CHEMICAL EQUILIBRIUM

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.

Reaction

Irreversible

Reversible

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 –

(a) Reactions in which reactant react to form product only.

(b) Reactions proceed in one single direction.

(c) Always proceed to completion.

(d) Always carried out in open vessel.

(e) 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 –

(a) All thermal decomposition in open vessel.

(b) All the neutralisation reaction of strong acid and strong base.

(c) All precipitation reactions.

(d) 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 –

(a) In these type of reactions, reactant react to form product and product further react to form reactant.

- (b) Reactions proceed in both directions.
- (c) These type of reactions never get completed.
- (d) Always carried out in closed vessel.

B. Some examples of reversible reactions are as follows –

(a) All thermal dissociation in closed vessel.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

 $PCI_5 \xrightarrow{} PCI_3 + CI_2$

(b) All types of salt hydrolysis except strong acid strong base salt.

$$NH_4CI + H_2O \implies NH_4OH + HCI$$

Salt of weak base

strong acid

(c) All gaseous reactions in closed vessel.

$$N_{2} + O_{2} = 2NO$$

$$H_{2} + I_{2} = 2HI$$

$$2 SO_{3} = 2SO_{2} + O_{2}$$

$$N_{2} + 3H_{2} = 2NH_{3}$$

(d) All the reactions of organic hydrolysis.

$$CH_3 - C - OC_2H_5 + H - OH$$

$$\leftarrow$$
 CH₃ - C - OH + C₂H₅ - OH \parallel

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. $N_{r}(q) + O_{r}(q) = \frac{2}{2} NO(q)$

$$CH_3 - C - O - C_2H_5(\ell) = 2 NO(g)$$

$$CH_3 - C - O - H(\ell) + C_2H_5 - OH(\ell)$$

Graphite (s)
$$\longrightarrow$$
 Diamond (s)
S_{Rh.} (s) \longrightarrow S_{mono.} (s)

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.

 $\begin{array}{cccc} CaCO_{3}(s) & \longleftarrow & CaO(s) + CO_{2}(g) \\ FeO(g) & + & CO(g) & \longleftarrow & Fe(s) + & CO_{2}(g) \\ Fe(s) & + & H_{2}O(\ell) & \longleftarrow & Fe(OH)_{2}(s) + & H_{2}(g) \\ FeCI_{3}(s) & + & 3H_{2}O(\ell) & \longleftarrow & Fe(OH)_{3}(s) + & 3HCI(\ell) \\ & & H_{2}O(\ell) & \longleftarrow & H_{2}O(g) \end{array}$

5. CHEMICAL EQUILIBRIUM

(a) State of reversible reaction at which rate of forward reaction becomes equal to the rate of backward reaction is called chemical equilibrium.
(b) State where rate of formation of product is equal to the rate of dissociation of reactant is known as chemical equilibrium.

(c) State of reversible reaction in which the concentration of reactant and concentration of product remain unchanged but not necessarily equal, is called chemical equilibrium.

(d) State where exchange of energy becomes zero is also called as chemical equilibrium.

5.1 Characteristics of chemical equilibrium :

(a) 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.
(b) On the stage of equilibrium the reaction proceeds both the side.

(c) At the state of equilibrium, both reactants and products are present and their concentration do not change with respect to time.

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





6. LAW OF MASS ACTION

(a) This law was given by Guldberg and Waage.

(b) 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. $A + B \longrightarrow C + D$

$$A + B \longrightarrow$$

$$\frac{-dA}{dt} \propto [A]$$

$$\frac{-dB}{dt} \propto [B]$$

$$\frac{dC}{dt} \propto [C]$$

$$\frac{dD}{dt} \propto [D]$$

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

r ∝ [A] [B]

r

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 $\mathrm{N_2}$ in 2 litre volume ?

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

eg. What is the active mass of 14 gm N₂ 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.

