

PHYSICAL CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



STUDY MATERIAL

Chemical Equilibrium

ENGLISH MEDIUM

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CHEMICAL EQUILIBRIUM

3.0 INTRODUCTION

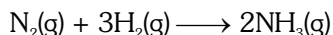
Chemical reaction : Symbolic representation of any chemical change in terms of reactants and products is called chemical reaction.

Types of chemical reactions :

(a) On the basis of physical state

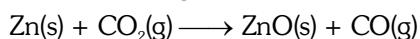
(I) Homogeneous reactions

All reactants and products are in same phase.



(II) Heterogeneous reactions

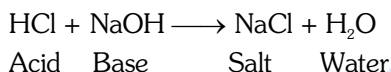
Reactants and products are in two or more phases.



(b) On the basis of speed.

(I) Fast reactions

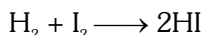
(i) Generally these reactions are ionic reactions.



(ii) Rate determination is almost impossible.

(II) Slow reactions

(i) Generally these reactions are molecular reactions.

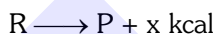


(ii) Rate determination is possible.

(c) On the basis of heat

(I) Exothermic reactions

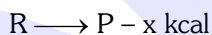
(i) Heat is evolved in these type of chemical reactions.



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

(II) Endothermic reactions

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

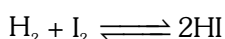
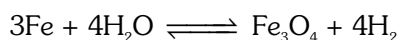
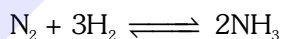


(ii) $\Delta H = (+)$ ve

(d) On the basis of direction

(I) Reversible reactions

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



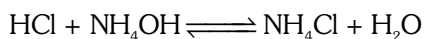
(ii) Proceed in forward as well as in backward direction.

(iii) Possible in closed container.

(iv) These can attain equilibrium.

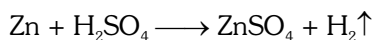
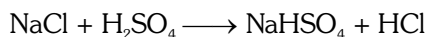
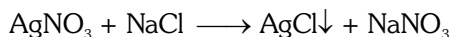
(v) Reactants are never completely converted into products.

(vi) Neutralisation reactions except of strong acid and strong base.

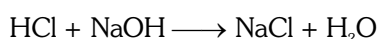


(II) Irreversible reactions

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



- (ii) Proceed 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.
 (vi) Neutralisation reactions of strong acid and strong base.


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

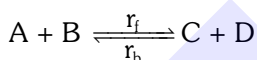
The change in concentration of reactants or products in unit time is known as rate of the reaction.

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

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,



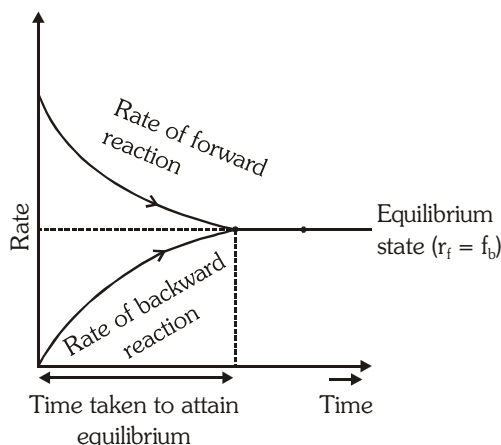
where, r_f = rate of forward reaction

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.

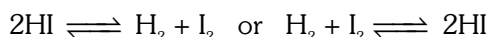
At a certain stage, rate of forward reaction becomes equal to the rate of backward reaction called equilibrium state.

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



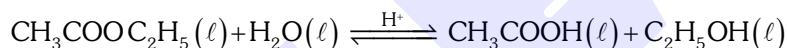
(B) Characteristics of chemical equilibrium :

- 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 disappear per second in the backward reaction.
- Chemical equilibrium is dynamic in nature i.e. the reaction although appears to be stopped but actually takes place in both the directions with the same speed.
- Chemical equilibrium can be approached from both sides

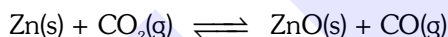


At equilibrium, each reactant and product has a constant concentration and this is independent of the fact whether the reaction starts from forward direction or backward direction with the reactant or with the product.

- 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.



