→ Chemical equilibrium: >

- It is found from experimental observations that most of chemical reactions when carried out in closed vessels do not go to completion. Under these conditions, a reaction starts by itself or by initiation, continues for some time at diminishing rates and ultimately appears to stop. The reactants may still be present but they do not appear to change into products any more. In this case, the products of the reaction start reacting at the same rate as the reactants. In other words, the rate of the back reaction becomes equal to the rate of the forward reaction.

  The composition of the reaction mixture is the same irrespective of the initial state of the system, i.e., irrespective of the fact whether we start with the reactants or the products. The reaction in such condition is said to be in a state of equilibrium.
- A chemical equilibrium can be defined as a dynamic state at which the rate of forward and backward reactions are the same and at that time all the reactants and products are present.
- Chemical equilibrium may be homogeneous or heterogeneous depending upon whether the reaction takes place (i) in one phase or (ii) in two or more phases.
- Example :-

$$2Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

$$H_2 + I_2 \rightleftharpoons 2HI$$

→ Characteristics of chemical equilibrium :→

- Chemical equilibrium, at a given temperature, can be characterised by constancy of certain observable properties like pressure, concentration, density or colour.
- Chemical equilibrium can be approached from either direction.
- A catalyst can speed up the approach of equilibrium but fails to alter the state of equilibrium.
- Chemical equilibrium is dynamic in nature because it involves two opposing reactions.

→ Law of mass action :→

- The relationship between the quantities of the reacting substances and the products formed can be determined with the help of law of mass action.
- This law was proposed by Guldberg and Waage in 1867.
- According to this law, "The rate at which substance reacts is proportional to its active mass and rate of a chemical reaction is directly proportional to the product of the active masses of the reacting substances."
- The term active mass means molecular concentration. Active mass of a substance is expressed by enclosing the symbol or the formula of a substance in square brackets [ ].
- Consider a general reversible chemical reaction

$$aA + bB \rightleftharpoons mM + nN$$

According to law of mass action

The rate of forward reaction $r_f \propto [A]^a [B]^b$

or $r_f = K_f [A]^a [B]^b$

and The rate of reverse reaction $r_r \propto [M]^m [N]^n$

$r_r = K_r [M]^m [N]^n$

where K_f and K_r are proportionality constant

K_f = The rate constant for forward reaction

K_r = The rate constant for reverse reaction

- At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction, that is,

$$K_f [A]^a [B]^b = K_r [M]^m [N]^n$$

$$K_{eq} = \frac{K_f}{K_r} = \frac{[M]^m [N]^n}{[A]^a [B]^b} \quad — ①$$

The constant K_{eq} is called the equilibrium constant of the reaction. Eq ① represents law of chemical equilibrium.

The equilibrium concentrations in eq. ① can be written in term of activities (a_i), partial pressures (P_i), molar concentrations (C_i) or mole fraction (x_i) of the species involved in the reaction. Consequently, K_{eq} will have different numerical values for a given chemical reaction.

→ Relation between K_p and K_c :→

– Consider a general reversible chemical reaction

$$aA + bB \rightleftharpoons mM + nN$$

Equilibrium constant for above reaction in term of molar concentrations and partial pressures are given by following equations respectively.

