Chapter – 10

CHEMICAL EQUILIBRIUM

1 EQUILIBRIUM

The term "equilibrium" in physical sense is defined as the ''no change of state of the body''. The state of the body can be either the state of rest or the state of uniform motion. Such static equilibrium can be further categorized into stable and unstable equilibriums. Let us take an example to understand these two type of equilibriums.

Consider a truncated cone resting on a horizontal surface in two different positions, (a) and (b) shown in figure 1. Both the positions are said to be in equilibrium state.

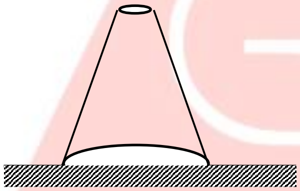

Fig 1. (a)

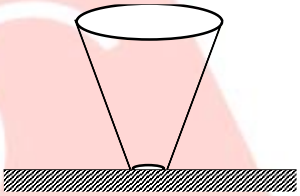

Fig 1. (b)

In position (a), if we displace cone slightly, it will retain its previous position while such a displacement in position (b), allow cone to change its position. Thus position (a) is referred as ***stable equilibrium*** while position (b) is termed as ***unstable equilibrium***.

You all must be acquainted with another well known equilibrium, equilibrium between liquid water and its vapour, $H_2O(\square) \rightleftharpoons H_2O(g)$. When $H_2O(l)$ is taken in a closed container, some water molecules go into the vapour phase (vaporization process) and simultaneously, water molecules return to the liquid phase (condensation process). Initially, the rate of vaporization is greater than the rate of condensation but after some time the rate of evaporation and the rate of condensation becomes equal. Thus, the number of water molecules leaving and the number of water molecules returning to the liquid phase are equal. At this stage, both the processes takes place but it seems that the changes are not occurring, as the composition of the system does not change. Such processes in which forward and backward changes are occurring at the same rate are referred as ***dynamic equilibrium***. This $H_2O(\square) \rightleftharpoons H_2O(g)$ equilibrium involving two phases of the same substance is called ***physical equilibrium*** because the changes that occur are physical changes.

In this lesson, we will be more concerned with the state of equilibrium attained in chemical reactions. Most of the chemical reactions are reversible in nature (i.e., occurs in both the directions). At the start of a reversible process containing only reactants, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, theoretically the reverse process also begins to take place and reactant molecules are formed from product molecules.

Chemical equilibrium is achieved when the rate of the forward and reverse reactions is equal and the concentrations of the reactants and products remain constant. Chemical equilibria are stable and dynamic in nature.

To understand chemical equilibrium, first we have to know about reversible reactions. The reversible reaction occurs in forward as well as reverse directions. The forward and reverse reactions are occurring in opposite direction. When the rates of two opposing reactions become equal, equilibrium is established. At equilibrium, no further change in the system is observed. This does not mean that the reaction has ceased, but a continuous cyclic situation result in which reactant gives product and products react to give original reactant.

Such equilibria are called dynamic equilibria.

Every chemical reaction has a tendency to attain equilibrium but there are certain chemical reactions, which remain unidirectional only. Such reactions are called ***irreversible reactions.*** Thus, there must be some criterion for a chemical reaction to become irreversible. When a chemical reaction follows any of the given two criterions, the reaction would be irreversible.

(a) If any of the product is insoluble (or gets precipitated).
(b) If the reaction is carried out in an open vessel and any of the product is in gaseous state.

The reactions of type (b) can be made reversible, if allowed to react in a closed vessel but for making reactions of type (a) to be reversible, we need very large excess of solvent to dissolve the insoluble product for the reverse reaction to take place. Thus, theoretically reactions of type
(b) are always considered irreversible.

2 REVERSIBLE REACTIONS AND CHEMICAL EQUILIBRIUM

REVERSIBLE REACTIONS

If the products of a certain reaction can give back the reactants under the same or different conditions, the reaction is said to be a reversible reaction. For example, when steam is passed over red hot iron, ferrosoferric oxide and hydrogen are formed.

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

On the other hand, when hydrogen is passed over heated ferrosoferric oxide, iron and steam are formed.

$$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

Now suppose, iron and steam are heated to a steady temperature ***in a closed vessel***, the reaction will not proceed to completion. To start with, we have only iron and steam and they would react to give Fe_3O_4 and H_2. As the concentrations of Fe and steam decrease with time, the rate of the reaction between iron and steam would decrease with time. At the same time, the amounts of Fe_3O_4 and H_2 increase with time. They would begin to react and the rate of this reaction would increase with time. After a sufficiently long time, it would be seen that the rate at which iron and steam react becomes equal to the rate at which Fe_3O_4 and H_2 react. Then we say that the system is in equilibrium. This equilibrium reaction is thus represented by

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

CHARACTERISTICS OF A CHEMICAL EQUILIBRIUM

- At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.
- Since both reactions take place at the same rate, the relative amounts of the reactants and products present at equilibrium will not change with time.
- The equilibrium is dynamic, i.e., the reactions do not cease. Both the forward and reverse reactions continue to take place, although at equal rates.
- Under the same conditions (temperature, pressure and concentration), the same state of equilibrium is reached. Thus when an equimolar mixture of H_2 and I_2 is heated to 440°C, 80% of the mixture would be converted to HI. If HI is heated at 440°C, only 20% would be converted into H_2 and I_2. This is an unfailing criterion of a chemical equilibrium.
- If one of the conditions (temperature, pressure or concentration) under which an equilibrium exists is altered, the equilibrium shifts and a new state of equilibrium is reached.
- A catalyst does not alter the position of equilibrium. It accelerates both the forward and reverse reactions to the same extent and so the same state of equilibrium is reached but quickly. So a catalyst hastens the attainment of equilibrium.

If the reactants and the products in a system are in the same phase, the equilibrium is said to be homogeneous.

For example,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

represents a homogeneous equilibrium in gaseous phase and

$$CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$$

represents a homogeneous equilibrium in solution phase.

A phase is a homogeneous (same composition and properties throughout) part of a system, separated from other phases (or homogeneous parts) by bounding surfaces.

- Any number of gases constitute only one phase.
- In liquid systems, the number of phases = number of layers in the system. Completely miscible liquids such as ethanol and water constitute a single phase. On the other hand, benzene - water system has 2 layers and so two phases.
- Each solid constitutes a separate phase, except in the case of solid solutions. [A solid solution, e.g., lead and silver, forms a homogeneous mixture.]

If more than one phase is present in a chemical equilibrium, it is said to be heterogeneous equilibrium.

For example,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

represents a heterogeneous equilibrium involving two solid phases and a gaseous phase.

3 THE LAW OF MASS ACTION

The law of mass action (given by Guldberg and Waage) states that the rate of a chemical reaction is proportional to the product of effective concentrations (active masses) of the reacting species, each raised to a power that is equal to the corresponding stoichiometric number of the substance appearing in the chemical reaction.

By the rate of a chemical reaction we mean the amount of reactant transformed into products in unit time. It is represented by dx/dt.

Active mass means the molar concentration, i.e., the number of moles in 1 litre. Suppose 3 moles of nitrogen are present in a 4 litre vessel, the active mass of nitrogen = 3/4 = 0.75 mole/litre. Active mass of a substance is represented by writing molar concentration in square brackets.

Active mass of reactant α molarity

Active mass of reactant = $\gamma \times$ molarity

where γ is the activity coefficient.

$\therefore$ $a = \gamma \times$ molarity

For very dilute solutions, the value of activity coefficient is unity.

