

# KEY CONCEPTS

## 1. GASEOUS STATE

When the molecular forces of attraction between the particles of a matter are minimum, the particles exist in a state known as gaseous state or a state of matter in which molecules are far away from each other and free to move in available space is called gaseous state.

### 1.1 Properties of Gases

- They do not have definite shape and volume.
- They can occupy whole space open to them.
- Gases have unlimited expansibility and high compressibility.
- They have very low densities because of negligible intermolecular forces.
- Gases exert pressure on the wall of the container with perfectly elastic collisions.
- They diffuse rapidly through each other to form homogeneous mixture against the electric, magnetic and gravitational field.

### 1.2 Parameters of Gases

The characteristics of gases are described in terms of four measurable parameters and it is also called as measurable properties of gases which are

- Mass
- Volume
- Pressure and
- Temperature

- Mass (m)**- The mass of a gas is denoted by 'm' which is related to the no of moles 'n'.

Therefore,

$$n \text{ (no of moles)} = \frac{m \text{ (mass in grams)}}{M \text{ (Molar mass)}}$$

$$\text{so, } m = n \times M$$

#### (b) Volume V-

- Gases occupy whole space available to them. The volume occupied by a gas is simply the volume of container in which it is filled.
- The volume of a gas is denoted by 'V' and it is measured in units of litre or cubic metre ( $\text{m}^3$ ) or  $\text{cm}^3$  or  $\text{dm}^3$ .
- 1 litre =  $1 \text{ dm}^3 = 1000 \text{ cm}^3 = 1000 \text{ ml}$

#### (c) Pressure (P)-

- It is force acting per unit area. A confined gas exerts uniform pressure on the walls of its container in all the direction.
- It is denoted by 'P' and specified in pascal ( $\text{Pa}$ ).
- Other units of pressure are atm, cm Hg, mmHg,  $\text{N/m}^2$ , bar, torr.
- $1 \text{ atm} = 76 \text{ cm Hg} = 760 \text{ mm Hg}$   
 $= 1.013 \times 10^5 \text{ N/m}^2 = 1.013 \times 10^5 \text{ Pa}$   
 $= 1.013 \text{ bar} = 760 \text{ torr}$

$$\begin{aligned} \text{(v) } P \text{ (Pressure)} &= \frac{F \text{ (Force)}}{A \text{ (Area)}} \\ &= \frac{\text{Mass} \times \text{Acceleration}}{\text{Area}} \end{aligned}$$

- Pressure exerted by a gas is due to kinetic energy ( $\text{K.E.} = \frac{1}{2} mv^2$ ) of the gases molecules.
- K.E. of the gas molecules increases, as the temperature is increased so, pressure of a gas is directly proportional to temperature.  $P \propto T$

#### (d) Temperature (T)-

- The temperature of a gas is denoted by 'T' and it is measured in the unit of kelvin (K).
- Other units of temperature are,  $^{\circ}\text{C}$ ,  $^{\circ}\text{F}$ ,  $^{\circ}\text{R}$ .
- $\text{K} = ^{\circ}\text{C} + 273.15$
- $\frac{x^{\circ}\text{C}}{5} = \frac{(y^{\circ}\text{F} - 32)}{9}$

## 2. Gas Laws

The certain laws which relate the four parameters are called gas laws.

### 2.1 Boyle's Law

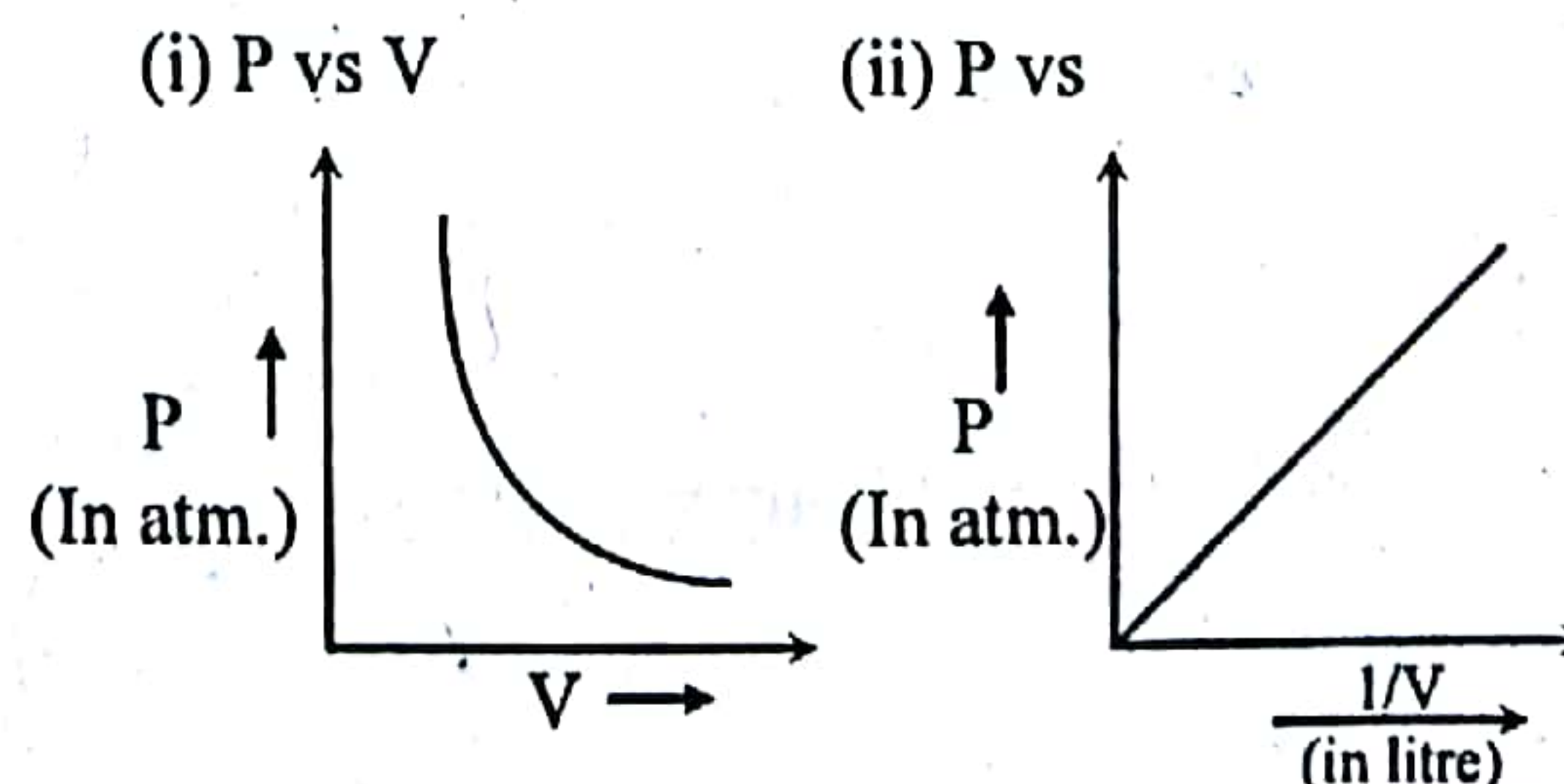
- It states that at constant temperature, the volume of a given mass of a gas is inversely proportional to the pressure.

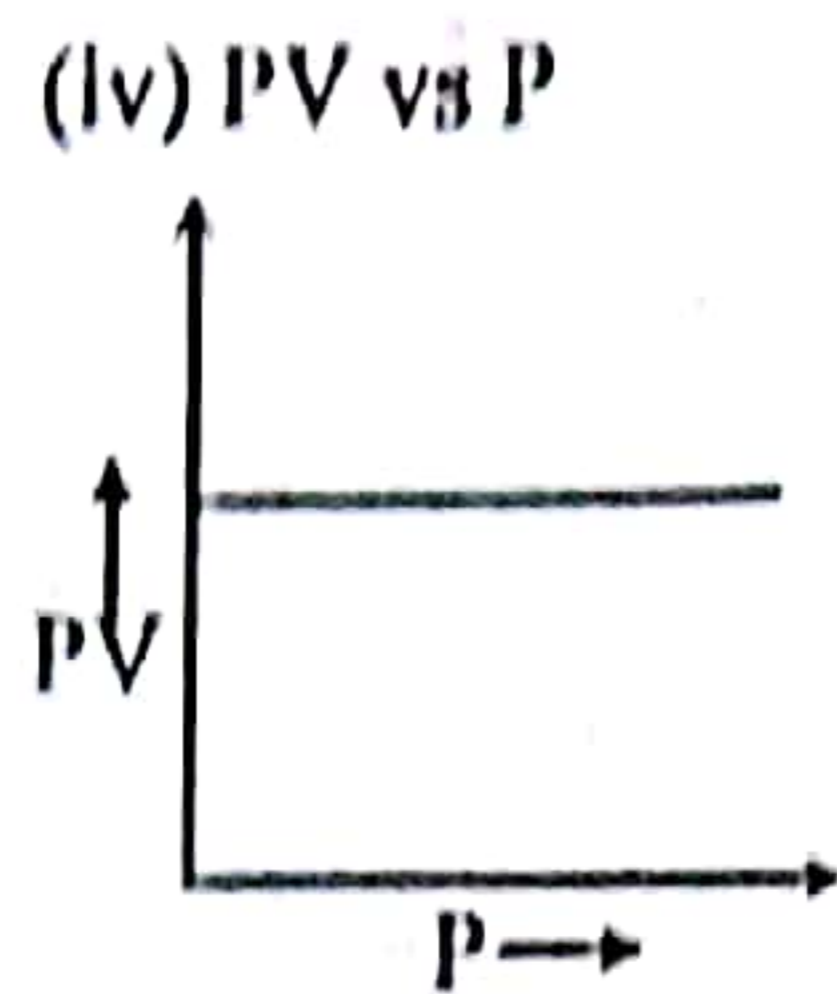
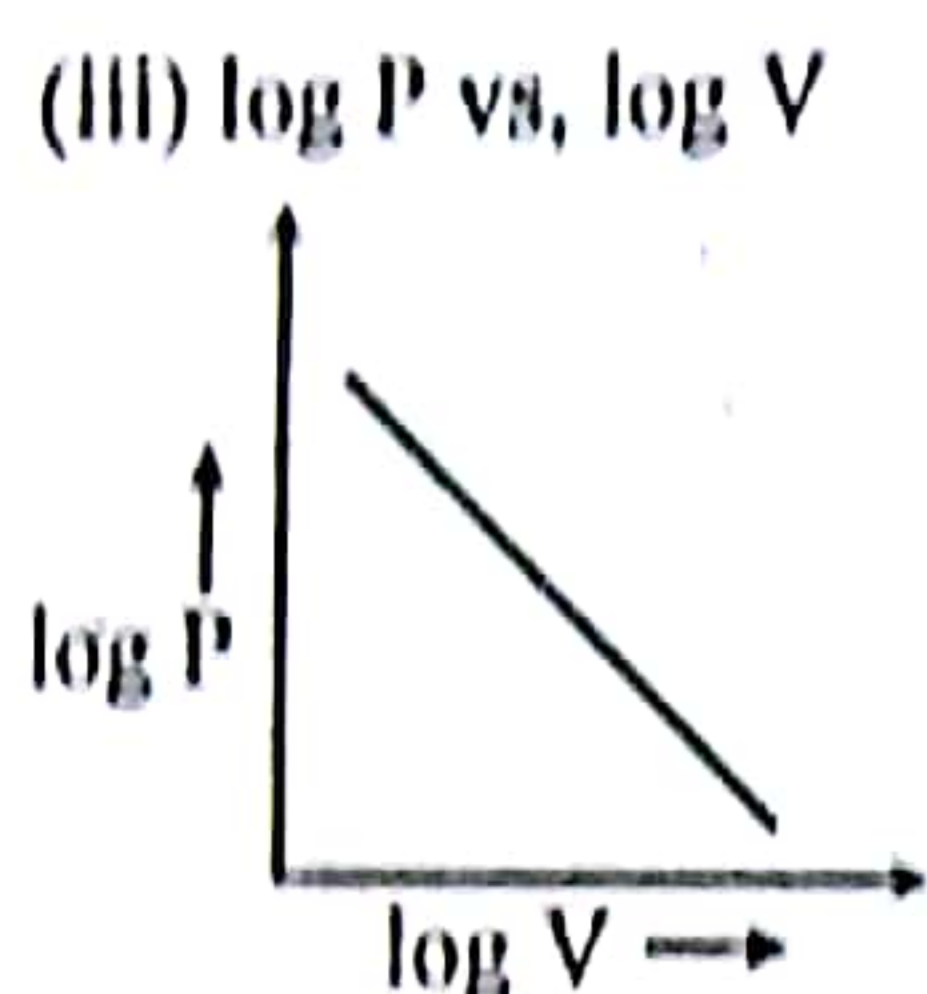
#### (b) Mathematically -

$$P \propto \frac{1}{V} \text{ (at constant temperature)}$$

$$\text{or } PV = K \text{ or } P_1V_1 = P_2V_2$$

#### (c) Graphical representations





## 2.2 Charles's law

(a) This law states that at constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature.

(Absolute temperature =  $^{\circ}\text{C} + 273.15$ )

(b) Mathematically -  $V \propto T$  (at constant pressure)

$V$  = volume of gas

$T$  = Absolute temperature

$V = KT$  or

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

Hence, if the volume of a gas of mass is  $V_1$  at temperature  $T_1$  changes to  $V_2$  at  $T_2$ , pressure remaining constant,

$$\text{then } \frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{constant}$$

$$\text{or } \log V - \log T = \text{constant}$$

(c) For each degree change of temperature the volume of sample of a gas changes by the fraction of  $\frac{1}{273.15}$  of its volume at  $0^{\circ}\text{C}$

$$\text{so } V_t = V_0 \left[ \frac{273.15 + t}{273.15} \right]$$

This equation is called Charles-gay-lussac equation.

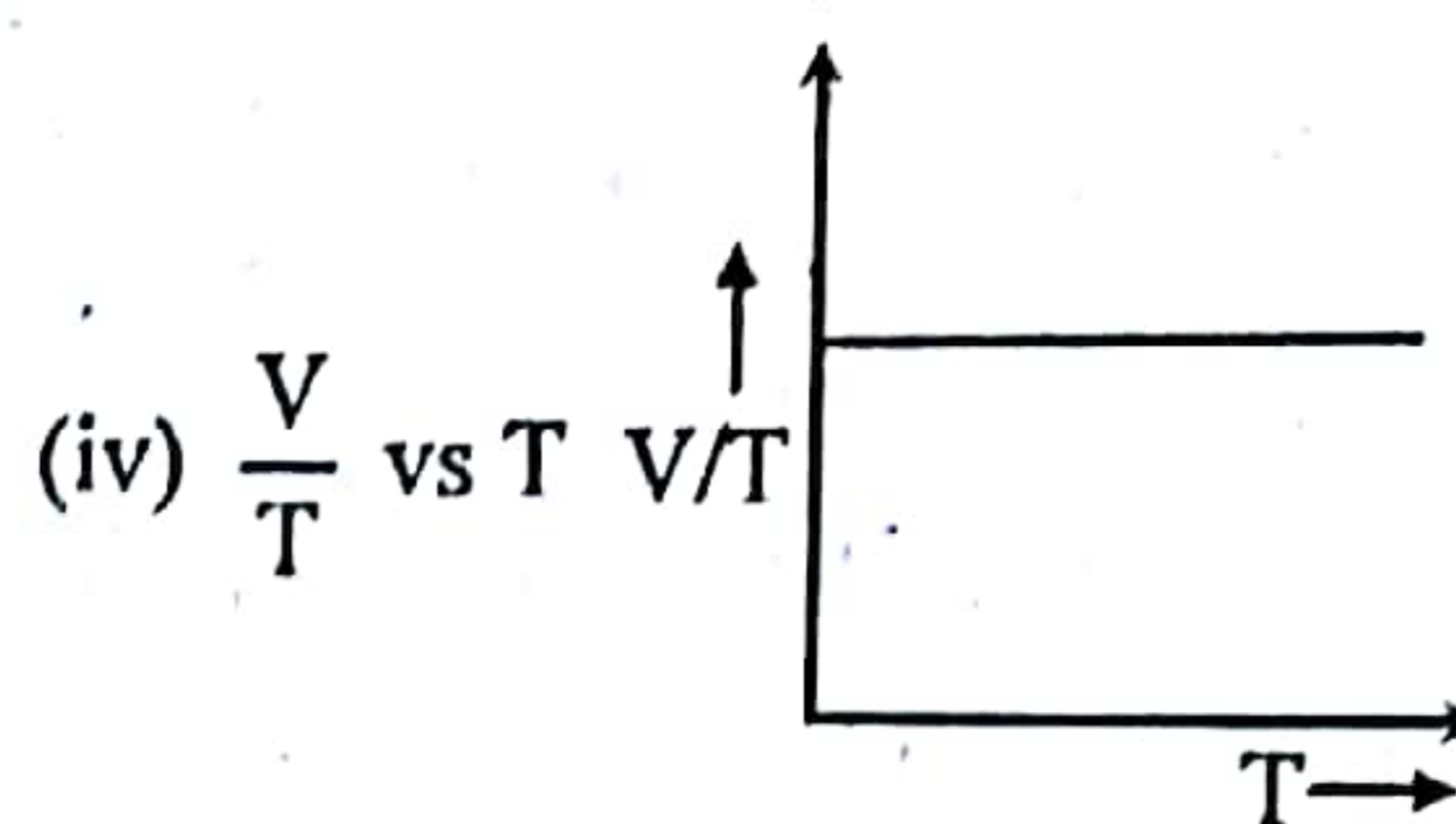
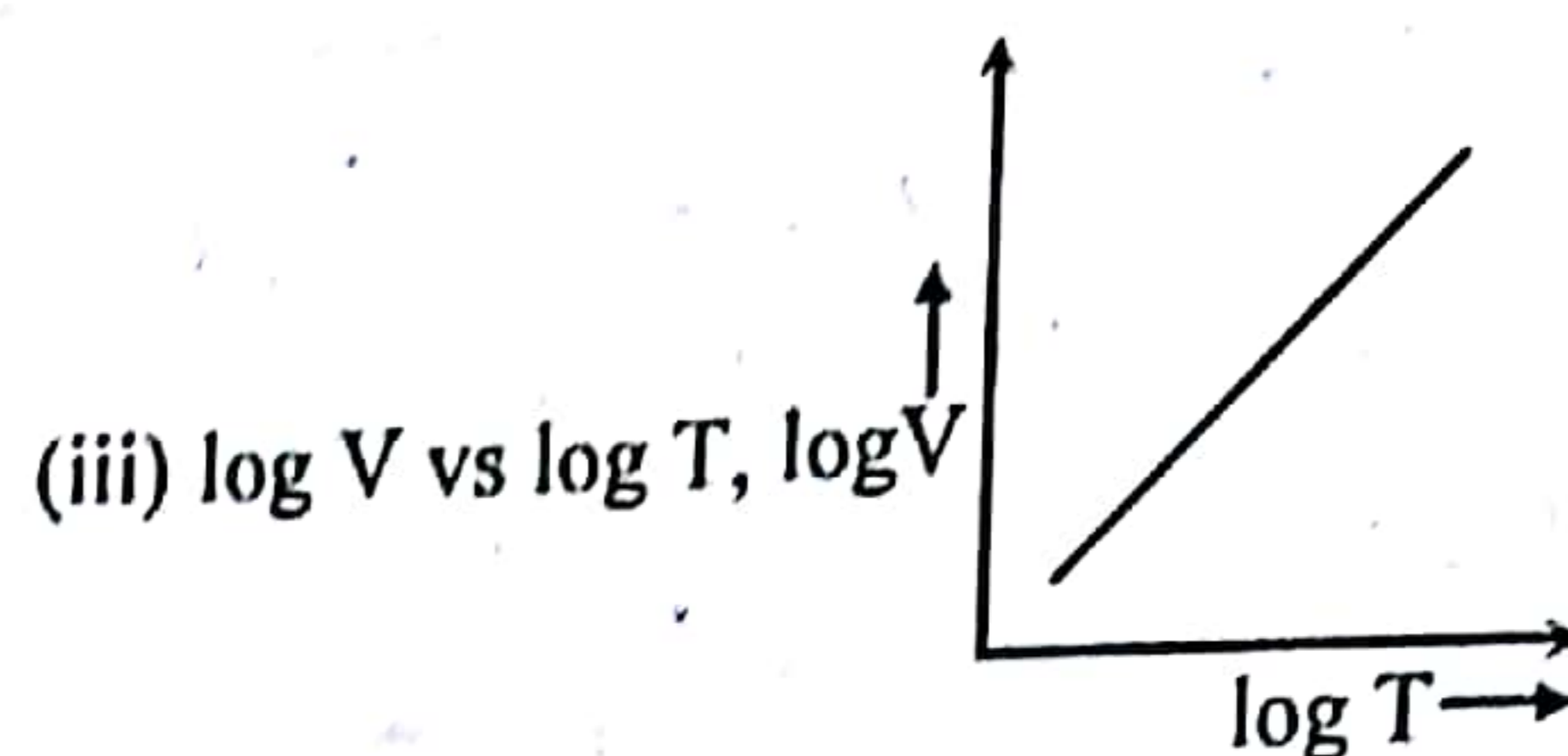
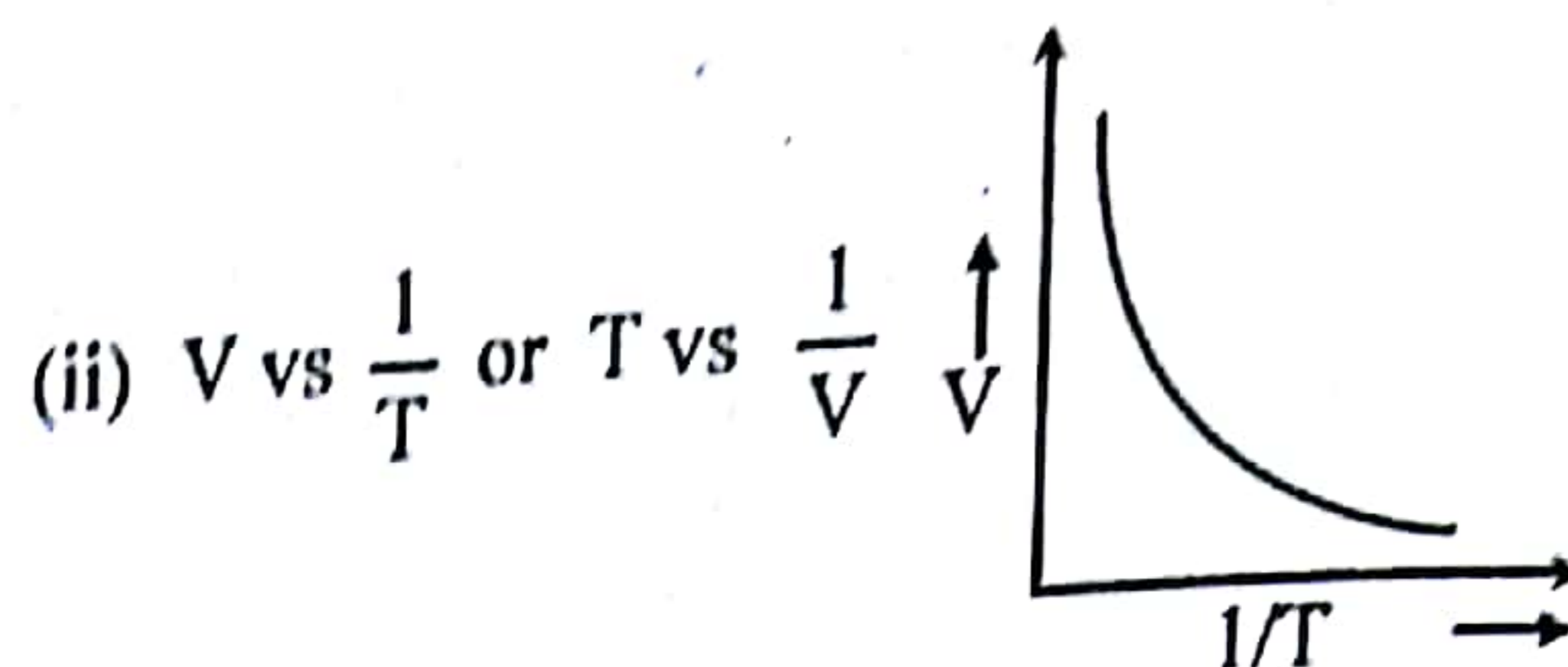
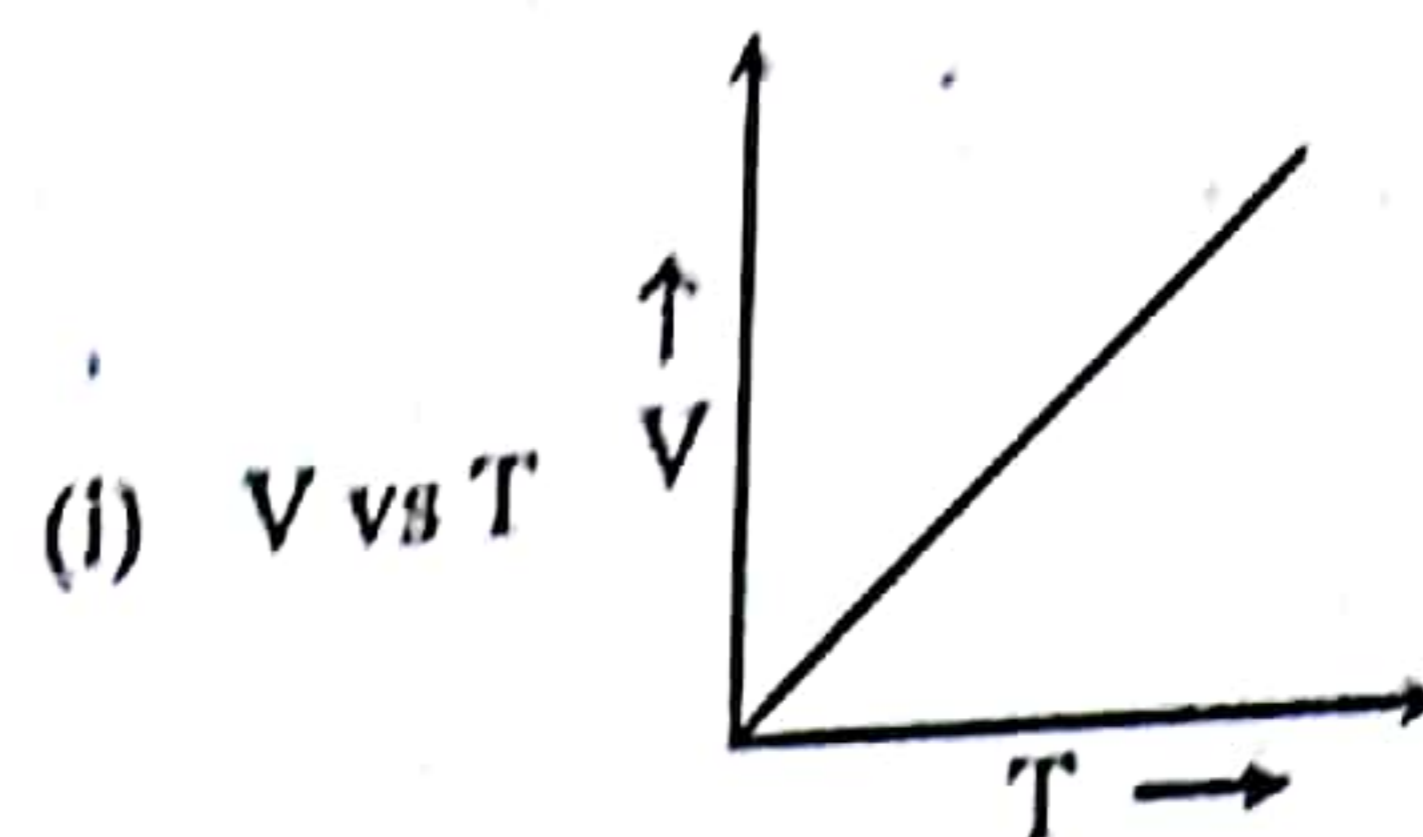
where

$V_t$  = volume of gas at temperature  $t^{\circ}\text{C}$

$V_0$  = volume of gas at  $0^{\circ}\text{C}$  temperature

$t$  = temperature in  $^{\circ}\text{C}$ .

(d) Graphical representations -



## 2.3 Gay-Lussac's Law or Amonton's Law

(a) It states that at constant volume, the pressure of a given mass of a gas is directly proportional to its absolute temperature.

(b) Mathematically -  $P \propto T$  (at constant volume)

where  $P$  = pressure of gas

$T$  = Absolute temperature

$P = KT$

$$\text{or } \frac{P}{T} = K$$

Hence, if the pressure of a gas is  $P_1$  at temperature  $T_1$  changes to  $P_2$  at  $T_2$ , volume remaining constant.

$$\text{then } \frac{P_1}{T_1} = \frac{P_2}{T_2} = \text{constant}$$

$$\log P - \log T = \text{constant.}$$

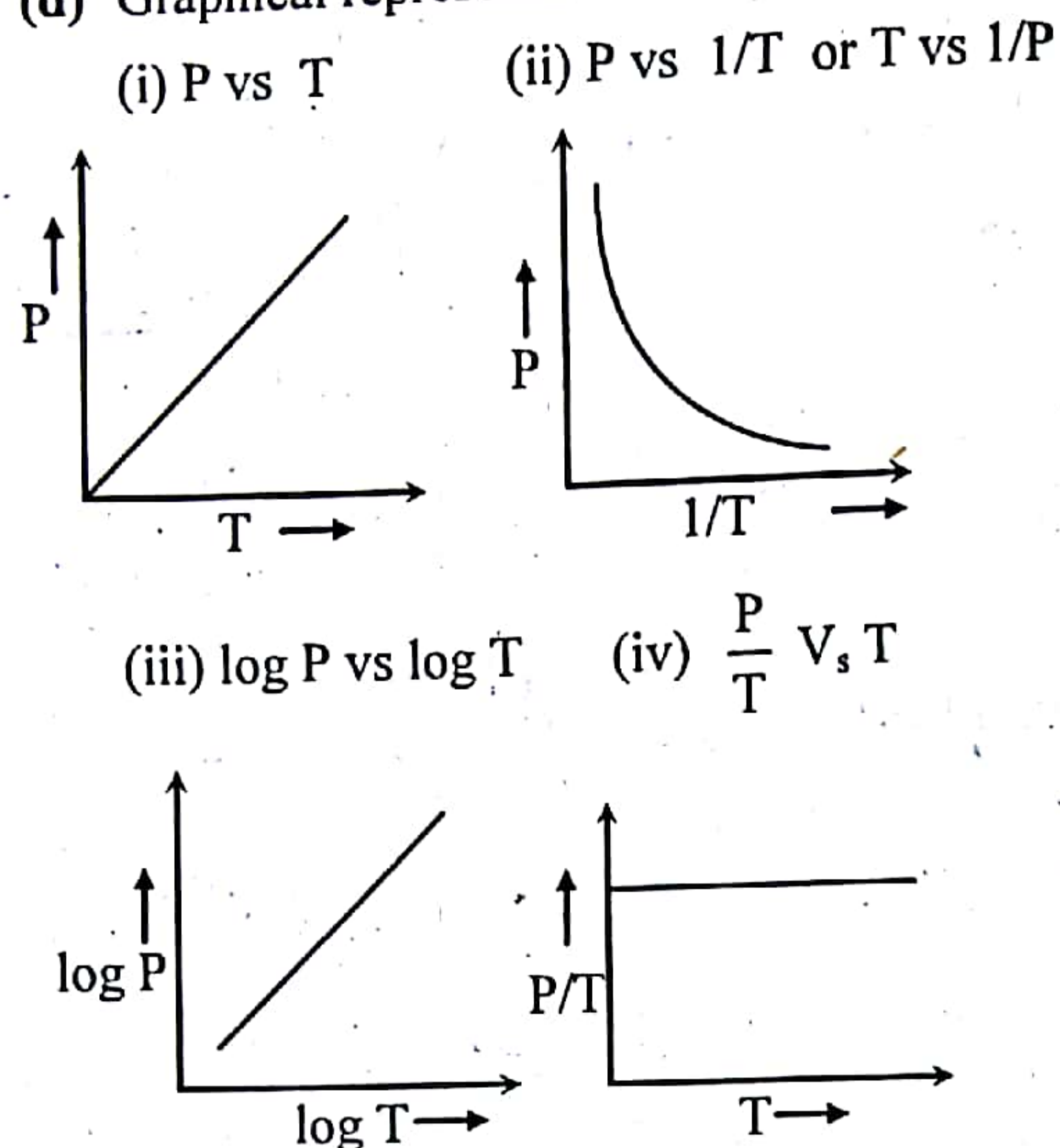
$$(c) P_t = P_0 \left( 1 + \frac{t}{273.15} \right)$$

where  $P_t$  = Pressure of gas at  $t^\circ\text{C}$   
 $P_o$  = Pressure of gas at  $0^\circ\text{C}$   
 $t$  = Temperature in  $^\circ\text{C}$ .

$$R = \frac{\frac{\text{force}}{\text{Area}} \times \text{volume}}{\text{mole} \times \text{Temperature}} = \frac{\text{force} \times \text{length}}{\text{mole} \times \text{Temperature}}$$

$$R = \frac{\text{work(energy)}}{\text{mole} \times \text{Temperature}}$$

(d) Graphical representation -



#### 2.4 Ideal gas equation

- (a) It correlates all the four parameters of a gas.  
 (b) It is the combination of Boyle's and Charles's law.  
 (c)  $PV = nRT$

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

The equation is called as ideal gas equation.