 $A + B \longrightarrow C + D$ 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

 $r_b \propto [C] [D]$ or $r_b = K_2 [C] [D]$ where K₂ 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]

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

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

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 concentration of N_2 and O_2 is a and b respectively. x is the degree of dissociation.

	$N_2 +$	$0_2 \rightarrow$	- 2NO
Initial	а	b	0
concentration moles at equilibrium	(a-x)	(b-x)	2x
Active mass	$rac{(a-x)}{V}$	$rac{(b-x)}{V}$	$\frac{2x}{V}$
(mol /-1)			

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:

C

n

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

$$N_2 + O_2 \implies 2 \text{ NO}$$

Initial a b 0
concentration
moles at (a-x) (b-x) 2x
equilibrium

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 $\ \mbox{P}_{NO}\,,\ \mbox{P}_{N_2}\,,\ \mbox{P}_{O_2}$ 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 Penta-chloride- $(\Delta n > 0)$ A. Calculation of $\mathbf{K}_{\mathbf{C}}$ - Suppose one mole of PCI_5 is take in a closed container of V litre. Further at equilibrium x mol of it dissociated PCI \longrightarrow PCl₃ + Cl₂ Initial 0 1 0 concentration moles at (1-x) Х х equilibrium $\frac{x}{v}$ Active mass $\frac{1-x}{y}$ х $(mol \ l^{-1})$

According to law of mass action

$$K_{C} = \frac{[PCI_3][CI_2]}{[PCI_5]}$$

Substituting the values in the above equation.

 $K_{C} = \overline{\left(\underline{1-x}\right)}$

K =	x ²	
'`C -	(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 $1 = x \approx 1$

So,
$$K_{C} = \frac{x^{2}}{v}$$

 $x^{2} = K_{C} \cdot V$
 $x^{2} \propto V$

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

B. Calculation of K_p -

PCI₅ = $+ Cl_2$ 0 initial 0 concentration moles at 1-x х х equilibrium

Total no. of moles at equilibrium,

(1 - x) + x + x = (1 + x) moles According to law of mass action

$$K_{P} = \frac{P_{PCI_{3}} \times P_{CI_{2}}}{P_{PCI_{5}}}$$

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 -

Page # 4

$$K_{P} = \frac{\left(\frac{x \times P}{1 + x}\right)\left(\frac{x \times P}{1 + x}\right)}{\frac{(1 - x) \times P}{(1 + x)}}$$
$$K_{P} = \frac{x^{2}P}{1 - x^{2}}$$

The equation of K_P is not independent of pressure.

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

The degree of dissociation of PCI₅ is inversely proportional to the square root of pressure so, decrease of pressure increases dissociation of PCl₅.

6.3.3 Formation of Ammonia – ($\Delta n < 0$) A. Calculation of K_c : –

+ $3H_2 \longrightarrow 2NH_3$ N_2 3 Initial 1 concentration moles at (1-x) (3-3x) 2x equilibrium Active mass $\left(\frac{1-x}{v}\right) \left(\frac{3-3x}{v}\right) \left(\frac{2x}{v}\right)$

Kp x²

x²

According to law of mass action

$$K_{C} = \frac{[NH_{3}]^{2}}{[N_{2}][H_{2}]^{3}}$$

Substituting the values in the above equation-

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



v

$$K_{C} = \frac{4x^{2}v^{2}}{(1-x)(3-3x)^{3}}$$
$$K_{C} = \frac{4x^{2}v^{2}}{27(1-x)^{4}}$$

The formula of K_C has V in the denominator, hence the equilibrium will be affected by V of the reaction container. endence If, x << 1 then, $(1 - x)^4 = 1$ Der

pendence if, x <

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

$$x^{2} = \frac{K_{C}}{v^{2}}$$

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

$$\boxed{x \propto \frac{1}{v}}$$

If we increase the volume of the container the degree of dissociation x is decreased. **B.** Calculation of K_{p} :