$$K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b} \quad — ①$$

and $$K_p = \frac{P_M^m \; P_N^n}{P_A^a \; P_B^b} \quad ②$$

For an ideal gaseous mixture,

$$PV = nRT$$

$$P = \frac{n}{V} RT$$

$$\text{or} \quad P = CRT \quad — ③ \qquad \because C = \frac{n}{V}$$

Thus $$P_M = [M]RT \quad , \qquad P_N = [N]RT$$

$$P_A = [A]RT \quad , \qquad P_B = [B]RT$$

Substitute values of partial pressures in eq. ②

$$K_p = \frac{[M]^m (RT)^m \; [N]^n (RT)^n}{[A]^a (RT)^a \; [B]^b (RT)^n}$$

or $$K_p = \frac{[M]^m [N]^n}{[A]^a [B]^b} \cdot \frac{(RT)^{m+n}}{(RT)^{a+b}}$$

From eq. ①

$$K_p = K_c \cdot \frac{(RT)^{m+n}}{(RT)^{a+b}}$$

or $$K_p = K_c (RT)^{(m+n)-(a+b)}$$

or $$K_p = K_c (RT)^{\Delta n} \quad — ④ \qquad \Delta n = (m+n)-(a+b)$$

Eq. ④ shows relationship between K_p and K_c

- If $\Delta n = 0$, then $m+n = a+b$, i.e. number of moles of products equals the number of moles of reactants. Thus

$$K_p = K_c$$

→ Thermodynamic derivation of law of mass action: Equilibrium constant and free energy: Reaction isotherm :→

- Consider a general reversible chemical reaction where the reactants and the products are assumed to be ideal gases

$$aA + bB \rightleftharpoons mM + nN$$

We know that chemical potential (i.e. Gibbs free energy) of reactants consisting of a moles of A and b moles of B is given by the expression

$$G_{reactants} = a\mu_A + b\mu_B \quad - ①$$

where μ_A and μ_B are the chemical potentials of A and B.

Similarly, for the products we have

$$G_{products} = m\mu_M + n\mu_N \quad - ②$$

In each case, pressure and temperature are constant. The free energy of the reaction is equal to the difference between the free energy of the products and that of the reactants, that is,

$$\Delta G_{reaction} = G_{products} - G_{reactants}$$

$$= (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) \quad - ③$$

At equilibrium $\Delta G = 0$

$$(m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) = 0 \quad - ④$$

- The chemical potential of the ith species in the gaseous state is given by

$$\mu_i = \mu_i^\circ + RT \ln P_i \quad — ⑤$$

Where P_i = Partial pressure of the ith component
μ_i° = standard chemical potential (i.e. when partial pressure of the ith component is unity)

From ④ and ⑤

$$[m(\mu_M^\circ + RT\ln P_M) + n(\mu_N^\circ + RT\ln P_N)] - [a(\mu_A^\circ + RT\ln P_A) + b(\mu_B^\circ + RT\ln P_B)] = 0$$

$$[m\mu^\circ_M + mRT\ln P_M + n\mu^\circ_N + nRT\ln P_N] - [a\mu^\circ_A + aRT\ln P_A + b\mu^\circ_B + bRT\ln P_B] = 0$$

$$[m\mu^\circ_M + n\mu^\circ_N + nRT\ln P_M + nRT\ln P_N] - [a\mu^\circ_A + b\mu^\circ_B + aRT\ln P_A + bRT\ln P_B] = 0$$

$$[mRT\ln P_M + nRT\ln P_N] - [aRT\ln P_A + bRT\ln P_B] = -[(m\mu^\circ_M + n\mu^\circ_N) - (a\mu^\circ_A + b\mu^\circ_B)]$$

$$[RT\ln P_M^m + RT\ln P_N^n] - [RT\ln P_A^a + RT\ln P_B^b] = -[(m\mu^\circ_M + n\mu^\circ_N) - (a\mu^\circ_A + b\mu^\circ_B)]$$

$$[RT\ln P_M^m P_N^n] - [RT\ln P_A^a P_B^b] = -[(m\mu^\circ_M + n\mu^\circ_N) - (a\mu^\circ_A + b\mu^\circ_B)]$$

$$RT\ln \frac{P_M^m P_N^n}{P_A^a P_B^b} = -[G^\circ_{products} - G^\circ_{reactants}]$$

$$RT\ln \frac{P_M^m P_N^n}{P_A^a P_B^b} = -\Delta G^\circ_{reaction} \quad — ⑥$$

$$\frac{p_M^m \, p_N^n}{p_A^a \, p_B^b} = e^{-\Delta G^\circ/RT} \quad — ⑦$$

- Since ΔG° depends upon only upon temperature and R is gas constant. hence the right hand side of eq. ⑦ is a constant at constant temperature. Thus.

$$\frac{p_M^m \, p_N^n}{p_A^a \, p_B^b} = \text{Constant} = K_p \quad — ⑧$$

Eq. ⑧ is called the law of chemical equilibrium.