$\therefore$ activity(a) = molarity.

Thus, in place of activity of any reactive species, molarity can be used for dilute solutions.

In IIT–JEE Syllabus, only dilute solutions are there, so everywhere we would be using the term molarity in place of active mass of a species.

4 EQUILIBRIUM CONSTANT, K_{eq}, K_C, K_P AND K_{PC}

(i) Let us have an equilibrium reaction as

$$X(g) + Y(g) \rightleftharpoons Z(g)$$

For this reaction, which is in equilibrium, there exist an equilibrium constant (K_{eq}) represented as

$$K_{eq} = \frac{[Z]}{[X]\,[Y]}$$

For the given equilibrium, irrespective of the reacting species (i.e, either X + Y or Z or X + Z or Y + Z or X + Y + Z) and their amount we start with, the ratio, $\frac{[Z]}{[X]\,[Y]}$ is always constant at a given temperature.

This really looks amazing. Isn't it? Let us see, how such a thing is possible.

We have learnt that at the equilibrium, rate of forward and reverse reactions are equal and we also know the law of mass action. Using this, we can write

Rate of forward reaction α [X] [Y]

Rate of forward reaction = k_f [X] [Y]

where k_f is the rate constant for the forward reaction.

Similarly, rate of reverse reaction α [Z]

Rate of reverse reaction = k_r [Z]

where k_r is the rate constant for the reverse reaction.

At equilibrium,

Rate of forward reaction = Rate of reverse reaction.

$$\therefore \quad k_f [X][Y] = k_r [Z]$$

$$\frac{k_f}{k_r} = \frac{[Z]}{[X][Y]}$$

Since, k_f and k_r are constants at a given temperature, so their ratio $\frac{k_f}{k_r}$ would also be a constant, referred as K_{eq}.

$$\therefore \quad K_{eq} = \frac{[Z]}{[X][Y]}$$

As K_{eq} is the ratio of rate constants for forward and reverse reaction, so the value of K_{eq} would always be a constant and will not depend on the species we have started with and their initial concentrations.

The given expression involves all variable terms (variable term means the concentration of the involved species changes from the start of the reaction to the stage when equilibrium is reached), so the ratio $\frac{[Z]}{[X][Y]}$ can also be referred as K_C.

$$\therefore \quad K_C = \frac{[Z]}{[X][Y]}$$

Thus, for the given equilibrium, it seems that K_{eq} and K_C are same but in actual practice for some other equilibrium, they are not same.

Assuming that the gases X, Y and Z behave ideally, we can use ideal gas equation for them.

$$PV = nRT$$

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

$$c = \frac{P}{RT}$$

$$\therefore \quad [X] = \frac{P_x}{RT}; \quad [Y] = \frac{P_y}{RT} \text{ and } [Z] = \frac{P_Z}{RT}$$

$$\therefore \quad K_C = \frac{\left(\frac{P_Z}{RT}\right)}{\left(\frac{P_X}{RT}\right)\left(\frac{P_Y}{RT}\right)} = \frac{P_Z \times RT}{P_X \times P_Y}$$

$$\frac{K_C}{RT} = \frac{P_Z}{P_X \times P_Y}$$

The LHS of the above expression is a constant since K_C , R and T, all are constant.

This implies that RHS is also a constant, which is represented by K_P.

$$\therefore \quad K_P = \frac{P_Z}{P_X \times P_Y}$$

Thus, expression of K_P involves partial pressures of all the involved species and represents the ratio of partial pressures of products to reactants of an equilibrium reaction.

(ii) Now, let us change the phase of reactant X from gaseous to pure solid. Then the equilibrium reaction can be shown as

$$X(s) + Y(g) \rightleftharpoons Z(g)$$

Its equilibrium constant (K_{eq}) would be

$$K_{eq} = \frac{[Z]}{[X][Y]}$$

Concentration of Y and Z is their respective number of moles per unit volume of the container (as the volume occupied by the gas is equal to the volume of the container). The concentration of X is the number of moles of X per unit volume of solid. As we know, the concentration of all pure solids (and pure liquids) is a constant as it is represented by d/M (where d and M represents its density and molar mass). This ratio of d/M will be a constant whether X is present initially or at equilibrium. This means that the concentration of X is not varying, but is a constant, which can be merged with K_{eq} to give another constant, called K_C.

$$K_{eq}[X] = \frac{[Z]}{[Y]}$$

$$\therefore \quad K_C = \frac{[Z]}{[Y]}$$

Thus expression of K_C involves only those species whose concentration changes during the reaction.
The distinction between K_{eq} and K_C is that the expression of K_{eq} involves all the species (whether they are pure solids, pure liquids, gases, solvents or solutions) while the K_C expression involves only those species whose concentration is a variable (like gases and solutions). Thus, expression of K_C is devoid of pure components (like pure solids and pure liquids) and solvents.

$$K_C = \frac{\frac{P_Z}{RT}}{\frac{P_Y}{RT}} = \frac{P_Z}{P_Y}$$

Since, LHS of the expression is a constant, so the ratio $\frac{P_Z}{P_Y}$ would also be a constant, represented by K_P.

$$\therefore \quad K_P = \frac{P_Z}{P_Y}$$

(iii) Now, let us change the phase of reactant X from pure solid to solution and add another gaseous product. The equilibrium reaction can now be represented as

$$X(soln.) + Y(g) \rightleftharpoons Z(g) + A(g)$$

$$K_{eq} = \frac{[Z][A]}{[X][Y]}$$

We have seen above that concentration of Y, Z and A is a variable but what about the concentration of X now. Let us see. X in solution phase means some moles of X (solute) are dissolved in a particular solvent. The concentration of X is thus given as the number of moles of X per unit volume of solution(volume of the solution has major contribution from the volume of solvent and the volume of solute hardly contributes to it). Let the number of moles of X taken initially are 'a', which are dissolved in 'V' litre of solvent. So, the initial concentration of X is $\frac{a}{V}$. Now at equilibrium, the moles of X reacted with Y be

'x'. Thus the concentration of X now becomes $\left(\frac{a-x}{V}\right)$. This shows that the concentration of X changes during the reaction and X is thus a variable.

Thus, given expression of K_{eq} involve all variable terms, so the ratio $\frac{[Z]\,[A]}{[X]\,[Y]}$ can also be referred as K_C.

$$\therefore \qquad K_C = \frac{[Z]\,[A]}{[X]\,[Y]}$$

Now, if we try to express the concentration of X, Y, Z and A in terms of partial pressures, we would be able to do it only for Y, Z and A but not for X, since it is a solution. As the concentration of X cannot be expressed in terms of its pressure or vapour pressure and constants, so it should be kept as concentration term only in the equilibrium constant expression.

$$\therefore \qquad K_C = \frac{\left(\frac{P_Z}{RT}\right)\left(\frac{P_A}{RT}\right)}{[X]\left(\frac{P_Y}{RT}\right)} = \frac{P_Z \times P_A}{[X]\,P_Y \times RT}$$

$$K_C(RT) = \frac{P_Z \times P_A}{[X]\,P_Y}$$

The LHS of the expression is a constant (as K_C, R and T all are constant), which implies that the RHS will also be a constant. But RHS of the expression can neither be called K_P (as all are not partial pressure terms) nor K_C (as all are not concentration terms), so such expression that involves partial pressure and concentration terms both are referred as K_{PC}.

$$\therefore \qquad K_{PC} = \frac{P_Z \times P_A}{[X]\,P_Y}$$

Thus, K_P can exist only for that equilibrium which satisfies these two conditions.

