



# Chemical Equilibrium

## Introduction :

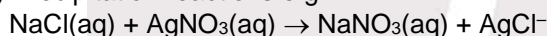
Equilibrium is a state in which there are no observable changes as time goes by. When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time and there are no visible changes in the system. However, there is much activity at the molecular level because reactant molecules continue to form product molecules while product molecules react to yield reactant molecules. This dynamic situation is the subject of this chapter. Here we will discuss different types of equilibrium reactions, the meaning of the equilibrium constant and its relationship to the rate constant and factors that can effect a system at equilibrium.

## Section (A) : Properties of equilibrium, active mass

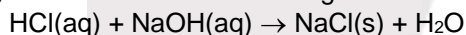
### Types of chemical reactions

The reaction which proceed in one direction only

(a) Precipitation reactions e.g.

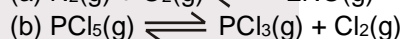
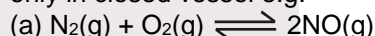


(b) Neutralization reactions e.g.



(c) Reactions in open vessels with one of the gaseous product

Reactions which proceed in both the direction. These are possible only in closed vessel e.g.



### Types of chemical reactions

Irreversible reaction		Reversible reaction	
1	The reaction which proceeds in one direction (forward direction) only.	1	The reaction which proceed in both the direction under the same set of experimental conditions.
2	Reactants are almost completely converted into products. Products do not react to form reactants again.	2	Reactants form products and products also react to form reactants in backward direction. These are possible in closed vessels .
3	Do not attain equilibrium state.	3	Attain the equilibrium state and never go to completion.
4	Such reactions are represented by single arrow {→}	4	Represented by double arrow (⇌) or (↔)
5	Examples –	5	Examples :–
(a)	Precipitation reactions e.g. $\text{NaCl(aq)} + \text{AgNO}_3(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{AgCl}\downarrow$	(a)	Homogeneous reactions- only one phase is present (i) Gaseous phase– $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ [Birkland eyde process ( $\text{HNO}_3$ )] $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ (Haber's process) (ii) Liquid phase $\text{CH}_3\text{COOH}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$
(b)	Neutralization reactions e.g. $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}$	(b)	<b>Heterogeneous reactions:</b> More than one phases are present $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$
(c)	$2\text{KClO}_3(\text{s}) \xrightarrow{\Delta} 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$		
(d)	<b>Reactions in open vessel:</b> Even a reversible reaction will become irreversible if it is carried out in open vessel. Ex. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$		Closed vessel

## State of Chemical equilibrium :

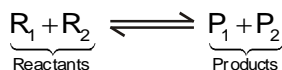
State of equilibrium means the balance of driving forces i.e. the factors taking the reaction in forward direction and the backward direction are balancing each other.

The equilibrium state represents a compromise between two opposing tendencies.

- Tendency to minimise energy.
- Molecules try to maximise entropy.



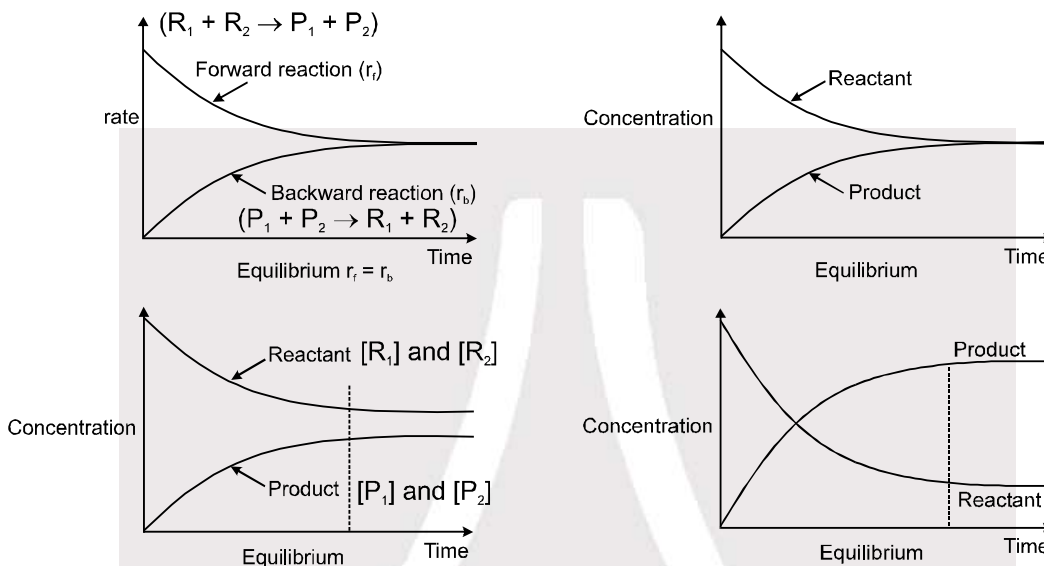
In a reversible reaction like :



Initially only reactants are present.  $R_1$  and  $R_2$  combine to form  $P_1$  and  $P_2$ . As soon as  $P_1$  and  $P_2$  are formed, they start the backward reaction. As concentrations of  $R_1$  and  $R_2$  decrease rate of forward reaction decreases and rate of backward reaction increases. Ultimately a stage is reached when both the rates become equal. Such a state is known as "Chemical Equilibrium" or "state of Equilibrium".

**At equilibrium :**

- (i) Rate of forward reaction ( $r_f$ ) = rate of backward reaction ( $r_b$ ) (dynamic nature)
- (ii) All measurable parameters become constant with respect to time.

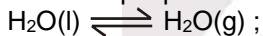


### Types of equilibria on the basis of process

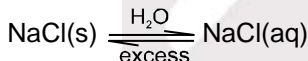
#### Physical Equilibrium

Equilibrium in physical process is called physical equilibrium.

For example phase changes like



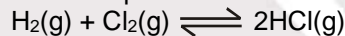
Solvation like



#### Chemical Equilibrium

Equilibrium in chemical process is called chemical equilibrium.

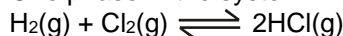
For example



### Types of equilibria on basis of physical state

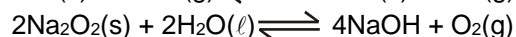
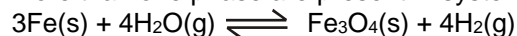
#### Homogeneous equilibrium

One phase in the system



#### Heterogeneous equilibrium

More than one phase are present in system



### Characteristics of chemical equilibrium :

- The nature and the properties of the equilibrium state are the same regardless of the direction from which it is achieved. It can be achieved in both directions.
- Equilibrium is dynamic in nature.  
It means that at microscopic level reaction has not stopped. It appears that no change is occurring but both the opposing reactions are proceeding at the same rate. So there is no net change. Thus equilibrium is not static in nature.

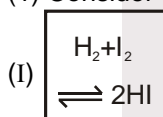




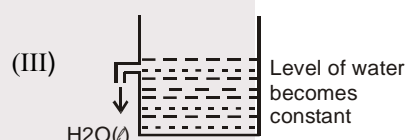
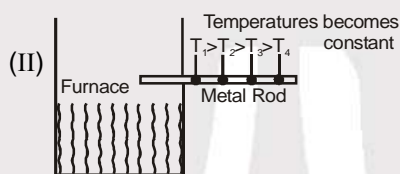
- A catalyst can alter the rate of approach of equilibrium but does not change the state of equilibrium. By using catalyst, the equilibrium can be achieved in different (more/less) time, but the relative concentrations of reactants and products are same irrespective of the presence or absence of a catalyst.
- Equilibrium can be observed by constancy of some observable properties like colour, pressure, concentration, density, temperature, refractive index etc. which may be suitable in a given reaction.
- At equilibrium, free energy change  $\Delta G = 0$
- Equilibrium state can be affected by altering factors like pressure, volume, concentration and temperature etc. (Le Chatelier's Principle).
- System moves toward an equilibrium state spontaneously even if it is disturbed. It will return to original state.

