# Chemical Equilibrium

#### **1. IRREVERSIBLE REACTION**

Reactions which proceed in such a way that reactants are completely converted (i. e. 100%) in to products are called irreversible reaction.

#### (A) Characterstics of Irreversible Reaction :-

- (i) Reactions moves in one direction i.e. in forward direction only i.e. from left to right.
- (ii) Products do not react together to produce reactants again i.e. no backward reaction.
- (iii) Always carried out in open vessel.
- (iv) In such reactions arrow ( $\rightarrow$ ) is placed between reactant and product which shows direction of chemical change. [Reactant  $\rightarrow$  Products]

#### (B) Examples of Irrevessible Reaction :-

(i) Thermal decomposition reaction :

**Example :**  $2 \text{ KCIO}_3(s) \xrightarrow{\text{MnO}_2} 2 \text{ KCI}(s) + 3 \text{O}_2(g)$  (decomposition of potassium chlorate)

(ii) **Precipitation reaction :** 

**Example :**  $AgNO_3(aq) + NaCI(aq) \longrightarrow AgCI(s) + NaNO_3(aq)$ white ppt.

- (iii) **Neutralisation reaction :** Reaction between strong acid and a strong base to give salt and water is called neutralisation reactions.
- Example : $H_2SO_4$ +2NaOH $\longrightarrow$  $Na_2SO_4$ + $2H_2O$ Strong AcidStrong BaseSaltWater
- (iv) Redox and combustion reactions :

Example :  $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$  $2Mg + O_2 \longrightarrow 2MgO$ 

#### 2. REVERSIBLE REACTION

The chemical reactions which take place in both directions i.e. in the forward direction as well as in backward direction under similar conditions are called reversible reactions.

Forward direction	$\Rightarrow$	Left to right	()
Backward direction	$\Rightarrow$	Right to left	()
	Or		

Reactions which proceed in both the directions and does not reach to completion are called reversible reactions.

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#### (A) Characterstics of Reversible Reaction :-

(i) In these reactions arrow (→) is replaced by two half arrows (→) pointing the reaction in both the directions.

Reactants - Products

- (ii) Always carried out in closed vessel.
- (iii) The reaction never reaches to completion.
- (iv) Characterised by the establishment of equillibrium.
- (v) Reactions occours in both the directions.
- (B) Examples of Reversible Reactions :-
- (i) Reaction between gases in closed vessel :

**Example :**  $2 SO_2(g) + O_2(g) \Longrightarrow 2 SO_3(g) + x k.cal$ 

 $N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g) + x k.cal$ 

(ii) Thermal decomposition reactions :

**Example :**  $CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g) + x k.cal$ 

$$PCl_{_{5}}(g) \Longrightarrow PCl_{_{3}}(g) + Cl_{_{2}}(g)$$

#### 3. TYPES OF REVERSIBLE REACTIONS

(A) Homogeneous Reactions :- The reversible reaction in which only one phase is present i.e. all the reactants and the products are in same physical state.

Example :

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

$$\mathsf{CH}_{3}\mathsf{COOH}\left(\ell\right) + \mathsf{C}_{2}\mathsf{H}_{5}\mathsf{OH}\left(\ell\right) \longleftrightarrow \mathsf{CH}_{3}\mathsf{COOC}_{2}\mathsf{H}_{5}\left(\ell\right) + \mathsf{H}_{2}\mathsf{O}\left(\ell\right)$$

Homogeneous reactions are of three types.

(i) **First Type :** When there is no change in number of molecules  $(\Delta n = 0)$ 

**Example :**  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ 

 $2 \operatorname{NO}(g) \rightleftharpoons N_2(g) + O_2(g)$ 

- (ii) Second Type : When there is increase in number of molecules.  $(\Delta n > 0)$
- **Example :**  $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

 $2NH_{3}(g) \implies N_{2}(g) + 3H_{2}(g)$ 

(iii) Third Type : When there is decrease in number of molecules. ( $\Delta n < 0$ )

Example :  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$  (B) Heterogeneous Reactions :- The reversible reaction in which more than one phases is present.

Example :  $MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$  $3Fe(s) + 4H_2O(\ell) \implies Fe_3O_4(s) + 4H_2(g)$ Example : æ 1 Which of the following is irreversible reaction - $[1] N_2(g) + O_2(g) \longrightarrow 2NO(g)$  $[2] 2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$  $[3] 2KCIO_{3}(s) \longrightarrow 2KCI(s) + 3O_{2}(g)$  $[4] H_2(g) + I_2(g) \longrightarrow 2HI(g)$ Ans. [3] 2 Which of the following is reversible reaction- $[2] H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$  $[1] MgCO_{3}(s) \longrightarrow MgO(s) + CO_{2}(g)$  $[3] 2Mg + O_2 \longrightarrow 2MgO$ Ans. [1] [4] None 3 Which of the following is homogeneous reversible reaction- $[1] 2NO(g) \longrightarrow N_2(g) + O_2(g)$  $[2] CaCO_{3}(s) \longrightarrow CaO(s) + CO_{2}(g)$  $[3] CH_3COOH(\ell) + C_2H_5OH(\ell) \longrightarrow CH_3COOC_2H_5(\ell) + H_2O(\ell)$ [4] All of the above Ans. [1] Which of the following is heterogeneous reversible reactions 4  $[1] 3Fe(s) + 4H_2O(\ell) \longrightarrow Fe_3O_4(s) + 4H_2(g)$  $[2] \operatorname{N}_2(g) + 3\operatorname{H}_2(g) \xrightarrow{} 2\operatorname{NH}_3(g)$  $[3] 2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ [4] None Ans. [1] 4. STATE OF CHEMICAL EQUILIBRIUM It can be shown graphically. Rate of forward Rate-Equilibrium state

Rate of backward reaction Time at which system has reached equilibrium Time -

At Ec	quilibrium	state
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Rate of forward reaction	=	Rate of backward reaction

 $R_{f}$ R<sub>b</sub>

#### (A) Defination's of Chemical Equilibrium :-

- 1. Chemical Equilibrium in a reversible reaction is a state at which both backward and forward reaction occour at the same speed.
- 2. The stage of the reversible reaction at which the concentrations of the reactants and products do not change with the time.
- (B) Characteristics of Equilibrium State :-
- 1. Equilibrium state can only be achived if a reversible reaction is carried out in closed vessel.
- 2. Free energy change is zero  $\Delta G^\circ = O$
- 3. Forward rate  $(R_i)$  = Backward rate  $(R_b)$
- 4. Equilibrium is dynamic in nature.
- Chemical Equilibrium can be attained from either of the side i.e. from side of reactants or products

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

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

- or
- 6. Equilibrium state can be attained in a lesser time by use of positive catalyst.