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



- **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 [].

$$\begin{aligned} \text{Active mass} &= \frac{\text{Number of gram moles of the substance}}{\text{Volume (L)}} \\ &= \frac{\text{Weight of substance (in grams)}}{\text{Molecular weight (M}_w\text{)} \times \text{Volume (L)}} = \frac{w}{M_w \times V(\text{L})} = \frac{w \times 1000}{M_w \times V(\text{mL})} \end{aligned}$$

- 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.

$$\begin{aligned} \text{Molar concentration} &= \frac{w}{M_w \times V(\text{L})} = \frac{\rho}{M_w} \quad (\text{where } \rho = \text{density (in gL}^{-1}\text{)}) \\ &= \frac{\rho}{M_w} \times 1000 \quad (\text{where } \rho = \text{density (in g mL}^{-1}\text{)}) \end{aligned}$$

$$\text{Active mass} = \frac{\text{density of the substance}}{\text{molecular mass of the substance}}$$

Pre-Medical

Following other names of active mass can also be used :

- | | | |
|-----------------------|----------------------|------------------------------|
| (i) mole/litre | (ii) gram mole/litre | (iii) gram molecules/litre |
| (iv) molarity | (v) Concentration | (vi) Effective 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. 8.5 g ammonia is present in a vessel of 0.5 litre capacity then find out the active mass of ammonia?

Solution. $[\text{NH}_3] = \frac{8.5}{17 \times 0.5} = 1 \text{ mol L}^{-1}$

BEGINNER'S BOX-1

1. Which of the following statement is correct regarding with chemical equilibrium :-
 - (1) Based on extent to which the reactions 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
 - (4) All of these
2. Find out the correct statement :-
 - (1) Equilibrium condition is a state of reversible reaction
 - (2) Chemical equilibrium are important in numerous biological process like transport and delivery of O_2
 - (3) Reversible reactions can be homogeneous 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 mol of NaCl kept in 4 litre vessel at NTP is :-

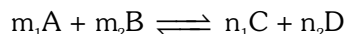
(1) 1	(2) 2	(3) $\frac{1}{2}$	(4) Not defined
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3.2 LAW OF MASS ACTION OR LAW OF CHEMICAL EQUILIBRIUM

- The law of mass action was given by Guldberg and Waage (1864).
- 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.

(A) Derivation of equilibrium constant :-

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



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 $(r_f) \propto [A]^{m_1} [B]^{m_2}$

Rate of backward reaction $(r_b) \propto [C]^{n_1} [D]^{n_2}$

$$r_f = k_f [A]^{m_1} [B]^{m_2} \quad \text{and} \quad r_b = k_b [C]^{n_1} [D]^{n_2}$$

Where k_f and k_b are forward and backward rate or velocity constants respectively.

At equilibrium state –

$$r_f = r_b$$

$$k_f [A]^{m_1} [B]^{m_2} = k_b [C]^{n_1} [D]^{n_2}$$

$$\frac{k_f}{k_b} = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$

$$K = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}} \quad \therefore K = \frac{k_f}{k_b}$$

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,

$$K = \frac{k_f}{k_b}$$

Forms of K

Concentration
(K_C)

Partial pressure
(K_P)

For reaction $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$K_C = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$

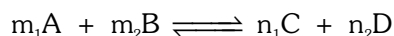
$$K_P = \frac{(P_C)^{n_1} \times (P_D)^{n_2}}{(P_A)^{m_1} \times (P_B)^{m_2}}$$

Unit of [] = mol L^{-1}

Unit of P = atm.

(B) Relation between K_P and K_C :

Consider a reversible homogeneous chemical equilibrium reaction



According to law of mass action (LOMA)

$$K_C = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$

$$K_P = \frac{(P_C)^{n_1} (P_D)^{n_2}}{(P_A)^{m_1} (P_B)^{m_2}}$$

For an ideal gas $PV = nRT$

Where –
 P = Pressure in atm
 V = Volume in litres
 n = Number of gaseous moles
 R = Gas constant = $0.0821 \text{ L atm mol}^{-1}\text{K}^{-1}$
 T = Temperature in kelvin

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

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

$$P_A = [A]RT, P_B = [B]RT, P_C = [C]RT \text{ and } P_D = [D]RT$$

Put all these values in K_p expression

$$\text{So } K_p = \frac{[C]^{n_1} (RT)^{n_1} [D]^{n_2} (RT)^{n_2}}{[A]^{m_1} (RT)^{m_1} [B]^{m_2} (RT)^{m_2}} = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}} \times \frac{(RT)^{n_1+n_2}}{(RT)^{m_1+m_2}}$$

$$K_p = K_c (RT)^{(n_1+n_2)-(m_1+m_2)}$$

$$\Delta n_g = (n_1 + n_2) - (m_1 + m_2)$$

= Sum of stoichiometric coefficient of gaseous products

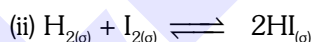
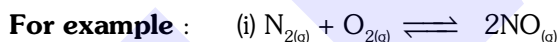
– sum of stoichiometric coefficient of gaseous reactants

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

- The K_c is expressed by the units $(\text{mol L}^{-1})^{\Delta n_g}$ and K_p by $(\text{atm})^{\Delta n_g}$.
- Following cases may arise :-

(a) When $\Delta n_g = 0$

$$K_p = K_c (RT)^0 = K_c$$

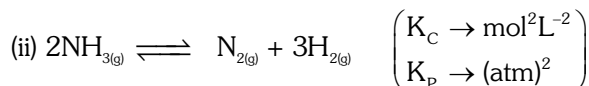
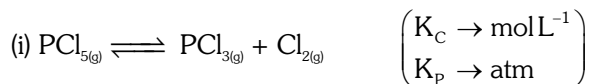


- K_c and K_p are unit less in this case.