## Solved Examples

Ex-1. (1) Consider the following cases—



Equilibrium state has been attained



The nature of flow of energy in case (I) is same as that in—

- (A) II (B) III (C) II and III (D) None

Sol. (D) None, because in II and III, the flow of energy or matter is taking place only in one direction. While in equilibrium state, the flow of energy takes place in both directions equally. Thus (I) is a dynamic equilibrium while states in II and III are called steady state (static equilibrium).

### Law of mass action : [By Guldberg and Waage]

Rate at which a substance reacts  $\propto$  [Active Mass of the substance]

Active Mass = Molar concentration i.e. Moles/Litres

$$= \frac{\text{Wt of substance (gram)}}{\text{Molar wt.} \times \text{Vol. (Litre)}}$$

It is represented in square brackets i.e. [ ] e.g. [A], [N<sub>2</sub>] etc.

**Note:** Active masses are dimensionless quantities but for our purposes we generally take them with dimensions of molarity, partial pressure, etc.

The rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers of their stoichiometric coefficients.

Ex.  $aA + bB \longrightarrow \text{products}$

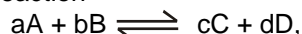
Rate of reaction  $\propto [A]^a [B]^b$

Rate =  $k [A]^a [B]^b$ , where  $k$  is the rate constant of the reaction.

### Section (B & C) : Homogeneous equilibrium: $K_C$ in gaseous system & $K_P$ in gaseous system

#### Equilibrium constant (K) :

For a general reaction



Forward reaction rate  $r_f = k_f [A]^a [B]^b$ ,

Backward reaction rate  $r_b = k_b [C]^c [D]^d$ ,

At equilibrium  $r_f = r_b$

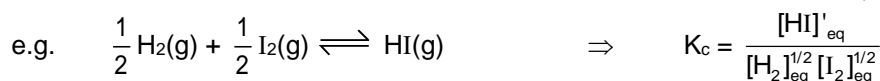
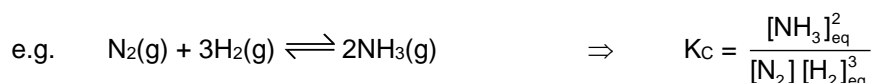
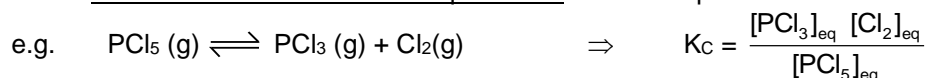
$$k_f [A]_{\text{eq}}^a [B]_{\text{eq}}^b = k_b [C]_{\text{eq}}^c [D]_{\text{eq}}^d$$

The concentrations of reactants & products at equilibrium are related by

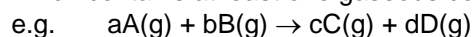
$$\frac{k_f}{k_b} = K_C = \frac{[C]_{\text{eq}}^c [D]_{\text{eq}}^d}{[A]_{\text{eq}}^a [B]_{\text{eq}}^b}$$



- $K_c$  is a constant and is called the **equilibrium constant in terms of concentration**, where all the concentrations are at equilibrium and are expressed in moles/litre.



- $K_p \rightarrow$  **Equilibrium constant in terms of partial pressure**. It is defined for the equilibrium reaction which contains at least one gaseous component.



$$K_p = \frac{[P_C]_{\text{eq}}^c [P_D]_{\text{eq}}^d}{[P_A]_{\text{eq}}^a [P_B]_{\text{eq}}^b}$$

Where various pressures are the partial pressures of various gases substances.

### Section (D) : Relation between $K_p$ and $K_c$

- **Relation between  $K_p$  &  $K_c$**

$$PV = nRT \quad \text{or,} \quad P = \frac{n}{V} RT$$

$$P = CRT \quad \text{where } C = \frac{n}{V} = (\text{moles per litre})$$

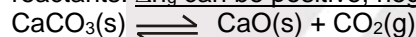
$$P_C = [C] RT ; \quad P_D = [D] RT ; \quad P_A = [A] RT ; \quad P_B = [B] RT$$

$$\Rightarrow K_p = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d) - (a+b)}$$

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

Where  $\Delta n_g = (c + d) - (a + b)$ , calculation of  $\Delta n$  involves only gaseous components.

- $\Rightarrow \Delta n_g =$  sum of the number of moles of gaseous products – sum of the number of moles of gaseous reactants.  $\Delta n_g$  can be positive, negative, zero or even fraction.



$\Delta n_g = 1$  (because there is only one gas component in the products and no gas component in the reaction)

$$\Rightarrow K_p = K_c \cdot (RT)$$

#### Unit of Equilibrium constants :

- Unit of  $K_p$  is  $(\text{atm})^{\Delta n}$
- Unit of  $K_c$  is  $(\text{mole/Lit})^{\Delta n} = (\text{conc.})^{\Delta n}$

- Note :** ○ In fact, equilibrium constant does not carry any unit because it is based upon the activities of reactants and products and activities are unitless quantities. Under ordinary circumstances, where activities are not known, above types of equilibrium constant and their units are employed.

- **For pure solids and pure liquids, although they have their own active masses but they remain constant during a chemical change (reaction). Therefore, these are taken to be unity for the sake of convenience.**



$$K_c = [\text{CO}_2], \quad K_p = P_{\text{CO}_2}$$



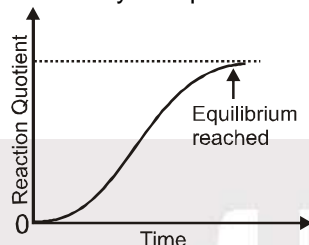
## Section (E) : Reaction quotient and Its applications

### ● Predicting the direction of the reaction

#### Reaction Quotient (Q)

At each point in a reaction, we can write a ratio of concentration terms having the same form as the equilibrium constant expression. This ratio is called the reaction quotient denoted by symbol Q. It helps in predicting the direction of a reaction.

The expression  $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$  at any time during reaction is called reaction quotient. The concentrations [C], [D], [A], [B] are not necessarily at equilibrium.



- The reaction quotient is a variable quantity with time.
- It helps in predicting the direction of a reaction.

- if  $Q > K_c$  reaction will proceed in backward direction until equilibrium is reached.
- if  $Q < K_c$  reaction will proceed in forward direction until equilibrium is established.
- if  $Q = K_c$  Reaction is at equilibrium.

eg.  $2A(g) + B(g) \rightleftharpoons C(g) + D(g)$

$Q_c$  = Reaction quotient in terms of concentration

$$Q_c = \frac{[C][D]}{[A]^2[B]}$$

$$K_c = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}^2[B]_{eq}} \quad [\text{Here all the conc. are at equilibrium}]$$

## Solved Examples

**Ex-2.** For the reaction  $NOBr(g) \rightleftharpoons NO(g) + \frac{1}{2} Br_2(g)$

$K_P = 0.15$  atm at  $90^\circ C$ . If NOBr, NO and  $Br_2$  are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 0.2 atm respectively, will  $Br_2$  be consumed or formed ?

