## 2.0 INTRODUCTION

**Chemical reaction :** Symbolic representation of any chemical change in term of reactants and products is called chemical reaction.

#### **Types of chemical reaction :**

## (a) On the basis of physical state

(I) Homogeneous reaction All reactants and products are in same phase.

$$N_2(g) + 3H_2(g) \div \uparrow \dagger 2NH_3(g)$$

#### (II) Heterogeneous reaction

Reactants and products are in two or more phases.

$$Zn(s) + CO_2(g) \stackrel{2}{\pm} \stackrel{2}{\uparrow} \stackrel{2}{\dagger} ZnO(s) + CO(g)$$

## (b) On the basis of speed

#### (I) Fast reactions

- (i) Generally these reactions are ionic reactions.
  - $HCl + NaOH \longrightarrow NaCl + H_2O$
  - Acid Base Salt Water
- (ii) Rate determination is impossible.

## (II) Slow reactions

- (i) Generally these reactions are molecular reactions.
  - $H_2 + I_2 \longrightarrow 2HI$
- (ii) Rate determination is possible.

## (c) On the basis of heat

## (I) Exothermic reaction

(i) Heat is evolved in these type of chemical reactions.

 $R \longrightarrow P + x \text{ kcal}$ 

(ii) Change in enthalpy,  $\Delta H = (-)$  ve

## (II) Endothermic reaction

Heat is absorbed in these type of chemical reactions.

 $R \longrightarrow P - x \text{ kcal}$ 

 $\Delta H = (+) ve$ 

## (d) On the basis of direction

## (I) Reversible reaction

(i) Chemical reaction in which products can be converted back into reactants.

 $N_2 + 3H_2 \ddagger \uparrow \dagger 2NH_3$ 

- (ii) Produced in forward as well as in backward direction.
- (iii) Possible in closed container
- (iv) These can attain equilibrium
- (v) Reactants are never completely converted into products
- (vi) Neutralization reaction except strong acid and strong base. HCl + NH<sub>4</sub>OH  $\frac{1}{2}$   $^{+}$  NH<sub>4</sub>Cl + H<sub>2</sub>O

## (II) Irreversible reaction

(i) Chemical reaction in which products cannot be converted back into reactants.

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 $AgNO_{3} + NaCl \longrightarrow AgCl \downarrow NaNO_{3}$  $NaCl + H_{2}SO_{4} \longrightarrow NaHSO_{4} + HCl$  $Zn + H_{2}SO_{4} \longrightarrow ZnSO_{4} + H_{2}\uparrow$ 

- (ii) Produced only in one direction (forward direction)
- (iii) Generally possible in open container
- (iv) These do not attain equilibrium
- (v) Reactants are nearly completely converted into products.

#### **GOLDEN KEY POINTS**

- We always take forward direction if direction is not specified.
- In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice-versa.

#### • Rate of Reaction

The change in concentration of reactants or products in unit time is known as rate of the reaction.

Rate of reaction  $= (\pm) \frac{\text{change in concentration}}{\text{time taken for the change}}$ 

#### 3.1 EQUILIBRIUM AND CHEMICAL PROCESS

#### (A) Chemical Equilibrium

The most important characteristic property of a reversible reaction is that it always attains a state of chemical equilibrium.

Consider a general reversible reaction in a closed vessel.

 $A + B \stackrel{2}{\ddagger} \stackrel{\sqrt{r}}{_{r}} \stackrel{2}{\uparrow} C + D$  Where,  $r_f = rate of forward reaction$ 

 $r_b = rate of backward reaction$ 

Initially reaction occurs in forward direction but as the concentration of products increases reaction also starts in backward direction.

At a certain stage, rate of forward reaction becomes equal to the rate of backward reaction called equilibrium state.

At equilibrium state : Rate of forward reaction  $(r_f) = Rate$  of backward reaction  $(r_b)$ 



## (B) Characteristic of equilibrium

- The concentrations of the reactants and products do not change with time.
- At this stage, number of moles of substances produced per second in the forward reaction is equal to the number of moles of substances which disapperar per second in the backward reaction.
- Chemical equilibrium is dynamic in nature i.e. the reaction although appears to be stopped but actually takes palace in both the directions with the same speed.
- Chemical equilibrium can be approached from both sides

2HI  $\frac{1}{2}$   $\uparrow$   $H_2 + I_2$  or  $H_2 + I_2$   $\frac{1}{2}$   $\uparrow$  2HI

At equilibrium, each reactant and product has a constant concentration and this is independent of the fact whether the reaction starts from forward direction or backward direction with the reactant or with the product.

- Equilibrium is not affected by the presence of catalyst. The catalyst only helps in attaining equilibrium rapidly.
- The measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time at the chemical equilibrium conditions.
- Homogeneous equilibrium is the equilibrium in which the reactants and products are in the same phase.

 $CH_{3}COOC_{2}H_{5}(\lambda) + H_{2}O(\lambda) \ddagger \uparrow^{H^{\lambda}} + CH_{3}COOH(\lambda) + C_{2}H_{5}OH(\lambda)$ 

• Heterogeneous equilibrium is the equilibrium in which the reactants and products are in two or more phases.

$$Zn(s) + CO_2(g) \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} T ZnO(s) + CO(g)$$

• **ACTIVE MASS :** The term active mass means the concentration of the reactants expressed in moles per litre (molar concentration) or the pressure of the reacting gas in atmosphere. In case of gases and solutions, the molar concentration means the number of gram molecules present per litre.

Active mass is usually expressed by enclosing the symbol of the reactant in square bracket [].

Active mass =  $\frac{\text{Number of gram moles of the substance}}{\text{Number of gram moles of the substance}}$ 

Volume in litres

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Weight of substance (in grams)	W	_ w×1000
$\overline{\text{Molecular weight}(M_w) \times \text{Volume}(\text{in litre})}$	$\frac{1}{S} = \frac{1}{M_w \times V(\text{litre})}$	$-\frac{1}{M_{w} \times V(mL)}$

The active mass of solids and pure liquids is a constant quantity (unity) because it is an intensive property i.e. number of molecules present per unit volume do not change because density and molecular weight of solids and pure liquids are constant. But it does not apply for gaseous substances because for them number of molecules present per unit volume change with change in volume of vessel.

Molar concentration =  $\frac{W}{M_w \times V(\text{litre})} = \frac{\rho}{M_w}$  (where  $\rho$  = density in gram/litre)  $= \frac{\rho}{M_w} \times 1000$  (where  $\rho$  = density in g/mL) Active mass =  $\frac{\text{density of the substance}}{\text{molecular mass of the substance}}$ 

Following other names of active mass can also be used :

(i) mole/litre	(ii) gram mole/litre	(iii) gram mo	olecules/litre
(iv) molarity	(v) concentration	(vi) effective	e concentration
(vii) active quantity	(viii) n/v	(ix) C	
(x) M	(xi) []		

## **Illustrations**

**Illustration 1.** In any chemical reaction, equilibrium is supposed to be established when :

(1) Mutual opposite reaction undergo.

(2) Concentration of reactants and resulting products are equal.

(3) Velocity of mutual reactions become equal.

(4) The temperature of mutual opposite reactions becomes equal.