(b) When $\Delta n_g = +ve$

$$K_p > K_c$$

For example :



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

$$K_p < K_c$$

For example :-



(d) Special point :

If $T = \frac{1}{R}$ then

$$K_p = K_c \left(R \times \frac{1}{R}\right)^{\Delta n_g}$$

$$K_p = K_c (1)^{\Delta n_g}$$

$$K_p = K_c$$

For any value of Δn_g

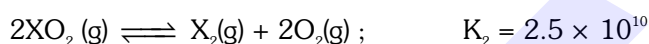
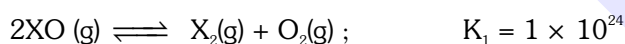
(C) Application of K

Stability of reactants and products :

Stability of reactants increases when value of K decreases

Stability of products increases when value of K increases

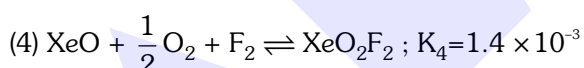
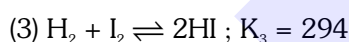
Ex : In the following reactions which one oxide is more stable.



$\therefore K_1 > K_2$ So the stability of $XO_2 > XO$

BEGINNER'S BOX-2

1. In which of the following reaction product is more stable :-



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 $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$ has $K_c = 4$ then what is the value of K_p for the same reaction:-

(1) $16 \times (800 R)^2$

(2) $\left(\frac{800R}{4}\right)^{-2}$

(3) $\left(\frac{1}{4 \times 800 R}\right)^2$

(4) None of these

4. For the equilibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$, what is the temperature at which $\frac{K_p(\text{atm})}{K_c(\text{M})} = 3$:-

(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 ΔH is the change in enthalpy then

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^0}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \text{ or } \log K_2 - \log K_1 = \frac{\Delta H^0}{2.303R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right]$$

(According to van't hof equation)

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

- (i)** When $\Delta H = +ve$ (endothermic reaction)

$$\log K_2 - \log K_1 > 0 \Rightarrow \log K_2 > \log K_1$$

$$\Rightarrow K_2 > K_1$$

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

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

$$\log K_2 - \log K_1 < 0$$

$$\Rightarrow \log K_2 < \log K_1$$

$$\Rightarrow K_2 < K_1$$

\therefore 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 $A + B \rightleftharpoons C + D$

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

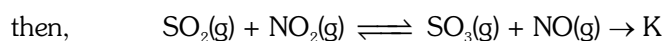
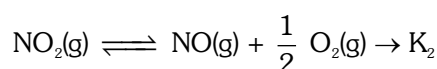
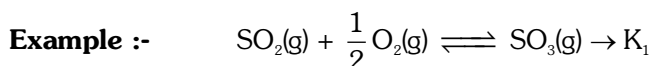
If the reaction is reversed $C + D \rightleftharpoons A + B$

$$\text{Equilibrium constant } K'_c = \frac{[A][B]}{[C][D]}$$

The equilibrium constant K'_c is actually the reciprocal of K_c

Thus, the two equilibrium constants are related as $\rightarrow K'_c = \frac{1}{K_c}$

- (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.

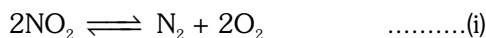


So, $K = K_1 \times K_2$

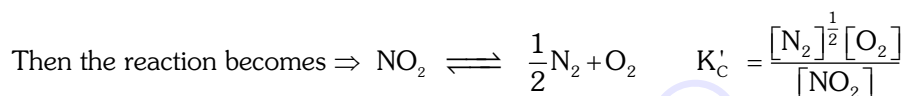
(d) Stoichiometry of the reaction :-

When a reversible reaction is multiplied or divided by a coefficient then the value of equilibrium constant will be numerically different in these cases.