**Sol.**  $Q_P = \frac{[P_{Br_2}]^{1/2} [P_{NO}]}{[P_{NOBr}]} = \frac{[0.2]^{1/2} [0.4]}{[0.50]} = 0.36$

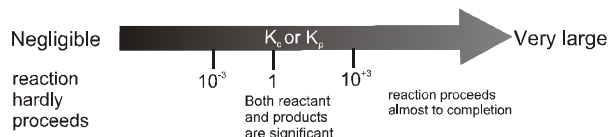
$$K_P = 0.15$$

$$\therefore Q_P > K_P$$

Hence, reaction will shift in backward direction  $\therefore Br_2$  will be consumed

### ● Predicting the extent of the reaction

$$K = \frac{[\text{Product}]_{eq}}{[\text{Reactant}]_{eq}}$$



**Case-I:** If K is large ( $K > 10^3$ ) then product concentration is very very larger than the reactant ( $[\text{Product}] \gg [\text{Reactant}]$ ) Hence concentration of reactant can be neglected with respect to the product. In this case, the reaction is product favourable and equilibrium will be more in forward direction than in backward direction.



**Case-II :** If  $K$  is very small ( $K < 10^{-3}$ )

$[\text{Product}] \ll [\text{Reactant}]$

Hence concentration of Product can be neglected as compared to the reactant.

In this case, the reaction is reactant favourable.

## Solved Examples

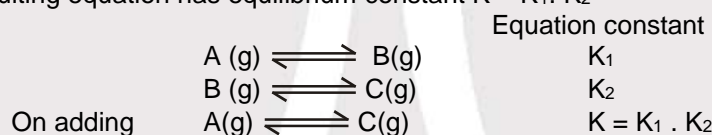
**Ex-3.** The  $K_p$  values for three reactions are  $10^{-5}$ , 20 and 300 then what will be the correct order of the percentage composition of the products.

**Sol.** Since  $K_p$  order is  $10^{-5} < 20 < 300$  so the percentage composition of products will be greatest for  $K_p = 300$ .

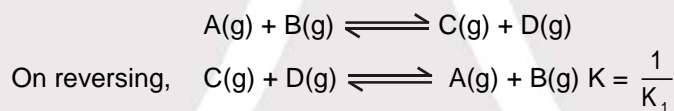
### Section (F) : Properties of equilibrium Constant

- Equilibrium constant does not depend upon concentration of various reactants, presence of catalyst, direction from which equilibrium is reached
- The equilibrium constant does not give any idea about time taken to attain equilibrium.
- **K depends on the stoichiometry of the reaction.**

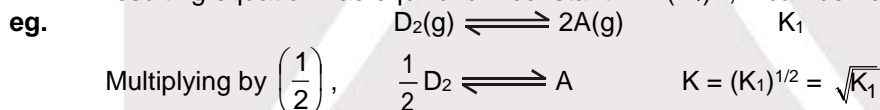
- If two chemical reactions at equilibrium having equilibrium constants  $K_1$  and  $K_2$  are added then the resulting equation has equilibrium constant  $K = K_1 \cdot K_2$



- If the reaction having eq. constant  $K_1$  is reversed then resulting equation has eq. constant  $\frac{1}{K_1}$



- If a chemical reaction having equilibrium constant  $K_1$  is multiplied by a factor  $n$  then the resulting equation has equilibrium constant  $K = (K_1)^n$ ,  $n$  can be fraction



- **Equilibrium constant is dependent only on the temperature.**

It means  $K_p$  and  $K_c$  will remain constant at constant temperature no matter how much changes are made in pressure, concentration, volume or catalyst.

- However if temperature is changed,

$$\log \frac{k_2}{k_1} = \frac{\Delta H}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]; \quad \Delta H = \text{Enthalpy of reaction}$$

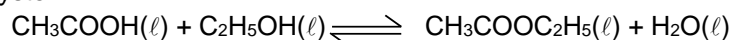
If  $T_2 > T_1$  then  $K_2 > K_1$  provided  $\Delta H = +ve$  (endothermic reaction)

$K_2 < K_1$  if  $\Delta H = -ve$  (exothermic reaction)

In the above equation, the unit of  $R$  and  $\Delta H/T$  should be same.

### Section (G) : Homogeneous Equilibrium (liquid system)

The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.



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





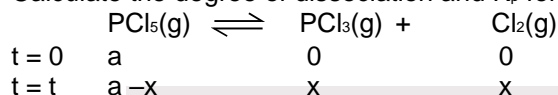
**Significance of n**

$$n = \frac{\text{sum of stoichiometric coefficient of product}}{\text{sum of coefficient of reactants}}$$

- (i) for  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$  ( $n = 2$ )  
 (ii) for  $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$  ( $n = \frac{3}{2} + \frac{1}{2} = 2$ )  
 (iii) for  $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$  ( $n = 1$ )

**Solved Examples**

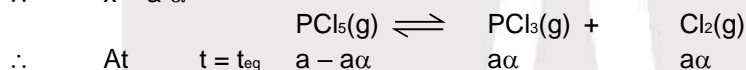
**Ex-5.** Calculate the degree of dissociation and  $K_p$  for the following reaction.



Since for a mole, x moles are dissociated

**Sol.** ∴ For 1 mole,  $\frac{x}{a}$  moles =  $\alpha$  are dissociated

$$\therefore x = a \alpha$$



Total no. of moles at equilibrium =  $a + a\alpha = a(1 + \alpha)$

$$P_{\text{PCl}_5} = \frac{a(1-\alpha)P}{a(1+\alpha)}, \quad P_{\text{PCl}_3} = \frac{a\alpha \cdot P}{a(1+\alpha)}, \quad P_{\text{Cl}_2} = \frac{a\alpha}{a(1+\alpha)} \cdot P$$

$$K_p = \frac{\left\{ \frac{\alpha P}{1+\alpha} \right\}^2}{\left( \frac{1-\alpha}{1+\alpha} \right) P} \quad K_p = \frac{\alpha^2 \cdot P}{1-\alpha^2} \quad (\text{Remember})$$

**Observed molecular weight and Observed Vapour Density of the mixture**

$$\text{Observed molecular weight of } A_n(\text{g}) = \frac{\text{molecular weight of } A_n(\text{g})}{\text{total no. of moles at equilibrium}} = \frac{aM_{\text{th}}}{a(1+(n-1)\alpha)}$$

$$\therefore M_{\text{obs}} = \frac{M_{\text{th}}}{[1+(n-1)\alpha]}$$

where  $M_{\text{th}}$  = theoretical molecular weight ( $n$  = atomicity)

$$M_{\text{mixture}} = \frac{M_{A_n}}{[1+(n-1)\alpha]}, \quad M_{A_n} = \text{Molar mass of gas } A_n$$

**Vapour density (V.D.) :** Density of the gas divided by density of hydrogen under same temp & pressure is called vapour density.

$$\text{○ } D = \text{vapour density without dissociation} = \frac{M_{A_n}}{2}$$

$$d = \text{vapour density of mixture} = \text{observed v.d.} = \frac{M_{\text{mix}}}{2}$$

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

$$\therefore \alpha = \frac{D-d}{(n-1) \times d} = \frac{M_T - M_0}{(n-1)M_0}$$

Where  $M_T$  = Theoretical molecular wt.,  $M_0$  = observed molecular wt. or molecular wt. of the mixture at equilibrium.