Solution Ans. (3)

**Illustration 2. Assertion :** The active mass of pure solids and pure liquids is taken unity.

Reason : The active mass of pure solids and pure liquids depends on density and molecular mass. The density and molecular mass of pure solids and pure liquids are constant.

(1) A (2) B (2) C(4) DSolution Ans. (1)

**Illustration 3.** 8.5 g ammonia is present in a vessel of 0.5 litre capacity the find out the active mass of ammonia?

 $[NH_3] = \frac{8.5}{17 \times 0.5} = 1$  mole/litre Solution

## **BEGINNER'S BOX-1**

Which of the following statement is correct regarding with chemical equilibrium :-1.

(1) Based on extent to which the reaction proceed to reach the equilibrium we may have negligible concentrations of reactants are left

(2) Equilibrium is not static

(3) Concentration of reactants and products becomes constant at equilibrium

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(4) All of these

- 2. Find out the correct statement :-
  - (1) Equilibrium condition is a state of reversible reaction

(2) Chemical equilibriums are important in numerous biological process like transport and delivery of O<sub>2</sub>

- (3) Reversible reactions can be homogenous and heterogeneous both
- (4) All of these
- 3. Which of the following reaction is endothermic reaction :-
  - (1) Bond formation by two unstable atoms at certain condition
  - (2) Combustion reactions
  - (3) Conversion of more stable allotrope to less stable allotropic element
  - (4) Condensation of vapour to its liquid state
- 4. Active mass of 2 mole of NaCl kept in 4 litre vessel at NTP is :-
  - $(3)\frac{1}{2}$ (4) Not defined (1)1(2) 2

#### LAW OF MASS ACTION OR LAW OF CHEMICAL EQUILIBRIUM 3.2

- The law of mass action was given by Guldberg and Waage (1864). ٠
- It states that the rate of a chemical reaction is directly proportional to the product of • active masses of the reacting substances raised to a power equal to the stoichiometric coefficient in the balanced chemical equation.

#### **Derivation of equilibrium constant :-(A)**

Consider a reversible homogeneous chemical reaction which has attained equilibrium state at a particular temperature :

$$M_1A + m_2B \stackrel{\circ}{\ddagger} \stackrel{\sim}{\uparrow} n_1C + n_2D$$

Let the active masses of A, b, C and D be [A] [B] [C] and [D] respectively at equilibrium.

According to law of mass action :-

Rate of forward reaction	$(\mathbf{r}_{\mathrm{f}}) \propto [\mathbf{A}]^{\mathrm{m}_{\mathrm{I}}} [\mathbf{B}]^{\mathrm{m}_{\mathrm{2}}}$
Rate of backward reaction	$(\mathbf{r}_{\mathbf{b}}) \propto [\mathbf{C}]^{\mathbf{n}_1} [\mathbf{D}]^{\mathbf{n}_2}$

 $\mathbf{r}_{f} = \mathbf{K}_{f} [\mathbf{A}]^{m_{1}} [\mathbf{B}]^{m_{2}}$  and  $\mathbf{r}_{b} = \mathbf{K}_{b} [\mathbf{C}]^{n_{1}} [\mathbf{D}]^{n_{2}}$ 

Where  $K_f$  and  $K_b$  are forward and backward rate or velocity constants respectively. At equilibrium state -

$$\begin{aligned} \mathbf{r}_{f} &= \mathbf{r}_{b} \\ \mathbf{K}_{f} \left[ \mathbf{A} \right]^{m_{1}} \left[ \mathbf{B} \right]^{m_{2}} &= \mathbf{K}_{b} \left[ \mathbf{C} \right]^{n_{1}} \left[ \mathbf{D} \right]^{n_{2}} \\ \frac{\mathbf{K}_{f}}{\mathbf{K}_{b}} &= \frac{\left[ \mathbf{C} \right]^{n_{1}} \left[ \mathbf{D} \right]^{n_{2}}}{\left[ \mathbf{A} \right]^{m_{1}} \left[ \mathbf{B} \right]^{m_{2}}} \qquad \Theta \qquad \mathbf{K} = \frac{\mathbf{K}_{f}}{\mathbf{K}_{b}} \end{aligned}$$

K is known as equilibrium constant and has a definite value for every chemical reaction at particular temperature.

The equilibrium constant at a given temperature is the ratio of the rate constants of forward and backward reactions.

$$\mathbf{K} = \frac{\mathbf{K}_{\mathrm{f}}}{\mathbf{K}_{\mathrm{b}}}$$

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#### (B) Relation between K<sub>P</sub> and K<sub>C</sub>:

Consider a reversible homogeneous chemical equilibrium reaction

 $m_1A + m_2B$   $\frac{1}{2}$   $\hat{T}$   $n_1C + n_2D$ 

According to law of mass action (LOMA)

$$K_{\rm C} = \frac{[{\rm C}]^{n_1} [{\rm D}]^{n_2}}{[{\rm A}]^{m_1} [{\rm B}]^{m_2}}$$
$$K_{\rm P} = \frac{({\rm P_{\rm C}})^{n_1} ({\rm P_{\rm D}})^{n_2}}{({\rm P_{\rm A}})^{m_1} ({\rm P_{\rm B}})^{m_2}}$$

Where –

For an ideal gas PV = nRT

P = Pressure in atm V = Volume in litres n = Number of gaseous moles R = Gas constant = 0.0821 L atm/mol/K T = Temperature in Kelvin

 $P = \frac{n}{V}RT = active mass \times RT$ 

 $\frac{n}{V}$  = molar concentration or active mass

 $P_A = [A]RT$ ,  $P_B = [B]RT$ ,  $P_C = [C]RT$  and  $P_D [D]RT$ Put all these values in  $K_P$  expression

$$K_{P} = \frac{[C]^{n_{1}}(RT)^{n_{1}} \times [D]^{n_{2}}(RT)^{n_{2}}}{[A]^{m_{1}}(RT)^{m_{1}} \times [B]^{m_{2}}(RT)^{m_{2}}} = \frac{[C]^{n_{1}}[D]^{n_{2}}}{[A]^{m_{1}}[B]^{m_{2}}} \times \frac{(RT)^{n_{1}+n_{2}}}{(RT)^{m_{1}+m_{2}}}$$

 $K_{\rm P} = K_{\rm C} ({\rm RT})^{(n_1 + n_2) - m_1 + m_2}$ 

 $\Delta n_{\rm g} = (n_1 + n_2) - (m_1 + m_2)$ 

= Sum of stoichiometric coefficient of gaseous products

- Sum of stoichiometric coefficient of gaseous reactants

$$K_{\rm P} = K_{\rm C} ({\rm RT})^{\Delta n}$$

• The K<sub>C</sub> is expressed by the units  $(mol L^{-1})^{\Delta n_g}$  and K<sub>P</sub> by  $(atm)^{\Delta n_g}$ .

