Equilibrium

4.1   Introduction

Equilibrium plays an important role in physical changes, chemical reactions, biological and environmental processes. e.g. evaproation of water, equilibrium between oxygen molecule and protein, production of ammonia etc. If certain changes and reactions are carried at constant temperature and pressure in closed vessels (closed systems), they remain incomplete. In the beginning of the reaction, the reactants which are in closed vessels, slowly change into products and the concentration of reactant decreases as the time proceeds. Along with this phenomenon, there is increase in concentration of product as the time proceeds. A certain point of time comes when there is no change in the concentration of reactant and product even if the time proceeds. This situation is called equilibrium state.

4.2   Dynamic Nature of Equilibrium

The most important matter in the case of equilibrium is that there is a continuous transformation of reactant to product and product to reactant. This state apprears to be steady but it is not so. This type of reaction which takes place in both the directions is called reversible reaction and it is expressed by the

symbol of two half-arrows $(\rightleftharpoons)$. This symbol indicates that such reaction occurs simultaneously in both (forward and reverse) directions. Generally, **the change of reactant to product is called forward reaction and the change of product to reactant is called the reverse reaction.** Thus, in reversible reactions, forward and reverse reactions continuously occur and we find it as equilibrium state. The mixture of reactants and products obtained at equilibrium time is called equilibrium mixture. The decomposition reaction of solid calcium carbonate in a closed vessel, at high temperature can be shown as below :

$$CaCO_{3(s)} \underset{}{\overset{\Delta}{\rightleftharpoons}} CaO_{(s)} + CO_{2(g)}$$
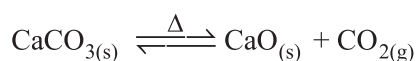
The equilibrium is dynamic and not steady or static as the forward and the reverse reactions occur with the same velocity at the equilibrium time in equilibrium reactions in closed vessels. In the above reaction obtaining CaO and CO_2 by decomposition of $CaCO_3$ and obtaining $CaCO_3$ by combination of CaO and CO_2 continuously take place. Suppose, if we deposit some amount in our bank account and withdraw the same amount, then balance in the account appears steady or static. But this can be considered operative or dynamic and not closed or static. It is very difficult to determine the dynamic nature of equilibrium, even then with the help of radioactive isotope, it can be proved viz. $^{14}CO_2$ gas containing radioactive isotope ^{14}C and $CaCO_3$ are taken in two different flasks and CO_2 obtained by decomposition is connected with vessel containing $^{14}CO_2$ gas, after some time, $Ca^{14}CO_3$ will be formed in the vessel of $CaCO_3$ and CO_2 will be obtained in the vessel containing $^{14}CO_2$. Thus, if the equilibrium would have been steady, there must not be exchange of ^{12}C and ^{14}C. With the help of suitable counter, the radioactivity can be measured and the proof for the dynamic nature of equilibrium can be obtained though the proportions of concentrations of reactants and products remain constant. The reaction can be fast or slow depending upon the nature of the reactant and the experimental conditions.

Equilibrium reactions can be divided into following three categories :

(i) Reactions which are almost at the extent of completion and concentration of reactants may be negligible. It is not possible to detect this experimentally.

(ii) Reactions in which the products are formed in very less proportions and most part of the reactant remains unchanged at the equilibrium.

(iii) Reactions in which the concentrations of reactants and products are in comparable proportions at equilibrium.

4.3 Types of Equilibrium

Physical Equilibrium : The equilibrium established in changes of pysical processes is called physical equilibrium. e.g. conversion of water into steam.

Chemical equilibrium : The equilibrium established in chemical reactions is called chemical equilibrium. e.g. Decomposition of calcium carbonate.

Equilibrium in Physical Process : At constant temperature, water in the liquid state taken in a closed vessel, gets converted into gaseous state of vapour (steam) as the time proceeds. Slowly, the concentration of vapour of water on the surface of water increases. After some time, the molecules of vapour of water get attracted to one another and converted into liquid state water. After certain time, the rates of formation of vapour from liquid water and the formation of liquid water from water vapour become equal and the equilibrium is called physical equilibrium or physical process equilibrium. In this type of process, there is no change in chemical structure of the molecule of the substance, only its physical state changes. The forward reaction of formation of water vapour from water is called evaporation of water and the reverse reaction of formation of water from vapours of water is called liquefaction.

$$H_2O_{(l)} \underset{\text{Liquefaction}}{\overset{\text{Evaporation}}{\rightleftharpoons}} H_2O_{(g)}$$
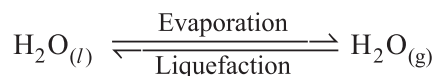
If there are changes in the factors like temperature, pressure or concentration in the physical reaction in equilibrium, there is a change in the equilibrium state.

As the substance changes from solid, liquid and gas into one another, three states can be established in physical process equilibrium.

(i) Solid-Liquid Process Equilibrium :

Take some ice and water in a thermos flask at 0^0 C (273 K). Now close the thermos flask with a cork. As you know that because of the wall having vacuum in the flask, there will not be exchange of heat between the system in the flask and the external surrounding. Hence, the quantity of ice in the thermos flask will remain constant but an equilibrium can be established between ice and water, which can be shown as below :

$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$$
Ice (solid)   Water (liquid)
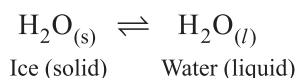
Experimentally, it is proved that even after establishment of the equilibrium in the flask, some molecules of ice get converted into water, and at the same time some amount of molecules of water get converted into ice. Hence, the quantity of ice and water in the thermos flask or the total number of molecules remain constant. This is one type of equilibrium, i.e. physical equilibrium between solid and liquid. It is important to note that there is no chemical change in the substance and therefore, this process is called physical equilibrium.