For example the dissociation of NO_2 can be represented as :

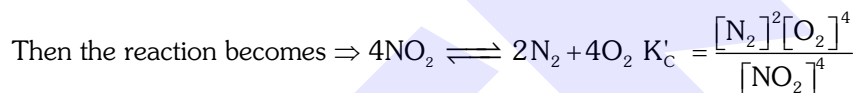


$$K_c = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}_2]^2}$$

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

Thus, the two equilibrium constants are related as $K'_c = \sqrt{K_c}$

So if reaction is divided by n then $K'_c = (K_c)^{\frac{1}{n}}$

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

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 presence of a catalyst. |
| (e) Presence of inert materials. | |

- The value of equilibrium constant depends only on temperature.**

Illustrations

Illustration 3 $\text{XeF}_6 + \text{H}_2\text{O} \rightleftharpoons \text{XeOF}_4 + 2\text{HF}$ constant = K_1 , $\text{XeO}_4 + \text{XeF}_6 \rightleftharpoons \text{XeOF}_4 + \text{XeO}_3\text{F}_2$ constant = K_2 . Then equilibrium constant for the reaction $\text{XeO}_4 + 2\text{HF} \rightleftharpoons \text{XeO}_3\text{F}_2 + \text{H}_2\text{O}$ will be—

- | | | | |
|-----------------------|-----------------|-----------------------|---------------------------|
| (1) $\frac{K_1}{K_2}$ | (2) $K_1 + K_2$ | (3) $\frac{K_2}{K_1}$ | (4) $\frac{K_1}{(K_2)^2}$ |
|-----------------------|-----------------|-----------------------|---------------------------|

Solution

Ans. (3)

Illustration 4

Assertion:- In the presence of catalyst, the value of equilibrium constant K increases.

Reason :- Catalysts increases the rate of forward and backward reaction to same extent.

- (1) Both (A) and (R) are true and (R) is the correct explanation of (A).
 (2) Both (A) and (R) are true and (R) is NOT the correct explanation of (A).
 (3) (A) is true but (R) is false.
 (4) (A) is false but (R) is true.

Solution

Ans. (4)

3.3 DEGREE OF DISSOCIATION

It is the fraction of moles of reactant dissociated $\alpha = \frac{x}{a}$

$$\% \alpha = \frac{x}{a} \times 100$$

Where α = Degree of dissociation
 x = Number of dissociated moles
 a = Initial number of moles (given)

Illustrations

Illustration 5 Initially 1 mole of PCl_5 is present. 40% of it is not dissociated at 300°C . The reaction is carried out in a flask of 1 litre capacity. The value of K_c would be :-

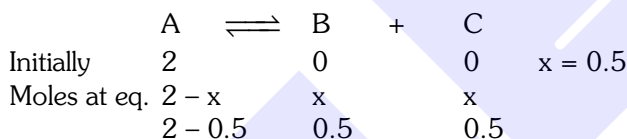
- (1) 3.2 (2) 1.6 (3) $(3.2)^{-1}$ (4) 0.9

Solution **Ans. (4)**

Illustration 6 In the beginning of the reaction, $\text{A} \rightleftharpoons \text{B} + \text{C}$, 2 moles of A are taken, out of which 0.5 moles gets dissociated. What is the amount of dissociation of A ?

- (1) 0.5 (2) 1 (3) 0.25 (4) 4.2

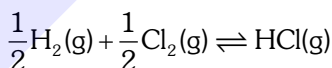
Solution **Ans. (3)**



Since, two moles dissociated into 0.5
 Therefore, one mole will dissociated into 0.25

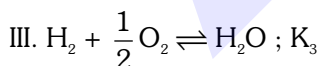
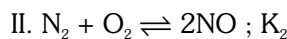
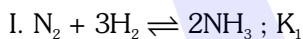
BEGINNER'S BOX-3

1. The equilibrium constant (K_c) for the reaction $2\text{HCl}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$ is 4×10^{-34} at 25°C . What is the equilibrium constant for the reaction :-



- (1) 2×10^{-17} (2) 2.5×10^{33} (3) 5×10^6 (4) None of these

2. Consider the following gaseous equilibrium given below



The equilibrium constant for the reaction $2\text{NH}_3 + \frac{5}{2}\text{O}_2 \rightleftharpoons 2\text{NO} + 3\text{H}_2\text{O}$ in terms of K_1 , K_2 and K_3 will be :-

- (1) $K_1 K_2 K_3$ (2) $\frac{K_1 K_2}{K_3}$ (3) $\frac{K_1 K_3^2}{K_2}$ (4) $\frac{K_2 K_3^3}{K_1}$

3. Using molar concentrations, what is the unit of K_c for the reaction $\text{CH}_3\text{OH}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 2\text{H}_2(\text{g})$:-

- (1) M^{-2} (2) M^2 (3) M^{-1} (4) M

4. If temperature is increased then equilibrium constant will be :-
 (1) Increased
 (2) Decreased
 (3) Remains constant
 (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 $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H = -46.06 \text{ kJ}$:-
 (1) 4×10^{-2} (2) 2×10^{-3} (3) 10^2 (4) 4×10^2
6. In which of the following equilibrium equation, $K_p > K_c$
 (1) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ (2) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
 (3) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (4) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
7. If $CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g)$, $K_1 = 60$; $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$, $K_2 = 180$ then the equilibrium constant of the reaction $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ will be—
 (1) 0.44 (2) 0.11 (3) 0.22 (4) 0.33