(a) At least one of the reactant or product should be in gaseous phase and

(b) No component of the equilibrium should be in solution phase (because when solution is present, the equilibrium constant would be called K_{PC}).

(iv) Let us consider a different equilibrium reaction of the type,

$$n_1A(g) + n_2B(g) \rightleftharpoons m_1C(g) + m_2D(g)$$

The equilibrium constant, K_{eq} would be

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

Since, in this expression all the terms involved are variables, so the ratio $\frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}}$ would also be a constant called K_c.

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

The concentration terms can be replaced by $\frac{P}{RT}$ for each gaseous species.

Thus,
$$K_C = \frac{\left[\frac{P_C}{RT}\right]^{m_1}\left[\frac{P_D}{RT}\right]^{m_2}}{\left[\frac{P_A}{RT}\right]^{n_1}\left[\frac{P_B}{RT}\right]^{n_2}}$$

Rearranging the expression gives

$$K_C(RT)^{(m_1+m_2)-(n_1+n_2)} = \frac{(P_C)^{m_1}(P_D)^{m_2}}{(P_A)^{n_1}(P_B)^{n_2}} \quad \text{.....(i)}$$

The LHS of the expression is a constant since K_C, R, T and all stoichiometric coefficients are constant. So, RHS of the expression would also be a constant called as K_P (as the RHS involved all partial pressure terms).

$$\therefore \quad K_P = \frac{(P_C)^{m_1}(P_D)^{m_2}}{(P_A)^{n_1}(P_B)^{n_2}} \quad \text{.....(ii)}$$

Using equation (i) and (ii), we can write

$$K_P = K_C(RT)^{(m_1+m_2)-(n_1+n_2)}$$

or **$K_P = K_C\,(RT)^{\Delta n}$**

where Δn = sum of the number of moles of gaseous products – sum of the number of moles of gaseous reactants.

R = gas constant

and T = absolute or Kelvin temperature at which equilibrium is established.

Since, partial pressures are generally noted in atm and concentrations are measured in $\left(\frac{\text{moles}}{\text{litre}}\right)$, so the value of R used in the given expression should be in ***litre–atm per mole per Kelvin***.

(a) When $\Delta n = 0$, then $K_P = K_C$.
For example, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(b) When $\Delta n > 0$, then $K_P > K_C$.
For example, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
where $\Delta n = 2 - 1 = 1$
and $N_4O_4(g) \rightleftharpoons 2NO_2(g)$
where $\Delta n = 2 - 1 = 1$

(c) When $\Delta n < 0$, then $K_P < K_C$.
For example, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
where $\Delta n = 2 - (3 + 1) = -2$.

5 UNITS OF K_P AND K_C

Although it is not customary to mention the units of equilibrium constants K_P and K_C but when required, the unit of K_C would be $\left(\frac{\text{moles}}{\text{litre}}\right)^{\Delta n}$ as the concentration of a species is generally expressed in moles/litre and the unit of K_P would be $(\text{atm})^{\Delta n}$ as the partial pressure is generally measured in atm.

- ***In problems, when the unit of K_P and K_C for equilibrium are given, do check that the value (magnitude) of equilibrium constant is given for the equilibrium in forward direction or reverse direction.***

6 PREDICTING THE DEIRECTION OF ATTAINMENT OF EQUILIBRIUM

The equilibrium constant, K_c for the reaction between $H_2(g)$ and $I_2(g)$ to form HI(g)

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 54.5 at 450°C.

Let the number of moles of H_2, I_2 and HI, taken in a 1 litre container at 450°C are 0.243, 0.146 and 1.98 respectively. Will there be a net reaction to form more H_2 and I_2 or more HI? This question can be answered by first calculating reaction quotient.

The reaction quotient is defined as the ratio of concentration of the reacting species at any point of time other than the equilibrium stage. It is represented by Q. Thus, inserting the starting concentrations of H_2, I_2 and HI in the equilibrium constant expression gives

$$Q = \frac{[HI]_0^2}{[H_2]_0[I_2]_0} = \frac{(1.98)^2}{(0.243)\,(0.146)} = 110.5$$

where the subscript 0 indicates initial concentrations (before equilibrium is reached).

As we know that every reaction has a tendency to attain equilibrium, so Q value should approach K_c value. In the present case, Q value is greater than K_c value, so value of Q can approach K_c value only when HI starts converting into H_2 and I_2. Thus, when $Q > K_c$, the net reaction proceeds from right to left to reach equilibrium.

To determine the direction in which the net reaction will proceed to achieve equilibrium, we compare the values of Q and K_c. The three possible cases are as follows:

(a) $Q > K_c$: For such a system, products must be converted to reactants to reach equilibrium. The system proceeds from right to left (consuming products, forming reactants) to reach equilibrium.

(b) $Q = K_c$: The initial concentrations are the equilibrium concentrations. So, the system is already at equilibrium.

(c) $Q_c < K_c$: For such a system, reactants must be converted to products to reach equilibrium. The system proceeds from left to right (consuming reactants, forming products) to attain equilibrium.

7 FACTORS AFFECTING EQUILIBRIUM CONSTANT

7.1 NATURE OF REACTANTS AND/OR PRODUCTS

The value of equilibrium constant depends on the nature of reactants as well as on the products. By changing reactant(s) or product(s) of a reaction, the equilibrium constant of the reaction changes.

For example,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)\ ;\ K_{c_1} = \frac{[NO]^2}{[N_2]\,[O_2]}$$

$$N_2(g) + 2O_2 \rightleftharpoons 2NO_2(g)\ ;\ K_{c_2} = \frac{[NO_2]^2}{[N_2]\,[O_2]^2}$$

Although the reactants are same in the two reactions but the products being different, the value of equilibrium constant for the two reactions will be different. If we start with ‘a’ and ‘b’ moles of N_2 and O_2 respectively in both the reactions, carried out in same vessel (V litre capacity), the extent of two reactions occurring will be different and thus, the K_C for the two reactions differ.

Similarly for reactions,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

The values of the equilibrium constant for the two reactions will be completely different as one of the reactant in the two reactions is different.

7.2 TEMPERATURE

The variation of equilibrium constant with temperature is given by the relation

$$\log\frac{K_2}{K_1}=\frac{\Delta H}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right).$$

This can be obtained by the help of Arrhenius equation.
The Arrhenius equation for the rate constant of forward reaction is

$$k_f=A_f e^{-E_{a(f)}/RT} \qquad \ldots\ldots\ldots(2)$$

where, k_f = rate constant for forward reaction, A_f = Arrhenius constant for forward reaction, and E_{a_f} = Energy of activation for forward reaction.
Similarly, Arrhenius equation for the rate constant of reverse reaction would be

$$k_r=A_r e^{-E_{a(r)}/RT} \qquad \ldots\ldots\ldots(3)$$

where, k_r = rate constant for reverse reaction, A_r = Arrhenius constant for reverse reaction, and E_{a_r} = Energy of activation for reverse reaction.
Dividing (2) by (3) we get,

$$\frac{k_f}{k_r}=\frac{A_f}{A_r}e^{\left(\frac{E_{a(r)}-E_{a(f)}}{RT}\right)}$$

We know that $\frac{k_f}{k_r}=K$ (equilibrium constant)

$$\therefore\ K=\frac{k_f}{k_r}=\frac{A_f}{A_r}e^{\left(\frac{E_{a(r)}-E_{a(f)}}{RT}\right)}$$