**Note :** It is not applicable for  $n = 1$  eg. Dissociation of HI & NO (as the total number of don't change during the dissociation.)





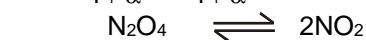
## Solved Examples

**Ex-6.** The vapour density of a mixture containing  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  is 38.3 at  $33^\circ\text{C}$  calculate the no. of moles of  $\text{NO}_2$  if 100g of  $\text{N}_2\text{O}_4$  were taken initially.

**Sol.**  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

$$M_{\text{mix}} = 2 \times 38.3 = 76.6$$

$$M_{\text{mix}} = \frac{M_{\text{th}}}{1 + \alpha} = \frac{92}{1 + \alpha} \Rightarrow \alpha = 0.2$$



$$t = 0 \quad a \quad 0$$

$$t = t \quad a - a\alpha \quad 2a\alpha$$

$$\text{no. of moles of } \text{NO}_2 = 2a\alpha = \frac{2 \times 100 \times 0.2}{92} = 0.435$$

### Section (J) : Thermodynamics of equilibrium

For a general reaction,  $m\text{A} + n\text{B} \rightleftharpoons p\text{C} + q\text{D}$ ,  $\Delta G$  is given by-

$$\Delta G = \Delta G^\circ + 2.303 RT \log_{10} Q$$

where  $\Delta G$  = Gibb's Free energy change

$\Delta G^\circ$  = Standard Gibb's Free energy change

$Q$  = reaction quotient

Since, at equilibrium,  $Q = K$

Here  $K$  is thermodynamic equilibrium constant replacing  $K_c$  or  $K_p$

$$K = \frac{(a_C)^p (a_D)^q}{(a_A)^m (a_B)^n}; \quad \text{Here } a_X \text{ denotes the activity of X.}$$

In fact, ' $a_x$ ' is the ratio of the activity of substance at equilibrium and its activity in standard condition. That is why it is unitless and  $K$  is also unitless.

- Note :** (i) Thermodynamic equilibrium constant is unitless since activity is unitless.  
(ii) For pure solids & pure liquids, activity is unity.  
(iii) For gases (ideal behaviour), the activity is its partial pressure (in atm).  
(iv) For components in solution, activity is molar concentration.

At equilibrium,  $\Delta G = 0$

$$\Rightarrow \Delta G^\circ = -2.303 RT \log_{10} K$$

$$\text{Now since, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

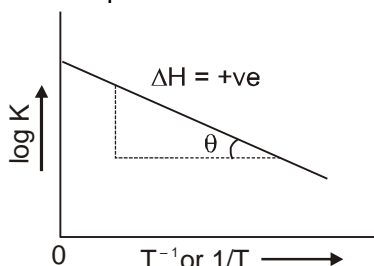
where  $\Delta H^\circ$  = Standard enthalpy change of the reaction

$\Delta S^\circ$  = Standard entropy change

$$\Rightarrow -2.303 RT \log_{10} K = \Delta H^\circ - T\Delta S^\circ$$

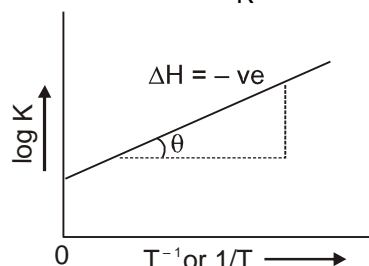
$$\Rightarrow \log_{10} K = -\frac{\Delta H^\circ}{2.303} \cdot \frac{1}{RT} + \frac{\Delta S^\circ}{2.303R}$$

If plot of  $\ln k$  vs  $\frac{1}{T}$  is plotted then it is a straight line with slope =  $-\frac{\Delta H^\circ}{R}$  and intercept =  $\frac{\Delta S^\circ}{R}$



Endothermic reaction

$$\text{Slope} = \frac{-\Delta H^\circ}{2.303R} = \tan \theta$$



Exothermic reaction

$$\text{y intercept} = \frac{\Delta S^\circ}{2.303R}$$



If at temperature  $T_1$ , equilibrium constant is  $K_1$  and at  $T_2$ , it is  $K_2$  then ;

$$\log_{10} K_1 = \frac{-\Delta H^\circ}{2.303R} \cdot \frac{1}{T_1} + \frac{\Delta S^\circ}{2.303R} \quad \dots\dots\dots (i)$$

$$\log_{10} K_2 = \frac{-\Delta H^\circ}{2.303R} \cdot \frac{1}{T_2} + \frac{\Delta S^\circ}{2.303R} \quad \dots\dots\dots (ii)$$

[Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  remains constant in this temperature range.]

Subtract eq. (ii) from (i) we get **Vant Hoff equation-**

$$\log \left( \frac{K_1}{K_2} \right) = \frac{\Delta H^\circ}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

- Note :**
- $\Delta H$  should be substituted with sign.
  - Unit of  $\Delta H/T$  and gas constant  $R$  should be same.
  - For endothermic ( $\Delta H > 0$ ) reaction value of the equilibrium constant increases with the rise in temperature
  - For exothermic ( $\Delta H < 0$ ) reaction, value of the equilibrium constant decreases with increase in temperature

**Condition for spontaneity :  $\Delta G < 0$  for spontaneous process or reaction.**

Since,  $\Delta G = \Delta H - T\Delta S$

$$\Rightarrow \Delta H - T\Delta S < 0 \quad \Rightarrow \quad T > \Delta H/\Delta S$$

\*  $\Delta G > 0$  for non-spontaneous process or reaction.

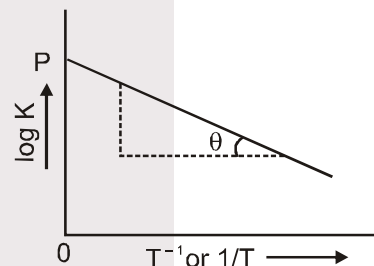
\*  $\Delta G = 0$  for equilibrium.

## Solved Examples

**Ex-7.** Variation of equilibrium constant  $K$  with temperature  $T$  is given by van't Hoff equation,

$$\log K = \log A - \frac{\Delta H^\circ}{2.303 RT}$$

A graph between  $\log K$  and  $T^{-1}$  was a straight line as shown in the figure and having  $\theta = \tan^{-1} (0.5)$  and  $OP = 10$ . Calculate :



- (a)  $\Delta H^\circ$  (standard heat of reaction) when  $T = 300$  K,
- (b)  $A$  (pre-exponential factor),
- (c) Equilibrium constant  $K$ , at  $300$  K,
- (d)  $K$  at  $900$  K if  $\Delta H^\circ$  is independent of temperature.

**Sol.** (a)  $\log_{10} K = \log_{10} A - \frac{\Delta H^\circ}{2.303 RT}$   
It is an equation of a straight line of the type  $y = c + mx$

$$\text{Slope 'm'} = \tan \theta = \frac{\Delta H^\circ}{2.303 R}$$

$$0.5 = \frac{\Delta H^\circ}{2.303 \times 8.314} \quad \Rightarrow \quad \Delta H^\circ = 9.574 \text{ J mol}^{-1}$$

(b) Intercept ' $c$ ' =  $\log_{10} A = 10 \quad \therefore \quad A = 10^{10}$

(c)  $\log K = 10 - \frac{9.574}{2.303 \times 8.314 \times 298} \Rightarrow \quad K = 9.96 \times 10^9$

(d)  $\log \left( \frac{K_2}{K_1} \right) = \frac{\Delta H}{2.303R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$

$$\log \frac{K_2}{9.96 \times 10^9} = \frac{9.574}{2.303 \times 8.314} \left\{ \frac{1}{298} - \frac{1}{798} \right\}$$

On solving  $K_2 = 9.98 \times 10^9$

**Ans. (a)  $9.574 \text{ J mol}^{-1}$ ; (b)  $A = 10^{10}$ ; (c)  $9.96 \times 10^9$ ; (d)  $9.98 \times 10^9$**

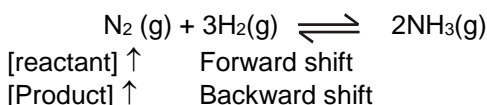


## Section (K) : Le-chatelier's principle

### Le Chatelier's Principle:

If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of change applied and the equilibrium is established again under new conditions.