#### Example :

- - [1] Complete conversion of A to B has taken place
  - [2] Conversion of A to B is only 50% complete
  - [3] Only 10% conversion of A to B has taken place
  - [4] The rate of transformation of A to B is just equal to the rate of transformation of B to A in the system

Ans. [4]

- 2 Chemical equilibrium has dynamic in nature because-
  - [1] The equilibrium becomes rapidly.
  - [2] The concentration of reactants and products become same at equilibrium.
  - [3] The concentration of reactants and products are constant but dissimilar in amount.
  - [4] None of these.

Ans. [4]

### 5. LAW OF CHEMICAL EQUILIBRIUM

(A) Defination :→ Law of Mass Action : "At a given temperature, the rate of reaction at a particular instant is proportional to the product of the active masses of the reactants at that instant raised to power which are numerically equal to their respective molecules in stoichiometric equation describing the reaction".

For the reaction :

nA + mB 🔶 zC + wD

- \* According to law of mass action
- \* Rf ∝ [A]<sup>n</sup> [B]<sup>m</sup>
- \* <sup>R</sup><sub>b</sub> ∝ [C]<sup>z</sup> [D]<sup>w</sup>
- \*  $R_f = K_1 [A]^n [B]^m$
- \*  $R_{b} = K_{2} [C]^{z} [D]^{w}$

• At equilibrium :  

$$R_{i} = R_{i}$$
  
 $K_{i} [A]^{n} [B]^{n} = K_{i} [C]^{n} [D]^{n}$   
 $\frac{K_{i}}{K_{i}} = \frac{[C]^{n} [D]^{n}}{[R^{n} = K_{i}] = \frac{R_{i}}{R_{v}} = \frac{R_{i}}{R_{v$ 

**Ex.1** The equilibrium constant of a reaction is 20.0. At equilibrium, the rate constant of forward reaction is 10.0. The rate constant for backward reaction is-

[1] 0.5 [2] 2.0 [3] 10.0 [4] 200.0 Ans.[1] Sol.  $K_c = 20$   $k_f = 10$   $k_b = ?$  $K_c = \frac{k_f}{k_b}$   $20 = \frac{10}{k_b}$  $\therefore K_b = \frac{10}{20} = 0.5$ 

#### Ex.2 At a given temperature, the equilibrium constant for the reactions

$$NO (g) + \frac{1}{2}O_{2} (g) NO_{2} (g) and 2 NO_{2} (g) 2 NO (g) + O_{2} (g) are K, and K_{2} respectively. If K, is 4 x 10-3, then K_{2} will be -
[1] 8 x 10-3 [2] 16 x 10-3 [3] 6.25 x 104 [4] 6.25 x 106 Ans.[3]
Sol.  $NO(g) + \frac{1}{2}O_{2}(g) NO_{2}(g)$   
 $K_{1} = \frac{[NO_{2}]}{[NO][O_{2}]^{1/2}} = 4 x 10^{-3}$   
Now for reaction  $2NO_{2}(g) \implies 2NO(g) + O_{2}(g)$   
 $K_{2} = \frac{[NO]^{2}[O_{2}]}{[NO_{2}]^{2}} = \frac{1}{K_{1}^{2}}$   
 $= \frac{1}{(4 \times 10^{-3})^{2}} = 6.25 \times 10^{4}$   
Ex.3 Equilibrium constant for the reaction :  $2NO(g) + Cl_{2}(g)$   $2NOCI (g) ; is correctly given by the expression$   
 $[1] K = \frac{[2NOCI]}{[2NO][Cl_{2}]}$   $[2] K = \frac{[NOC]^{2}}{[NO]^{2}[Cl_{2}]}$   
 $[3] K = \frac{[NO]^{2}[Cl_{2}]}{[NO]^{2} + [Cl_{2}]}$   $[4] K = \frac{[NO]^{2} + [Cl]^{2}}{[NOCI]}$  Ans.[2]  
Ex.4 Molar concentration of 96 g of O<sub>2</sub> contained in 2 litre vessel is -  
[1] 16 mol/litre [2] 1.5 mol/litre [3] 4 mol/litre [4] 24 mol/litre Ans.[2]$$

Molar concentration =  $\frac{\text{Number of mol}}{\text{Volume in litre}} = \frac{3}{2} = 1.5 \text{ mol/litre}$ 

#### 7. EQUILIBRIUM CONSTANT IN TERMS OF PRESSURE :

\* It is denoted by K<sub>P</sub>

\* Partial pressure =  $\frac{\text{no.of moles}}{\text{Totalmoles}} \times \text{Totalpressure}$ 