From eq. ⑥ and ⑧

$$RT \ln K_p = -\Delta G^\circ$$

or
$$\Delta G^\circ = -RT \ln K_p \quad — ⑨$$

Eq. ⑨ is known as the van't Hoff reaction isotherm and this equation shows relation between equilibrium constant and free energy.

- If the chemical potentials are expressed in terms of mole fractions (x_i), then

$$\mu_i = \mu_i^\circ + RT \ln x_i \quad , \quad K_x = \frac{x_M^n \, x_N^n}{x_A^a \, x_B^b} \quad , \quad \Delta G^\circ = -RT \ln K_x$$

- If the chemical potentials are expressed in terms of molar concentrations (c_i), then

$$\mu_i = \mu_i^\circ + RT \ln c_i \quad , \quad K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b} \quad , \quad \Delta G^\circ = -RT \ln K_c$$

→ Temperature-dependance of the equilibrium constant : Reaction isochore :→

– The relation between equilibrium constant and free energy (reaction isotherm) is given by

$$\Delta G^\circ = -RT \ln K_p \quad — ①$$

Differentiate eq. ① with respect to temperature at constant pressure

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

multiply both sides by T

$$T\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_p = -RT\ln K_p - RT^2\frac{d\ln K_p}{dT}$$

or

$$T\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_p = \Delta G^\circ - RT^2\frac{d\ln K_p}{dT} \quad — ③ \qquad \because \Delta G^\circ = -RT\ln K_p$$

From Gibbs-Helmholtz equation

$$\Delta G^\circ = \Delta H^\circ + T\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_p \quad — ④$$

From eq. ③ and ④

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

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

or $\frac{d\ln K_p}{dT} = \frac{\Delta H^o}{RT^2}$ — ⑤

Eq. ⑤ is called van't Hoff reaction isochore.

→ Integrated form of the van't Hoff equation: →

- The integration of eq. ⑤ depends upon the manner in which ΔH^o depends upon temperature. If, over a short temperature range, ΔH^o is assumed to be temperature - independent. eq. ⑤ can be written as

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

On integration

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

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

or $\ln K_p = -\frac{\Delta H^o}{RT} + I$ — ⑥

where I is the integration constant. According to eq. ⑥, a plot of $\ln K_p$ verses $1/T$ gives a straigh line with slope = $-\Delta H^o/R$. Thus from the, ΔH^o can be determined

$$\Delta H^o = -R \times \text{slople}$$

- On integrating eq. ⑤ between T_1 and T_2 when equilibrium constants are $K_{p,1}$ and $K_{p,2}$, assuming that ΔH° is constant over this temperature range

$$\int_{K_{p,1}}^{K_{p,2}} d\ln K_p = \frac{\Delta H^\circ}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

or $$\ln\frac{K_{p,2}}{K_{p,1}} = \frac{\Delta H^\circ}{R}\left[-\frac{1}{T_2}-\left(-\frac{1}{T_1}\right)\right]$$

or $$\ln\frac{K_{p,2}}{K_{p,1}} = \frac{\Delta H^\circ}{R}\left[\frac{T_2-T_1}{T_1T_2}\right] \quad - ⑦$$

This is integrated van't Hoff equation.

→ Clapeyron equation:→

- An important equation for one-component two-phase system was derived in the nineteenth century by Clapeyron from the second law of thermodynamics. It is known as the Clapeyron equation.
- The two phases in equilibrium may be any of the following-

(i) Solid and liquid, $S \rightleftharpoons L$, at the melting point of solid.