 $N_2 + 3H_2 = 2NH_3$ Initial concentration 1 3 0 moles at equilibrium (1 - x) (3 - 3x)2x Total number of moles at equilibrium = (1 - x) + (3 - 3x) + 2x = (4)- 2x) According to the law of mass action

$$K_{P} = \frac{(P_{NH_{3}})^{2}}{(P_{N_{2}}) \times (P_{H_{2}})^{3}}$$

/D

At equilibrium $P_{NH_3} =$

$$P_{N_{2}} = \frac{(1-x).P}{(4-2x)}$$
$$P_{H_{2}} = \frac{(3-3x).P}{(4-2x)}$$

Substituting the values in the above equation of K_P.

$$K_{p} = \frac{\left(\frac{2x}{4-2x}.P\right)^{2}}{\left(\frac{1-x}{4-2x}.P\right)\left(\frac{3-3x}{4-2x}.P\right)^{3}}$$

$$K_{\rm P} = \frac{4x^{-}(4-2x)^{-}}{(1-x)^{3}(3-3x)^{2}{\rm P}^{2}}$$
$$K_{\rm P} = \frac{16x^{2}(2-x)^{2}}{27(1-x)^{4}{\rm P}^{2}}$$

The equation of K_p is not independent of pressure

suppose, x << 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 Bartholate and Gill. In this reaction all the reactants and products are in liquid state.

(mole ℓ^{-1})

I

Μ

e

According to law of mass action

$$K_{C} = \frac{[CH_{3}COOC_{2}H_{5}][H_{2}O]}{[CH_{3}COOH][C_{2}H_{5}OH]}$$

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) :

It 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 $p_A = Partial pressure of A$

$$p_B = Partial pressure of B$$

 $p_{\rm C}$ = Partial pressure of C

 $p_D = Partial pressure of D$

Partial pressure of a gas given by the following formula.

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

or $p = mole fraction \times P$.

Here, P is the total pressure.

7.3 Factors which do not influence equilibrium constant :

- (a) Concentration of reactants and products.
- (b) Pressure and volume.
- (c) Presence of catalyst.

(d) Addition of the inert gas at constant Pressure and volume.

7.4 Factors influence the equilibrium constant :

- **A**. Mode of representation of chemical reaction.
- **B**. Stoichiometry of reaction.
- C. Temperature.

A. Mode of representation of reaction -

If we take reaction $2HI \longrightarrow H_2 + I_2$ Then, we write the value of equilibrium constant

 $K_{\text{C}_{1}}$ for the above reaction as following.

$$K_{C_1} = \frac{[H_2][I_2]}{[H]|^2}$$

Now, if we take reaction $H_2 + I_2 \implies 2HI$ Then, we write the value of equilibrium constant

 K_{C_2} for above reaction as following

$$K_{C_2} = \frac{[HI]^2}{[H_2][I_2]} = \frac{1}{K_{C_1}}$$
(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 $H_2(g)$ and $I_2(g)$.

$$H_2 + I_2 \stackrel{\Delta}{\longleftarrow} 2HI$$

The expression of its equilibrium constant is-

$$K_{C_1} = \frac{[HI]^2}{[H_2][I_2]}$$

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

$$\frac{1}{2}$$
 H₂(g) + $\frac{1}{2}$ I₂(g) \longrightarrow HI(g)

The expression for the equilibrium constant is -

$$K_{C_2} = \frac{[HI]}{[H_2]^{\frac{1}{2}}[I_2]^{\frac{1}{2}}}$$

on the basis of comparing both the equilibrium constant equation.

$$K_{C_2} = \sqrt{K_{C_1}}$$
 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.

A + B $\stackrel{\sim}{\longrightarrow}$ C + D is K₁ then for the reaction

$$\frac{1}{n} A + \frac{1}{n} B \Longrightarrow \frac{1}{n} C + \frac{1}{n} D$$

the value of the equilibrium constant K_2 is equal to $n\sqrt{K_1}$ 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 $\rm K_c$ and $\rm K_p$ decrease with rise in temperature while for endothermic reactions, the value of $\rm K_c$ and $\rm K_p$ increases with rise in temperature. This type of variation in equilibrium constant with temperature given by **Van't Hoff** equation as follows -

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

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 ΔH = Energy of reaction of constant



1

temperature

R = Molar gas constant

According to the temperature, reaction are of three types.