Exam	nple - PCl <sub>5</sub>	$PCl_3 + Cl_2$		
*	Initial moles no. of	1	0	0
*	Moles of equilibrium	1 – x	х	x
*	Total moles	1 - x + x + x = 1 +	х	
	$P_{pCl_5} = \frac{1-x}{1+x} \times P$	$P_{Cl_2} = \frac{x}{1+x} \times P$	P <sub>PC</sub>	$I_3 = \frac{x}{1+x} \times P$
	$K_{P} = \frac{P_{PCI_3} \cdot P_{CI_2}}{P_{PCI_5}}$			
	Unit of K <sub>c</sub> = (Conc	centration) <sup>∆n</sup>	Uni	t of $K_p = (atm)^{\Delta n}$
	$\Delta n$ = no. of moles of gas	eous product – no. c	of mol	es of gaseous reactant
8. U		IUM CONSTANT	-	
Ē	Example :			
Ex.1	The unit of $K_c$ for the rea	ction $2SO_3$ $2SO_2$	<sub>2</sub> + O <sub>2</sub>	
	[1] mole <sup>2</sup> lit <sup><math>-2</math></sup> [2] mo	le per litre [3]	mole	e x litre [4] litre per mole Ans. [2]
Sol.	Unit fo $K_c = [M]^{\Delta n}$			
	where M = mole/litre		C	9
	$\Delta n = Number of gaseous$	s mole of product – Nu	umbei	of gaseous mole of reactant
	Here $\Delta n = (2 + 1) -$	2 = 1		
	∴ unit of	$K_c = [mole/litre]^1$		= mole per litre.
9. \$	SIGNIFICANCE O	F EQUILIBRI	JM	CONSTANT
	(A) High value of $K_c$ :-	Denotes high concer	ntratio	on of the products relative to the reactants, at equilibrium
	5	K <sub>c</sub> >>> 1 bu	t	$K_c \neq \infty$
	conce	ntration of product > c	conce	ntration of reactant
	(B) Low value of $K_c :=$	Denotes high value o	of con	centration of reactants relative to products at the equilibrium
	K <sub>c</sub> <<<	< 1 but $K_c \neq O$		
	conce	ntration of product < c	conce	ntration of reactant
	(C) Suppose there are the	nree reaction having e	quilibr	ium constant $K_1, K_2$ and $K_3$ and $K_1 > K_2 > K_3$
	Hence the order of the te	ndency of the reactio	n to p	roceed in forward direction (i.e. formation of product)
	React	ion 1 > Reaction 2 > I	React	ion 3
	In short			

 $\mathbf{K}\uparrow$  , forward reaction  $\uparrow$ 



# 11. STANDARD FREE ENERGY CHANGE OF A REACTION AND ITS EQUILIBRIUM CONSTANT

Let  $\Delta G^{\circ}$  be the difference in free energy of the reaction when all the reactants and products are in standard state (1 atm pressure and 298 K) and K<sub>c</sub> and K<sub>p</sub> be the thermodynamic equilibrium constant of the reaction. Both are related to each other at temperature T by following relation.

#### $\Delta G^{\circ} = -2.303 \text{ RT log K}_{c}$

#### & $\Delta G^{\circ} = -2.303 \text{ RT log K}_{a}$

Equation relates equilibrium constant of a reaction to a thermochemical property.

where  $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$ 

here  $\Delta H^{\circ} =$  Standard enthalpy change

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

Three cases may arise :

(i)  $\Delta G^{\circ} = 0$  then  $K_{c} = 1$ 

(ii)  $\Delta G^{\circ} > 0$  i.e. + ve then K<sub>c</sub> < 1

In this case reverse reaction is feasible i.e. less concentration of products at equilibrium state.

(iii)  $\Delta G^{\circ} < 0$  i.e. -ve then  $K_c > 1$ 

In this case forward reaction is feasible i.e. large concentration of products at equilibrium state.

In short :

Free energy change Equilibrium constant Concentration of rectants and Products

$\Delta G^{\circ} = 0$	$K_c = 1$	Reactants = Products
$\Delta G^{\circ} > 0$	K <sub>c</sub> < 1	Reactants > Products
$\Delta G^{\circ} < 0$	K <sub>c</sub> > 1	Reactants < Products

Example :

1. The  $K_p$  for a homogeneous gaseous reaction is  $10^{-8}$ . The standard Gibb's free energy change  $\Delta G^\circ$  for the reaction is-

[3] –4.145 k cals

[4] 4.145 k cals Ans. [1]

#### 12. EQULIBRIUM CONSTANT EXPRESSIONS FOR SOME REACTIONS

[2] –1.8 k cal

Case I :

Homogeneous gaseous equilibria when  $(\Delta n = 0)$ 

Synthesis of hydrogen iodide

(a) Calculation of K<sub>c</sub>:

Suppouse the initial concentration of  $H_2$  and  $I_2$  is 'a' and 'b' respectively, x is degree of dissociation and 'v' is volume in litre of container.

N.	$H_{_{2}}(g)$ +	$I_2(g)$	<b>≥</b> 2HI (g)
Intial conc.	а	b	0
Moles at equilibrium	a-x	b-x	2x
Active mass	$\frac{a-x}{v}$	$\frac{b-x}{v}$	$\frac{2x}{v}$

According to law of mass action.

$$K_{c} = \frac{[HI]^{2}}{[H_{2}][I_{2}]}$$

$$K_{c} = \frac{[2x/v]^{2}}{\left[\frac{a-x}{v}\right]\left[\frac{b-x}{v}\right]} \quad ; \qquad K_{c} = \frac{4x^{2}}{(a-x)(b-x)}$$

(b) Calculation of  $K_p$ : The equilibrium constant  $K_p$ , can also be calculated considering partial pressure of reactants and products at equilibrium.



 $\Delta n = 0$  ;  $K_p = K_c$ Here

i.e. for all gaseous reaction of this type, K<sub>p</sub> and k<sub>c</sub> are equal and have no units.

#### Effect of pressure : $K_c \alpha$ pressure° (i)

As the equation does not include volume term, K is independent of pressure.

#### (ii) Effect of adding substansces : (Reactant and products)

On adding reactant rate of forward reaction increase on adding product rate of backward reaction increase

Concentraion of reactant  $\uparrow$  Rate of forward reaction  $\uparrow$ 

Concentraion of product  $\uparrow$  Rate of backward reaction  $\uparrow$ 

(iii) Effect of temperature : The formation of HI from H<sub>2</sub> and I<sub>2</sub> is an exothermic reaction i.e. by increasing temperature the value of K<sub>c</sub> decreases.