• Three cases may rise :-

(a) When  $\Delta n_g = 0$ 

$$\mathbf{K}_{\mathbf{P}} = \mathbf{K}_{\mathbf{C}}(\mathbf{R}\mathbf{T})^0 = \mathbf{K}_{\mathbf{C}}$$

For example : (i)  $N_{2(g)} + O_{2(g)} \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} \stackrel{2}{\downarrow} 2NO_{(g)}$ 

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So

(ii) 
$$H_{2(g)} + I_{2(g)} \ddagger \uparrow \uparrow 2HI_{(g)}$$
  
•  $K_C$  and  $K_P$  are unit less in this case.  
When  $\Delta n_g = +ve$   
 $K_P > K_C$ 

For example : (i) 
$$PCl_{5(g)} \ddagger \uparrow PCl_{3(g)} + Cl_{2(g)} \begin{pmatrix} K_{C} \rightarrow mol L^{-1} \\ K_{P} \rightarrow atm \end{pmatrix}$$
  
(ii)  $2NH_{3(g)} \ddagger \uparrow N_{2(g)} + 3H_{2(g)} \begin{pmatrix} K_{C} \rightarrow mol^{2} L^{2} \\ K_{P} \rightarrow (atm)^{2} \end{pmatrix}$ 

(c) When 
$$\Delta n_g = -ve$$
  
 $K_P = K_C$ 

**(b)** 

For example :

mple: (i)  $N_{2(g)} + 3H_{2(g)} \stackrel{+}{\ddagger} \stackrel{+}{\uparrow} 2NH_{3(g)} \begin{pmatrix} K_{C} \rightarrow mol^{2} L^{2} \\ K_{P} \rightarrow atm^{-2} \end{pmatrix}$ (ii)  $PCl_{3(g)} + Cl_{2(g)} \stackrel{+}{\ddagger} \stackrel{+}{\uparrow} PCl_{5(g)} \begin{pmatrix} K_{C} \rightarrow mol^{-1} L^{1} \\ K_{P} \rightarrow atm^{-1} \end{pmatrix}$ 

- (d) Special point :
  - If  $T = \frac{1}{R}$  then

$$K_{\rm P} = K_{\rm C} \left( \mathbf{R} \times \frac{1}{\mathbf{R}} \right)^{\Delta n_{\rm g}}$$
$$K_{\rm P} = K_{\rm C} (1)^{\Delta n_{\rm g}}$$

$$K_P = K_C$$

For any value of  $\Delta n_g$ 

#### (C) Application of K :-

Stability of reactants and products : Stability of reactants increases when value of K decreases Stability of products increases when value of K increases In the following reactions which one oxide is more stable

**Ex :** In the following reactions which one oxide is more stable.

#### **BEGINNER'S BOX-2**

1. In which of the following reaction product is more stable :-(1)  $N_2 + 3H_2$   $\ddagger \uparrow \uparrow 2NH_3$ ;  $K_1 = 2.3 \times 10^{-2}$ 

(2) 
$$N_2 + O_2$$
  $\ddagger \uparrow \uparrow 2NO$ ;  $K_2 = 2 \times 10^2$   
(3)  $H_2 + I_2$   $\ddagger \uparrow \uparrow 2HI$ ;  $K_3 = 294$   
(4)  $XeO + \frac{1}{2}O_2 + F_2$   $\ddagger \uparrow \uparrow XeO_2F_2$ ;  $K_4 = 1.4 \times 10^{-3}$ 

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**2.** Equilibrium constant is :-

(1) 
$$\frac{K_b}{K_f}$$
 (2)  $\frac{K_f}{K_b}$  (3)  $K_f \times K_b$  (4)  $\frac{1}{K_f K_b}$ 

3. At 527°C, the reaction  $NH_3(g)$   $\ddagger \uparrow \uparrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$  has  $K_C = 4$  then what is the value of  $K_P$  for the same reaction :-

(1) $160 \times (800 \text{R})^2$	$(2)\left(\frac{800R}{4}\right)^2$
$(3)\left(\frac{1}{4\times 800R}\right)^2$	(4) None of these

4. For the equilibrium  $SO_2Cl_2(g) \ddagger \uparrow \dagger SO_2(g) + Cl_2(g)$ , what is the temperature at which

$$\frac{K_{P}(atm)}{K_{C}(M)} = 3:-$$
(1) 0.027 K (2) 0.36 K (3) 36.54 K (4) 273 K

#### (D) Factors affecting the equilibrium constant :-

(a) **Temperature :** The value of equilibrium constant changes with the change of temperature. If  $K_1$  and  $K_2$  be the equilibrium constants of a reaction at absolute temperatures  $T_1$  and  $T_2$  and  $\Delta H$  is the change in enthalpy then

$$\log\left(\frac{K_{2}}{K_{1}}\right) = \frac{\Delta H^{0}}{2.303R} \left[\frac{1}{T_{1}} - \frac{1}{T_{2}}\right] \text{ or } \log K_{2} - \log K_{1} = \frac{\Delta H^{0}}{2.303R} \left[\frac{T_{2} - T_{1}}{T_{1}T_{2}}\right]$$

(According to van't hoff equation)

If the temperature 
$$T_2$$
 is higher than  $T_1$  then  $\left(\frac{T_2 - T_1}{T_1 T_2}\right) > 0$ .

(i) When  $\Delta H = +ve$  (endothermic reaction) log  $K_2 - log K_1 > 0$  or  $log K_2 > log K_1$  $K_2 > K_1$ 

> The value of equilibrium constant increases when temperature increases in case of endothermic reactions.

(ii) When  $\Delta H = -ve$  (exothermic reaction)

 $\log K_2 - \log K_1 < 0$ 

 $\log K_2 - \log K_1$ 

$$K_2 < K_1$$

The value of equilibrium constant decreases when temperature increases in the case of exothermic reactions.

## (b) The mode of representation of the reaction :-

Consider the reversible chemical equilibrium reaction  $A + B \ddagger \uparrow \dagger C + D$ 

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

If the reaction is reversed  $C + D \ddagger \hat{T} A + B$ 

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

The equilibrium constant  $K_C$  is actually the reciprocal of  $K_C$ .

Thus, the two equilibrium constants are related as  $\rightarrow \mathbf{K}_{C} = \frac{1}{\mathbf{K}_{C}}$ 

(c) Multi step reaction : If a reaction can be expressed as the sum of two or more reactions then overall  $K_C$  will be equal to the product of the individual equilibrium constants of the reactions.

**Example :-**  $SO_2(g) + \frac{1}{2}O_2(g) \ddagger \uparrow \dagger SO_3(g) \rightarrow K_1$ 

**NO<sub>2</sub>(g)** 
$$\ddagger \uparrow \uparrow NO(g) + \frac{1}{2}O_2(g) \rightarrow K_1$$

Then,  $SO_2(g) + NO_2(g) \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} SO_3(g) + NO(g) \rightarrow K$ 

So,  $K = K_1 \times K_2$ 

(d) Stoichiometry of the reaction :-

When a reversible reaction can be written with the help of two or more stoichiometric equation then the value of equilibrium constant will be numerically different in these cases.

