# Chemical Equilibrium

#### Section (A) : Equilibrium and its properties

#### **Introduction :**

of the gaseous product

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 from 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 disrupt a system at equilibrium.



#### Types of chemical reactions

	Irreversible reaction		Reversible reaction
1	The reaction which proceeds in one direction (forward	1	The reaction which proceed in both the direction under the same
	direction) only.		set of experimental conditions.
2	Reactants are almost completely converted into products.	2	Reactants form products and products also react to form
	Products do not react to form reactants again.		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 $\{\rightarrow\}$	4	Represented by double arrow ( $\implies$ ) or ( $\implies$ )
5	Examples –	5	Examples :-
(a)	Precipitation reactions e.g.	(a)	Homogeneous reactions- only one phase is present
	$NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl \downarrow$		(i) Gaseous phase-
(b)	Neutralization reactions e.g		$H_2(g) + I_2(g) \longrightarrow 2HI(g)$
	$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$		$N_2(g) + O_2(g)$ 2NO(g) [Birkland eyde process (HNO <sub>3</sub> )]
(C)	$2\text{KCIO}_3(s) \xrightarrow{\Delta} 2\text{KCI}(s) + 3\text{O}_2(g)$		$N_2(g) + 3H_2(g)$ 2NH <sub>3</sub> (g) (Haber's process)
(d)	Reactions in open vessel :-		$CH_3 COOH(I) + C_2H_5OH(I) CH_3COOC_2H_5(I) + H_2O(I)$
	Even a reversible reaction will become irreversible if it is		Heterogeneous reactions- More than one phases are present
	carried out in open vessel. Ex.		$CaCO_3(s)$ $CaO(s) + CO_2(g)$
	$CaCO_3(s) \iff CaO(s) + CO_2(g)$ Open		$NH_4HS(s) \longrightarrow NH_3(g) + H_2S(g)$
	$NH_4HS(s) \implies NH_3(q) + H_2S(q)$ vessel	(b)	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 backword direction are balancing each other.

The equilibrium state represents a compromise between two opposing tendencies.

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

In a reversible reaction like-

 $\begin{array}{c} R_{1} \downarrow \downarrow R_{2} \\ Reactants \end{array} \xrightarrow{P_{1} \downarrow \downarrow P_{2}} Products$ 

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  $(r_b)$ 

(ii) Concentration (mole/litre) of reactant and product remains constant with respect to time.



#### Types of equilibria on basis of physical state



#### 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 from both direction.
- Equilibrium is <u>dynamic in nature.</u>

It means that reaction has not stopped. It appears that no change is occuring but 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 chateliers Principle).
- System moves toward an equilibrium state spontaneously even if it is disturbed. It will return to original state.

Solved Examples

Ex-1. Consider the following cases :



equilibrium while states in II and III are called steady state (static equilibrium).

Sol.

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 = Molar wt. × Vol.(Litre)

It is represented in square brackets i.e. [] e.g. [A], [N2] 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.  $aA + bB - \rightarrow$  products

Rate of reaction a [A]<sup>a</sup> [B]<sup>b</sup>

Rate = k [A]<sup>a</sup> [B]<sup>b</sup>,

where k is the rate constant of the reaction.

Ex-2. Four vessel each of volume V = 10 Lilres contains  
(1) 16 g CH<sub>4</sub> (2) 18 g H<sub>2</sub>O (3) 35.5 g Cl<sub>2</sub> (4) 44 g CO<sub>2</sub>  
Which container will contain same molar concentration and same active mass as that in (1)?  
Sol. (1) 
$$\Rightarrow$$
 [ CH<sub>4</sub>] =  $\frac{16}{16 \times 10}$  = 0.1 M (2)  $\Rightarrow$  [H<sub>2</sub>O] =  $\frac{18}{18 \times 10}$  = 0.1 M  
(3)  $\Rightarrow$  [Cl<sub>2</sub>] =  $\frac{35.5}{71 \times 10}$  = 0.05 M (4)  $\Rightarrow$  [CO<sub>2</sub>] =  $\frac{44}{44 \times 10}$  = 0.1 M  
Hence, (2) and (4) has same molar concentration as that in (1).

#### Equilibrium constant (K) :

For a general reaction

 $\begin{array}{c} aA+bB \overleftarrow{\frown} cC+dD,\\ \\ \mbox{Forward reaction rate } r_f=k_f\,[A]^a\,\,[B]^b\,,\\ \\ \mbox{Backward reaction rate } r_b=k_b\,[C]^c[D]^d\,,\\ \\ \mbox{At equilibrium } r_f=r_b\\ \\ k_f\,[A]^a\,[B]^b=k_b\,[C]^c\,[D]^d \end{array}$ 

The concentrations of reactants & products at equilibrium are related by

$$\frac{K_{f}}{K_{b}} = \frac{[C]^{c} [D]^{d}}{[A]^{a} [B]^{b}}$$

0

 $K_c$  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.

e.g. 
$$PCI_{5}(g) \rightleftharpoons PCI_{3}(g) + CI_{2}(g) \Rightarrow K_{C} = \frac{\begin{bmatrix} PCI_{3} \end{bmatrix} & \begin{bmatrix} CI_{2} \end{bmatrix}}{\begin{bmatrix} PCI_{5} \end{bmatrix}}$$
  
e.g.  $N_{2}(g) + 3H_{2}(g) \rightleftharpoons 2NH_{3}(g) \Rightarrow K_{C} = \frac{\begin{bmatrix} NH_{3} \end{bmatrix}^{2}}{\begin{bmatrix} NL_{2} \end{bmatrix} & K_{C} = \frac{\begin{bmatrix} NH_{3} \end{bmatrix}^{2}}{\begin{bmatrix} NL_{2} \end{bmatrix} & K_{C} = \frac{\begin{bmatrix} NH_{3} \end{bmatrix}^{2}}{\begin{bmatrix} NL_{2} \end{bmatrix} & K_{C} = \frac{\begin{bmatrix} NH_{3} \end{bmatrix}^{2}}{\begin{bmatrix} NL_{2} \end{bmatrix}}$   
e.g.  $\frac{1}{2}H_{2}(g) + \frac{1}{2}I_{2}(g) \rightleftharpoons HI(g) \Rightarrow K_{C} = \frac{\begin{bmatrix} HI \end{bmatrix}}{\begin{bmatrix} HL_{2} \end{bmatrix}^{1/2} [I_{2}]^{1/2}}$   
Solved Examples

- **Ex-3.** In a reaction A (g) + B (g)  $\rightleftharpoons$  C (g)+ D(g) , A, B, are mixed in a vessel at temperature T. The initial concentration of A was twice the initial concentration of B. After the equilibrium is reached, concentration of C was thrice the concentration of B Calculate K<sub>c</sub>.
- **Sol.** Let concentration of B initially is 'a' mole/litre

$$A + B \rightleftharpoons C + D \Rightarrow \Delta n = 0$$
at t = 0 2a a 0 0  
at t = t<sub>eq</sub> 2a - x a - x x x  
Given that
$$x = 3 (a - x) \Rightarrow x = \frac{3}{4}a \qquad K_{c} = \frac{\begin{bmatrix} C \end{bmatrix} \begin{bmatrix} D \\ A \end{bmatrix}}{K_{c} = \begin{bmatrix} C \end{bmatrix} \begin{bmatrix} D \\ A \end{bmatrix}}$$

$$\frac{\left(\frac{3a}{4}\right)^{2}}{\left(2a - \frac{3a}{4}\right)\left(a - \frac{3a}{4}\right)} \Rightarrow K_{c} = \frac{9}{5} = 1.8$$

- O  $K_P \rightarrow Equilibrium constant in terms of partial pressure.$  It is defined for the equilibrium reaction which contains at least one gaseous component.
  - e.g.  $aA(g) + bB(g) \rightarrow cC(g) + dD(g)$

$$\mathsf{K}_{\mathsf{P}} = \frac{\left[\mathsf{P}_{\mathsf{C}}\right]^{\mathsf{c}} \quad \left[\mathsf{P}_{\mathsf{D}}\right]^{\mathsf{d}}}{\left[\mathsf{P}_{\mathsf{A}}\right]^{\mathsf{a}} \quad \left[\mathsf{P}_{\mathsf{B}}\right]^{\mathsf{b}}}$$

where various pressures are the partial pressures of various gases substancs.

### Solved Examples.

 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ 

**Ex-4.** Calculate the expression for K<sub>c</sub> and K<sub>p</sub> if initially a moles of N<sub>2</sub> and b moles of H<sub>2</sub> is taken for the following reaction.

 $(\Delta n < 0)$  (P, T, V given)

given)

Sol.

$$N_{2}(g) + 3H_{2}(g) \stackrel{\sim}{\longrightarrow} 2NH_{3}(g) \qquad (\Delta n < 0) (P, T, V)$$
At t = 0 a b 0  
t = t eq (a - x) (b - 3x) 2x  

$$[N_{2}] = \frac{a - x}{V}, \qquad [H_{2}] = \frac{b - 3x}{V}, \qquad [NH_{3}] = \frac{2x}{V}$$

$$\frac{\left(\frac{2x}{V}\right)^{2}}{\left(\frac{a - x}{V}\right)\left(\frac{b - 3x}{V}\right)^{3}} = \frac{4x^{2}V^{2}}{(a - x)(b - 3x)^{3}}$$
Total no. of moles at equilibrium = a + b - 2x  

$$(a - x) \qquad (b - 3x) \qquad (2x).$$

$$\begin{bmatrix} P_{N_2} \end{bmatrix}_{=} \frac{(a-x)}{a+b-2x} \cdot P, \quad \begin{bmatrix} P_{H_2} \end{bmatrix}_{=} \frac{(b-3x)}{a+b-2x} \cdot P, \quad \begin{bmatrix} P_{NH_3} \end{bmatrix}_{=} \frac{(2x) \cdot P}{a+b-2x} \cdot P = \frac{\left(\frac{2x}{a+b-2x} \cdot P\right)^2}{\left[\left(\frac{a-x}{a+b-2x}\right) \cdot P\right]^2} = \frac{\left[\left(\frac{a-x}{a+b-2x}\right) \cdot P\right]^2}{\left[\left(\frac{a-x}{a+b-2x}\right) \cdot P\right]^2}$$

$$K_{P} = \frac{\frac{4x^{2} \cdot P^{2}}{(a+b-2x)^{2}}}{P^{4} \cdot \frac{(a-x)(b-3x)^{3}}{(a+b-2x)^{4}}} = \frac{(a+b-2x)^{2} \cdot 4x^{2}}{P^{2}(a-x)(b-3x)^{3}}$$

#### $\mathbf{O}$ Relation between K<sub>P</sub> & K<sub>c</sub>

P = VRTPV = nRTor n P = CRT where C = V = (moles per litre)  $P_D = [D] RT$ ;  $P_A = [A] RT$ ;  $P_B = [B] RT$  $P_{c} = [C] RT;$  $[C]^{c}(RT)^{c}[D]^{d}(RT)^{d}$  $K_{P} = \frac{\overline{[A]^{a}(RT)^{a}[B]^{b}(RT)^{b}}}{[A]^{a}[B]^{b}} = \frac{\overline{[A]^{a}[B]^{b}}}{[RT)^{(c+d)-(a+b)}}$  $K_p = K_c(RT)^{\Delta n}$ 

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

 $\Delta n =$  sum of the number of moles of gaseous products – sum of the number of moles of gaseous ⇒ reactants. An can be positive, negative, zero or even fraction.