Where  $n$  = no of moles of the gas  
 $m$  = mass of the gas  
 $M$  = Mol. wt. of the gas  
 $R$  = Molar gas constant.

- (d) For 1 mole of the gas  $n = 1$

$$PV = RT$$

$$\text{So } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = R \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Where  $P_1, V_1, T_1$  are the initial pressure, volume and temperature and  $P_2, V_2, T_2$  are final.

The above equation is called as ideal gas equation.

- (e) The unit of  $R$  is the unit of work or energy per degree per mole as -

$$R = \frac{PV}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{mole} \times \text{Temperature}}$$

(f) Numerical values of  $R$  in different units -

- (i)  $R = 0.0821 \text{ litre atm. deg.}^{-1} \text{ mole}^{-1}$   
 (ii)  $R = 62.4 \text{ litres mm. deg.}^{-1} \text{ mole}^{-1}$   
 (iii)  $R = 8.314 \times 10^7 \text{ ergs deg.}^{-1} \text{ mole}^{-1}$   
 (iv)  $R = 82.05 \text{ C.C.atm. deg.}^{-1} \text{ mole}^{-1}$   
 (v)  $R = 2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$   
 (vi)  $R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$

### 3. Dalton's Law of Partial Pressure

- (a) According to this law, when two or more than two chemically inert gases are kept in a closed container, the total pressure exerted by the gaseous mixture is equal to the sum of the partial pressures of individual gases - i.e.-

$$P = P_1 + P_2 + P_3 + \dots + P_n$$

- (b) Let  $n_1$  &  $n_2$  be the no. of moles of two inert gases A and B which is filled in a container of volume 'V' at temperature T. So the total pressure of container 'P' may be calculated as -

$$PV = (n_1 + n_2) RT \dots (i)$$

Partial pressure of individual gas calculates as -

$$P_A V = n_1 RT \dots (ii)$$

$$P_B V = n_2 RT \dots (iii)$$

On the addition of eq. (ii) & (iii) we get -

$$(P_A + P_B) V = (n_1 + n_2) RT \dots (iv)$$

On the comparison of eq. (i) & (iv)

$$P = P_A + P_B$$

Dividing by equation (ii) by (i), we get

$$\frac{P_A}{P} = \frac{n_1}{n_1 + n_2} = x_A$$

$$P_A = x_A \times P$$

where  $x_A$  = mole fraction of 'A'

Similarly dividing (iii) by (i), we get

$$P_B = x_B \times P$$

so

Partial pressure of a component = mole fraction  $\times$  total pressure

### 3.1 Applications of Dalton's Law of Partial pressure

(a) mole fraction of a gas in a mixture of gas

$$= \frac{\text{partial pressure of gas}}{\text{Total pressure of the mixture of gas}}$$

(b) % of a gas in a mixture

$$= \frac{\text{partial pressure of gas}}{\text{Total pressure}} \times 100$$

(c) Pressure of dry gas which is collected over the water is-

$$P_{\text{Total}} = P_{\text{moist air}} = P_{\text{dry gas}} + P_{\text{water vapour}}$$

(Note :  $P_{\text{water vapour}}$  is called aqueous tension)

$$\text{so } P_{\text{dry gas}} = P_{\text{Total}} - P_{\text{Water vapour}}$$

(Note: Aqueous tension is directly proportional to absolute temperature)

### 3.2 Limitations of Dalton's law of partial pressure

(a) It is applicable only inert gases like  $N_2$  and  $O_2$ ,  $N_2$  and  $Cl_2$  etc.

(b) It is not applicable for chemically reactive gases like  $H_2$  and  $Cl_2$ ,  $CO$  and  $Cl_2$  etc.

### Avogadro's Law

(a) According to this law under the same condition of temperature and pressure, equal volumes of all gas contains equal no. of molecules.

$$V \propto n \text{ (At constant temperature \& pressure)}$$

Where  $V$  = volume

$n$  = no of molecules

(b) Molar Volume or gram molecular volume - 22.4 litres or 22400 ml of every gas at NTP is the volume occupied by its one gram mole and it is called molar volume or gram molecular volume.

(c) The mole Concept - Mole is defined as the total amount of substance that contains as many basic units as there are atoms in 12 g of the isotopes of carbon -12. Thus a mole will be defined as

the Avogadro no of particles which is equal to  $6.023 \times 10^{23}$ .

(d) Loschmidt number - It the no of molecules present in the volume of a gas at S.T.P. Its value is  $2.617 \times 10^{19}$  per c.c.

### Graham's Law of Diffusion of Effusion

**Diffusion:** It is the ability of a gas to mix spontaneously and to form a homogenous mixture is known as diffusion.

**Effusion:** It is a process in which a gas is allowed to escape under pressure through a fine orifice from closed container.

#### LAW

(a) This law was proposed by Thomas Graham.

(b) According to this law, at constant temperature and pressure, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its density. Thus and directly proportional to its pressure.

$$\text{Rate of diffusion (r)} \propto \frac{P}{\sqrt{d}}$$

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{d_2}{d_1}}$$

It pressure is constant

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

where  $r_1$  &  $r_2$  are rates of diffusion of two gases and  $d_1$  &  $d_2$  are densities.

$\therefore 2 \times \text{vapour density} = \text{Molecular mass}$

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

where  $M_1$  &  $M_2$  are the molecular masses of two gases.

$$(c) \text{ Rate of diffusion} = \frac{\text{Volume of gas diffused}}{\text{Time taken for diffusion}}$$

### 5.1 Applications of graham's law of diffusion

(a) To the Detection of marsh gas in mines.

(b) Separation of isotopes

(c) Determination of density and molecular mass of gases.

- (a) It was a commonly given for ideal gases.
- (b) This theory was proposed by Bernoulli and next to developed by Clausius, Maxwell, Kroning and Boltzman.

### 6.1 Assumptions of Kinetic Theory of gases

- (a) All the gases are made up of molecules moving randomly in all the directions.
- (b) The volume of the individual molecule is negligible as compared to the total volume of the gas.
- (c) Pressure exerted by gas is due to collision of gas molecules with the wall of the container so.  
Pressure  $\propto$  No of collisions per unit time per unit area by the molecules on the wall of the container
- (d) All collisions between two molecules or between a molecule and a wall are perfectly elastic.
- (e) All the molecules obey Newton's laws of motion.
- (f) Gas molecules neither attract nor repel each other.
- (g) Kinetic energy of gas molecules depend upon the absolute temperature so.  
Kinetic energy  $\propto$  absolute temperature
- (h) The force of gravity has no effect on the speed of gas molecules.

### 6.2 Calculation of Kinetic energy

According to postulates of kinetic gas equation-

$$PV = \frac{1}{3} mnv^2$$

where P = pressure of the gas

V = volume of the gas

n = no of molecules present in the given amount of gas

v = Root mean square speed.

for one mole of the gas -

$$PV = RT \quad \text{and } n = N$$

$$\frac{1}{3} mNv^2 = RT$$

$$\text{or } \frac{2}{3} \cdot \frac{1}{2} mNv^2 = RT$$

$$\left( \because \frac{1}{2} mNv^2 = \text{K.E. per mole} \right)$$

$$\therefore \text{K.E.} = RT$$

$$\text{K.E.} = \frac{3RT}{2} \Rightarrow \text{K.E. per mole / Avg. K.E. per mole.}$$

$$\therefore \text{Boltzmann constant } K = \frac{R}{N} \\ = 1.38 \times 10^{-16} \text{ ergs K}^{-1} \text{ molecules}^{-1}$$

$$\text{K.E.} = \frac{3KT}{2} \Rightarrow \text{K.E. per molecule / Avg. K.E. per molecule}$$

### 6.3 Velocities related to gaseous state

#### (A) Root mean square velocity (RMS velocity) -

Square root of the mean of the squares of the speed of all the molecules present in the given sample of the gas is called root mean square speed.

$$u = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

#### (b) Average Speed -

It is the arithmetic mean of the various speeds of the molecules

$$\text{Average speed } (\bar{v}) = \sqrt{\frac{8RT}{\pi m}}$$

$$\text{Average speed} = .9213 \times \text{RMS speed}$$

$$\text{RMS speed} = 1.085 \times \text{Average speed}$$

#### (c) Most Probable Speed-

Speed possessed by maximum number of molecules of a gas at a given temperature.

$$\text{Most probable speed } (\alpha) = \sqrt{\frac{2RT}{M}}$$

$$\text{MPS} = .816 \times \text{RMS}; \text{RMS} = 1.224 \text{ MPS}$$

$$\text{MPS} : \text{A.V. speed} : \text{RMS} = 1 : 1.128 : 1.224$$

S.N.	Ideal gas	Real gas
1.	Obeys gas law under all condition	Obeys only at low P and high T
2.	Obeys ideal gas	Does not obeys ideal gas equation
3.	Intermoleuclar interaction between	Intermolecular interaction between

	gaseous molecules are negligible.	gaseous molecules not negligible.
4.	Volume of a particle is negligible as compared to total volume of the gas.	Volume of a particle is not be negligible as compared to total volume of the gas.
5.	Exists only high temperature and low pressure	Exists only at low temperature and high pressure

### 7.1 Explanation of deviation

Kinetic theory of gases do not hold good at all condition mostly these two assumptions

- (a) The force of attraction between gaseous molecules are negligible
- (b) The volume occupied by the gaseous molecules is negligible compared to total volume of gas at high pressure. Both the assumptions do not hold good hence deviating from ideal gas.

### SPECIFIC HEAT OF GASES ::

(a) Specific Heat - It is the amount of heat required to raise the temperature of one gm of the substance through one degree centigrade. It is usually expressed in "Calories".

(b) Calorie - A calorie is defined as the amount of heat required to raise the temperature of one gm of water through 1°C (more accurately from 15.5 °C to 16.5 °C.).

The heat so supplied is used up in increasing the internal energy of the molecule, i.e. in raising the temperature or in raising the average K.E. of the molecules.

(c) Specific Heat of a gas at constant volume ( $C_v$ ) -

The amount of heat required to raise the temperature of one gm of the gas by 1 °C when the volume is kept constant and pressure is allowed to increase.

(d) Specific Heat of a gas at constant Pressure ( $C_p$ ) -

The amount of heat required to raise the temperature of one gm of the gas by 1 °C when the pressure is kept constant and volume is allowed to increase.

$$C_v = c_v \times M \text{ and } C_p = c_p \times M$$

Where  $C_v$  and  $C_p$  are molar specific heat or heat capacity per mole at constant volume and at constant pressure.

(e) Ratio for Molar Heats -

(i) For monoatomic gases  $\frac{C_p}{C_v} = g$

$$= \frac{5.0}{3.0} = 1.66$$

∴ Molar heat capacity at constant volume ( $C_v$ )

$$= \text{K.E.} = \frac{3RT}{2}$$

$$\text{at } 1^\circ\text{C} \Rightarrow \text{K.E.} = \frac{3}{2} R$$

$$\text{K.E.} = \frac{3}{2} \times 2 = 3.$$

Therefore  $\Rightarrow C_v = 3$  calories.

$$\& C_p = \text{Increase in K.E.} \left( \frac{3}{2} R \right) + \text{work done}$$

$$= \frac{3}{2} R + R = \frac{5}{2} R \text{ (Since } R = 2)$$

$$C_p = \frac{5}{2} \times 2 = 5 \text{ calories.}$$

(ii) For diatomic gases  $\frac{C_p}{C_v} = \frac{5+x}{3+x}$

In case of diatomic gases x in many cases is 2.

$$\frac{C_p}{C_v} = \frac{7}{5} = 1.40$$

(iii) For triatomic gases  $\frac{C_p}{C_v} = \frac{5+3}{3+3}$

$$= \frac{8}{6} = 1.33$$

### VANDER WAAL'S EQUATION - A MODIFICATION OF IDEAL GAS EQUATION ::

According to Vander Waal Maxwell has made two wrong assumptions in his kinetic theory of gases which lead to wrong results.

- (a) The forces of attractions between gaseous molecules are negligible under all conditions.
- (b) The volume occupied by the gaseous molecules is negligible as compared to total volume of gas.
- (c) Volume Correction - The observed volume is greater than ideal volume & correction term 'nb' has to be subtracted from observed volume in order to get ideal volume.

$$V_{\text{ideal}} = V - nb$$

Where 'n' is no. of moles of real gas & 'b' is constant which depends on nature of real gas.

### 10. CRITICAL CONSTANTS

- (a) **Critical temperature ( $T_C$ )** - The temperature above which gas cannot be liquified whatever pressure is applied is called critical temperature.

$$T_C = \frac{8a}{27bR}$$

- (b) **Critical pressure ( $P_C$ )** - The minimum pressure required to liquefy a gas at its critical temperature is called critical pressure.

$$P_C = \frac{a}{27b^2}$$

- (c) **Critical volume ( $V_C$ )** - The volume occupied by one mole of a gas at the critical temperature and critical pressure is called critical volume.

$$V_C = 3b$$

### 11. LIQUIFICATION OF GASES

- (a) On increasing the pressure gas can be easily liquified because intermolecular attraction between gaseous molecule increases.
- (b) On decreasing the temperature K.E. of gaseous molecules decrease That's why gas can be easily liquified.
- (c) Temperature of gas must be lower than critical temperature ( $T_C$ ).

### 12. BOYLE'S TEMPERATURE

The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range.

$$T_B = \frac{a}{Rb}$$

### 13. INVERSION TEMPERATURE

It is the temperature at which any real gas is expanded adiabatically and no effect of cooling or heating is observed.

$$T_i = \frac{2a}{Rb}$$

# KEY CONCEPTS

## 1. REACTION ::

The transformation of one substance into another is known as reaction.

## 2. REACTANT ::

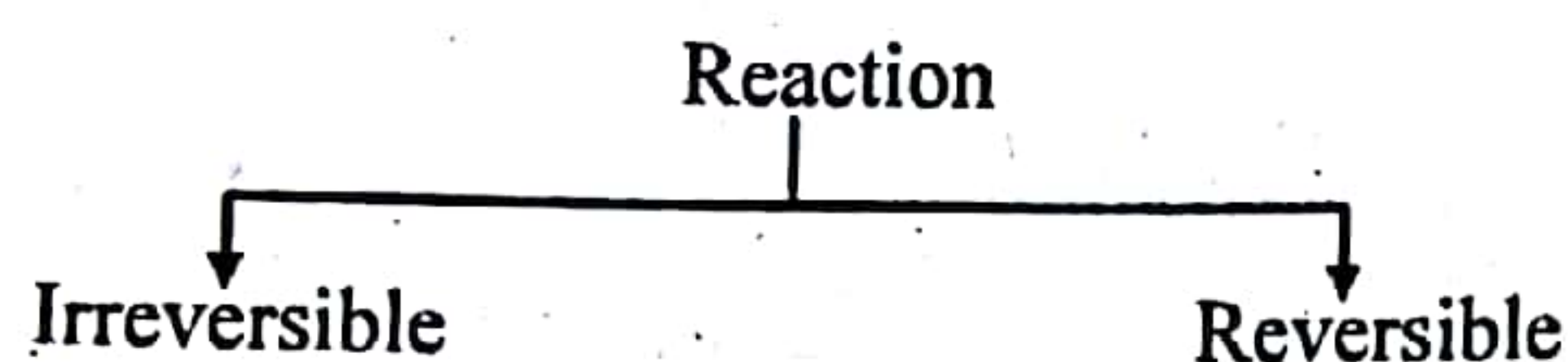
The substances used at initial stage of reaction are known as reactant.

## 3. PRODUCT ::

The substances formed at final stage of reaction are known as product.

## 4. TYPES OF REACTIONS ON THE BASIS OF DIRECTION ::

On the basis of the direction, reactions are of two types.



### 4.1 Irreversible reactions :

The chemical reactions in which the products formed do not combine to give back the reactants are known as irreversible reaction.

#### A. Properties of irreversible reactions –

- Reactions in which reactant react to form product only.
- Reactions proceed in one single direction.
- Always proceed to completion.
- Always carried out in open vessel.
- In these type of reactions, If product are gaseous in state, then they can escape from reacting site. If they are solid in state they will precipitate.

#### B. Some examples of irreversible reactions are as follows –

- All thermal decomposition in open vessel.
- All the neutralisation reaction of strong acid and strong base.
- All precipitation reactions.
- All gaseous reactions in open vessel.

### 4.2 Reversible reactions :

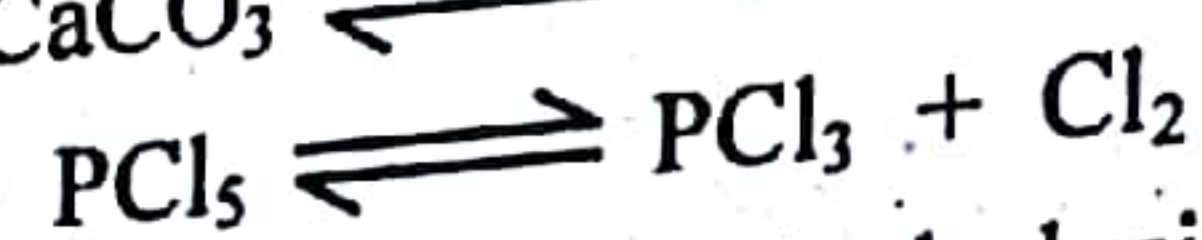
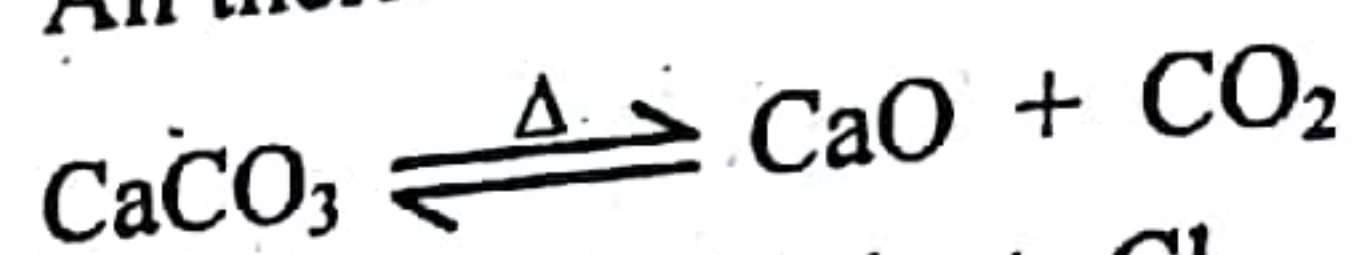
The reactions in which the products can react with one another to give back the reactants again under suitable conditions called as reversible reaction.

#### A. Properties of reversible reactions –

- In these type of reactions, reactant react to form product and product further react to form reactant.
- Reactions proceed in both directions.
- These type of reactions never get completed.
- Always carried out in closed vessel.

#### B. Some examples of reversible reactions are as follows –

- All thermal dissociation in closed vessel.



- All types of salt hydrolysis except strong acid strong base salt.

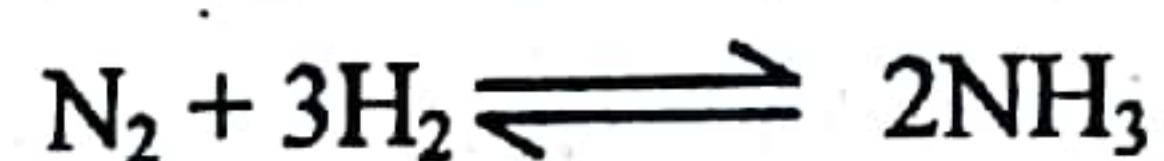


Salt of weak base

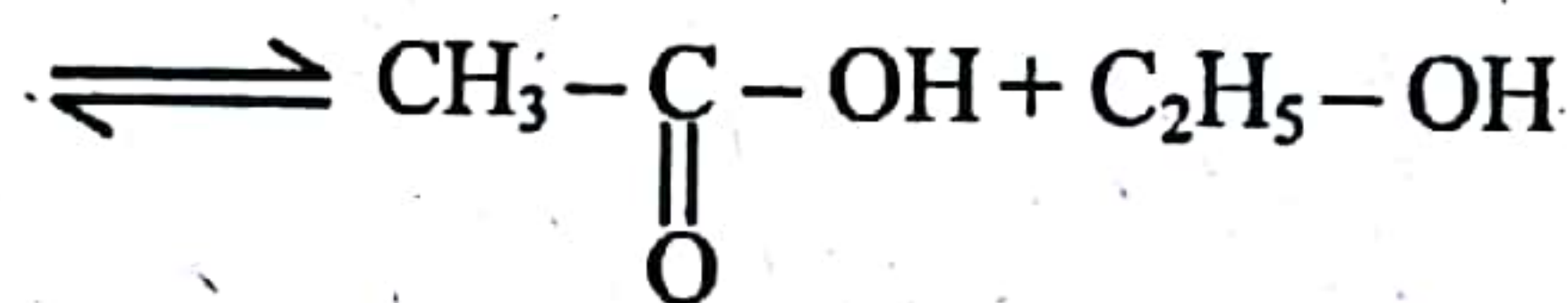
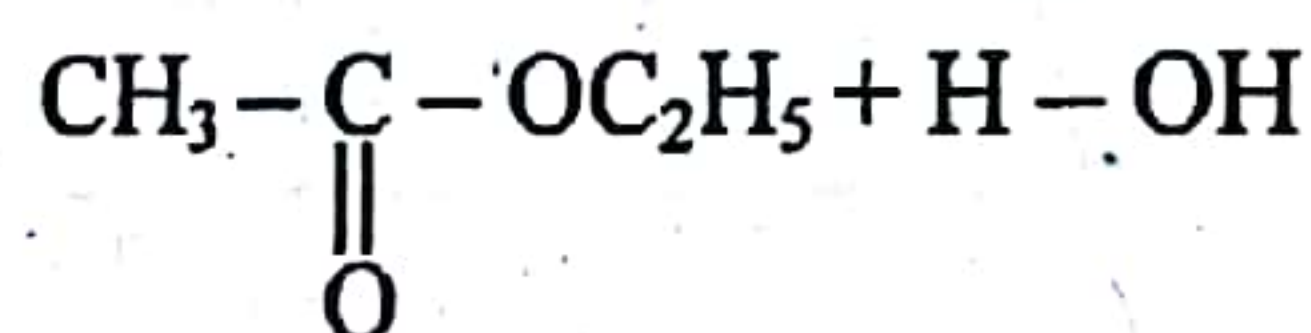
+

strong acid

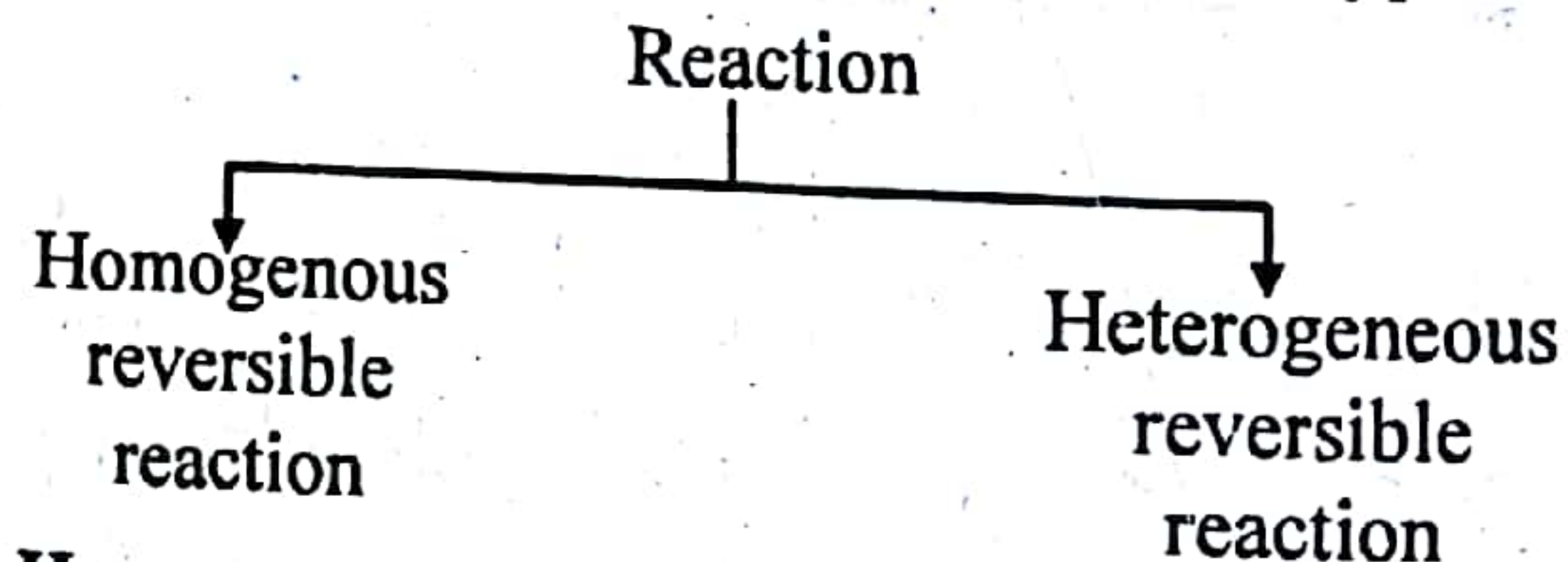
- All gaseous reactions in closed vessel.



- All the reactions of organic hydrolysis.

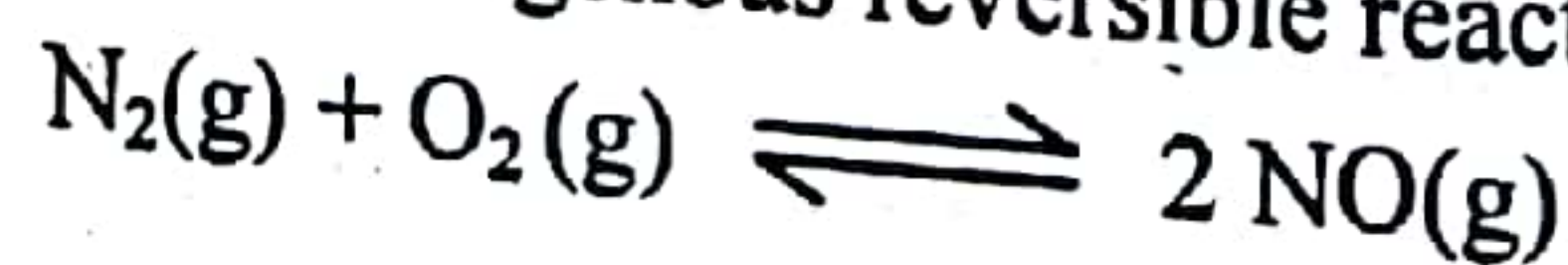


Reversible reactions are also of two type-

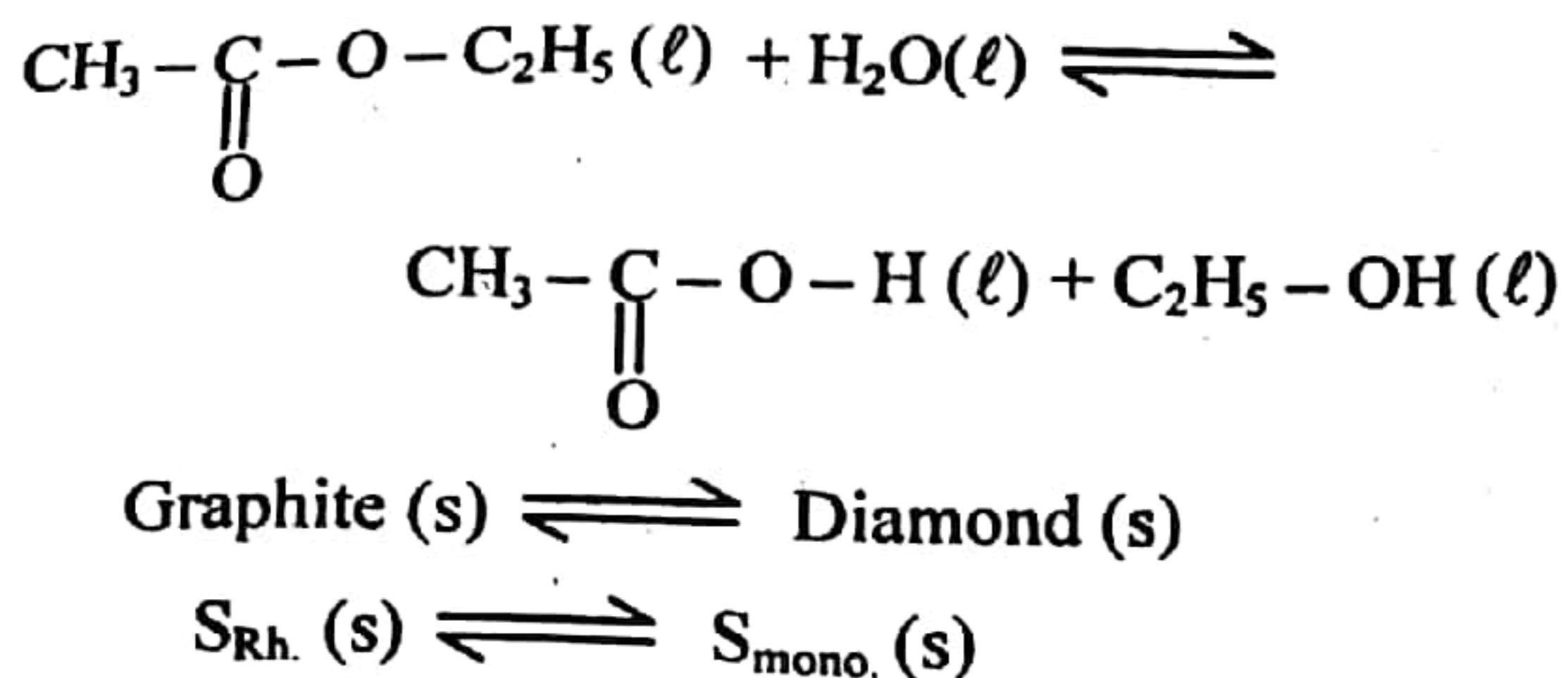


### 4.2.1 Homogenous reversible reactions :

If in the reversible reactions physical state of all reactants and products are same, it is known as called as homogenous reversible reaction.