(ii) Liquid and Vapour, $L \rightleftharpoons V$, at the boiling point of liquid.

(iii) Solid and vapour, $S \rightleftharpoons V$, at the sublimation temperature of solid.

(iv) one crystalline form and another crystalline form as, for example, rhombic and monoclinic sulphur, $S_R \rightleftharpoons S_M$, at the transistion temperature of the two alltropic forms.

- In case of equilibrium state, equal amounts of a given substance must have exactly the same free energy in the two phases.
- Consider, in general, the change of a pure substance from phase A to another phase B in equilibrium with it at given temperature and pressure.

If G_A = free energy per mole of the substance in the initial phase A.

G_B = free energy per mole of the substance in the final phase B.

At equilibrium

$$G_A = G_B$$

i.e. $$\Delta G = G_B - G_A = 0$$

- If the temperature of such a system is raised, say, from T to T + dT, the pressure will also have to change, say, from P to P + dP, in order to maintain the equilibrium. The relationship between dT and dP can be derived from thermodynamics.
- Let the free energy per mole of the substance in phase A at the new temperature and be $G_A + dG_A$ and in phase B be $G_B + dG_B$. Since the two phases are still in equilibrium, hence,

$$G_A + dG_A = G_B + dG_B$$

According to thermodynamics,

$$dG = VdP - SdT \quad — \quad ①$$

For phase A

$$dG_A = V_A dP - S_A dT \quad — \quad ②$$

and for phase B

$$dG_B = V_B dP - S_B dT \quad — \quad ③$$

Since $G_A = G_B$, hence

$$dG_A = dG_B$$

$$V_A dP - S_A dT = V_B dP - S_B dT$$

or $$S_B dT - S_A dT = V_B dP - V_A dP$$

or $$dT (S_B - S_A) = dP (V_B - V_A)$$

or $$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} \quad — \quad ④$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad — ⑤$$

where $\Delta S = S_B - S_A$ = Change in entropy

and $\Delta V = V_B - V_A$ = Change in volume

If q is the heat exchanged reversibly per mole of the substance during the phase transformation at temperature T, then the change in entropy (ΔS) in this process is given by

$$\Delta S = \frac{q}{T}$$

Hence, from eq. ⑤

$$\frac{dP}{dT} = \frac{q}{T\Delta V}$$

Thus, $$\frac{dP}{dT} = \frac{q}{T(V_B - V_A)} \quad — ⑥$$

Eq. ⑥ is called the Clapeyron equation, named after the French engineer Benoit P. Clapeyron (1799-1864).

Eq. ⑥ gives change in pressure dp with change in temperature dT, in the case of a system containing two phases of a pure substance in equilibrium with each other.

Eq. ⑥ is useful in phase equilibria.

- Suppose the system consist of water in the two phases, viz., liquid and vapour, in equilibrium with each other at the temperature T, i.e.

$$\text{Water (liquid)} \rightleftharpoons \text{Water (vapour)}$$

Then $q =$ Molar heat of vaporisation, ΔH_{vap}

$V_B =$ Volume of one mole of water in vapour state, V_g

$V_A =$ Volume of one mole of water in liquid state, V_l

From eq. ⑥

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T(V_g - V_l)} \quad — ⑦$$

- If the system consist of water at its freezing point, then, the two phases in equilibrium will be

$$\text{Water (solid)} \rightleftharpoons \text{Water (liquid)}$$

Then $q =$ Molar heat of fusion, ΔH_{fus}

$V_B =$ Volume of one mole of water in liquid state, V_l

$V_A =$ Volume of one mole of water in solid state, V_s

From eq. ⑦

$$\frac{dP}{dT} = \frac{\Delta H_{fus}}{T(V_l - V_s)} \quad — ⑧$$

→ Clausius - Clapeyron equation :→ Integrated form of Clapeyron equation for liquid ⇌ Vapour equilibrium :→

– Clapeyron equation for liquid ⇌ vapour equilibrium is

$$\frac{dP}{dT} = \frac{\Delta H vap}{T(V_g - V_l)} \quad — ①$$

The molar volume of a substance in the vapour state is considerably greater than that in liquid state. In case of water, for example, value of V_g at 100°c is 30060 ml while that of V_l is only a little more than 18 ml.