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

 $\begin{array}{rrrr} \log \ \mathrm{K}_2 \ - \ \log \ \mathrm{K}_1 \ = \ 0 \\ \log \ \mathrm{K}_2 \ = \ \log \ \mathrm{K}_1 \end{array}$

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

(b) Endothermic reaction $\Rightarrow \Delta H = (+)$ ve log K₂ - log K₁ = (+) ve, means K₂ > K₁

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

(c) Exothermic reaction $\Rightarrow \Delta H = (-)$ ve log K₂ - log K₁ = (-) ve, means K₂ < K₁

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)^{Δn}.

Value of Δn	Units of K _p	Units of K_c
0	No Un <mark>it</mark>	No unit
> 0	(atm) ^{∆n}	(moles ⁻¹) ^{∆n}
< 0	(atm) ^{∆n}	(moles ⁻¹) ^{∆n}

7.6 Relation between K_p and K_c :

Let us consider the following reaction $n_1 A + n_2 B = m_1 C + m_2 D.$

The value of K_c for the reaction is,

 $K_{c} = \frac{[C]^{m_{1}}[D]^{m_{2}}}{[A]^{n_{1}}[B]^{n_{2}}}$

According to gas law PV = n RT

$$P = \left(\frac{n}{v}\right) RT \qquad \dots \dots (i)$$

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

 $\therefore \quad K_{P} = \frac{(P_{C})^{m_{1}} (p_{D})^{m_{2}}}{(p_{A})^{n_{1}} (p_{B})^{n_{2}}}$

on putting the value of 'p' in the formula of K_p by the equation(i)

$$\begin{split} \mathsf{K}_{\mathsf{P}} &= \frac{(\mathbf{C})^{m_1} (\mathbf{D})^{n_1} (\mathbf{B}) \mathbf{RT})^{n_2}}{([\mathbf{A}] \mathbf{RT})^{n_1} ([\mathbf{B}] \mathbf{RT})^{n_2}} \\ \mathsf{K}_{\mathsf{P}} &= \frac{[\mathbf{C}]^{m_1} [\mathbf{D}]^{m_2} (\mathbf{RT})^{m_1 + m_2}}{[\mathbf{A}]^{n_1} [\mathbf{B}]^{n_2} (\mathbf{RT})^{n_1 + n_2}} \\ \mathsf{K}_{\mathsf{P}} &= \mathsf{K}_{\mathsf{C}} (\mathbf{RT})^{(m_1 + m_2) - (n_1 + n_2)} \\ \mathsf{K}_{\mathsf{P}} &= \mathsf{K}_{\mathsf{C}} (\mathbf{RT})^{\Delta n} \\ [\Delta n &= (m_1 + m_2) - (n_1 + n_2)] \\ \Delta n &= \text{number of moles of product - number of moles of reactant.} \\ \mathsf{T} &= \text{Absolute temperature.} \end{split}$$

([C] RT)^{m1} ([D]RT)^{m2}

Note : ∆n only includes gaseous moles.

I. on the basis of Δn , the reactions are of three types.

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

 $N_2 + O_2 = 2NO$ $\Delta n = 2 - 2 = 0$
By the relation of
 $K_P = K_C (RT)^{\Delta n}$ $\therefore \Delta n = 0$
 $K_P = K_C (RT)^0$
So, $K_P = K_C$

(b) Reaction in which the value of Δn is negative-

$$2 \text{ CO} + 0_2 \implies 2 \text{ CO}_2$$

 $\Delta n = 2 - 3 = -$

By the relation of
$$K_{\rm P} = K_{\rm C} (\rm RT)^{\Delta n}$$

 $K_{\rm P} = K_{\rm C} (\rm RT)^{-1}$

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 Δn is positive-2 SO₃ \implies 2 SO₂ + O₂

