

CHAPTER
6

Reaction
- Reversible reaction
- Irreversible reaction
- Reactants & Products

CHEMICAL EQUILIBRIUM

6.1.0 INTRODUCTION

Substances react with each other to form products. In some of the reactions, the reactants are completely converted into products at the end of the reactions. Such reactions are called irreversible.

Anyhow, there are certain reactions which do not proceed to completion. Actually, the products which are produced, recombine with each other to form the original substances. They are generally represented as



'A' and 'B' are the reactants for the forward step while 'C' and 'D' are the reactants for the backward step.

6.1.1 Dynamic nature of chemical equilibrium:

If we start the reaction with 'A' and 'B' as reactants in a closed vessel, then the reaction is fast at the beginning to form 'C' and 'D'. The concentrations of 'A' and 'B' decrease while those of 'C' and 'D' increase continuously. At the same time, the rate of the backward step increases. A stage reaches when the rates of two opposing reactions become equal. This is state of dynamic equilibrium.

So, the state of dynamic equilibrium is the state of reversible reaction when two opposing reactions occur at same rate and the concentrations of reactants and products do not change with time.

6.1.2 Explanation of dynamic nature of chemical equilibrium:

This can be understood on the basis of kinetic molecular model. The molecules of the substance 'A' and 'B' at equilibrium state collide with each other to form 'C' and 'D'. In a similar way, 'C' and 'D' collide to give 'A' and 'B'. It is a known fact that the collisions of molecules in a closed system is a ceaseless phenomenon. So, this continues to occur, even at equilibrium and the concentrations remain unchanged.

6.1.3 Graphical explanation of chemical equilibrium:

If we plot a graph between time on x-axis and the concentrations of reactants and products on y-axis, then the rising curves are obtained for the products and falling curves and obtained for the reactants. Fig. (1)

- Backward
- Forward

- Equilibrium?

- Rate?
- Concentration?

- Product?
- Collision?

- Ceaseless process

→ static equilibrium

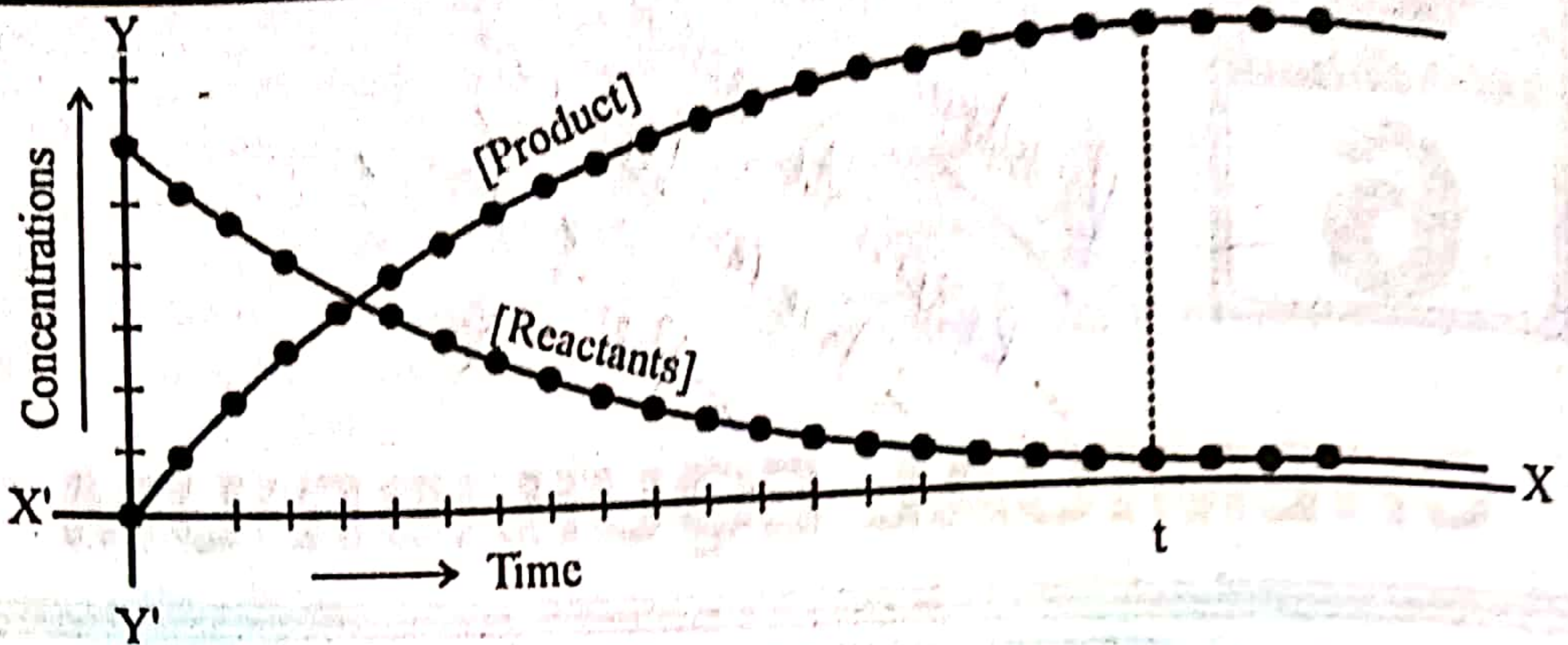


Fig. (1) Time of equilibrium.

The steepness of the rising curve for the products decreases with the passage of time. In the long run, it becomes parallel to the time axis. This is the time of chemical equilibrium. From this time onwards the concentrations of the products do not increase further. Similar type of the parallel graph is obtained for the reactants. It becomes parallel to the time axis at equilibrium stage.

If the reaction attains the equilibrium stage after 50% completion, then the graphs can touch each other and they merge into each other to give a single graph at the time of equilibrium.

6.1.4 Characteristics of chemical equilibrium:

All the chemical reactions which have the reversibility and attain the chemical equilibrium at a certain stage have the following characteristics.

(i) Concentrations remains the same:

The mixture of reactants and products at equilibrium stage is called equilibrium mixture and the concentrations are called equilibrium concentrations. They do not change after the attainment of equilibrium stage.

(ii) Equilibrium constant is independent of initial concentration:

Whatever concentrations of reactants are taken at the start of reactions, the values of ' K_p ' or ' K_c ' remain the same under the given conditions.

(iii) Equilibrium can be established from either side:

The concentration of the species at equilibrium stage, attain the same values whether we start the reaction in the vessel in the forward direction or backward direction.

(iv) Vessel should be closed:

A reversible chemical reaction can attain the equilibrium, if the reaction vessel is closed. No part of the reactants or products may be allowed to escape out. If the reactants or products or both are gases and any of them escapes from the vessel, then equilibrium is disturbed.

(v) A catalyst does not change the equilibrium position:

A catalyst increases the rate of both forward and backward steps equally by lowering the energy of activation of the reaction, but it does not change the equilibrium position.

— Reactants & Product Rates? Completion?

(vi) Free energy change is zero:

At equilibrium position of the chemical reaction, Gibb's free energy change is minimum. Any change taking place at equilibrium proceeds without the change in free energy. In other words,

$$\Delta G = 0, \text{ at equilibrium stage.}$$

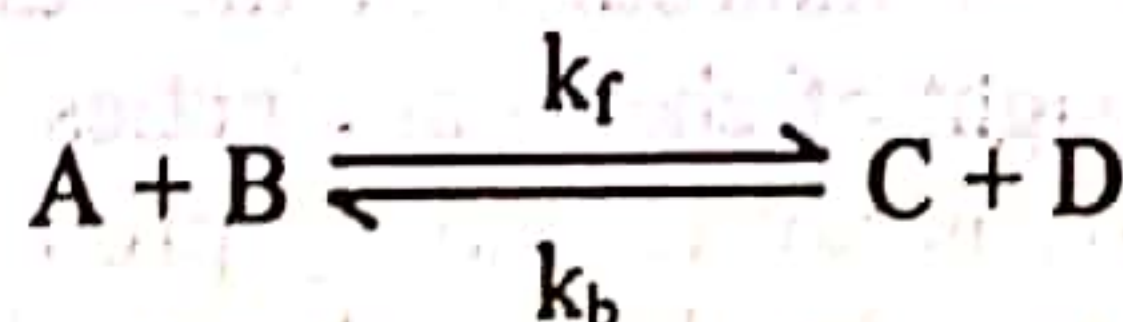
6.2.0 LAW OF MASS ACTION

This law was given by C.M. Guldberg and P. Waage in 1864. They studied a lot of reversible reactions and gave a generalization. A more general statement of law of mass action is that the rate of a chemical reaction is proportional to the product of molar concentrations raised to a power equal to the number of times, the particular substance appears in stoichiometric equation.

6.2.1 Equilibrium constant or equilibrium law:

Keeping in mind the law of mass action, we can have relationship between concentrations of reactants and products with the rate constants of forward and backward steps.

Let us consider a general reaction,



The co-efficients for the reactants and products are unity for the sake of convenience. The rates of reactions at equilibrium stage depend upon the concentrations of reactants.

$$\text{Rate of forward reaction} \propto [A][B]$$

$$\text{Rate of forward reaction} = k_f[A][B]$$

$$\text{Rate of backward reaction} \propto [C][D]$$

$$\text{Rate of backward reaction} = k_b[C][D]$$

' k_f ' and ' k_b ' are the rate constants for the forward and the reverse reactions.