At temperature T_1,

$$K_{T_1}=\frac{A_f}{A_r}e^{\left(\frac{E_{a(r)}-E_{a(f)}}{RT_1}\right)} \qquad \ldots\ldots\ldots(4)$$

At temperature T_2 (with the change of temperature, the Arrhenius constant and activation energies of the forward and reverse reactions do not change),

$$K_{T_2}=\frac{A_f}{A_r}e^{\left(\frac{E_{a(r)}-E_{a(f)}}{RT_2}\right)} \qquad \ldots\ldots\ldots(5)$$

Dividing (5) by (4) we get

$$\frac{K_{T_2}}{K_{T_1}}=e^{\left(\frac{E_{a(r)}-E_{a(f)}}{R}\right)\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

Taking log of both the sides,

$$\log\frac{K_{T_2}}{K_{T_1}}=\frac{E_{a(r)}-E_{a(f)}}{2.303\,R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

The enthalpy of a reaction is defined in terms of activation energies of forward and reverse reactions as $E_{a(r)}-E_{a(f)}=-\Delta H$

$$\therefore\quad \log\frac{K_{T_2}}{K_{T_1}}=\frac{-\Delta H}{2.303\,R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\therefore\quad \log\frac{K_{T_2}}{K_{T_1}}=\frac{\Delta H}{2.303\,R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad \ldots\ldots\ldots(6)$$

(a) When ΔH is positive (endothermic reactions), an increase in temperature ($T_2 > T_1$) will make $K_{T_2} > K_{T_1}$, i.e. the reaction goes more in the forward direction and with decrease in temperature, reaction goes in reverse direction.

(b) When ΔH is negative (exothermic reactions), an increase in temperature ($T_2 > T_1$), will take $K_{T_2} < K_{T_1}$ i.e., the reaction goes in the reverse direction and with decrease in temperature, reaction goes in the forward direction.

(c) The calculation of equilibrium constant from kinetic consideration is only one of the many approaches. Since equilibrium constant is a thermodynamic quantity its definition and calculation involve detailed thermodynamical consideration which is beyond the scope of IIT–JEE syllabus.

7.3 STOICHIOMETRY OF THE EQUILIBRIUM REACTION

The value of K_P and K_C depends upon the stoichiometry of reaction since the law of mass reaction makes use of the given stoichiometric coefficients of the reaction.

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

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad \text{………(i)}$$

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

$$K'_C = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} \qquad \text{………(ii)}$$

From equation (i) and (ii)

$$K'_C = \sqrt{K_C}$$

Thus, in general if an equilibrium reaction is multiplied by 'n', the equilibrium constant of the new reaction would become nth power of the equilibrium constant of old reaction.

$$\therefore (K_C)_{new} = (K_C)^n_{old}$$

7.4 MODE OF WRITING A CHEMICAL EQUATION

The value of K_P and K_C also depend on the method of representing a chemical equation.

For example,

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

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

When the equilibrium reaction is reversed,

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

$$K''_C = \frac{[N_2]\,[H_2]^3}{[NH_3]^2} = \frac{1}{K_C}$$

Now, if we write the equilibrium reaction as,

$$NH_3(g) \rightleftharpoons \tfrac{1}{2}N_2(g) + 3/2\ H_2(g)$$

$$K'''_C = \frac{[N_2]^{1/2}\ [H_2]^{3/2}}{[NH_3]} = \sqrt{\frac{1}{K_C}}$$

8 DEGREE OF DISSOCIATION

Degree of dissociation is the fraction of a mole of the reactant that underwent dissociation. It is represented by 'α'.

$$\alpha = \frac{\text{no. of moles of the reactant dissociated}}{\text{no. of moles of the reac tan t present initially}}$$

For example,

Let the equilibrium reaction is the dissociation equilibrium of NH_3 into N_2 and H_2.

$$NH_3\,(g) \rightleftharpoons \frac{1}{2}\,N_2\,(g) + \frac{3}{2}\,H_2(g)$$

Let the initial moles of NH_3 taken be 1 and the moles of NH_3 dissociated at equilibrium be ‘x’. Then,

	$NH_3\,(g) \rightleftharpoons$	$\frac{1}{2}\,N_2\,(g)$ +	$\frac{3}{2}\,H_2(g)$
Moles initially	1	0	0
Moles at equilibrium	$1-x$	$\frac{x}{2}$	$\frac{3x}{2}$

Here, x represents the degree of dissociation (α). If we would have started with ‘a’ moles of NH_3 and the moles of NH_3 dissociated is taken as ‘x’, then the degree of dissociation of NH_3 will not be ‘x’ but it would be $\frac{x}{a}$.

And if out of ‘a’ moles of NH_3 taken, moles of NH_3 dissociated would be taken as $2x'$, then the degree of dissociation of NH_3 would be $\frac{2x'}{a}$.

The degree of dissociation is defined only for those equilibrium in which dissociation takes place. For example, the degree of dissociation cannot be defined for the reverse reaction in which N_2 and H_2 combine to give NH_3.

9 EQUILIBRIUM CONSTANTS OF VARIOUS EQUILIBRIA

The term homogeneous equilibrium applies to reactions in which all reacting species are in the same phase.

9.1 HOMOGENEOUS EQUILIBRIA IN GASEOUS PHASE

(i) Formation of hydrogen iodide

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Suppose a mixture of ‘a’ moles of hydrogen and ‘b’ moles of iodine be heated at a steady temperature in a sealed tube of capacity ‘V’ litres until equilibrium is established. Let ‘x’ moles of hydrogen react at equilibrium. Then x moles of I_2 would also react in the same time and produce $2x$ moles of HI.

	$H_2(g)$ +	$I_2(g) \rightleftharpoons$	$2HI(g)$
Moles initially	a	b	0
Moles at equil.	$a-x$	$b-x$	$2x$
Molar conc. at equil.	$\frac{a-x}{V}$	$\frac{b-x}{V}$	$\frac{2x}{V}$

$$K_C = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

Let P_T be the total pressure at the equilibrium.

$$K_P = \frac{(P_{HI})^2}{(P_{H_2})\,(P_{I_2})} = \frac{\left(\frac{2x}{a+b}\times P_T\right)^2}{\left(\frac{a-x}{a+b}\times P_T\right)\left(\frac{b-x}{a+b}\times P_T\right)} = \frac{4x^2}{(a-x)(b-x)}$$

Thus, $K_p = K_c$

Also from the relation, $K_p = K_c(RT)^{\Delta n}$

Since, Δn for this equilibrium reaction is zero,

$\therefore K_p = K_c$

(ii) Thermal dissociation of PCl_5

When PCl_5 is heated in a closed vessel at a steady temperature (above 200°C), the following equilibrium is established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Moles at equil. $\quad 1-\alpha \qquad \alpha \qquad \alpha$

Let α be the degree of dissociation. Then at equilibrium we will have $(1-\alpha)$ mole of PCl_5, α mole of PCl_3 and α mole of Cl_2. If 'V' litres is the capacity of the vessel, then molar concentration of various species would be

$$[PCl_5] = \frac{1-\alpha}{V}; \quad [PCl_3] = \frac{\alpha}{V}; \quad [Cl_2] = \frac{\alpha}{V}$$

$$K_C = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{V(1-\alpha)}$$

Let P_T be the total pressure of the equilibrium system.

$$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{\left(\frac{\alpha}{1+\alpha}\right)P_T \times \left(\frac{\alpha}{1+\alpha}\right)P_T}{\left(\frac{1-\alpha}{1+\alpha}\right)P_T} = \frac{\alpha^2 P_T}{1-\alpha^2}$$

$\therefore K_P \neq K_C$ (since Δn is not zero)

9.3 EQUILIBRIUM CONSTANT FOR VARIOUS HETEROGENEOUS EQUILIBRIA

Heterogeneous equilibrium results from a reversible reaction involving reactants and products that are in different phases. The law of mass action applicable to a homogeneous equilibrium is also applicable to a heterogeneous system.