Thus, $V_g >>> V_l$, Eq. ① can be written as

$$\frac{dP}{dT} = \frac{\Delta H vap}{T V_g} \quad — ②$$

Ideal gas equation for one mole

$$PV = RT$$

or $V_g = \frac{RT}{P}$

Hence, eq. ② becomes

$$\frac{dP}{dT} = \frac{\Delta H vap}{T} \times \frac{P}{RT}$$

or $\frac{dP}{dT} = P \frac{\Delta H vap}{RT^2} \quad — ③$

$$\text{or} \quad \frac{1}{P} \times \frac{dP}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

$$\text{or} \quad \frac{d(\ln P)}{dT} = \frac{\Delta H_{vap}}{RT^2} \quad — ④$$

Assuming that ΔH_v remains constant over a small range of temperature, we have

$$d(\ln P) = \frac{\Delta H_{vap}}{R} \cdot \frac{dT}{T^2}$$

$$\int d(\ln p) = \frac{\Delta H_{vap}}{R} \int \frac{dT}{T^2} \quad — ⑤$$

$$\text{or} \quad \ln P = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \quad — ⑥$$

where C is integration constant

Eq. ⑥ is the equation of straight line. Hence, the plot of $\ln p$ against $1/T$ should yield a straight line with slope $= -\Delta H_{vap}/R$ and intercept $= C$. Thus using slope ΔH_{vap} can be easily calculated.

Eq. ⑤ can also be integrated between limits of pressures P_1 and P_2 corresponding to temp T_1 and T_2. Thus,

$$\int_{P_1}^{P_2} d(\ln p) = \frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2} = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{\Delta H_{vap}}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad — ⑦$$

Eq. ⑦ is called Clausius-Clapeyron equation.

→ Applications of Clausius - Clapeyron equation :→

1. Calculation of molar heat of vaporisation, ΔH_{vap} :→

— If the pressures P_1 and P_2 at temperatures T_1 and T_2 are known then, ΔH_{vap} can be calculated easily.

Example:- vapour pressures of water at 95°C and 100°C are 634 and 760 mm, respectively. Calculate the molar heat of vaporisation, ΔH_{vap}, of water between 95°C and 100°C.

Solution:- Given data $T_1 = 95°C\ (368\,K)$ $T_2 = 100°C\ (373\,K)$

$P_1 = 634\ mm$ $P_2 = 760\ mm$ $\Delta H_{vap} = ?$

Substituting the given data in following eq.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\ln \frac{760\ mm}{634\ mm} = \frac{\Delta H_{vap}}{8.314\ J K^{-1} mol^{-1}}\left[\frac{373\,K - 368\,K}{(368\,K)(373\,K)}\right]$$

$$0.1812 = \frac{\Delta H_{vap}}{8.314}\left[\frac{5}{137264}\right]$$

$$\Delta H_{vap} = \frac{0.1812 \times 8.314 \times 137264}{5}$$

$$\Delta H_{vap} = 41357.5\ J\ mol^{-1}$$

2. Effect of temperature on vapour pressure of a liquid :→

- If vapour pressure of a liquid at one temperature is known, that at another temperature can be calculated.

Example:- The vapour pressure of water at 100°c is 760 mm. what will be vapour pressure at 95°c ? The heat of vaporisation of water in this temperature range is 41.27 KJ per mole.