At equilibrium stage the two rates are equal.

$$k_f[A][B] = k_b[C][D]$$

$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} \quad \dots\dots (1)$$

According to this equation (1), the concentrations of reactants and products have a certain ratio and this ratio depends upon the forward and backward rate constants.

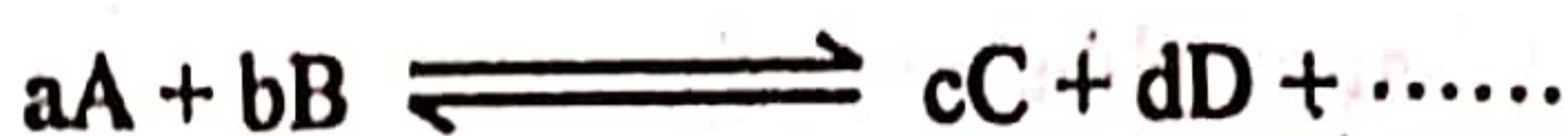
If the ratio of two rate constants ' k_f ' and ' k_b ' is put equal to another constant ' K_c ', then

$$K_c = \frac{k_f}{k_b} \quad \dots\dots (2)$$

This ' K_c ' in equation (2) is called equilibrium constant.

The square brackets denote the concentrations in moles dm^{-3} . So, symbol ' K_c ' is used, when concentrations of 'A', 'B', 'C', and 'D' are taken in moles dm^{-3} .

If the reversible reaction has co-efficients in the balanced equations as,



$$\text{Then } K_c = \frac{[C]^c [D]^d \dots}{[A]^a [B]^b \dots} \quad \dots \quad (3)$$

Hence equilibrium constant is the product of equilibrium concentrations of products divided by the product of equilibrium concentrations of reactants and each concentration term is raised to the power equal to the co-efficients of the substance in the balanced equation.

This above equation is called law of chemical equilibrium.

6.2.2 Explanation of law of chemical equilibrium:

We have noted above that, while we write down the relationships of equilibrium constant then the concentrations of each reactant is raised to the power corresponding to the number of molecules in the balanced equation. It appears contradictory to the basic thought of chemical kinetics. In the chemical kinetics we say that the rate of a reaction is not essentially proportional to the concentration raised to the power indicated by balanced equations. However, the power relationship is valid for equilibrium constant expression. The reason is that the factors in the rate expressions for the opposing reactions always cancel in such a way as to give the indicated expression for the equilibrium constants.

6.2.3 Law of chemical equilibrium for non-ideal solutions:

It should be made clear at this stage, that the expression for ' K_c ', which has been derived above is strictly true for ideal dilute solutions. It is not applicable to non-ideal solutions. If the solutions are non-ideal, then the chemical reactions depend on the effective concentrations and not actual concentrations. We should not consider the molar concentration. We know that non-ideal behaviour is shown by a solution of substances in the case of ionic species. In that case, activities must be used in the expression, if exact calculations are required. The equilibrium constant is denoted by ' K_a ' in such cases.

$$K_a = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

6.2.4 Equilibrium constant in terms of partial pressures:

Those reversible reactions which involve the gases should be handled by measuring their partial pressures and equilibrium constant is indicated by ' K_p '.

$$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

6.3.0 RELATIONSHIP BETWEEN DIFFERENT TYPES OF EQUILIBRIUM CONSTANTS

The values of equilibrium constants for a certain reaction depend upon the units of concentration chosen. Equilibrium constant ' K_p ' is employed when the concentrations are in partial pressures, ' K_c ' when concentrations are moles dm^{-3} , ' K_x ' when we have mole fractions and K_n is used when we have simple number of moles of reactants and products. Suppose we have a general reaction.



The reaction under consideration is consisted of ideal gases. The activity of each substance is proportional to the partial pressure and to its molar concentration.

For an ideal system, we shall be able to write down the expressions of ' K_p ', ' K_c ', ' K_x ', and ' K_n ' as follows.

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

$$K_c = \frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b}$$

$$K_x = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b}$$

$$K_n = \frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b}$$

In these expressions the symbol p , C , X and n stand for partial pressure, moles dm^{-3} , mole fraction and number of moles respectively

6.3.1 Relationship between K_p and K_c :

Keeping in view the general gas equation, and the Dalton's law of partial pressures, we can write down

$$p_i V = n_i RT \quad \dots \dots (1)$$

' i ' is the name of any one of the component.

$$\text{or} \quad p_i = \frac{n_i RT}{V}$$

Since $\frac{n_i}{V} = C_i = \text{conc. in moles dm}^{-3}$

$$p_i = C_i RT \quad \dots \dots (2)$$

' p_i ' is the partial pressure of the gas ' i ' in the mixture of gases, n_i is its number of moles, $\frac{n_i}{V}$ is in the moles dm^{-3} and has a unit of concentration. The volume and temperature as ' V ' and ' T ' are same for all gases.

$\rightarrow n \propto p$ are same

In our reaction there are gaseous substances as 'A', 'B', 'C', 'D'. According to the above equation (1) their partial pressures are

$$\left. \begin{aligned} p_A &= \frac{n_A}{V} RT = C_A RT \\ p_B &= \frac{n_B}{V} RT = C_B RT \\ p_C &= \frac{n_C}{V} RT = C_C RT \\ p_D &= \frac{n_D}{V} RT = C_D RT \end{aligned} \right\} \dots\dots (3)$$

Let us substitute their values of partial pressures from set of equations (3) in the expression of ' K_p ', i.e;

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \dots\dots (4)$$

Putting values of partial pressures from equations (3) into equations (4)

$$K_p = \frac{(C_C RT)^c (C_D RT)^d}{(C_A RT)^a (C_B RT)^b} = \frac{C_C^c C_D^d (RT)^{c+d}}{C_A^a C_B^b (RT)^{a+b}}$$

$$K_p = K_c (RT)^{(c+d)-(a+b)}$$

$$K_p = K_c (RT)^{n_p - n_R}$$

$$K_p = K_c (RT)^{\Delta n} \dots\dots (5)$$

Where Δn is the difference of number of moles of products (n_p) and number of moles of reactants n_R . So, $n_p - n_R = \Delta n$. With the help of equation (5) we can interconvert K_p and K_c .

6.3.2 Relationship between K_p and K_x :

In order to derive the relationship between ' K_p ' and ' K_x ', we take the help from Dalton's law of partial pressures, that is

$$p_i = X_i P \dots\dots (6)$$

Where p_i is the partial pressure of a gas 'i' in a mixture and ' X_i ' is its mole fraction.

According to this equation, the partial pressure of any gas depends upon the mole fraction of that gas and total pressure 'P' of the mixture. The values of partial pressures of four substances i.e. 'A', 'B', 'C' and 'D' are as follows.

$$\left. \begin{aligned} p_A &= X_A P \\ p_B &= X_B P \\ p_C &= X_C P \\ p_D &= X_D P \end{aligned} \right\} \dots\dots (7)$$

Putting these values of equation (7) in the expression of K_p of equation (4)

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \dots\dots (4)$$

$$K_p = \frac{(X_C P)^c (X_D P)^d}{(X_A P)^a (X_B P)^b}$$

$$K_p = \frac{X_C^c X_D^d P^{(c+d)}}{X_A^a X_B^b P^{(a+b)}}$$

$$K_p = K_x (P)^{(c+d)-(a+b)}$$

When $\Delta n = 0$

Let $\Delta n = (c + d) - (a + b)$

$$K_p = K_x \dots\dots (8)$$

This equation (8) shows that if we multiply ' K_x ' with pressure of the system with a certain power, then we get ' K_p '. So in order to interconvert ' K_p ' and ' K_x ', we should know the total pressure of reaction mixture at equilibrium stage and the difference of number of moles of reactants and products, i.e. ' Δn '.

6.3.3 Relationship between K_p and K_n :

We again take the help of Dalton's law of partial pressures:

Since, $p_i = X_i P$

Where, $X_i = \frac{n_i}{N}$

N = total number of moles of reactants and products at equilibrium stage

n_i = number of moles of component 'i'

So, $p_i = \frac{n_i}{N} P \dots\dots (9)$

Let us apply this relationship to calculate the partial pressures of four components.

$$\left. \begin{aligned} p_A &= \frac{n_A}{N} P \\ p_B &= \frac{n_B}{N} P \\ p_C &= \frac{n_C}{N} P \\ p_D &= \frac{n_D}{N} P \end{aligned} \right\} \dots\dots (10)$$

Putting these values of partial pressures from the set of equations (10) in the expression of ' K_p ' in equation (4).

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \quad \dots\dots (4)$$

$$K_p = \frac{\left(\frac{n_C}{N} P\right)^c \left(\frac{n_D}{N} P\right)^d}{\left(\frac{n_A}{N} P\right)^a \left(\frac{n_B}{N} P\right)^b}$$

$$K_p = \frac{n_C^c n_D^d}{n_A^a n_B^b} \left(\frac{P}{N}\right)^{(c+d)-(a+b)}$$

$$K_p = K_n \left(\frac{P}{N}\right)^{(c+d)-(a+b)}$$

$$K_p = K_n \left(\frac{P}{N}\right)^{\Delta n} \quad \dots\dots (11)$$

In order to know the relationship between ' K_p ' and ' K_n ', we should know the values of total pressure, total number of moles of reactants and products, and the difference of number of moles of reactants and products. When we join all these relationships, then we can say that

$$K_p = K_c (RT)^{\Delta n} = K_x (P)^{\Delta n} = K_n \left(\frac{P}{N}\right)^{\Delta n} \quad \dots\dots (12)$$

If the number of moles of reactants and products are equal, then $\Delta n = 0$

$$\text{Hence, } (RT)^0 = 1 \quad (P)^0 = 1 \quad \left(\frac{P}{N}\right)^0 = 1$$

$$\text{So, } K_p = K_c = K_x = K_n \quad \dots\dots (13)$$

We reach the important conclusion that when the number of moles of reactants and products in a reaction are equal, then all equilibrium constants have the same values.