 $CaCO_3$  (s)  $\subset$  CaO (s) + CO<sub>2</sub>(q)

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

 $\Rightarrow$  K<sub>p</sub> = K<sub>c</sub>.(RT)

 $\Rightarrow$ 

#### Unit of Equilibrium contants :

- Unit of K<sub>p</sub> is (atm)<sup>∆n</sup>
- Unit of K<sub>c</sub> is  $(mole/Lit)^{\Delta n} = (conc.)^{\Delta n}$

Note: O 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.

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

e.g. 
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
  
 $K_0 = I CO_2 I \qquad K_0 = \frac{P_{CO_2}}{r_0}$ 

$$\mathsf{K}_{\mathsf{C}} = [\mathsf{C}\mathsf{O}_2], \quad \mathsf{K}_{\mathsf{P}} =$$

Calculate kp and Kc if initially a moles of PCI5 is taken Ex-5.

$$PCI_5(g) \longrightarrow PCI_3(g) + CI_2(g)$$

Sol.

 $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$ At t = 0а 0

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Calculating equilibrium concentrations

The concentration of various reactants and products can be calculated using the equilibrium constant and the initial concentrations.

 $\label{eq:constraint} \textbf{Ex-6.} \quad 1 \text{ mole of } N_2 \text{ and } 3 \text{ moles of } H_2 \text{ are placed in } 1L \text{ vessel. Find the concentration of } NH_3 \text{ at equilibrium, if } NH_3 \text{ at equilibrium, } NH_3 \text{ at equil$ 

equilibrium pressure is 1 atm and the equilibrium constant at 400K is  $\overline{27}$ 

Sol. N<sub>2</sub> (g) + 3H<sub>2</sub>(g) 
$$\rightleftharpoons$$
 2NH<sub>3</sub>(g) ( $\Delta n < 0$ )  
1mol 3 mol 0  
(1-x) (3-3x) 2x  
P<sub>eq</sub> = 1 atm, T = 400 K  
 $K_{C} = \frac{[NH_{3}]^{2}}{[N_{2}] [H_{2}]^{3}} = \frac{(2x)^{2}}{(3-3x)^{3}(1-x)} = \frac{4}{27}$   
 $\frac{x^{2}}{(1-x)^{4}} = 1 \Rightarrow x = (1-x)^{2} \Rightarrow x^{2}-3x+1=0$   
 $\Rightarrow x = \frac{3 \pm \sqrt{9-4}}{2} \Rightarrow x = \frac{3 \pm \sqrt{5}}{2}$   
 $x = \frac{3 \pm 2.24}{2} \text{ or } x = \frac{3 \pm \sqrt{5}}{2}$   
 $x = \frac{5.24}{2} = 2.62 \text{ or, } x = \frac{0.76}{2}$   
 $\Rightarrow x = 0.38 \text{ (since x cannot be greater than 1)}$   
 $[NH_{3}] = 0.38 \times 2 = 0.76$ 

#### Characteristics of equilibrium constant & factors affecting it :

• Equilibrium constant <u>does not depend</u> upon concentration of various reactants, presence of catalyst, direction from which equilibrium is reached

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- The equilibrium constant does not give any idea about time taken to attain equilibrium.
- K depends on the stoichiometry of the reaction.
  - O If two chemical reactions at equilibrium having equilibrium constants  $K_1$  and  $K_2$  are added then the resulting equation has equilibrium constant  $K = K_1 \cdot K_2$

Equation constant

On adding

 $\circ$  If the reaction having eq. constant K<sub>1</sub> is reversed then resulting equation has eq. constant  $K_1$ 

$$A(g) + B(g) \longleftarrow C(g) + D(g)$$

On reversing,  $C(g) + D(g) = A(g) + B(g) = \overline{K_1}$ 

O 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

eg.

$$D_{2}(g) \stackrel{\frown}{\longrightarrow} 2A(g) \qquad \qquad K_{1}$$
Multiplying by  $\left(\frac{1}{2}\right), \quad \frac{1}{2} D_{2}(g) \stackrel{\frown}{\longrightarrow} A(g) \qquad \qquad K = (K_{1})^{1/2} = \sqrt{K_{1}}$ 

**Ex-7.** The value of  $K_c$  for the reaction,  $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$  at a certain temperature is 400. calculate the value of equilibrium constant for.

(i)  $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$ ; (ii)  $1/2 N_2(g) + O_2(g) \rightleftharpoons NO_2(g)$ 

Sol. Equilibrium constant (K<sub>c</sub>) for the reaction N<sub>2</sub> (g) + 2O<sub>2</sub>(g)  $\rightleftharpoons$  2NO<sub>2</sub>(g) is  $\begin{aligned}
& K_{c} = \frac{[NO_{2}]^{2}}{[N_{2}][O_{2}]^{2}} = 400
\end{aligned}$ (i) For the reaction 2NO<sub>2</sub>(g)  $\rightleftharpoons$  N<sub>2</sub>(g)+ 2O<sub>2</sub>(g) , K'c =  $\frac{[N_{2}][O_{2}]^{2}}{[NO_{2}]^{2}} = \frac{1}{K_{c}}$   $K'_{c} = \frac{1}{400} = 0.0025 \text{ mole litre}^{-1}$ (ii) For the reaction 1/2 N<sub>2</sub>(g) + O<sub>2</sub>(g)  $\rightleftharpoons$  NO<sub>2</sub>(g)  $K''_{c} = \frac{[NO_{2}]}{[N_{2}]^{1/2}[O_{2}]} = \sqrt{K_{c}} \Rightarrow K''_{c} = \sqrt{400} = 20 \text{ litre}^{-1/2} \text{ mole}^{-1/2}$ 

#### • 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.

O However if temperature is changed,

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

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.

• Relation between equilibrium constant & standard free energy change.

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

Where  $\Delta G^{\circ}$  = standard free energy change

T = Absolute temperature,

R = universal gas constant.

Ex-8. From the following data :

(i)  $H_2(g) + CO_2(g) \longrightarrow H_2O(g) + CO(g)$  $K_{2000K} = 4.4$ (ii)  $2H_2O(g) \longrightarrow 2H_2(g) + O_2(g)$  $K_{2000K} = 5.31 \times 10^{-10}$ (iii)  $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$  $K_{1000K} = 2.24 \times 10^{22}$ State whether the reaction (iii) is exothermic or endothermic?

**Sol.** Equation (iii) = 
$$-[2 \times (i) + (ii)]$$

$$\therefore \qquad K_{2000 \text{ (iii)}} = \frac{1}{K_1^2 K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

 $\mathbb{X} \qquad \mathsf{T} \uparrow \mathsf{K}^{\downarrow} \Rightarrow \text{reaction is exothermic.}$ 

#### Section (B) : Calculation of K<sub>P</sub> & K<sub>c</sub> in homogenous equilibrium

#### Homogeneous liquid system : Formation of ethyl acetate :

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

 $CH_{3}COOH(l) + C_{2}H_{5}OH(l) \xrightarrow{} CH_{3}COOC_{2}H_{5}(l) + H_{2}O(l)$   $\frac{[CH_{3}COOC_{2}H_{5}][H_{2}O]}{[CH_{3}COOH][C_{2}H_{5}OH]}$ 

**Ex-9.** In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at T<sup>o</sup>C, the equilibrium mixture on analysis shows that 54.3% of the acid is esterfied. Calculate the equilibrium constant of this reaction.

 $CH_3COOH(l) + C_2H_5OH(l) \leftarrow CH_3COOC_2H_5(l) + H_2O(l)$ Sol. Initial 1 1 0 1 At equilibrium 1 - x1 – x 1 + x Х 1 - 0.5431 - 0.5430.543 1 + 0.5431 x 54.3 100 (54.3% of 1 mole = = 0.543 mole) Hence given x = 0.543 mole

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Applying law of mass action :  $K_c = \frac{[ester][water]}{[acid][alcohol]} = \frac{0.543 \times 1.543}{0.457 \times 0.457} = 4.0$ 

### Section (C) : Reaction quotient Applications of Equilibrium constant :

#### • 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  $Q = \begin{bmatrix} A \end{bmatrix}^a \begin{bmatrix} B \end{bmatrix}^b$  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.
  - o if Q > K<sub>c</sub> reaction will proceed in backward direction until equilibrium in reached.
  - o if Q < K<sub>c</sub> reaction will proceed in forward direction until equilibrium is established.
  - $\circ$  if Q = K<sub>c</sub> Reaction is at equilibrium.

eg.  $2A(g) + B(g) \stackrel{\frown}{=} C(g) + D(g)$ 

 $Q_C$  = Reaction quotient in terms of concentration

 $\begin{aligned} Q_{C} &= \frac{\begin{bmatrix} C \end{bmatrix} \begin{bmatrix} D \end{bmatrix}}{\begin{bmatrix} A \end{bmatrix}^{2} \begin{bmatrix} B \end{bmatrix}} \\ K_{C} &= \frac{\begin{bmatrix} C \end{bmatrix}_{eq} \begin{bmatrix} D \end{bmatrix}_{eq}}{\begin{bmatrix} A \end{bmatrix}_{eq}^{2} \begin{bmatrix} B \end{bmatrix}_{eq}} \\ \begin{bmatrix} Here & all & the conc. & are & at & equilibrium \end{bmatrix} \end{aligned}$ 

**Ex-10.** For the reaction NOBr (g)  $\Longrightarrow$  NO(g) +  $\frac{1}{2}$  Br<sub>2</sub> (g)

 $K_P = 0.15$  atm at 90°C. If NOBr, NO and Br<sub>2</sub> are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 0.2 atm respectively, will Br<sub>2</sub> be consumed or formed ?