As T  $\uparrow$ , K  $\downarrow$  (exothermic reaction)

#### Case II:

#### Homogeneous gaseous reactions when $\Delta n > 0$

#### Dissocation of PCI,

#### (a) Calculation of K<sub>c</sub>:

Let 'a' moles of PCI<sub>5</sub> be taken in a closed vessel of volume 'v' litre. Suppose 'x' mole is dissociated at equilibrium.



when

$$k_{c} = \frac{x^{2}}{(1-x)v}$$

(b) Calculation of  $K_p$ : Let the total pressure at equilibrium be P. Then total number of moles at equilibrium = (a - x) + x + x = a + xThe partial pressure of each reactant and product

$$P_{PCl_{5}} = \left(\frac{a-x}{a+x}\right) P$$
$$P_{Cl_{2}} = \left(\frac{x}{a+x}\right) P$$
$$P_{PCl_{3}} = \left(\frac{x}{a+x}\right) P$$

Applying law of mass action

$$\mathsf{K}_{\mathsf{p}} = \frac{\mathsf{P}_{\mathsf{PCI}_3} \times \mathsf{P}_{\mathsf{CI}_2}}{\mathsf{P}_{\mathsf{PCI}_5}} = \frac{\left(\frac{\mathsf{x}}{\mathsf{a} + \mathsf{x}}\right) \mathsf{P} \times \left(\frac{\mathsf{x}}{\mathsf{a} + \mathsf{x}}\right) \mathsf{P}}{\left(\frac{\mathsf{a} - \mathsf{x}}{\mathsf{a} + \mathsf{x}}\right) \mathsf{P}}$$

$$K_{p} = \frac{x^{2} P}{(a - x)(a + x)}$$
$$a = 1,$$
$$K_{p} = \frac{x^{2} P}{1 - x^{2}}$$

when

(i) Effect of pressure :-

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

suppose x <<< 1 then  

$$K_p = x^2 p$$
  
 $x^2 \alpha \frac{1}{P}$   
 $x \alpha \frac{1}{\sqrt{P}}$ 
 $p \downarrow , x \uparrow$ 

Degree of dissociation of PCI<sub>5</sub> is inversely proportional to square root of pressure so decrease in pressure increase dissociation of PCI<sub>5</sub>

 $\uparrow$ 

 $\uparrow$ 

(ii) Effect of concentration :-

concentraion of  $PCI_5$ 

concentraion of PCl<sub>3</sub> & Cl<sub>2</sub>

Rate of forward reaction  $\uparrow$ Rate of backward reaction  $\uparrow$ 

(iii) Effect of temperature :- The dissocation of PCl<sub>5</sub> is endothermic reaction. The value of equilibrium constant increase with increase in temperature

Homogeneous gaseous reaction  $\Delta n < 0$ 

Synthesis of Ammonia

(a) Calculation of K<sub>c</sub>:

	$N_{2}(g) +$	$3H_2(g) \rightleftharpoons 2NH_3$	(g)	
Initial conc.	a	b	0	
Moles at eq.	a – x	b – 3x	2x	
Active mass	$\frac{a-x}{v}$	$\frac{b-3x}{v}$	$\frac{2x}{v}$	
Applying law of mas	s action			
INH <sub>1</sub> <sup>2</sup>				

$$K_{c} = \frac{\left[2x/V\right]^{2}}{\left[\frac{a-x}{V}\right]\left[\frac{b-3x}{V}\right]^{3}}; \qquad K_{c} = \frac{\left[\frac{4x^{2}}{V}\right]\left[\frac{b-3x}{V}\right]^{3}}{\left[\frac{a-x}{V}\right]\left[\frac{b-3x}{V}\right]^{3}};$$

If a = 1 and b = 3 then

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

If x <<< 1 then  $(1 - x)^4 = 1$ 

$$K_{c} = \frac{4x^{2}v^{2}}{27}$$
$$x^{2} \alpha \frac{1}{v^{2}}$$
$$x \alpha \frac{1}{v^{2}}$$

#### (b) Calculation of Kp :

Let total pressure at equilibrium be P.

Total no. of moles at equilibrium = (a - x) + (b - 3x) + 2x = (a + b - 2x)

$$p_{NH_3} = \frac{2x}{(a+b-2x)} \times P \qquad p_{N_2} = \frac{a-x}{(a+b-2x)} \times P$$

$$p_{H_2} = \frac{b-3x}{(a+b-2x)} \times P$$

$$K_p = \frac{[p_{NH_3}]^2}{[p_{N_2}][p_{H_2}]^3} = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3p^2}$$

If a = 1 and b = 3 then

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

Suppose x <<< 1 then  $(1 - x)^4 = 1$ ;  $(2 - x)^2 = 4$ 

$$K_{p} = \frac{64x^{2}}{27p^{2}}$$
$$x^{2} \alpha p^{2}$$
$$x \alpha p$$

(i) Effect of pressure : With increase in pressure the volume term decrease therefore x increase.

(ii) Effect of temperature : On increasing temperature value of equilibrium constant decreases.

**T**  $\uparrow$  **K**  $\downarrow$  exothermic reaction

## (A) Homogeneous liquid system :-

Formation of ethyl acetate

$$\begin{array}{c|c} CH_{3}COOH\left(\ell\right)+C_{2}H_{5}OH\left(\ell\right) & \longleftrightarrow & CH_{3}COOC_{2}H_{5}\left(\ell\right)+H_{2}O\left(\ell\right) \\ \hline \\ \mbox{Initial conc.} & a & b & 0 & 0 \\ \mbox{Moles at eq.} & a-x & b-x & x & x \\ \mbox{Moles at eq.} & a-x & b-x & x & x \\ \hline \\ \mbox{Active mass} & v & \frac{b-x}{v} & \frac{x}{v} & \frac{x}{v} \\ \hline \end{array}$$

Applying law of mass action

a = b = 1

lf

Here V = total volume

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$$K_{c} = \frac{[CH_{3}COOC_{2}H_{5}][H_{2}O]}{[CH_{3}COOH][C_{2}H_{5}OH]} = \frac{[x / v] \times [[x / v]]}{\left[\frac{a - x}{v}\right] \times \left[\frac{b - x}{v}\right]}$$
$$K_{c} = \frac{x^{2}}{(a - x)(b - x)}$$
then 
$$K_{c} = \frac{x^{2}}{(1 - x)^{2}}$$

This does not involve volume term thus K<sub>c</sub> is not affected by change in volume

-0

#### (B) Heterogeneous Equilibrium :-

The decomposition of solid NaHCO<sub>3</sub> to produce solid Na<sub>2</sub>CO<sub>3</sub>, CO<sub>2</sub> gas and H<sub>2</sub>O

$$2 \text{ NaHCO}_3(s) \longrightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)$$

Applying law of mass action

$$K_{c}' = \frac{[Na_{2}CO_{3}][H_{2}O][CO_{2}]}{[NaHCO_{3}]^{2}}$$

It involves two pure solids, Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>. It is customary not to include concentration of of pure solid in equilibrium expression.