(ii) Liquid - Gas Process Equilibrium :

At constant temperature, take water in a closed vessel (system). As the time proceeds, water slowly changes into vapour (steam) depending upon the value of temperature. As the water gets converted into water vapour, vapour of water increases and the vapour pressure also increases. After sometime vapour pressure becomes constant because the temperature is constant and the change in vapour pressure stops and some constant value of vapour pressure is obtained. This equilibrium state can be expressed as below :

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$
Water (liquid)   Vapour of water (gas)
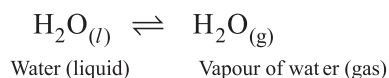
As this process is carried out in a closed vessel (system) some molecules of water change into water vapour. At the same time same number of molecules of water vapour change into water liquid. Hence, the amount of water and water vapours remain constant. Thus, this is one type of equilibrium between liquid (water) and gas (water vapour) and it is physical equilibrium.

It is important to note here that as there is no chemical change in the substance, it is the example of physical equilibrium.

### (iii) Equilibrium Involving Dissolution of Solid in Solution :

For the study of this type of equilibrium the example of sugar and its solution in water can be taken. At constant temperature, take some water. Add some sugar into it and stir. In the beginning sugar easily dissolves, but as more and more amount of sugar is added, it dissolves according to its solubility and then some amount of sugar remains in solid form without dissolution. We know this state as saturated solution but in this system the equilibrium is also established between sugar (solid) and liquid (solution of sugar). This can be expressed as below :

$$Sugar_{(s)} \rightleftharpoons Sugar\ solution_{(aq)}$$
Solid   Liquid
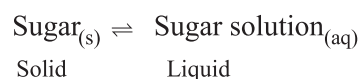
As studied earlier, equilibrium is dynamic because the forward and the reverse reactions continuously occur in each system. In this system, the amount of sugar that dissolves in water, same amount of sugar separates from solution of sugar. Hence, the number of molecules of sugar and number of aqueous molecules of sugar in the solution remain constant in this system.

(iv) Equilibrium Involving Gas and Solution :

At constant temperature and pressure, carbon dioxide can be dissolved in water in a closed vessel (system), so that a system containing gas and solution of carbon dioxide can be formed. As temperature and pressure are constant, carbon dioxide dissolves according to its pressure and temperature and forms solution of carbon dioxide and the excess carbon dioxide gas remains in equilibrium with it. Equilibrium is dynamic and so molecules of carbon dioxide gas that dissolve in water is the same as the number of molecules of the gas that release from the solution in the system. Thus, in this closed system, the total number of molecules (amount) of carbon dioxide in gaseous form and those that have dissolved in water remain constant. This equilibrium can be shown as below :

$$CO_{2(g)} \rightleftharpoons CO_{2(soln)}$$
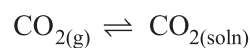
All the reactions studied above are processes in which only physical change takes place and so they all are examples of physical process equilibrium.

(v) Solid - Gas Process Equilibrium : You know that when certain solid substances are heated, they get converted into gaseous state and on cooling are converted directly into solid from gaseous state. This process is known as sublimation. For the study of the equilibrium of this let us take example of solid iodine (I_2). In a closed vessel (system) some amount of solid iodine is taken and it is heated. At constant temperature, vapour of iodine is formed from solid iodine, which appears as a violet coloured gas. If the temperature is constant equilibrium can be expressed as below :

$$I_{2(s)} \rightleftharpoons I_{2(vap)}$$
Solid   Gas
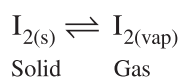
As equilibrium is dynamic at constant temperature, the number of molecules (amount) of iodine that are changed from solid iodine to vapour of iodine remain the same as the number of molecules (amount) of iodine vapour to solid iodine. Thus, in the closed vessel, the amount of iodine (solid and gaseous form) remains constant.

Table 4.1 Some Characteristics of Physical Process Equilibrium

Process	Conclusion (characteristic)
(1) Liquid $\rightleftharpoons$ Gas $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$	At constant temperature, P_{H_2O} remains constant.
(2) Solid $\rightleftharpoons$ Liquid $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$	At constant temperature melting point remains constant
(3) Solid $\rightleftharpoons$ Solution $sugar_{(s)} \rightleftharpoons$ solution of $sugar_{(aq)}$	At constant temperature, the solubility of solute in the solution remains constant.
(4) Gas $\rightleftharpoons$ Liquid $CO_{2(g)} \rightleftharpoons CO_{2(Vap)}$	At constant temperature the rates of concentration of gas dissolved in solution and concentration of gas in gaseous state remain equal.

4.4 General Characteristics of Equilibrium Involved in Physical Processes

The following are the general characteristics of systems in equilibrium for the physical systems discussed earlier.

(i)   At constant temperature, equilibrium is possible only in closed system.

(ii) Both the processes (reactitons) opposite to each other that is, the forward and the reverse reactions occur at the same rates and the equilibrium involved in it remains dynamic but condition remains steady (static).

(iii) All the properties of the system which can be measured remain constant.

(iv) For physical process, when equilibrium is obtained then at constant temperature, the value of one of the factors remains constant. The list of these properties is shown in Table 4.1

(v)   At any stage magnitude of such quantities show to what extent the physical process has advanced before reaching to equilibrium.

4.5 Chemical Process (Reaction) Equilibrium

Like physical processes, equilibrium state is also obtained in chemical processes (reactions). Equilibrium state is obtained when the chemical reactions occur in opposite directions to each other i.e. forward and reverse reactions and the rates of the reactions become equal. Hence concentrations of reactants and products remain constant. Chemical equilibrium is dynamic like physical equilibrium. i.e. The conversion of reactants to products and products to reactants continuously occur, and as a result all the reactants and products are present at equilibrium.