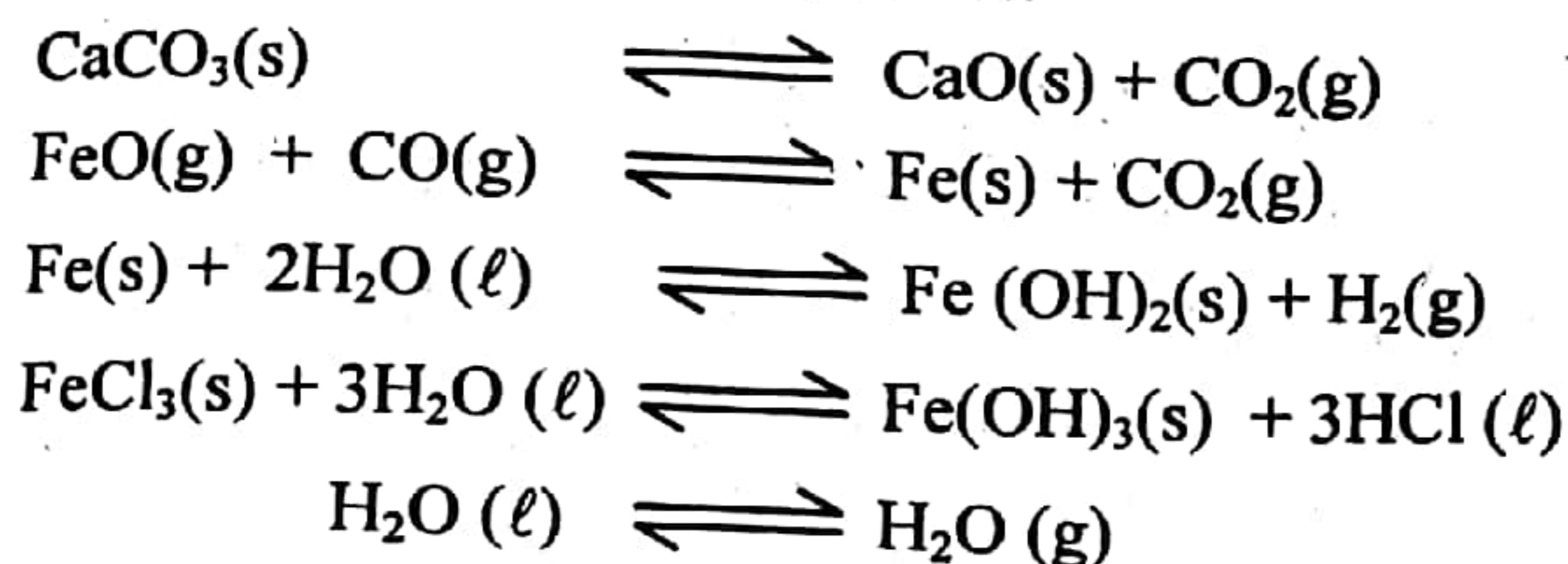






#### 4.2.2 Heterogenous reversible reaction :

If in the reversible reaction, physical state of reactant and product are different, it is known as heterogeneous reversible reaction.



### 5. CHEMICAL EQUILIBRIUM :

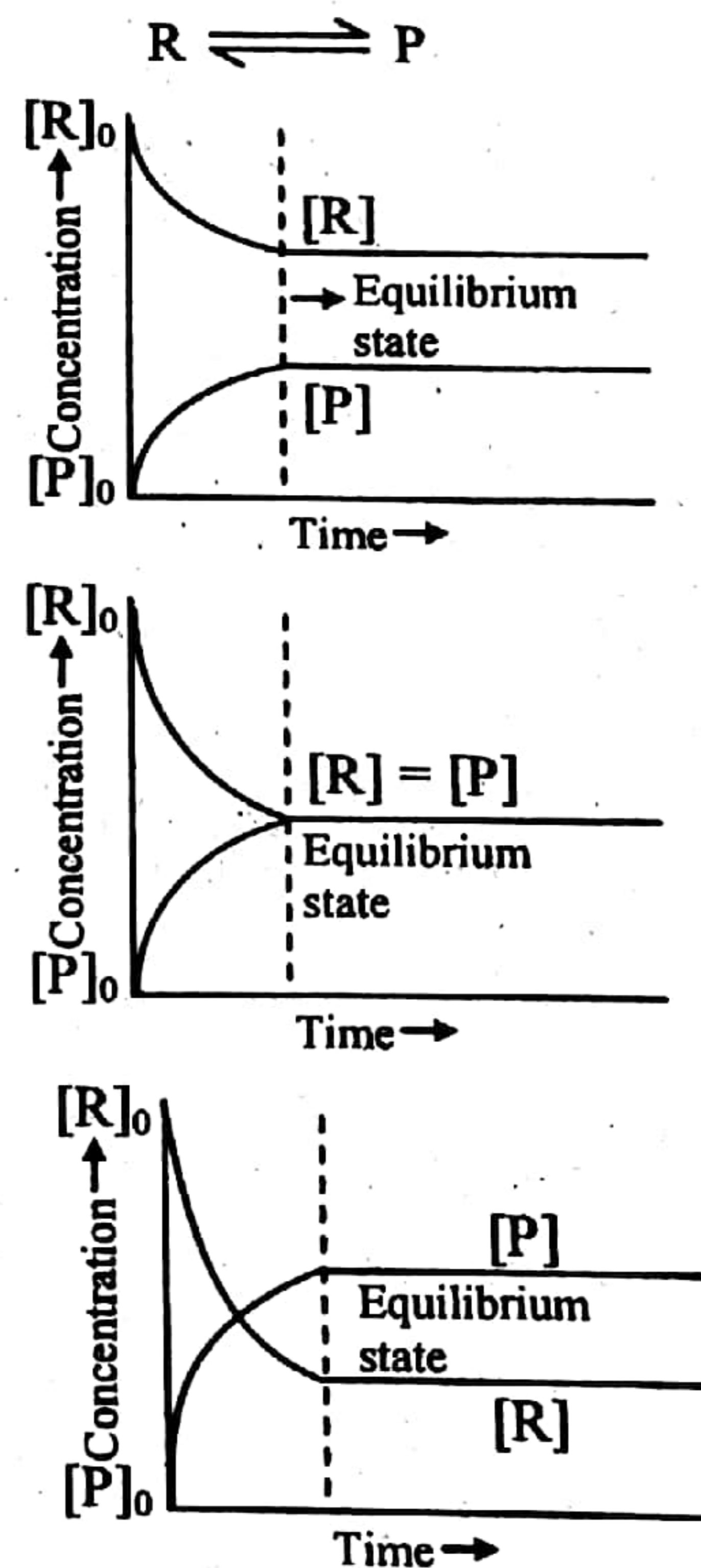
- State of reversible reaction at which rate of forward reaction becomes equal to the rate of backward reaction is called chemical equilibrium.
- State where rate of formation of product is equal to the rate of formation of reactant is known as chemical equilibrium.
- State of reversible reaction in which the concentration of reactant and concentration of product remain unchanged but not necessarily equal, is called chemical equilibrium.
- State where exchange of energy becomes zero is also called as chemical equilibrium.

#### 5.1 Characteristics of chemical equilibrium :

- It is a dynamic equilibrium i.e. at this stage of reaction takes place in both the directions of same speed although appears to be stopped.
- On the stage of equilibrium the reaction proceeds both the side.
- At the state of equilibrium, both reactants and products are present and their concentration do not change with respect to time.
- The state of equilibrium is not effected by the presence of catalyst : It only helps to attain the equilibrium state in less or more time.

- Change in pressure, temperature or concentration favours one of the reactions and thus shifts the equilibrium point in one direction.
- Change in free energy is equal to zero at the state of equilibrium ( $\Delta G = 0$ ).

#### 5.2 Graphical representation of chemical equilibrium –



### 6. LAW OF MASS ACTION :

- This law was given by **Guldberg and Waage**.
- According to this law, the rate of dissociation of reactant and the rate of formation of product is directly proportional to active mass of itself at constant temperature.



$$\frac{-d\text{A}}{dt} \propto [\text{A}]$$

$$\frac{-d\text{B}}{dt} \propto [\text{B}]$$

$$\frac{d\text{C}}{dt} \propto [\text{C}]$$

$$\frac{d\text{D}}{dt} \propto [\text{D}]$$

While, the rate of a chemical reaction is directly proportional to the product of active masses of reactants.

$$r \propto [A][B]$$

$$r = K[A][B]$$

### 6.1 Active Mass or activity or effective concentration or molar concentration -

- (a) It is the molecular concentration of a substance i.e. the no. of gram moles per litre.  
 (b) It is represented by enclosing its formula in square brackets ( [ ] ) of a substance.

Active mass = Molar concentration =

$$\frac{\text{No. of moles}}{\text{volume (in litres)}} = \frac{\text{No. of grams of substance}}{\text{Mol. wt.} \times \text{volume (in litre)}}$$

**Note:** The active mass of solids is one.

eg. What is the active mass of 4 gm  $H_2$  in 2 litre volume?

$$[H_2] = \frac{4}{2 \times 2} = 1$$

eg. What is the active mass of 14 gm  $N_2$  in 2 litre volume?

$$[N_2] = \frac{14}{28 \times 2} = \frac{1}{4}$$

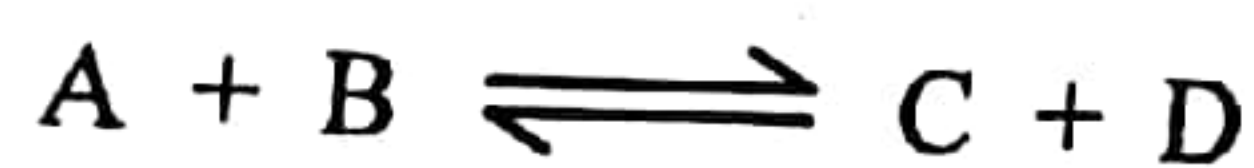
eg. What is the active mass of 14 gm  $N_2$  in  $\frac{1}{2}$  litre volume?

$$[N_2] = \frac{14}{28 \times \frac{1}{2}} = \frac{14 \times 2}{28} = 1$$

**Note:** - Law of mass action is applicable only for reversible reaction.

### 6.2 Mathematical Expression of law of mass action :

At the constant temperature, let us consider the following reversible reaction.



According to law of mass action -

Rate of forward reaction

$$r_f \propto [A][B] \text{ or } r_f = K_1[A][B]$$

where  $K_1$  is the rate constant of the forward reaction.

Rate of backward reaction

$$r_b \propto [C][D] \text{ or } r_b = K_2[C][D]$$

where  $K_2$  is the rate constant of the backward reaction.

At equilibrium :

Rate of forward reaction = Rate of backward reaction

$$K_1[A][B] = K_2[C][D]$$

$$\text{or } \frac{K_1}{K_2} = \frac{[C][D]}{[A][B]}$$

$$\text{or } K = \frac{[C][D]}{[A][B]}$$

Here,  $k$  is equilibrium constant of given reversible reaction.

### 6.3 Applications of law of mass action :-

#### 6.3.1 Formation of Nitric Oxide : ( $\Delta n = 0$ )

##### A. Calculation of $K_C$ :-

Suppose the initial moles of  $N_2$  and  $O_2$  is  $a$  and  $b$  respectively.  $x$  mole of each  $N_2$  and  $O_2$  is dissociated at equilibrium.

	$N_2$	+	$O_2$	$\rightleftharpoons$	$2NO$
Initial moles	$a$		$b$		$0$
moles at equilibrium	$(a-x)$		$(b-x)$		$2x$
Active mass ( $\text{mol l}^{-1}$ )	$\frac{(a-x)}{V}$		$\frac{(b-x)}{V}$		$\frac{2x}{V}$

Here,  $V$  is the volume of container in litre.

According to the law of mass action

$$K_C = \frac{[NO]^2}{[N_2][O_2]}$$

Substituting the values in the above equation

$$K_C = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

$$K_C = \frac{4x^2}{(a-x)(b-x)}$$

##### B. Calculation of $K_P$ :

All the things being same as above, except pressure. Let  $P$  atmosphere is the pressure at equilibrium.

	$N_2$	+	$O_2$	$\rightleftharpoons$	$2NO$
Initial moles	$a$		$b$		$0$
moles at equilibrium	$(a-x)$		$(b-x)$		$2x$

Total no. of moles =  $(a-x) + (b-x) + 2x = (a+b)$   
 Now, the partial pressure of the above three species can be calculated as below-

$$P_{N_2} = \frac{(a-x)P}{(a+b)}$$

$$P_{O_2} = \frac{(b-x)P}{(a+b)}$$

$$P_{NO} = \frac{(2x)P}{(a+b)}$$

According to the law of mass action

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})}$$

substituting the value of partial pressure in the above equation of  $K_p$  -

$$K_p = \frac{\left(\frac{(2x)P}{(a+b)}\right)^2}{\left(\frac{(a-x)P}{(a+b)}\right)\left(\frac{(b-x)P}{(a+b)}\right)}$$

$$K_p = \frac{4x^2}{(a-x)(b-x)}$$

### 6.3.2 Thermal Dissociation of Phosphorus Pentachloride- ( $\Delta n > 0$ )

A. Calculation of  $K_c$  - Suppose one mole of  $PCl_5$  is taken in a closed container of  $V$  litre. Further at equilibrium  $x$  mol of it dissociated

	$PCl_5$	$\rightleftharpoons$	$PCl_3$	+	$Cl_2$
Initial moles	1		0		0
moles at equilibrium	$(1-x)$		$x$		$x$
Active mass	$\frac{1-x}{V}$		$\frac{x}{V}$		$\frac{x}{V}$

(mol  $l^{-1}$ )

According to law of mass action

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Substituting the values in the above equation.

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1-x}{V}\right)}$$

$$K_c = \frac{x^2}{(1-x)V}$$

The formula of  $K_c$  has  $V$  in the denominator, hence the equilibrium will be affected by  $V$  of the reaction container.

If  $x \ll 1$  then  $1-x \approx 1$

$$\text{So, } K_c = \frac{x^2}{V}$$

$$x^2 = K_c \cdot V$$

$$x^2 \propto V$$

$$x \propto \sqrt{V}$$

If we increase the volume, the dissociation  $x$  is also increased.

#### B. Calculation of $K_p$ -

	$PCl_5$	$\rightleftharpoons$	$PCl_3$	+	$Cl_2$
initial concentration moles at equilibrium	1		0		0
	$1-x$		$x$		$x$

Total no. of moles at equilibrium,

$$(1-x) + x + x = (1+x) \text{ moles}$$

According to law of mass action

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

$$\text{At equilibrium } P_{PCl_3} = \frac{x \times P}{(1+x)}$$

$$P_{Cl_2} = \frac{x \times P}{(1+x)}$$

$$P_{PCl_5} = \frac{(1-x)P}{(1+x)}$$

Substituting the values in the above equation of  $K_p$  -

$$K_p = \frac{\left(\frac{x \times P}{1+x}\right)\left(\frac{x \times P}{1+x}\right)}{\frac{(1-x) \times P}{(1+x)}}$$

$$K_p = \frac{x^2 P}{1-x^2}$$

The equation of  $K_p$  is not independent of pressure.

suppose,  $x \ll 1$  then  $1-x^2 \approx 1$

$$K_p = x^2 P$$

$$x^2 = \frac{K_p}{P}$$

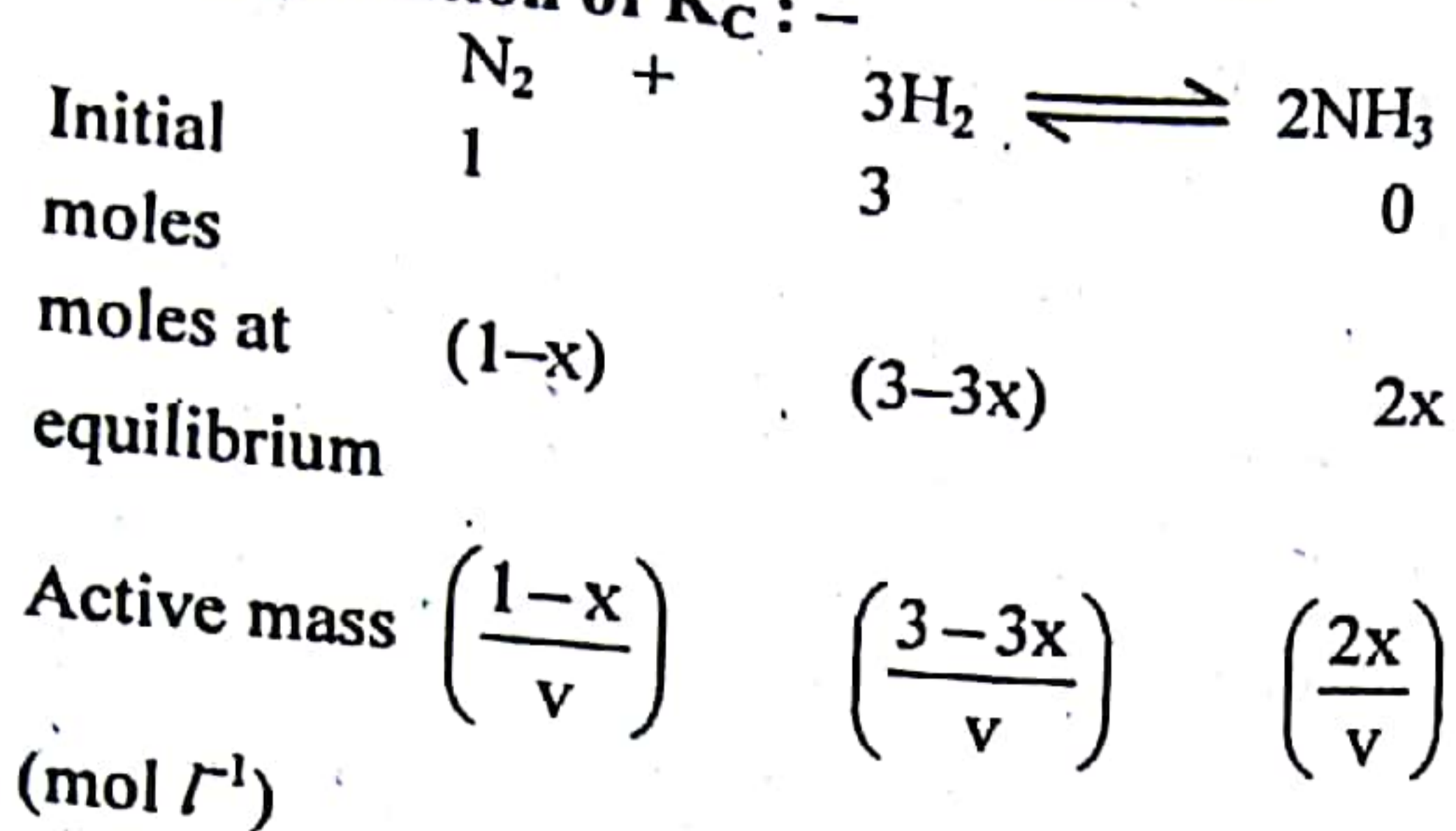
$$x^2 \propto \frac{1}{P}$$

$$x \propto \frac{1}{\sqrt{P}}$$

The degree of dissociation of  $PCl_5$  is inversely proportional to the square root of pressure so, decrease of pressure increases dissociation of  $PCl_5$ .

### 6.3.3 Formation of Ammonia - ( $\Delta n < 0$ )

#### A. Calculation of $K_C$ :-



According to law of mass action

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Substituting the values in the above equation-

$$K_C = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{1-x}{v}\right)\left(\frac{3-3x}{v}\right)^3}$$

$$K_C = \frac{4x^2 v^2}{(1-x)(3-3x)^3}$$

$$K_C = \frac{4x^2 v^2}{27(1-x)^4}$$

The formula of  $K_C$  has  $V$  in the numerator, hence the equilibrium will be affected by  $V$  of the reaction container.

Dependence If,  $x \ll 1$  then,  $(1-x)^4 = 1$

$$K_C = \frac{4x^2 v^2}{27}$$

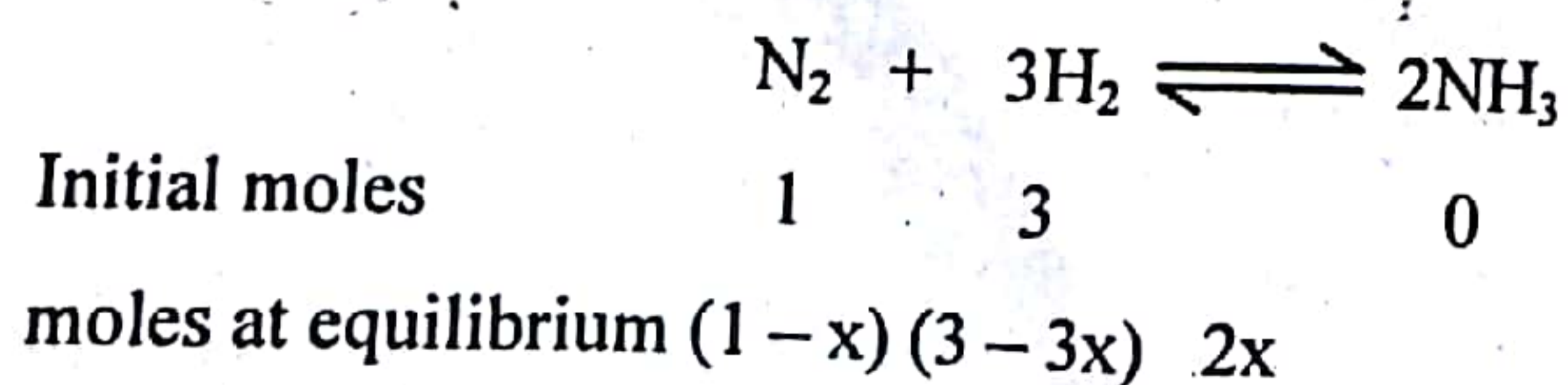
$$x^2 = \frac{K_C}{V^2}$$

$$x^2 \propto \frac{1}{V^2}$$

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

If we increase the volume of the container the degree of dissociation  $x$  is decreased.

#### B. Calculation of $K_P$ :



Total number of moles at equilibrium  
 $= (1-x) + (3-3x) + 2x = (4-2x)$   
 According to the law of mass action

$$K_P = \frac{(P_{NH_3})^2}{(P_{N_2}) \times (P_{H_2})^3}$$

At equilibrium  $P_{NH_3} = \frac{(2x) \cdot P}{(4-2x)}$

$$P_{N_2} = \frac{(1-x) \cdot P}{(4-2x)}$$

$$P_{H_2} = \frac{(3-3x) \cdot P}{(4-2x)}$$

Substituting the values in the above equation of  $K_P$ .

$$K_P = \frac{\left(\frac{2x \cdot P}{4-2x}\right)^2}{\left(\frac{1-x \cdot P}{4-2x}\right) \left(\frac{3-3x \cdot P}{4-2x}\right)^3}$$

$$K_P = \frac{4x^2 (4-2x)^2}{(1-x)(3-3x)^3 P^2}$$

$$K_P = \frac{16x^2 (2-x)^2}{27(1-x)^4 P^2}$$

The equation of  $K_P$  is not independent of pressure suppose,  $x \ll 1$  then,

$$(1-x)^4 = 1, (2-x)^2 = 4$$

$$K_P = \frac{64x^2}{27P^2}$$

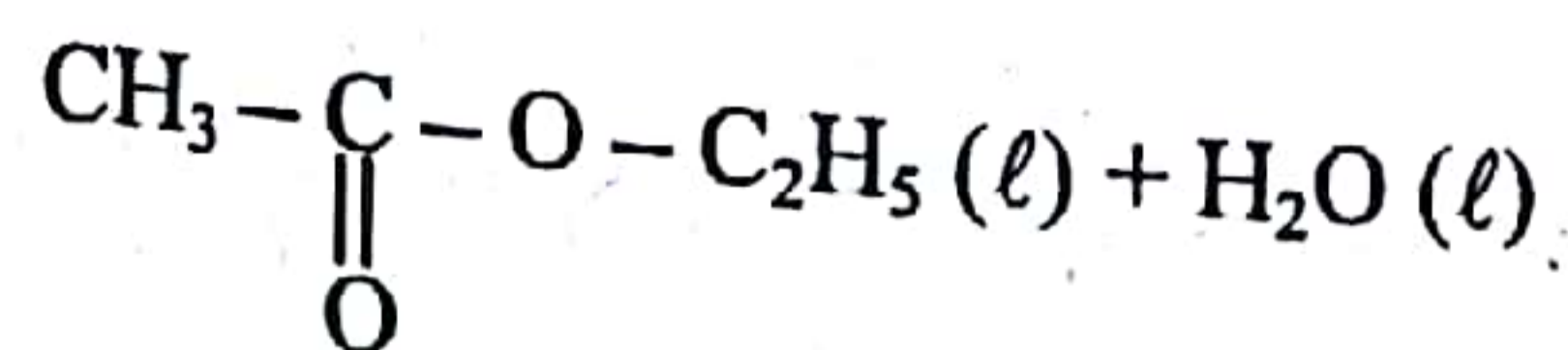
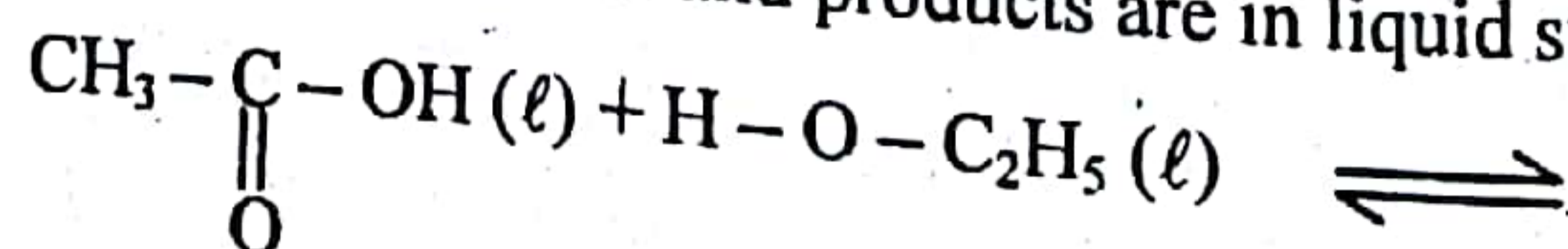
$$x^2 \propto P^2$$

$$x \propto P$$

If we increase the pressure the degree of dissociation  $x$  is also increased.

### 6.3.4 Liquid equilibrium (Ester formation) -

It is proposed by Bartholote and Gill. In this reaction all the reactants and products are in liquid state.



Initial moles	a	b	0	0
Moles at equilibrium	(a-x)	(b-x)	x	x
Active mass (mole l <sup>-1</sup> )	$\frac{a-x}{v}$	$\frac{b-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

According to law of mass action

$$K_C = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

Substituting the values in the above equation

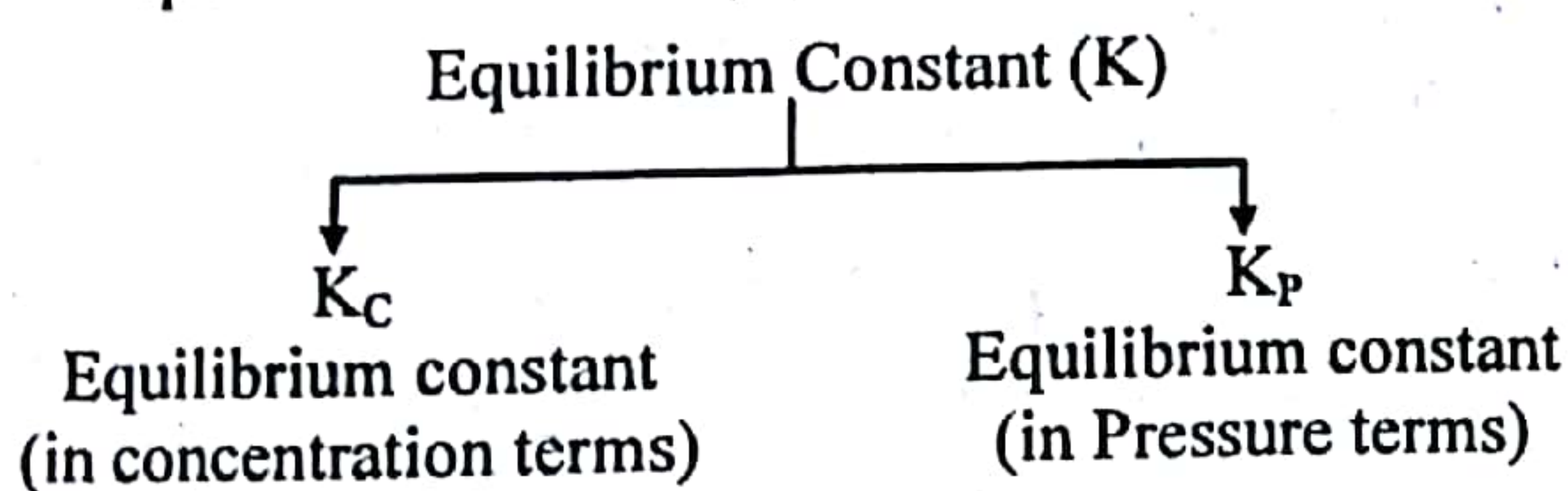
$$K_C = \frac{\left(\frac{x}{v}\right) \times \left(\frac{x}{v}\right)}{\left(\frac{a-x}{v}\right) \left(\frac{b-x}{v}\right)}$$

$$K_C = \frac{x^2}{(a-x)(b-x)}$$

Note: The value of  $K_P$  is equal to unity in liquid and solid equilibrium.

## 7. TYPES OF EQUILIBRIUM CONSTANT

Equilibrium constant (K) is also of two types



### 7.1 Equilibrium concentration constant ( $K_C$ ):

If we use the term concentration in given reaction with the equilibrium constant (K) is called equilibrium concentration constant ( $K_C$ ).

$$K = K_C = \frac{[C][D]}{[A][B]}$$

### 7.2 Equilibrium Pressure constant ( $K_P$ ):

If we use the term pressure in given reaction with the equilibrium constant (K) is called equilibrium pressure constant ( $K_P$ ).

$$K_P = \frac{P_C \times P_D}{P_A \times P_B}$$

where  $p_A$  = Partial pressure of A  
 $p_B$  = Partial pressure of B

$p_C$  = Partial pressure of C  
 $p_D$  = Partial pressure of D

Partial pressure of a gas given by the following formula.

$$p = \frac{\text{No. of mole of given gas at equilibrium}}{\text{Total no. of moles at equilibrium}} \times P$$

or  $p = \text{mole fraction} \times P$ .