6.3.4 Comparison of various equilibrium constant values:

If the number of moles are different, then the relative sizes of different equilibrium constants can be only estimated if we know the pressure, temperature and the difference of number of moles of reactants and products.

$$\text{For example, } K_p = K_c (RT)^{\Delta n}$$

(i) When number of moles of products are greater than those of reactants, then Δn is positive. So,

$$K_p > K_c$$

(ii) When the number of moles of products are less than those of reactants, then Δn is negative. So,

$$K_p < K_c$$

Anyhow, the amount of smallness of K_p than K_c depends upon the temperature of the reversible reaction.

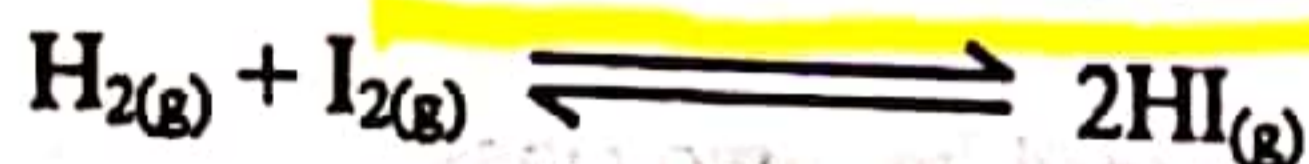
6.3.5 Units of equilibrium constants:

For reversible reactions we write down the equilibrium constant expression in terms of concentrations. The concentrations of the substances are given in units of mol dm^{-3} or atm in the case of gases. The units of ' K_p ' and ' K_c ' depend upon the specific reactions.

Let us discuss two situations when the number of moles of reactants and products in the reversible reaction are equal and then consider when they are unequal.

Equal number of moles of reactants and products:

In such cases, the units cancel with each other and K_c or K_p have no units.



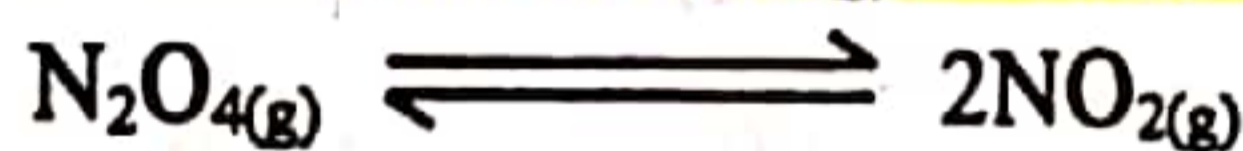
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(\text{mol / dm}^3)^2}{(\text{mol / dm}^3)(\text{mol / dm}^3)} \longrightarrow \text{No units}$$

$$K_p = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})} \longrightarrow \text{No units}$$

Unequal number of moles of reactants and products:

Again there are two situations that whether the number of moles of products are greater or less than those of reactants.

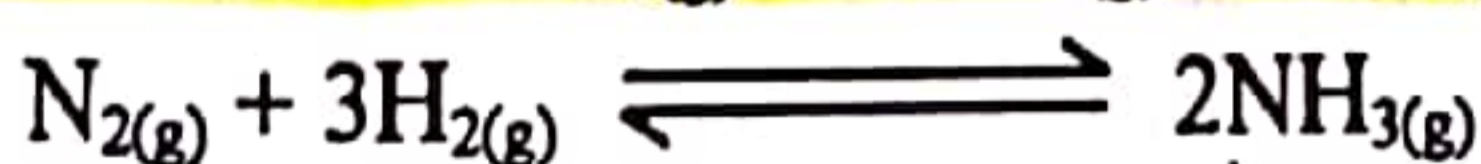
(a) The dissociation of $\text{N}_2\text{O}_{4(g)}$ into $\text{NO}_{2(g)}$ has the following units



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(\text{mol / dm}^3)^2}{(\text{mol / dm}^3)} = \text{mol / dm}^3 = \text{mol dm}^{-3}$$

$$K_p = \frac{(p_{\text{NO}_2})^2}{(p_{\text{N}_2\text{O}_4})} = \frac{(\text{atm})^2}{(\text{atm})} = \text{atm}$$

(b) The formation of $\text{NH}_{3(g)}$ from $\text{N}_{2(g)}$ and $\text{H}_{2(g)}$.



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(\text{mol / dm}^3)^2}{(\text{mol / dm}^3)(\text{mol / dm}^3)^3} = (\text{mol / dm}^3)^{-2} \\ = \text{mol}^{-2} \text{dm}^{+6}$$

$$K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})^3} = (\text{atm})^{-2}$$

6.4.0 TYPES OF CHEMICAL EQUILIBRIUM

Chemical equilibrium are two types.

(i) Homogeneous equilibria

(ii) Heterogeneous equilibria

(i) Homogeneous Equilibria:

In this equilibria, all components are in one phase. A system containing only gases or totally miscible liquids are the best examples.

(ii) Heterogeneous Equilibria:

In this equilibria, more than a single phase exist. Equilibrium between

- (i) solid and gas
- (ii) liquid and gas
- (iii) solid and liquid
- (iv) solid and solid
- (v) immiscible liquids

are the some good examples.

6.4.1 Homogeneous equilibrium and law of mass action:

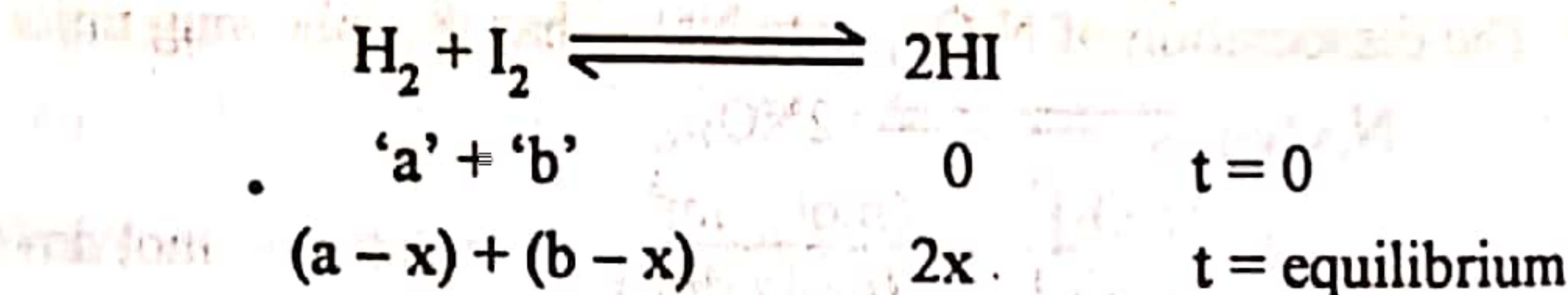
The gas phase reactions:

The gaseous reactions may be divided into two classes.

- (i) Those reactions in which there is no change in the number of moles after reaction.
- (ii) Those reactions in which number of moles either increase or decreases.

6.4.2 Reaction with no change in the number of moles:

Let us take the reaction between hydrogen and iodine. If number of moles of 'H₂' and 'I₂' are 'a' and 'b' respectively at initial stage of reaction, then



Let 'x' moles of H₂ disappear at equilibrium position. Since one mole of H₂ reacts with one mole I₂ to produce two moles of HI, so 'x' moles of H₂ will react with 'x' order of I₂ to produce 2x moles of HI at equilibrium. Total number of moles, (a + b) do not change in this case, because at equilibrium stage

$$(a - x) + (b - x) + x + x = a + b.$$

(A) Expression for K_c:

Let us suppose that the total volume of the gaseous mixture is 'V' dm³. At equilibrium stage, the equilibrium molar concentrations of various species involved are

$$\left. \begin{array}{l}
 [\text{H}_2] = \frac{(a - x)}{V} \text{ moles dm}^{-3} \\
 [\text{I}_2] = \frac{(b - x)}{V} \text{ moles dm}^{-3} \\
 [\text{HI}] = \frac{2x}{V} \text{ moles dm}^{-3}
 \end{array} \right\} \dots\dots (1)$$

Remember that molar concentrations are denoted by square brackets [].

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Putting set of equations (1) in this expression of K_c

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{(a-x)}{V}\right)\left(\frac{(b-x)}{V}\right)}$$

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

The factor of volume has cancelled, so change of volume at equilibrium stage does not disturb the K_c value.

(B) Expression for K_p :

The expression for partial pressures will be obtained by taking total pressure as 'P' and multiplying mole fraction of substances with 'P'.

Since, $p_i = X_i P$

So,

$$\left. \begin{aligned} p_{H_2} &= \frac{(a-x)}{(a+b)} P \\ p_{I_2} &= \frac{(b-x)}{(a+b)} P \\ p_{HI} &= \frac{2x}{(a+b)} P \end{aligned} \right\} \dots\dots (3)$$

The expression of K_p is obtained, when concentrations are put as partial pressures in the following equation.

$$K_p = \frac{p_{HI}^2}{p_{H_2} p_{I_2}} \dots\dots (4)$$

Now put values of partial pressures from set of equations (3) into equation (4)

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

or $K_p = \frac{4x^2}{(a-x)(b-x)} \dots\dots (5)$

The factor of total pressure 'P' has cancelled out. It means that ' K_p ' value is independent of pressure of reaction.