$$\frac{K_{c}'[NaHCO_{3}]^{2}}{[Na_{2}CO_{3}]} = [CO_{2}][H_{2}O]$$
$$K_{c} = [CO_{2}][H_{2}O]$$

#### **Example :**

**Ex.1** For the reaction  $N_2O_4 \iff 2NO$ , degree of dissociation is  $\alpha$ . The number of moles at equilibirum will be –

	$[1] (1 - \alpha)^2$	[2] (1 + α)	[3] 3		[4] 1	Ans. [2]
Sol.		$N_2O_4$	2NO	C)		
	Initially	1 0				
	Moles at equilib	prium $1-\alpha$ 20	x-O			
	Total number of moles	at equilibrium 🔹 1	$-\alpha + 2\alpha$			
		0	= 1 + 0	X		

**Ex.2** 4 mole of A are mixed with 4 mole of B, when 2 mole of C are formed at equilibrium according to the reaction, A  $+ B \rightleftharpoons C + D$ . The equilibrium constant is -

[1] 4 [2] 1 [3] 
$$\sqrt{2}$$
 [4]  $\sqrt{4}$  Ans. [2]  
Sol.  
A + B C + D  
Initially 4 4 0 0  
At equilibrium  $4 - \alpha \ 4 - \alpha \ \alpha \ \alpha$   
Given at equilibrium mole of C = 2 ( $\therefore \alpha = 2$ )  
 $\therefore$  [A] = 4 - 2 = 2 mole  
[B] = 4 - 2 = 2 mole  
[D] =  $\alpha = 2$  mole

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

**Ex.3** At a certain temperature,  $2HI \iff H_2 + I_2$  only 50% HI is dissociated at equilibrium. the equilibrium constant is -

[1] 1.0 [2] 3.0 [3] 0.5 [4] 0.25 Ans.[4]

Sol.

2HI  $H_2 + I_2$ 0 Initially 1 0 Moles at equilibrium α/2  $1 - \alpha$ α/2

50% of HI is dissociated therefore  $\alpha = .5$ 

$$[HI] = 1 - .5 = .5$$
$$[H_2] = .5/2$$
$$[I_2] = .5/2$$
$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{.5/2 \times .5/2}{[.5]^2} = \frac{1}{4} = 0.25$$

$$[H_{2}] = .5/2$$

$$[I_{2}] = .5/2$$

$$[I_{2}] = .5/2$$

$$K_{c} = \frac{[H_{2}][I_{2}]}{[HI]^{2}} = \frac{.5/2 \times .5/2}{[.5]^{2}} = \frac{1}{4} = 0.25$$
**Ex.4** One mole of ethyl alcohol was treated with one mole of acetic acid at 25°C. 2/3 of the acid changes into ester at equilibrium. The equilibrium constant for the reaction of hydrolysis of ester will be -

$$\begin{bmatrix} 1 \end{bmatrix} 1 \qquad \begin{bmatrix} 2 \end{bmatrix} 2 \qquad \begin{bmatrix} 3 \end{bmatrix} 3 \qquad \begin{bmatrix} 4 \end{bmatrix} 4 \qquad \text{Ans. [4]}$$
Sol.  $C_2H_5OH(\ell) + CH_3COOH(\ell) = CH_3COOC_2H_5(\ell) + H_2O(\ell)$ 
Initially  $1 \qquad 1 \qquad 0 \qquad 0$ 
Moles of equilibrium  $1 - \alpha \qquad 1 + \alpha \qquad \alpha \qquad \alpha$ 
Given  $\alpha = 2/3$ 
Therefore  $C_2H_5OH = 1 - 2/3 = 1/3$ 
 $CH_3COOH = 1 - 2/3 = 1/3$ 
 $CH_3COOC_2H_5 = 2/3$ 
 $H_2O = 2/3$ 
 $K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{2/3 \times 2/3}{1/3 \times 1/3} = 4$ 

**Ex.5** For the reaction,  $C(s) + CO_2(g) \implies 2CO(g)$ , the partial pressures of  $CO_2$  and CO are 2.0 and 4.0 atm respectively at equiibrium. The  $K_{\scriptscriptstyle P}$  for the reaction is -

[4] 32.0 [1] 0.5 [2] 4.0 [3] 8.0 Ans.[3]

**Sol.**  $K_{p} = \frac{[p_{co}]^{2}}{[p_{co_{2}}]} = \frac{[4]^{2}}{[2]}$ 

∴ K<sub>p</sub> = 8

#### **13. LECHATELIER'S PRINCIPLE**

According to this principle, "If a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shift in a direction that tends to undo the effect of the change".

#### (A) Effect of change in concentration :-

- In a chemical equilibrium, increasing the concentration of the reactants result in shifting the equilibrium in favour of products (i.e. equilibrium shift in forward direction).
- Increasing concentration of the products results in shifting the equilibrium in favour of reactants (i.e in the backward direction).

Concentration	Equilibrium shift
Concentration of reactant $\uparrow$	Forward direction
Concentration of product $\uparrow$	Backward direction

#### (B) Effect of change in pressure :-

According to lechatelier's principal if the pressure is increased reaction will take place in that direction, which will bring lowering of pressure or lowering in number of mole.

- (i) Increase of pressure shifts the equilibrium in that direction where number of moles decreases.  $(\Delta n < 0)$ 
  - eg.  $N_{1} + 3H_{2} \Longrightarrow 2NH_{2}$

i.e.

on 1 pressure

$$\Delta n = 2 - 4 = -2 < 0$$

equilibrium shift in forward directin.

- (ii) Decrease of pressure shifts the equilibrium in that direction where number of mole increase.  $(\Delta n > 0)$ 
  - eg.  $PCI_5 \longrightarrow PCI_3 + CI_2$   $\Delta n = 2 1 = + ve$ i.e.  $\downarrow$  in pressure equilibrium shift in forward direction
- (iii) Change of pressure has no effect if  $\Delta n = 0$

eg.  $H_2 + I_2 \Longrightarrow 2HI$   $\Delta n = 2 - 2 = 0$ 

- (C) Change in temperature :-
- (i) For endothermic reaction : If we increase the temperature equilibrium shift in forward direction which proceed with absorption of heat.
- (ii) For exothermic reaction : If we increased the temperature the equilibrium shifts in backward direction which proceed with evolution of the heat.
- (D) Role of Catalyst :- Positive catalyst increase the rate of both the forward and backward reaction equally so the equilibrium will be attained in less time. Negative catalyst decrease the rate of both forward and backward reaction so equilibrium will be attained in more time.