Here, P is the total pressure.

### 7.3 Factors which do not influence equilibrium constant:

- Concentration of reactants and products.
- Pressure and volume.
- Presence of catalyst.
- Addition of the inert gas at constant Pressure and volume.

### 7.4 Factors influence the equilibrium constant:

- Mode of representation of chemical reaction.
- Stoichiometry of reaction.
- Temperature.

#### A. Mode of representation of reaction –

If we take reaction  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$

Then, we write the value of equilibrium constant for the above reaction as following.

$$K_{C_1} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \quad \dots\dots (i)$$

Now, if we take reaction  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$

Then, we write the value of equilibrium constant  $K_{C_2}$  for above reaction as following

$$K_{C_2} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{1}{K_{C_1}} \quad \dots\dots (ii)$$

#### B. Stoichiometry of the reaction –

Method of writing the equation of the reversible reaction is called as stoichiometry of the reaction.

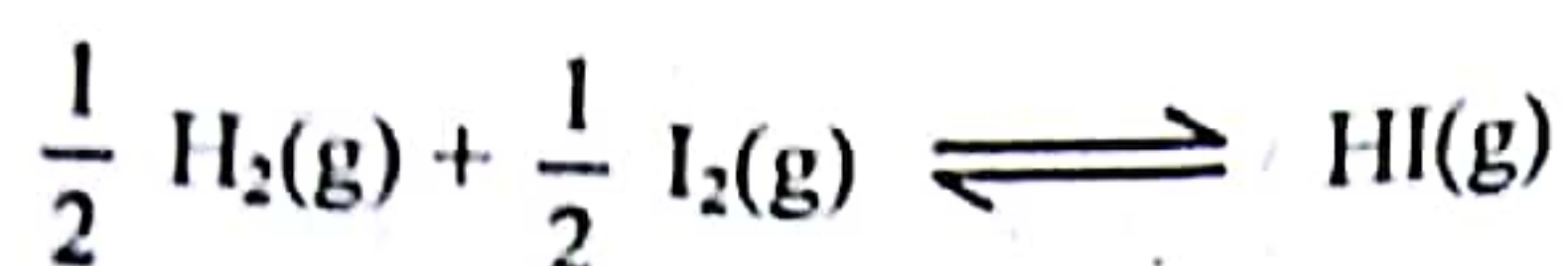
Now, we consider the formation of HI(g) by the combination of  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$ .



The expression of its equilibrium constant is-

$$K_{C_1} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

If the equation of above reaction is written by following method –



The expression for the equilibrium constant is -

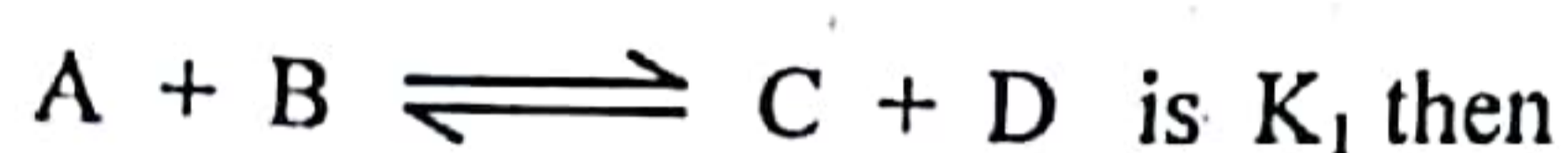
$$K_{C_2} = \frac{[\text{HI}]}{[\text{H}_2]^{1/2} [\text{I}_2]^{1/2}}$$

on the basis of comparing both the equilibrium constant equation.

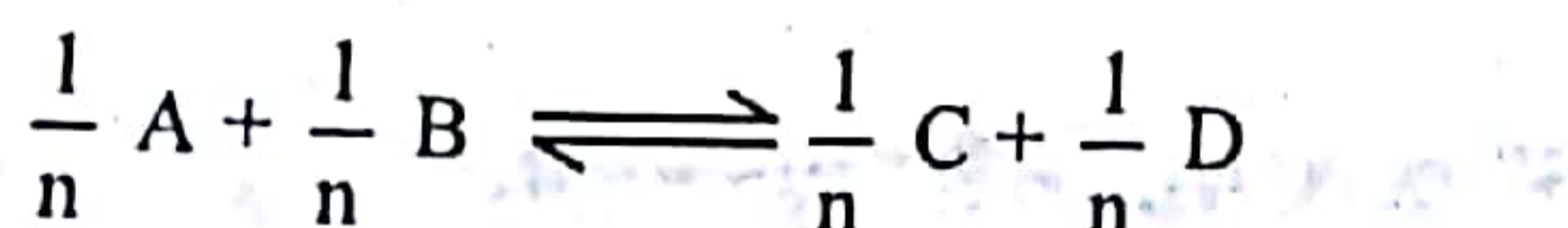
$$K_{C_2} = \sqrt{K_{C_1}} \text{ or } (K_{C_1})^{1/2}$$

**Result** - When we divide a reaction by a factor 'n' in the equation, the value of new equilibrium constant is equal to the root of n of the previous equilibrium constant.

**For Example** - Suppose, the equilibrium constant for the following reaction.



for the reaction



the value of the equilibrium constant  $K_2$  is equal to  $\sqrt[n]{K_1}$  or  $(K_1)^{1/n}$ .

**C Temperature** - Increase in temperature favours the endothermic reaction and decrease in temperature favours the exothermic reaction for the forward reaction.

Means for exothermic reactions, the value of  $K_c$  and  $K_p$  decrease with rise in temperature while for endothermic reactions, the value of  $K_c$  and  $K_p$  increases with rise in temperature. This type of variation in equilibrium constant with temperature given by **Van't Hoff** equation as follows -

$$\log K_2 - \log K_1 = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\text{or } \log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

Where,

$K_2$  = equilibrium constant at temperature  $T_2$

$K_1$  = equilibrium constant at temperature  $T_1$

$\Delta H$  = Energy of reaction at constant temperature

$R$  = Molar gas constant

According to the temperature, reaction are of three types.

(a) Athermic or Non-thermic reaction means  $\Delta H = 0$

$$\log K_2 - \log K_1 = 0$$

$$\log K_2 = \log K_1$$

**Result** : - There is no effect of temperature on this type of reaction.

(b) Endothermic reaction  $\Rightarrow \Delta H = (+)$  ve

$$\log K_2 - \log K_1 = (+) \text{ ve,}$$

$$\text{means } K_2 > K_1$$

**Result** : - On increase of temperature equilibrium constant will also increase for this type of reaction.

(c) Exothermic reaction  $\Rightarrow \Delta H = (-)$  ve

$$\log K_2 - \log K_1 = (-) \text{ ve,}$$

$$\text{means } K_2 < K_1$$

**Result** - On the increase of temperature equilibrium constant will decreases for exothermic reaction.

### 7.5 Units of $K_p$ and $K_c$

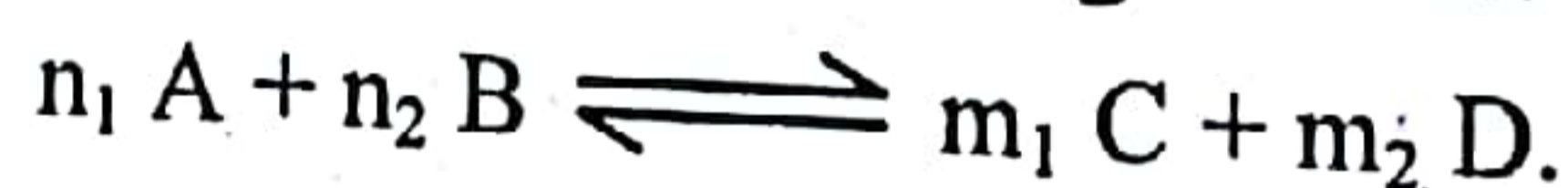
Partial pressure are measured by the unit of atmospheres and therefore units of  $K_p$  will be (Atmospheres) $^{\Delta n}$ .

In the same way, the concentration is expressed in the term of moles per litre. Therefore, units of  $K_c$  will be (moles litre $^{-1}$ ) $^{\Delta n}$ .

Value of $\Delta n$	Units of $K_p$	Units of $K_c$
0	No Unit	No unit
> 0	(atm) $^{\Delta n}$	(moles $\ell^{-1}$ ) $^{\Delta n}$
< 0	(atm) $^{\Delta n}$	(moles $\ell^{-1}$ ) $^{\Delta n}$

### 7.6 Relation between $K_p$ and $K_c$ :

Let us consider the following reaction



The value of  $K_c$  for the reaction is,

$$K_c = \frac{[\text{C}]^{m_1} [\text{D}]^{m_2}}{[\text{A}]^{n_1} [\text{B}]^{n_2}}$$

According to gas law  $PV = nRT$

$$P = \left( \frac{n}{V} \right) RT \quad \dots\dots (i)$$

Here  $\frac{n}{V} = \frac{\text{no. of moles}}{\text{lit.}} = [ ] = \text{Active mass}$

$$K_p = \frac{(p_C)^{m_1} (p_D)^{m_2}}{(p_A)^{n_1} (p_B)^{n_2}}$$

on putting the value of 'p' in the formula of  $K_p$  by the equation.

..... (i)

$$K_p = \frac{([C]RT)^{m_1} ([D]RT)^{m_2}}{([A]RT)^{n_1} ([B]RT)^{n_2}}$$

$$K_p = \frac{[C]^{m_1} [D]^{m_2} (RT)^{m_1+m_2}}{[A]^{n_1} [B]^{n_2} (RT)^{n_1+n_2}}$$

$$K_p = K_c (RT)^{(m_1+m_2)-(n_1+n_2)}$$

$$K_p = K_c (RT)^{\Delta n}$$

$$[\Delta n = (m_1 + m_2) - (n_1 + n_2)]$$

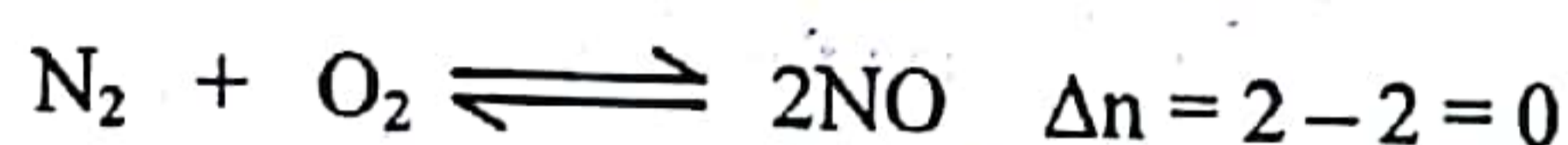
$\Delta n$  = number of moles of product – number of moles of reactant.

T = Absolute temperature.

Note :  $\Delta n$  only includes gaseous moles.

I. on the basis of  $\Delta n$ , the reactions are of three types.

(a) Reaction in which  $\Delta n = 0$



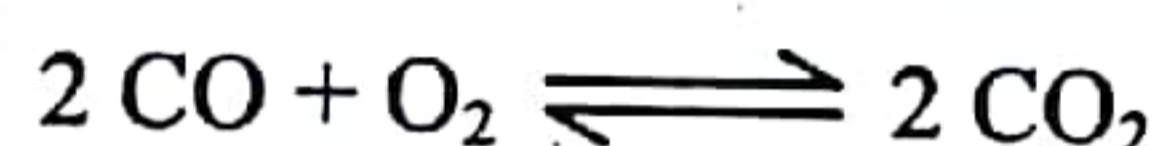
By the relation of

$$K_p = K_c (RT)^{\Delta n} \quad \because \Delta n = 0$$

$$K_p = K_c (RT)^0$$

So,  $K_p = K_c$

(b) Reaction in which the value of  $\Delta n$  is negative-



$$\Delta n = 2 - 3 = -1$$

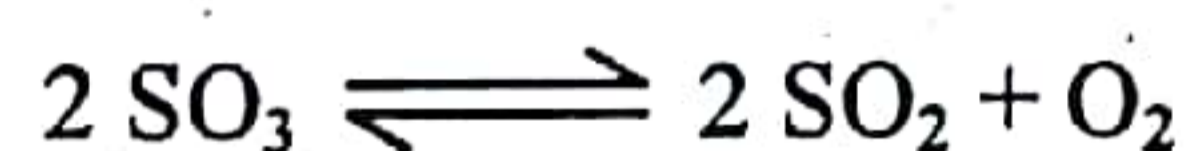
By the relation of  $K_p = K_c (RT)^{\Delta n}$

$$K_p = K_c (RT)^{-1}$$

or  $K_p = \frac{K_c}{RT}$  means  $K_p \times RT = K_c$

So,  $K_c > K_p$

(c) Reaction in which the value of  $\Delta n$  is positive-



$$\Delta n = 3 - 2 = +1$$

By the relation of  $K_p = K_c (RT)^{\Delta n}$

$$K_p = K_c (RT)^{+1}$$

means  $K_p = K_c \times RT$

So,  $K_p > K_c$

II. On the basis of the value of pressure, reactions are also of three types as follows-

(a) Reaction in which the value of  $\Delta n = 0$



$$\Delta n = 2 - 2 = 0$$

$$K_p = K_c (RT)^{\Delta n}$$

According to relationship

$$K_p = K_c (RT)^0 \quad \text{means } K_p = K_c$$

In this type of reaction, there is no effect of pressure.

(b) Reaction in which the value of  $\Delta n$  is (+)ve.



$$\Delta n = 2 - 1 = +1$$

In this type of reaction, when pressure is increases then the degree of dissociation decreases.

(c) Reaction in which the value of  $\Delta n$  is (-)ve.



$$\Delta n = 2 - 3 = -1$$

In this type of reaction, when the pressure is increases then the degree of dissociation is also increases.

## 8. LE-CHATELIER'S PRINCIPLE

(a) According to this principle, if a system in equilibrium is subjected to a change of temperature, pressure or concentration, then the equilibrium shifts in a direction, as the effect of the changed condition is nullified.

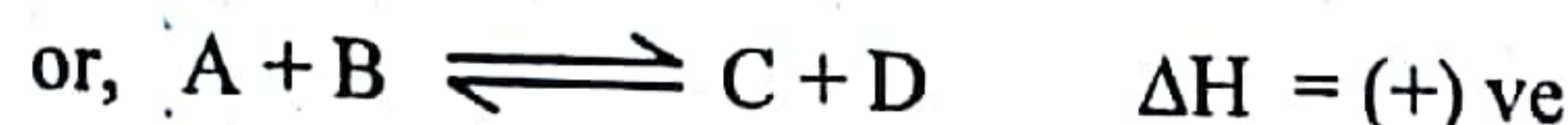
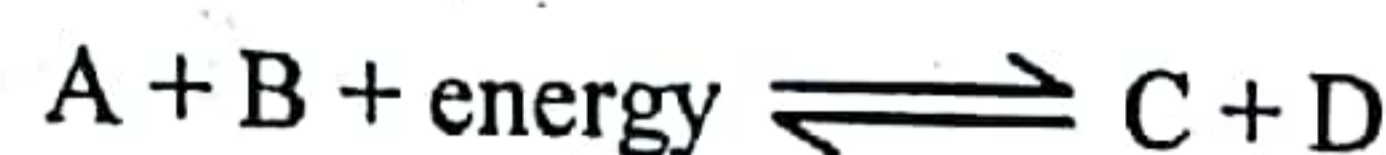
(b) It explains the effect of changes in temperature, pressure and concentrations on various reactions in equilibrium.

### A. Effect of change in temperature -

(a) If the temperature is raised, reaction will proceed in that direction in which the effect of raised heat can be destroyed so that the temperature on the system remains constant.

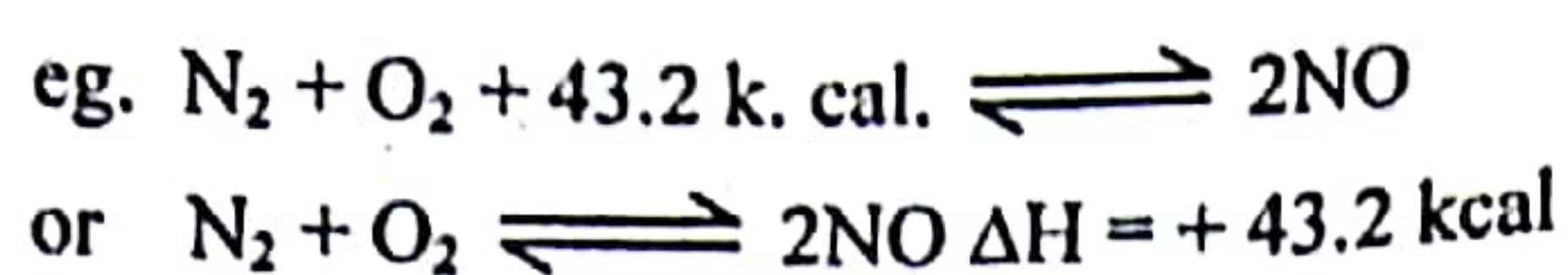
(b) Athermic or nonthermic reaction not affected by the change in temperature.

(i) Endothermic reaction -

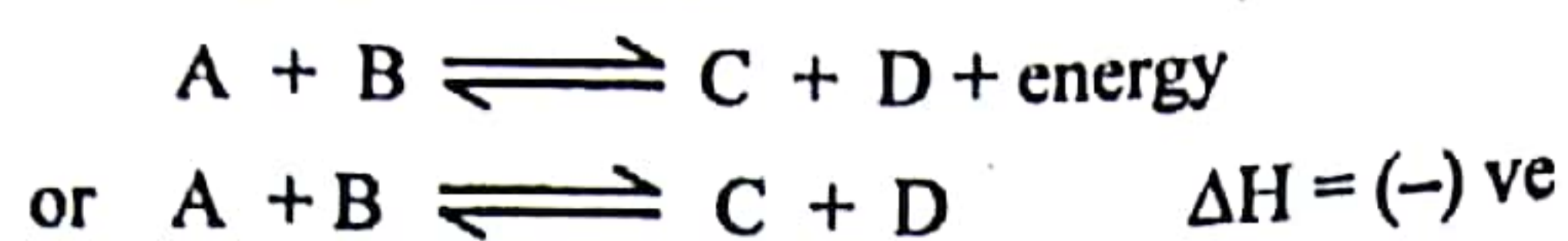


Here,  $K = \frac{[C][D]}{[A][B]}$

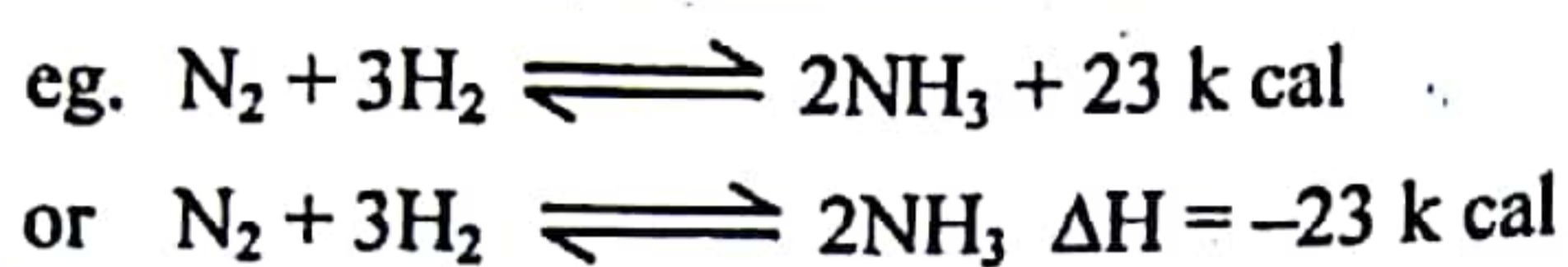
If we increase in temperature, the equilibrium shifts in forward direction of endothermic reaction which proceed with absorption of heat.



(ii) Exothermic reaction :-



If we increase in temperature, the equilibrium shifts in backward direction of exothermic reaction which proceed with evolution of heat.

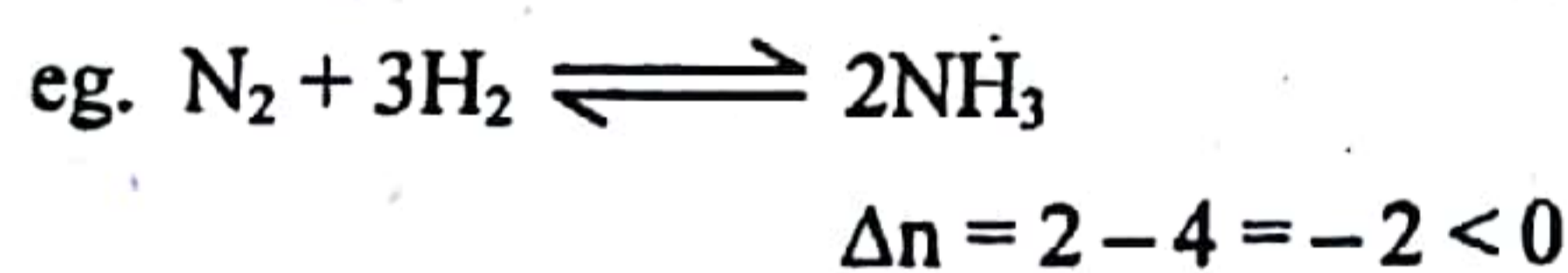


### B. Effect of change in pressure :

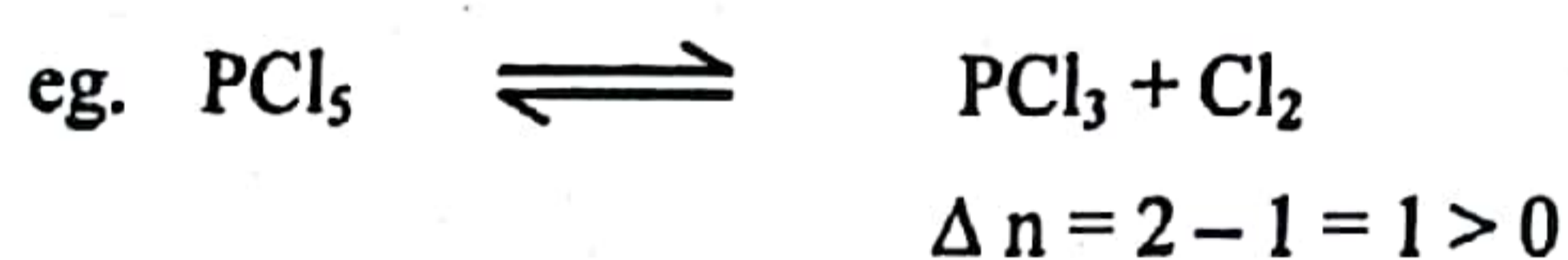
According to Le-Chatelier's principle, if the pressure is increased, reaction will take place in that direction, which will bring about lowering of pressure or lowering in number of moles.

This implies that -

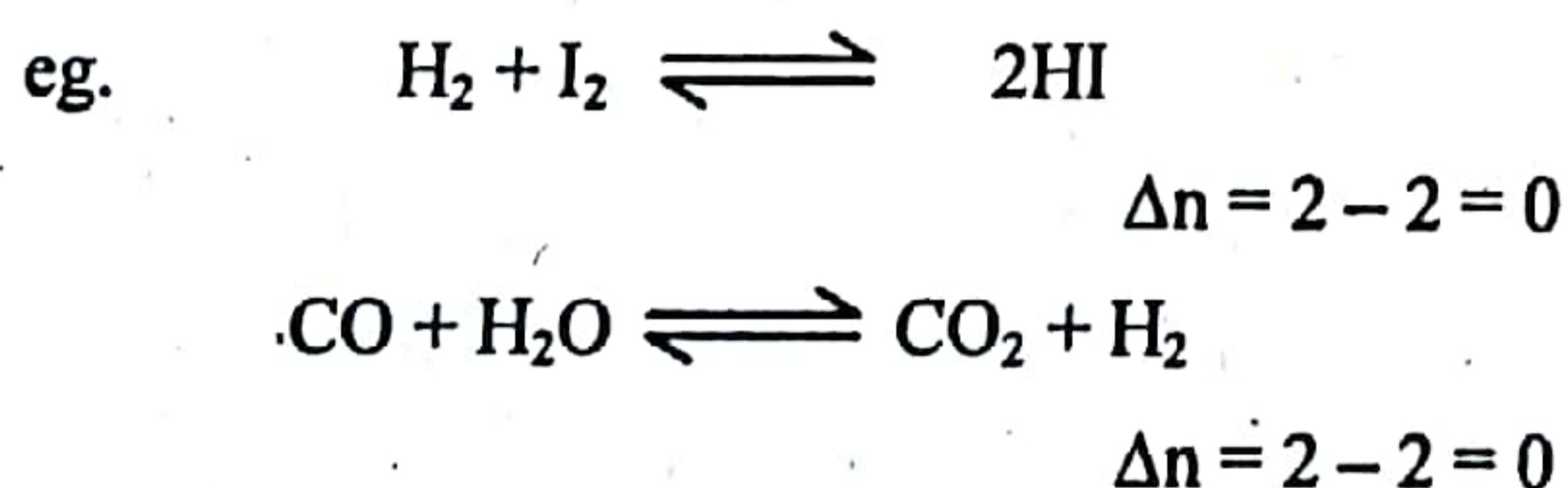
(i) Increase of pressure shifts the equilibrium in that direction where the number of moles decreases or  $\Delta n < 0$ .



(ii) Decrease of pressure shifts the equilibrium in that direction where the number of moles increase or  $\Delta n > 0$ .



(iii) Change of pressure has no effect, if the number of moles of gaseous product remain same as the gaseous reactants i.e.  $\Delta n = 0$



### C. Effect of change in concentration :

If in any reversible reaction, concentration of the reactants is increased at equilibrium state, the equilibrium shifts in the forward direction, means more product are formed. It is due to the fact that increase in concentration of reactant increases the number of effective collisions between the reactant molecule.

Similarly, if the concentration of products is increased, then to maintain the equilibrium constant, concentration of reactant has to increase and backward reaction is favoured.

Thus, it implies as -

(i) Increase in the concentration of any reactants, the equilibrium shifts in the forward direction.  
 (ii) Increase in the concentration of products, the equilibrium shifts in the backward direction.

Note : addition or removal of gaseous species only can affect equilibrium position.

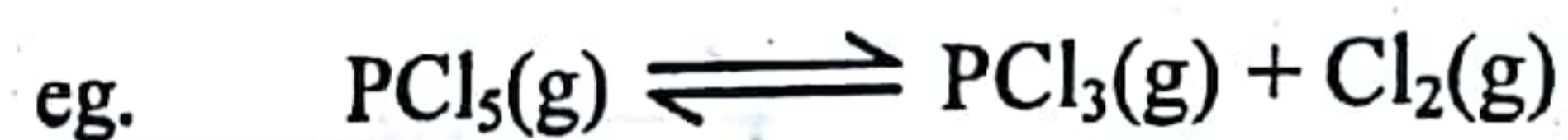
### D. Effect of addition of catalyst :

There is no effect on equilibrium by the addition of catalyst. It is due to the fact that the catalyst increase the rate of forward and backward reaction equally i.e. the catalyst helps in acquiring the equilibrium state quickly.

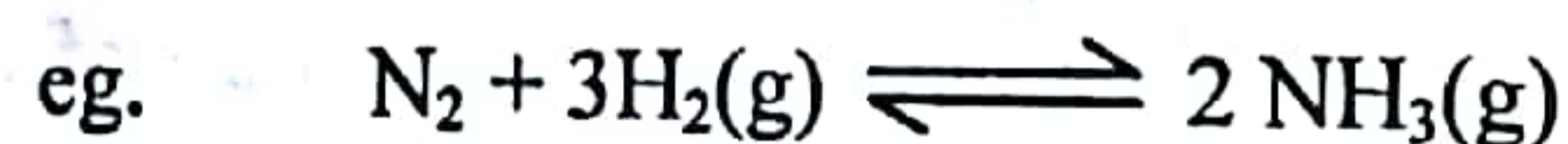
### E. Effect of addition of inert gas :

Addition of inert gas at constant pressure to the equilibrium system causes the under mentioned effect.

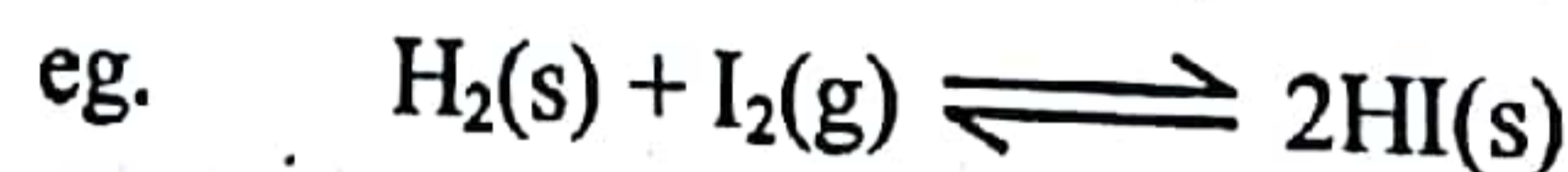
(i) For the equilibrium system where the  $\Delta n > 0$ , the addition of inert gas at constant pressure increases the total volume of the system and decreases the molar concentration of reactant and product and the dissociation of reactant increases.



(ii) For the equilibrium system where  $\Delta n < 0$ , the addition of inert gas at constant pressure will shift the equilibrium to the backward direction.



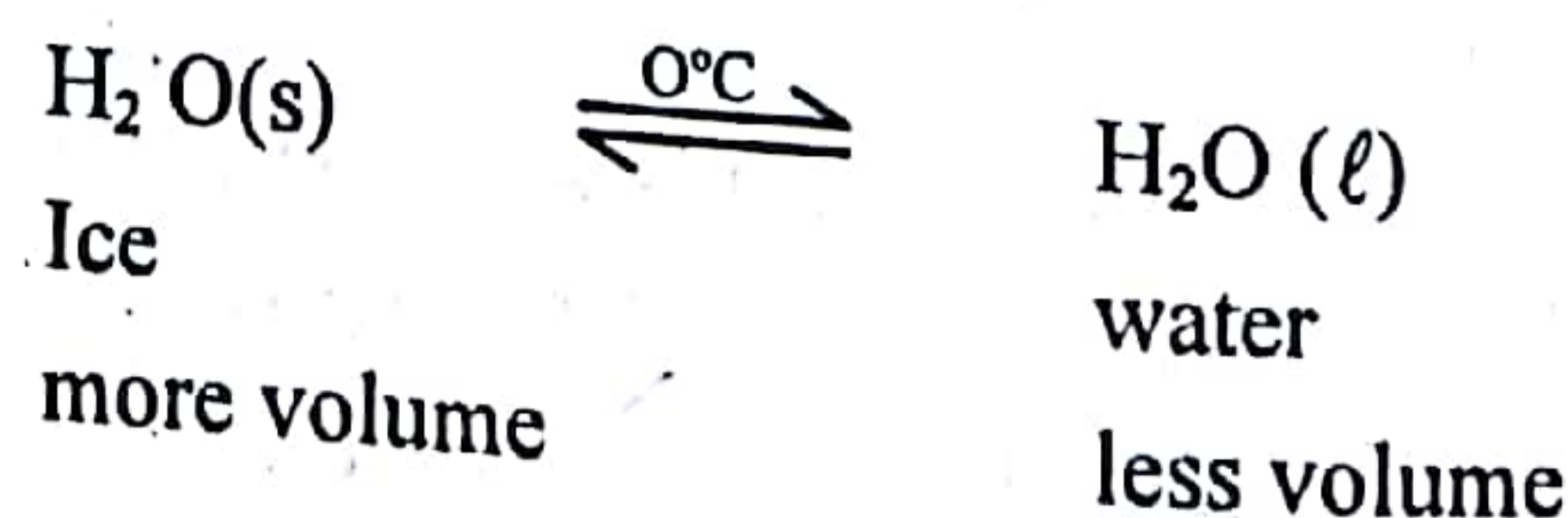
(iii) For the equilibrium system where  $\Delta n = 0$ , the addition of inert gas at constant pressure has no effect.