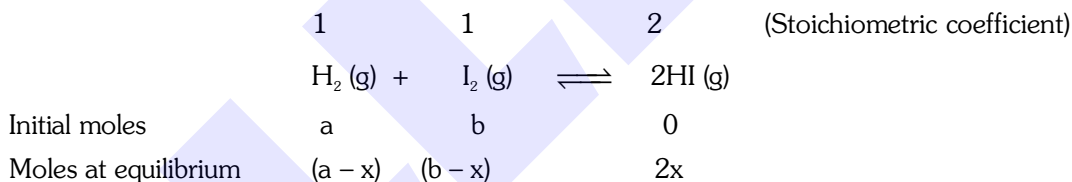
3.4 APPLICATIONS OF LAW OF MASS ACTION

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

(A) Homogeneous Gaseous Reactions of Type-I ($\Delta n_g = 0$)

Synthesis of HI :-

- (i) **Expression for K_c** : The formation of HI from H_2 and I_2 is represented by following 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

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$$

$$\Rightarrow K_c = \frac{4x^2}{(a-x)(b-x)}$$

- When $a = b = 1$, x becomes degree of formation of HI or degree of dissociation of H_2 (or I_2).

$$K_c = \frac{4x^2}{(1-x)^2}$$

Let if $x \ll 1$ then $1-x \simeq 1$ So $K_c = 4x^2$

$$x = \sqrt{\frac{K_c}{4}} \quad \text{i.e.} \quad \boxed{x \propto V^0}$$

At equilibrium the degree of dissociation is independent 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 $HI = \frac{2x}{(a + b)} P$

$$K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} = \frac{\left(\frac{2x}{a+b}\right)^2 P^2}{\left(\frac{a-x}{a+b}\right)\left(\frac{b-x}{a+b}\right) P^2}$$

$$K_p = \frac{4x^2}{(a-x)(b-x)} \quad \text{Thus } K_p = K_c$$

Let if $x \ll 1$ then $1 - x \simeq 1$ So $K_p = 4x^2$

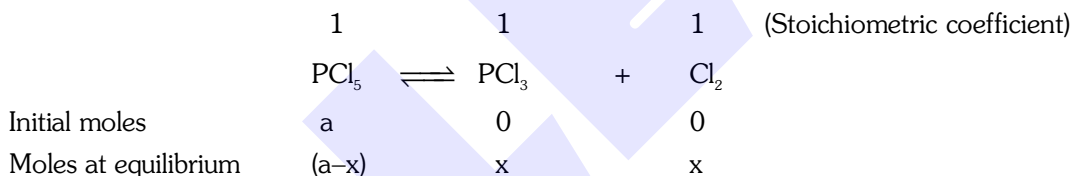
$$x = \sqrt{\frac{K_p}{4}} \quad \text{i.e. } \boxed{x \propto P^0}$$

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

(B) Homogeneous Gaseous reactions of Type-II ($\Delta n_g > 0$)

Dissociation of PCl_5 :-

- (i) **Expression for K_c** : The dissociation of PCl_5 takes place according to the equation



Let a moles of PCl_5 be taken in a closed vessel of volume V . At equilibrium x moles of PCl_5 are dissociated into x moles of each PCl_3 and Cl_2 .

$$[PCl_5] = \frac{(a-x)}{V} ; \quad [PCl_3] = \frac{x}{V} ; \quad [Cl_2] = \frac{x}{V}$$

$$\text{Apply law of mass action } K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$$

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

$$\text{If } \alpha \ll 1 \text{ then } 1 - \alpha \approx 1 \quad K_c \approx \frac{\alpha^2}{V} \quad \text{or} \quad \boxed{\alpha \propto \sqrt{V}}$$

The degree of dissociation of PCl_5 at equilibrium is directly proportional to the square root of the volume.

- (ii) **Expression for K_p** :

Let the total pressure at equilibrium be P .

Total number of moles at equilibrium = $(a - x) + x + x = a + x$

$$p_{PCl_5} = \left(\frac{a-x}{a+x}\right)P, \quad p_{PCl_3} = \left(\frac{x}{a+x}\right)P, \quad p_{Cl_2} = \left(\frac{x}{a+x}\right)P$$

Apply law of mass action

$$K_p = \frac{p_{\text{PCl}_3} \cdot p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{x^2 p}{(a+x)(a-x)}$$