#### 14. APPLICATION OF LE CHATELIER PRINICPAL ON PHYSICAL EQUILIBRIA

(A)	Melting of Ice :-	H <sub>2</sub> O (s)	$H_2O(\ell)$
		Ice	Water
		(More volume)	(Less volume)

With increase in pressure melting point of ice is decreased and equilibrium will be shifted in a direction of less volume.

(B) Vaporisation of liquid :-

H₂O (ℓ)	100°C	H <sub>2</sub> O (g)	and a
Water		Vapour	G
(less volume)		(more volume)	ò.

Vaporisation of liquid is endothermic process in the nature i.e. the evaporation of liquid in to its vapour is completed by absorption of heat so rise of temperature will favour vaporisation and equilibrium is shifted in forward direction.

On the other hand on increasing the pressure the equilibrium will be shifted in direction of less volume means water cannot be converted in to vapour and boiling point increases.

	On <sup>↑</sup> temperature	Vaporisation $\uparrow$	forward shift
	On ↑ pressure	B.P ↑	Backward shift
(C)	Melting of Sulphur :-		
	Sulphur (s)	sulphur ( $\ell$ )	
	Less volume	More volume	

On increasing pressure the equilibrium will shift towards less volume, means **Sol.** id will be not converted in to liquid, thus melting point of sulphur increases.

#### Example :

2

[1] Decrease with decrease in pressure	[2] Decrease with increase pressure	
[3] Is unaffected by pressure	[4] None of these	Ans. [1]
For equilibrium $2NO_2(g) \longrightarrow N_2O_4(g) + 14.6 K.$	cal. increase of temperature would -	
[1] Favour the formation of $N_2O_4$	[2] Favour the decomposition of $N_2O_4$	

[3] Not alter the equilibrium [4] Stop the reaction Ans. [2]

#### **15. CALCULATION OF DEGREE OF DISSOCIATION BY DENSITY MEASUREMENT**

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

Let us consider the following reaction.

	PCI <sub>5</sub>	$PCI_3 + C$	1 <sub>2</sub>			
Initially	1	0	0			
Moles at equilibrium	1 – α	α	α	$(\alpha \rightarrow degree of dissociation)$		
Total number of moles at equilibrium = $(1 - \alpha) + \alpha + \alpha = (1 + \alpha)$						

Now, 'V' is the volume occupied by 1 mole of  $PCI_5$  which have vapour density 'D' before dissociation and after dissociation is 'd'. So under same conditions, the voulme occupied by  $(1 + \alpha)$  moles at equilibrium will be  $(1 + \alpha)$  V litre.



When one mole of reactant on dissociation gives 'n' moles of gaseous products the above equation takes in the form of.

$$\alpha = \frac{D-d}{(n-1)d}$$
Remote :--
(i) Example  $n_1A \longrightarrow n_2B + n_3C$ 

$$\alpha = \frac{n_1}{\Delta n} \left[ \frac{D-d}{d} \right] ; \qquad \text{Here } \Delta n = (n_2 + n_3) - n_1$$
(ii)  $\Delta n = + \text{ve}$  'd' always decreases  $D > d$   
 $\Delta n = - \text{ve}$  'd' always increases  $d > D$ .

☞ Example :

Ex.1At 250°C the vapour density of pcl<sub>5</sub> is 100 calculate the degree of dissociation at this temperature-<br/>[1] 4[2] .04[3] .02[4] 2Ans. [2]

Sol. D for PCl<sub>5</sub> = 
$$\frac{\text{Molecular mass}}{2} = \frac{208.5}{2} = 104.25$$
  
d for PCl<sub>5</sub> = 100  
 $\alpha = \frac{D-d}{d} = \frac{104.25 - 100}{100} = 0.0425$ 

C

#### 16. REACTION QUOTIENT AND EQUILIBRIUM CONSTANT

Consider the following reversible reaction

The reaction quotient (Q<sub>c</sub>) is the ratio of the product of active masses of the products and product of active masses of the reactants.

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

The concentration are not necessarily equilibrium concentration.

[At equilibrium  $Q_c = K_c$ ]

Case I :

*.*..

If Q<sub>c</sub> < K<sub>c</sub> then : [Reactants] > [Products]

then the system is not at equilibrium

The value of  $\frac{[Pr oduct]}{[Reactant]}$  is small.

:. For establishment of equilibrium the reaction will go in forward direction.[Reactants -> Products]

#### Case II :

If  $Q_c = K_c$  then : The system is at equilibrium and the concentration of the species C, D, B,A are at equilibrium.

#### Case III :

The system is not at equilibrium.

The value of [Product] [Reactant] is large

: For establishment of equilibrium the reaction will go in backward direction [Products -> Reactants]

#### ☞ Example :

1 When two reactants A and B are mixed to give products C and D, the reaction quotient Q, at the initial stages of the reaction -

[1] Is zero	[2] Decreases with time		
[3] Is independent of time	[4] Increases with time	Ans. [1]	