Sol. 
$$Q_{P} = \frac{\left[P_{Br_{2}}\right]^{1/2} \left[P_{NO}\right]}{\left[P_{NOBr}\right]} = \frac{\left[0.2\right]^{1/2} \quad [0.4]}{\left[0.50\right]} = 0.36$$
  
 $K_{P} = 0.15$   
 $\therefore \qquad Q_{P} > K_{P}$ 

- Hence, reaction will shift in backward direction
- $\therefore$  Br<sub>2</sub> will be consumed

#### • Predicting the extent of the reaction



- **Case-I** : If K is large (k > 10<sup>3</sup>) then product concentration is very very larger than the reactant ([Product] >>[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 <  $10^{-3}$ )

[Product] << [Reactant]

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

In this case, the reaction is reactant favourable.

### Solved Examples

- **Ex-11.** 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 (D) : Degree of dissociation (a)

It is the fraction of one mole dissociated into the products. (Defined for one mole of substance)

So,  $\alpha = no.$  of moles dissociated / initial no. of moles taken

= fraction of moles dissociated out of 1 mole.

#### Note : % dissociation = $\alpha \times 100$

Suppose 5 moles of PCI<sub>5</sub> is taken and if 2 moles of PCI<sub>5</sub> dissociated then  $\alpha = \overline{5} = 0.4$ Let a gas A<sub>n</sub> dissociates to give n moles of A as follows-

$$A_{n}(g) \qquad n A(g)$$

$$t = 0 \qquad a \qquad 0$$

$$t = t_{eq} \qquad a - x \qquad n.x \qquad \alpha = \overline{a} \Rightarrow \qquad x = a\alpha.$$

$$a - a \alpha = a(1 - \alpha) \qquad n a \alpha$$
Total no. of moles =  $a - a \alpha + n a \alpha$ 

$$= [1 + (n - 1) \alpha] a$$
Significance of n

sum of stoichiometric coefficient of product

n = sum of coefficient of reactants

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(i)	for PC	l₅(g) <del>⊂</del> PCl₃(g) + C	2 <b>(g)</b>	(n = 2)	
		,		$\frac{3}{2}$ $\frac{1}{2}$	
(ii)	for 2N	$H_3(g) \longrightarrow N_2(g) + 3H_2$	(g)	(n = 2 + 2 = 2)	1
(iii)	for 2H	$(g) \rightleftharpoons H_2(g) + I_2(g)$		(n = 1)	
	5	Solved Examp	ples ——		
Ex-12.	Calcul	ate the degree of disso	ociation and $K_p$ for t	he following read	ction.
		PCl₅(g) ← PCl₃	$(g) + Cl_2(g)$		
	t = 0	a 0	0		
	t = t	a –x x	х		
	Since	or a mole, x moles are	dissociated		
		х			
Sol.	<i>.</i>	For 1 mole, a moles	$s = \alpha$ are dissociate	d	
	<i>.</i>	x = a α			
		PCI <sub>5</sub>	(g) $\Longrightarrow$ PCl <sub>3</sub> (g)	) + Cl <sub>2</sub> (g)	
	<i>.</i>	At t = t <sub>eq</sub> a - a	α α	aα	
	Total r	o. of moles at equilibri	um = a + aα = a (1	+ α )	
		a(1-α) P	aα.	Р	a α
		$P_{PCI_{5}} = \frac{a(1+\alpha)}{a(1+\alpha)},$	P <sub>PCl3</sub> = a (1+	α)	$P_{Cl_2} = \overline{a (1+\alpha)}$ . P
		$\frac{\left\{\left(\frac{\alpha P}{1+\alpha}\right)\right\}^2}{\left(1-\alpha\right)}$	a <sup>2</sup> F		
		$K_{P} = \left[ \frac{1-\alpha}{1+\alpha} \right] P$	$K_{P} = \frac{\alpha \cdot r}{1 - \alpha^{2}}$	(Remember)	
	Obser	ved molecular weigh	t and Observed V	apour Density o	of the mixture
	30001		m	lecular weight	$M_{\alpha}$ of A (a)
			total	no of moles	$\frac{1}{at} = \frac{1}{a(1+(n-1)a)}$
	Obser	ved molecular weigh	t of $A_n(g) = \frac{10121}{1012}$		$a = a(1 + (1 - 1)\alpha)$

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

where  $M_{th}$  = theoritical molecular weight (n = atomicity)

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

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

O D = vapour density without dissociation = 
$$\frac{M_{A_n}}{2}$$
  
d = vapour density of mixture = observed v.d. =  $\frac{M_{mix}}{2}$   
 $\frac{D}{d}$  = 1 + (n - 1)  $\alpha$ 

$$\alpha = \frac{D-d}{(n-1) \times d} = \frac{M_{T} - M_{o}}{(n-1)M_{o}}$$

where  $M_T$  = Theoritical 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].

## Solved Examples .

**Ex-13.** The vapour density of a mixture containing NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> is 38.3 at 33°C calculate the no. of moles of NO<sub>2</sub> if 100g of N<sub>2</sub>O<sub>4</sub> were taken initially.

Sol.

$$N_{2}O_{4}(g) \stackrel{\longrightarrow}{\longrightarrow} 2NO_{2}(g)$$

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

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

$$N_{2}O_{4} \stackrel{\longrightarrow}{\longrightarrow} 2NO_{2}$$

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

$$t = t \quad a - a\alpha \qquad 2a\alpha$$
no. of moles of NO<sub>2</sub> =  $2a\alpha = \frac{2 \times 100 \times 0.2}{92} = 0.435$ 

#### Section (E) : Heterogenous Equilibrium

For pure solid and pure liquid, active mass is taken to be unity i.e. 1 as they remain constant throughout the reaction

• CaCO<sub>3</sub> (s) <del>CaC</del>CaO (s) + CO<sub>2</sub> (g)

$$\begin{split} \mathsf{K}_{\mathsf{P}} &= \overset{\mathsf{P}_{\mathsf{CO}_2}}{\underset{\mathsf{V}}{\mathsf{N}_{\mathsf{C}}}}, \, \mathsf{K}_{\mathsf{C}} &= [\mathsf{CO}_2\left(g\right)] \\ & [\mathsf{CaCO}_3(s)] = \overset{\mathsf{moles}}{\underset{\mathsf{V} \text{olume}}{\mathsf{volume}}} = \overset{\mathsf{M}_{\mathsf{CaCO}_3}}{\underset{\mathsf{V}}{\mathsf{N}_{\mathsf{CaCO}_3}}} = \overset{\mathsf{density}}{\underset{\mathsf{M}_{\mathsf{CaCO}_3}}{\mathsf{M}_{\mathsf{CaCO}_3}}} = \mathsf{constant} \\ & \frac{[\mathsf{CaO}(s)][\mathsf{CO}_2(g)]}{[\mathsf{CaCO}_3(s)]} \\ & \mathsf{K} &= \overset{\mathsf{[CaCO}_3(s)]}{\underset{\mathsf{[CaCO}_3(s)]}{\mathsf{I}_{\mathsf{C}}}} = [\mathsf{CO}_2(g)] \\ & \mathsf{K}_{\mathsf{C}} &= [\mathsf{CO}_2(g)] \end{split}$$

 $H_2O(l) \rightleftharpoons H_2O(g)$ 

 $K_{P} = , K_{C} = [H_{2}O(g)]$ 

[For pure solid and pure liquid active mass is taken as unity i.e. = 1]

**Ex-14.** In a reaction  $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ ,<br/>Calculate  $K_P$ .the equilibrium pressure is 12 atm. If 50% of  $CO_2$  reacts.<br/>Calculate  $K_P$ .**Sol.** $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ 

t = 0 a 0

t = t<sub>eq</sub> a - 
$$\frac{a}{2}$$
 2 $\frac{a}{2}$   
P<sub>eq</sub> = 12 atm  
X<sub>CO<sub>2</sub></sub> =  $\frac{1}{3}$ , X<sub>CO</sub> =  $\frac{2}{3}$ ; P<sub>CO<sub>2</sub></sub> =  $\frac{1}{3}$  x 12 = 4 ; P<sub>CO</sub> =  $\frac{2}{3}$  x 12 = 8  
∴ K<sub>P</sub> =  $\frac{8 \times 8}{4}$  = 16

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#### EQUATION INVOLVING IONS :

Equilibrium involving ions always take place in aquous medium . In case of expression of  $K_C$  concentration of ion is taken.

$$Ag^{+}(aq.) + CI^{-}(aq.) \longleftrightarrow AgCI(s) K_{c} = \frac{1}{[Ag^{+}][CI^{-}]}$$

#### Section (F) : Thermodynamics of Equilibrium

For a general reaction,  $mA + nB \stackrel{\longrightarrow}{\longrightarrow} pC + qD$ ,  $\Delta G$  is given by-

 $\Delta G = \Delta G^0 + 2.303 \text{ RT } \log_{10} Q$ 

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

 $\Delta G^0$  = Standard Gibb's Free energy change

Q = reaction quotient

Since, at equiibrium, Q = K

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

$$K = \frac{(a_{c})^{p} (a_{D})^{q}}{(a_{A})^{m} (a_{B})^{n}}; \qquad \text{Here } a_{X} \text{ denotes the activity of } X.$$