(a) Decomposition of solid $CaCO_3$ into solid CaO and gaseous CO_2

Let 'a' moles of $CaCO_3$ are taken in a vessel of volume 'V' litre at temperature 'T' K.

	$CaCO_3(s)$	$\rightleftharpoons$ $CaO(s)$	+ $CO_2(g)$
Moles initially	a	0	0
Moles at equilibrium	$a-x$	x	x

$$K_{eq} = \frac{[CaO] \times [CO_2]}{[CaCO_3]}$$

As $CaCO_3$ and CaO(s) are pure solids, so their d/M is a constant and their concentrations do not change as long as they are present. Thus the equilibrium expression can be rearranged as

$$K_{eq}\frac{[CaCO_3]}{[CaO]} = [CO_2]$$

It can be seen that left hand side of the equation is a constant represented by K_c.

$$\therefore K_c = [CO_2] = \frac{x}{V} \qquad \text{........(i)}$$

Assuming CO_2 gas to behave ideally at the temperature & pressure of the reaction, the molar concentration of CO_2 can be written using ideal gas equation as $\frac{P_{CO_2}}{RT}$.

$$\therefore K_c = \frac{P_{CO_2}}{RT}$$

$$K_c(RT) = P_{CO_2}$$

Since K_c, R and T are constants, their product will also be a constant referred as K_p.

$$\therefore K_p = P_{CO_2} = \frac{xRT}{V} \qquad \text{........(ii)}$$

From equation (i) and (ii), it is clear that whenever the equilibrium would be attained at 'T' K, in a vessel of volume 'V' litre, the moles of CO_2 present at equilibrium should be x (which can exert a pressure equal to P_{CO_2}) If rather than starting with 'a' mole of $CaCO_3$, we start with x moles of $CaCO_3$ in the vessel of volume 'V' at 'T'K, then the entire $CaCO_3$ would have decomposed to give CO_2 but the equilibrium can not be maintained as there would be no $CaCO_3$ left. Further if the moles of $CaCO_3$ taken in the same vessel at same temperature were less than x, the equilibrium would never be attained. Thus, any amount (moles) of $CaCO_3$ more than x would be sufficient to establish the equilibrium. So the minimum moles of $CaCO_3$ required would be x, as any moles more than this would be sufficient to establish the equilibrium. So the minimum moles of $CaCO_3$ required to attain equilibrium under given conditions would be x.

The given equilibrium can be made to move in the forward direction by either removing some moles of CO_2 or by increasing the volume of the container or by increasing the temperature of the reaction (as the reaction is endothermic). Addition of solid $CaCO_3$ or CaO to the equilibrium mixture will not affect the equilibrium at all.

For such equilibria, at any temperature, there will be a fixed value of the pressure of CO_2, which is called as ***dissociation pressure.*** The dissociation pressure of heterogeneous equilibria is defined as the total pressure exerted by the gaseous species in equilibrium with the solid species. The relation giving the variation of Kp with temperature is

$$\log \frac{(K_p)_{T_2}}{(K_p)_{T_1}} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

(b) Reaction of solid phosphorous with gaseous Cl_2 to form liquid PCl_3

$P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$

The equilibrium constant is given by

$$K_{eq} = \frac{[PCl_3]^4}{[P_4][Cl_2]^6}$$

Since, pure solids and pure liquids do not appear in the equilibrium constant expression, thus expression can be rearranged as

$$K_{eq}\frac{[P_4]}{[PCl_3]^4} = \frac{1}{[Cl_2]^6}$$

$$\therefore K_c = \frac{1}{[Cl_2]^6}$$

Alternatively, we can express the equilibrium constant in terms of the pressure of Cl_2.

$$K_p = \frac{1}{(p_{Cl_2})^6}$$

(iii) Dissociation of ammonium hydrogen sulfide

Let the moles of $NH_4HS(s)$ taken in a vessel of volume 'V' litre be 'a' at temperature 'T'K. At equilibrium, x moles of NH_4HS dissociates to give $NH_3(g)$ and $H_2S(g)$.

	$NH_4HS(s) \rightleftharpoons$	$NH_3(g)$ +	$H_2S(g)$
Moles initially	a	0	0
Moles of equilibrium	$a - x$	x	x

$$K_{eq} = \frac{[NH_3]\,[H_2S]}{[NH_4HS]}$$

As the concentration of NH_4HS is a constant, so it can be merged with K_{eq} to get K_C.

$$K_{eq}\,[NH_4HS] = [NH_3]\,[H_2S]$$

$$\therefore\ K_C = [NH_3]\,[H_2S] = \left(\frac{x}{V}\right)\times\left(\frac{x}{V}\right) = \left(\frac{x}{V}\right)^2$$

Assuming H_2S and NH_3 to behave ideally at the given temperature and pressure of the reaction, the molar concentration of the gas can be written as $\frac{P}{RT}$.

$$\therefore\ [NH_3] = [H_2S] = \frac{P_{NH_3}}{RT} = \frac{P_{H_2S}}{RT}$$

$$\therefore\ K_C = \left(\frac{P_{NH_3}}{RT}\right)\times\left(\frac{P_{H_2S}}{RT}\right)$$

$$K_C(RT)^2 = P_{NH_3}\times P_{H_2S}$$

Since, LHS of the expression is a constant, it can be represented by another constant, K_P.

$$\therefore\ K_P = P_{NH_3}\times P_{H_2S}\,.$$

If the dissociation pressure measured for NH_4HS be P_T atm, then

$$P_{NH_3} = P_{H_2S} = \frac{P_T}{2}$$

$$\therefore\ K_P = \left(\frac{P_T}{2}\right)\times\left(\frac{P_T}{2}\right) = \frac{(P_T)^2}{4}$$

10 MULTIPLE EQUILIBRIA

We have so far considered relatively simple equilibrium reactions. Let us take a slightly complicated situation, in which the product molecules(s) in one equilibrium system are involved in a second equilibrium process.

$$A(g) + B(g) \rightleftharpoons C(g) + D(g) \quad ; \quad K_{C_1} = \frac{[C]\,[D]}{[A]\,[B]}$$

$$C(g) + E(g) \rightleftharpoons F(g) + G(g) \quad ; \quad K_{C_2} = \frac{[F]\,[G]}{[C]\,[E]}$$

Overall reaction: $$A(g) + B(g) + E(g) \rightleftharpoons D(g) + F(g) + G(g) \quad ; \quad K_{C_3} = \frac{[D]\,[F]\,[G]}{[A][B]\,[E]}$$

In this case, one of the product molecule, C(g) of the first equilibrium reaction combines with E(g) to give F(g) and G(g) in another equilibrium reaction, so in the overall reaction, C(g) will not appear on either side.