II. On the basis of the value of pressure, reactions are also of three types as follows-(a) Reaction in which the value of $\Delta n = 0$

$$N_2 + O_2 \implies 2 NC$$

$$\Delta n = 2 - 2 = 0$$
$$K_{\rm p} = K_{\rm c} (\rm RT)^{\Delta n}$$

According to relationship

 $K_P = K_C (RT)^0$ means $K_P = K_C$

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

(b) Reaction in which the value of Δn is (+)ve.

 $\begin{array}{cccc} {\sf PCI}_5 & \longrightarrow & {\sf PCI}_3 \,+\, {\sf CI}_2 \\ & & \Delta n \,=\, 2 \,-\, 1 \,=\, +\, 1 \\ \\ \mbox{In this type of reaction, when pressure is} \end{array}$ increases then the degree of dissociation decreases.

(c) Reaction in which the value of
$$\Delta n$$
 is (-)ve.
N₂ + 3H₂ \implies 2NH₃

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

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

 $A + B + energy \longrightarrow C + D$

or, $A + B \implies C + D \quad \Delta H = (+) ve$

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

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

eg. N₂ + O₂ + 43.2 k. cal. \implies 2NO

or
$$N_2 + O_2 = 2NO \Delta H = + 43.2$$
 kcal

(ii) Exothermic reaction : -

 $A + B \longrightarrow C + D + energy$

or A + B \longrightarrow C + D \triangle H = (-) ve If we increase in temperature, the equilibrium shifts in backward direction of exothermic reaction which proceed with evolution of heat. eg. N₂ + $3H_2 \implies 2NH_3 + 23$ k cal or $N_2 + 3H_2 \implies 2NH_3 \quad \Delta H = -23 \text{ k cal}$

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 $\Delta n < 0$.

eg.
$$N_2 + 3H_2 = 2NH_3$$

 $\Delta n = 2$

-4 = -2 < 0

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

 $PCl_3 + Cl_2$ $\Delta n = 2 - 1 = 1 > 0$

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

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

$$CO + H_2O = CO_2 + H_2$$

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

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.

0

α

(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.

 $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$ eg.

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

 $N_2 + 3H_2(g) \implies 2 NH_3(g)$ eg.

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

 $H_2(s) + I_2(g) \longrightarrow 2HI(s)$ eg.

(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 -

 $H_2O_{(q)}$ $H_2 O_{(\ell)}$ water vapour less volume more volume

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 :

 $\mathsf{Sulphur}_{(s)} \mathchoice{\longleftarrow}{\leftarrow}{\leftarrow} \mathsf{Sulphur}_{(\ell)}$ less volume more volume 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.

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 -

 $PCI_{5} \leq$ $PCI_3 + CI_2$ Initially moles at (1 α) equilibrium

(Here ' α ' is the degree of dissociation) Total number of moles at equilibrium = $(1 - \alpha) + \alpha + \alpha = (1 + \alpha)$

α

Now, the V is the volume occupied by 1 mol of PCl₅(s) which have vapour density is 'D' before dissociation and after dissociation is 'd'. So, under the same conditions, the volume occupied by $(1 + \alpha)$ moles at equilibrium would be $(1 + \alpha)$ α) V litre.

ince Density
$$\propto \frac{1}{Volume}$$

S

or

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

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

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

	_ D – d
α	[–] (n – 1)d



Power by: VISIONet Info Solution Pvt. Ltd Website : www.edubull.com Mob no. : +91-9350679141

is the value of 'K' ?