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) Themodynamic 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,  $\Delta G = 0$ 

$\Delta G^0 = -2.303 \text{ RT} \log_{10} \text{K}$		
$\Delta G^{0} = \Delta H^{0} - T \Delta S^{0}$		
$\Delta H^0$ = Standard enthalpy change of the reaction		
$\Delta S^{\circ}$ = Standard entropy change		
$-2.303 \text{ RT} \log_{10}\text{K} = \Delta H^0 - T\Delta S^0$		
$\log_{10}K = -\frac{\Delta H^{\circ}}{2.303} \cdot \frac{1}{RT} + \frac{\Delta S^{\circ}}{2.303R}$		
1	$\Delta H^{\circ}$	$\Delta S^{\circ}$
T is plotted then it is a straight line with slope = $-$	R , and intercept =	R
	$\begin{split} &\Delta G^{0} = -2.303 \text{ RT } \log_{10} \text{K} \\ &\Delta G^{0} = \Delta H^{0} - T\Delta S^{0} \\ &\Delta H^{0} = \text{Standard enthalpy change of the reaction} \\ &\Delta S^{\circ} = \text{Standard entropy change} \\ &-2.303 \text{ RT } \log_{10} \text{K} = \Delta H^{0} - T\Delta S^{0} \\ &\log_{10} \text{K} = -\frac{\Delta H^{0}}{2.303} \cdot \frac{1}{\text{RT}} + \frac{\Delta S^{o}}{2.303\text{R}} \\ &\frac{1}{\text{T}} \text{ is plotted then it is a straight line with slope} = - \end{split}$	$\begin{split} &\Delta G^{0} = -2.303 \ \text{RT} \ \text{log}_{10}\text{K} \\ &\Delta G^{0} = \Delta H^{0} - T\Delta S^{0} \\ &\Delta H^{0} = \text{Standard enthalpy change of the reaction} \\ &\Delta S^{\circ} = \text{Standard entropy change} \\ &- 2.303 \ \text{RT} \ \text{log}_{10}\text{K} = \Delta H^{0} - T\Delta S^{0} \\ &\log_{10}\text{K} = - \frac{\Delta H^{0}}{2.303} \cdot \frac{1}{\text{RT}} + \frac{\Delta S^{o}}{2.303\text{R}} \\ &\frac{1}{\text{T}} \text{ is plotted then it is a straight line with slope} = - \frac{\Delta H^{o}}{\text{R}} \text{ , and intercept} = - \frac{\Delta H^{o}}{\text{R}} \end{split}$



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

$$\log_{10}K_{1} = \frac{-\Delta H^{\circ}}{2.303R} \cdot \frac{1}{T_{1}} + \frac{\Delta S^{\circ}}{2.303R} \qquad .....(i)$$
$$\log_{10}K_{2} = \frac{-\Delta H^{\circ}}{2.303R} \cdot \frac{1}{T_{2}} + \frac{\Delta S^{\circ}}{2.303R} \qquad .....(ii)$$

[Assuming  $\Delta H^0$  and  $\Delta S^0$  remains constant in this temperature range.]

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

$$\log \left(\frac{\mathsf{K}_{1}}{\mathsf{K}_{2}}\right) = \frac{\Delta \mathsf{H}^{\mathsf{o}}}{2.303\mathsf{R}} \left(\frac{1}{\mathsf{T}_{2}} - \frac{1}{\mathsf{T}_{1}}\right)$$

Note :  $O \Delta H$  should be substituted with sign.

O Unit of  $\Delta$ H/T and gas constant R should be same.

O For endothermic ( $\Delta H > 0$ ) reaction value of the equilibrium constant increases with the rise in temperature

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

- $\Rightarrow \quad \Delta H T\Delta S < 0 \qquad \Rightarrow \qquad T > \Delta H/\Delta S$
- ΔG > 0 for non-spontaneous process or reaction.

A I 10

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

Ex-15. Variation of equilibrium constant K with temperature T is given by van't Hoff equation,

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

A graph between log K and T<sup>-1</sup> 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.



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

#### External factors affecting equilibrium :

#### 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.

 $\begin{array}{c} N_2 \left(g\right) + 3H_2 \left(g\right) & \longrightarrow & 2NH_3 \left(g\right) \\ \mbox{[reactant]}^{\uparrow} & & \mbox{Forward shift} \\ \mbox{[Product]}^{\uparrow} & & \mbox{Backward shift} \end{array}$ 

- O If concentration of reactant is increased at equilibrium then reaction shifts in the forward direction
- O 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 :

O 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.

O 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.  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$  (No effect)

#### **Explanation :**

#### • 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  $\propto$  no. of moles

#### 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 :

#### At constant volume : Inert gas addition has no effect at constant volume (i)

(ii) 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

- $\Delta n_g > 0$ , reaction will shift in the forward direction (i)
- $\Delta n_q < 0$ , reaction will shift in the backward direction (ii)

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

#### Effect of temperature :

A(g) + B(g) 
$$\subset$$
 C(g) + D(g) + Heat  $\Delta H = -ve$   
N<sub>2</sub>(g) + 3H<sub>2</sub>(g)  $\subset$  2NH<sub>3</sub>(g) + Heat

 $T^{\uparrow} \Rightarrow$  K' will decrease (from vant' hoff equation)

$$\log \frac{\frac{K_1}{K_2}}{\frac{K_1}{K_2}} = \frac{\Delta H^o}{2.303 R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$\log \frac{\frac{K_1}{K_2}}{\frac{K_2}{K_2}} < 0 \implies \log K_1 - \log K_2 > 0$$
$$\implies \log K_1 > \log K_2$$
$$\implies K_1 > K_2$$

Reaction will shift in backward direction.

 $T \downarrow \Rightarrow K$  will increases.

Reaction will shift in forward direction.

(ii) Endothermic reaction : energy consumed.

$$\begin{array}{ll} A(g) + B(g) & \overleftarrow{\phantom{a}} C(g) + D(g) - \text{Heat} & \therefore \Delta H = + \text{ ve} \\ T \uparrow \Rightarrow K \uparrow \Rightarrow \text{ Forward} & ; & T \downarrow \Rightarrow & K \downarrow \Rightarrow \text{ Backward} \end{array}$$

## Solved Examples -

- **Ex-16.** The volume of a closed reaction vessel in which the equilibrium,  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$  is halved, Now
  - (1) The rates of forward and backward reactions will remains the same.
  - (2) The equilibrium will not shift.
  - (3) the equilibrium will shift to the right.
  - (4) The rate of forward reaction will become double that of reverse reaction and the equilibrium will shift to the right.

 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ Sol. (4) In the reaction,

> In this reaction three moles (or volumes) of reactants are converted into two moles (or volumes) of products i.e. there is a decreases in volume and so if the volume of the reaction vessel is halved the

#### **CHEMISTRY FOR JEE**

equilibrium will be shifted to the right i.e. more product will be formed and the rate of forward reaction will incerases i.e. double that of reverse reaction.

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

#### • Vapour Pressure of Liquid :

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

 $H_2O(\ell) \longrightarrow H_2O(g)$ ;  $K_P = P_{H_2O} = constant$  at fixed temperature

Hence V.P. of liquid is independent of pressure, volume and concentration change. e.g. at 25°C, vapour pressure of water 24 mm of Hg

Partial pressure of  $H_2O$  vapours

**Relative Humidity** = Vapour pressure of  $H_2O$  at that temp.

#### Formation of diamond :

C (graphite)  $\leftarrow$  C (diamond) – Heat;  $\Delta H = + ve$   $\downarrow \qquad \downarrow$ Density Low Density High

Density Low Volume High

Volume Low

Formation of diamond is favourable at high pressure and high temperature

#### • Melting of ice :

 $\begin{array}{ccc} H_2O\left(s\right) & \overleftarrow{\phantom{aaaa}} & H_2O\left(\ell\right) \; ; & \Delta H = + \; ve \\ \downarrow & \downarrow & \\ Density \; Low & Density \; High \\ Volume \; High & Volume \; Low \end{array}$ 

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

#### • Boiling of water :

 $H_2O(\ell) \qquad \longrightarrow \qquad H_2O(g)$   $\downarrow \qquad \qquad \downarrow$ Density High Density Low

Volume Low Volume High

On incerasing pressure, equilibrium will shift in the direction in which volume is decreasing i.e. backward. Hence, on incerasing pressure, the boiling point increases.

#### Formation of ammonia by Haber's process :

 $N_2(g) + 3 H_2(g) \xrightarrow{} 2NH_3(g) \Delta H = -22.4 \text{ Kcal/mol.}$ 

(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

<u>-2SO<sub>2</sub>(g) + O<sub>2</sub>(g) = 2SO<sub>3</sub>(g) + 45.2 kcal\_</u>

High pressure (1.5 to 1.7 atm), Low temperature (500°C), Higher qunatity of  $SO_2$  and  $O_2$  are favourable conditions for the formation of  $SO_3$ .

#### Manufacturing of NO by Birkeland–Eyde process

 $N_2(g) + O_2(g) \stackrel{\longrightarrow}{\longleftarrow} 2 NO(g) - 43.2 \text{ kcal}$ 

- O No effect on change of pressure
- O High temperature (1200 °C to 2000 °C), High concentration of  $N_2$  and  $O_2$  are favourable condition
- for

the formation of NO.

Solved Examples -

Ex-17. The equilibrium constant of the reaction at 25°C

 $CuSO_{4.5}H_{2}O(s) \xleftarrow{} CuSO_{4.3}H_{2}O(s) + 2H_{2}O(g)$ 

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 loosing its water of crystallization according to above reaction. (Vapour pressure of water at 25°C is 24 mm of Hg).

Sol. 
$$K_{P} = (P_{H_2O})^2$$
 so  $P_{H_2O} = \sqrt{1.084 \times 10^{-4}} = 1.041 \times 10^{-2}$  atm 8 mm of Hg

O 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.