(iv) The addition of inert gas at constant volume has no effect on the equilibrium system.

## 8.1 Application of Le chatelier principle on physical equilibria -

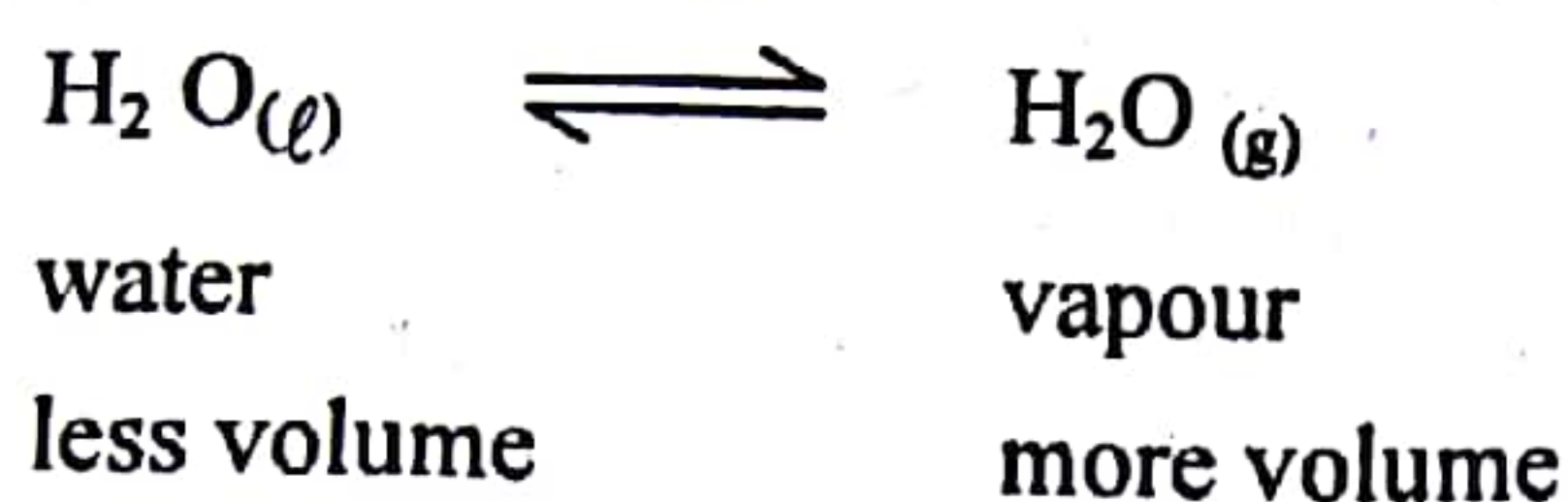
### A. Melting of Ice :





Since, if we increase the pressure, the equilibrium will be shifted in the direction of less volume. Hence, the rise of pressure, more ice will melt into water i.e. melting point of ice is decreased by rise of pressure.

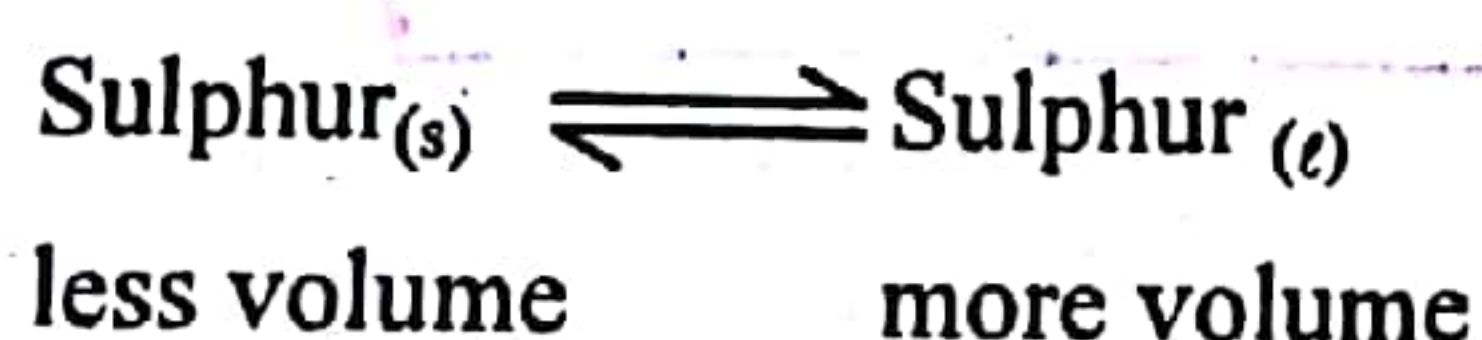
### B. Vaporization of liquid -



Vaporization of a liquid is endothermic process in the nature i.e. the evaporation of a liquid into its vapour is completed by absorption of heat, so the rise of temperature will favour vaporization.

On the other hand in this process, on increase of pressure the equilibrium will shift in the direction of less volume means water cannot be converted into vapour and boiling point increases.

### C. Melting of Sulphur :



On increase in pressure, the equilibrium will shift towards less volume means solid is not converted into liquid and thus, melting point of sulphur increases.

under the same conditions, the volume occupied by  $(1 + \alpha)$  moles at equilibrium would be  $(1 + \alpha) V$  litre.

Since  $\text{Density} \propto \frac{1}{\text{Volume}}$

Therefore  $D \propto \frac{1}{V}$

$$d \propto \frac{1}{(1+\alpha)V}$$

or  $\frac{D}{d} = \frac{1}{\frac{1}{(1+\alpha)V}} = (1 + \alpha)$

or  $\alpha = \frac{D}{d} - 1 = \frac{D-d}{d}$

or  $\alpha = \frac{D-d}{(n-1)d}$

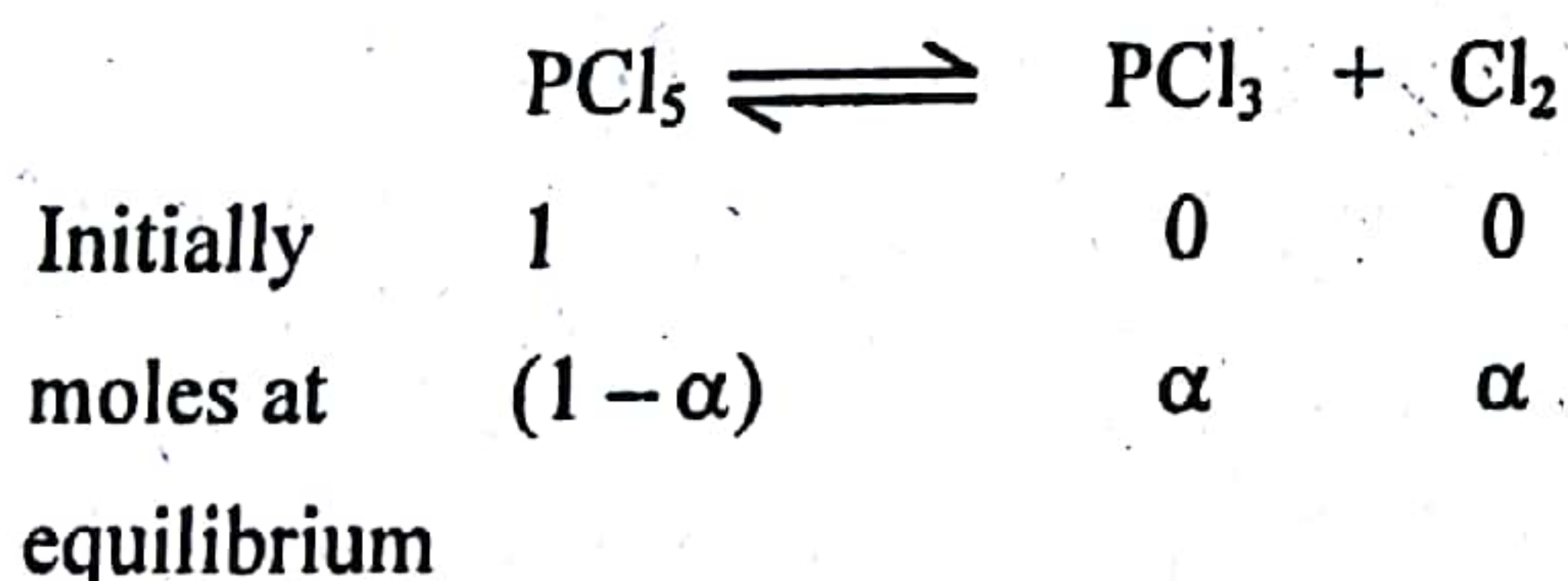
**Note:** When one mole of a reactant on dissociation gives 'n' moles of gaseous products, the above equation takes in the form of

$$\alpha = \frac{D-d}{(n-1)d}$$

## 9. CALCULATION OF DEGREE OF DISSOCIATION BY VAPOUR DENSITY MEASUREMENT :

In those type of reactions in which there is a change in the number of moles after dissociation, the extent of dissociation can be determined by vapour density measurement.

Let us, consider the following reaction -



(Here ' $\alpha$ ' is the degree of dissociation)

Total number of moles at equilibrium

$$= (1 - \alpha) + \alpha + \alpha = (1 + \alpha)$$

Now, the V is the volume occupied by 1 mol of  $\text{PCl}_5(g)$  which have vapour density is 'D' before dissociation and after dissociation is 'd'. So,

# KEY CONCEPTS

Those substance which allow the electric current to pass through them are called electric conductors and property is called electric conductivity.

On the basis of Electric conductivity, substances are of two types -

## 1.1 Nonconductors :

Those substance which do not allow the electric current to pass through them are called nonconductors. eg. All covalent compounds & nonmetals.

## 1.2 Conductors :

Those substance which allow the electric current to pass through them are called conductors. eg. all metals, alloys, all acid and bases, salt and graphite etc.

On the basis of conducting units conductors are of two types -

### 1.2.1 Metallic or Electric Conductors :

Electricity conduct them due to the presence of free and mobile electron which act as electricity conducting unit called metallic or electric conductors. eg. Metals, Alloys, Graphite, Gas, Carbon etc.

### 1.2.2 Ionic Conductors or Electrolytes :

Conductors in which the current is passes through them due to the presence of free ions are called **Ionic Conductors or Electrolyte or Electrolytic conductors.**

Ionic conductors are further divided into two types on the basis of their strengths -

#### (a) Strong electrolytes :

(i) Those substance which are almost completely ionize into ions in their aqueous solution are called strong electrolytes.

(ii) Degree of ionisation for this type of electrolyte is one i.e.  $\alpha \cong 1$ . eg. HCl, H<sub>2</sub>SO<sub>4</sub>, NaCl, HNO<sub>3</sub>, KOH, NaOH, HNO<sub>3</sub>, AgNO<sub>3</sub>, CuSO<sub>4</sub>, etc. Means all strong acids and bases and all types of salts.

#### (b) Weak electrolytes :

(i) Those substance which are ionize to a small extent in their aqueous solution are known weak electrolytes. eg. H<sub>2</sub>O, CH<sub>3</sub>COOH, NH<sub>4</sub>OH,

HCN, HCOOH, Liq. SO<sub>2</sub> etc. Means all weak acids and bases.

(ii) Degree of ionization for this types of electrolytes in  $\alpha \lll 1$ .

## IONISATION OF WEAK ELECTROLYTES :

### 2.1 Ionisation :

The process in which molecules of acids bases and salts when melted or dissolve in water dissociate into ions is called ionization.

#### 2.1.1 Ionic Equilibrium :

Weak electrolytes are partially ionised in aqueous solution and an equilibrium is situated between the ionised and unionised electrolyte. This type of equilibrium is known as ionic equilibrium.

Let us consider an acid HA which when dissolved in water, an equilibrium will setup between ionised and unionised acid molecule as below -



On applying the law of mass action, the equilibrium constant K is written as -

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

Since in an aqueous solution, the molar concentration of water is constant i.e. [H<sub>2</sub>O] = constant. Therefore K [H<sub>2</sub>O] replaced by a new constant K<sub>a</sub> which is known as ionisation acid constant or dissociation constant of acid. Thus,

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

'K<sub>a</sub>' is the characteristic of the individual acid. From the above equation K<sub>a</sub> is directly proportional to [H<sup>+</sup>] concentration hence, greater the K<sub>a</sub> of an acid, more will be acidity.

Assume that the initial concentration of C is moles/lit. and  $\alpha$  is the degree of ionization then

	$HA + H_2O \rightleftharpoons H^+ + A^-$		
Initial concentration	C	0	0
Equilibrium concentration	$(1 - \alpha)C$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{\alpha^2 C}{(1-\alpha)}$$

The degree of ionisation  $\alpha$  is very small as compared to 1 means  $\alpha \ll 1$ . So,  $1 - \alpha = 1$

Thus,  $K_a = \alpha^2 c$ ;  $\alpha^2 = \frac{K_a}{C}$

or  $\alpha = \sqrt{\frac{K_a}{C}}$   $\therefore \frac{1}{C} = V$

So,  $\alpha = \sqrt{K_a \times V}$

This equation is known as Ostwald dilution law equation.

Similarly, for a weak base we have

$\alpha = \sqrt{\frac{K_b}{C}}$   $\therefore \frac{1}{C} = V$

So,  $\alpha = \sqrt{K_b \times V}$

Where,

- $K_b$  is the dissociation constant of weak base.
- $C$  is the initial concentration
- $\alpha$  is the degree of dissociation of weak base.

Hence, according to Ostwald dilution law, the degree of ionization of weak electrolyte is directly proportional to the square root of volume containing one mole of electrolyte or Inversely proportional to the square root of its molar concentration.

**3. ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION OR IONIZATION**

- (a) When an electrolyte dissociates into water, it gives two types of charged particles called ions.
- (b) Ions which carry (+) ve charge and move towards cathode are called as 'Cations' while ions carrying (-) ve charge and moving towards anode called as 'anion'.
- (c) Every electrolytic solution is always neutral in nature.
- (d) Quantity or part of electrolyte which is ionized or decomposed or dissociate called as "Degree of Ionisation".
- (e) Electrolyte which gives  $H^+$  ions after dissociation in the aqueous solution is called as acid while that which gives  $OH^-$  after dissociation in the aqueous solution is called as base.

(f) Acidic strength of acids is directly proportional to the dissociation constant  $k_a$ .

$pk_a = -\log k_a$

Thus, Acidic strength  $\propto k_a$

$\propto \frac{1}{pk_a}$

$\propto pk_b$

$\propto \frac{1}{k_b}$

(g) Similarly basic strength of bases is directly proportional to  $K_b$ .

$pk_b = -\log k_b$

Basic strength of base  $\propto k_b$

$\propto \frac{1}{pk_b}$

$\propto pk_a$

$\propto \frac{1}{k_a}$

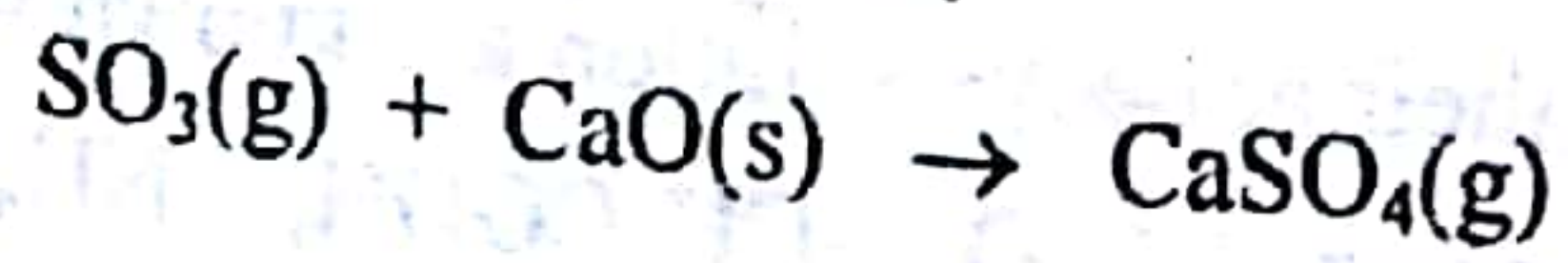
(h) Conductivity of solution depends upon the number of ions produced by the electrolyte, such as -

Conduction of solution  $\propto$  number of ions produced by the electrolyte

- (i) Solution of strong electrolyte has more electric conductivity property as compared to weak electrolyte.
- (j) Only weak electrolyte followed the law of mass action and Ostwalds dilution law.
- (k) When electricity passed through in the electrolytic solution, it gives only direction to movement of ions towards the electrodes.
- (l) Movement of ions is inversely proportional to the molecular mass or atomic mass of ions.

**3.1 Limitations of Arrhenius Concept :-**

- (a)  $H^+$  and  $OH^-$  ions exist as hydrated ions.
- (b) He was unable to explain the acidic nature of  $CO_2$ ,  $SO_2$  etc. and basic nature of  $NH_3$ ,  $CaO$ ,  $Na_2CO_3$  etc.
- (c) He could not explain the acid base reaction in the absence of water.



### 3.2 Factors affecting the degree of ionisation :-

(a) **Temperature** – With the rise in temperature, the degree of dissociation of an electrolyte in solution increased. Thus,

$$\text{Degree of dissociation} \propto \text{Temperature}$$

(b) **Dilution** :- On the increasing of dilution, the degree of dissociation increases. But at infinite dilution, there is no effect on the degree of dissociation.

(c) **Concentration of the solution** :-

Degree of dissociation

$$\propto \frac{1}{\text{Concentration of solution}}$$

$$\propto \frac{1}{\text{Amount of solute in given volume or wt. of solution}}$$

$$\propto \text{Amount of solvent}$$

(d) **Nature of Solvent** :- Higher the dielectric constant of a solvent, more is its dissociation power or ionising power. Thus

Degree of ionisation or dissociation of an electrolyte  $\propto$  dielectric constant of solvent.

**Dielectric constant** :- The dielectric constant of solvent is a measure of its tendency to weaken the forces of attraction between oppositely charged ions of the given electrolyte or the force of attraction applied by solvent molecules on solute molecule is defined as Dielectric constant of solvent.

Note :- Water is the most powerful ionizing solvent as its dielectric constant is highest.

(e) **Presence of Common Ion** :- In the presence of a strong electrolyte having common ion, the degree of dissociation of an electrolyte decreases. eg. Ionisation of  $\text{CH}_3\text{COOH}$  is suppressed in the presence of  $\text{HCl}$  due to common  $\text{H}^+$  ions.

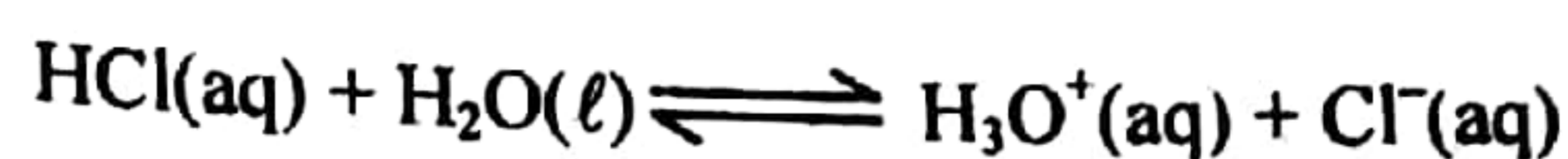
(f) **Nature of Electrolyte** :- At constant temperature, electrolytes ionize to a different extent in their solutions of same concentration.

## 4. BRONSTED AND LOWRY CONCEPT OF ACIDS & BASES

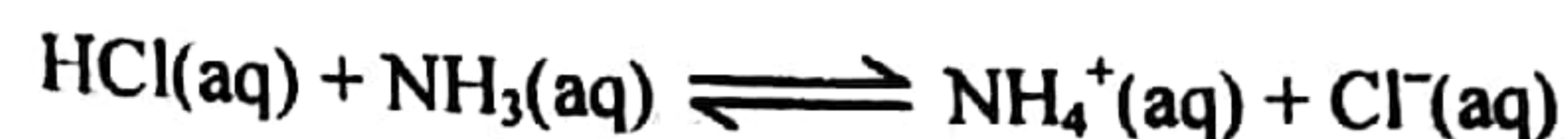
### 4.1 Postulates :-

- (1) Acid - Proton ( $\text{H}^+$ ) donor
- (2) Base - Proton ( $\text{H}^+$ ) acceptor

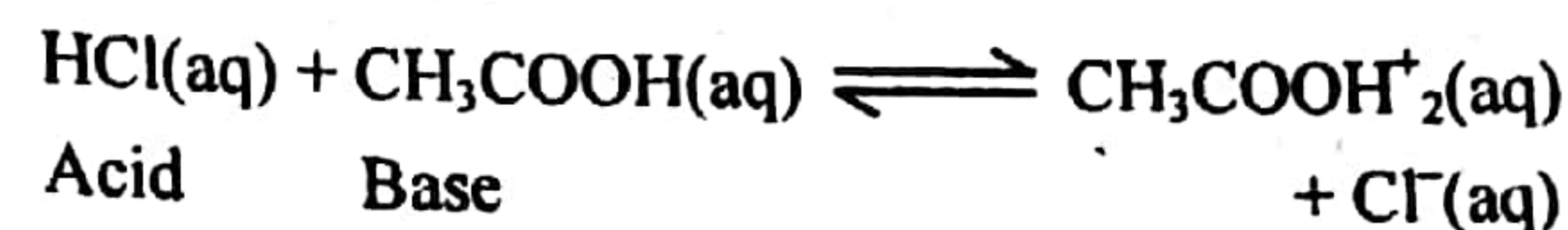
e.g.



Acid      Base



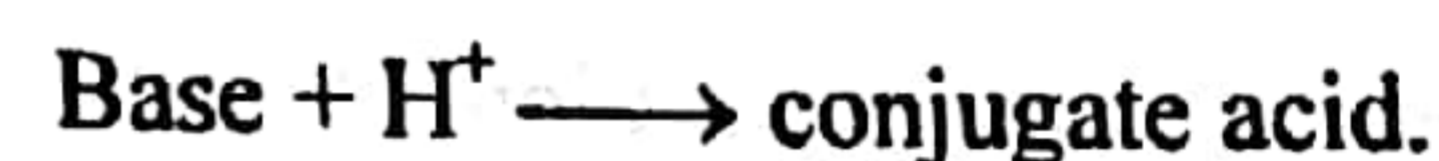
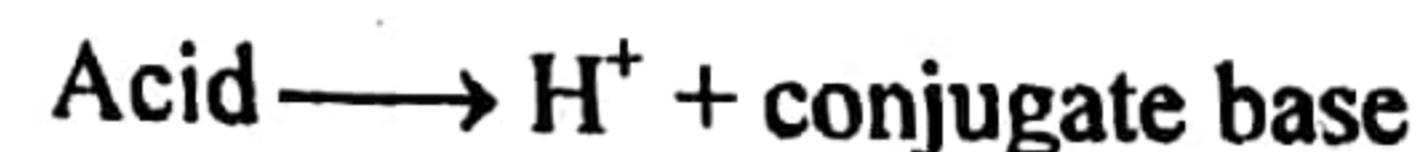
Acid      Base



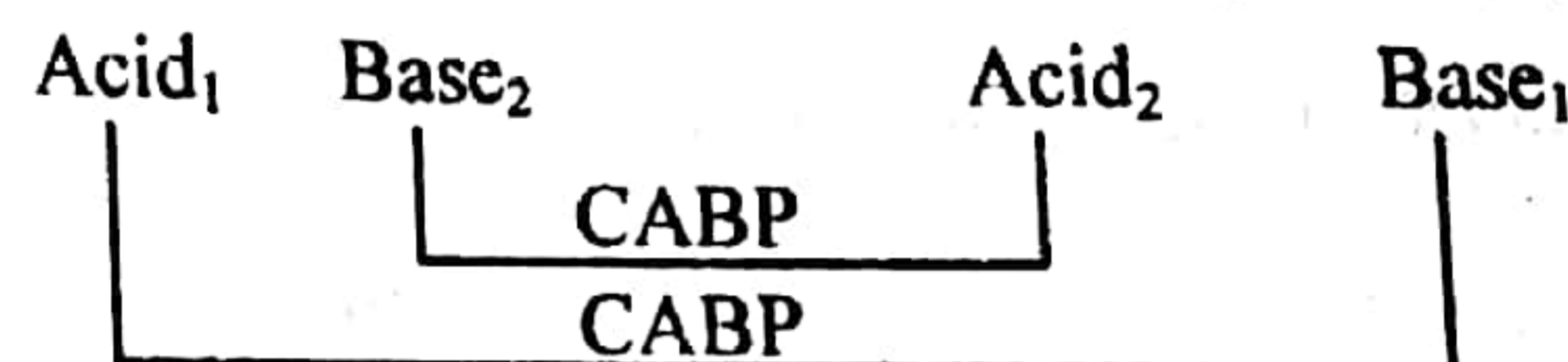
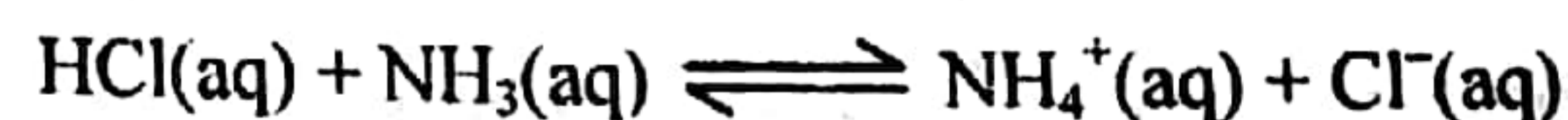
Note :- Here  $\text{CH}_3\text{COOH}$  has a less tendency to donate  $\text{H}^+$  than  $\text{HCl}$ , therefore  $\text{CH}_3\text{COOH}$  acts as a weak base.

### 4.2 Conjugate Acid-Base Pair (CABP) :-

In an acid-base reaction



e.g.



Note:- A CABP is different from each other only by single proton.

e.g.

$\text{HSO}_4^-$  is the conjugate base of  $\text{H}_2\text{SO}_4$  but  $\text{SO}_4^{2-}$  is not.

### 4.3 Relative strength of Acids/Bases :-

Any Species and its conjugate species are opposite of each other in terms of strength. e.g.

<u>Acid (or Base)</u>	<u>Conjugate Base (or Acid)</u>
(i) Weak	Strong
(ii) Strong	Weak

(i) Weak

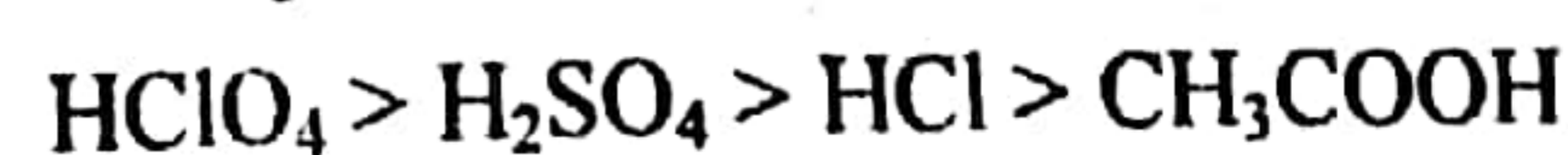
Strong

(ii) Strong

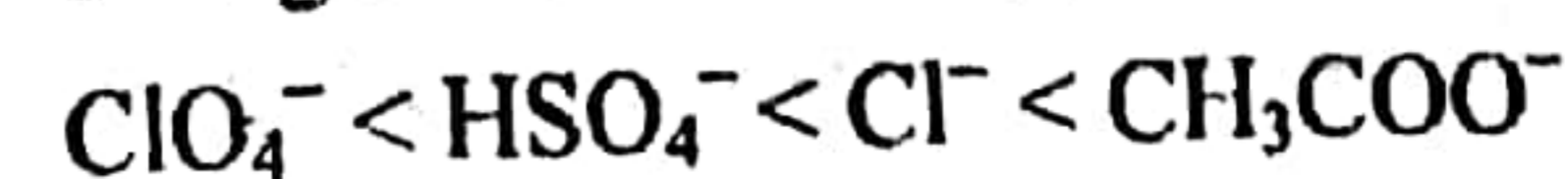
Weak

e.g.

Strength order of acids.

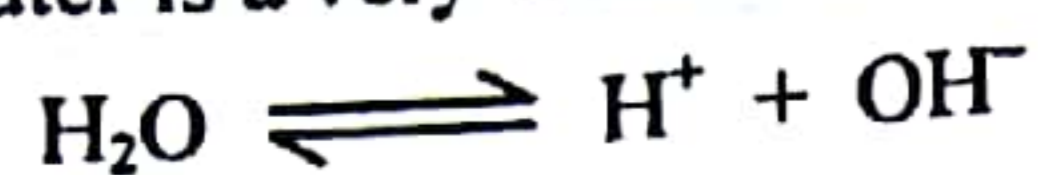


strength order of conjugate bases



## 5. IONIC PRODUCT OF WATER

Pure water is a very weak electrolyte -



on applying the law of mass action at equilibrium,

$$\text{Then } K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$\text{or } [\text{H}^+][\text{OH}^-] = K[\text{H}_2\text{O}]$$

Since, ionization takes place to a very small extent, so the concentration of unionized water molecule is regarded as constant. Thus the product of  $K[\text{H}_2\text{O}]$  gives another constant  $K_w$ .

$$\text{So, } [\text{H}^+][\text{OH}^-] = K_w$$

The product of concentration of  $\text{H}^+$  and  $\text{OH}^-$  ion in water at a particular temperature is known as ionic product of water.

$$K_w = 10^{-7} \times 10^{-7}$$

$$K_w = 10^{-14}$$

*Note* : - The value of  $K_w$  is increases with the increase in temperature i.e. the ionisation of water increases with increase in temperature and finally the concentration of  $\text{H}^+$  and  $\text{OH}^-$  ion increases.

(a) Values of  $K_w$  at various temperature :-

	Temperature (°C)	Value of $K_w$
(1)	0	$0.11 \times 10^{-14}$
(2)	10	$0.31 \times 10^{-14}$
(3)	20-35 or 25° (Room temp.)	$1 \times 10^{-14}$
(4)	60	$2.9 \times 10^{-14}$
(5)	80	$5.6 \times 10^{-14}$
(6)	90	$1 \times 10^{-12}$

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$-\log K_w = -\log [\text{H}^+] + (-) \log [\text{OH}^-]$$

$$pK_w = \text{pH} + \text{pOH}$$

$$\boxed{14 = \text{pH} + \text{pOH}}$$

The acidity and basicity depend upon the concentration of  $\text{H}^+$  and  $\text{OH}^-$  ions.