The equilibrium constant (K_{C_3}) of the overall reaction can be obtained if we take the product of the expressions of (K_{C_1}) and (K_{C_2}).

$$K_{C_1}\times K_{C_2} = \frac{[C]\,[D]}{[A]\,[B]}\times\frac{[F]\,[G]}{[C]\,[E]} = \frac{[D]\,[F][G]}{[A]\,[B]\,[E]}$$

$$\therefore \qquad K_{C_1}\times K_{C_2} = K_{C_3}$$

Thus, ***if a equilibrium reaction can be expressed as the sum of two or more equilibrium reactions, then the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.***

11 SIMULTANEOUS EQUILIBRIA

When more than one equilibrium are established in a vessel at the same time and any one of the reactant or product is common in more than one equilibrium, then the equilibrium concentration of the common species in all the equilibrium would be same.

For example, if we take $CaCO_3(s)$ and C(s) together in a vessel of capacity 'V' litre and heat it at temperature 'T' K, then $CaCO_3$ decomposes to CaO(s) and $CO_2(g)$. Further, evolved CO_2 combines with the

C(s) to give carbon monoxide. Let the moles of $CaCO_3$ and carbon taken initially be ‘a’ and ‘b’ respectively.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Moles at equilibrium $a - x$ x $(x - y)$

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Moles at equilibrium $(x - y)$ $(b - y)$ $2y$

Thus, as CO_2 is common in both the equilibrium so its concentration is same in both the equilibrium constant expressions.

Equilibrium constant for first equilibrium, $K_{C_1} = [CO_2] = \frac{x-y}{V}$

Equilibrium constant for second equilibrium, $K_{C_2} = \frac{[CO]^2}{[CO_2]} = \frac{(2y)^2 V}{V^2(x-y)} = \frac{\mathbf{4y^2}}{\mathbf{V(x-y)}}$

POINTS TO BE REMEMBERED FOR WRITING EQUILIBRIUM CONSTANT EXPRESSIONS

- The concentration of the reacting species in the solution phase is expressed in mol/litre.
- The concentration of the reacting species in the gaseous phase can be expressed either in mol/litre or in atm.
- The concentration of pure solid, pure liquids (in heterogeneous equilibria) and solvents (in homogeneous equilibria) are constant and do not appear in the equilibrium constant expression of a reaction.
- K_p and K_c are related as, $K_p = K_c(RT)^{\Delta n}$ where Δn = number of moles of gaseous product– number of moles of gaseous reactant.
- It is not customary to write units of equilibrium constants (K_p and K_c) but when mentioned, the units of K_p are $(atm)^{\Delta n}$ and units of K_c are $\left(\frac{moles}{litre}\right)^{\Delta n}$.
- In quoting the value of equilibrium constant, we must specify the balanced equation and the temperature at which equilibrium is established.
- If a reaction can be expressed as the sum of two or more reactions, the product of the equilibrium constants of the individual reactions gives the equilibrium constant for the overall reaction.
- If two equilibria have been established in a vessel and any reactant or product is common to both the equilibria, then the equilibrium concentration of the common species will be same in both the equilibria.

12 THE LE CHATELIER – BRAUN PRINCIPLE

Chemical equilibrium represents a balance between forward and reverse reactions. In most cases, this balance is quite delicate. Changes in concentration, pressure, volume and temperature may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed. There is a general rule (named Le Chatelier principle) that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume or temperature occurs.

Le Chatelier’s principle states that if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset.

The word “stress” here implies a change in concentration, pressure, volume, addition of an inert gas or temperature that removes a system from the equilibrium state.

The Le Chatelier principle can be explained using the following equilibrium reaction.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Let the moles of PCl_5, PCl_3 and Cl_2 at equilibrium be a, b and c respectively. Also let the volume of the container in which equilibrium is established be 'V' litre and the total pressure of the system at equilibrium be P_T atm.

$$K_P = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = \frac{\left(\frac{b}{a+b+c}\times P_T\right)\left(\frac{c}{a+b+c}\times P_T\right)}{\left(\frac{a}{a+b+c}\times P_T\right)}$$

$$\therefore \quad K_P = \frac{bc\times P_T}{a\,(a+b+c)} \qquad \text{....(i)}$$

The total pressure of the system (P_T) can be given as (assuming all gases at equilibrium behave ideally under the given conditions)

$$P_T = \frac{(a+b+c)\,RT}{V}$$

$$\therefore \quad \frac{P_T}{(a+b+c)} = \frac{RT}{V}$$

Inserting the value of $\frac{P_T}{(a+b+c)}$ in equation (i), we get

$$K_P = \frac{bc\times RT}{a\times V} \qquad \text{....(ii)}$$

Now, let us examine the effect of change of certain parameters like moles of reactant, moles of product, volume, temperature, addition of inert gas and addition of catalyst on the given equilibrium.

12.1 CHANGE IN NUMBER OF MOLES OF REACTANT

If we add 'd' moles of PCl_5 to the equilibrium mixture, the equilibrium would be disturbed and the expression $\frac{bc\times RT}{(a+d)\,V}$ becomes Q_P. As $Q_P < K_P$, so the net reaction moves in the forward direction till Q_P becomes equal to K_P.

Thus for any equilibrium, when more reactant is added to (or some product is removed from) an equilibrium mixture, the net reaction moves in the forward direction (as Q < K) to establish a new equilibrium state.

12.2 CHANGE IN NUMBER OF MOLES OF PRODUCT

Let 'd' moles of PCl_3 (or Cl_2) are added to the equilibrium. The equilibrium would be under stress and thus the expression $\frac{(b+d)\,c\times RT}{a\times V}$ would become Q_P. Since, $Q_P > K_P$, so the net reaction moves in the reverse direction till Q_P becomes same as K_P.

Thus for any equilibrium, when product is added to (or some reactant is removed from) an equilibrium mixture, the net reaction moves in the reverse (backward) direction (as Q > K) to establish a new equilibrium state.

12.3 CHANGE IN VOLUME

Let the volume of the container be increased from V to V′ litre. The equilibrium would be disturbed and the expression $\frac{bc\times RT}{a\times V'}$ becomes Q_P. The value of Q_P is less than K_P, so the net reaction moves in the forward direction to establish new equilibrium. But when the volume of the container is decreased, the reaction moves in the backward direction to again attain the equilibrium state.

Thus for any equilibrium, on increasing the volume of the container, the net reaction shifts in the direction of more moles of the gases while on decreasing the volume of the vessel, the reaction goes in the direction of fewer moles of the gases.

12.4 ADDITION OF AN INERT GAS

The effect of addition of an inert gas can be studied under two conditions i.e., at constant volume and at constant pressure.

Let us first see the effect of addition of an inert gas (gas that does not react with any of the component of the equilibrium mixture under the given conditions of the equilibrium. That's why they are also refereed as non-reacting gases) to the equilibrium system at constant volume and then at constant pressure.

Let 'd' moles of an inert gas are added to the equilibrium mixture at constant volume. The total number of moles of the system increases so too the pressure of the system but the partial pressure of all the species would still be same. Let the total pressure becomes P_T' then $\frac{P_T'}{(a+b+c+d)} = \frac{RT}{V}$. As R, T and V are constant, so the expression $\frac{bc \times RT}{a \times V}$ would still be equal to K_P. As, $Q_P = K_P$, the net reaction does not move at all.

Thus for any equilibrium, when an inert gas is added at constant volume, the equilibrium remains unaffected whether the equilibrium reaction have Δn equal to zero or non–zero.