(C) Expression for K_x :

For this purpose, we put concentrations in terms of mole fractions.

$$K_x = \frac{X_{HI}^2}{X_{H_2} X_{I_2}}$$

Substances at equilibrium have following values of mole fractions.

$$\left. \begin{aligned} X_{\text{H}_2} &= \frac{(a-x)}{(a+b)} \\ X_{\text{I}_2} &= \frac{(b-x)}{(a+b)} \\ X_{\text{HI}} &= \frac{(2x)}{(a+b)} \end{aligned} \right\} \dots\dots (6)$$

Put the values from set of equations (6)

$$K_x = \frac{[2x/(a+b)]^2}{(a-x)/(a+b) \cdot (b-x)/(a+b)}$$

$$K_x = \frac{4x^2}{(a-x)(b-x)} \dots\dots (7)$$

Relationship between K_p , K_x and K_c :

The three expressions derived above are identical i.e.,

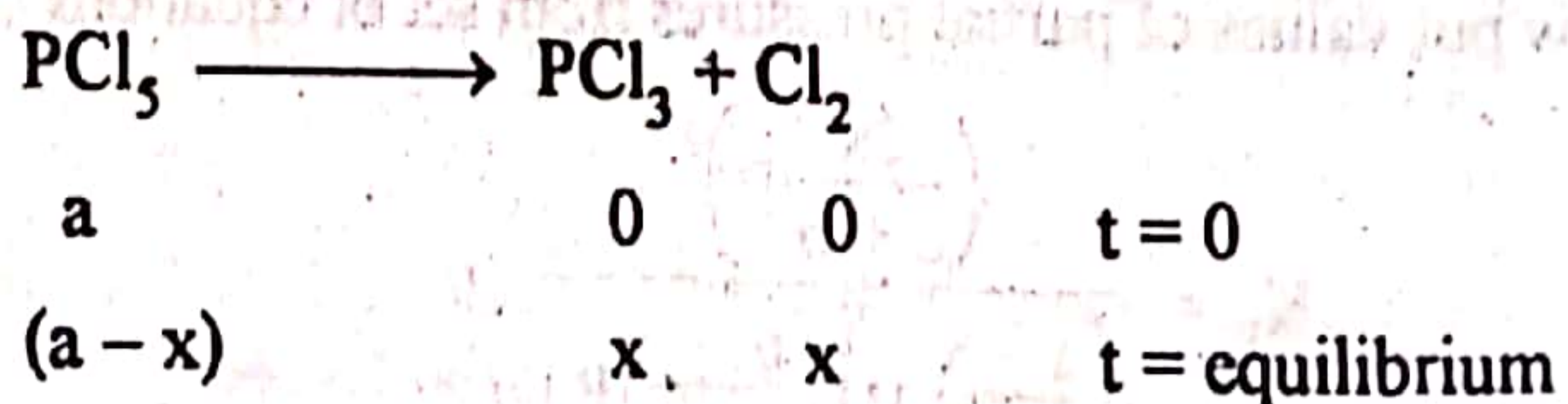
$$K_p = K_c = K_x$$

If in a reaction, 'C' moles of HI are already present at the start of the reaction, then the amount of HI at equilibrium will be $(C + 2x)$, and the equilibrium constants can be expressed by,

$$K_p = K_c = K_x = \frac{(C + 2x)^2}{(a-x)(b-x)} \dots\dots (8)$$

6.4.3 The Reactions in which the number of moles increase:

Let us consider the thermal decomposition of the PCl_5 . Suppose initial concentration of PCl_5 is 'a' moles and at equilibrium stage $(a - x)$ moles of PCl_5 are left behind



Now, total number of moles at the start = a

The total number of moles at the equilibrium stage = $(a - x) + x + x = (a + x)$

The mole fractions of various gases at equilibrium stage are

$$\left. \begin{aligned} X_{\text{PCl}_5} &= \frac{(a-x)}{(a+x)} \\ X_{\text{PCl}_3} &= \frac{x}{(a+x)} \\ X_{\text{Cl}_2} &= \frac{x}{(a+x)} \end{aligned} \right\} \dots\dots (1)$$

The expressions for ' K_x ', ' K_p ' and ' K_c ' are derived as follows:

(A) Expression of K_c :

The concentration in moles dm^{-3} of various gases are

$$\left. \begin{aligned} [\text{PCl}_5] &= \frac{(a-x)}{V} \\ [\text{PCl}_3] &= \frac{x}{V} \\ [\text{Cl}_2] &= \frac{x}{V} \end{aligned} \right\} \dots\dots (2)$$

Since,
$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\frac{(a-x)}{V}}$$

$$K_c = \frac{x^2}{(a-x)V} \dots\dots (3)$$

The increase of 'V' will decrease ' K_c ', so to keep ' K_c ' constant, we have to increase 'x'. It means that the reaction moves to the forward direction by increasing volume.

(B) Expression of K_p :

The partial pressures are obtained by taking the help of set of equations (1) i.e. when mole fractions are multiplied by total pressure of the mixture

$$\left. \begin{aligned} p_{\text{PCl}_5} &= \frac{(a-x)}{(a+x)} P \\ p_{\text{PCl}_3} &= \left(\frac{x}{a+x}\right) P \\ p_{\text{Cl}_2} &= \frac{x}{(a+x)} P \end{aligned} \right\} \dots\dots (4)$$

Since,
$$K_p = \frac{p_{\text{PCl}_3} p_{\text{Cl}_2}}{p_{\text{PCl}_5}}$$

Putting the values of partial pressure from set of equations (4)

$$K_p = \frac{\left(\frac{x}{a+x}\right)^2 P^2}{\left(\frac{a-x}{a+x}\right) P}$$

$$K_p = \frac{x^2}{(a^2 - x^2)} P \dots\dots (5)$$

Increase of pressure increases ' K_p '. To keep ' K_p ' constant, 'x' has to decrease. It means that reaction is pushed to backward direction, by increasing pressure.

(C) Expression of K_x :

The value of ' K_x ' can be obtained by putting set of equation (1) in the expression of ' K_x '.

$$K_x = \frac{X_{\text{PCl}_3} X_{\text{Cl}_2}}{X_{\text{PCl}_5}}$$

Putting values of mole fractions

$$K_x = \frac{\left(\frac{x}{a+x}\right)\left(\frac{x}{a+x}\right)}{\left(\frac{a-x}{a+x}\right)}$$

$$K_x = \frac{x^2}{(a^2 - x^2)}$$

Relationship of K_p and K_c :

Since, $PV = nRT$ for one mole of a gas

$$\text{So, } V = \frac{nRT}{P} = \frac{(a+x)RT}{P} \quad \dots\dots (7)$$

because, $n = (a+x)$

Putting the value of ' V ' in equation (3)

$$K_c = \frac{x^2 P}{(a-x)(a+x) RT}$$

$$K_c = \frac{x^2 P}{(a^2 - x^2) RT} \quad \dots\dots (8)$$

Divide equation (5) of ' K_p ' by that of ' K_c ' equation (8)

$$\text{As } K_p = \frac{x^2 P}{(a^2 - x^2)} \quad \dots\dots (4)$$

$$K_c = \frac{x^2 P}{(a^2 - x^2) RT} \quad \dots\dots (8)$$

$$\text{So, } \frac{K_p}{K_c} = RT$$

$$K_p = K_c (RT)$$

Since, in this reaction $\Delta n = 1$,

the general relation $K_p = K_c (RT)^{\Delta n}$ is obtained.

Effect of pressure:

It is same as derived earlier. Equation (4) shows, that at a constant temperature an increase of pressure would result in a decrease of ' x '. This means that if pressure is increased, the dissociation of PCl_5 must decrease.

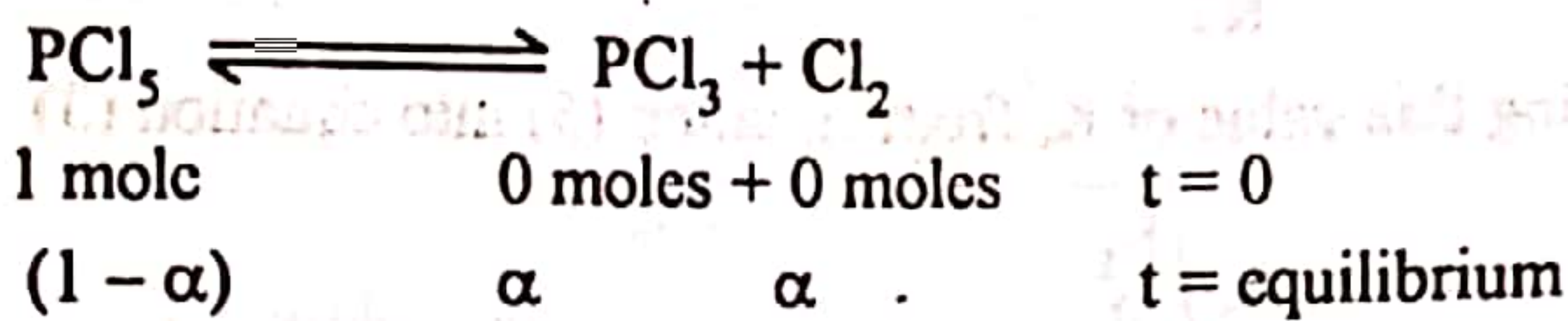
Effect of adding of any one component of the reaction at equilibrium stage:

If any of three (PCl_5 , PCl_3 or Cl_2) is added to the system already at equilibrium, leads to a new equilibrium position. For example, if Cl_2 gas is introduced into the system, the partial pressure of chlorine increases. Since K_p is a

constant in its values, the partial pressure of PCl_3 must decrease. This means that the equilibrium would tend to move in the reverse direction. It decreases the degree of dissociation of PCl_5 .