CHEMICAL EQUILIBRIUM



(A) $3/4 = 0.75 \text{ mol}^2 \ell^{-2}$ (B) $3/2 = 1.5 \text{ mol}^2 \ell^{-2}$ (C) $27/16 = 1.7 \text{ mol}^2 \ell^{-2}$ (D) $27/64 = 0.42 \text{ mol}^2 \ell^{-2}$ Ans. [C] Sol. Let α be the degree of dissociation : Hence we have : $2NH_3(g) \implies N_2(g) + 3H_2(g)$ $2 \qquad 0 \qquad 0$ $2-2\alpha \qquad \alpha \qquad 3\alpha$ At equilibrium : $[NH_3] = 2 - 2\alpha = 1$ or $\alpha = 1/2$ $[N_2] = \frac{1}{2}, [H_2] = \frac{3}{2}, [NH_3] = 1$ $\therefore \quad \mathsf{K} = \frac{[\mathsf{N}_2][\mathsf{H}_2]^3}{[\mathsf{N}\mathsf{H}_3]^2}$ $= \frac{\frac{1}{2} \times \frac{3}{2} \times \frac{3}{2} \times \frac{3}{2}}{\frac{1}{2} \times \frac{3}{2}} = \frac{27}{16} = 1.7 \text{ mol}^2 \ell^{-2}$ Ex.7 In a 2 litre flask, the reaction takes place as : $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ The equilibrium conc. of [COCl₂] was found to be 0.4. If the excess of COCI, is added to the system, the equilibrium reestablishes and [COCl₂] becomes 1.6. What is the equilibrium conc. of [CO] ? (A) Half of the former value (B) Thrice of the former value (C) Remains unaltered (D) Twice of the former value Ans. [D] $COCl_2(g) \implies CO(g) + Cl_2(g)$ Sol. $\frac{[CO][Cl_2]}{[COCl_2]} = K_C$ Let [CO] = x, then $[CI_2] = x$ $\frac{x^2}{[COCl_2]} = K_C \text{ or } \frac{x^2}{0.4} = K_C$ Again $K_{C} = \frac{x^{2}}{0.4} = \frac{[CO][Cl_{2}]}{[COCl_{2}]}$ $\frac{x^2}{0.4} = \frac{[CO]^2}{1.6} ; \{ [CO] = [CI] \}$ $x^2 \times 4 = [C0]^2$ 2x = [CO]Ex.8 4.0 gms of hydrogen react with

Ex.8 4.0 gms of hydrogen react with 9.023×10²³ molecules of chlorine to form HCl gas. The total pressure after the reaction was found to be 700 mm. The S partial pressure of HCl will be – (A) 3900 mm (B) 600 mm (C) 700 mm (D) 350 mm Ans. [B]

Sol.
$$H_2 + Cl_2 \longrightarrow 2HCl$$

 $\frac{4}{2} \frac{9.023 \times 10^{23}}{6.02 \times 10^{23}} = 0$ Initially
 $3/2$ moles of Cl_2 will react with $3/2$ moles of H_2 to give $\frac{3}{2} \times 2 = 3.0$ moles of HCl. So the total number of moles in the reaction
 $= \left(2 - \frac{3}{2}\right) + 0 + 3 = 3.5$
Partial pressure of HCl = $\frac{3 \times 700}{3.5} = 600$ mm
Ex.9 The equilibrium constant 'K' for the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$ is 16. What would be value of equilibrium constant 'K' for the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$ is 16. What would be value of equilibrium constant 'K' for the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$ is 16. What would be value of equilibrium constant 'K' for the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$ is 16. What would be value of equilibrium constant 'K' for the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$ is 16. What would be value of equilibrium constant 'K' for the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$ is 16. What would be value of equilibrium constant 'K' for the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$ is 16. What would be value of equilibrium constant or the reaction $N_1 \longrightarrow N_1 \longrightarrow \frac{1}{2}$
K = $\frac{1}{\sqrt{K}} = \frac{1}{\sqrt{16}} = \frac{1}{4} = 0.25$
Ex.10 1.0 mole of PCl_3(g) and 2.0 moles of Cl_2 (g) were placed in a 3 litre flask and heated to 400 K. When equilibrium was established , only 0.70 mole of PCl_3 (g) remained. What is the value of equilibrium constant for the reaction : PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g) at 400 K ? (A) 0.25 (B) 1.31 (C) 0.76 (D) 2.6 Ans. [C]
Sol. PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g) at 400 K ? (A) 0.25 (B) 1.31 (C) 0.76 (D) 2.6 Ans. [C]
Sol. PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g), The moles of each component PCl_3 PCl_3 and Cl_2 at equilibrium were found to be 2. If the total pressure is 3 atm. The K_p will be - (A) 1 atm. (B) 2 atm. (C) 3 atm. (D) 1.5 atm. Ans. [A]
Sol. Total Moles = 2 + 2 + 2 = 6