Now, let 'd' moles of an inert gas are added to the equilibrium mixture at constant pressure. To keep the pressure constant, volume of the vessel should increase. Let the volume of the vessel increases from V to V′ litre. So, the expression $\frac{bc \times RT}{a \times V'}$ becomes Q_P. As the value of $Q_P < K_P$, so the net reaction moves in the forward direction to establish new equilibrium state. Thus, addition of an inert gas at constant pressure has the same effect as produced by the increased volume of the container.

Thus, for equilibrium having $\Delta n = 0$, when an inert gas is added at constant pressure, the equilibrium remains unaffected (since V does not appear in the expression of K_P) while for equilibrium having $\Delta n \neq 0$, the addition of an inert gas at constant pressure causes reaction to move in the direction of more moles of the gases.

12.5 ADDITION OF A CATALYST

We know that a catalyst enhances the rate of a reaction by lowering the reaction's activation energy. Actually a catalyst lowers the activation energy of the forward reaction and the reverse reaction to the same extent. We can thus conclude that the ***presence of a catalyst does not alter the equilibrium constant nor does it shift the position of an equilibrium system.*** Adding a catalyst to a reaction mixture that is not at equilibrium will simply cause the mixture to reach equilibrium sooner. The same equilibrium mixture could be obtained without the catalyst, but we might have to wait much longer for it to happen.

12.6 CHANGE IN TEMPERATURE

If we increase the temperature of the reaction from T K to T′K, equilibrium would be disturbed and the expression $\frac{bc \times RT'}{a \times V}$ becomes Q_P. Therefore, it seems that the reaction moves in the backward direction as $Q_P > K_P$ but actually it is not so. According to such predictions, no change in the equilibrium reaction would be observed on increasing temperature for reactions having $\Delta n = 0$, as T would not appear in the expression of K_P, but in actual practice such reactions also move in a particular direction (either backward or forward) on increasing the temperature.

Answer to these facts lie in the truth that K_P is temperature dependent and with the increase of temperature, K_P either increases or decreases.

For the given equilibrium, with the increase of temperature from T K to T′K, Q_P increases.

$$\therefore \quad Q'_{P_T} = \frac{bc \times RT'}{a \times V} \text{ and } Q_{P_T} = \frac{bc \times RT}{a \times V}$$

$$Q'_{P_T} > Q_{P_T} \quad (\text{as } T' > T)$$

With the increase of temperature, K_P also changes, which can either increase or decrease. If K_P decreases, then $K'_{P_T} < Q'_{P_T}$ and net reaction moves in the backward direction but if K_P increases, then K'_{P_T} could either be equal to Q'_{P_T} or > Q'_{P_T} or < Q'_{P_T}. The magnitude of K'_{P_T} can be compared with that of Q'_{P_T} by looking at the dependence of K_P and Q_P on temperature. We have seen that K_P depends on temperature exponentially while Q depends on T raised to the power
1, 2, 3, 4 etc. Thus, variation in K_P would be more than the variation in Q_P on increasing temperature. Therefore, K'_{P_T} would always be greater than Q'_{P_T} and the net reaction moves in the forward direction.

Thus, to examine the temperature effect, we need to look at the variation at K_P only and not at Q_P. If K_P increases, the net reaction moves forward while if K_P decreases, the net reaction moves backward.
The variation of K_P with temperature is given by Von't Hoff equation as

$$\log\frac{K'_T}{K_T} = \frac{\Delta H}{2.303R}\left[\frac{1}{T} - \frac{1}{T'}\right] \qquad \text{where } T' > T$$

All reactions are either endothermic or exothermic in nature. For an endothermic reaction, ΔH is positive and with an increase in temperature of the system to T′ K from T K, the RHS of the expression becomes positive. Thus, equilibrium constant at higher temperature (K'_T) would be more than the equilibrium constant at lower temperature (K_T).

But for an exothermic reaction, ΔH is negative and on increasing the temperature of the system from T K to T′K, the RHS of the expression becomes negative. So, the equilibrium constant at higher temperature would be less than the equilibrium constant at lower temperature.

The given equilibrium, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is endothermic in nature. So, with the increase of temperature from T K to T′ K, K_P and Q_P both increases. Therefore, equilibrium shifts in the forward direction.

Thus, for an endothermic reaction (ΔH = positive), with the increase of temperature, net reaction moves in the forward direction and the decrease in temperature favours backward reaction white for an exothermic reaction (ΔH = negative), net reaction moves in the backward direction with the increase of temperature and in forward direction with the decrease of temperature.

In general, with the increase of temperature, net reaction moves in that direction where the heat is absorbed and the effect of increasing temperature is nullified.

12.7 CHANGE IN MORE THAN ONE PARAMETER

For the given equilibrium, if the number of moles of PCl_3 is increased four folds and the volume of the vessel is doubled, then the equilibrium would be disturbed. The expression $\frac{4b \times c \times RT}{a \times 2V}$ would become Q_P.
Since, $Q_P > K_P$, so the net reaction moves in reverse direction till Q_P becomes equal to K_P.

Thus, when two or more parameters are simultaneously changed for any equilibrium, find the changed value of Q and K and compare them. If Q = K, there will be no effect on the reaction, if Q > K, the net reaction moves in the backward direction while if Q < K, net reaction moves in the forward direction.

12.8 APPLICATION OF LE CHATELIER'S PRINCIPLE

Solubility

Some solids, on dissolution in water, absorb heat (endothermic process) and ΔH is +ve. Solubilities of such solids will increase with temperature. When the heat of solution is –ve, the solubility decreases with temperature.

Melting of ice

In the system, ice $\rightleftharpoons$ water, when ice starts melting, there is absorption of heat and the volume decreases. Thus, the melting is favoured by increase of temperature and increase of pressure.

Synthesis of ammonia

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ \Delta H = -46\ \text{kJ mol}^{-1}$$

On going from reactants to products, there is decrease in volume ($\Delta n = -2$) and so application of high pressure will favour forward reaction. Since forward reaction is exothermic low temperature favours forward reactions.

Formation of nitric oxide

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)\ ;\ \Delta H = 43.2\ \text{kcal mol}^{-1}$$

Since $\Delta n = 0$, there is no effect on changing the pressure. High temperature favours forward reaction.

Dissociation of PCl_5

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)\ ;\ \Delta H = +ve$$

Conditions favourable for forward reactions are **(i)** low pressure, **(ii)** high temperature. Oxidation of carbon monoxide by steam:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)\ ;\ \Delta H = -ve$$

$\Delta n = 0$ and so pressure has no effect. Low temperature favours forward reaction and so by employing excess of steam.

13 RELATION BETWEEN VAPOUR DENSITY AND DEGREE OF DISSOCIATION

The relation between vapour density and the degree of dissociation can be established only for a gaseous equilibrium whose K_P exists. For example,

	$A(g) \rightleftharpoons$	$nB(g)$
Initial conc.	c	0
Conc. at equilibrium	$c(1-\alpha)$	$nc\alpha$

Total concentration at equilibrium $= c - c\alpha + nc\alpha = c\,[1 - \alpha + n\alpha] = c\,[1 + \alpha\,(n-1)]$

Assuming that all the gaseous components at equilibrium behave ideally, we can apply ideal gas equation.

$$PV = nRT = \frac{w}{M} \times RT$$

$$M = \frac{w}{V} \times \frac{RT}{P} = \frac{\rho RT}{P}$$

$$\therefore\ \ V.D = \frac{\rho RT}{2P} \qquad \text{....(i)} \quad [\text{since molar mass} = 2 \times V.D]$$

As pressure of the system is given by, $P = \dfrac{nRT}{V}$, so putting the value of P in equation (i) gives

$$V.D = \frac{\rho RT}{2nRT} \times V = \frac{\rho V}{2n}$$

where ρ is the density of the gas or gaseous mixture expressed in g/litre.