O If  $P_{H_2O}$  < 8 mm of Hg then CuSO<sub>4</sub>.5H<sub>2</sub>O will loose water of crystallization and reaction will move in forward direction.

i.e. If relative humidity  $< \frac{8}{24} < 33.33\%$ then CuSO<sub>4.5</sub>H<sub>2</sub>O will loose water of crystallization.

#### Simultaneous Equilibrium :

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.

e.g.

 $A(s) \stackrel{\longrightarrow}{\longleftarrow} X(g) + Y(g)$ t = 0а 0 0  $t = t_{eq}$ a-t t t + u  $B(s) \stackrel{\longrightarrow}{\longrightarrow} Z(g) + Y(g)$ b 0 0 b – u u u + t  $K_{C1} = t (u + t)$  $K_{C2} = (u + t) u$ 

**Ex-18.** 102 g of solid NH<sub>4</sub>HS is taken in the 2L evacuated flask at 57°C. Following two equilibrium exist simultaneously

 $NH_4HS$  (s)  $\overrightarrow{}$   $NH_3$  (g) +  $H_2S$  (g)

Sol.

$$NH_{3}(g) \stackrel{1}{\longleftrightarrow} \frac{1}{2}N_{2}(g) + \frac{3}{2}H_{2}(g)$$

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.

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

$$NH_4HS (s) \longrightarrow NH_3 (g) + H_2S (g) \qquad K_{C_1}$$

$$2 \qquad 0 \qquad 0$$

$$1 \qquad 1-x \qquad 1$$

$$NH_3 (g) \longrightarrow N_2 (g) + \frac{3}{2} H_2 (g) \qquad K_{C_2}$$

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

$$K_{C1} = \frac{1}{2} \frac{(1-x)}{2} = \frac{1}{8} \qquad [Since V = 2 L]$$

$$\frac{\left(\frac{3x}{4}\right)^{3/2} \left(\frac{x}{4}\right)^{3/2}}{\left(\frac{1-x}{2}\right)} = \frac{\left(\frac{3}{8}\right)^{3/2} \left(\frac{1}{8}\right)^{5/2}}{\frac{1}{4}} = \frac{(3)^{3/2} \frac{1}{64} \times \frac{4}{1} = \frac{(3)^{3/2}}{16}}{16}$$

### **MISCELLANEOUS SOLVED PROBLEMS (MSPS)**

A vessel contain 5 mole of A & 10 mople of B, total pressure of vessel is 18 atm. Calculate the P<sub>B</sub> & P<sub>A</sub>
 5 10

**Ans.**  $P_A = \frac{5}{5+10} \times 18 = 6$   $P_B = \frac{10}{15} \times 18 = 12$ 

2. What should be the relationship between K<sub>2</sub> and K<sub>1</sub>, if the equilibrium constant of the reaction given below are K<sub>1</sub> and K<sub>2</sub> respectively ?

$$2SO_{2}(g) + O_{2}(g) \stackrel{\frown}{=} 2SO_{3}(g) \qquad SO_{2}(g) + \frac{1}{2}O_{2}(g) \stackrel{\frown}{=} SO_{3}(g)$$
(1)  $K_{2} = K_{1}$ 
(2)  $K_{2} = \sqrt{K_{1}}$ 
(3)  $K_{2} = K_{1}$ 
(4)  $2K_{2} = K_{1}$ 
**Ans.**  $2SO_{2}(g) + O_{2}(g) \stackrel{\frown}{=} 2SO_{3}(g) + \frac{1}{2}O_{2}(g) \stackrel{\frown}{=} SO_{3}(g)$ 

$$K_{1} = \frac{[SO_{3}]^{2}}{[SO_{2}]^{2}[O_{2}]} \qquad K_{2} = \frac{[SO_{3}]}{[SO_{2}][O_{2}]}$$
Therefore,  $K_{2} = \sqrt{K_{1}}$ 
**3.** What should be the value of Kc for the reaction  $2SO_{2}(g) + O_{2}(g) \stackrel{\frown}{=} 2SO_{3}(g)$ . If the amount are  $SO_{3} = 48g$ ,  $SO_{2} = 12.8$  and  $O_{2} = 9.6$  at equilibrium and the volume of the container is one litre ?  
(1)  $64$ 
(2)  $0.30$ 
(3)  $42$ 
(4)  $8.5$ 
**Ans.**  $2SO_{2}(g) + O_{2}(g) \stackrel{\frown}{=} 2SO_{3}(g)$ 

[SO <sub>3</sub> ] <sup>2</sup>	
$K_{c} = [SO_{2}]^{2}[O_{2}]$	Concentration in gram mole/litre, therefore
48	
$[SO_3] = \frac{80 \times 1}{100}$	(Where 80 is molecular weight of SO <sub>3</sub> )
128	
$[SO_2] = \overline{64 \times 1}$	(Where 64 is molecular weight of SO <sub>2</sub> )
9.6	
$[O_2] = \overline{32 \times 1}$	(Where 32 is molecular weight of O2)
$\left(\frac{48}{80}\right)^2$	
Thus, K <sub>c</sub> = $\overline{\left(\frac{12.8}{64}\right)^2 \left(\frac{9.6}{32}\right)} = 0.30$	)

4. If 0.5 mole H<sub>2</sub> is reacted with 0.5 mole I<sub>2</sub> in a ten-litre container at 444°C and at same temperature value of equilibrium constant K<sub>c</sub> is 49, the ratio of [H] and [I<sub>2</sub>] will be :

(1) 7 (2) 
$$\frac{1}{7}$$
 (3)  $\sqrt{\frac{1}{7}}$  (4) 49  
Ans.  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$   
 $K_C = \frac{[HI]^2}{[H_2][I_2]}$  if  $[H_2] = [I_2]$   
 $K_C = \frac{[HI]^2}{[I_2]^2}$  [HI]<sup>2</sup> =  $K_C \times [I_2]^2$   
 $r = \frac{[HI]^2}{[I_2]^2} K_C$  or  $\frac{[HI]}{[I_2]} = \sqrt{K_C} = \sqrt{49} = 7$ 

1.1 mole of A mixed with 2.2 mole of B and the mixture is kept in a 1 litre at the equilibrium A + 2B =
 2C + D is reached. At equilibrium 0.2 mole of C is formed then the value of K<sub>c</sub> will be :

Ans.		А	+	2B	$\rightarrow$	2C	+	D	
	Initial mole	1.1		2.2		0		0	
	At Eq.	1.1 –	х	2.2 – 2x			2x		х
		1.1 –	0.1	2.2 – 0.2		0.2		0.1	
		1		2		0.2		0.1	
		1		2					
	Active mass	1		1		0.2		0.1	
	V	[C]²[ [A][B	$\frac{D}{D^2}$ $\frac{2}{10}$	$\frac{2}{10} \times \frac{2}{10} \times \frac{1}{10}$ $\frac{1}{10}$ $\frac{1}{10}$	$\frac{1}{100}$ 0.001				
	$\mathbf{r}_{\mathrm{C}} =$		- =		= 0.001				

6. For the reaction  $A + 2B \stackrel{\sim}{=} 2C + D$ , initial concentration of A is a and that of B is 1.5 times that of A. Concentration of A and D are same at equilibrium. What should be the concentration of B at equilibrium ?