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

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

If $\alpha \ll 1$ then $1 - \alpha^2 \approx 1$, $K_p \approx \alpha^2 P$

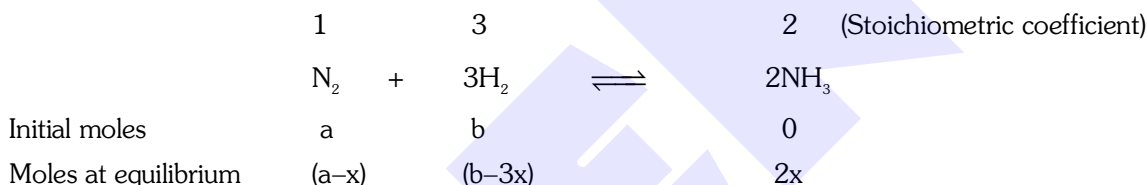
$$\alpha^2 \propto \frac{1}{P} \Rightarrow \boxed{\alpha \propto \frac{1}{\sqrt{P}}}$$

- The degree of dissociation of PCl_5 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 :



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_3 .

At equilibrium $[\text{N}_2] = \frac{(a-x)}{V}$; $[\text{H}_2] = \frac{(b-3x)}{V}$; $[\text{NH}_3] = \frac{2x}{V}$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$

If $a = 1$, $b = 3$ then $K_c = \frac{4x^2 V^2}{27(1-x)^4}$

If $x \ll 1$ then $1 - x \approx 1$

$$K_c = \frac{4x^2 V^2}{27} \quad \text{i.e.} \quad \boxed{x \propto \frac{1}{V}}$$

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 = $a - x + b - 3x + 2x = a + b - 2x$

If total pressure is P at equilibrium then

$$p_{\text{N}_2} = \frac{(a-x)}{(a+b-2x)} P, \quad p_{\text{H}_2} = \frac{(b-3x)}{(a+b-2x)} P, \quad p_{\text{NH}_3} = \frac{2x}{(a+b-2x)} P$$

According to Law of mass action

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = \frac{\left(\frac{2x}{a+b-2x}P\right)^2}{\left(\frac{a-x}{a+b-2x}\right)\left(\frac{b-3x}{a+b-2x}\right)^3}$$

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

If $a = 1$, $b = 3$ then $K_p = \frac{16x^2(2-x)^2}{27(1-x)^4 P^2}$

If $x \ll 1$ then $2-x \approx 2$ and $1-x \approx 1$

$$K_p = \frac{64x^2}{27P^2} \text{ i.e. } x^2 \propto P^2 \Rightarrow \boxed{x \propto P}$$

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.

$$\alpha \propto (V)^{\frac{\Delta n_g}{\text{sum of stoichiometric coefficient of gaseous products}}} \text{ or } \alpha \propto \left(\frac{1}{P}\right)^{\frac{\Delta n_g}{\text{sum of stoichiometric coefficient of gaseous products}}}$$

Effect	$\Delta n_g = 0$	$\Delta n_g > 0$ or +ve	$\Delta n_g < 0$ or -ve
	$\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$	$\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$	$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
	$x \propto (v)^\circ \propto (P)^\circ$	$x \propto (v)^{1/2} \propto \left(\frac{1}{P}\right)^{1/2}$	$x \propto \left(\frac{1}{v}\right) \propto (P)$
(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 decreases	x decreases
(b) constant volume	x unchanged	x unchanged	x unchanged

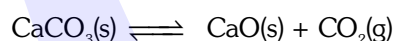
BEGINNER'S BOX-4

1. $A + B \rightleftharpoons C + D$ If initially A and B 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) $\frac{9}{4}$ (3) $\frac{1}{9}$ (4) 4
2. At a certain temperature, only 50% HI is dissociated at equilibrium in the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ 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 $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ 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
4. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ 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) $\frac{p}{8}$
5. For the reaction $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$, 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 substances only.

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



$$K_p = p_{CO_2}$$

- (ii) $2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$

$$K_p = (p_{H_2})^2 (p_{O_2})$$

- (iii) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$$K_p = \frac{(p_{H_2})^4}{(p_{H_2O})^4}$$

Illustrations

Illustration 7 Two sample of HI each of 5 g 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 (2) More in 10 litre vessel
 (3) Equal in both vessel (4) None of these

Solution Ans. (3)

Illustration 8 What will be the amount of dissociation, if the volume is increased 16 times of initial volume in the reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$?

- (1) 4 times (2) $\frac{1}{4}$ times (3) 2 times (4) $\frac{1}{5}$ times

Solution Ans. (1)

$x \propto \sqrt{V}$ or $x \propto \sqrt{16}$ Thus, 4 times.

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 favour of products while increasing concentrations of the products results in shifting the equilibrium in favour 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 increases. According to Le-Chatelier's principle, the equilibrium shifts in that direction in which there is decrease 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 that 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.