For example the dissociation of  $NO_2$  can be represented as :

$$2NO_{2} \stackrel{*}{\ddagger} \stackrel{^{\wedge}}{\dagger} \stackrel{N_{2}}{=} 2O_{2} \qquad \dots \dots \dots (i)$$
$$K_{C} = \frac{[N_{2}][O_{2}]^{2}}{[NO_{2}]^{2}}$$

(1) If reaction (i) is divided by 2-

Then the reaction becomes  $-NO_2$   $\ddagger \uparrow \uparrow = \frac{1}{2}N_2 + O_2 K_C = \frac{[N_2]^2[O_2]}{[NO_2]}$ 

Thus, the two equilibrium constants are related as  $K_{\rm C} = \sqrt{K_{\rm C}}$ 

So if reaction is divided by n then  $K_C = (K_C)^{\frac{1}{n}}$ 

(2) If reaction (i) is multiplied by 2

Then the reaction becomes  $4NO_2$   $\ddagger$   $\uparrow \uparrow 2N_2 + 4O_2 K_C \ddagger \uparrow \uparrow \frac{[N_2]^2[O_2]^4}{[NO_2]^4}$ 

Thus, the two equilibrium constants are related as  $K_C = (K_C)^2$ So if reaction is multiplied by n then  $K_C = (K_C)^n$ 

## **GOLDEN KEY POINTS**

• Factors not affecting the equilibrium constant :

The value of equilibrium constant is independent of the following factors :-

- (a) Concentration of reactants and products (b) Pressure
- (c) Volume

(d) The pressure of a catalyst

- (d) Presence of inert materials
- The value of equilibrium constant depends only on temperature.

# Illustrations

Illustration	$4. XeF_6 + H_2O$	î_î† XeOF₄	+ 2HF c	constan	$t = K_1,$	$XeO_4 + XeF_6 \ddagger \uparrow \uparrow$	$XeOF_4 + XeC$	)F <sub>2</sub>
	$constant = K_2$	2. Then equilibr	rium co	nstant f	for the r	eaction XeO <sub>4</sub> + 2HF	$\hat{f} \hat{f} \hat{T} XeO_3F_2$	2 +
	H <sub>2</sub> O will be-							
(1) $\frac{\mathbf{k}}{\mathbf{k}}$	$\frac{X_1}{X_2}$	(2) K <sub>1</sub> + K <sub>2</sub>		$(3) \frac{k}{k}$	$\frac{\mathbf{X}_2}{\mathbf{X}_1}$	(4) $\frac{K_1}{(K_2)^2}$		
Solution	Ans. (3)							
Illustration (1) A	5. Assertion :- Reason :- Ca	In the presence talysts increase (2) B	of cata es the ra	lyst, the te of fo (3) C	e value o orward a	of equilibrium const and backward reaction (4) D	ant K increases. on to same exter	nt.
Solution	<b>Ans.</b> (4)							
3.3 DEG	REE OF DISS	OCIATION						
It is t	he fraction mole	es of reactant d	issociat	ed $\alpha =$ % $\alpha =$	$\frac{x}{a} = \frac{x}{a} \times 10$	00		
When	$\begin{array}{ll} \alpha = D \\ x = N \\ a = In \end{array}$	egree of dissoc umber of disso itial number of	ciation ciated n moles (	noles (given) ratio	ns			
Illustration	<b>6.</b> 40% of PCl <sub>5</sub>	is not dissocia	ted at 3	00°C. 7	The read	ction is carried out in	n a flask of 1 li	tre
	capacity. The	value of K <sub>C</sub> w	ould be	:-	1			
(1) 3. Solution	<sup>2</sup> Ans. (4)	(2) 1.6		(3) (3	3.2)-1	(4) 0.9		
Illustration	7. In the beginn	ing of the reac	tion, A	<u>}</u> ^†	B + C,	2 moles of A are ta	ken, out of whi	ich
(1) 0.	0.5 moles get	s dissociated. V (2) 1	What is	the am (3) 0.	ount of 0 25	dissociation of A? (4) 4.2		
Solution	Ans. (3)		D		G			
		A ţî	В	+	C			
	Initially Moles at eq.	$2 \\ 2 - x \\ 2 - 0.5$	0 x 0.5		0 x 0.5	x = 0.5		
	Since, two m Therefore, on	oles dissociated le mole will dis	d into 0. ssociated	5 d into (	0.25			
		R	GINNE	CR'S B	OX-3_			
1 The	equilibrium cor	$(K_{a})$ for	the re-	action	2HCl(g)	) $\hat{*}$ $\hat{*}$ H <sub>2</sub> ( $\alpha$ ) $\pm$ C1	$a(\alpha)$ is $4 \times 10^{-34}$	ot

**1.** The equilibrium constant (K<sub>C</sub>) for the reaction  $2\text{HCl}(g) \ddagger \uparrow \dagger H_2(g) + \text{Cl}_2(g)$  is  $4 \times 10^{-34}$  at 25°C. What is the equilibrium constant for the reaction :-

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$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \stackrel{+}{2} \stackrel{+}{\wedge} HCl(g)$$
(1) 2×10<sup>-17</sup> (2) 2.5×10<sup>33</sup> (3) 5×10<sup>6</sup> (4) None of these  
Consider the following gaseous equilibrium given below  
I. N<sub>2</sub> + 3H<sub>2</sub>  $\stackrel{+}{2} \stackrel{+}{\wedge} \stackrel{+}{2} 2NH_3$ ; eq. constant = K<sub>1</sub>  
II. N<sub>2</sub> + O<sub>2</sub>  $\stackrel{+}{2} \stackrel{+}{\wedge} \stackrel{+}{2} 2NO$ ; eq. constant = K<sub>2</sub>  
III. H<sub>2</sub> +  $\frac{1}{2} O_2 \stackrel{+}{2} \stackrel{+}{\wedge} \stackrel{+}{H_2O}$  eq. constant = K<sub>3</sub>  
The equilibrium constant for the reaction  $2NH_3 + \frac{5}{2} O_2 \stackrel{+}{2} \stackrel{+}{\wedge} \stackrel{+}{2} 2NO + 3H_2$  in terms of K<sub>1</sub>, K<sub>2</sub>  
and K<sub>3</sub> will be :-  
(1) K<sub>1</sub> K<sub>2</sub> K<sub>3</sub> (2)  $\frac{K_1K_2}{K_3}$  (3)  $\frac{K_1K_3^2}{K_2}$  (4)  $\frac{K_2K_3^2}{K_1}$   
Using molar concentration, what is the unit of K<sub>c</sub> for the reaction  
CH<sub>3</sub>OH(g)  $\stackrel{+}{2} \stackrel{+}{\wedge} CO(g) + 2H_2(g)$  :-  
(1) M<sup>-2</sup> (2) M<sup>2</sup> (3) M<sup>-1</sup> (4) M  
If temperature is increased then equilibrium constant will be :-  
(1) Increased  
(2) Decreased  
(3) Remains  
(4) May increased or decreased depends on exothermic or endothermic nature

5. What will be the equilibrium constant at 127°C. If equilibrium constant at 27°C is 4 for reaction N<sub>2</sub> + 3H<sub>2</sub>  $\ddagger$   $\uparrow \uparrow$  2NH<sub>3</sub>;  $\Delta H = -46.6 \text{ kJ}$  :-

(1) 
$$4 \times 10^{-2}$$
 (2)  $2 \times 10^{-3}$  (3)  $10^{2}$  (4)  $4 \times 10^{2}$ 

6. According to the law of chemical equilibrium,

> (1) The rate of forward reaction becomes equal to the rate of backward reaction when the chemical system attains equilibrium

(2) A system can achieve the equilibrium state through forward as well as backward reaction

(3) Both (1) and (2)

2.

3.

4.