If the equilibrium reaction is established in a closed vessel, then vapour density will be inversely proportional to the number of moles of the gaseous species as the density of the gaseous mixture (ρ) is a constant.

$$\therefore \qquad \frac{\text{Initial vapour density}}{\text{Vapour density at equilibrium}} = \frac{\text{Total moles of gases at equilibrium}}{\text{Initial moles of gaseous reactant}}$$

Let the initial vapour density and vapour density at equilibrium be ‘D’ and ‘d’ respectively, then for the given equilibrium

$$\frac{D}{d} = \frac{c\,[1+\alpha\,(n-1)]}{c}$$

or $$\frac{D}{d} = [1+\alpha\,(n-1)]$$

or $$\frac{D}{d} - 1 = \alpha\,(n-1)$$

∴ $$\alpha = \frac{(\mathbf{D}-\mathbf{d})}{(\mathbf{n}-1)\,\mathbf{d}}$$

where ‘n’ represents the number of moles of gaseous product given by 1 mole of the gaseous reactant. Knowing D, d and n, the degree of dissociation (α) can be calculated.

The vapour density measurement is used for the determination of degree of dissociation of only those equilibria in which 1 mole of the gaseous reactant gives more than one mole of gaseous products. Because when one mole of the gaseous reactant gives only one mole of gaseous product, then ‘D’ and ‘d’ would be same and ‘α’ can not be determined.

14 RELATION BETWEEN FREE ENERGY CHANGE & EQUILIBRIUM CONSTANT

As you might be aware, every process in nature occurs in order to reduce the energy of a system. This is because reduced energy state has fewer tendencies to undergo change thereby it brings stability. When an object falls from a certain height, the process reduces the potential energy of the system. Where as, if the object is to be taken to a certain height the potential energy increases. That’s why the former occurs on its own, while for the latter work has to be done.

Chemical reactions too occur with decrease in energy. One might of course wonder how does an endothermic reaction occur? Well, even endothermic reactions occur with decrease in energy! This statement may contradict the very definition of endothermic reactions. Not so if you read on.

The energy that decreases in a chemical reaction, which brings about stability, is called *Free Energy*. It is the decrease in free energy that causes a reaction to happen. For endothermic reactions also, the free energy decreases, even though the total energy increases. This can be understood by figuring out what is free energy?

Free energy of a system, say for example a molecule like CH_4, is the ***total intrinsic electrostatic potential energy of the system.*** In a CH_4 molecule, there are in total 10 protons (6 of C and 1 each of H) and 10 electrons (6 of C and 1 each of H). If we were to calculate the total electrostatic potential energy of the system by calculating the potential energy of all charges due to all other charges and adding the sum, the result would be the free energy of CH_4 molecule.

For this, one needs to know the distance between all the charges, which is not practically possible. But the concept of free energy is very useful to understand the direction of reactions. Free energy represents the stability of a system. Lower the value of free energy; more are the attractive forces in the system and consequently more is the stability. If one were to ask why methane is a tetrahedron then a safe answer would be that it is the tetrahedral shape that allows methane to have the least possible free energy. With temperature free energy is likely to change as bond distances and angles may get altered.

Let us consider a reaction,

	A	+	B	$\rightleftharpoons$	C	+	D
Free Energy per mole (in kJ)	3		6		2		5
No. of mole	2		3		4		1

If we look at this reaction we can see that the total Free Energy on the left is $[2 \times (3)] + [3 \times (6)] = 24$. On the other hand, the free energy on the right side is $[4 \times (2)] + [1 \times (5)] = 13$. This means that the left side of the reaction has greater instability than the right side. So to bring about stability, the free energy lowers itself by moving the reaction to the forward direction. The corollary of this is that the reverse reaction does not occur because this would bring about instability. As the forward reaction occurs the number of mole of A & B decreases while that of C & D increases. This makes the number on the left side smaller and that of the right side bigger. Finally a stage is reached when the free energy of the left and the right become equal. This is the stage when equilibrium is established. At this juncture the reverse reaction starts to occur (because free energy while going reverse is not taking the reaction to the side of instability) with the same speed as that of the forward reaction.

Therefore, free energy change is zero when the reaction is at equilibrium ($\Delta G = 0$).

When the concentration of all reactants and products is 1 mole/litre, the change in Free Energy is represented as ΔG^0. For the reaction shown $\Delta G^0 = -2$.

Thus, ΔG is the free energy change at any given concentration of reactants and products.

If all the reactants and products are taken at a concentration of one mol per litre, the free energy change of the reaction is called ΔG^0 (standard free energy change). Remember that ΔG^0 is not necessarily the free energy change at equilibrium.

$$\Delta G^\circ = \Sigma\ \Delta G_f^0 \text{ of products} - \Sigma\, \Delta G_f^0 \text{ of reactants}$$

and $\Delta G = \Sigma\Delta G_f$ of products $- \Sigma\ \Delta G_f$ of reactants.

If $\Delta G = -ve$, reaction goes in the forward direction

$\Delta G = +ve$, reaction goes in the backward direction

$\Delta G = 0$, reaction is at equilibrium

It has been proved (proof not required) that $\Delta G^0 = -RT \ln K$.

where T is always in Kelvin, and if R is in joules, ΔG^0 will be in joules, and if R is calories then ΔG^0 will be in calories.

*[**Note:** K may either be K_C or K_P or any other equilibrium constant. The use of this relation between ΔG^0 and equilibrium constant (K) will also be seen in the lesson "Electrochemistry".]*

MIND MAP

CHEMICAL EQUILIBRIUM

1. Chemical equilibrium is a reversible process in which the rates of forward and reverse reactions are equal and the concentration of reactants and products do not change with time.

2. Equilibrium constant is the ratio of rate constant for forward reaction to that of the reverse reaction. There are two types of equilibrium constants generally used, K_p and K_c. They are related as $K_p = K_c(RT)^{\Delta n}$.

3. The concentrations of pure solids, pure liquids and solvents are constant and do not appear in the equilibrium constant expression of a reaction.

4. If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

5. Degree of dissociation is the fraction of a mole of the reactant that underwent dissociation. It is represented by 'α'. If we start with 'a' moles of NH_3 and the moles of NH_3 dissociated is taken as 'x', then the degree of dissociation of NH_3 will not be 'x' but it would be x/a.

6. The reaction quotient (Q) has the same form as the equilibrium constant but it applies to a reaction that may not be at equilibrium. If $Q > K$, the reaction will proceed from right to left to achieve equilibrium. If $Q < K$, the reaction will proceed from left to right to attain equilibrium.

7. Le Chatelier's principle state that if an external stress is applied to a system at chemical equilibrium, the system will adjust to partially offset the stress.

8. Only a change in temperature changes the value of equilibrium constant of a particular reaction. Changes in concentration, pressure, or volume may change the equilibrium concentrations of reactants and products. The addition of a catalyst hastens the attainment of equilibrium but does not affect the equilibrium concentrations of reactants and products.

9. The relation between ΔG° and equilibrium constant (K) is given by $\Delta G^\circ = -RT \ln K$ where T is always in Kelvin, and if R is in joules, ΔG° will also be in joules, and if R is in calories, then ΔG° will also be in calories. K may either be K_C or K_P or any other equilibrium constant.