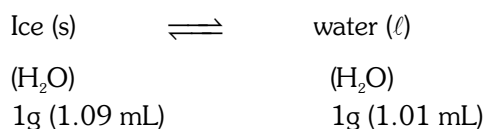
(B) PHYSICAL EQUILIBRIUM

Physical reaction :- Those reaction in which change in only and only physical states (solid, liquid and gas) of substance takes place without any chemical change, is called physical reaction.

Example :

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

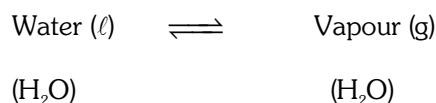
Melting of ice is accompanied by absorption of heat (endothermic) and decrease in volume



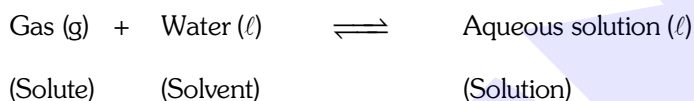
Hence both increase of temperature and pressure will favour the melting of ice into water.

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

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



- 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 :

- **Effect of pressure** → Solubility of such gases increases with increasing pressure which dissolves in a solvent with a decrease in volume.

Illustrations

Illustration 9 On applying pressure to the equilibrium $\text{ice} \rightleftharpoons \text{water}$, 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 10 Which of the following conditions should be more favourable for increasing the rate of forward reaction in the equilibrium $\text{H}_2 \rightleftharpoons \text{H} + \text{H}$ ($\Delta H = +ve$) ?

- (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 $\text{H}_2 \rightleftharpoons \text{H} + \text{H}$, heat has to be provided to dissociate H_2 into H . Therefore, the reaction is endothermic (ΔH will positive). So, temperature should be high. Since, one mole of H_2 forms two moles of H -atoms, so volume is increasing (Δn is positive) so pressure should be low for increasing the rate of forward reaction.

Illustration 11 The reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ goes to completion in lime kiln because :

- | | |
|-------------------------------------|--|
| (1) of the high temperature | (2) CaO is more stable than CaCO_3 |
| (3) CaO is not dissociated | (4) CO_2 escapes continuously |

Solution Ans. (4)

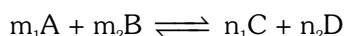
BEGINNER'S BOX-5

- Which of the following equilibrium remains unaffected by a change in pressure (or volume) ?
 (1) $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(s)} + \text{Cl}_2\text{(g)}$ (2) $\text{H}_2\text{(g)} + \text{CO}_2\text{(g)} \rightleftharpoons \text{H}_2\text{O(g)} + \text{CO(g)}$
 (3) $3\text{PbS(s)} + 3\text{O}_2\text{(g)} \rightleftharpoons 2\text{PbO(s)} + 2\text{SO}_2\text{(g)}$ (4) $\text{PCl}_5\text{(g)} \rightleftharpoons \text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)}$
- Consider the following equilibrium system; $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)}$; 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.
 (2) Less SO_2 is produced.
 (3) Addition of inert gas does not affect equilibrium.
 (4) system moves to new equilibrium position which cannot be predicted theoretically.
- Which of the following is not true for the equilibrium reaction; $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)}$; $\Delta H = 180\text{kJ mol}^{-1}$.
 (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.
- Consider the following equilibrium system; $\text{SO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightleftharpoons \text{SO}_3\text{(g)}$; 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 $\text{SO}_3\text{(g)}$ is produced.
 (3) More $\text{SO}_3\text{(g)}$ is produced.
 (4) The system moves to new equilibrium position which cannot be predicted theoretically.
- 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.
- Which of the following equilibrium is dynamic ?
 (1) $\text{Solid} \rightleftharpoons \text{Liquid}$ (2) $\text{Liquid} \rightleftharpoons \text{Vapour}$ (3) $\text{Solid} \rightleftharpoons \text{Vapour}$ (4) All of these
- Which of the following is not true for solid-liquid equilibrium ?
 (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 change with time.
 (4) There is no exchange of heat between the system and its surrounding.

8. Which of the following substances can be placed in a closed vessel to establish (solid \rightleftharpoons vapour) equilibrium?
 (1) Ammonium chloride (2) Camphor (3) Iodine (4) All of these
9. Which of the following solutions kept in contact with undissolved solute is an example of solid-solution equilibrium?
 (1) Aqueous solution (2) Saturated solution (3) Unsaturated solution (4) Nonaqueous solution
10. Which of the following is correct regarding the gas-solution equilibrium ?
 (1) The solubility of gas increases with the increase of pressure and decreases with the increase of temperature.
 (2) The solubility of gas increases with the increase of pressure as well as temperature.
 (3) The solubility of gas decreases with the increase of pressure and increases with the increase of temperature.
 (4) The solubility of gas decreases with the increase of pressure as well as temperature.