(4) The equilibrium constant  $K_{eq}$  is defined as the product of the equilibrium active masses of the products, each raised to the power that corresponds to its coefficient in the balanced equation, divided by the product of the equilibrium active masses or reactants, each raised to the power that corresponds to its coefficient in the balanced equation.

In which of the following equilibrium equation,  $K_p > K_c$ 7.

(1)  $2SO_3(g) \ddagger \uparrow \dagger 2SO_2(g) + O_2(g)$ (2)  $PCl_3(g) + Cl_2 \ddagger \uparrow \dagger PCl_5(g)$ (3)  $H_2(g) + I_2(g) \ddagger \uparrow \dagger 2HI(g)$ (4)  $N_2(g) + 3H_2(g) \ddagger \uparrow \dagger 2NH_3(g)$ 

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If  $CoO(s) + H_2(g) \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} Co(s) + H_2O(g)$ ,  $K_1 = 60$ ;  $CoO(s) + CO(g) \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} Co(s) + CO_2(g)$ , 8.  $K_2 = 180$  then the equilibrium constant of the reaction  $CO_2(g) + H_2(g)$   $\frac{1}{2}$   $\dot{T}$   $CO(g) + H_2O(g)$ will be -(1) 0.44(2) 0.11(4) 0.33(3) 0.22

#### 3.4 APPLICATIONS OF LAW OF MASS ACTION

Initial moles

[Relation of dissociation (x) with volume (V) and pressure (P)]

- Homogeneous Gaseous Reactions of Type-I ( $\Delta n_g = 0$ ) **(A)** Synthesis of HI :-
- **Expression for K\_C:** The formation of HI from  $H_2$  and  $I_2$  is represented by following (i) reaction

Let us start with 'a' moles of  $H_2$  and 'b' moles of  $I_2$  in a closed bulb of V volume. If at equilibrium x moles of each of  $H_2$  and  $I_2$  have reacted, then 2x moles of Hi will be formed so active masses.

$$[H_2] = \frac{(a-x)}{V}$$
;  $[I_2] = \frac{(b-x)}{V}$ ;  $[HI] = \frac{2x}{V}$ 

Applying law of mass action  $K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$ 

$$K_{\rm C} = \frac{4x}{(a-x)(b-x)}$$

When a = b = 1, x becomes degree of formation of HI or degree of dissociation of H<sub>2</sub> (or I<sub>2</sub>). K<sub>C</sub>  $\frac{4x^2}{(1-x)^2}$ 

Let if 
$$x \ll 1$$
 then  $1 - x \propto 1$  so  $K_C = 4x^2$   
 $x = \sqrt{\frac{K_C}{4}}$  i.e.  $x \propto V^\circ$ 

At equilibrium the degree of dissociation is dependent to the volume.

(ii) **Expression for K\_P:** The equilibrium constant  $K_P$  can also be calculated considering partial pressures of reactants and products at equilibrium.

Total number of moles at equilibrium = (a - x) + (b - x) + 2x = (a + b)If total pressure of the system at equilibrium be P then

Partial pressure of 
$$H_2 = \frac{(a-x)}{(a+b)}P$$
; Partial pressure of  $I_2 = \frac{(b-x)}{(a+b)}P$ ; Partial pressure of  $HI = \frac{2x}{(a+b)}P$ 

$$K_{P} = \frac{(p_{HI})^{2}}{(p_{H_{2}})^{2}(p_{I_{2}})} = \frac{\left(\frac{2x}{a+b}\right)^{2}P^{2}}{\left(\frac{a-x}{a+b}\right)\left(\frac{b-x}{a+b}\right)P^{2}}$$

$$K_{P} = \frac{4x^{2}}{(a-x)(b-x)} \quad \text{Thus } K_{P} = K_{C}$$
Let if  $x <<<1 \text{ then } 1-x \propto 1 \quad \text{so } K_{P} = 4x^{2}$ 

$$X = \sqrt{\frac{K_{P}}{4}} \quad \text{i.e.} \quad \boxed{x \propto P^{\circ}}$$

At equilibrium the degree of dissociation is independent to the pressure also.

#### Homogeneous Gaseous reactions of Type-II ( $\Delta n_g > 0$ ) **(B) Dissociation of PCl<sub>5</sub>:-**

1

(i) **Expression for K\_C:** The dissociation of PCl<sub>5</sub> takes place according to the equation (Stoichiometric coefficient) 1

1

$$[PCl_{5}] = \frac{(a-x)}{V} ; [PCl_{3}] = \frac{x}{V} ; [Cl_{2}] = \frac{x}{V}$$
Apply law of mass action  $K_{C} = \frac{[PCl_{3}][Cl_{2}]}{[PCl_{5}]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^{2}}{(a-x)V}$ 

When a = 1, x becomes degree of dissociated ( $\alpha$ )  $K_C = \frac{\alpha^2}{(1-\alpha)V}$ 

 $K_C \approx \frac{\alpha^2}{V}$  or  $\alpha \propto \sqrt{V}$ If  $\alpha < < < 1$  then  $1 - \alpha \approx 1$ 

The degree of dissociation of PCl<sub>5</sub> at equilibrium is directly proportional to the square root of the volume.

#### **(ii) Expression for K**<sub>P</sub>:

Let the total pressure at equilibrium be P. Total number of moles at equilibrium = (a - x) + x + x = a + x

$$p_{PCl_{5}} = \left(\frac{a-x}{a+x}\right)P , \qquad p_{PCl_{3}} = \left(\frac{x}{a+x}\right)P, \qquad p_{Cl_{2}} = \left(\frac{x}{a+x}\right)P$$
Apply law of mass action
$$K_{P} = \frac{p_{PCl_{3}} \cdot P_{Cl_{2}}}{p_{PCl}} = \frac{x^{2}p}{(a+x)(a-x)}$$

When a = 1, x becomes degree of dissociation (a)

$$=\frac{\alpha^2 P}{(1+\alpha)(1-\alpha)}=\frac{\alpha^2 P}{1-\alpha^2}$$

 $p_{PCl_5}$ 

K<sub>P</sub>

If 
$$\alpha < < < 1$$
 then  $1 - \alpha^2 \approx 1$ ,  $K_P \approx \alpha^2 P$   
 $\alpha^2 \propto \frac{1}{P} \implies \alpha \propto \frac{1}{\sqrt{P}}$ 

• The degree of dissociation of PCl<sub>5</sub> is inversely proportional to the square root of the total pressure at equilibrium.

#### (C) Homogeneous Gaseous reactions of Type-III ( $\Delta n_g < 0$ ) Synthesis of Ammonia :-

(i) **Expression for K\_C :** The formation of ammonia from nitrogen and hydrogen is represented by the equation :

$$1 \qquad 3 \qquad 2 \qquad \text{(Stoichiometric coefficient)}$$

$$N_2 + 3H_2 \stackrel{\circ}{\ddagger} \stackrel{\circ}{\uparrow} \stackrel{\circ}{} 2NH_3$$
Initial moles a b 0
Moles at equilibrium (a-x) (b-3x) 2x
Let us start with 'a' males of N and 'b' males of H in a closed wavel of Volume V. At

Let us start with 'a' moles of  $N_2$  and 'b' moles of  $H_2$  in a closed vessel of Volume V. At equilibrium x moles of  $N_2$  has combined with 3x moles of  $H_2$  and produced 2x moles of NH<sub>3</sub>.