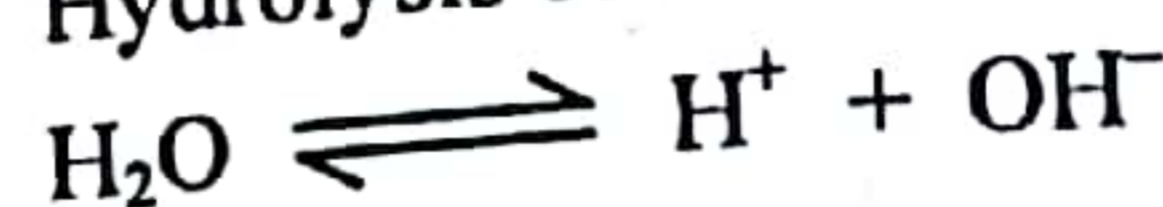
$$\text{If, } [\text{H}^+] > [\text{OH}^-] = \text{Acidic solution}$$

$$[\text{OH}^-] > [\text{H}^+] = \text{Basic solution}$$

$$[\text{OH}^-] = [\text{H}^+] = \text{Neutral solution}$$

## Some Important Points to Remember :-

- Mass of 1 litre of water = 997 gm.
- Molar concentration of water = 55.5 gm-mole / litre.
- Number of water molecule in 1 litre of water =  $55.5 \times 6.023 \times 10^{23} = 3.34 \times 10^{25}$ .
- Concentration of  $\text{H}^+$  ion in litre of neutral water =  $10^{-7}$  moles / litre.
- Concentration of  $\text{OH}^-$  ion in litre of neutral water =  $10^{-7}$  moles / litre.
- Number of  $\text{H}^+$  ion in one litre of neutral water =  $6.023 \times 10^{16}$ .
- Number of  $\text{OH}^-$  ion in one litre of neutral water =  $6.023 \times 10^{16}$ .
- Hydrolysis constant of water -



$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$= \frac{10^{-7} \times 10^{-7}}{55.5} = 1.8 \times 10^{-16} \text{ Ans.}$$

## 6. NEUTRALISATION

A reaction between acid and base to form salt and water molecule is known as neutralisation. In this type of reaction acid gives  $\text{H}^+$  ion and base gives  $\text{OH}^-$  ion.

### 6.1 Salts :

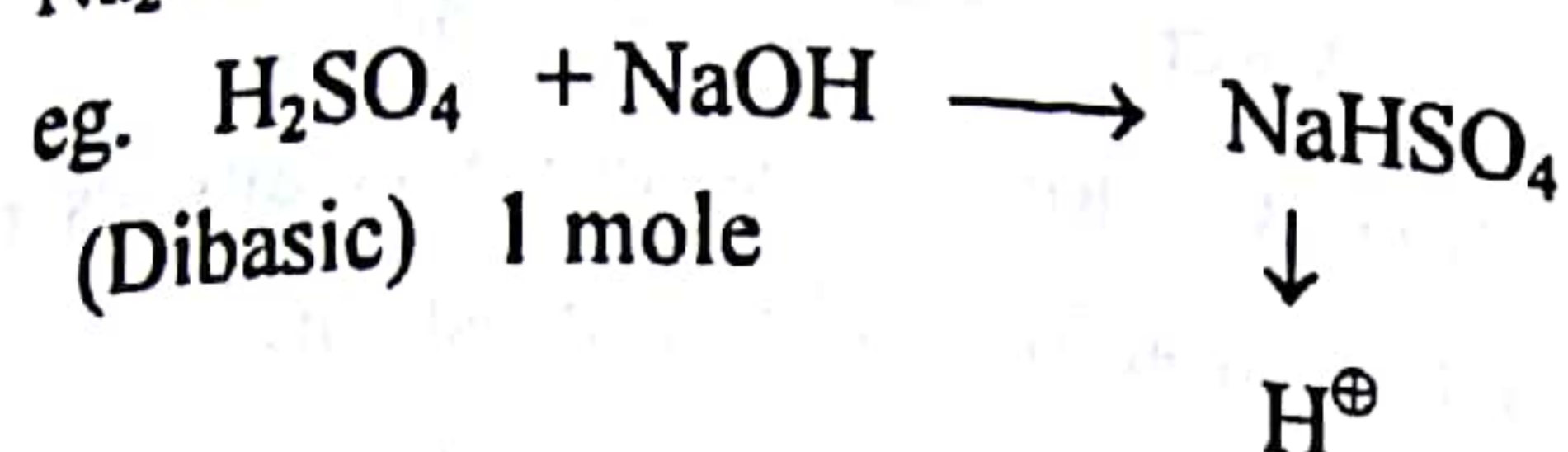
- Species formed by the reaction of neutralization of acid and base is called as salt.
- salt formation is the exothermic process and released energy by this reaction is called as the heat of neutralization for 1 eq. monoacidic base and 1 eq. monobasic acid.
- The value of heat of neutralization is equal to 13.6 kcal.
- Salts are generally crystalline solid.
- Salts are classified into following four types.

#### 6.1.1 Simple Salts :

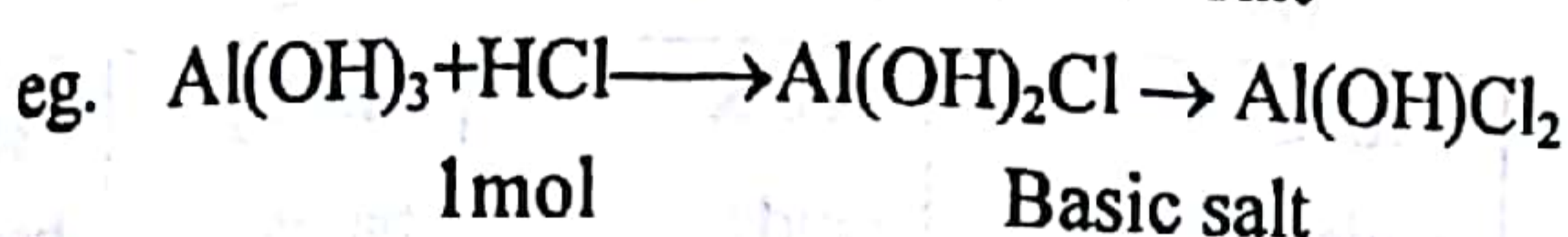
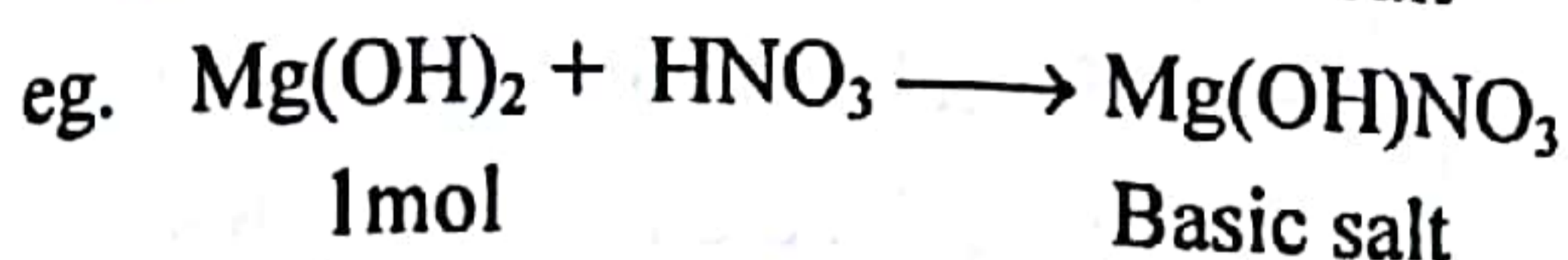
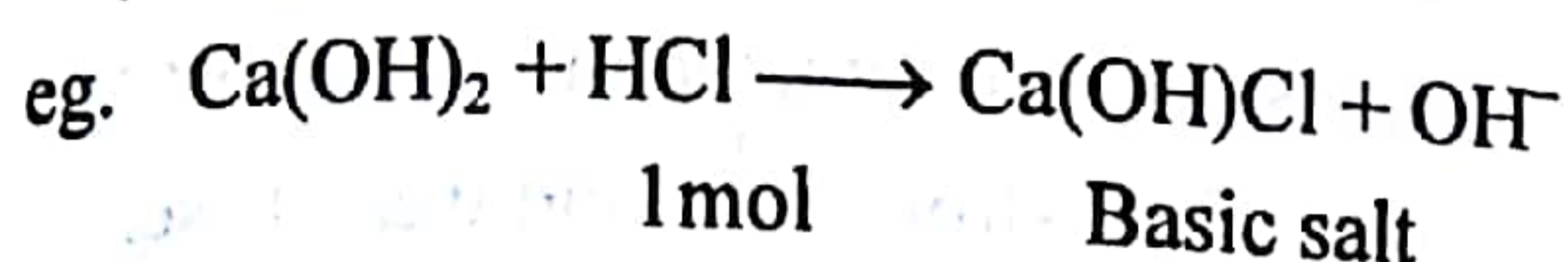
These salts formed by the neutralisation process, which are of three types.

- Normal Salt : These salts are formed by the neutralization reaction of simple acid and simple base, like -  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{KNO}_3$  etc.

(b) Acid Salt : It is formed by the incomplete neutralization reaction of acid with the base is called the acidic salt and gives proton in aqueous solution. Like -  $\text{NaHCO}_3$ ,  $\text{NaHSO}_4$ ,  $\text{Na}_2\text{HPO}_4$ .

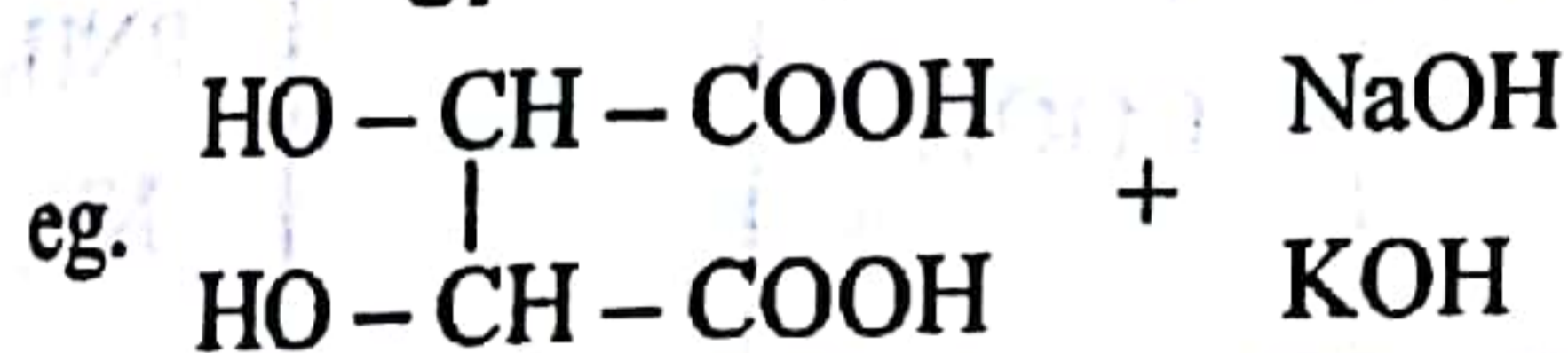
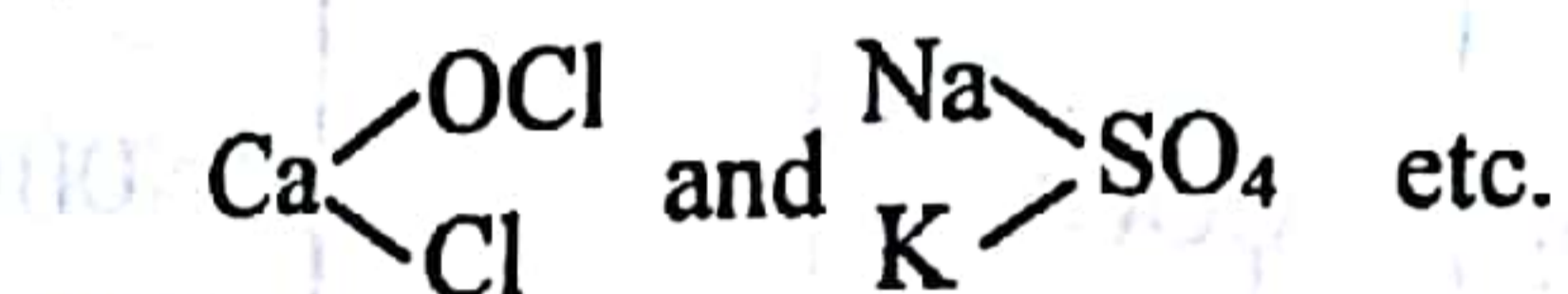


(c) Basic salt : Salt which is formed by the incomplete neutralization reaction of base with acid called the basic salt and gives  $\text{OH}^-$  ion in aqueous solution. Like-  $\text{Zn}(\text{OH})\text{Cl}$ ,  $\text{Mg}(\text{OH})\text{Cl}$ ,  $\text{Fe}(\text{OH})_2\text{Cl}$  etc.

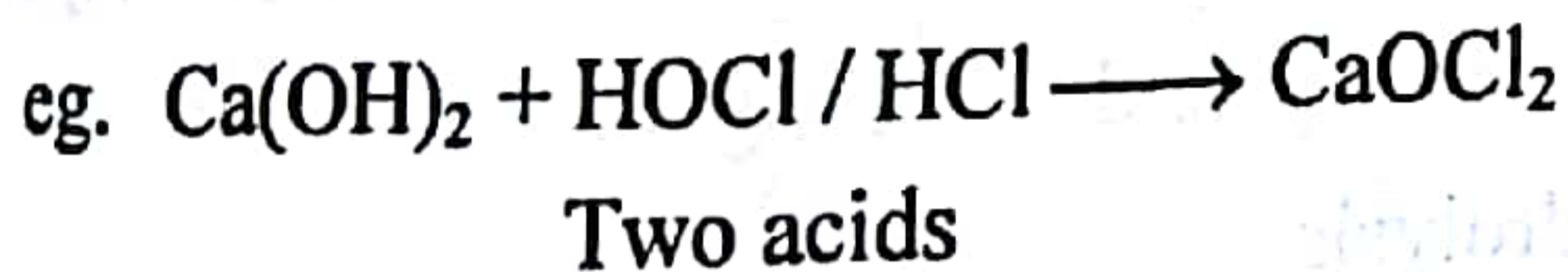
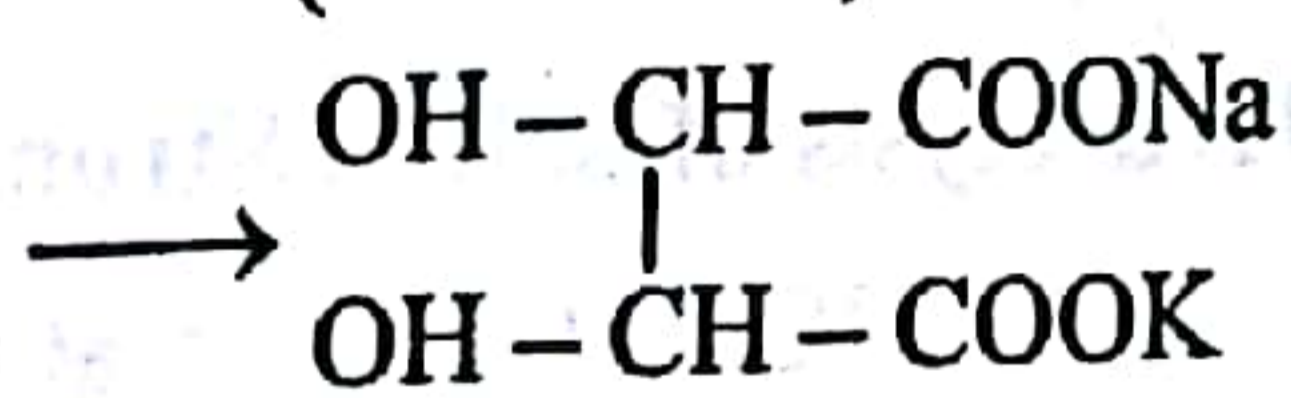


### 6.1.2 Mixed Salts :

Salt which are formed by the neutralisation reaction of more than two different acids and bases are called mixed salt. Or Salts which furnish more than one cation or more than one anion when dissolved in water are also as mixed salt. Like Rochelle salt,

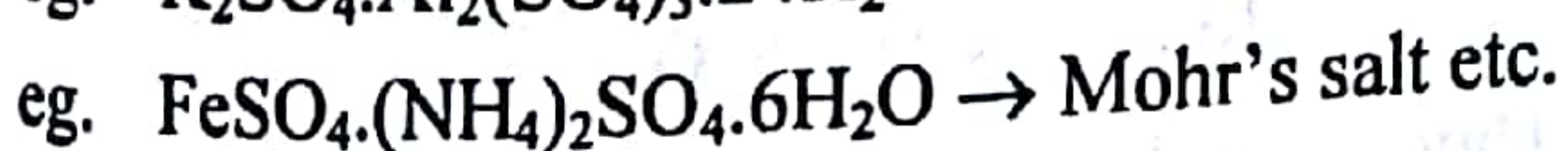
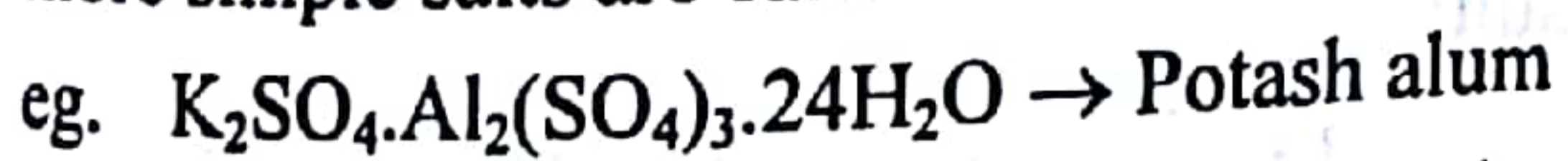


(Two bases)



### 6.1.3 Double salts :

Salts which are formed by the addition of two or more simple salts are called as double salt.



### 6.1.4 Complex salts : -

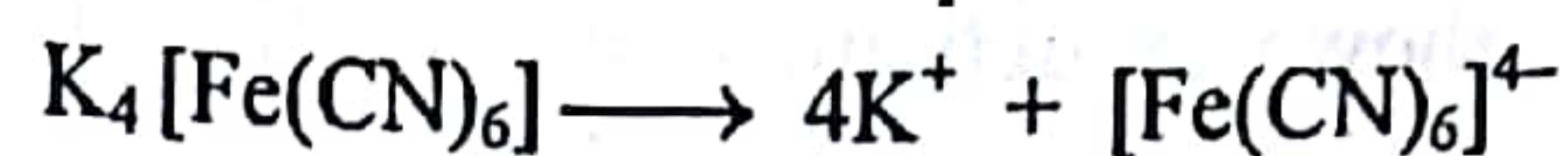
(a) Salt which are formed by the donation of electron pair by the legand molecule with the metal ion are called as complex salts. Or salts which are formed by the combination of simple salts or molecular compounds.

(b) Complex salts are stable in solid state.

(c) On dissolving the water, complex salts. Give minimum one complex ion -



or all coordination compound



## 7. pH SCALE :

(i)  $\text{H}^+$  concentration in any solution can vary within a wide range from  $1 \text{ mol dm}^{-3}$  to  $10^{-14} \text{ mol dm}^{-3}$ . So a logarithmic notation has been devised by Sorensen in 1909 to simplify the expression of these quantities.

(ii) The above notation is termed is  $\text{p}^{\text{H}}$  scale. According to the scale the hydrogen ion concentrations  $[\text{H}^+]$  are expressed in terms of the numerical value of negative power to which 10 must be raised. i.e.

$$[\text{H}^+] = 10^{-\text{pH}}$$

$$\text{or } \text{pH} = -\log [\text{H}^+] = \log \left( \frac{1}{[\text{H}^+]} \right)$$

Note :

(i)  $[\text{H}^+]$  should be taken always in  $\text{mol dm}^{-3}$  or  $\text{mol L}^{-1}$ .

(ii) Similarly  $[\text{OH}^-]$  is also expressed i.e.

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

$$\text{since we know } [\text{H}^+][\text{OH}^-] = K_w = 10^{-14}$$

$$\text{or } \text{pH} + \text{pOH} = 14 \text{ at } 25^\circ\text{C}$$

(iii)

$[\text{H}^+]$	$[\text{OH}^-]$	pH	pOH	Nature of solution
$10^0=1$	$10^{-14}$	0	14	Strongly Acidic
$10^{-2}$	$10^{-12}$	2	12	Acidic
$10^{-5}$	$10^{-9}$	5	9	Weakly acidic
$10^{-7}$	$10^{-7}$	7	7	Neutral
$10^{-9}$	$10^{-5}$	9	5	Weakly basic
$10^{-11}$	$10^{-3}$	11	3	Basic
$10^{-14}$	$10^0=1$	14	0	Strongly basic

(iv) pH values of the solutions do not give immediate idea of the relative strength of the solution. e.g.

(a) For a solution of  $\text{pH} = 1$  has a  $[\text{H}^+]$  100 times that of a solution of  $\text{pH} = 3$ . (not three times)

(b) A  $4 \times 10^{-5}$  N HCl is twice concentrated as a  $2 \times 10^{-5}$  N HCl solution but their pH values will be 4.4 and 4.7. (not double)

(v) A solution of an acid having very low concentration, say  $10^{-8}$  N HCl, can not have pH = 8 as shown by definition but the pH will be less than 7.

### 7.1 Applications of pH

#### (a) pH of strong acid or strong base.

(i) pH of a strong acid or strong base can be calculated directly by its normality, since they are completely ionised.

e.g.

(a) For  $10^{-2}$  M HCl  $\equiv 10^{-2}$  N HCl

$$[H^+] = 10^{-2} \text{ M}$$

$$\text{or } \text{pH} = -\log(10^{-2}) = 2$$

(b) For  $10^{-3}$  M NaOH  $\equiv 10^{-3}$  N NaOH

$$[H^+] = \frac{10^{-14}}{[OH^-]} = 10^{-11}$$

$$\text{or } \text{pH} = -\log(10^{-11}) = 11$$

(c) For  $10^{-2}$  M  $\text{H}_2\text{SO}_4 \equiv 2 \times 10^{-2}$  N  $\text{H}_2\text{SO}_4$

$$[H^+] = 2 \times 10^{-2} \text{ M}$$

$$\text{or } \text{pH} = -\log(2 \times 10^{-2}) = 1.699$$

(d) For  $10^{-3}$  M  $\text{Mg}(\text{OH})_2 \equiv 2 \times 10^{-3}$  N  $\text{Mg}(\text{OH})_2$

$$[H^+] = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12} \text{ M}$$

$$\text{or } \text{pH} = -\log(5 \times 10^{-12}) = 11.3$$

**Note:** Normality = Acidity or Basicity  $\times$  Molarity

#### (b) pH of weak acid or weak base

(i) For weak acid or base  $[H^+]$  can not be calculated by its concentration only since they are partially ionised.

(ii) For  $[H^+]$  calculation either  $K_a$  (or  $K_b$ ) or degree of dissociation will be required in addition to its concentrations (C).

(iii) As we know for weak acids

$$[H^+] = \sqrt{K_a \cdot C} \text{ or } [H^+] = C\alpha$$

$$\text{so } \text{pH} = \frac{1}{2} (\text{p}K_a - \log C)$$

(iv) For weak bases,  $[OH^-] = \sqrt{K_b \cdot C}$

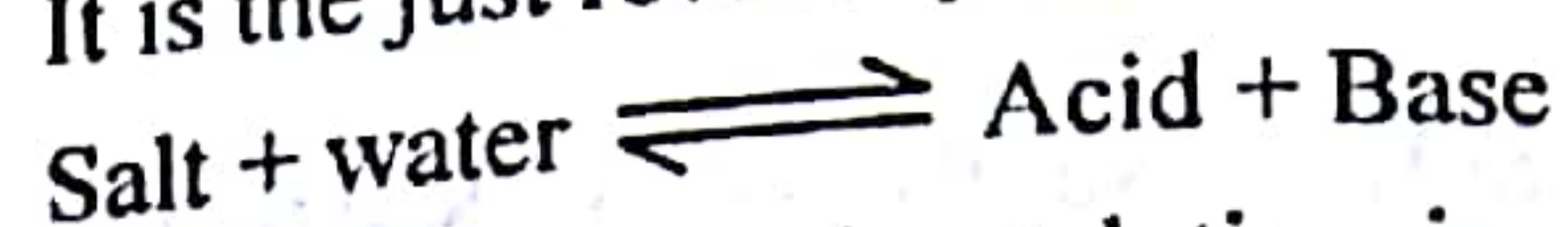
$$\text{or } [OH^-] = C\alpha$$

$$\text{so } \text{pOH} = \frac{1}{2} (\text{p}K_b - \log C)$$

## 8. HYDROLYSIS

It is defined as a process involving the reaction of water on a salt to form mixture of acid and base.

(a) It is the just reverse process of neutralization



(b) In this reaction the solution is always neutral when both acid and base are strong.

(c) If acid is stronger than base, the solution is acidic and if base is stronger than acid, the solution is basic.

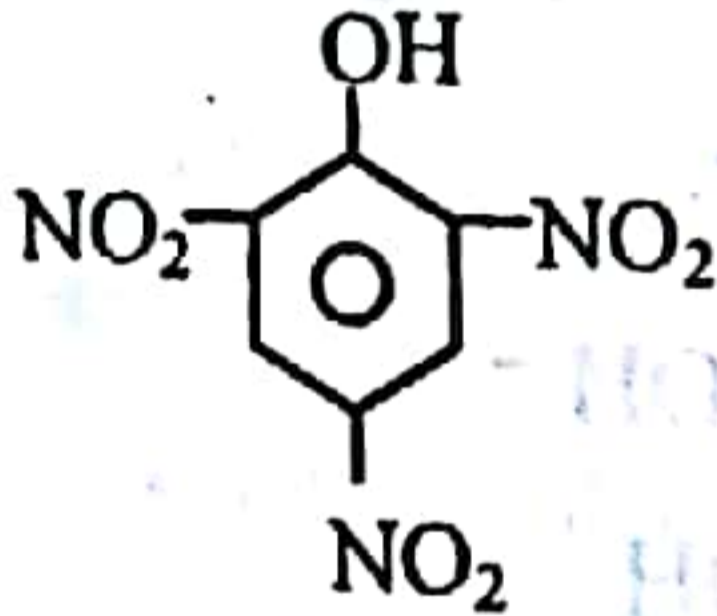

(d) Depending upon the nature of an acid or a base, there can be four types of salt -

(i) Salt of strong acid and strong base.

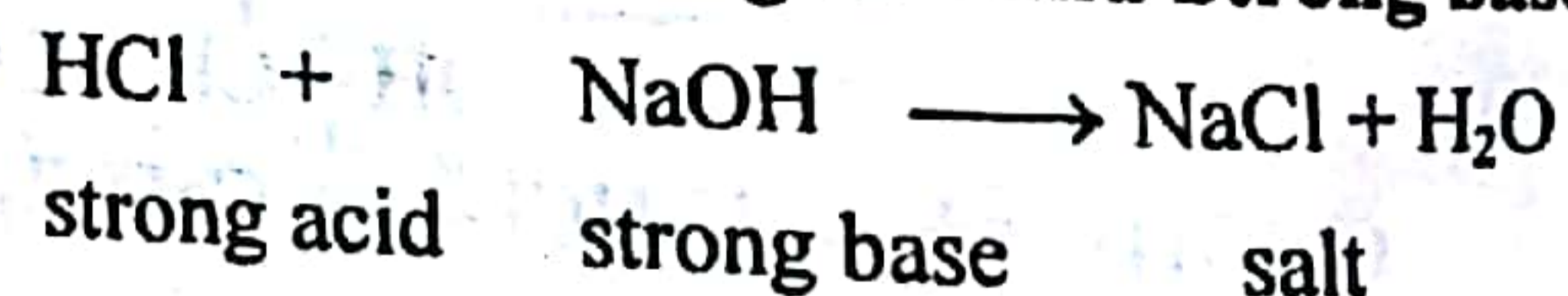
(ii) Salt of strong acid and weak base.

(iii) Salt of weak acid and weak base.

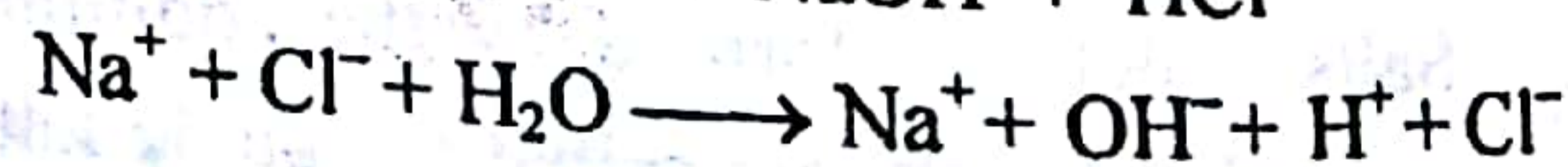
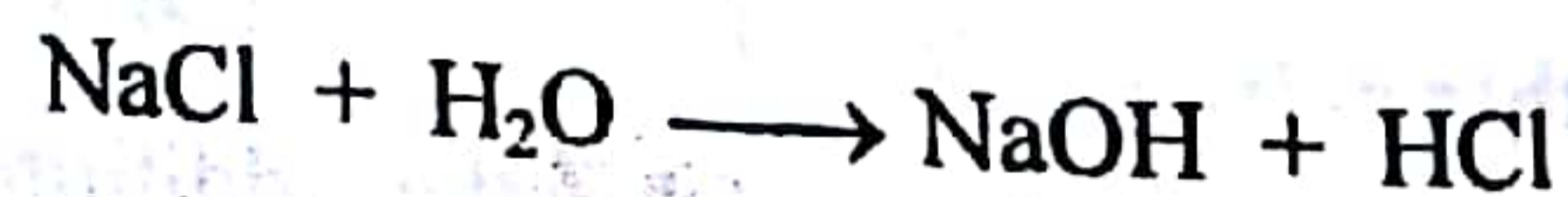
(iv) Salt of weak acid and strong base.