Let us think of a simple reversible reaction :

$$A + B \rightleftharpoons C + D$$
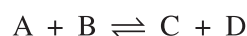
With the passing of the time, the products C and D increase and the reactants A and B decrease which is shown in Fig 4.1.
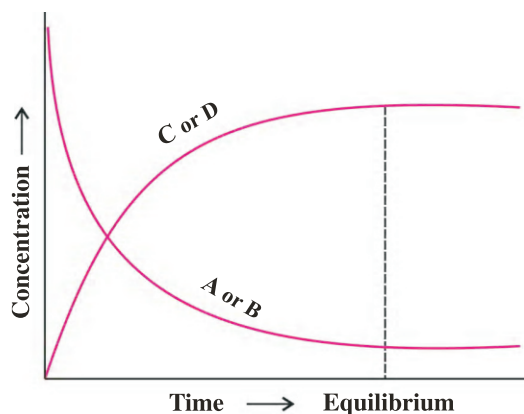
Fig. 4.1 Attainment of chemical equilibrium

It shows that at some point there is decrease in rate of forward reaction and increase in rate of reverse reaction. By chance, if both the reactions occur at the same rate, the system reaches to equilibrium state.

Suppose if we start by taking products C and D in the above reaction, even then equilibrium can be obtained. This means that even if the reaction occurs from any direction, equilibrium can be obtained.

Dynamic Nature of Chemical Equilibrium : The dynamic nature of chemical equilibrium can be demonstrated by taking example of the production of ammonia. By keeping known quantities of dinitrogen gas and dihydrogen gas at high temperature and pressure in a closed vessel, the amount of ammonia gas formed can be determined at constant intervals by a series of experiments. The quantities of unreacted dinitrogen and dihydrogen also can be determined. From this it is concluded that even if the reactants and products are in different proportions, their concentrations are same at equilibrium. This constancy in composition indicates dynamic nature of equilibrium. For this, in synthesis of ammonia, deuterium (D_2) instead of dihydrogen, (H_2) is used and ammonia gas is produced by Haber process and it is studied. The results obtained are similar to those obtained above. In the mixture proportions of N_2, D_2 and ND_3 instead of N_2, H_2, NH_3 can be determined and equilibrium can be obtained. If D_2 is added after the formation of ammonia by reaction of N_2 and H_2, the reaction may not occur but H in NH_3 is displaced by D and ND_3 can be determined by mass spectrometer. Thus, it is proved that in the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ that the reactions from reactants to products and products to reactants that is forward and reverse reactions continuously occur with the same rates and so ND_3 instead of NH_3 is obtained. By the use of radioactive isotope, the dynamic nature of equilibrium can be proved viz. For the reaction, $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ radioactive isotope ^{131}I of iodine can be used to study the dynamic nature of chemical equilibrium. As the equilibrium is dynamic, certain properties or factors are found similar. e.g. Intensity of colour, constant pressure, constant concentration etc.

4.6 Law of Chemical Equilibrium and Equilibrium Constant

The mixture of reactants and products at equilibrium is called equilibrium mixture. We shall study the relation between concentrations of reactants and products at equilibrium state.

Let us take a simple reversible reaction as follows : A + B $\rightleftharpoons$ C + D

In this reaction A and B are reactants and C and D are products. This means that in this reaction moles of reactants and products are one each but in all reactions this may not happen. Hence, it is necessary that their moles are expressed. Balanced reaction determines their moles. viz. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

From the experimental studies of many reversible reactions scientists of Norway, Guldberg and Waage mentioned in 1864 that the concentrations of substances in equilibrium mixture can be expressed by following equilibrium equation.

$$K_c = \frac{[C][D]}{[A][B]} = \frac{\text{Multiplication of concentrations of products}}{\text{Multiplication of concentrations of reactants}}$$

where K_c is equilibrium constant and [ ] bracket expresses concentration of reactant or product in $mollit^{-1}$ or M. The equilibrium equation is also known as law of active masses because in the early years of chemistry, concentration was said to be 'active mass'.

Now, we shall derive the equation for equilibrium constant of a general reaction. Suppose, if a reaction takes place, as given below in which the reactants and products are shown in balanced form with their proper moles (a, b, c or d).

aA + bB $\rightleftharpoons$ cC + dD
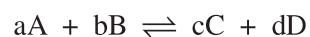
On the basis of Guldberg and Waage's law the rate of forward reaction

$v_f \propto [A]^a [B]^b$....4.2 **or**

$V_f = K_f [A]^a [B]^b$....4.3

where K_f is the proportionality constant for forward reaction.

The rate of reverse reaction $V_r \propto [C]^c [D]^d$ 4.4

$$\text{or} \qquad V_r = K_r [C]^c [D]^d ....4.5$$

where V_r is the proportionality constant for reverse reaction.

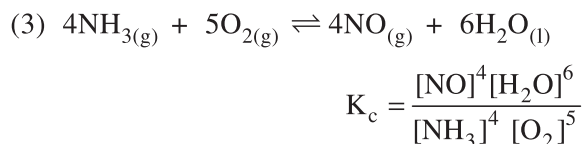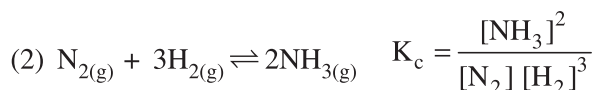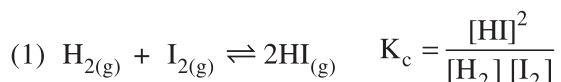At equilibrium the rates of forward and reverse reaction will be equal and so $V_f = V_r$

that is, $K_f [A]^a [B]^b = K_r [C]^c [D]^d$

$$\therefore \quad \frac{K_f}{K_r} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_c \qquad ......4.6$$

where $\quad K_c = \dfrac{K_f}{K_r}$

Thus, when equilibrium is attained if we determine the concentration of the reactants and the products in any reaction and their stoichiometric multiples, the equilibrium constant K_c can be obtained.