- **Effect of concentration :** If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration. e.g. In the following example.



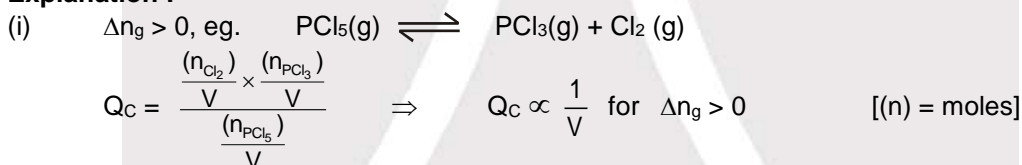
- If concentration of reactant is increased at equilibrium then reaction shifts in the forward direction.
- If concentration of product is increased then reaction shifts in the backward direction

**Note :** The addition of any solid component does not affect the equilibrium.

- **Effect of volume :**

- If volume is increased, pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
- If volume is increased then, for  
 $\Delta n_g > 0$  reaction will shift in the forward direction  
 $\Delta n_g < 0$  reaction will shift in the backward direction  
 $\Delta n_g = 0$  reaction will not shift. eg.  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  (No effect)

### Explanation :

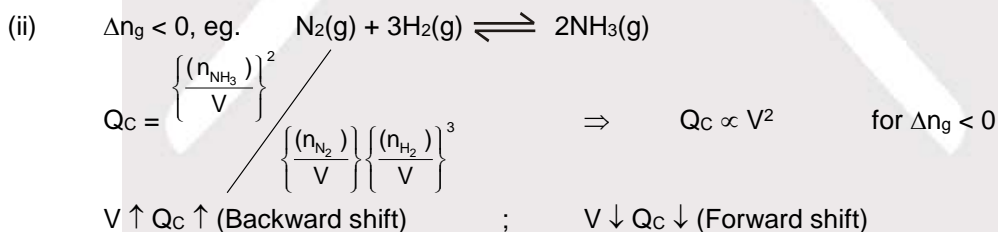


On increasing V,  $Q_c$ , decreases.

Now, for  $Q_c < K_c$  reaction will shift in forward direction.

Thus, if, Volume ↑  $Q_c$  ↓ (Forward shift)

Volume ↓  $Q_c$  ↑ (Backward shift)



- **Effect of pressure :**

On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e. no. of moles in the reaction decreases and vice versa.

∴  $P \propto \text{no. of moles}$

(i) For  $\Delta n_g = 0 \rightarrow$  No. effects

(ii) For  $\Delta n_g > 0$ ,  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

$$Q_p = \frac{(X_{\text{PCl}_3} \cdot P) \cdot (X_{\text{Cl}_2} \cdot P)}{(X_{\text{PCl}_5} \cdot P)} \Rightarrow Q_p \propto P \quad [( ) = \text{mole fraction}]$$

$P \downarrow$ ;  $Q_p \downarrow$ ; (Forward shift)

$P \uparrow$ ;  $Q_p \uparrow$ ; (Backward shift)



$$Q_P = \frac{[(X_{\text{NH}_3})P]^2}{[(X_{\text{N}_2}) \cdot P][X_{\text{H}_2}]^3} \Rightarrow Q_P \propto \frac{1}{P^2}$$

$P \uparrow$ ;  $Q_P \downarrow$ ; (Forward shift) ;  $P \downarrow$ ;  $Q_P \uparrow$ ; (Backward shift)

● **Effect of catalyst :**

Due to catalyst, the state of equilibrium is not affected i.e. no shift will occur as catalyst lowers the activation energy of both the forward & reverse reaction by same amount, thus altering the forward & reverse rate equally and hence, the equilibrium will be attained faster i.e time taken to reach the equilibrium is less.

● **Effect of inert gas addition :**

(a) **At constant volume :** Inert gas addition has no effect at constant volume

(b) **At constant pressure :** If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

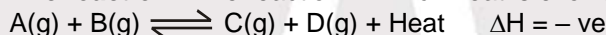
(i)  $\Delta n_g > 0$ , reaction will shift in the forward direction

(ii)  $\Delta n_g < 0$ , reaction will shift in the backward direction

(iii)  $\Delta n_g = 0$ , no effect

● **Effect of temperature :**

(i) **Exothermic reaction :** The reaction in which heat is evolved



eg.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{Heat}$

$T \uparrow \Rightarrow K' \text{ will decrease}$

$$\log \frac{K_1}{K_2} = \frac{\Delta H^\circ}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (\text{from vant' hoff equation})$$

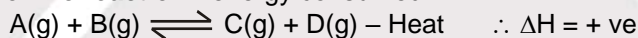
$$\log \frac{K_1}{K_2} < 0 \Rightarrow \log K_1 - \log K_2 > 0 \Rightarrow \log K_1 > \log K_2 \Rightarrow K_1 > K_2$$

Reaction will shift in backward direction.

$T \downarrow \Rightarrow K \text{ will increase.}$

Reaction will shift in forward direction.

(ii) **Endothermic reaction :** energy consumed.

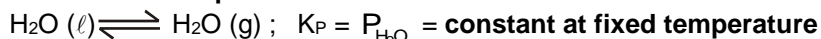


$T \uparrow \Rightarrow K \uparrow \Rightarrow \text{Forward}; \quad T \downarrow \Rightarrow K \downarrow \Rightarrow \text{Backward}$

**Application of le chatelier's principle : Practical equilibrium situations :**

**Section (L) : Vapour pressure and Relative Humidity**

● It is the pressure exerted by the vapours over its liquid when it is in equilibrium with the liquid. Vapour pressure of water is also called **aqueous tension**.



Hence V.P. of liquid is independent of pressure, volume and concentration change.

e.g. at 25°C, vapour pressure of water  $\approx 24$  mm of Hg

$$\text{Relative Humidity} = \frac{\text{Partial pressure of H}_2\text{O vapours}}{\text{Vapour pressure of H}_2\text{O at that temp.}}$$

● **Formation of diamond :**

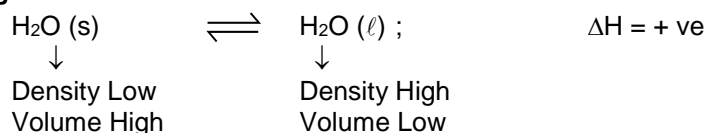


$\downarrow$	$\downarrow$
Density Low	Density High
Volume High	Volume Low

Formation of diamond is favourable at high pressure and high temperature

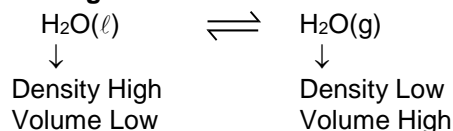


● **Melting of ice :**



Melting of ice is favourable at high temperature and high pressure.