Strong acids	Weak acids	Strong bases	Weak bases
HCl	$\text{CH}_3\text{COOH}$	NaOH	$\text{NH}_4\text{OH}$
$\text{H}_2\text{SO}_4$	HCN	KOH	LiOH
$\text{HNO}_3$	$\text{H}_2\text{CO}_3$	RbOH	$\text{Ca}(\text{OH})_2$
$\text{HClO}_4$	$\text{H}_3\text{PO}_4$	CsOH	$\text{Be}(\text{OH})_2$
HI	$\text{H}_3\text{PO}_3$	$\text{Ba}(\text{OH})_2$	$\text{Zn}(\text{OH})_2$
$\text{H}_2\text{SO}_3$	HOCl		$\text{Al}(\text{OH})_3$
			$\text{Fe}(\text{OH})_3$
			$\text{RNH}_2$
			$\text{NH}_3$

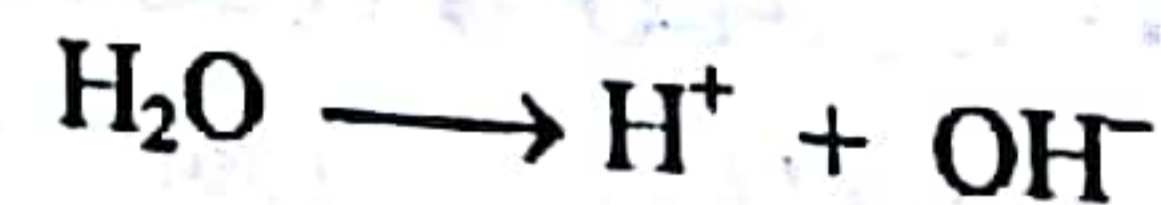
### 8.1 Hydrolysis of Salt of Strong acid and Strong base :



on Hydrolysis,



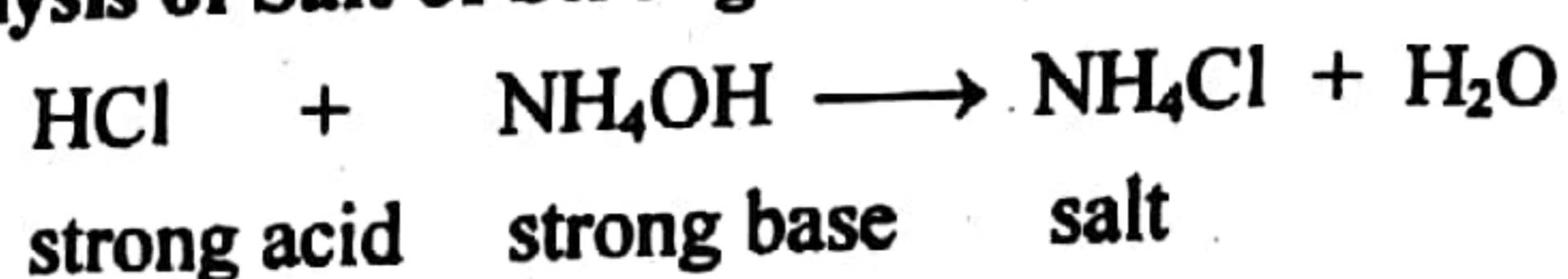
Result:



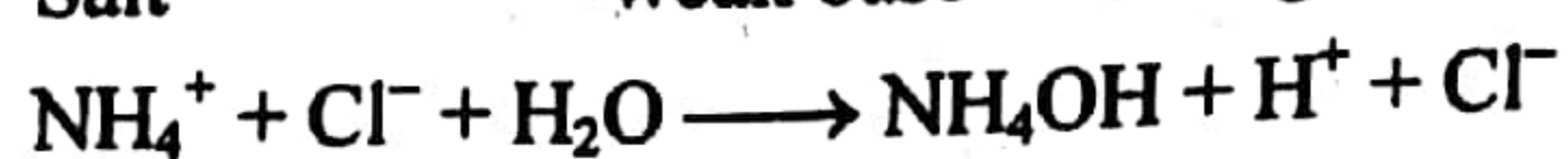
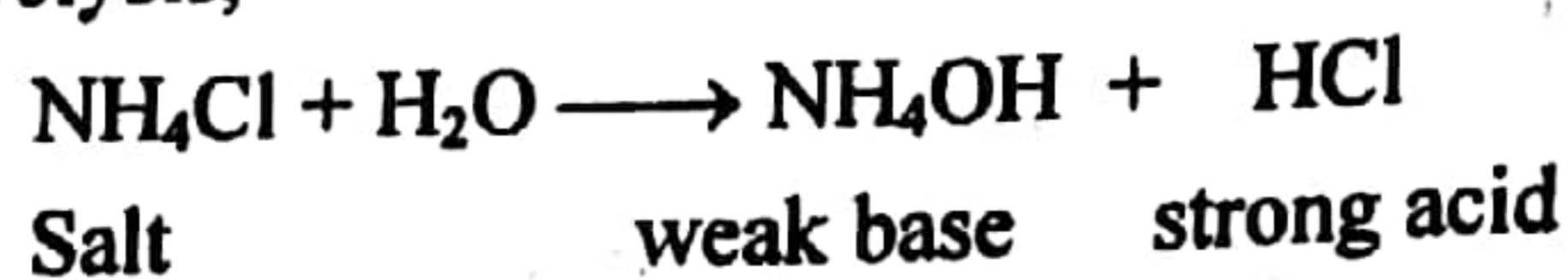
Thus, hydrolysis does not occur. So, the solution is neutral in nature i.e. salt of strong acid and strong base does not hydrolysed.

**Note :** No hydrolysis reaction takes place due to conjugate acid and base of this type of salt, which are weak.

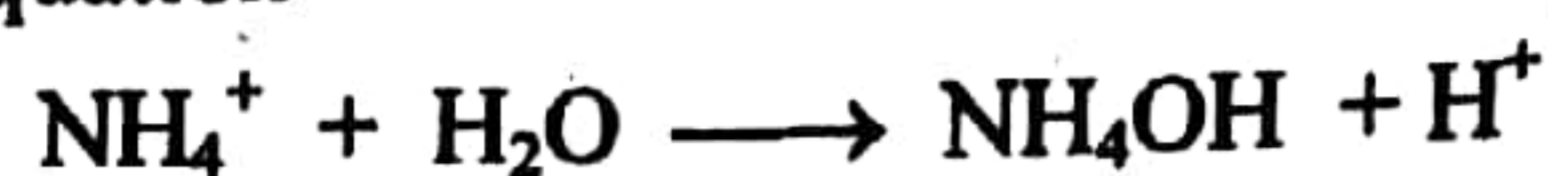
### 8.2 Hydrolysis of Salt of Strong acid and Weak base :



on hydrolysis,

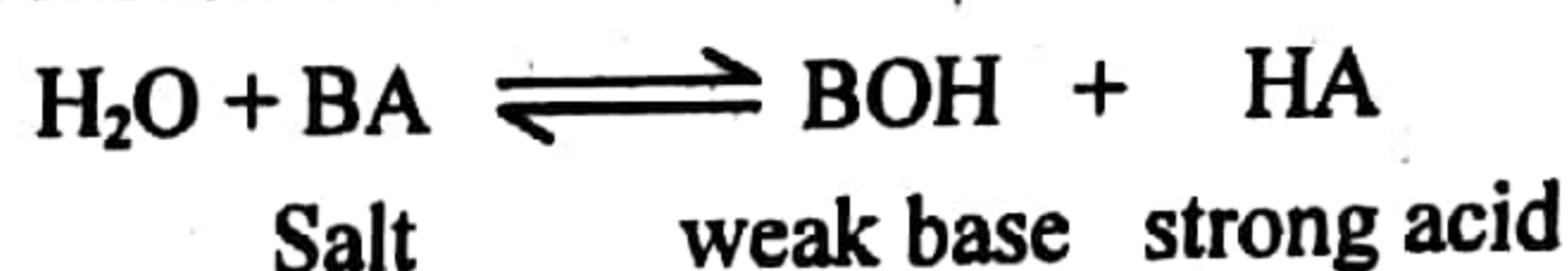


Final equation



#### A. Relation between hydrolysis constant of water ( $K_h$ ), weak base dissociation constant ( $K_b$ ) and ionic product of water ( $K_w$ ):

Let us consider a salt - BA



on applying the law of mass action

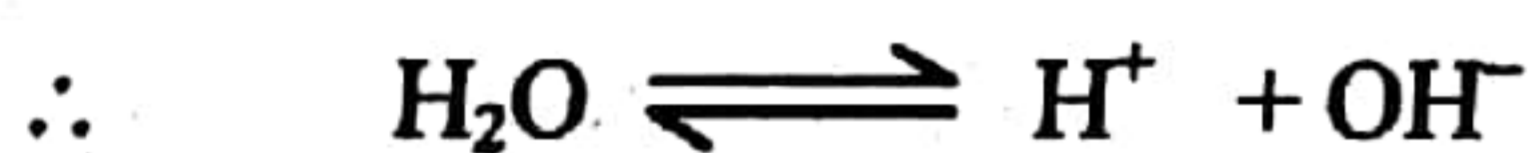
$$K = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+][\text{H}_2\text{O}]}$$

concentration of  $[\text{H}_2\text{O}]$  remains almost constant means only one  $\text{H}_2\text{O}$  molecule is ionized out of 55 crore molecule of  $\text{H}_2\text{O}$ .

So,  $K[\text{H}_2\text{O}] = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+]}$

$$K_h = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+]} \quad \text{----(1)}$$

Some part of  $\text{H}_2\text{O}$  would be ionized otherwise reaction will not be reversible.



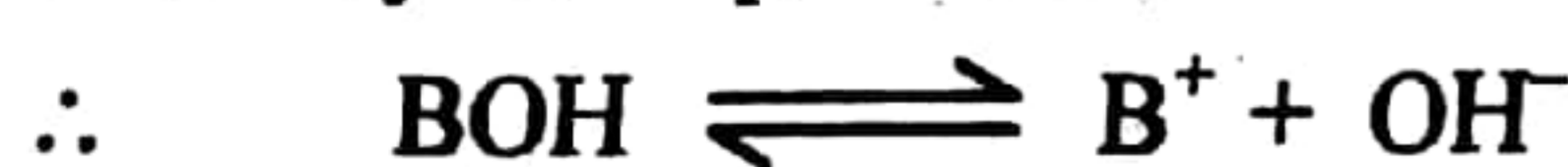
$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K[\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} \quad \text{----(2)}$$

Similarly some part of BOH will be also ionized -



$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}$$

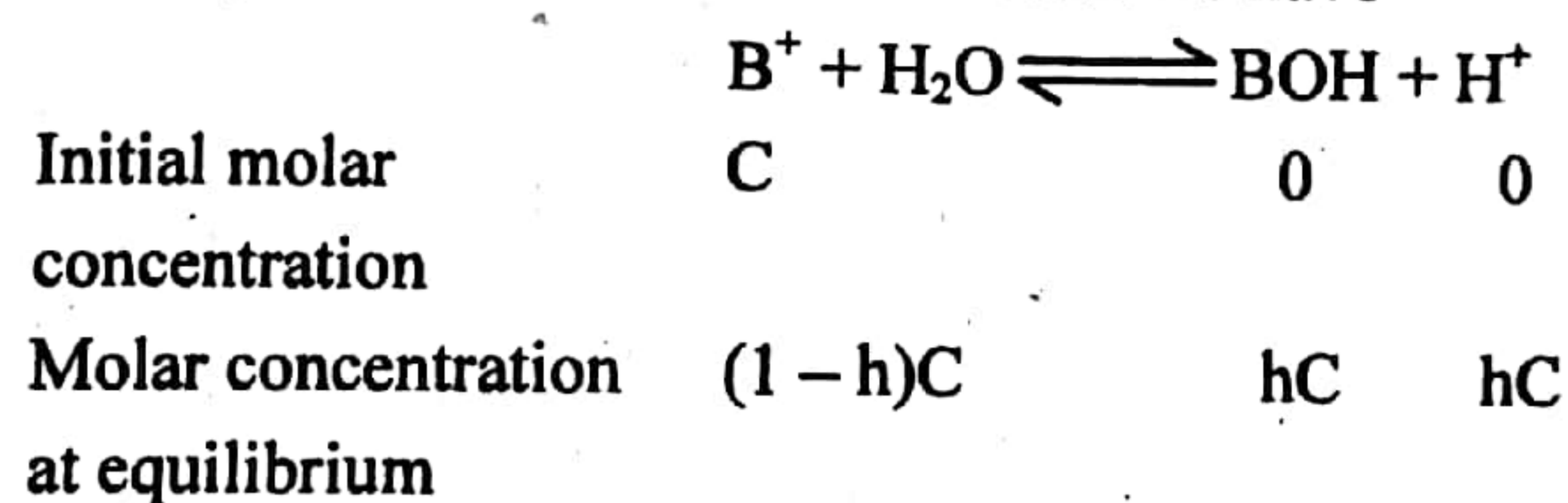
$$[\text{B}^+] = \frac{K_b \times [\text{BOH}]}{[\text{OH}^-]} \quad \text{----(3)}$$

On putting the value of  $[\text{H}^+]$  and  $[\text{B}^+]$  on the equation (1) by the equation (2) and (3), we get -

$$\boxed{K_h = \frac{K_w}{K_b}}$$

#### B. Calculation of degree of hydrolysis : -

Assume the original concentration of the salt in the solution is C moles / lit. and h is its degree of hydrolysis at this concentration. Then we have -



$$\therefore \frac{1-h}{V} \qquad \frac{h}{V} \qquad \frac{h}{V}$$

$$K = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+][\text{H}_2\text{O}]}$$

$$K[\text{H}_2\text{O}] = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+]}$$

$$K_h = \frac{\frac{h}{V} \times \frac{h}{V}}{\frac{1-h}{V}} = \frac{h^2}{(1-h)V}$$

Since,  $h \ll 1$ , therefore  $1-h = 1$ ,

$$K_h = \frac{h^2}{V}$$

$$h^2 = K_h \times V$$

$$h = \sqrt{K_h V}$$

$\therefore K_h = \text{Hydrolysis constant}$

Then,  $h \propto \sqrt{V}$

Hence, the degree of hydrolysis is directly proportional to the square root of volume, inversely proportional to the square root of C.

$$\therefore h^2 = K_h \times V \qquad \therefore V = 1/C$$

$$h^2 = \frac{K_h}{C}$$

$$\boxed{h = \sqrt{\frac{K_h}{C}}}$$

on putting the value of  $K_h$  in the above equation -

$$\boxed{h = \sqrt{\frac{K_w}{K_b \times C}}}$$







We know that,

$$K_w = [H^+][OH^-] \quad \text{---(4)}$$

Dividing (4) by (2) and (3) -

$$\begin{aligned} \frac{K_w}{K_a \times K_b} &= \frac{[H^+][OH^-][HA][BOH]}{[H^+][A^-][B^+][OH^-]} \\ &= \frac{[HA][BOH]}{[B^+][A^-]} \end{aligned} \quad \text{---(5)}$$

from equation (1) and (5) -

$$K_h = \frac{K_w}{K_a \times K_b} \quad \text{---(6)}$$

### B. Calculation of degree of hydrolysis :

Assume again, the original concentration of salt in the solution is C moles / litre and h is its degree of hydrolysis at this concentration. Then we have

	$B^+$	$A^- + H_2O$	$\rightleftharpoons$	$HA + BOH$
Initial molar concentration	C	C		0      0
Molar concentration at equilibrium	$(1-h)C$	$(1-h)C$		$hC$ $hC$

$$\begin{aligned} \therefore K_h &= \frac{[HA][BOH]}{[B^+][A^-]} \\ &= \frac{hC \times hC}{(1-h)C \times (1-h)C} \\ K_h &= \frac{h^2}{(1-h)^2} \end{aligned}$$

If h is very small as compared to 1 then  $(1-h)$  is equal to 1. Hence the above equation becomes,

$$K_h = h^2$$

$$\text{or } h = \sqrt{K_h}$$

Thus, the degree of hydrolysis in this case is independent of concentration or dilution of the salt.

on putting the value of  $K_h$  from equation (6)

$$h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

### C. Calculation of hydrogen ion concentration or calculation of pH :

In this type of cases, the hydrogen ion concentration may be calculated from the following equation of weak acid HA.



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

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

$$[H^+] = K_a \frac{hC}{(1-h)C} = K_a \frac{h}{(1-h)}$$

Since,  $h \ll 1$  then  $(1-h) = 1$   
on putting the value of h

$$[H^+] = K_a \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{K_w \cdot K_a}{K_b}}$$

We know that

$$pH = -\log [H^+]$$

$$= -\log \sqrt{\frac{K_w \cdot K_a}{K_b}}$$

$$= -\log \left( \frac{K_w \cdot K_a}{K_b} \right)^{1/2}$$

$$= -\frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} pK_b$$

$$= \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

## 9. BUFFER SOLUTIONS

- (i) In certain applications of chemistry and biochemistry we require solutions of constant pH. Such solution are called buffer solution.
- (ii) A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid ( $H^+$  ions) or a base ( $OH^-$  ions) is called buffer solution.
- (iii) Buffer solutions are also called solutions of reverse acidity or alkalinity.
- (iv) Following are the characteristics of buffer solutions
  - (a) It must have constant pH.
  - (b) Its pH should not be changed on long standing
  - (c) Its pH should not be changed on dilution.
  - (d) It pH should not be changed to any great extent on addition of small quantity of acid or base.

(v) Buffer solutions can be classified as follows.

(A) Simple buffer

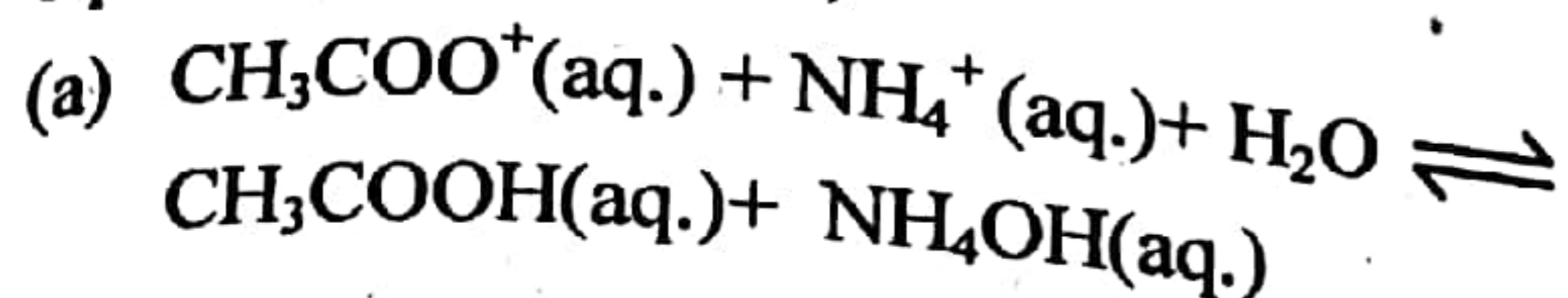
(B) Mixed buffer

### 9.1 Simple buffer

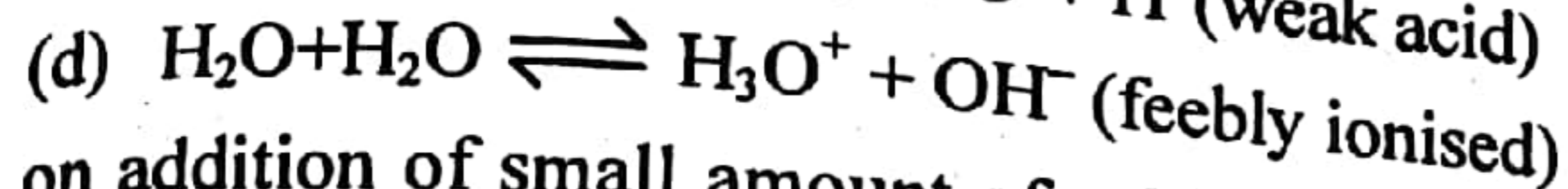
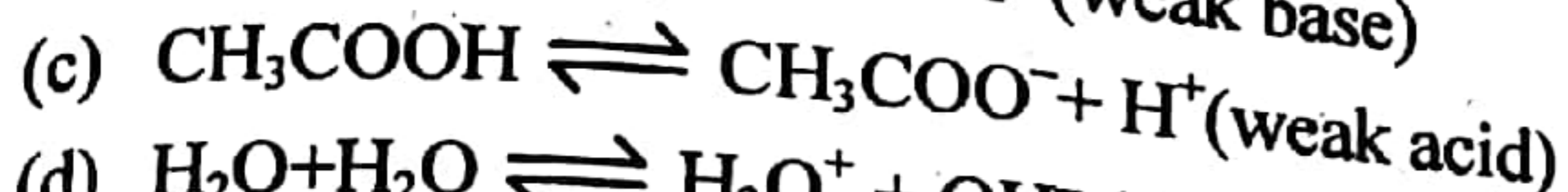
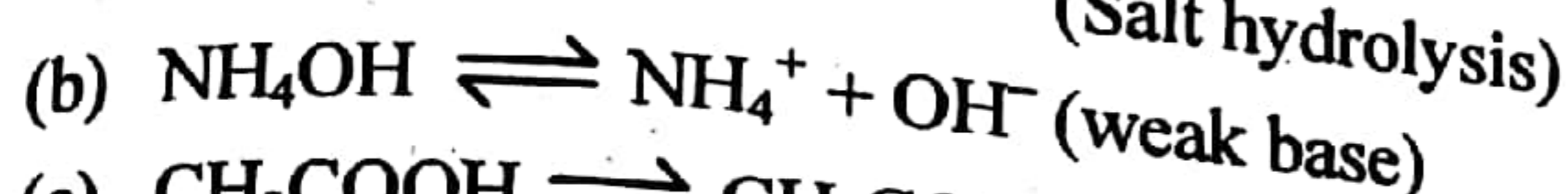
(i) It is a solution of one compound i.e. salts of WA + WB (Refer salt hydrolysis.)

(ii) Buffer action of such solution can be explained as follows,

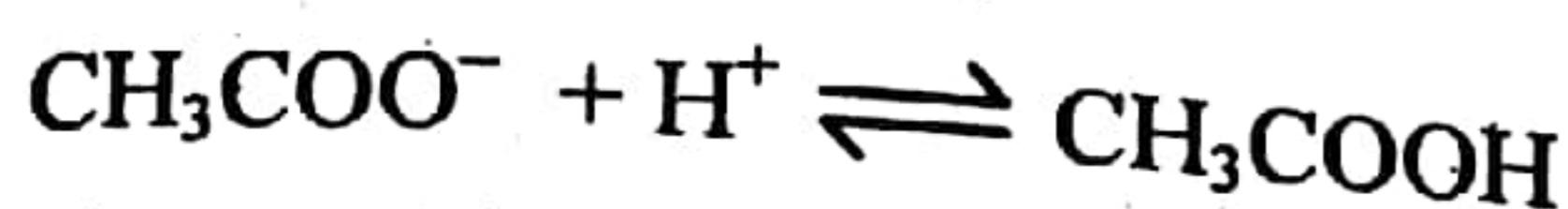
In the salt solution of  $\text{CH}_3\text{COONH}_4$  following equilibria will be there,



(Salt hydrolysis)



on addition of small amount of acid the  $[\text{H}^+]$  in solution will increase and

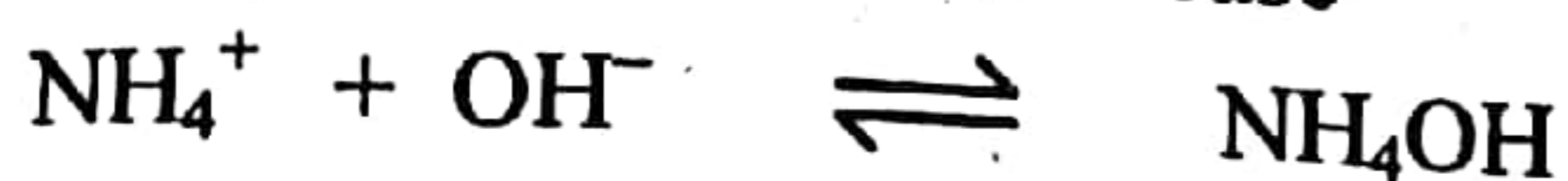


(from acid)

(very less ionised)

equilibria will shift in forward direction.

Similarly on addition of small amount of base, the  $[\text{OH}^-]$  in solution will increase



(from base)

(very less ionised)

equilibria will shift in forward direction Hence

one can conclude that there will be no change (almost) in the pH of the solution.

(iii) Simple buffer solutions have very little

significance since  $\text{pH} = 7 + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b$  so

solution of desired pH can not be prepared.

### 9.2 Mixed buffer

Mixed buffers are solutions of more than one compounds. They can be further classified as

(a) Acidic buffer

(b) Basic buffer

(c) A mixture of an polyprotic acid and its acidic salt

(d) Solution of ampholyte or amphoteric electrolyte viz. Proteins and Amino acids.

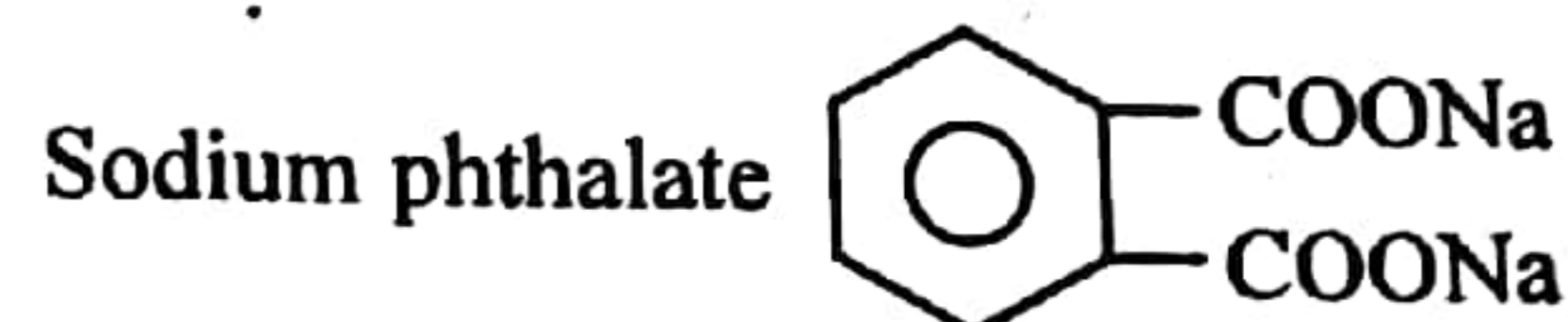
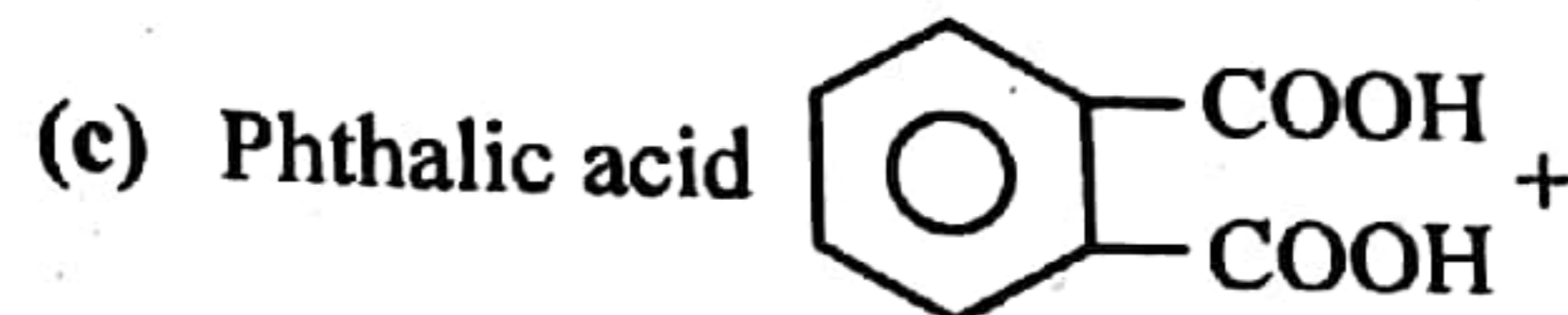
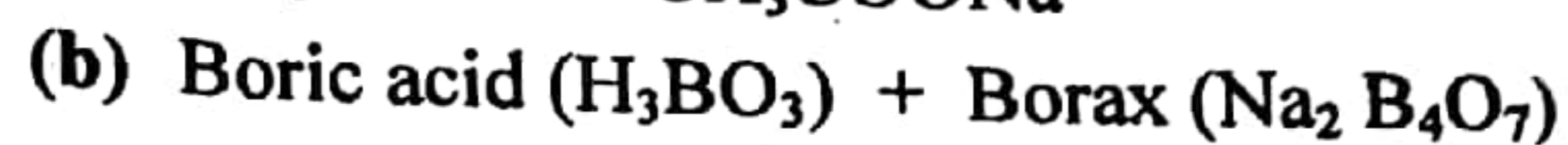
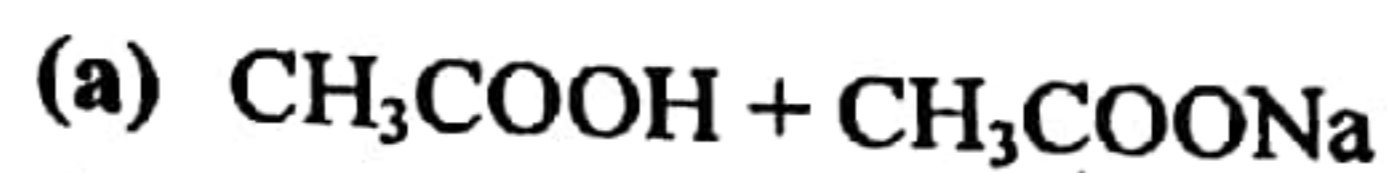
Note :

(i) Ampholyte or amphoteric electrolytes are those which can show properties of both acid and base.

### 9.2.1 Acidic buffer

(i) These are the mixture of a weak acid and its salt with strong base.

e.g.



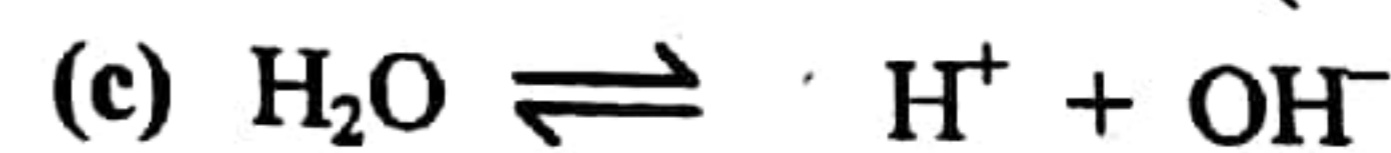
(ii) Buffer action of acidic buffer can be explained with following equilibria,



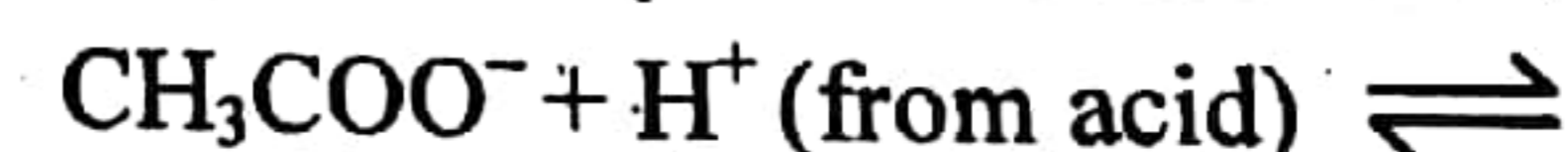
(Feebly ionised.)



(completely ionised.)