а	а	3a	
(1) 4	(2) 2	(3) 4	(4) All of the above

Ans.	A +	2B	$\rightleftharpoons$	2C	+	D				
	а	1.5a		0		0	No. of	initial mole		
	(a–x)	(1.5a –	2x)	2x		х	No. of	moles at equilibrium		
	Concentration of A and D are same at equilibrium.									
	ax = x									
	2x = a									
	а									
	$x = \overline{2}$									
	Therefore, con	centratio	n of B =	1.5 (a) -	- 2(a/2)					
	[B] = 0.5 a									
	а									
	[B] = 2									
7.	In the reaction	, N <sub>2</sub> + O	₂ ╤ 2	NO, the	moles/li	tre of N <sub>2</sub> , C	2 and NO re	spectively 0.25, 0.05 and 1.0	at	
	equilibrium, the	e initial co	oncentra	tion of N	$I_2$ and $O_2$	2 will respe	ctively be :			
	(1) 0.75 mol/lit	re, 0.55 r	nole/litre	)		(2) 0.50 m	ole/litre, 0.75	o mole/litre		
	(3) 0.25 mole/li	itre, 0.50	mole/ lit	re		(4) 0.25 m	ole/litre, 1.0	mole/litre		
Ans.	N2 +	<b>O</b> <sub>2</sub>	$\rightarrow$	2NO		2x = 1.0 m	nole/litre			
	а	b		0		x = 1.0/2 r	nole/litre = 0.	50 mole/litre		
	(a – x)	(b–x)		2x						
	If $a - x = 0.25$ ,	b - x = 0	0.05							
	$[N_2] = a = a - x$	x + x = 0.1	25 + 0.5	0 = 0.75	mole/lit	re				
0		200°C fo				) x 10-4 on	l og uilibrium	amounto of N and O are use	۰.d	
8.	Value of K <sub>C</sub> at	300°C fo	or $N_2 + C$		2NO is §	9 × 10 <sup>-4</sup> and	d equilibrium	amounts of $N_2$ and $O_2$ are use	∍d.	
8.	Value of $K_c$ at The concentrat	300°C fo tion of N	or N₂ + C O at equ	ilibrium	2NO is 9 will be	9 × 10 <sup>-4</sup> and	d equilibrium	amounts of $N_2$ and $O_2$ are use	∍d.	
8.	Value of $K_c$ at The concentrat (1) 0.0148 a	300°C fo	or N <sub>2</sub> + O O at equ (2) 0.29	) <sub>2</sub>	2NO is 9 will be	9 × 10 <sup>-4</sup> and (3) 0.148 ;	d equilibrium a	amounts of $N_2$ and $O_2$ are use (4) 0.0296 a	∍d.	
8. Ans.	Value of $K_c$ at The concentrat (1) 0.0148 a N <sub>2</sub> +	300°C fo tion of NG O2	or N <sub>2</sub> + C O at equ (2) 0.29	ilibrium 96 a	2NO is 9 will be 2NO	9 × 10 <sup>-4</sup> and (3) 0.148 ; Ka	d equilibrium a $c = 9 \times 10^{-4}$	amounts of $N_2$ and $O_2$ are use (4) 0.0296 a	əd.	
8. Ans.	Value of $K_c$ at The concentrat (1) 0.0148 a N <sub>2</sub> + a	300°C fo tion of No O <sub>2</sub> a	or N <sub>2</sub> + C O at equ (2) 0.29	$b_2 \longrightarrow$ ilibrium $b_2 = b_2$	2NO is 9 will be 2NO 0	9 × 10 <sup>–4</sup> and (3) 0.148 a Ka In	d equilibrium a $c = 9 \times 10^{-4}$ itial mole	amounts of N₂ and O₂ are use (4) 0.0296 a	əd.	
8. Ans.	Value of $K_c$ at The concentrat (1) 0.0148 a $N_2$ + a (a - x)	300°C fo tion of No O <sub>2</sub> a (a-x)	or N <sub>2</sub> + C O at equ (2) 0.29	$p_2 \longrightarrow$ ilibrium v 96 a	2NO is 9 will be 2NO 0 2x	9 × 10 <sup>–4</sup> and (3) 0.148 ; Ka In M	d equilibrium a $c = 9 \times 10^{-4}$ itial mole ole at equilib	amounts of N₂ and O₂ are use (4) 0.0296 a rium	ed.	
8. Ans.	Value of K <sub>C</sub> at The concentrat (1) 0.0148 a N <sub>2</sub> + a (a - x) [NO] <sup>2</sup>	300°C fc tion of No $O_2$ a (a-x) $4x^2$	or N <sub>2</sub> + C O at equ (2) 0.29	$p_2 \longrightarrow$ ilibrium 96 a	2NO is 9 will be 2NO 0 2x	9 × 10 <sup>–4</sup> and (3) 0.148 ; Ka In M	d equilibrium a $c = 9 \times 10^{-4}$ itial mole ole at equilib	amounts of N₂ and O₂ are use (4) 0.0296 a rium	ed.	
8. Ans.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) K <sub>c</sub> = $\frac{[NO]^2}{[N_2][O_2]}$ =	300°C fo tion of No $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$	or N <sub>2</sub> + C O at equ (2) 0.29	$p_2 \longrightarrow$ ilibrium v 96 a	2NO is 9 will be 2NO 0 2x	9 × 10 <sup>–4</sup> and (3) 0.148 ; Ka In M	d equilibrium a c = 9 × 10 <sup>-4</sup> itial mole ole at equilib	amounts of N₂ and O₂ are use (4) 0.0296 a rium	∋d.	
8. Ans.	Value of K <sub>c</sub> at The concentrat (1) 0.0148 a N <sub>2</sub> + a (a - x) K <sub>c</sub> = $\frac{[NO]^2}{[N_2][O_2]}$ =	300°C fo tion of No $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$	or N <sub>2</sub> + C O at equ (2) 0.29	$p_2 \longrightarrow$ ilibrium $p_6 a$	2NO is 9 will be 2NO 0 2x	9 × 10 <sup>–4</sup> and (3) 0.148 : Ki In M	d equilibrium a c = 9 × 10 <sup>-4</sup> itial mole ole at equilib	amounts of N₂ and O₂ are use (4) 0.0296 a rium	əd.	
8. Ans.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) K <sub>c</sub> = $\frac{[NO]^2}{[N_2][O_2]}$ = $\frac{2x}{a - x} = \sqrt{9 \times 10}$	300°C fo tion of N $O_2$ a $(a-x)$ $\frac{4x^2}{(a-x)^2}$ $\overline{(a-x)^2}$	or N <sub>2</sub> + C O at equ (2) 0.29 $= 9 \times 10^{-2}$	$p_2 \longrightarrow$ ilibrium v $p_6 a$	2NO is 9 will be 2NO 0 2x	9 × 10 <sup>–₄</sup> and (3) 0.148 ; Ka In M	d equilibrium a c = 9 × 10 <sup>-4</sup> itial mole ole at equilib	amounts of N₂ and O₂ are use (4) 0.0296 a rium	ed.	
8. Ans.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) K <sub>c</sub> = $\frac{[NO]^2}{[N_2][O_2]}$ = $\frac{2x}{a - x} = \sqrt{9 \times 10}$ 2x = 0.03 (a - x)	300°C for tion of N( $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$ $\overline{O_2}^{-4} = 3 \times 10^{-4}$	or $N_2 + C$ O at equ (2) 0.29 = 9 × 10 $10^{-2}$	$p_2 \longrightarrow$ ilibrium $p_6$ a	2NO is 9 will be 2NO 0 2x	9 × 10 <sup>–4</sup> and (3) 0.148 : Ki In M	d equilibrium a c = 9 × 10 <sup>-4</sup> itial mole ole at equilib	amounts of N₂ and O₂ are use (4) 0.0296 a rium	əd.	
8. Ans.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) $\frac{[NO]^2}{K_c = \frac{[N_2][O_2]}{a - x} = \sqrt{9 \times 100}}$ $\frac{2x}{a - x} = \sqrt{9 \times 100}$ $2x = 0.03 (a - x)$ $2x = 0.03x = 0$	300°C fo tion of N( $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$ $\overline{)^{-4}} = 3 \times (a)$	or N <sub>2</sub> + C O at equ (2) 0.29 $= 9 \times 10^{-2}$	$p_2 \longrightarrow$ ilibrium v $p_6 a$	2NO is 9 will be 2NO 0 2x	9 × 10 <sup>-4</sup> and (3) 0.148 ; Ka In M	d equilibrium a c = 9 × 10 <sup>-4</sup> itial mole ole at equilib	amounts of N₂ and O₂ are use (4) 0.0296 a rium	∍d.	
8. Ans.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) K <sub>c</sub> = $\frac{[NO]^2}{[N_2][O_2]}$ = $\frac{2x}{a - x} = \sqrt{9 \times 10}$ 2x = 0.03 (a -x) 2x = 0.03 x = 0 2x + 0.03 x = 0	300°C fo tion of N( $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$ $\overline{O^{-4}} = 3 \times (a)$ .03a 0.03 a	or $N_2 + C$ O at equ (2) 0.29 = 9 × 10 $10^{-2}$	$p_2 \longrightarrow$ ilibrium $p_6$ a -4 or or	2NO is 9 will be 2NO 0 2x	9 × 10 <sup>-4</sup> and (3) 0.148 : Ki In M 2x = 0.03a 2 03x = 0	d equilibrium $a = 9 \times 10^{-4}$ itial mole ole at equilib $a = 0.03 \times 10^{-4}$	amounts of N₂ and O₂ are use (4) 0.0296 a rium	∍d.	
8. Ans.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) $K_c = \frac{[NO]^2}{[N_2][O_2]} =$ $\frac{2x}{a - x} = \sqrt{9 \times 10}$ 2x = 0.03 (a - x) 2x = 0.03 x = 0 2x + 0.03 x = 0 x = 0.0148 a	300°C fo tion of N( $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$ $\overline{O^{-4}} = 3 \times (a^2)$ .03a 0.03 a	or N <sub>2</sub> + C O at equ (2) 0.29 $= 9 \times 10^{-2}$	$p_2$ ilibrium v $p_6$ a -4 or or Therefo	2NO is 9 will be 2NO 0 2x	$9 \times 10^{-4}$ and (3) 0.148 ; Ka In M 2x = 0.03a 2.03x = 0. 2x = 0.029	d equilibrium $a = 9 \times 10^{-4}$ itial mole ole at equilib $a = 0.03 \times 10^{-4}$ 03 a 26a	amounts of N₂ and O₂ are use (4) 0.0296 a rium	əd.	
8. Ans.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) $\frac{[NO]^2}{K_c} = \frac{2x}{a - x} = \sqrt{9 \times 100}$ 2x = 0.03 (a - x) 2x = 0.03 x = 0 2x + 0.03 x = 0 x = 0.0148 a	300°C fo tion of N( $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$ $\overline{O^{-4}} = 3 \times (a^2)$ .03a 0.03 a	or N <sub>2</sub> + C O at equ (2) 0.29 $= 9 \times 10^{-2}$	or or Therefo	2NO is 9 will be 2NO 0 2x	$9 \times 10^{-4}$ and (3) 0.148 = (3) 0.148 = (3) 0.148 = (4) 0.148 = (1) 0.148 =	d equilibrium a $c = 9 \times 10^{-4}$ itial mole ole at equilib a - 0.03 x 03 a 96a	amounts of N₂ and O₂ are use (4) 0.0296 a rium	ed.	
8. Ans. 9.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) $K_c = \frac{[NO]^2}{[N_2][O_2]} =$ $\frac{2x}{a - x} = \sqrt{9 \times 10}$ 2x = 0.03 (a - x) 2x = 0.03x = 0 2x + 0.03 x = 0 x = 0.0148 a One mole PCI	300°C fo tion of N( $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$ $\overline{O^{-4}} = 3 \times (a - x)^2$ .03a 0.03 a	or N <sub>2</sub> + C O at equ (2) 0.29 $= 9 \times 10^{-2}$ ted in a	or or Therefo	2NO is 9 will be 2NO 0 2x 2x	9 × 10 <sup>-4</sup> and (3) 0.148 ; Ka In M 2x = 0.03a 2.03x = 0. 2x = 0.029 er of one lit	d equilibrium $a = 9 \times 10^{-4}$ itial mole ole at equilib $a = 0.03 \times 10^{-4}$ 03 a 96a re capacity.	amounts of N₂ and O₂ are use (4) 0.0296 a rium At equilibrium 20% PCI₅ is r	əd.	
8. Ans. 9.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) $\frac{[NO]^2}{K_c = [N_2][O_2]} =$ $\frac{2x}{a - x} = \sqrt{9 \times 10}$ 2x = 0.03 (a - x) 2x = 0.03x = 0 2x + 0.03x = 0 x = 0.0148 a One mole PCI dissociated. W	300°C fo tion of N( $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$ $\overline{O^{-4}} = 3 \times (a - x)^2$ .03a 0.03 a a $b_5$ is heat hat shou	or N <sub>2</sub> + C O at equ (2) 0.29 $= 9 \times 10^{-2}$ ted in a Id be the	or or Therefo e value o	2NO is 9 will be 2NO 0 2x 2x bre containe	$9 \times 10^{-4}$ and (3) 0.148 : Ki In M 2x = 0.03a 2.03x = 0. 2x = 0.028 er of one lit	d equilibrium $a = 9 \times 10^{-4}$ itial mole ole at equilib $a = 0.03 \times 10^{-4}$ $a = 0.03 \times 10^{-4}$	amounts of N₂ and O₂ are use (4) 0.0296 a rium At equilibrium 20% PCI₅ is r	∍d. not	
8. Ans. 9.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) $K_c = \frac{[NO]^2}{[N_2][O_2]} =$ $\frac{2x}{a - x} = \sqrt{9 \times 10}$ 2x = 0.03 (a - x) 2x = 0.03 x = 0 2x + 0.03 x = 0 x = 0.0148 a One mole PCI dissociated. W (1) $(3 - 2)^{-1}$	300°C fo tion of N( $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$ $\overline{O^{-4}} = 3 \times (a - x)^2$ $\overline{O^{-4}} = 3 \times (a - x)^2$ $\overline{O^{-4}}$	or N <sub>2</sub> + C O at equ (2) 0.29 $= 9 \times 10$ $10^{-2}$ ted in a ld be the (2) 3.2	or or Therefo e value o	2NO is 9 will be 2NO 0 2x 2x Dre containe	$9 \times 10^{-4}$ and (3) 0.148 ; Ka In M 2x = 0.03a 2.03x = 0. 2x = 0.029 er of one lift (3) 2.4	d equilibrium $a = 9 \times 10^{-4}$ itial mole ole at equilib $a = 0.03 \times 10^{-4}$ 03 a 96a re capacity.	amounts of N₂ and O₂ are use (4) 0.0296 a rium At equilibrium 20% PCI₅ is r (4) 42	∍d.	
8. Ans. 9.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) $\frac{[NO]^2}{K_c = [N_2][O_2]} =$ $\frac{2x}{a - x} = \sqrt{9 \times 10}$ 2x = 0.03 (a - x) 2x = 0.03 (a - x) 2x = 0.03 x = 0 2x + 0.03 x = 0 x = 0.0148 a One mole PCI dissociated. W (1) (3 - 2)^{-1} PCI <sub>5</sub>	300°C fo tion of N( $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$ $\overline{O^{-4}} = 3 \times (a - x)^2$ .03a 0.03 a $A_5$ is heat hat shou	or N <sub>2</sub> + C O at equ (2) 0.29 = 9 × 10 $10^{-2}$ ted in a ld be the (2) 3.2 PCl <sub>3</sub>	or or or Therefo e value o +	2NO is 9 will be 2NO 0 2x 2x Dre containe of Kc ?	$9 \times 10^{-4}$ and (3) 0.148 a Ka In M 2x = 0.03a 2.03x = 0. 2x = 0.028 or of one lift (3) 2.4 (20% is not	d equilibrium $a = 9 \times 10^{-4}$ itial mole ole at equilib $a = 0.03 \times 10^{-4}$ $a = 0.03 \times 10^{-4}$ a	amounts of N <sub>2</sub> and O <sub>2</sub> are use (4) 0.0296 a rium At equilibrium 20% PCI <sub>5</sub> is r (4) 42 I, i.e., 80% is dissociated)	ed.	
8. Ans. 9.	Value of K <sub>c</sub> at The concentration (1) 0.0148 a N <sub>2</sub> + a (a - x) $\frac{[NO]^2}{K_c} = \frac{2x}{[N_2][O_2]} =$ $\frac{2x}{a-x} = \sqrt{9 \times 10}$ 2x = 0.03 (a - x) 2x = 0.03 (a - x) 2x = 0.03 x = 0 2x + 0.03 x = 0 x = 0.0148 a One mole PCI dissociated. W (1) $(3 - 2)^{-1}$ PCI <sub>5</sub> 1	300°C fo tion of N( $O_2$ a (a-x) $\frac{4x^2}{(a-x)^2}$ $\overline{O^{-4}} = 3 \times (a - x)^2$ $\overline{O^{-4}} = 3 \times (a - x)^2$ $\overline{O^{-4}}$	or N <sub>2</sub> + C O at equ (2) 0.29 $= 9 \times 10$ $10^{-2}$ ted in a Id be the (2) 3.2 PCl <sub>3</sub> 0	or or or Therefo e value o +	2NO is 9 will be 2NO 0 2x 2x Dre containe of Kc ?	$9 \times 10^{-4}$ and (3) 0.148 ; Ka In M 2x = 0.03a 2.03x = 0. 2x = 0.025 er of one lift (3) 2.4 (20% is not	d equilibrium $a = 9 \times 10^{-4}$ itial mole ole at equilib $a = 0.03 \times 10^{-4}$ $a = 0.03 \times 10^{-4}$ a	amounts of N₂ and O₂ are use (4) 0.0296 a rium At equilibrium 20% PCI₅ is r (4) 42 I, i.e., 80% is dissociated)	∍d.	