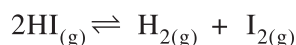Equilibrium constants of some reaction are as shown below :

(1) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

(2) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

(3) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(l)}$

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

Let us think about reaction between H_2 and I_2. This reaction can be written as follows:

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ (From reactants to products)

$$\therefore K_c = \frac{[HI]^2}{[H_2][I_2]} ....4.7$$

Now, we write the reaction as follows :

$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

$$\therefore K_c' = \frac{[H_2][I_2]}{[HI]^2} .... 4.8$$

Equations 4.7 and 4.8 are inverse of each other. Hence $K_c' = \frac{1}{K_c}$. Thus, the equilibrium constant of forward reaction is the inverse of the equilibrium constant of reverse reaction.

The above reaction can also be written as follows :

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)}$$
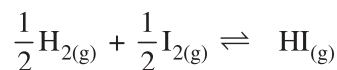
If we write the equilibrium constant for this reaction then,

$$\therefore K_c' = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}}$$

$$= \left[\frac{[HI]^2}{[H_2][I_2]}\right]^{\frac{1}{2}} ....4.9$$

$$\therefore K_c' = K_c^{1/2}$$

Multiplying reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ by n.

$$nH_{2(g)} + nI_{2(g)} \rightleftharpoons 2nHI_{(g)}$$
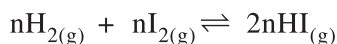
Equilibrium constant will be K_c^n

Hence, it can be written as follows :

Equation of chemical reaction	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K_c
$cC + dD \rightleftharpoons aA + bB$	$K_c' = \dfrac{1}{K_c}$
$(n)aA + (n)bB \rightleftharpoons (n)cC + (n)dD$	$K_c^n = (K_c)^n$

Example 1 : The following reaction can be carried out in a closed vessel at 400 K. The concentration of hydrogen is 0.6 mol lit^{-1}, the concentration of iodine is 0.8 mol lit^{-1} and concentration of hydrogen iodide is 0.14 mol lit^{-1} at equilibrium state. Calculate the equilibrium constant of this reaction.

Solution :

Reaction $\qquad H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
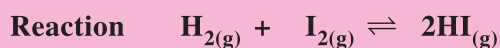
Concentration at equilibrium :

mol lit^{-1} 0.6   0.8   0.14

Equilibrium constant $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

$= \dfrac{(0.14)^2}{(0.6)(0.8)}$

$= 4.1 \times 10^{-2}$

What will be the unit of K_c? Think and verify.

In gaseous reaction, if concentrations are expressed in partial pressures, then equilibrium constant can be obtained from partial pressures of reactants and products, and it is expressed as K_p. Let us think about a gaseous reaction :

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

If we express partial pressures of reactants and products as p_A, p_B, p_C, and p_D respectively then the equation for chemical equilibrium K_p can be shown as below :

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

4.7 Relation between K_p and K_c

As seen earlier the equilibrium constant of a gaseous reaction can be written as

$$\therefore K_p = \dfrac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \quad \text{........ 4.10}$$
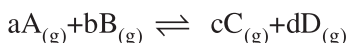
But we know that according to simple gas equation $pV = nRT$. Hence, it can be written as

$$\therefore p = \dfrac{n}{V}RT = CRT$$

(where $\dfrac{n}{V} = C = $ concentration in mol lit^{-1}) Substituting the values of p in the above equation 4.10, it can be written as

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

$$= \dfrac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b} \cdot \dfrac{(RT)^{c+d}}{(RT)^{a+b}} \quad \text{.........4.11}$$

$$= \dfrac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{(c+d)-(a+b)} \text{.........4.12}$$

$$= K_c \cdot (RT)^{\Delta n_g} \text{.........4.13}$$

where $\Delta n_g = (c + d) - (a + b)$

means number of total moles of gaseous products minus number of total moles of gaseous reactants.

Hence, it can be written as

$$K_p = K_c \cdot (RT)^{\Delta n_g} \text{..........4.14}$$

It is necessary to remember that in gaseous reaction, pressure depends on number of moles and so their partial pressures can be taken as concentrations. Atmosphere is the unit used for pressure but according to SI unit it is expressed as Pascal. A summary of K_p and K_c with respect to values Δn_g, can be written as follows : **(1) if $\Delta n_g = 0$ then $K_p = K_c$ (2) if $\Delta n_g > 0$ then $K_p > K_c$ (3) if $\Delta n_g < 0$ then $K_p < K_c$**

Example 2 : 1 mole H_2O and 1 mole CO are heated in a colsed vessel of 10 litres at 725 K temperature. At equilibrium H_2O 40% by mass reacts with CO gas as follows :

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

Calculate equilibrium constants K_p and K_c for this reaction :

Solution :

Reaction : $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$

Initial concentration mol lit^{-1}

| $\frac{1}{10}$ | $\frac{1}{10}$ | 0 | 0 |

Concentration at equilibrium mol

| $\frac{1(100-40)}{100}$ | $\frac{1(100-40)}{100}$ | $\frac{40}{100}$ | $\frac{40}{100}$ |
| $= 0.6$ | $= 0.6$ | $= 0.4$ | $= 0.4$ |

concentration mol lit^{-1}

| $\frac{0.6}{10}$ | $\frac{0.6}{10}$ | $\frac{0.4}{10}$ | $\frac{0.4}{10}$ |
| $= 0.06$ | $= 0.06$ | $= 0.04$ | $= 0.04$ |