At equilibrium 
$$[N_{2}] = \frac{(a-x)}{V}; \qquad [H_{2}] = \frac{(b-3x)}{V}; \qquad [NH_{3}] = \frac{2x}{V}$$
$$K_{C} = \frac{[NH_{3}]^{2}}{[N_{2}][H_{2}]^{2}} = \frac{\left(\frac{2x}{V}\right)^{2}}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^{3}} = \frac{4x^{2}V^{2}}{(a-x)(b-3x)^{3}}$$
If  $a = 1, b = 3$  then  $K_{C} = \frac{4x^{2}V^{2}}{27(1-x)^{4}}$ If  $x < < 1$  then  $1 - x \approx 1$ 
$$K_{C} = \frac{4x^{2}V^{2}}{27}$$
i.e.  $x \propto \frac{1}{V}$ 

At equilibrium, the degree of dissociation is inversely proportional to the volume of vessel.

#### (ii) **Expression** for $K_P$ :-

Total number of moles at equilibrium = a - x + b - 3x + 2x = a + b - 2xIf total pressure is P at equilibrium then

$$p_{N_2} = \frac{(a-x)}{(a+b-2x)}P, \quad p_{H_2} = \frac{(b-3x)}{(a+b-2x)}P, \quad p_{NH_3} = \frac{2x}{(a+b-2x)}P$$

According to Law of mass action

$$K_{P} = \frac{p_{NH_{3}}^{2}}{P_{N_{2}}P_{NH_{2}}^{3}} = \frac{\left(\frac{2x}{a+b-2x}P\right)^{2}}{\left(\frac{a-x}{a+b-2x}\right)\left(\frac{b-3x}{a+b-2x}\right)^{3}}$$
$$K_{P} = \frac{4x^{2}(a+b-2x)^{2}}{(a-x)(b-3x)^{3}P^{2}}$$

If a = 1, b = 3 then 
$$K_P = \frac{16x^2(2-x)^2}{27(1-x)^4 P^2}$$
  
If x < < < 1 then 2 - x  $\approx$  2 and 1 - x  $\approx$  1  
 $K_P = \frac{64P^2}{27P^2}$  i.e.  $x^2 \propto P^2 \implies x \propto P$ 

At equilibrium, the degree of dissociation is directly proportional to the pressure.

#### **GOLDEN KEY POINTS**

• If inert gas mixed at constant temperature and constant volume in an equilibrium chemical reaction then total number of moles of gases are present in a container increases i.e. total pressure of gases increases but concentration in terms of mol  $L^{-1}$  and partial pressure of reacting substances are unchanged so dissociation (x) unchanged.

• 
$$\alpha \propto (V)^{\frac{}{\text{sum of stoichiometric coefficient of gaseous product}}$$

Effect	$\Delta n_g = 0$	$\Delta n_g > 0 \text{ or } + ve$	$\Delta n_g < 0 \text{ or } -ve$
	$H_2 + I_2 \hat{\ddagger} \hat{\uparrow} 2HI$	$\frac{\mathbf{PCl}_5}{2} \stackrel{\circ}{+} \stackrel{\circ}{+} \frac{\mathbf{PCl}_3}{\mathbf{PCl}_3} + \mathbf{Cl}_2$	$N_2 + 3H_2 \ddagger \uparrow \uparrow$
	$x \propto (v)^{\circ} \propto (P)^{\circ}$	$(1)^{1/2}$	$2NH_3$
		$\mathbf{x} \propto (\mathbf{v})^{1/2} \propto \left(\frac{1}{\mathbf{P}}\right)$	$x \propto \left(\frac{1}{V}\right) \propto (P)$
(i) Pressure (increases)	x unchanged	x decreases	x increases
(ii) Volume (increases)	x unchanged	x increases	x decreases
(iii) Mixing of inert gas at			
(a) constant pressure	x unchanged	x increases	x decreases
(b) constant volume	x unchanged	x unchanged	x unchanged

#### **BEGINNER'S BOX-4**

1.  $A + B \ddagger \hat{\dagger} \hat{\phantom{\dagger}} C + D$  if initially of A and Bare both are taken in equal amount but at equilibrium concentration of D will be twice of that of A then what will be the equilibrium constant of reaction :-

(1) 
$$\frac{4}{9}$$
 (2)  $\frac{1}{9}$  (3)  $\frac{9}{4}$  (4) 4

2. At a certain temperature, only 50% HI is dissociated at equilibrium in the reaction  $2HI(g) \stackrel{\circ}{\ddagger} \stackrel{\wedge}{\dagger} H_2(g) + I_2(g)$ . The equilibrium constant for the reaction is :-

(1) 0.25 (2) 1.0 (3) 3.0 (4) 0.5

3. The equilibrium constant  $K_P$  for the reaction  $H_2(g) + CO_2(g) \ddagger \uparrow H_2O(g) + CO(g)$  is 4.0 at 1660°C. Initially 0.80 mole  $H_2$  and 0.80 mole  $CO_2$  are injected into a 5.0 liter flask. What is the equilibrium concentration of  $CO_2(g)$  :-(1) 0.533 M (2) 0.0534 M (3) 5.34 M (4) None of these

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- 5.  $N_2(g) + 3H_2(g) \ddagger \uparrow \dagger 2NH_3(g)$  for the reaction initially the mole ratio was 1:3 of  $N_2: H_2$ . At equilibrium 50% of each has reacted. If the equilibrium pressure is p, the partial pressure of  $NH_3$  at equilibrium is :-
  - (1)  $\frac{p}{3}$  (2)  $\frac{p}{4}$  (3)  $\frac{p}{6}$  (4)  $\frac{p}{8}$
- 6. For the reaction  $H_2(g) + CO_2(g) \ddagger \uparrow CO(g) + H_2O(g)$ , if the initial concentration of  $[H_2] = [CO_2]$  and x moles/litre of hydrogen is consumed at equilibrium, the correct expression of  $K_P$  is:-

(1) 
$$\frac{x^2}{(1-x)^2}$$
 (2)  $\frac{(1+x)^2}{(1-x)^2}$  (3)  $\frac{x^2}{(2-x)^2}$  (4)  $\frac{x^2}{1-x^2}$ 

## (D) Law of Mass Action as Applied to Heterogeneous Equilibrium :-

In such cases the active mass of pure solids and pure liquids is taken as unity and the value of equilibrium constant is determined by the gaseous substance only.

(i) The dissociation of  $CaCO_3$  in closed vessel.

$$\begin{aligned} & CaCO_{3}(s) \stackrel{*}{\ddagger} \stackrel{*}{\uparrow} CaO(s) + CO_{2}(g) \\ & K_{P} = p_{CO_{2}} \\ (ii) & 2H_{2}O(\lambda) \stackrel{*}{\ddagger} \stackrel{*}{\uparrow} 2H_{2}(g) + O_{2}(g) \\ & K_{P} = (p_{H_{2}})^{2}(p_{O_{2}}) \\ (iii) & 3Fe(s) + 4H_{2}O(g) \stackrel{*}{\ddagger} \stackrel{*}{\uparrow} Fe_{3}O_{4}(s) + 4H_{2}(g) \end{aligned}$$

$$K_{\rm P} = \frac{(p_{\rm H_2})^4}{(p_{\rm H_2O})^4}$$

# Illustrations

**Illustration 8** Two sample of HI each of 5 gm. were taken separately into vessels of volume 5 and 10 litres respectively at 27°C. The extent of dissociation of HI will be :-

(1) More in 5 litre vessel

(3) Equal in both vessel

(2) More in 10 litre vessel(4) None of these

Solution Ans. (3)

**Illustration 9** What will be the amount of dissociation, if the volume is increased 16 times of initial volume in the reaction  $PCl_5 \stackrel{\circ}{\ddagger} \stackrel{\wedge}{\uparrow} PCl_3 + Cl_2$ ?