Solution:- Data given $\Delta H_{vap} = 41.27 \text{ KJ mol}^{-1} = 41270 \text{ J mol}^{-1}$

$T_1 = 100°c \ (373 \text{ K})$, $T_2 = 95°c \ (368 \text{K})$, $P_1 = 760 \text{ mm}$ $P_2 = ?$

Substituting the given data in following eq.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\ln \frac{P_2}{760 \text{ mm}} = \frac{41270 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-} \text{mol}^{-1}} \left[\frac{368\text{K} - 373\text{K}}{(373\text{K})(368\text{K})} \right]$$

$$\ln P_2 - 6.63 = \frac{41270}{8.314} \left[\frac{-5}{137264} \right]$$

$$\ln P_2 - 6.63 = -0.1808$$

$$\ln P_2 = 6.63 - 0.1808$$

$$\ln P_2 = 6.4492$$

$$P_2 = 632.2 \text{ mm}$$

3. Effect of pressure on boiling point:→

- If the boiling point of a liquid at one pressure is known, that at another pressure can be calculated.

Example:- Ether boils at 33.5°c at 760 mm pressure. At what temperature will it boil at a pressure of 750 mm, given that the heat of vaporisation of ether is 369.86 joules per gram.

Solution:- Data given $T_1 = 33.5°c\ (306.5\ K)$ $T_2 = ?$ $P_1 = 760\ mm$, $P_2 = 750\ mm$

$\Delta H_{vap} = 369.86\ J\ gm^{-1}$, $369.86 \times 74 = 27369.64\ J\ mol^{-1}$

Substituting the given data in following eq.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln \frac{750\ mm}{760\ mm} = \frac{27369.64\ J\ mol^{-1}}{8.314\ J\ K^{-1}\ mol^{-1}}\left[\frac{1}{306.5K} - \frac{1}{T_2}\right]$$

$$-0.0132 = 3292\left[\frac{1}{306.5} - \frac{1}{T_2}\right]$$

$$-0.0132 = \frac{3292}{306.5} - \frac{3292}{T_2}$$

$$-0.0132 = 10.74 - \frac{3292}{T_2}$$

$$\frac{3292}{T_2} = 10.74 + 0.013$$

$$T_2 = \frac{3292}{10.753} = 306.1\ K = 33.1°\ C$$

→ Le Chatelier's principle :→

- Henri Louis Le Chatelier (1850-1936), the french chemist, studied the effect of concentration, temperature and pressure on a large number of chemical equilibria. He summed up this conclusion in the form of generalisation known as Le Chatelier's principle.
- According to this principle," If an equilibrium is subjected to a stress, the equilibrium shifts in such a way as to reduce the stress."

  Thus, if a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of change.
- This principle follows from the van't Hoff equation for the temperature dependence of the equilibrium constant.

→ Effect of change of concentration:→

- Consider the following equilibrium

$$\underset{\text{Pale yellow}}{Fe^{+3}(aq)} + (SCN^-)(aq) \rightleftharpoons \underset{\text{Dark brown}}{[Fe(SCN)]^{2+}(aq.)}$$

- Suppose, some ferric salt ($FeCl_3$) is added to this equilibrium. The colour of the solution will darken immediately showing that there is increase in the concentration of the coloured complex $[Fe(SCN)]^{2+}$. This change is accordance with Le chatelier's principle.
- Similarly, some sulphocyanide salt (potassium sulphocyanide) is added to the equilibrium, the colour will darken again due to the formation of more of the ferri-sulphocyanide ion. Here again the addition of one of the reactants has led to the formation of the product.

- Now, suppose a small amount of potassium ferri-sulphocyanide capable of giving the complex ion, $[Fe(SCN)]^{2+}$ is added to the equilibrium. The solution becomes less coloured showing that the dark coloured $[Fe(SCN)]^{2+}$ complex ion has been changed into Fe^{+3} and $(SCN)^-$ ions. Thus, increasing the concentration of the product shift the equilibrium in favour of the reactants.