Now, $K_c = \dfrac{[H_2][CO_2]}{[H_2O][CO]} = \dfrac{0.04 \times 0.04}{0.06 \times 0.06} = 0.44$

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

In this reaction (number of moles of gaseous products) − (number of moles of gaseous reactants)

$(1 + 1) - (1 + 1) = \Delta n_g = 0$

Hence, $K_p = K_c \cdot (RT)^0 = K_c$

Hence, the values of K_p and K_c will be same i.e. 0.44

Example 3 : The equilibrium constant of the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ at 700 K temperature is 54.8. The concentration of HI at equilibrium is 0.5 mollit^{-1}. Suppose reaction is carried by taking $HI_{(g)}$ find concentrations of $H_{2(g)}$ and $I_{2(g)}$ at equilibrium.

Solution :

Reaction : $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
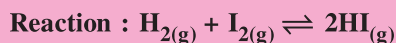
$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.5)^2}{[H_2][I_2]}$$

i.e. $54.8 = \dfrac{(0.5)^2}{[H_2][I_2]}$

$\therefore [H_2][I_2] = \dfrac{(0.5)^2}{54.8}$ But at equilibrium

$H_{2(g)} = I_{2(g)}$ and

$[H_2][I_2] = \dfrac{(0.5)^2}{54.8} = 4.56 \times 10^{-3}$

$[H_2] = [I_2] = \sqrt{4.56 \times 10^{-3}} = 0.0675$ mollit^{-1}

Activity : Derive relation amongst K_c, K_p and K_x.

Hint : According to Dalton's law of partial pressures, if the total pressure is P atmosphere, the partial pressures of reactants A and B and partial pressures of products C and D will be $X_A \cdot p_A$, $X_B \cdot p_B$, $X_C \cdot p_C$ and $X_D \cdot p_D$ respectively, where X is mole fraction. Using this derive the following relations :

$$K_p = K_x \cdot P^{\Delta n_g} \text{ and } K_c = K_x \cdot V^{-\Delta n_g}$$

4.8   Types of Chemical Equilibrium

The equilibrium is of two types :

(i) Homogeneous equilibrium and

(ii) Heterogeneous equilibrium.

(i) Homogeneous equilibrium : In **homogeneous system all the reactants and the products are in one similar phase** viz.

The product ammonia produced by reaction of reactants dinitrogen and dihydrogen, all are in gaseous phase. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. Similarly, the hydrolysis of methyl acetate is also homogeneous equilibrium because, the reactants and the products in it are also in the same phase (liquid phase).

$$CH_3COOCH_{3(l)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(l)} + CH_3OH_{(l)}$$
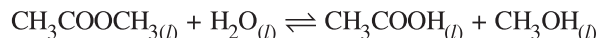
In addition to this, the reaction between aqueous solution containing Fe^{3+} ions and aqueous solution containing SCN^- ions is also an example of homogeneous equilibrium. But the only change in it is that this equilibrium is ionic equilibrium.

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)}$$
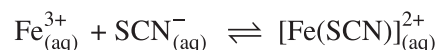
We shall study this, later on in this unit.

All the equilibrium reactions and their equilibrium constants that we discussed earlier are the examples of homogeneous equilibrium and also derived from the relations between K_p, K_c and K_x related to them. For calculation of values of K_p pressures must be expressed in unit of bar because, bar is the unit in standard condition but in SI unit it is pascal. The relation between them is as follows :

1 Pascal Pa = 1 Nm^{-2} (Newton meter^{-2}) and 1 bar = 10^5 Pa.

For calculation of equilibrium constants of homogeneous equilibrium constant, we understand the following examples :

Example 4 : $PCl_{5(g)}$ can be obtained by chemical reaction between $PCl_{3(g)}$ and $Cl_{2(g)}$ in closed vessel. The concentrations of PCl_3, Cl_2, and PCl_5 in this reaction at 500 K are 1.59 m, 1.59 M and 1.41 M respectively, calculate equilibrium constant of this reaction.

Solution :

Reaction : $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$
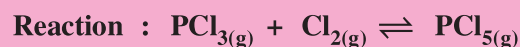
$$Kc = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{1.41}{1.59 \times 1.59}$$

$$= 5.58 \times 10^{-3} \text{ mollit}^{-1}$$

Suppose, we want to calculate K_p for this reaction. According to relation,

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

$$K_p = 5.58 \times 10^{-3} (0.0831 \times 500)^{-1}$$

because Δn_g = number of moles of gaseous product − number of moles of gaseous reactants = 1 − 2 = −1

$$\therefore K_p = \frac{5.58 \times 10^{-3}}{(0.0831 \times 500)}$$

$$= 1.3 \times 10^{-4} \ bar^{-1}$$

Example 5 : Ethyl acetate is obtained by reaction of ethanol with acetic acid in presence of H^+ ions. Suppose 1 mole acetic acid and 0.18 mole ethanol are taken in this reaction. At equilibrium 0.171 mole ethylacetate is obtained. Calculate equilibrium constant of this esterification reaction.

Solution :

Reaction :

$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$

Initial

concentration :

  1 mol   0.18 mole   0   0

concentration

at equilibrium

(1-0.171)mole (0.18-0.171)mole 0.171mole 0.171mole

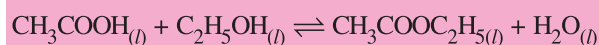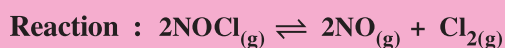0.829mol   0.009mole   0.171mole 0.171mole

$$K_c = \frac{[CH_3COOC_2H_5] \ [H_2O]}{[CH_3COOH] \ [C_2H_5OH]}$$

$$= \frac{0.171 \times 0.171}{0.829 \times 0.009} = 3.92$$

Example 6 : The value of equilibrium constant for the reaction $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$ is obtained as 0.033 bar at 1060 K temperature, then what will be the value of K_c for this reaction ?