$$P_{PCl_3} = \frac{2}{6} \times 3, P_{PCl_5} = \frac{2}{6} \times 3, P_{Cl_2} = \frac{2}{6} \times 3$$

$$K_{P} = \frac{P_{PCl_{3}} \times P_{Cl_{2}}}{P_{PCl_{5}}} = \frac{1 \times 1}{1} = 1 \text{ atmosphere.}$$

Ex.12 For the reaction

 $H_2 + I_2 \rightleftharpoons 2HI$ The value of equilibrium constant is 9.0. The degree of dissociation of HI will be – (A) 2 (B) 2/5 (C) 5/2 (D) 1/2 Ans. [B]

Sol. Equilibrium constant of the reaction $H_2 + I_2 \implies 2HI \text{ is } 9.0$ So the equilibrium constant for the dissociation of HI i.e. $2HI \implies H_2 + I_2$ will be 1/9.

2HI
1

$$H_2 + I_2$$

 $1 - x$
 $K_C = \frac{x}{2} \times \frac{x}{2}$
 $\frac{1}{(1-x)} \times \frac{1}{(1-x)}$
 $\frac{1}{9} = \frac{x^2}{2 \times 2(1-x)^2};$
 $\frac{1}{3} = \frac{x}{2(1-x)}$
or $2 - 2x = 3x$
 $5x = 2$

x = 2 / 5

Ex.13 For the reaction $N_2 \implies 2NH_3$, N_2 : H_2 were taken in the ratio of 1 : 3. Up to the point of equilibrium 50% each reactant has been reacted. If total pressure at equilibrium is P. The partial pressure of ammonia would be – (A) P/3 (B) P/6 (C) P/4 (D) P/8

Ans. [A] Sol. $3H_2$ 2NH3 Initially 1 3 0 At equilibrium 1-0.5 3 - 1.5 2×0.5 Total moles = (1 - 0.5) + (3 -1.5) + 1 = 3; $P_{NH_3} = \frac{1}{3}P$

Ex.14 In a reaction	vessel of 2 litre capacity 3
moles of N ₂ re	eacts with 2 moles of O_2 to
produce 1 mo	le of NO. What is the molar
concentration	of N ₂ at equilibrium ?
(4) 1 25	(R) 1 50

(A) 1120 (D) 1100
(C) 0.75 (D) 2.0 Ans. [A]
Sol.
$$N_2 + O_2 = 2NO$$

 $3 -x - 2 - x - 2x$
 $\therefore 2x = 1 ; x = 0.5$
 $[N_2] = \frac{3 - 0.5}{2} = 1.25$

Ex.15 HI was heated in a sealed tube at 440°C till the equilibrium was established. The dissociation of HI was found to be 22%. The equilibrium constant for dissociation

is –	
(A) 0.282	(B) 0.0786
(C) 0.0199	(D) 1.99

Ans. [C]

Sol. The equilibrium of the dissociation of

2HI	<u>→</u> H ₂	+ I ₂
1	0	0
1 22	22	22
100	100×2	100×2
0.78	0.11	0.11

 $K_{C} = \frac{0.11 \times 0.11}{0.78 \times 0.78} \approx 0.0199$