6.4.4 Expression for the degree of dissociation of PCl_5 :

If ' α ' is a degree of dissociation of PCl_5 , then $(1 - \alpha)$ of PCl_5 is left behind from one mole of PCl_5 .



Since, $K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$

The concentrations in moles dm^{-3} are obtained, by dividing the number of moles by total volume of mixture V

So, $K_c = \frac{\left(\frac{\alpha}{V}\right)\left(\frac{\alpha}{V}\right)}{(1 - \alpha)} = \frac{\alpha^2}{V(1 - \alpha)}$ (1)

Total number of moles at equilibrium stage = $(1 - \alpha) + \alpha + \alpha = (1 + \alpha)$

Applying the general gas equation for $(1 + \alpha)$ number of moles of reactants and products at equilibrium position.

$PV = (1 + \alpha)RT$

or $V = \frac{(1 + \alpha) RT}{P}$

Putting this value of ' V ' in above equation (1)

$K_c = \frac{\alpha^2 P}{(1 - \alpha^2) RT} \approx \frac{\alpha^2 P}{RT}$ (2)

or $K_c = \frac{\alpha^2 P}{RT}$ (α being very small, can be ignored in the denominator)

or $\alpha^2 = \frac{K_c RT}{P}$

or $\alpha = \sqrt{K_c \frac{RT}{P}}$ (3)

According to equation (3), K_c and R are constants. So,

$\alpha \propto \sqrt{\frac{T}{P}}$

At constant temperature

$\alpha \propto \sqrt{\frac{1}{P}}$ (4)

So, the degree of dissociation at any temperature varies inversely to the square root of the pressure of the system.

The increase of pressure will decrease the degree of dissociation of PCl_5 . We know that

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

$$\text{so, } K_c = \frac{K_p}{RT} \quad \dots\dots (5)$$

Putting this value of K_c from equation (5) into equation (3)

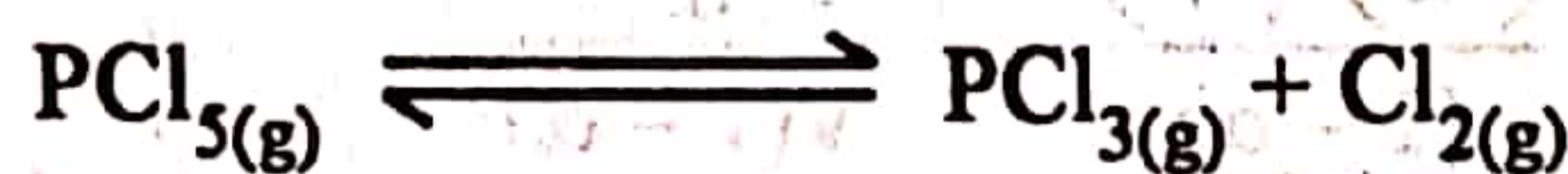
$$\alpha = \sqrt{\frac{K_p}{P}}$$

$$\text{or } \alpha \propto \frac{1}{\sqrt{P}} \quad \dots\dots (4)$$

In this way we obtain the same results.

6.4.4 Degree of dissociation from density measurements:

PCl_5 dissociates according to the reaction



This reaction proceeds with an increase in volume at constant temperature and pressure and the total mass remains constant. The density must decrease with the extent of dissociation.

Let the initial concentration of PCl_5 is 'a' moles. The total numbers of moles of all the compounds are 'a(1 + α)', at equilibrium position, where ' α ' is the degree of dissociation. So, the total volume depends upon the number of moles present in any system. The density of the system will be proportional to the reciprocal of the total number of moles present in the system.

Let the density of the pure PCl_5 is 'd'

$$d \propto \frac{1}{a}$$

Suppose the density of the system at equilibrium is ' d_e '.

$$\text{So, } d_e \propto \frac{1}{a(1 + \alpha)}$$

Divide these two equations

$$\frac{d}{d_e} = 1 + \alpha$$

$$\alpha = \frac{d}{d_e} - 1$$

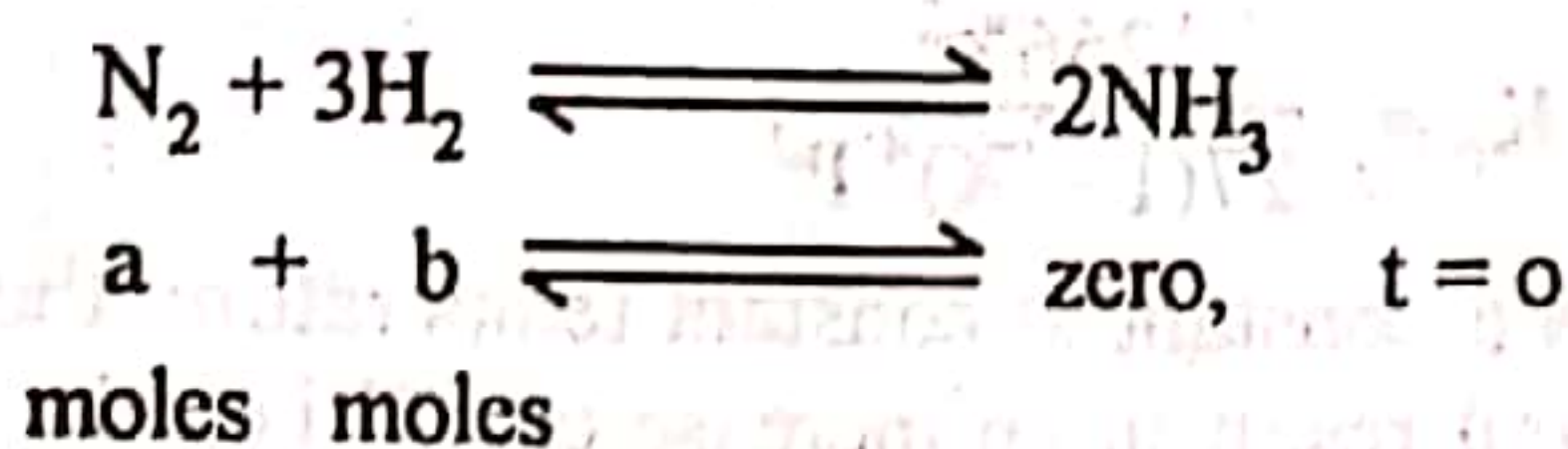
$$\text{Hence, } \alpha = \frac{d - d_e}{d_e}$$

So degree of dissociation of PCl_5 can be measured, if we know the density of PCl_5 and that of mixture at equilibrium stage.

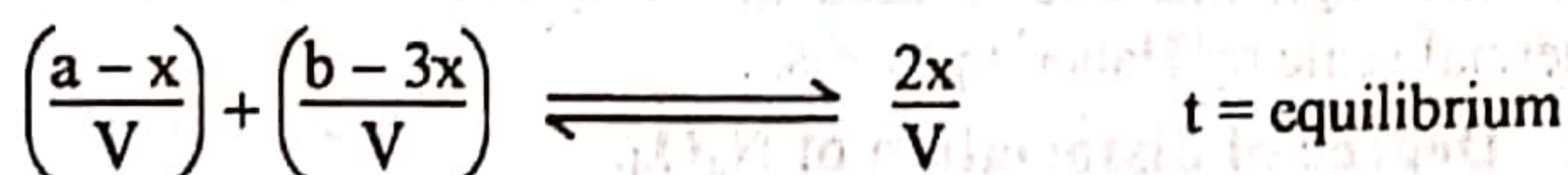
6.4.5 The reaction in which the number of moles decrease:

Synthesis of Ammonia:

A typical example of reaction proceeding with a decrease in the number of moles is of ammonia synthesis. If 'x' moles of 'N₂' are converted to products, then '3x' moles of 'H₂' are consumed to give '2x' mole of NH₃. The initial concentration of N₂ is 'a' moles and that of H₂ is 'b' moles



Let the volume of reaction mixture at equilibrium is 'V' dm³, then the equilibrium concentrations in moles dm⁻³



The expression of K_c, is

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Putting the values

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3}$$

$$K_c = \frac{4x^2V^2}{(a-x)(b-3x)^3} \quad \dots \dots (1)$$

If the volume of reaction vessel is increased at equilibrium stage then 'x' has to be decreased to keep 'K_c' constant. It mean reaction section goes back.

Effect of pressure on K_p of Ammonia Synthesis:

Suppose that the reactants N₂ and H₂ are taken in the molar ratio of 1 : 3 at the start and at equilibrium the mole fraction of NH₃ is X, then at equilibrium stage the combined mole fraction of the reactants is (1 - X).