→ Effect of change of temperature: →

- A chemical equilibrium involves two opposing reactions: one favouring the products and the other favouring the reactants. If one of these is exothermic, the other must be enothermic.
- Consider the equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \; ; \quad \Delta H = +59.0 \text{ KJ}$$

In this equilibrium, the reaction favouring the product (NO_2) is seen to be endothermic. Therefore, the opposing reaction favouring the reactant (N_2O_4) must be exothermic. Now suppose the system is heated and its temperature is allowed to rise. According to Le Chatelier's principle, the equilibrium will shift in the direction which tends to undo the effect of heat, i.e., which tends to produce cooling. Therefore, the equilibrium will shift in favor of NO_2, i.e., the dissociation of N_2O_4 into NO_2 will increase

If system is cooled, the equilibrium will shift in the direction which tends to produce heat. Therefore, the equilibrium will shift in the direction which tends to produce heat. Therefore, the equilibrium will shift in the reverse direction, i.e. in favour of N_2O_4. The dissociation of N_2O_4 will decrease.

→ Effect of change of pressure :→

- If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure.
- Consider dissociation of N_2O_4 into NO_2

$$\begin{array}{ccc} N_2O_4\,(g) & \rightleftharpoons & 2NO_2\,(g) \\ 1 \text{ mole} & & 2 \text{ moles} \end{array}$$

Suppose the pressure on the system is increased. The volume of the system will decrease proportionately. The total number of moles per unit volume will now be more than before. The change can be counteracted if equilibrium shifts in that direction in which the total number of moles is decreased. This can be take place by the combination of NO_2 molecules to produce N_2O_4 molecules. Thus, application of pressure on the above system tends to shift the equilibrium in favour of N_2O_4.

→ Le Chatelier's principle and physical equilibria :→

– Le chatetier's principle is applicable to all types of equilibria involving not only chemical but physical change as well. A few examples of its application to physical equilibria are discussed below.

1. Vapour pressure of a liquid :→

– Consider the equilibrium

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

The change of a liquid into its vapour is accompanied by absorption of heat whereas the conversion of vapour into liquid is accompanied by evolution of heat. According to Le chatelier's principle, therefore, addition of heat to such a system will shift the equilibrium towards the right. On raising the temperature of the system, liquid will evaporate. This will raise the vapour pressure of the system. Thus, the vapour pressure of a liquid increases with rise in temperature.

2. Effect of pressure on the boiling point of a liquid :→

– Consider the equilibrium

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

The conversion of liquid into vapour is accompanied by increase of pressure (vapour pressure). Therefore, if pressure on the system is increased, some of the vapour will change into liquid so as to lower the pressure. Thus, the application of pressure on the system to condense the vapour into liquid state at a given temperature. In order to counteract it, a higher temp is needed. This explains the rise of boiling point of a liquid on the application of pressure.

3. Effect of pressure on the freezing point of a liquid (or the melting point of a solid):→

- At the melting point, solid and liquid are in equilibrium

$$\text{Solid} \rightleftharpoons \text{liquid}$$

When a solid melts, there is a usually a change, either increase or decrease of volume. For example, when ice melts, there is a decrease in volume, or at constant volume, there is decrease in pressure. Thus, increase of pressure on ice $\rightleftharpoons$ water system at a constant temperature will cause the equilibrium to shift towards the right, i.e., it will cause the ice to melt. Hence, in order to retain ice in equilibrium with water at the high pressure, it will be necessary to lower the temperature. Thus, the application of pressure will lower the melting point of ice.

4. Effect of temperature on solubility:→

- In most of cases, when a solute dissolves into solution, heat is absorbed, i.e., cooling results. Therefore, according to Le Chatelier's principle, when heat is supplied to a saturated solution, the change will take place in the direction which absorbs heat i.e. which tends to produce cooling. Therefore, some more of the solute will dissolve. In other words, the solubility of the substance increases with rise in temperature.

Dissolution of some salts is accompained by evolution of heat. Here, the solubility decreases with rise in temperature.