S.No.	Reaction	n	Relation between $K_p$ and $K_c$	Values of K <sub>p</sub> and K <sub>c</sub>	Kc	Kp	Unitof K <sub>c</sub>	UnitofKp	Relation between Amount of dissociation Volume(V)and Pr essure	н	Conditions for obtaining more product
1.	$H_2^+ I_2 \rightleftharpoons 2HI$	0	$K_p = K_c (RT)^6$	K <sub>p</sub> =K <sub>c</sub>	$\frac{4x^2}{(a x)(b x)}$	$\frac{4x^2}{(a x)(b x)}$	None	None		ve (Endothermic)	High Temperatur NoPressure Hig Concentration
2.	2HI <del>←</del> H <sub>2</sub> +I <sub>2</sub>	0	$K_p = K_c (RT)^6$	K <sub>p</sub> = K <sub>c</sub>	$\frac{x^2}{4(1-x)^2}$	$\frac{x^2}{4(1 x)^2}$	None	None		ve (Endothermic)	Low Temperatur Nopressure Hig Concentration
3.	PCl <sub>5</sub> ← PCl <sub>3</sub> + Cl <sub>2</sub>	1	$K_p = K_c (RT)^1$	K <sub>p</sub> >K <sub>c</sub>	$\frac{x^2}{(1 x)v}$	$\frac{x^2P}{(1 x^2)}$	gram mol <sup>1</sup> lit <sup>1</sup>	(Atm.press.) <sup>1</sup>	$x \sqrt{v}$ or $x \frac{1}{\sqrt{P}}$	ve (Endothermic)	High Temperatur No Pr essure Hig Concentration
4.	$N_2O_4 \rightleftharpoons 2NO_2$	1	$K_p = K_c (RT)^1$	K <sub>P</sub> > K <sub>c</sub>	$\frac{4x^2}{(1 x)v}$	$\frac{4x^2P}{(1 x^2)}$	gram mol <sup>1</sup> lit <sup>1</sup>	(Atm.Press.) <sup>1</sup>	$x \sqrt{v}$ or $x \frac{1}{\sqrt{P}}$	ve (Endothermic)	High Temperatur No Pr essure Hig Concentration
5.	$2NH_3 \rightleftharpoons N_2 + 3H_2$	2	$K_p \equiv K_c (RT)^2$	K <sub>p</sub> >K <sub>c</sub>	$\frac{27x^4}{4(1 \ x)^2 v^2}$	27x <sup>4</sup> P <sup>2</sup> 16	gram mol <sup>2</sup> lit <sup>2</sup>	(Atm.Press.) <sup>2</sup>	$x \sqrt{v}$ or $x \frac{1}{\sqrt{P}}$	ve (Endothermic)	High Temperatur Low PressureHi Concentration
6.	N₂+ 3H₂ <del>←</del> 2NH₃	2	$K_p = K_c (RT)^2$	K <sub>P</sub> <k<sub>c</k<sub>	$\frac{4x^2v^2}{27(1 \ x)^2}$	64x <sup>2</sup> 27P <sup>2</sup>	gram mol <sup>2</sup> lit <sup>2</sup>	(Atm.Press.) <sup>2</sup>	x 1 or x P	ve (Exothermic)	Low Temperatur HighPr essure Hi Concentration
7.	PCl <sub>3</sub> +Cl <sub>2</sub> ⇔PCl <sub>5</sub>	1	$K_p = K_c (RT)^{1}$	K <sub>p</sub> < K <sub>c</sub>	$\frac{xv}{(1 x)^2}$	<u>x 2 x</u> (1 x <sup>2</sup> )P	gram mol <sup>1</sup> lit <sup>1</sup>	(Atm.Press.) <sup>1</sup>	x 1 v or x P	ve (Exothermic)	Low Temperatur HighPr essure Hi Concentration
8.	2SO <sub>2</sub> + O <sub>2</sub> → 2SO <sub>3</sub>	1	$K_p = K_c (RT)^{1}$	K <sub>P</sub> < K <sub>c</sub>	$\frac{x^3}{2(1-x)^2v}$	$\frac{x^{3}P}{(2  x)(1  x)^{2}}$	gram mol <sup>1</sup> lit <sup>1</sup>	(Atm.Press.) <sup>1</sup>	x 1 v or x P	ve (Exothermic)	Low Temperatur HighPr essure Hi Concentration

## Equiibrium constant expressions for some reactions



**Ex.1** 6 gram hydrogen reacts with 9.023 × 10<sup>23</sup> chlorine molecules to form HCI. If total pressure of the reaction is 800 mm then partial pressure of HCI will be

	(1) 400 mm		(2) 533 mm		(3) 600 mn	n	(4) 153.3 mm	Ans: (2)		
Sol.	H <sub>2</sub> +	$\operatorname{Cl}_2$								
	3 mole	9.023 6.023	$\frac{8 \times 10^{23}}{8 \times 10^{23}}$ 0 ln	itial mole						
	3 – 1.5 mole Total mole at e	1.5–1. equilibriu	5 mole 3.0 m = 1.5 + 3.0 -	Mole at eq · 4.5 mole	uilibrium		2	,		
	Partial pressu	re of HCI	$=\frac{3.0}{4.5}$ × 800 =	$\frac{1600}{3} = 53$	3 mm		0			
Ex.2	20% part of N (1) 0.29	<sub>2</sub> O <sub>4</sub> is dis	sociated in NC (2) 16.0	$D_2$ at 1 atmosphere	ospheric pres (3) 1.60	sure, then th	e value of K <sub>p</sub> will be (4) None of these	Ans: (4)		
Sol.	$N_2O_4 \rightleftharpoons 2N_2$	٥٥,	K_ =	$=\frac{4x^2P}{4x^2}$						
	P = 1 atm. pre	essure. >	k = 20% i.e. 2	1– x <sup>2</sup> mole		$\mathbf{O}$				
	$K_{p} = \frac{4 \times 0.2 \times 1}{1 - (0.1)}$	$\frac{02 \times 1}{2)^2} =$	$\frac{0.16}{0.96} = 0.17$		2					
Ex.3	In the reactior	In the reaction, $A + B \iff C + D$ , the equilibrium constant K is determined by taking 1 mole of A and 1 mole								
	of B as initial a	of B as initial amounts. If 2 moles of A and 3 moles of B are taken, then the equilibrium constant will be								
	(1) Two times		(2) Three tim	ies	(3) Six tim	es	(4) Unchanged	Ans: (4)		
Sol.	Equilibrium co	onstant (k	$K_{c}$ ) will remain $u$	inchanged	l					
Ex.4	Vaporization c will be the valu	of 1 mole ue of equi	of PCl₅ is done ilibrium consta	in a one-li nt	tre container.	If 0.2 mole C	$I_2$ is formed at equilib	rium, then what		
	(1) 0.15		(2) 0.05		(3) 1.78		(4) 0.2	Ans: (2)		
Sol.		2		PCL +	CL					
	Initial mole		1	0	0					
	Mole at equilib	orium	1–0.2	0.2	0.2					
	$K_{p} = \frac{[PCI_{3}][C}{[PCI_{5}]}$	$\frac{\left  \mathbf{s} \right _2}{\left  \right _2} = \frac{0}{\mathbf{s}}$	$\frac{2\times0.2}{0.8} = \frac{1}{20} =$	= 0.5						
Ex.5	$C(s) + H_2O(g)$	──────────────────────────────	2(g) + CO(g)							
	What will be the effect of pressure on the above equilibrium process?									
	(1) Remains u	naffected	I		(2) It will go in backward direction					
	(3) It will go in	forward	direction		(4) Unpred	ictable		Anc. (2)		
Sol.	There is no ef	fect of p	ressure of soli	ds. Volume	e of gases is	increasina in	the forward reaction	n. Therefore on		

**Sol.** There is no effect of pressure of solids. Volume of gases is increasing in the forward reaction. Therefore on increasing pressure, equilibrium will shift towards backward direction.