	[PCl <sub>3</sub> ][Cl <sub>2</sub>	$2] 0.8 \times 0.8$						
	$K_{C} = [PCI_5]$		3.2					
10.	In the reaction pressure is 3 a	, PCl₅ <del>Cl</del> ₂, t atmosphere. The	he amount of eavent of the value of KP will be	ach PCl₅ be	, PCl₃ ar	nd Cl₂ is	2 mole	at equilibrium and total
	(1) 1.0 atm	(2) 3.0	atm	(3) 2.9	atm		(4) 6.0	atm
Ans.	PCI <sub>5</sub>	PCl <sub>3</sub> +	Cl <sub>2</sub>					
	2	2	2					
	Total mole of e	equilibrium = 2 +	2 + 2 = 6 mole					
	and total press	sure (P) = 3 atm						
	$p_{PCl_3}p_{Cl_2}$							
	$K_P = P_{PCI_5}$							
	2		2			2	2	
	$(p_{PCl_3}) = 6 \times 3$	= 1 ;	$(p_{Cl_2}) = 6 \times 3 =$	= 1	;	$(p_{PCl_5})$	$3 = \times 3$	= 1
	1×1							
	∴ K <sub>P</sub> = 1 1 a	atm						
44		lee ner litre of DC	l haa ta ha taka	a ta abtai	in 0 1 ma		the volu	o of aquilibrium contant
			15 Has to be take	110 0018	III U. I IIIC		line valu	le of equilibrium containt
	(1) 1 15		(2) 0 25		(3) 0 35	5		(4) 0 05
<b>A</b> no	(1) 1110	$DCL(\mathbf{a})$					$Cl_{\alpha}(\alpha)$	(1) 0.00
AIIS.	Initial mole	PC15(9)		0	PC13(g)	+	C12(9)	Here a = ?
	Mole at	a a-x		0	x	0	x	$K_{\rm C} = 0.04$
	equilibrium	u A			X		X	
		<b>x</b> <sup>2</sup>	0.1×0.1					
		$k_{a} = \overline{(a-x)V}$	$\frac{V(a-x)}{V(a-x)}$					
	0 1×0	1 1						
	$a - x - \frac{1 \times 0.04}{1 \times 0.04}$	$\frac{1}{4} - \frac{1}{4} - 0.25$						
	a = a - x + x =	0.25 + 0.10 = 0.25	35					
12.	At 227°C, 60%	of 2 gram moles	s of PCl₅ gets dis	sociated	l in a two	litre cor	ntainer.	The value of $K_p$ will be
	(1) 450 R	(2) 400	) R	(3) 50 l	R			(4) 100 R
Ans.	PCl₅	$\rightleftharpoons$	PCl <sub>3</sub> +	$CI_2$			Initial m	nole
	<u>2-12</u>		<u>12</u>	12				
	2		2	2			Mole at	t equilibrium
	<b>x</b> <sup>2</sup>	12×12						
	$K_c = V(a - x) =$	2(2-12)						
	12×12							
	$K_{\rm C} = \overline{2 \times 0.80} =$	: 0.9						
	$K_p = K_C \times (RT)$	$^{1} = 0.9 \times (R \times 50)$	0) = 450 R					
40	<b>T</b> I			<b>f</b> 1		-: h	المعادلية المع	

**13.** The reaction,  $PCI_5 \rightleftharpoons PCI_3 + CI_2$  is statted in a five litre container by taking one mole of  $PCI_5$ . If 0.3 mole of  $PCI_5$  is there at equilibrium, the total mole and concentration of  $PCI_5$  and  $K_c$  will respectively be

		49			23	
	(1) 0.70, 0.14,	150		(2) 0.3	0, 0.12, <sup>100</sup>	
		23			49	
	(3) 0.10, 0.07,	100		(4) 0.0	5, 20, 150	
Ans.	PCI <sub>5</sub>	$\rightleftharpoons$	PCl₃	+	Cl <sub>2</sub>	
	1		0		0	Initial mole
	1-0.7		0.7		0.7	
	5		5		5	Conc. at equilibrium
	Total mole of I	$PCI_3 = 0.7$				
	Concentration	= 0.14				
	X <sup>2</sup>	0.7×0.7 49				
	$K_{c} = (1 - x)V_{=}$	$= 0.3 \times 5 = 150$				

**14.** When sulphur in the form of  $S_8$  is heated at 900 K, the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of some  $S_8$  to  $S_2$ . Find the value of equilibrium constant for this reaction.

Sol. Sol.  $S_8(g) \leftarrow 4S_2(g)$ Initial pressure 1 atm 0 Eq. Pressure (1-x) atm 4x atm But x = 0.29 atm  $\therefore P_{S_8} = 1 - x = 1 - 0.29 = 0.71$  atm P\_

$$^{S_2} = 4x = 4 \times 029 = 1.16 \text{ atm}$$
  
 $K_p = \frac{(pS_2)^4}{pS_8} = \frac{(1.16)^4}{0.71} = 2.55 \text{ atm}^3$ 

**15.** The  $K_p$  for the reaction,  $N_2O_4 \rightleftharpoons 2NO_2$  is 640 mm at 775K. Calculate the percentage dissociation of  $N_2O_4$  at equilibrium pressure of 160 mm. At what pressure the dissociation will be 50% ?