Solution :

Reaction : $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$

As we know, that $K_p = K_c \ (RT)^{\Delta n_g}$

Δn = Moles of $NO_{(g)}$ + Moles of $Cl_{2(g)}$ − $\left(\text{Moles of } NOCl_{(g)}\right)$

$= (2 + 1 - 2) = 3 - 2 = 1$

Putting the values, $0.033 = K_c \ (0.0831 \times 1060)^1$

$$\therefore K_c = \frac{0.033}{0.0831 \times 1060}$$

$$= 3.7 \times 10^{-4} \ mol.lit^{-1}$$

(ii) Heterogeneous Equilibrium : If reactants and products, possess more than one phase, the equilibrium is called heterogeneous equilibrium. The equilibrium between water (liquid) and water vapour (steam) in a closed vessel is the example of heterogeneous equilibrium.

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$
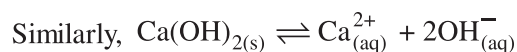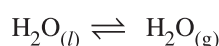
Similarly, $Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$ is also the example of heterogeneous equilibrium. (Equilibrium between solid and liquid). It is necessary to note here that this is an example for ionic equilibrium.

Generally, in heterogeneous equilibrium, pure solid or liquid are associated, the concentrations of reactants and products can be separated, viz. The concentration of pure solid or liquid is its density and density is constant at constant temperature. Hence, concentration can also be taken as constant or the pure solid or liquid which are present will be independent of concentration. Suppose, some substance X is involved in this, then concentrations $X_{(s)}$ and $X_{(l)}$ will be taken as constant in whatever proportion they are present while concentrations of $X_{(g)}$ and $X_{(aq)}$ will change and will vary with volume.

Let us take example of thermal decomposition of calcium carbonate.
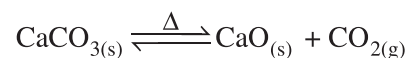
$$CaCO_{3(s)} \underset{\longleftarrow}{\overset{\Delta}{\longrightarrow}} CaO_{(s)} + CO_{2(g)}$$

If we write the equation for heterogeneous equilibrium on the basis of stoichiometry then,

$$K_c = \frac{[CaO_{(s)}] \ [CO_{2(g)}]}{[CaCO_{3(s)}]} \qquad ....4.15$$

As discussed earlier, $CaO_{(s)}$ and $CaCO_{3(s)}$ are in solid state, their concentrations can be taken equal to their densities, i.e. they remain constant. Hence, the above equation can be written as below :

$$K_e \times K_1 = K_c = [CO_{2(g)}] \qquad ....4.16$$

where, $\quad K_1 = \dfrac{[CaCO_{3(s)}]}{[CaO_{(s)}]} \quad$ or $\quad K_p = p_{CO_2}$

where P_{CO_2} is the concentration or pressure of CO_2 gas at equilibrium. The equilibrium constant of above reaction is found to be 2.0×10^5 at 1100 K temperature. Hence, $K_p = P_{CO_2} = 2.0 \times 10^5$ Pa. Converting it into bars,

$$\dfrac{2 \times 10^5 \text{ Pa}}{1 \times 10^5 \text{ Pa / bar}} = 2.0 \text{ bar}$$

It is necessary to remember that in heterogeneous equilibrium, even if the solid and liquid are in very less proportion, their concentrations or partial pressures are not considered in equilibrium constant, viz. For the reaction,

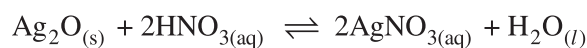$$Ag_2O_{(s)} + 2HNO_{3(aq)} \rightleftharpoons 2AgNO_{3(aq)} + H_2O_{(l)}$$

$$K_c = \dfrac{[AgNO_{3(aq)}]^2 \, [H_2O_{(l)}]}{[Ag_2O_{(s)}] \, [HNO_{3(aq)}]^2}$$

$$= \dfrac{[AgNO_{3(aq)}]^2}{[HNO_{3(aq)}]^2}$$

because, $[H_2O_{(l)}]$ and $[Ag_2O_{(s)}]^2 =$ constant.

4.9 Characteristics of Equilibrium

(i) During chemical equilibrium, the properties like colour, concentration, pressure or temperature of the system remain constant and they are similar in the total area of the system.

(ii) When chemical equilibrium is attained, the rates of forward and reverse reactions become equal.

(iii) If the factors like concentration, pressure, temperature etc. which affect the chemical equilibrium are changed, they produce effect on equilibrium.

(iv) Even if the initial concentrations are different, the equilibrium constant remains constant at constant temperature.

(v) The value of equilibrium constant changes if the temperature changes.

(vi) For attainment of equilibrium, the reaction can be carried out from left to right (reactants to products) or from right to left (products to reactants).

(vii) There is no effect of catalyst on the equilibrium constant and so the proportions of products remain same but the rate of reaction to attain equilibrium increases.