Since N₂ and H₂ react in the ratio of 1 : 3, so the mole fractions of N₂ and H₂ at equilibrium are $\frac{1}{4}(1 - X)$ and $\frac{3}{4}(1 - X)$ respectively

Now, $p_{\text{N}_2} = \frac{1}{4}(1 - X)P$ "Since partial pressure of any gas is mole fraction × total pressure"

$p_{\text{H}_2} = \frac{3}{4}(1 - X)P$

$p_{\text{NH}_3} = XP$

$$\text{As, } K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3}$$

$$K_p = \frac{X^2 P}{\left\{ \frac{1}{4} (1 - X) P \right\} \left\{ \frac{3}{4} (1 - X) P \right\}^3}$$

$$K_p = \frac{256X^2}{27(1 - X)^4 P^2}$$

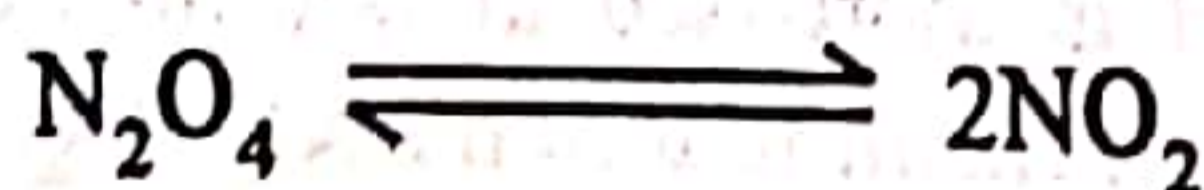
Since, K_p is a constant at constant temperature, therefore an increase in the total pressure 'P' will result in an increase of 'X' i.e., the mole fraction of NH_3 at equilibrium. Thus an increase of pressure favours the formation of NH_3 . This is the reason why high pressure is used in the synthetic manufacture of ammonia on commercial scale by Haber's process.

6.4.6 Degree of dissociation of N_2O_4 :



In this reaction the reactants and products are both gases. The reaction is happening with unequal number of moles, so the volume of the reaction system increases. In other words, we can say that value of ' K_p ' is disturbed momentarily. When the pressure is increased the number of moles of NO_2 decrease and that of N_2O_4 increase. It means that the increase of pressure suppresses the dissociation of N_2O_4 . This is just in accordance will be Le-Chatlier's principle.

In order to have a quantitative relationship between pressure of the system and the extent of dissociation, let us consider that we have one mole of N_2O_4 in 1 dm^3 of volume. Suppose that ' α ' is the fraction of '1' mole which is dissociated into NO_2 . This α is called degree of dissociation.



1 mole

0 moles

$t = 0$

$(1 - \alpha)$ moles

2α moles

$t = \text{equilibrium}$

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

From the individual number of moles of reactants and products and total number of moles of mixture, let us determine the mole fractions of two components.

$$X_{\text{N}_2\text{O}_4} = \frac{1 - \alpha}{1 + \alpha} \quad X_{\text{NO}_2} = \frac{2\alpha}{1 + \alpha} \quad \dots\dots (1)$$

The partial pressures of two components are obtained by multiplying the mole fractions of equations(1) with total pressure of the mixture i.e., P

$$\left. \begin{aligned} p_{\text{N}_2\text{O}_4} &= \frac{1 - \alpha}{1 + \alpha} P \\ p_{\text{NO}_2} &= \frac{2\alpha}{1 + \alpha} P \end{aligned} \right\} \dots\dots (2)$$

The expression of K_p for this reaction is

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}}$$

Now put the set of equation (2) in the expression of K_p .

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

$$\text{So, } K_p = \frac{4\alpha^2 P}{1-\alpha^2} \dots\dots (3)$$

According to this equation (3) the value of ' K_p ' depends upon degree of dissociation ' α ' and external pressure ' P ' of the system. If pressure is increased at equilibrium stage, then ' α ' has to be decreased to keep ' K_p ' constant. In other words, we say that increase of pressure pushes the reaction to the backward direction.

It should be kept in mind that all such calculations are based upon the assumption that all gases behave ideally over the whole range of pressure. We can rearrange the above equation by bringing ' α ' on one side and all the other factors on the right hand side.

$$\frac{4\alpha^2}{(1-\alpha^2)} = \frac{K_p}{P}$$

Inverting the both sides of equation.

$$\frac{1-\alpha^2}{4\alpha^2} = \frac{P}{K_p}$$

$$\frac{1-\alpha^2}{\alpha^2} = \frac{4P}{K_p}$$

$$\left(\frac{1}{\alpha^2} - 1\right) = \frac{4P}{K_p}$$

$$\frac{1}{\alpha^2} = \frac{4P}{K_p} + 1 = \frac{4P + K_p}{K_p}$$

Inverting again

$$\text{or } \alpha^2 = \frac{K_p}{4P + K_p}$$

Taking square root

$$\text{or } \alpha = \sqrt{\frac{K_p}{4P + K_p}} \dots\dots (5)$$

According to this equation, the degree of dissociation α is inversely proportional to the pressure of the system.

6.4.7 Addition of an inert gas to a system at equilibrium:

An inert gas is that which has no relation to the reaction. When it is added to an equilibrated system, the equilibrium may shift to a new position. The added

inert gas increases the total pressure and as a result, the partial pressures of the other gaseous constituents are affected.

Let us try to discuss this effect quantitatively. Consider a reaction in which all the agents are in gaseous phase.



The expression of K_p for this gaseous reactions is

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

Since, $p_i = X_i P$

Hence $p_A = X_A P$ $p_C = X_C P$

$p_B = X_B P$ $p_D = X_D P$

So let us replace all the partial pressures by mole fraction and total pressure.

$$\text{So, } K_p = \frac{X_C^c X_D^d}{X_A^a X_B^b} (P)^{\Delta n} = K_x (P)^{\Delta n} \quad \dots\dots (1)$$

Since $X_i = \frac{n_i}{N}$

So, we can get the K_p as

$$K_p = \frac{n_C^c n_D^d}{n_A^a n_B^b} \left(\frac{P}{N}\right)^{\Delta n} = K_n \left(\frac{P}{N}\right)^{\Delta n} \quad \dots\dots (2)$$

Where 'n' represents the number of moles of any of the constituent. 'N' is the total number of moles and 'P' is the total pressure of the system.

' K_p ' is constant at constant temperature. The number of moles of the products and the reactants control the the factor $\left(\frac{P}{N}\right)^{\Delta n}$. Obviously, when $\Delta n = \text{zero}$, there is no change in the number of moles due to the reaction. The first factor in the R.H.S. of equation (2) will remain the same irrespective of the fact that whether N increases or decreases. The following conclusions are drawn.

- (1) In those reactions where there is no change in the number of moles the addition of inert gas to an equilibrated system cannot affect the position of equilibrium.
- (2) If the inert gas is added to a system at constant volume, the increase in the total number of moles will result in a corresponding increase in pressure and the ratio $\frac{P}{N}$ will remain the same. So, the equilibrium is not affected in any way.
- (3) When the inert gas is added to an equilibrated system at constant pressure then as a result of increase in the values of 'N', the factor $\frac{P}{N}$ will decrease, hence the first factor on the R.H.S. of equation (2) will either

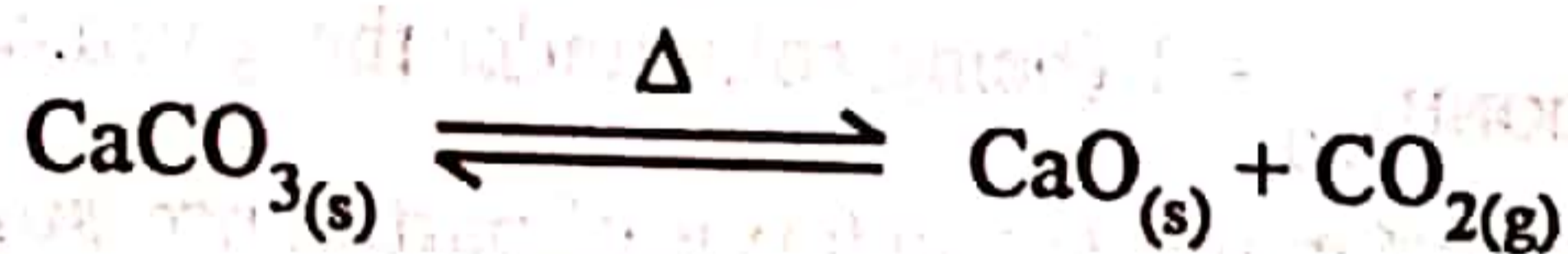
decrease or increase, depending whether ' Δn ' is positive or negative. If ' Δn ' is positive, $\left(\frac{P}{N}\right)^{\Delta n}$ decreases and in order to maintain the constancy of K_p , the first factor should increase. It mean K_n should increase. This can only happen if the forward reaction is favoured, resulting in an increase in the number of mole of products. If ' Δn ' is negative, reverse will be the case.

6.5.0 APPLICATION OF LAW OF MASS ACTION TO HETEROGENEOUS EQUILIBRIUM

Those chemical systems in which more than one phases are present at equilibrium stage are called heterogeneous equilibria. While studying the heterogeneous system, the activity terms are employed. The activity of a pure solid is taken as unity. The gases are generally assumed to be ideal. This assumption helps us to covert the activities into their partial pressures. In order to illustrate it, let us take some typical examples of some heterogeneous equilibria.

1. Dissociation of CaCO_3 :

CaCO_3 dissociates to give CaO and CO_2 . CO_2 is a gas and the other two substances are solid. So, at equilibrium stage, the system is heterogeneous, when the reaction is happening in a closed vessel.