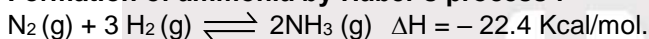
● **Boiling of water :**



On increasing pressure, equilibrium will shift in the direction in which volume is decreasing i.e. backward.

Hence, on increasing pressure, the boiling point increases.

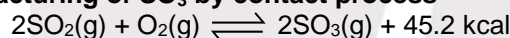
● **Formation of ammonia by Haber's process :**



(i) The reaction will shift in the forward direction at low temperature, but at very low temperature the rate of reaction becomes very low; thus moderate temperature is used for this reaction.

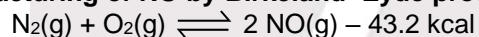
(ii) At high pressure, reaction will shift in forward direction to form more product.

● **Manufacturing of SO<sub>3</sub> by contact process**



High pressure (1.5 to 1.7 atm), Low temperature (500°C), higher quantity of SO<sub>2</sub> and O<sub>2</sub> are favourable conditions for the formation of SO<sub>3</sub>.

● **Manufacturing of NO by Birkeland–Eyde process**

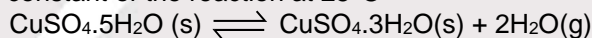


○ No effect on change of pressure

○ High temperature (1200°C to 2000°C), High concentration of N<sub>2</sub> and O<sub>2</sub> are favourable condition for the formation of NO.

## Solved Examples

**Ex-8.** The equilibrium constant of the reaction at 25°C



is  $1.084 \times 10^{-4} \text{ atm}^2$ . Find out under what conditions of relative humidity, CuSO<sub>4</sub>·5H<sub>2</sub>O will start losing its water of crystallization according to above reaction. (Vapour pressure of water at 25°C is 24 mm of Hg).

**Sol.**  $K_P = (P_{\text{H}_2\text{O}})^2$  so  $P_{\text{H}_2\text{O}} = \sqrt{1.084 \times 10^{-4}} = 1.041 \times 10^{-2} \text{ atm} \approx 8 \text{ mm of Hg}$

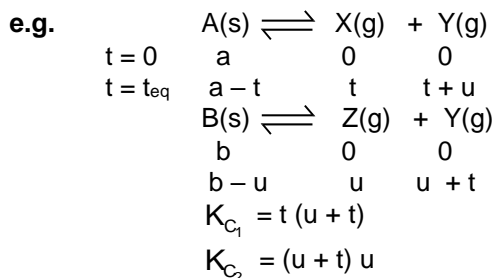
○ If in a room, pressure of water is greater than 8 mm of Hg then CuSO<sub>4</sub>·3H<sub>2</sub>O will absorb water from air and will form CuSO<sub>4</sub>·5H<sub>2</sub>O & will keep absorbing until partial pressure of H<sub>2</sub>O becomes 8 mm of Hg.

○ If  $P_{\text{H}_2\text{O}} < 8 \text{ mm of Hg}$  then CuSO<sub>4</sub>·5H<sub>2</sub>O will lose water of crystallization and reaction will move in forward direction.

i.e. If relative humidity  $< \frac{8}{24} < 33.33\%$  then CuSO<sub>4</sub>·5H<sub>2</sub>O will lose water of crystallization.

## Section (M) : Simultaneous equilibria

If in any container there are two or more equilibria existing simultaneously involving one or more than one common species. Then in both/all equilibrium the concentration of common species is the total concentration of that species due to all the equilibria under consideration.



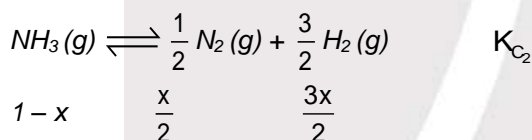
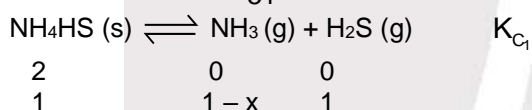
## Solved Examples

**Ex-9.** 102 g of solid  $NH_4HS$  is taken in the 2L evacuated flask at  $57^\circ C$ . Following two equilibrium exist simultaneously



one mole of the solid decomposes to maintain both the equilibrium and 0.75 mole of  $H_2$  was found at the equilibrium then find the equilibrium concentration of all the species and  $K_C$  for both the reaction.

**Sol.** Moles of  $NH_4HS = \frac{102}{51} = 2$



Given that moles of  $H_2 = \frac{3x}{2} = 0.75 \Rightarrow x = \frac{1}{2}$

$$K_{C_1} = \frac{1(1-x)}{2 \cdot 2} = \frac{1}{8} \quad [\text{Since } V = 2 \text{ L}]$$

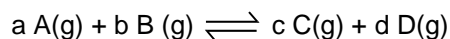
$$K_{C_2} = \frac{\left(\frac{3x}{4}\right)^{3/2} \left(\frac{x}{4}\right)^{1/2}}{\left(\frac{1-x}{2}\right)} = \frac{\left(\frac{3}{8}\right)^{3/2} \left(\frac{1}{8}\right)^{1/2}}{\frac{1}{4}} = (3)^{3/2} \frac{1}{64} \times \frac{4}{1} = \frac{(3)^{3/2}}{16}$$





## SUMMARY

Chemical equilibrium is a dynamic state in which the concentration of reactants and products remain constant because the rates of the forward and the reverse reaction are equal. For the general reaction



concentrations in the equilibrium mixture are related by the equilibrium equation :

$$K_c = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b}$$

The ratio on the right side of the equation is called the equilibrium constant expression. The equilibrium constant  $K_c$  is the number obtained when equilibrium concentrations (in mol/L) are substituted into the equilibrium constant expression. The value of  $K_c$  varies with temperature and depends upon the form of the balanced chemical equation.

The equilibrium constant  $K_p$  can be used for gas phase reactions. It is defined in the same way as  $K_c$  except that the equilibrium constant expression contains partial pressures (in atmospheres) instead of molar concentrations. The constants  $K_p$  and  $K_c$  are related by the equation,