(1) 4 (2)  $\frac{1}{4}$  times (3) 2 (4)  $\frac{1}{5}$  times Solution Ans. (1)

**Illustration 10 Assertion :-** For the reaction,  $N_2 + O_2 \ddagger \uparrow \uparrow \uparrow 2NO$ , increase in pressure at equilibrium

has no effect on the reaction.

**Reason :-** The reaction is not accompanied by any change in number of moles of gaseous species.

(1) A (2) B (3) C (4) D Solution Ans. (1)

## 3.5 LE-CHATELIER'S PRINCIPLE

**PRINCIPLE :-** According to this principle, if a system at equilibrium is subjected to a change of concentration, pressure or temperature then the equilibrium is shifted in such a way as to nullify the effect of change.

• Le-Chatelier's principle is applicable for both chemical and physical equilibrium.

## (A) CHEMICAL EQUILIBRIUM

#### (a) Change in concentration :-

In an equilibrium increasing the concentrations of reactants results in shifting the equilibrium in fovour of products while increasing concentrations of the products results in shifting the equilibrium in fovour of the reactants.

#### (b) Change in pressure :-

When the pressure on the system is increased, the volume decreases proportionately i.e. the total number of moles present per unit volume increase. According to Le-Chatelier's principle, the equilibrium shifts in that direction in which there is decreases in number of moles.

• If there is no change in number of moles of gases in a reaction then a pressure change does not affect the equilibrium.

## (c) Change in temperature :-

If the temperature of the system at equilibrium is increased then reaction will proceed in the direction in which heat can be used. Thus increase in temperature will favour the forward reaction for endothermic reaction.

Similarly, increase in temperature will favour the backward reaction for exothermic reactions.

## (A) PHYSICAL EQUILIBRIUM

**Physical reaction :**- Those reaction in which change in only and only physical states (solid, liquid and gas) of substance takes place with out any chemical change, is called physical reaction.

## Example :

## (a) Ice-water system (melting of ice) :

Melting of ice is accompanied by absorption of heat (endothermic) and decrease in volume

Ice (s)	<u>}</u> ^†	water ( $\lambda$ )
(H <sub>2</sub> O)		(H <sub>2</sub> O)
1 g (1.09 ml	L)	1 g (1.09 mL)

Hence both increase of temperature and pressure will favour the melting of ice into water.

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(b) Water-water vapour system (Vapourisation of water) :

Vapourisation of water is an endothermic and condensation of vapour into water is an exothermic reaction :

Water (l) $\hat{\ddagger} \hat{\phantom{a}} \hat{\phantom{a}}$ Vapour (g)(H2O)(H2O)

- The equilibrium shifts towards right side when the temperature is increased so rise in temperature will increase the vapour.
- The equilibrium shifts towards left side when the pressure is increased (i.e. volume is decreased) so increase in pressure will favour the rate of condensation of vapour into water.
- Thus favourable conditions for conversion of water into vapour are high temperature and low pressure.
- (c) Solubility of gases :

Gas(g)+Water (λ) $\frac{1}{4}$  ^†Aqueous solution (λ)(Solute)(Solvent)(Solution)**Effect of pressure**Solubility of such press increase with

• Effect of pressure  $\rightarrow$  Solubility of such gases increase with increasing pressure which dissolves in a solvent with a decrease in volume.

# Illustrations

**Illustration 11** On applying pressure to the equilibrium ice  $\hat{\uparrow}$  water, which phenomenon will

happen :

- (1) More ice will be formed
- (2) More water will be formed
- (3) Equilibrium will not be disturbed
- (4) Water will evaporate

Solution Ans.(2)

**Illustration 12** Which of the following conditions should be more favourable for increasing the rate of forward reaction in the equilibrium H<sub>2</sub>  $\ddagger \uparrow \dagger$  H + H ( $\Delta$ H = +ve) ?

(1) 2000°C temperature and 760 mm of Hg pressure.

- (2) 3500°C temperature and 100 cm of Hg pressure.
- (3) 3500°C temperature and 1 mm of Hg pressure.
- (4) All are wrong

Solution Ans.(3)

In H<sub>2</sub>  $\ddagger$   $\uparrow$  H + H, heat has to be provided to dissociate H<sub>2</sub> into H. Therefore, the reaction is endothermic ( $\Delta$ H will positive). So, temperature should be high. Since, one mole of H<sub>2</sub> forms two atoms of H, so volume is increasing ( $\Delta$ n is positive) so pressure should be low for increasing the rate of forward reaction.

**Illustration 13 Assertion :**  $SO_2(g) + \frac{1}{2}O_2(g) \ddagger \uparrow \uparrow SO_3(g) + heat ; Forward reaction is favoured at$ 

low temperature and high pressure. **Reason :** Reaction is endothermic.

(1) A (2) B (3) C (4) D

Solution Ans.(3)

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**Illustration 14** The reaction CaCO<sub>3</sub> (s)  $\ddagger \uparrow \uparrow$  CaO (s) + CO<sub>2</sub> (g) goes to compension in lime kiln

because : (1) of the high temperature (3) CaO is not dissociated

(2) CaO is more stable than  $CaCO_3$ 

(4) CO<sub>2</sub> escapes continuously

Solution Ans.(4)

**Illustration 15 Assertion :** For a reversible exothermic reaction, extent of reaction decreases with increase in temperature.

**Reason :** In reversible exothermic reaction temperature is favourable for more formation of product. **Ans.(3)** 

Solution

## **BEGINNER'S BOX-5**

1. Which of the following equilibrium remains unaffected by a change in pressure (or volume)? (1) 2NOCl (g)  $\ddagger \uparrow \dagger 2NO(s) + Cl_2(g)$ 

(2)  $H_2(g) + CO_2(g) \stackrel{2}{:} \stackrel{2}{:} \stackrel{1}{:} H_2O(g) + CO(g)$ 

- (3)  $3PbS(s) + 3O_2(g) \ddagger \uparrow \dagger 2PbO(s) + 2SO_2(g)$
- (4)  $PCl_{5}(g) \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} PCl_{3}(g) + Cl_{2}(g)$
- 2. Consider the following equilibrium system ;  $2SO_2(g) + O_2(g) \ddagger \uparrow \dagger 2SO_3(g)$ ; some inert gas is added to the above system at constant volume. Predict which of the following is true?