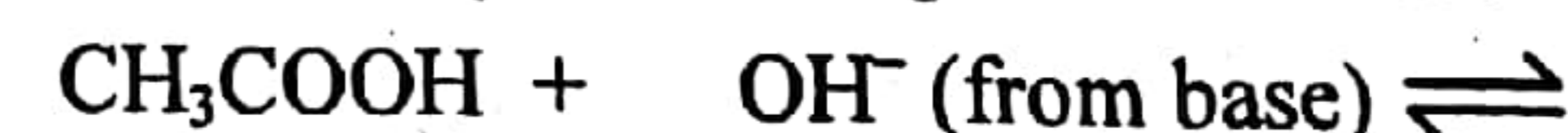


When a strong acid is added in the solution  $[\text{H}^+]$  increases, which will combine with  $\text{CH}_3\text{COO}^-$  to form feebly ionised  $\text{CH}_3\text{COOH}$ , which is also suppressed by common ion effect,



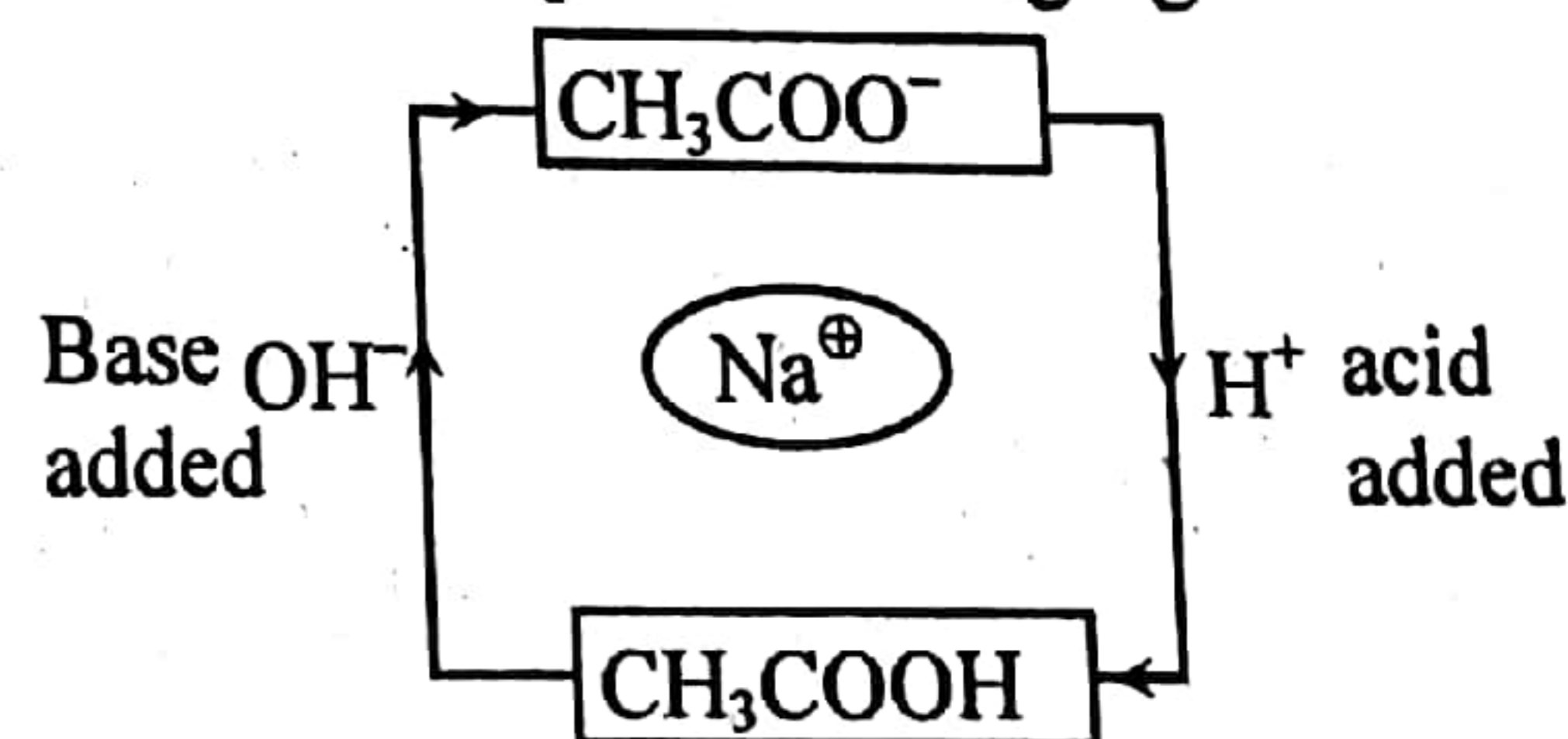
$\text{CH}_3\text{COOH}$  (Weak Acid)

Again when strong base is added in the solution it will attack on unionised acid  $\text{CH}_3\text{COOH}$  to form feebly ionised  $\text{H}_2\text{O}$  molecules

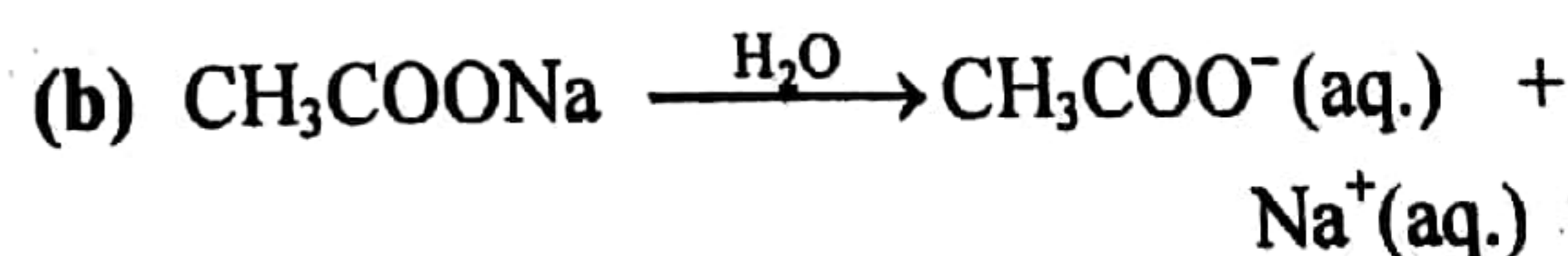


$\text{CH}_3\text{COO}^- + \text{H}_2\text{O}$

(iii) One can remember the buffer action of acidic buffer with the help of following figure -



(iv) pH of such acidic buffer can be calculated as follows.



CH<sub>3</sub>COOH is feebly ionised and its ionisation is also suppressed by presence of common ion (CH<sub>3</sub>COO<sup>-</sup>). So one can fairly assume [CH<sub>3</sub>COO<sup>-</sup>] = [salt] and [CH<sub>3</sub>COOH] = [Acid] taken initially in buffer solution.

$$\text{so } K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$\text{or } [H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

$$\begin{aligned} \log[H^+] &= \log K_a + \log[CH_3COOH] - \log[CH_3COO^-] \\ -\log[H^+] &= \\ -\log K_a - \log[CH_3COOH] + \log[CH_3COO^-] \end{aligned}$$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

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

Above equation called Henderson's equation.

- \* If we increase the concentration of given salt in acidic buffer, pH will also increase.
- \* If we increase the concentration of acid in acidic buffer, pH will decrease.
- \* If conc. and volume are given for salt and acid then the pH is given by the following formula-

$$pH = pK_a + \log \frac{[N_2V_2]}{[N_1V_1]}$$

Where N<sub>2</sub>V<sub>2</sub> = conc. & volume of salt

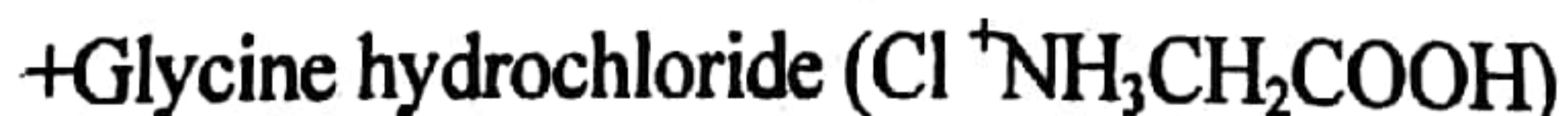
N<sub>1</sub>V<sub>1</sub> = conc. & volume of acid

**Note :** Mixture of weak acid and strong base solution can also act as an acidic buffer, if value of N<sub>1</sub>V<sub>1</sub> of weak acid is greater than the value of N<sub>2</sub>V<sub>2</sub> of strong base.

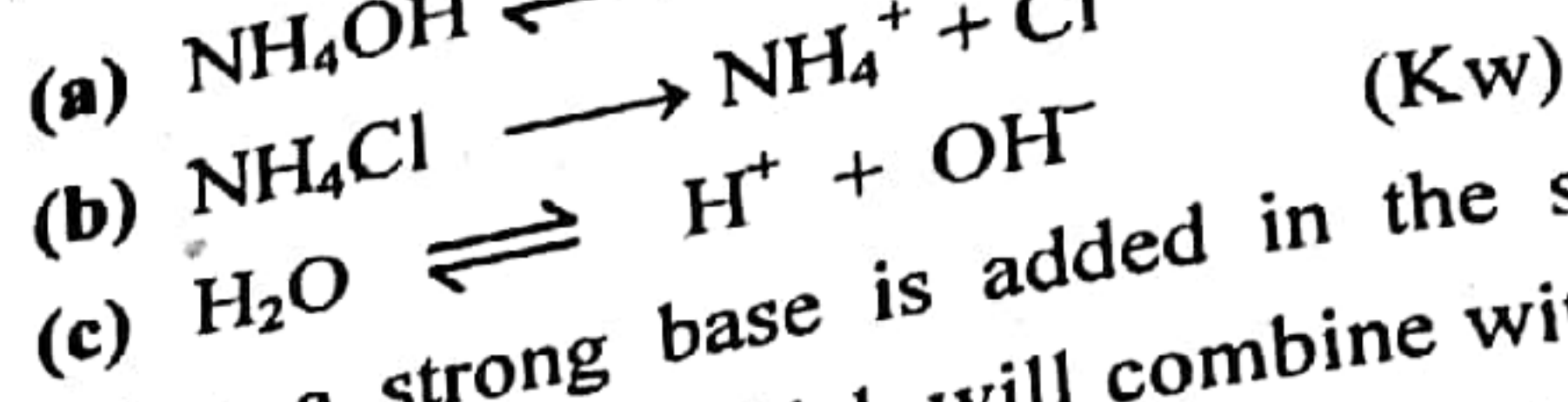
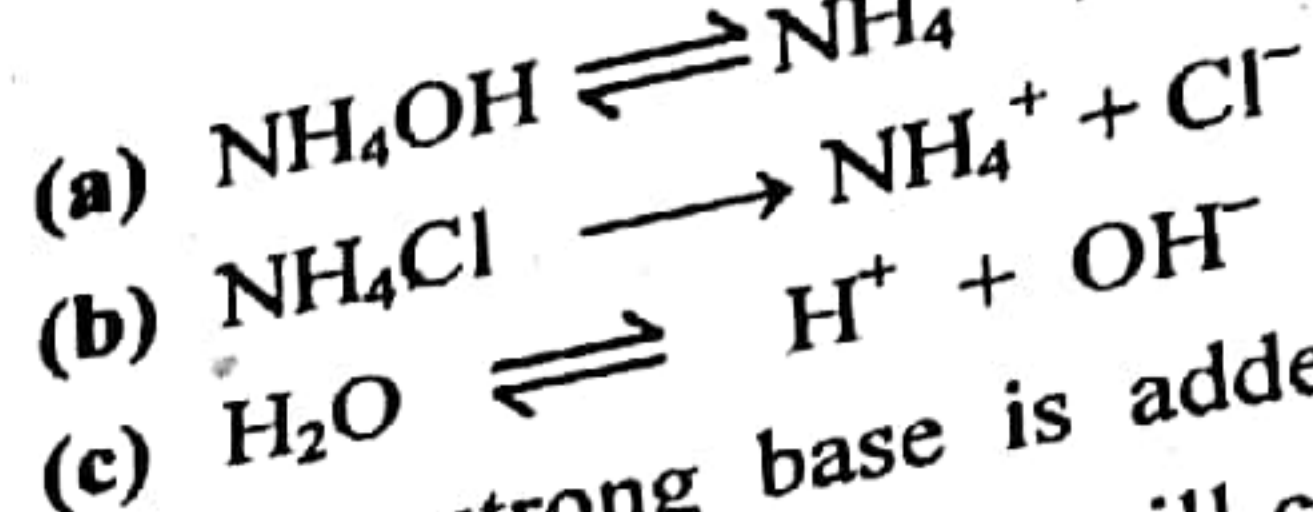
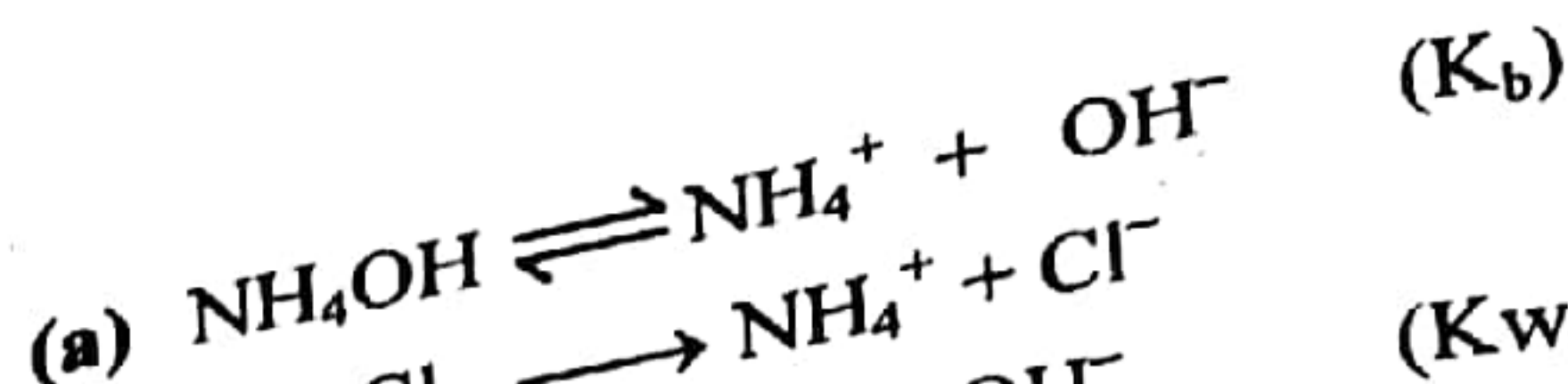
### 9.2.2 Basic Buffer

- (i) These are the mixture of a weak base and its salt with strong acid.

e.g.



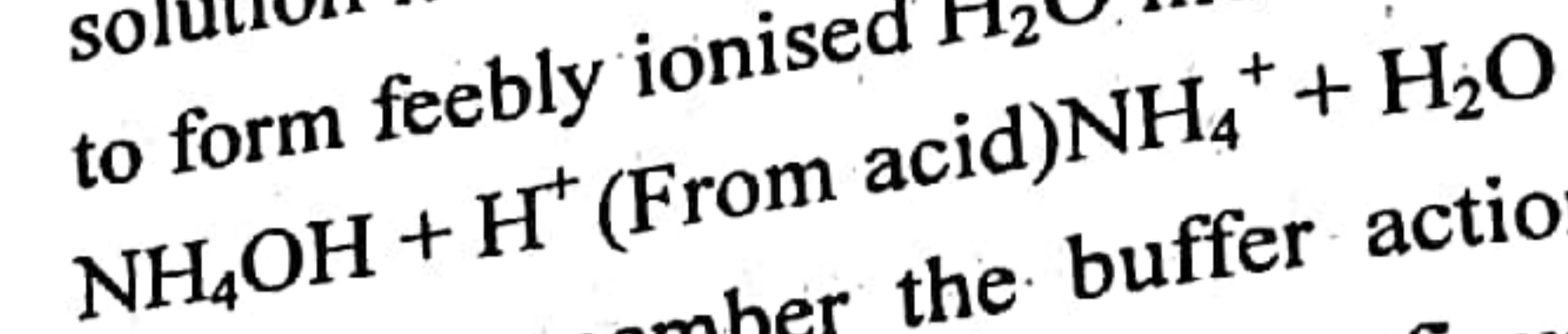
- (ii) Buffer action of basic buffer can be explained with the help of following equilibria



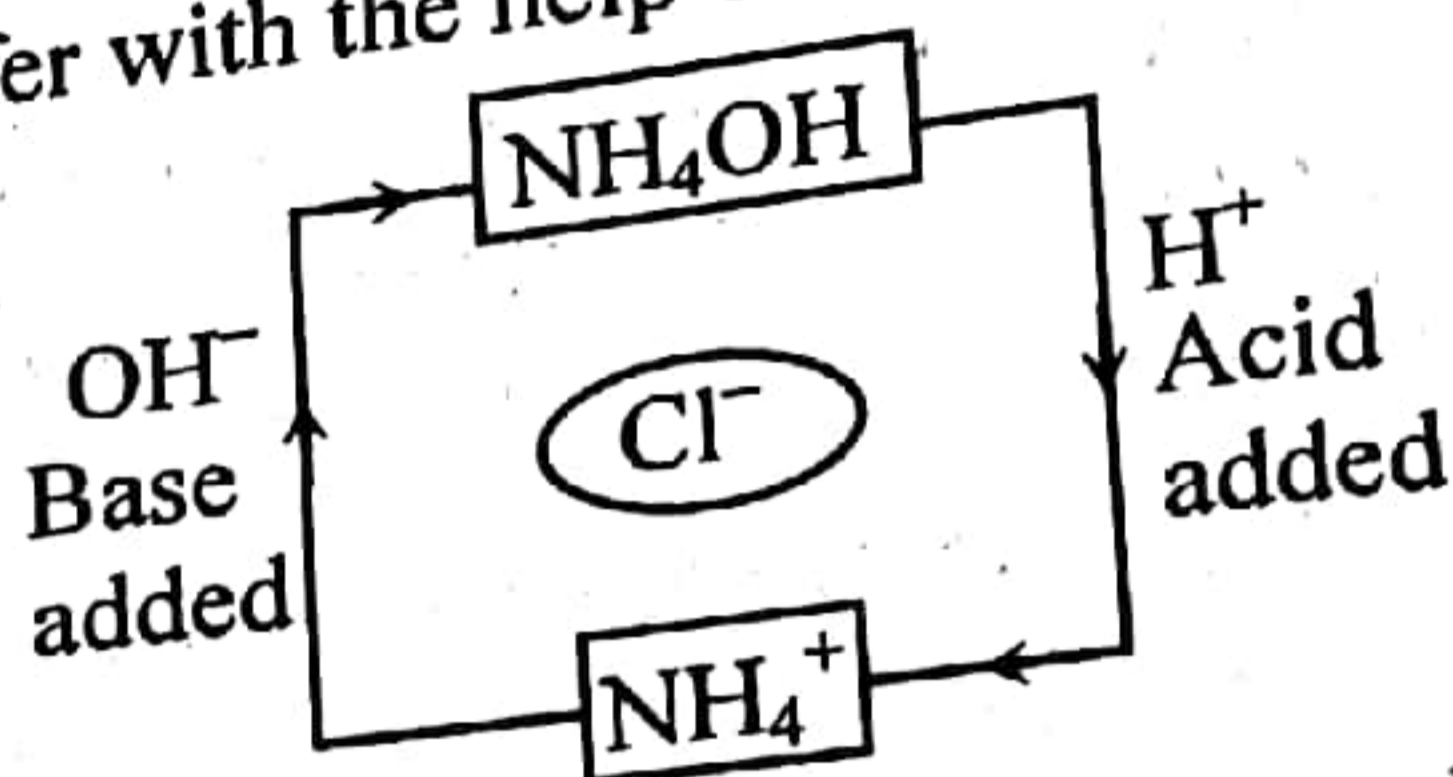
When a strong base is added in the solution [OH<sup>-</sup>] increases, which will combine with NH<sub>4</sub><sup>+</sup> to form feebly ionised NH<sub>4</sub>OH, which is also suppressed by common ion effect.

NH<sub>4</sub><sup>+</sup> + OH<sup>-</sup> (From base) ⇌ NH<sub>4</sub>OH (Weak base)

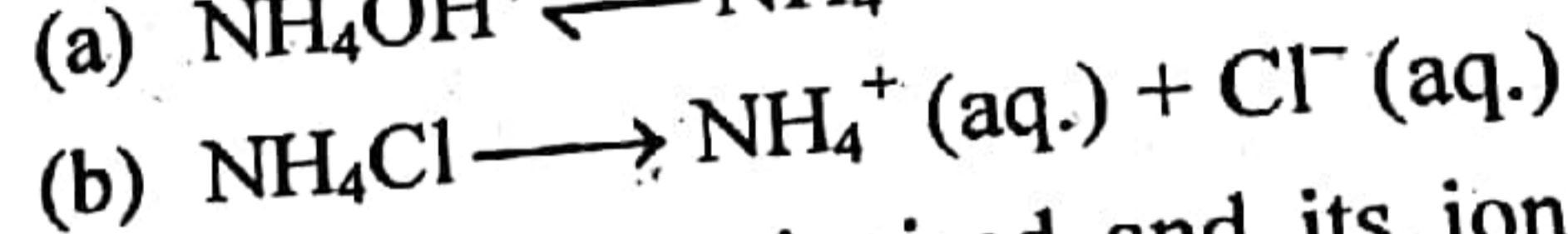
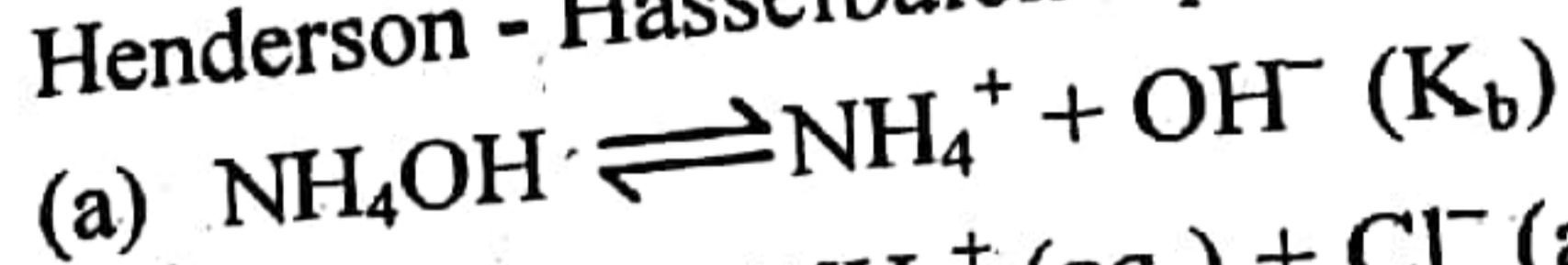
Again when strong acid is added in the solution it will attack on unionised base NH<sub>4</sub>OH to form feebly ionised H<sub>2</sub>O molecules.



- (iii) One can remember the buffer action of basic buffer with the help of following figure -



- (iv) p<sup>H</sup> of such basic buffer can be calculated from Henderson - Hasselbalch equation as follows.



NH<sub>4</sub>OH is feebly ionised and its ionisation is also suppressed by presence of common ion (NH<sub>4</sub><sup>+</sup>). So one can fairly assume [NH<sub>4</sub><sup>+</sup>] = [Salt] and [NH<sub>4</sub>OH] = [Base] taken initially in buffer solution.

$$\text{so } K_b = \frac{[OH^-][NH_4^+]}{[NH_4OH]}$$

$$\text{or } [OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]}$$

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

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

$$\text{or } pH = 14 - pOH$$

### 9.3 Buffer Capacity

- (i) The property of a buffer solution to resist alteration in its pH value is known as buffer capacity.

- (ii) Buffer capacity is number moles of acid or base added in one litre of solution as to change the pH by unity, i.e.

Buffer capacity ( $\phi$ )

=

$$\frac{\text{Number of moles acid or base added to 1 lit. sol.}}{\text{Change in pH}}$$

$$\text{or } \phi = \frac{\partial b}{\partial(\text{pH})}$$

where  $\partial b$  is number of moles of acid or base added and  $\partial(\text{pH})$  is change in pH.

#### 9.4 Applications of Buffer solutions in analytical chemistry.

- For the removal of  $\text{PO}_4^{3-}$  ion after second group using  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$  buffer.
- For the precipitation of lead chromate quantitatively in gravimetric analysis using  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$  buffer.
- For the precipitation of hydroxides of III<sup>rd</sup> group using  $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$  buffer.
- A buffer solution of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  is used for precipitation of carbonates of V<sup>th</sup> group.

#### 10. SOLUBILITY (S) :

At a constant temperature, the mass of a solute or electrolyte dissolved in the 100 gm of solvent in its saturated solution is called as solubility. Or number of gm mole of a solute dissolved in one litre of water at constant temperature is called as solubility of that solute.

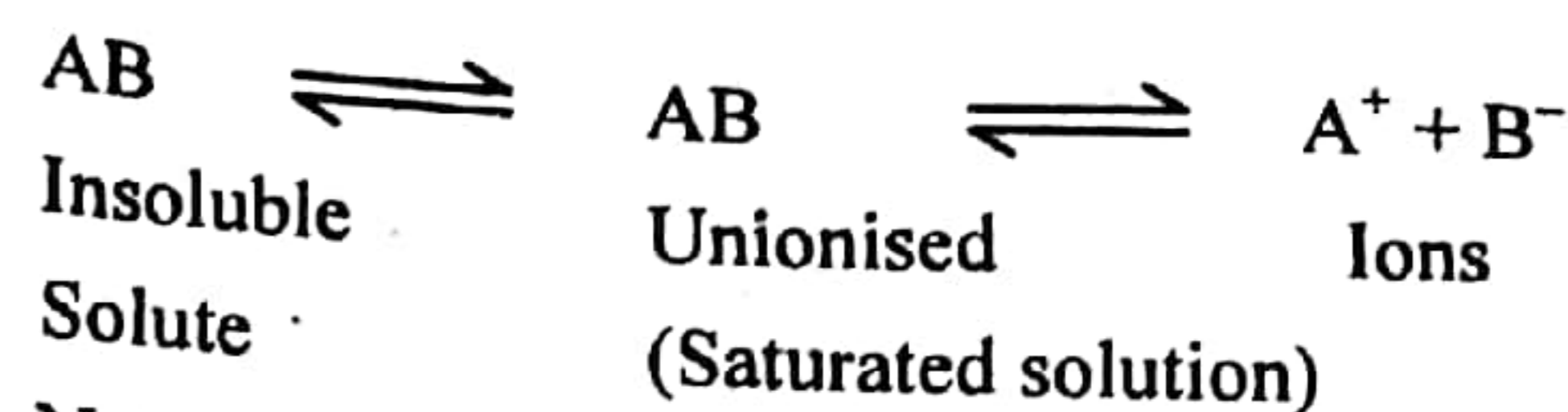
Solubility of a solute in moles / litre

$$= \frac{\text{Solubility of solute in gm / litre}}{\text{molecular weight of the solute}}$$

#### 10.1 Solubility product ( $K_{SP}$ ) :

It is the product of the ionic concentration of the ions of binary solid electrolyte in saturated state at constant temperature.

- (a) Let solubility of a compound  $A_x B_y$  be  $s$  moles  $\text{L}^{-1}$  it means that if more than  $s$  moles are dissolved in solvent (one litre) only  $s$  moles will be soluble, rest will be insoluble, following equilibrium is established,



Note : - In the solubility  $s$  moles  $\text{L}^{-1}$ , moles of only unionised are counted moles of ions and insoluble solute do not have anything to do.

- (b) According to law of mass action -

$$K_1 = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]}$$

$$\text{or } K_1 [\text{AB}] = [\text{A}^+][\text{B}^-] = K_{SP}$$

This  $K_{SP}$  is called **solubility product**.

- (c) At a certain temperature solubility product of a compound is constant, it means that ions are formed in the manner that product of their concentration is always a constant. However, it becomes clear that if one of ions ( $\text{A}^+$  or  $\text{B}^-$ ) is added from outside, it would tend to increase  $K_{SP}$  because  $[\text{A}^+]$  or  $[\text{B}^-]$  has get increased, so that extra ions will react with other ions to convert in insoluble part and this will get precipitated.

- (d)  $K_{SP}$  increases with increase in temperature.

- (e) In a saturated solution.

$$K_{SP} = [\text{A}^+][\text{B}^-]$$

- (f) In an unsaturated solution of AB

$$K_{SP} > [\text{A}^+][\text{B}^-]$$

i.e. more solute can be dissolved.

- (g) In a supersaturated solution

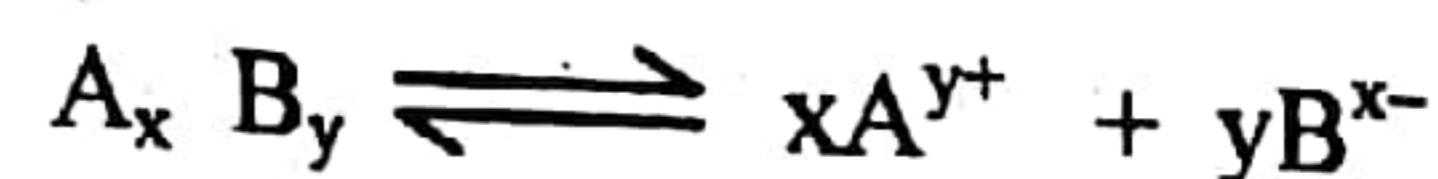
$$K_{SP} < [\text{A}^+][\text{B}^-]$$

i.e. precipitation will start to occur.

#### 10.2 Relationship between Solubility and Solubility

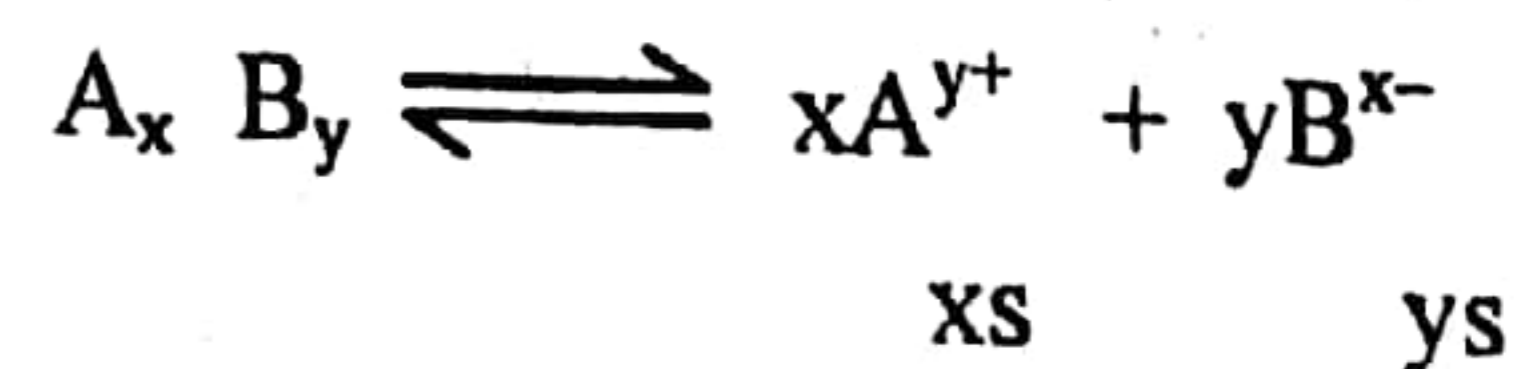
**Product :**

The equilibrium for a saturated solution of a salt  $A_x B_y$  may be expressed as,



Thus, solubility product  $K_{SP} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$

Let the solubility of the salt  $A_x B_y$  in water at a particular temperature be 's' moles per litre then



$$\text{So, } K_{SP} = [xs]^x [ys]^y$$

$$K_{SP} = x^x \cdot y^y (s)^{x+y}$$