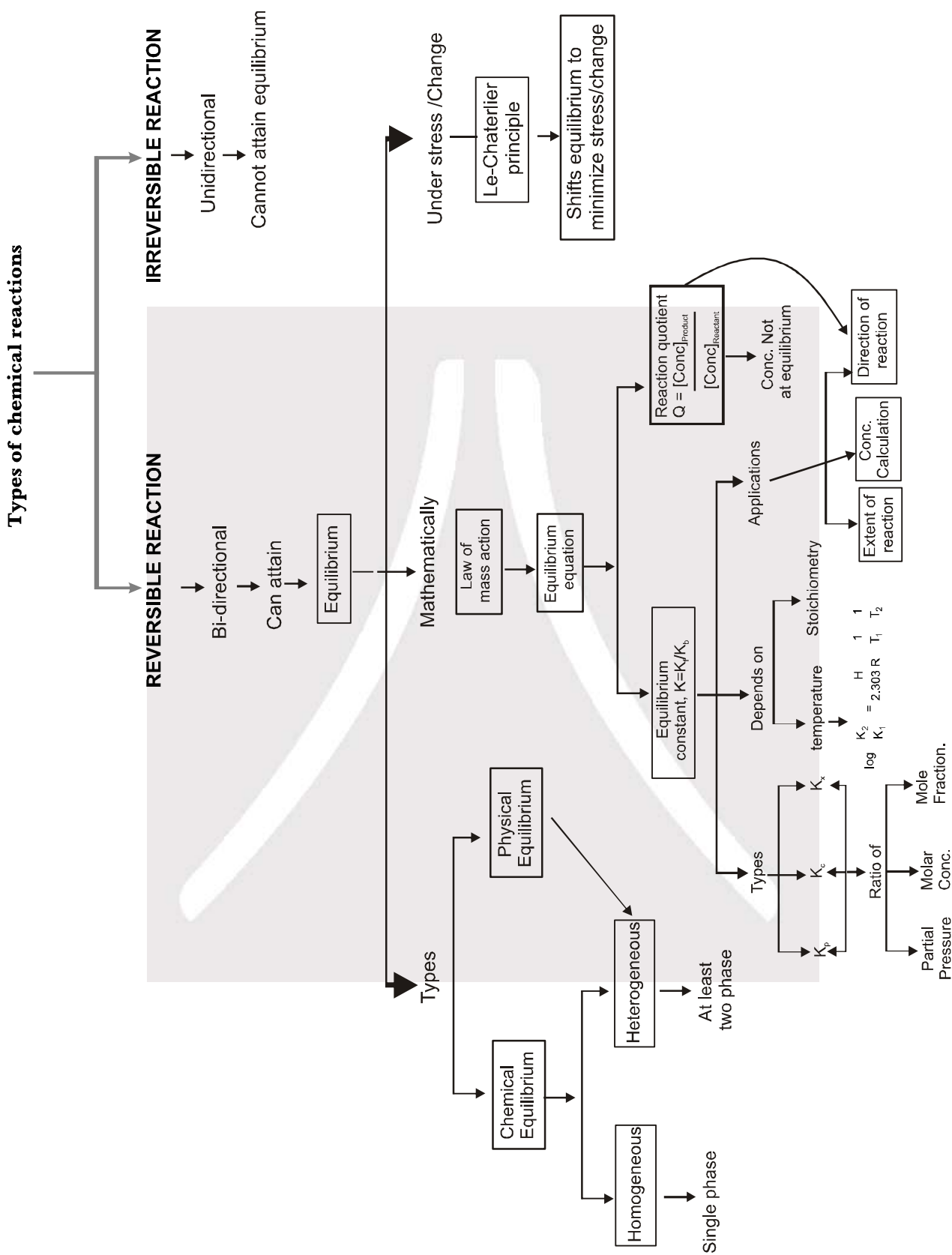
$$K_p = K_c (RT)^{\Delta n_g}, \text{ where } \Delta n_g = (c + d) - (a + b).$$

Homogeneous equilibrium are those in which all reactants and products are in a single phase; heterogeneous equilibria are those in which reactants and products for heterogeneous equilibrium does not include concentrations of pure solids or pure liquids.

The value of the equilibrium constant for a reaction makes it possible to judge the extent of reaction, predict the direction of reaction, and calculate equilibrium concentrations (or partial pressures) from initial concentration (or partial pressures) . The farther the reaction proceed towards completion, the larger the value of  $K_c$ . The direction of a reaction not at equilibrium depends on the relative values of  $K_c$  and the reaction quotient  $Q_c$  which is defined in the same way as  $K_c$  except that the concentrations in the equilibrium constant expression are not necessarily equilibrium concentrations. If  $Q_c < K_c$ , net reaction goes from left to right to attain equilibrium; if  $Q_c = K_c$ , the system is at equilibrium.

The composition of an equilibrium mixture can be altered by changes in concentration, pressure (volume), or temperature. The qualitative effect of these changes is predicted by Le Chatelier's principle, which says that if a stress is applied to a reaction mixture at equilibrium, net reaction occurs in the direction that relieves the stress. Temperature changes affect equilibrium concentrations because  $K_c$  is temperature-dependent. As the temperature increases,  $K_c$  for an exothermic reaction decreases, and  $K_c$  for an endothermic reaction increases.

A catalyst increases the rate at which chemical equilibrium is reached, but it does not affect the equilibrium constant or the equilibrium concentration. The equilibrium constant for a single-step reaction equals the ratio of the rate constants for the forward and reverse reactions :  $K_c = k_f / k_b$ .





### MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. An example of a reversible reaction is :  
 (A)  $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{NaI}(\text{aq}) \rightleftharpoons \text{PbI}_2(\text{s}) + 2\text{NaNO}_3(\text{aq})$   
 (B)  $\text{AgNO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightleftharpoons \text{AgCl}(\text{s}) + \text{HNO}_3(\text{aq})$   
 (C)  $2\text{Na}(\text{s}) + \text{H}_2\text{O}(\ell) \rightleftharpoons 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$   
 (D)  $\text{KNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightleftharpoons \text{KCl}(\text{aq}) + \text{NaNO}_3(\text{aq})$

**Ans. (D)**

**Sol.** Precipitation reactions, acid base reactions and reactions in which gases are liberated and are taking place in open container will be irreversible reactions.

2. For the reaction,  $\text{A} + \text{B} \rightleftharpoons 3\text{C}$ , if 'a' mol/litre of each 'A' & 'B' are taken initially then at equilibrium the incorrect relation is :

(A)  $[\text{A}] - [\text{B}] = 0$       (B)  $3[\text{B}] + [\text{C}] = 3a$       (C)  $3[\text{A}] + [\text{C}] = 3a$       (D)  $[\text{A}] + [\text{B}] = 3[\text{C}]$

**Ans. (D)**

**Sol.** At equilibrium :

$$[\text{A}] = [\text{B}]$$

$$[\text{A}] + \frac{1}{3}[\text{C}] = a$$

3. The equilibrium constant for the decomposition of water  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$  is given by :

( $\alpha$  = degree of dissociation of  $\text{H}_2\text{O}(\text{g})$ ;  $p$  = Total equilibrium pressure )

$$(A) K = \frac{\alpha^2 p^{1/2}}{(1+\alpha)(2-\alpha)^{1/2}}$$

$$(B) K = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$$

$$(C) K = \frac{\alpha^3 p^{1/2}}{\sqrt{2}}$$

$$(D) K = \frac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$$

**Ans. (B)**

**Sol :**  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

$$\begin{array}{ccc} 1 & 0 & 0 \\ 1-\alpha & \alpha & \alpha/2 \end{array}$$

Total moles at equilibrium =  $1 - \alpha + \alpha + \alpha/2 = 1 + \alpha/2$

Let the total pressure at equilibrium be =  $p$

$$\text{So, } p_{\text{H}_2\text{O}} = \frac{1-\alpha}{1+\alpha/2} \times p$$

$$p_{\text{H}_2} = \frac{\alpha}{1+\alpha/2} \times p$$

$$p_{\text{O}_2} = \frac{\alpha/2}{1+\alpha/2} \times p$$

$$\text{So } K_p = \frac{(p_{\text{O}_2})^{1/2} (p_{\text{H}_2})}{(p_{\text{H}_2\text{O}})}$$

4. The reaction quotient  $Q$  for  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  is given by  $Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$ . The reaction will

proceed in backward direction, when:

(A)  $Q = K_c$       (B)  $Q < K_c$       (C)  $Q > K_c$       (D)  $Q = 0$

**Ans. (C)**

**Sol.** When  $Q > K$ , reaction will favour backward direction and when  $Q < K$ , it will favour forward direction.

5. 0.96 g of HI were heated to attain equilibrium  $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ . The reaction mixture on titration requires 15.7 mL of N/10 hypo solution. Calculate degree of dissociation of HI.