The equilibrium constant of this reaction can be written as follows.

$$K_d = \frac{a_{\text{CaO}(s)} a_{\text{CO}_2(g)}}{a_{\text{CaCO}_3(s)}}$$

The activities of solid substances are taken as unity, so

$$K_a = a_{\text{CO}_2}$$

The activity of CO_2 is best measured in terms of partial pressures of CO_2 .

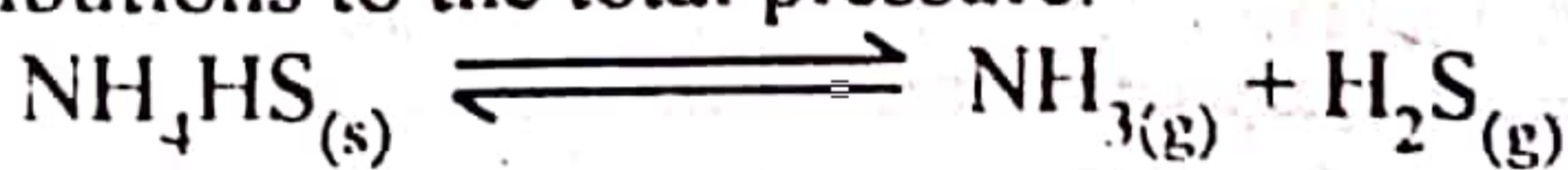
In that case, a_{CO_2} should be replaced by p_{CO_2} .

$$\text{So, } K_p = p_{\text{CO}_2}$$

This partial pressure of CO_2 is simply the dissociation pressure of CaCO_3 .

2. Dissociation of ammonium hydrogen sulphide:

NH_4HS is solid at room temperature. It dissociates into NH_3 and H_2S gas in a reversible manner. This system is consisted of one solid and two gases. The total pressure of the system is due to two gases which are formed. Since the two gases are produced to the same extent keeping in view their number of moles, so they have equal contributions to the total pressure.



$$K_a = \frac{a_{\text{NH}_3(g)} a_{\text{H}_2\text{S}(g)}}{a_{\text{NH}_4\text{HS}(s)}}$$

Since, $a_{\text{NH}_4\text{HS}(s)} = 1$ (being solid under the reaction conditions)

$$\text{So, } K_a = a_{\text{NH}_3(g)} a_{\text{H}_2\text{S}(g)}$$

The activity of two gases are best expressed in terms of their partial pressures. So,

$$K_p = P_{\text{NH}_3} P_{\text{H}_2\text{S}}$$

Partial pressures of both gases are $\frac{P}{2}$ and $\frac{P}{2}$

$$\text{So } K_p = \frac{P}{2} \times \frac{P}{2} = \frac{P^2}{4}$$

It means that if we know the total pressure of mixture, we can calculate the equilibrium constant ' K_p '.

3. Dissociation of ammonium carbamate:

Ammonium carbonate is solid substance, and it dissociates in a reversible manner to give NH_3 and CO_2 .



This system is consisted of one solid and two gases

$$K_a = \frac{a_{\text{NH}_{3(g)}}^2 a_{\text{CO}_{2(g)}}}{a_{\text{NH}_2\text{COONH}_{4(s)}}$$

Since $a_{\text{NH}_2\text{COONH}_{4(s)}} = 1$ (being solid under the given conditions)

Activities are best expressed in terms of partial pressures, so

$$K_p = P_{\text{NH}_{3(g)}}^2 P_{\text{CO}_{2(g)}}$$

Total pressure of the system is due to two moles of NH_3 and 1 mole of CO_2 . So, the contribution of NH_3 is twice than that of CO_2 towards the total pressure.

$$P_{\text{NH}_3} = \frac{2}{3} P$$

$$P_{\text{CO}_2} = \frac{1}{3} P$$

$$K_p = \left(\frac{2}{3} P\right)^2 \left(\frac{1}{3} P\right) = \frac{4}{27} P^3$$

So the equilibrium constant can be calculated from the total pressure of the reaction mixture.

6.6.0 QUANTITATIVE EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

Le-Chatelier's principle helps us to understand the effect of temperature on equilibrium constants of all the reactions. Exothermic reactions go to the backward direction on heating and endothermic reactions go to the forward direction on heating. This is a qualitative discussion of effect of temperature on chemical equilibrium.

In order to do the quantitative discussion, we have to consider thermodynamic aspects of chemical equilibrium. With this help, we will be able to estimate the value of K_p at any temperature. Moreover, we can estimate the rate of change of equilibrium constant with respect to temperature. We can also calculate the value of exothermicity or endothermicity of reaction by calculating the K_p values at various temperatures.

Let us take the help of following equation

$$\Delta G^\circ = -RT \ln K_p \quad \dots\dots (1)$$

This equation tells us that how the ' K_p ' value of a reaction decides the spontaneity of chemical reaction. Greater the negative value of ' ΔG° ', greater the spontaneity of reaction.

Differentiate this equation with respect to temperature at constant pressure. The right side of this equation is differentiated by using 'U x V' formula, because we have two variables on the right hand side.

$$\left(\frac{\partial(\Delta G^\circ)}{\partial T}\right)_P = -R \ln K_p - RT \left[\frac{\partial \ln K_p}{\partial T}\right] \quad \dots\dots (2)$$

Left side of equation (2) shows that it is the rate of change of standard free energy change with respect to temperature.

Multiply this equations by 'T', we get

$$T \left(\frac{\partial(\Delta G^\circ)}{\partial T}\right)_P = -RT \ln K_p - RT^2 \left[\frac{\partial \ln K_p}{\partial T}\right] \quad \dots\dots (3)$$

The first term on the right hand side of equation (3) is simply equal to ΔG° according to equation (1). So,

$$T \left(\frac{\partial(\Delta G^\circ)}{\partial T}\right)_P = \Delta G^\circ - RT^2 \left[\frac{\partial \ln K_p}{\partial T}\right] \quad \dots\dots (4)$$

Equation (4) is applicable on certain reversible reactions. If all the substances which are reactants and products are in their standard states, then the Gibbs-Helmholtz equation can be written as follows

$$\Delta G^\circ - \Delta H^\circ = T \left(\frac{\partial(\Delta G^\circ)}{\partial T}\right)_P \quad \dots\dots (5)$$

Let us compare equation (4) and (5)

$$RT^2 \frac{d \ln K_p}{dT} = \Delta H^\circ$$

$$\text{or} \quad \frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \quad \dots\dots (6)$$

The partial differentiation is converted to total one because there is only one independent variable and one dependent.

This equation (6) is called Van't Hoff equation or Van't Hoff isochore. ' ΔH° ' is the standard enthalpy change of chemical reaction. Left side of this equation is the rate of change of equilibrium constant with respect to temperature. It means that when the temperature of reaction changes, then its equilibrium

constant changes. This rate of change depends upon the enthalpy change of chemical reaction.

6.6.1 Integration of Van't Hoff's equation:

This equation (6) can be integrated subject to the condition that ' ΔH° ' is the constant over a small range of temperature. The integration will help us to calculate the value of equilibrium constant at any temperature, if we know the heat of chemical reaction ' ΔH° '. Actually, this aspect is the quantitative relationship of ' K_p ' and temperature T .

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

Separate the variables, by taking ' dT ' on R.H.S.

$$d \ln K_p = \frac{\Delta H^\circ}{R} \left(\frac{dT}{T^2} \right)$$

Let us integrate this equation. $\frac{\Delta H^\circ}{R}$ is constant so, it may be kept outside the integration sign

$$\int d \ln K_p = \frac{\Delta H^\circ}{R} \int \frac{dT}{T^2}$$

$$\int \frac{dT}{T^2} = \int T^{-2} dT = \frac{T^{-2+1}}{-2+1} = \frac{-1}{T}$$

$$\text{So, } \ln K_p = -\frac{\Delta H^\circ}{RT} + C \quad \dots\dots (7)$$

'C' is constant of integration.

Taking antilog on both sides

$$K_p = e^{\left(-\frac{\Delta H^\circ}{RT} + C\right)} = e^C \cdot e^{-\frac{\Delta H^\circ}{RT}} = A e^{-\frac{\Delta H^\circ}{RT}}$$

(where $e^C = A$, another constant)

$$K_p = A e^{-\frac{\Delta H^\circ}{RT}} \quad \dots\dots (8)$$

'A' is constant. According to this equation (8), value of ' K_p ' depends upon temperature. When the temperature increases, the ' K_p ' also increases, if ' ΔH° ' is positive. If ' ΔH° ' is negative, then increase of temperature, decreases the ' K_p ' value.