3.6 REACTION QUOTIENT (Q)

Consider a general homogeneous reversible reaction :

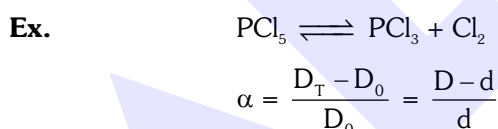


$$\text{Reaction Quotient (Q)} = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}, \text{ (Applied at any stage of reaction)}$$

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

- (i) When $Q = K$ then reaction is in equilibrium state.
 (ii) When $Q < K$ then reaction shift in the forward direction.
 (iii) When $Q > K$ then reaction shift in the backward direction.

3.7 Calculation of degree of dissociation from vapour density :-



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 temp.

α = Degree of dissociation

$\text{Vapour density} = \frac{\text{Molecular weight}}{2}$

Reversible reaction	$\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$	Total moles	Volume at NTP	Vapour density
Let initial moles	1 0 0	1	$V_T = 22.4$	$D_T \propto \frac{1}{V_T}$
Moles at equilibrium	$(1-\alpha)$ α α	$1+\alpha$	$V_0 = 22.4 (1+\alpha)$	$D_0 \propto \frac{1}{V_0}$

If α is the degree of dissociation

$$\frac{D_T}{D_0} = \frac{V_0}{V_T} = \frac{22.4(1+\alpha)}{22.4}$$

$$\frac{D_T}{D_0} = 1 + \alpha \quad \text{or} \quad \alpha = \frac{D_T}{D_0} - 1 \quad \boxed{\alpha = \frac{D_T - D_0}{D_0}}$$

So for a general reversible reaction $n_1A \rightleftharpoons n_2B + n_3C$

$$\boxed{\alpha = \frac{n_1}{\Delta n} \left(\frac{D_T - D_0}{D_0} \right)} \quad \Delta n = (n_2 + n_3) - (n_1)$$

OR

$$\boxed{\alpha = \frac{n_1}{\Delta n} \left(\frac{M_T - M_0}{M_0} \right)}$$

M_T = Theoretical molecular weight

M_0 = Observed or experiment molecular weight

Illustrations

Illustration 12 The vapour density of undecomposed N_2O_4 is 46. When heated, vapour density decreases to 24.5 due to its dissociation to NO_2 . The percentage dissociation of N_2O_4 at the final temperature is -

- (1) 87 (2) 60 (3) 40 (4) 70

Solution Ans. (1)

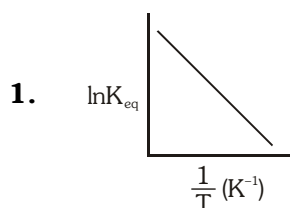
Illustration 13 If PCl_5 is 80% dissociated at 250°C then its vapour density at room temperature will be

- (1) 56.5 (2) 104.25 (3) 101.2 (4) 52.7

Solution Ans. (2)

$$\alpha = \frac{D_T - D_0}{D_0} ; D_T = \frac{\text{Molecular weight}}{2}$$

Vapour density at room temperature (D_T) is 104.25, which is fixed.

BEGINNER'S BOX-6


According to this graph reaction will be :-

- (1) Endothermic (2) Exothermic
 (3) Spontaneous at room temperature (4) ΔH is negligible
2. For the reaction $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$
 If $K_p = K_c (RT)^x$, when the symbols have usual meaning the value of x is (assuming ideality) :-
 (1) -1 (2) $-\frac{1}{2}$ (3) $+\frac{1}{2}$ (4) +1
3. For the equilibrium $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$ $K_p = 63 \text{ atm}$ at 1000 K. If at equilibrium $P_{\text{CO}} = 10 P_{\text{CO}_2}$ then total pressure at equilibrium is :-
 (1) 6.30 atm (2) 0.693 atm (3) 6.93 atm (4) 69.3 atm
4. A(g) is 90 % converted in to B according to the reaction $\text{A}(\text{g}) \rightleftharpoons 3\text{B}(\text{g})$ value of $\left(\frac{D}{d}\right)$ at this point is :-
 (1) 1.0 (2) 2.0 (3) 2.5 (4) 2.8
5. What will be the direction of reaction if concentration of H_2 , I_2 and HI are 2 mol L^{-1} , 2 mol L^{-1} and 8 mol L^{-1} respectively. K_c for reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ is 4.
 (1) forward direction (2) backward direction
 (3) equilibrium condition (4) reaction will be completed

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4						
	Ans.	4	4	3	1						
BEGINNER'S BOX-2	Que.	1	2	3	4						
	Ans.	3	2	4	3						
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7			
	Ans.	4	4	2	4	1	1	4			
BEGINNER'S BOX-4	Que.	1	2	3	4	5					
	Ans.	4	1	2	1	1					
BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	2	3	4	2	3	4	1	4	2	1
BEGINNER'S BOX-6	Que.	1	2	3	4	5					
	Ans.	1	2	3	4	2					