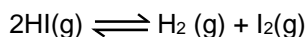
**Ans.** 20.9%





**Sol.** meq of  $I_2 = \frac{W_{I_2}}{127} \times 1000 = 1.57$

$$w_{I_2} = \frac{127 \times 1.57}{1000} \quad n_{I_2} = \frac{1.57}{2000}$$



$$a - a\alpha \quad \frac{a\alpha}{2} \quad \frac{a\alpha}{2} \quad \frac{0.96}{256} \times \alpha = \frac{1.57}{2000}$$

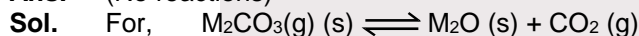
$$\alpha = 0.209 \quad \text{Ans.}$$

6. Would 1%  $CO_2$  by volume in air be sufficient to prevent any loss in weight when  $M_2CO_3$  is heated at  $120^\circ C$  ?



$K_p = 0.0095$  atm at  $120^\circ C$ . How long would the partial pressure of  $CO_2$  have to be to promote this reaction at  $120^\circ C$  ?

**Ans.** (No reactions)



$$\therefore CO_2 \text{ is } 1\% \text{ in air ; } \therefore P_{CO_2} = \frac{1}{100} \times P_{air} = \frac{1}{100} \times 1 \text{ atm.} = 0.01 \text{ atm.}$$

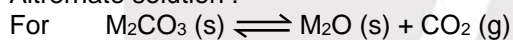
$$\text{Also for equilibrium } K_p = P_{CO_2} = 0.0095 \text{ atm.}$$

$$\therefore \text{ Given, } P_{CO_2} = 0.01 \text{ atm.}$$

Since decomposition is carried out in presence of  $P_{CO_2}$  of 0.01 atm and  $K_p = 0.0095$  atm, thus, practically no decomposition of  $M_2CO_3$ . Thus, 1%  $CO_2$  is sufficient to prevent any loss in weight.

If at all reaction is desired, the  $P_{CO_2}$  must be lesser than 0.0095 atm as  $P_{CO_2}$  at equilibrium cannot be more than 0.0095 atm.

Alternate solution :



$$\left( \frac{1}{100} + P \right)$$

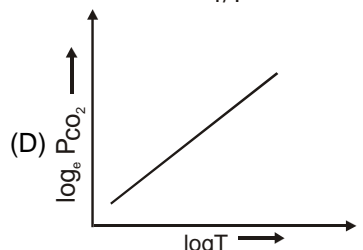
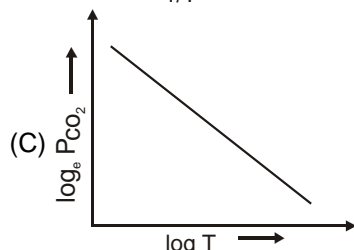
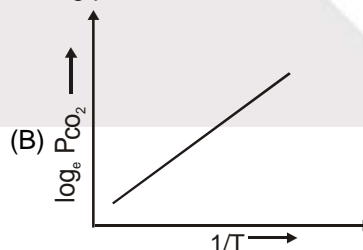
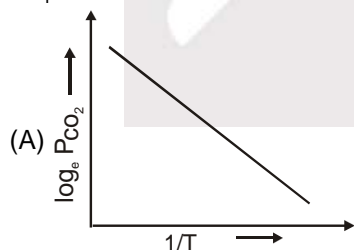
$\therefore K_p = P_{CO_2}$  and the pressure of  $CO_2$  already present in  $1/100$  atm. Let the decomposition of  $M_2CO_3$  produces the  $CO_2$  of pressure  $P$ , then

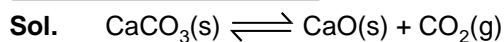
$$\therefore K_p = \frac{1}{100} + P \quad \text{or} \quad 0.0095 = P + 0.01 \quad \text{or} \quad P = -0.0005.$$

The value of pressure comes negative and thus, it may be concluded that  $M_2CO_3$  will not dissociate in pressure of  $CO_2$  of pressure 0.01 atm.

7. For the chemical equilibrium,  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$\Delta H_f^\circ$  can be determined from which one of the following plots ?





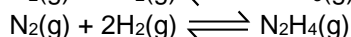
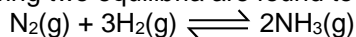
$$K_p = P_{\text{CO}_2}$$

$$\log K_p = \log A - \frac{\Delta H_r^\circ}{2.303RT}$$

$$\log P_{\text{CO}_2} = \log A - \frac{\Delta H_r^\circ}{2.303} \cdot \frac{1}{RT} \dots\dots\dots (i)$$

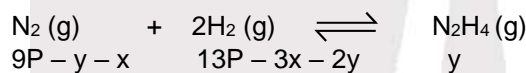
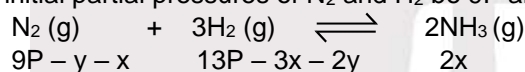
Graph (a) represents (i) and its slope will be used to determine the heat of the reaction.  
So, Ans. (A).

**8.** In a container of constant volume at a particular temperature  $\text{N}_2$  and  $\text{H}_2$  are mixed in the molar ratio of 9:13. The following two equilibria are found to be coexisting in the container



The total equilibrium pressure is found to be 3.5 atm while partial pressure of  $\text{NH}_3(\text{g})$  and  $\text{H}_2(\text{g})$  are 0.5 atm and 1 atm respectively. Calculate of equilibrium constants of the two reactions given above.

**Sol.** Let the initial partial pressures of  $\text{N}_2$  and  $\text{H}_2$  be 9P and 13 P respectively



$$\begin{aligned} \text{Total pressure} &= P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{NH}_3} + P_{\text{N}_2\text{H}_4} = 3.5 \text{ atm} \\ &= (9\text{P} - x - y) + (13\text{P} - 3x - 2y) + 2x + y = 3.5 \text{ atm} \quad \dots(1) \end{aligned}$$

$$P_{\text{NH}_3} = 2x = 0.5 \text{ atm} \quad \dots(2)$$

$$P_{\text{H}_2} = (13\text{P} - 3x - 2y) = 1 \text{ atm} \quad \dots(3)$$

$$\begin{aligned} \text{from (1)} \quad &\Rightarrow (9\text{P} - x - y) + 1 \text{ atm} + 0.5 + y = 3.5 \\ &\Rightarrow (9\text{P} - x) = 2 \text{ atm} \end{aligned}$$

$$\begin{aligned} \text{so} \quad 9\text{P} &= 2.25 \\ \text{P} &= 0.25 \text{ atm} \end{aligned}$$

$$\begin{aligned} \text{from (3) equation} \quad 2y &= 1.5 \\ y &= 0.75 \text{ atm} \end{aligned}$$

$$\text{so} \quad P_{\text{N}_2} = 9\text{P} - x - y = 1.25 \text{ atm}$$

$$P_{\text{H}_2} = 1 \text{ atm}$$

$$P_{\text{NH}_3} = 0.5 \text{ atm}$$

$$P_{\text{N}_2\text{H}_4} = 0.75 \text{ atm}$$

$$\text{So, } K_{P_1} = \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 \cdot P_{\text{N}_2}} = \frac{0.5 \times 0.5}{1 \times 1 \times 1 \times 1.25} = 0.2 \text{ atm}^{-2}$$

$$K_{P_2} = \frac{P_{\text{N}_2\text{H}_4}}{P_{\text{N}_2} \cdot P_{\text{H}_2}^2} = \frac{0.75}{1 \times 1 \times 1.25} = 0.6 \text{ atm}^{-2}$$