The equation (7) is the equation of a straight line. $\frac{1}{T}$ is independent variable and

' $\ln K_p$ ' is dependent variable. When a graph is plotted between $\frac{1}{T}$ on x-axis and

' $\ln K_p$ ' on y-axis, then a straight line with negative slope is obtained Fig. (2). The

slope of the straight line corresponds to $\frac{\Delta H^\circ}{R}$. If we put the values of slope and 'R'

we can calculate the value of ' ΔH° '.

$$\frac{\Delta H^\circ}{R} = \text{slope}$$

$$\text{or } \Delta H^\circ = R (\text{slope})$$

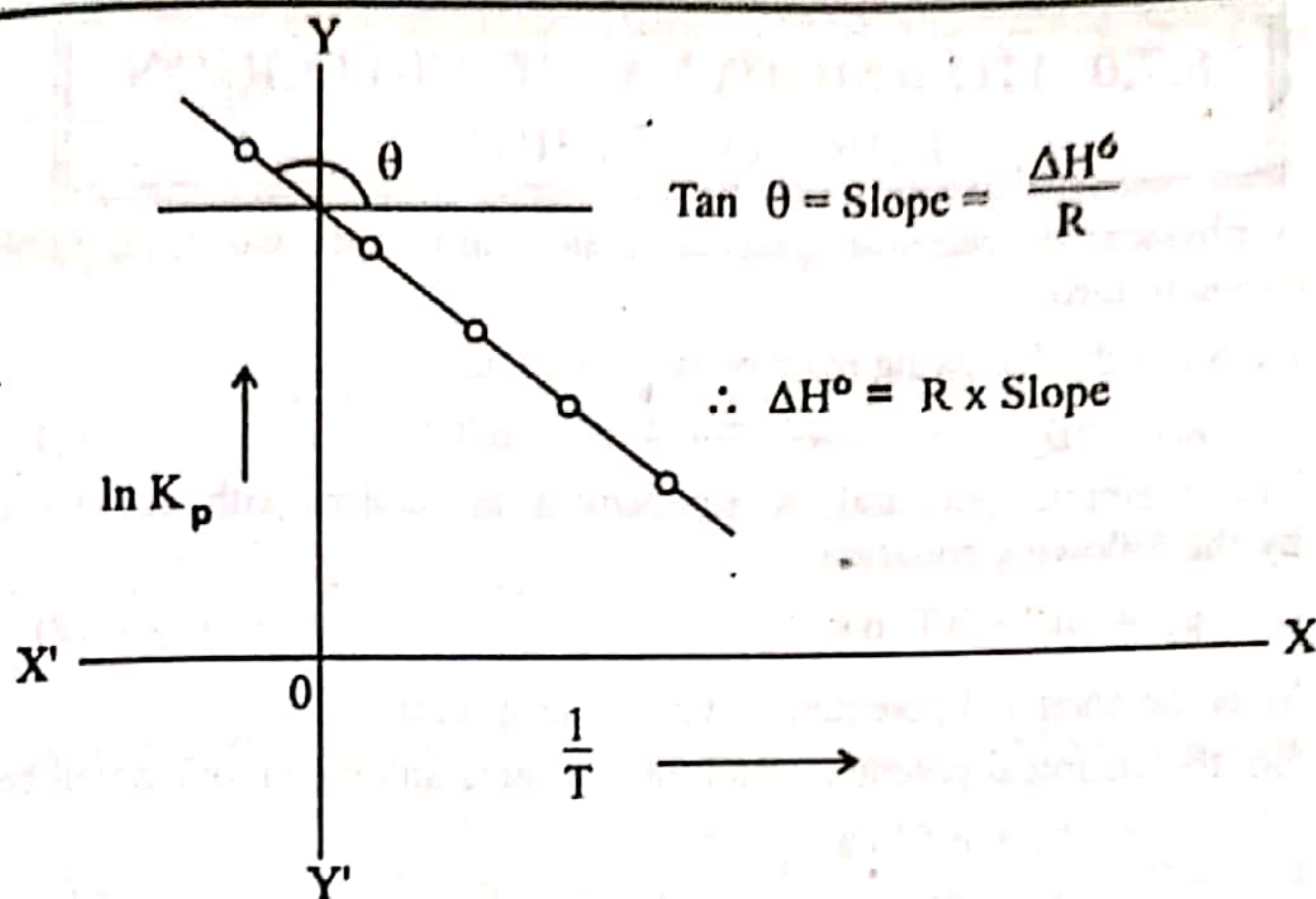


Fig. (2) A graph plotted between $\ln K_p$ and $\frac{1}{T}$ to find ΔH° .

This graph is for those reactions which are endothermic, if the reaction is exothermic, then the slope of straight line will be positive.

6.6.2 Definite Integration of Van't Hoff equation:

When we plot the above graph of equation (7) we have to measure at least five to six ' K_p ' values at different temperatures, and then we are able to calculate ' ΔH° ' for the reaction.

For practical applications, it is more convenient to integrate the Van't Hoff equation between two temperatures ' T_1 ' and ' T_2 '. We suppose that at temperature ' T_1 ', the equilibrium constant is ' K_{p_1} ' and at ' T_2 ', equilibrium constant is ' K_{p_2} '.

$$\int_{K_{p_1}}^{K_{p_2}} d \ln K_p = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

Doing the integration and putting the limits

$$\ln \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

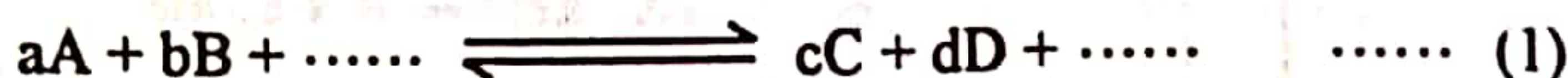
$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

It means that if we know two temperatures and two equilibrium constants, then we can calculate the enthalpy change ' ΔH° ' of reaction under standard conditions.

6.7.0 THERMODYNAMIC CRITERION FOR EQUILIBRIUM

A physical or chemical process is in equilibrium, when the Gibbs free energy change is zero.

Consider the following reaction in general, as



The chemical potential of an element is related with activity of that element by the following equation.

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad \dots (2)$$

' μ ' is the chemical potential of any of the species.

So, the chemical potential of all the reactants and the products will be

$$\left. \begin{aligned} \mu_A &= \mu_A^\circ + RT \ln a_A \\ \mu_B &= \mu_B^\circ + RT \ln a_B \\ \mu_C &= \mu_C^\circ + RT \ln a_C \\ \mu_D &= \mu_D^\circ + RT \ln a_D \end{aligned} \right\} \dots (3)$$

Free energy change of a reaction is the difference of free energies of reactions and products

$$\Delta G = \sum G_P - \sum G_R \quad \dots (4)$$

Actually, free energy change is the difference of chemical potentials of reactants and products.

$$\Delta G = (c\mu_C + d\mu_D + \dots) - (a\mu_A + b\mu_B + \dots)$$

Putting the set of equations (3)

$$\begin{aligned} \Delta G &= [c(\mu_C^\circ + RT \ln a_C) + d(\mu_D^\circ + RT \ln a_D) + \dots] \\ &\quad - [a(\mu_A^\circ + RT \ln a_A) + b(\mu_B^\circ + RT \ln a_B) + \dots] \end{aligned}$$

$$\begin{aligned} \Delta G &= (c\mu_C^\circ + d\mu_D^\circ + \dots - a\mu_A^\circ - b\mu_B^\circ - \dots) \\ &\quad + (RT \ln a_C^c + RT \ln a_D^d + \dots - RT \ln a_A^a - RT \ln a_B^b + \dots) \end{aligned}$$

$$\text{Now, } (c\mu_C^\circ + d\mu_D^\circ + \dots) - (a\mu_A^\circ + b\mu_B^\circ + \dots) = \Delta G^\circ$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_C^c a_D^d \dots}{a_A^a a_B^b \dots} \quad \dots (5)$$

Where 'a' represents the activities. ' ΔG° ' which is equal to ' ΔG ', when each of substances involved in the reaction is in its unit activity state, is called standard free energy change of the reaction. When the system is at equilibrium, ' ΔG ' must be zero. Hence,

$$0 = \Delta G^\circ + RT \ln \left(\frac{a_C^c a_D^d \dots}{a_A^a a_B^b \dots} \right) \quad \dots (6)$$

The quotient in the parenthesis is equal to K , which is called the equilibrium constant.

$$\text{So, } \Delta G^\circ = -RT \ln K \quad \dots\dots (7)$$

Substituting this value of ΔG° in equation (5), we get

$$-\Delta G = RT \ln K - RT \ln \frac{a^c_C a^d_D \dots\dots}{a^a_A a^b_B \dots\dots}$$

$$-\Delta G = RT \ln K - RT \sum n \ln a \quad \dots\dots (8)$$

$$\text{Where } \sum n \ln a = \ln \frac{a^c_C a^d_D \dots\dots}{a^a_A a^b_B \dots\dots} \quad \dots\dots (9)$$

Equation (8), is called the reaction isotherm or Van't Hoff's isotherm.

If the reaction involves gases and also if all gases involved in the reaction behave ideally, then activities may be replaced by the partial pressures and hence from equation (8), we get

$$-\Delta G = RT \ln K_p - RT \sum n \ln p \quad \dots\dots (10)$$

Where ' $\sum n \ln p$ ' is given by a similar expression as equation (9) using partial pressure notation 'p' instead of 'a'.

Similarly, for molar concentration and mole fraction we get

$$-\Delta G = RT \ln K_c - RT \sum n \ln C \quad \dots\dots (11)$$

$$-\Delta G = RT \ln K_x - RT \sum n \ln X \quad \dots\dots (12)$$

Equation (10), (11) and (12) are also the expression for a reaction isotherm.

The condition for spontaneous occurrence of reaction is that the free energy of the system should decrease. i.e., ' ΔG ' should assume a negative value. This is the case when $\ln K < \sum n \ln a$. Therefore, when $\ln K < \sum n \ln a$, the reaction will occur spontaneously.

When $\ln K = \sum n \ln a$, $\Delta G = 0$, the system will be in equilibrium. Under such conditions, no net reaction will occur in the system.

Applications:

- (i) The free energy change gives the spontaneity of reaction.
- (ii) It is related with E.M.F. of the cells.
- (iii) K_c or K_p can be calculated.
- (iv) ΔH and ΔS can be calculated

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