(1) More of  $SO_3$  is produced

- (1) More of  $SO_3$  is produced (2) Less  $SO_2$  is produced
- (2) Addition of inert gas does not affect equilibrium
- (4) System moves to new equilibrium position which cannot be predicted theoretically.
- **3.** Which of the following is not true for the equilibrium reaction;  $N_2(g) + O_2(g) \ddagger \uparrow \dagger 2NO(g)$ ;

 $\Delta H = 180 \text{ kJ mol}^{-1}$ 

- (1) The formation of NO is increased at higher temperature.
- (2) The volume change at constant pressure does not affect the equilibrium.
- (3) The pressure change at constant volume does not affect the equilibrium
- (4) The formation of NO is decreased at higher temperature

4. Consider the following equilibrium system ; SO<sub>2</sub> (g)  $\frac{1}{2}$  O<sub>2</sub> (g)  $\frac{1}{2}$   $\stackrel{?}{\to}$  SO<sub>3</sub> (g) ; set up in a

cylinder fitted with a piston. Some inert gas is added and the piston is moved outwards to keep the total gaseous pressure constant. Predict which of the following is true ?

- (1) Addition of inert gas does not affect the equilibrium
- (2) Less  $SO_3$  (g) is produced
- (3) More  $SO_3$  (g) is produce
- (4) The system moves to new equilibrium position which cannot be predicted theoretically.

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5.	When a volatile liquid is introduced into an evacuated closed vessel at a particular temperature, both evaporation and condensation take place simultaneously. The system reaches equilibrium state when-								
	(1) The liquid is completely transformed into the corresponding vapour								
	(2) Equal amounts of liquid and vapour are present in the system								
	(3) The rate of evaporation becomes equal to the rate of condensation.								
	(4) Liquid cannot be converted into	vapour and vice versa							
6.									
	(1) Solid <sup>2</sup> î î Liquid	(2) Liquid ‡ˆ⁺ V	apor						
	(3) Solid ‡ î† Vapor	(4) All of these							
7.	Which of the following is not true f	for solid-liquid equilibrium?							
	(1) It can be established at any give	(1) It can be established at any given temperature.							
	(2) The mass of solid does not change with time.								
	(3) The mass of liquid does not cha	inge with time.	ounding						
	(4) There is no exchange of heat be	stween the system and its surr	Sunding.						
8.	Which of the following substances	s can be placed in a closed v	ressel to establish (solid $\frac{2}{3}$ $$						
	vapour) equilibrium ?								
	(1) Ammonium chloride	(2) Camphor							
	(3) lodine	(4) All of these							
9.	Which of the following solutions solid-solution equilibrium ?	kept in contact with undiss	olved solute is an example of						
	(1) Aqueous solution	(2) Saturated solution	on						
	(3) Unsaturated solution	(4) Nonaqueous sol	ution						
10.	Which of the following is correct re	egarding the gas-solution equi	ilibrium?						
200	(1) The solubility of the dissolved	l gas increases with the incre	ease of pressure and decreases						
	with the increases of temperature.								
	(2) The solubility of the dissolve	d gas increases with the ind	creases of pressure as well as						
	temperature.								
	(3) The solubility of the dissolve	d gas decreases with the in-	creases of pressure as well as						
	(4) The solutility of the dissolute	d and doornoond with the in							
	(4) The solubility of the dissolve	ed gas decreases with the in	crease of pressure as well as						
	temperature.								
3.6	<b>REACTION QUOTIENT (O)</b>								
	Consider a general homogeneous re	eversible reaction :							

 $m_1A + m_2B \ddagger \uparrow \uparrow n_1C + n_2D$ 

Reaction Quotient (Q) =  $\frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$ , (Applied at any stage of reaction)

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Equilibrium constant  $K = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$ , (Applied only at equilibrium state)

- (i) When Q = K then reaction is in equilibrium state.
- When Q < K then rate of forward reaction increases. (ii)
- (iii) When Q > K then rate of backward reaction increases.

#### 3.7 Calculation of degree of dissociation from vapour density:-

 $PCl_5 \stackrel{\circ}{\pm} \stackrel{\circ}{\uparrow} \stackrel{\bullet}{\dagger} PCl_3 + Cl_2$ Ex.

$$\alpha = \frac{\mathbf{D}_{\mathrm{T}} - \mathbf{D}_{\mathrm{0}}}{\mathbf{D}_{\mathrm{0}}} = \frac{\mathbf{D} - \mathbf{d}}{\mathbf{d}}$$

Where :

 $D_T$  or D = Principle or theoretical vapour density or normal vapour density  $D_0$  or d = Observed or practical vapour density or experimental vapour density or vapour density at higher temperature.

 $\alpha$  = Degree of dissociation Vapour density =  $\frac{\text{Molecular weight}}{\text{Molecular weight}}$ 

Reversible reaction $PCl_5 f$		$PCl_3 + Cl_3$	2 Total moles	Volume at NTP	Vapour density
Let initial moles	1	0 0	1	$V_{\rm T} = 22.4$	$D_T \propto \frac{1}{V_{_T}}$
Moles at equilibrium	(1-α)	αα	$1 + \alpha$	$V_0 = 22.4 (1+\alpha)$	$D_0 \propto rac{1}{V_0}$

2

If  $\alpha$  is the degree of dissociation

$$\frac{D_{T}}{D_{0}} = \frac{V_{0}}{V_{T}} = \frac{22.4(1+\alpha)}{22.4}$$

$$\frac{D_{T}}{D_{0}} = 1 + \alpha \text{ or } \alpha = \frac{D_{T}}{D_{0}} - 1 \qquad \alpha = \frac{D_{T} - D_{0}}{D_{0}}$$
So for a general reversible reaction

So for a general reversible reaction

$$n_1 A \stackrel{2}{\ddagger} \stackrel{2}{\uparrow} n_2 B + n_3 C$$

$$a = \frac{n_1}{\Delta n} \left( \frac{D_T - D_0}{D_0} \right) \qquad \Delta n = (n_2 + n_3) - (n_1)$$

# Illustrations

**Illustration 16** The vapour density of undecomposed  $N_2O_4$  is 46. When heated. Vapour density decreases to 24.5 due to its dissociation to NO<sub>2</sub>. The percentage dissociation of  $N_2O_4$  at the final temperature is :

(1) 87(2) 60(3) 40(4)70Solution **Ans.** (1)

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ANSWER KEY										
	BEGINNER'S BOX-1									
1.	(4)	2.	(4)	3.	(3)	4.	(1)			
					BI	EGINN	ER'S B	OX-2		
1.	(3)	2.	(2)	3.	(4)	4.	(3)			
					BI	EGINN	ER'S B	OX-3		
1. 8.	(4) (4)	2.	(4)	3.	(2)	4.	(4)	5.	(1)	<b>6.</b> (3) <b>7.</b> (1)
					BI	EGINN	ER'S B	OX-4		
1.	(4)	2.	(1)	3.	(2)	4.	(3)	5.	(1)	<b>6.</b> (1)
BEGINNER'S BOX-5										
1.	(2)	2.	(3)	3.	(4)	4.	(2)	5.	(3)	<b>6.</b> (4) <b>7.</b> (1)
8.	(4)	9.	(2)	10.	(1)					
					BI	EGINN	ER'S B	OX-6		
1.	(1)	2.	(2)	3.	(3)	4.	(4)	5.	(2)	

EXERCISE-I (Conceptual Questions)

Build Up Your Understanding

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