Units of Equilibrium Constant : To express equilibrium constant K_c, the concentrations are required in mol lit^{-1} or M and for K_p, Pa, kPa, bar or atmosphere is taken. Hence, after selecting these units, if the numerator and denominator become equal, then there will be no unit or equilibrium constant and will be unitless and ratio will become 1. But if the concentrations of substances are expressed in their stoichiometric proportions, and are written accordingly, then the unit will be there. Some reactions and units of their K are expressed below :

Reaction :	Unit
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	Unitless

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$\dfrac{(mol.lit^{-1})^2}{(mol.lit^{-1})(mol.lit^{-1})^3}$$

$$= (mol.\ lit^{-1})^{-2}$$

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons$$

$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \quad \text{Unitless}$$
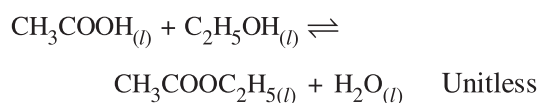
Example 7 : The equilibrium constant of the reaction $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$, K_c is 4.25 at 810 K. Suppose, if this reaction begins with reactants having concentrations 0.1 mol.lit^{-1} or M, then calculate the concentrations of $CO_{(g)}$, $H_2O_{(g)}$, $CO_{2(g)}$ and $H_{2(g)}$ at equilibrium at 810 K.

Solution :

Reaction : $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

Initial concentration

       0.1M   0.1M   0   0

Concentration at equilibrium

     $(0.1 - x)$M $(0.1 - x)$M xM xM

where xM is the concentration of $CO_{2(g)}$ and $H_{2(g)}$ at equilibrium. Now, equilibrium constant

$$K_c = \frac{[CO_{2(g)}] \, [H_{2(g)}]}{[CO_{(g)}] \, [H_2O_{(g)}]}$$

$$= \frac{[x] \, [x]}{[0.1-x] \, [0.1-x]}$$

$$\therefore \ 4.25 = \frac{x^2}{[0.1-x]^2}$$

$$\therefore \ x^2 = 4.25(0.01 - 0.2x + x^2)$$

$$\therefore \ x^2 = 0.0425 - 0.850x + 0.0425x^2 = 0$$

$$\therefore \ 3.25x^2 - 0.850x + 0.0425 = 0$$

The coefficients of quadratic equation are a = 3.25, b = − 0.850 and c = 0.0425. The solution of quadratic equation $ax^2 + bx + c = 0$ is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{+0.850 \pm \sqrt{(0.85)^2 - 4\,(3.25)\,(0.0425)}}{(2 \times 3.25)}$$

$$\therefore \ x = \frac{0.850 \pm 0.41}{6.50}$$

$\therefore$ One out of the two solutions

$x_1 = \dfrac{0.850 + 0.41}{6.50} = 0.19$ and second solution

$x_2 = \dfrac{0.850 - 0.41}{6.50} = 0.068$. But initial concentration is 0.1M. Hence, the value 0.19M is not acceptable. Hence, $x = 0.068$M is acceptable.

Thus, $x = [CO_{2(g)}] = [H_{2(g)}] = 0.068$M and concentration of $CO_{(g)}$ at equilibrium will be $(0.1 - x) = (0.1 - 0.068) = 0.032$ M. and concentration of $H_{2(g)}$ at equilibrium will be $(0.1 - x) = (0.1 - 0.068) = 0.032$M.

4.10 Applications of Equilibrium Constant

Some of the important applications of equilibrium constants are as follows :

(i) Prediction of completion of reaction : The value of equilibrium constant shows proportion of completion of the reaction. If the value of $K_c > 1$, then more proportion of products will be obtained, i.e. the reaction of getting products from the reactants will be towards completion. If the value of K_c is less than 1, then the proportions of reactants will be more as compared to products and so there will be decrease in the tendency for the completion of the reaction. If value of K_c is 1, then the proportions of reactants and products will be in equilibrium state.

(ii) Prediction about the forward or reverse direction of the reaction : The prediction about the reaction at any stage will occur in which direction can be decided from the value of equilibrium constant. For this we have to calculate the reaction quotient (Q_c). As mentioned earlier, the value of K_c for the reaction $aA + bB \rightleftharpoons cC + dD$.

$$K_c = \frac{[C]^c \, [D]^d}{[A]^a \, [B]^b} = Q_c$$

If $Q_c < K_c$, or $K_c > Q_c$, then reaction will occur in forward direction, i.e. from reactants to products. If $Q_c > K_c$ or $K_c < Q_c$, then the reaction will occur in reverse reaction, i.e. from products to reactants. If $Q_c = K_c$, the reaction will remain in equilibrium.

Example 8 : The value of K_c for the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ is found to be 57.0 at 700 K temperature. Suppose in reaction mixture the concentrations of reactants and products at some determined time are as follows : $[H_2] = 0.05$M, $[I_2] = 0.10$M and $[HI] = 0.20$M. Determine in which direction the reaction will proceed :

Solution :

Reaction : $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
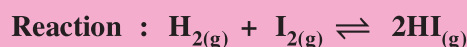
$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = Q_c$$

$$Q_c = \frac{(0.20)^2}{(0.05)\,(0.1)} = \frac{0.04}{0.005} = 8$$

Thus, $Q_c = 8$ and $K_c = 57.0$. Hence, $Q_c < K_c$ i.e. The reaction will occur in forward direction which means that reaction will occur in the direction of obtaining product from reactant.

(iii) Calculation of Equilibrium Concentration : If we know the concentrations of reactants and products at equilibrium time we can calculate the value of equilibrium constant and if the initial concentration of the reactants and the value of equilibrium constant are known, equilibrium concentrations can be calculated. For this the following steps are to be followed.

Step 1 : Write chemical reaction in balanced form.

Step 2 : (a) Mention the initial concentrations of reactants and products below them and (b) Mention the changes that take place when equilibrium is reached. Mention concentration in mollit^{-1} or pressure in bar. Write x for the unknown concentrations and then mention their stoichiometry.

Step 3 : Put the values of equilibrium concentration in the equation of chemical equilibrium and solve the equation. If quadratic equation is obtained, find out the two values using formula for it and determine the acceptable value.