**Ex.6** If pressure is increased in the following reaction  $N_2 + 3H_2$   $2NH_3$ ,  $\Delta H = -22.4$  kcal then the equilibrium will

(1) be stable (2) Shift towards left side

- (3) Shift towards right side (4) Shift first towards left side, then right side **Ans: (3)**
- **Sol.** On increasing pressure in the reaction, equilibrium will shift towards the direction where volume gets decreased i.e towards forward (right) direction.

**Ex.7** In which case does the reaction go farthest to completion : K=1;  $K = 10^{10}$ ;  $K = 10^{-10}$  and why

**Sol.** The ratio 
$$\frac{[Pr oduct]}{[Reactant]}$$
 is maximum when K = 10<sup>10</sup> and thus reaction goes farthest to completion when K = 10<sup>10</sup>

**Ex.8** The equilibrium constant  $K_c$  for  $A_{(q)}$   $B_{(q)}$  is 1.1. Which gas has a molar concentration greater than 1?

**Sol.** For  $A_{(g)}$   $B_{(g)}$ ;  $K_c = \frac{[B]}{[A]} = 1.1 \implies [B] > [A]$ . If [B] = 1; [A] = 0.91

Case I	0.91 < [A] ≤ 1	Only [B] > 1
Case II	[A] > 1	Both [A] and [B] > 1

**Ex.9** 0.1 mole of  $N_2O_{4(g)}$  was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mole of  $NO_{2(g)}$  present, if the equilibrium  $N_2O_{4(g)}$   $2NO_{2(g)}$ , (K<sub>p</sub> = 0.14) is reached after some time.

Sol. 
$$N_2O_4$$
  $2NO_2$   
 $0.1$   $0$   
 $(0.1 - \alpha)$   $2\alpha$   
 $K_p = \frac{(2\alpha)^2}{(0.1 - \alpha)} \times \left[\frac{P}{0.1 + \alpha}\right]^1$  or  $K_p = \frac{40\alpha^2}{(0.1 - \alpha)}$  or  $\frac{40\alpha^2}{(0.1 - \alpha)} = 0.14$   
 $\therefore \quad \alpha = 0.017$   $\therefore \quad NO_2 = 0.017 \times 2 = 0.034$  mole

**Ex.10** What concentration of  $CO_2$  be in equilibrium with  $2.5 \times 10^{-2}$  mol litre<sup>-1</sup> of CO at 100° C for the reaction

0

$$FeO(s) + CO(g)$$
  $Fe(s) + CO_2(g)$ ;  $K_c = 5$ .

Sol.

$$\therefore \qquad 5 = \frac{[CO_2]}{2.5 \times 10^{-2}}$$

 $K_{c} = \frac{[CO_{2}]}{[CO]}$ 

:.  $[CO_2]$  at equilibrium =  $2.5 \times 10^{-2} \times 5 = 12.5 \times 10^{-2}$  mol litre<sup>-1</sup>

**C**;

Ex.11 What is the % dissociation of H<sub>2</sub>S if 1 mole of H<sub>2</sub>S is introduced into a 1.10 litre vessel at 1000 K ? K<sub>c</sub> for the  $2H_{2(g)} + S_{2(g)}$  is 1 × 10<sup>-6</sup> reaction :  $2H_2S_{(q)}$ 

0

 $2H_{2(g)} + S_{2(g)}$ 

Sol.

·..

·..

 $2H_2S_{(g)}$ 

Mole before dissociation 1 0

α Mole after dissociation  $(1-\alpha)$ α 2

Where  $\alpha$  is degree of dissociation of H<sub>2</sub>S

Volume of container = 1.10 litre

$$K_{c} = \frac{[H_{2}]^{2}[S_{2}]}{[H_{2}S]^{2}} = \frac{\left[\frac{\alpha}{1.1}\right]^{2}\left[\frac{\alpha}{2\times 1.1}\right]}{\left[\frac{1-\alpha}{1.1}\right]^{2}} = 1 \times 10^{-6}$$

Assuming  $1 - \alpha = 1$  since  $\alpha$  is small because K<sub>c</sub> =  $10^{-6}$ 

$$\frac{\alpha^3}{2(1.1)} = 10^{-6} \qquad \alpha = 1.3 \times 10^{-2} = 1.3\%$$

In the reaction,  $C(s) + CO_2(g)$ 2CO(g), the equilibrium pressure is 12 atm. If 50% of CO<sub>2</sub> reacts, calculate Ex.12  $K_P$ .

2CO(g) CO<sub>2</sub>(g) Sol. C(s) Gaseous mole before dissociation -0 50 2×50 Gaseous mole after dissociation 100 100 0.5 1 · . . Total mole = 1.5 Total pressure given at equilibrium = 12 atm

Partial pressure of CO = 
$$\frac{1}{1.5} \times 12 = 8$$

Partial pressure of 
$$CO_2 = \frac{.5}{1.5} \times 12 = 4$$

$$K_{p} = \frac{P_{CO}^{2}}{P_{CO_{2}}} = \frac{(8)^{2}}{4} = 16 \text{ atm}$$

When  $\alpha$ -d glucose is dissolved in water, it undergoes a partial conversion to  $\beta$ -d glucose to exhibit mutarota-Ex.13 tion. This conversion stops when 63.6% of glucose is in β from. Assuming that equilibrium has been attained, calculate  $K_c$  for mutarotation.

Sol.  $\alpha$  –d glucose β-d glucose

> At equilibrium 36.4 63.6

$$\therefore \qquad \qquad \mathsf{K}_{\mathsf{C}} = \frac{63.6}{36.4} = 1.747$$