Suppose number of moles of  $N_2O_4$  taken = 1 mol

Degree of dissociation =  $\alpha$ 

	$N_2O_4$	2NO2
Initial moles	1 mol	0
At Eq.	(1–x) mol	2a mol

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

Let P be the total pressure at equilibrium, then = 
$$P_{N_2O_4} = \frac{(1-\alpha)}{(1+\alpha)} \times P$$

$$P_{NO_2} = \frac{2\alpha}{(1+\alpha)} \times P$$

$$K_{p} = \frac{\frac{P_{NO_{2}}^{2}}{P_{N_{2}O_{4}}}}{\frac{P_{N_{2}O_{4}}}{P_{1}}} = \frac{\left[\frac{2\alpha}{(1-\alpha)} \times P\right]}{\left[\frac{1-\alpha}{1+\alpha} \times P\right]} = \frac{4\alpha^{2}}{(1+\alpha)(1-\alpha)} \times P$$

Substituting  $K_p = 640$  mm and P = 160 mm

$$640 = \frac{4\alpha^2}{1 - \alpha^2} \times 160$$

Sol.

 $\alpha = 0.707$  ot 70%

For 50% dissociation, a = 0.5, Substituting the value of K<sub>p</sub> and a in equation (i)  $\frac{4(0.5)^2}{640} = \frac{4(0.5)^2}{1-(0.5)^2} \times P \quad \Rightarrow \quad P = 480 \text{ mm}$ At 540 K, 0.10 mol of PCI<sub>5</sub> are heated in a 8.0 L flask. The pressure of the equilibrium mixture is found to

Sol.

16.

be 1.0 bar. Calcualted  $K_p$  and  $K_c$  for the reaction.

$$n = \frac{PV}{RT} = \frac{1 \text{ bar } \times 8L}{0.083 \text{ L bar } \text{mol}^{-1} \text{ K}^{-1} \times 540\text{K}} = 0.18$$

$$0.1 + x = 0.18$$

$$x = 0.08$$

$$[PCl_5] = \frac{0.1 - 0.08}{8} \text{ M} = 2.5 \times 10^{-3} \text{ M}$$

$$[PCl_3] = \frac{0.08}{8} \text{ M} = 0.01 \text{ M}$$

$$[Cl_2] = \frac{0.08}{8} \text{ M} = 0.01 \text{ M}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.01 \times 0.01}{2.5 \times 10^{-3}} = 4 \times 10^{-2}$$

$$K_p = K_c (RT)^{\Delta n} = 4 \times 10^{-2} \times (0.083 \times 540) = 1.79 \text{ bar}$$

**17.** The  $K_p$  value for the reaction  $H_2 + I_2 \rightleftharpoons 2HI$  at 460°C is 49. If the initial pressure of  $H_2$  and  $I_2$  is 0.5 bar respectively, determine the partial pressure of each has at equilibrium.

Sol.  
H<sub>2</sub> + I<sub>2</sub> 2 2HI  
Initial pressure (bar) 0.5 0.5 0  
Eq. Pressure (0.5-x) (0.5-x) 2x  

$$K_{p} = \frac{(P_{H_{1}})^{2}}{P_{H_{2}} \times P_{I_{2}}} = \frac{(2x)^{2}}{(0.5-x)(0.5-x)}$$

$$49 = \frac{(2x)^{2}}{(0.5-x)^{2}}$$

$$7 = \frac{2x}{(0.5-x)} \text{ or } x = 0.389$$

$$P_{H_{2}} = 0.5 - x = 0.5 - 0.389 = 0.111 \text{ bar}$$

$$P_{H_{2}} = 0.5 - x = 0.5 - 0.389 = 0.111 \text{ bar}$$

$$P_{H_{1}} = 2x = 2 \times 0.389 = 0.788 \text{ bar}$$

#### **CHEMISTRY FOR JEE**

**18.** When 3.06 g of solid NH<sub>4</sub>HS is introduced into two litre evacualted flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

(i) Calculate  $K_p$  and  $K_p$  for the reaction at 27°C.

(ii) What would happen to the equilibrium when more solid NH4HS is introduced into the flask ?

Moles of  $H_2S$  formed = 0.018

**Sol.** (i)  $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ 

mass of NH<sub>4</sub>HS decomposed =  $\frac{3.06 \times 30}{100}$  = 0.918 g

0.918

Moles of NH<sub>4</sub>HS decomposed = 51 = 0.018Moles of NH<sub>3</sub> formed = 0.018 Moles

 $[NH_3] = \frac{0.18}{2} = 0.009 \text{ M} \qquad [H_2S] = \frac{0.018}{2} = 0.009 \text{ M}$  $[NH_3][H_2S] = 0.009 \times 0.009$ 

 $K_c = [NH_4HS] = 1 = 8.1 \times 10^{-5}$ 

 $K_p = K_c \times (RT)^{\Delta_n} = 8.1 \times 10^{-5} \times (0.083 \times 300)^2 = 5.02 \times 10^{-2} \text{ bar}^2$ 

(ii) Since conc. of solid NH<sub>4</sub>HS remains same no matter how much of it is present, addition of solid NH<sub>4</sub>HS would not distrub the equilibrium.

**19.** At certain temperature, the equilibrium constant (K<sub>c</sub>) is 16 for the reaction,

 $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g).$ 

If we take one molw each each of all the four gases in 1 L container, what be comcentration of NO and  $NO_2$  at equilibrium ?

**Sol.**  $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) = NO(g)$ 

Suppose x moles of SO<sub>2</sub> react with x moles of NO<sub>2</sub> to form x moles of SO<sub>3</sub> and x moles of No to attain equilibrium. The equilibrium concentration, therefore woud be

$$[SO_{2}] = (1 - x) \text{ mol } L^{-1}; \qquad [NO_{2}] = (1 - x) \text{ mol } L^{-1}; [SO_{3}] = (1 + x) \text{ mole } L^{-1}; \qquad [NO] = (1 + x) \text{ miole } L^{-1}; [NO] = (1 + x) \text{ miole } L^{-1}; [NO] = (1 + x) \text{ miole } L^{-1}; [NO] = (1 + x) \text{ miole } L^{-1}; [NO] = (1 + x)^{2} = 16 \qquad \text{or} \qquad \frac{(1 + x)}{(1 - x)^{2}} = 16 \\ \frac{(1 + x)^{2}}{(1 - x)^{2}} = 16 \qquad \text{or} \qquad \frac{(1 + x)}{(1 - x)} = 4 \\ 1 + x = 4 - 4x \text{ or } 5x = 3 \qquad \text{or} \qquad x = \frac{3}{5} = 0.6 \text{ mole} \\ [NO_{2}] = (1 - x) = (1 - 0.6) = 0.4 \text{ mol } L^{-1} \\ [NO] = (1 + x) = (1 + 0.6) = 1.6 \text{ mol } L^{-1}$$

**20.** At 340 K,  $K_p$  for the reaction,  $N_2O_4$  (g)  $\rightleftharpoons$  2NO<sub>2</sub>(g) is 0.8 bar. Calculate the per cent dissociation of  $N_2O_4$  at 340 K and a total pressure of 1 bar.

Sol.

	1102
	$K_p = (P_{N_2O_4}) = 0.8 \text{ bar}$
	$P_{NO_2} + P_{N_2O_4} = 1 \text{ bar}$
Let	$P_{NO_2}$ be x bar

 $(P_{NO})^{2}$ 

*:*..

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

$$0.8 = \frac{x^{2}}{1-x}$$
or
$$x^{2} + 0.8 x - 0.8 = 0 \text{ or } x = 0.58$$

$$P_{NO_{2}} = 0.58 \text{ bar}$$
and
$$P_{N_{2}O_{4}} = (1 - 0.58) = 0.42 \text{ bar}$$

Since each mole of N<sub>2</sub>O<sub>4</sub> on dissociation producess 2 moles of NO<sub>2</sub>, the initial pressure of N<sub>2</sub>O<sub>4</sub> ( $P_{N_2O_4}$ ) is given as

p° N<sub>2</sub>O<sub>4</sub> = 
$$P_{N_2O_4} + \frac{1}{2}P_{NO_2} = 0.42 + \frac{0.58}{2} = 0.71$$
 bar  
Percent dissociation =  $\frac{\frac{1}{2}p_{NO_2}}{p^{\circ}N_2O_4} \times 100 = \frac{0.29}{0.71} \times 100 = 40.8\%$ 

- **21.** Nitrogen and hydrogen react to form ammonia as per the reaction,  $2 N_2(g) + 3/2H_2(g) \rightleftharpoons NH_3(g)$ When the mixture of the three gases is in equilibrium predict whether the amount of ammonia increases or decreases if
  - (i) The pressure on the system is increased,
  - (ii) The temperature of the system is raised,
  - (iii) The concentration of hydrogen is increased.
- **Sol.** (i) When pressure is increased, equilibrium shifts to that direction in which pressure decreases i.e. in the direction in which the number i of moles of gases decreases. hence, the reaction shifts in the forward direction and thus the amount of NH<sub>3</sub> increases.

(ii) As the forward reaction is exthormic, increases of temperature will shifts the equilibrium in the back directiuon (endothermic direction) and thus the amout of Nh<sub>2</sub> decreases.

(iii) On increasing the concentration of  $H_2$  the equilibrium will shifts in the forward direction and thus the amount of  $NH_3$  increases.

- 22. An endothermic reaction, A(g) + 2B(g) 2C(g) is in equilibrium at a certain temperature. can we increase the amount of C by (i) adding catalyst (ii) Increasing pressure (iii) Increasing temperature
- Sol. No, because catalyst does not distrub the equilibrium state
   (ii) Yes, because increase in pressure will shift the equilibrium in forward direction as the number of moles of products is less than that of reactants.
   (iii) Yes, because increase in temperature would shift the reaction in the forward direction Condethermin

(iii) Yes, because increase in temperature would shift the reaction in the forward direction 9endothermic direction)