Step 4 : From the value of x, determine the acceptable value.

Step 5 : Verify the value of equilibrium constant by putting the values of equilibrium concentrations in the equation for equilibrium constant.

Example 9 : 6.9 gram N_2O_4 is taken in a closed versel of 0.5 litre volume. Temperature is 400 K. Required time passes to obtain equilibrium. If the reaction is $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ and at equilibrium total pressure is 9.15 bar, calculate K_c, K_p and partial pressures at equilibrium. R = 0.082 lit atm mol^{-1} kelvine

Solution :

Reaction : $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

Moles of N_2O_4 = $\dfrac{\text{Mass of } N_2O_4}{\text{Molecular mass}}$

$= \dfrac{6.9}{92} = 0.075$

The volume of closed vessel is 0.5 lit.

Now, PV = nRT

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

$= \dfrac{0.075}{0.5} \times 0.082 \times 400 = 4.92 \, \text{bar}$

At equilibrium total presure is 9.15.

Reaction : $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
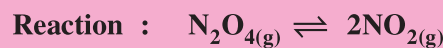
Initial concentration 4.92 bar   0 bar (pressure)

At equilibrium

concentration (pressure)

$(4.92 - x)$ bar $2x$ bar

where x = concentration (pressure) of NO_2

Now, total pressure = partial pressure of $N_2O_{4(g)}$ + partial pressure of $NO_{2(g)}$

$\therefore$ $9.15 = (4.92 - x) + 2x$

$\therefore$ $9.15 = 4.92 - x + 2x = 4.92 + x$

$\therefore$ $x = 9.15 - 4.92 = 4.23$ bar

Partial pressure of $N_2O_{4(g)}$ at equilibrium

$p_{N_2O_4} = 4.92 - 4.23 = 0.69$ bar

Partial pressure of $NO_{2(g)}$, at equilibrium.

$p_{NO_2} = 2x = 2 \times 4.23 = 8.46$ bar

Now, $K_p = \dfrac{(p_{NO_2})^2}{(p_{N_2O_4})}$

$= \dfrac{(8.34)^2}{0.69} = 103.73$ bar

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

$\therefore$ $103.73 = K_c \, (0.082 \times 400)^1$

Here Δn_g = (moles of gaseous NO_2 − moles of gaseous N_2O_4)

$= (2 - 1) = 1$

$\therefore$ $K_c = \dfrac{103.73}{0.082 \times 400}$

$= 3.162 \approx 3.2 \, \text{mol lit}^{-1}$

4.11 Relation Between Reaction Quotient Q_c, Equilibrium Constant K and Gibbs' Free Energy

Chemical equilibrium has no relation with chemical kinetics, but it is definitely related to thermodynamics. In thermodynamics, the change in free energy ΔG is known as Gibbs free energy change. This difference is the difference

between total free energy of products and total free energy of reactants. Three possibilites are there : negative, zero and positive. We shall discuss its relation with equilibrium constant.

(i) If the value of ΔG is negative, then the reaction will be spontaneous (will occur of its own) and it will always proceed in the direction toward products i.e. forward reaction.

(ii) If the value of ΔG is positive then the reaction will not be spontaneous and will always proceed in the direction from products to reactants.

(iii) If the value of ΔG is zero, then the reaction will be in equilibrium i.e. the concentrations of reactants and products will be in equilibrium and the reaction will not proceed towards either of the forward or reverse reactions.

In the thermodynamics, the relation between changes in free energy and concentration Quotient (Q_c) is as follows :

$$\Delta G = \Delta G^0 + RT \ln Q_c \ \text{....... 4.17}$$

where ΔG^0 = standard Gibbs free energy change or it is the value of Gibbs standard free energy change.

As we have seen, $\Delta G = 0$ at equilibrium,

Hence, $Q_c = K_c$ and in putting the value equation 4.17,

$$\Delta G = \Delta G^0 + RT \ln K = 0 \ \text{...... 4.18}$$

$$\text{or } \Delta G^0 = - RT \ln K \ \text{...... 4.19}$$

If we write this equation by taking antilogaritham it can be written as

$$K = e^{-\Delta G^0/RT} \ \text{...... 4.20}$$

Hence, equation 4.20 can be used and related to the spontaneity and ΔG of the reaction.

(i) If $\Delta G^0 < 0$, then $-\Delta G^0/RT$ will be positive. Hence, it can be said that $K > 1$ or the values of ΔG is negative, the reaction will always proceed in the direction of forward reaction and proportions of products will be more.

(ii) If $\Delta G^0 > 0$ then $-\Delta G^0/RT$ will be negative and so $K < 1$. This shows that the reaction will not be spontaneous and the proportion of products will be less than those of reactants.

Example 10 : The value of equilibrium constant in reaction of phosphorylation of glucose during glycolysis was obtained 3.8×10^{-3} at 298 K temperature. Calculate the value of ΔG^0 for this reaction and mention your opinion about this reaction.

Solution : $K = 3.8 \times 10^{-3}$ and $T = 298$ K

Now, $\Delta G^0 = - RT \ln K$

$= - 2.303 RT \log K$

$= -2.303 \times 8.314 \times 298 \times \log 3.8 \times 10^{-3}$

$= -2.303 \times 8.314 \times 298 \times (-2.4202)$

$= 13809 \ \text{Jmol}^{-1} \approx 13.81 \ \text{kJmol}^{-1}$

The value of ΔG^0 being positive, the reaction will not be spontaneous.

4.12 Factors Affecting Chemical Equilibrium

In industries, the intention is to obtain maximum product with minimum expenses. Hence, the study of factors affecting the equilibrium constant and their aggregation (interpretation) becomes more important in the method to keep the equilibrium. In the study of factors affecting equilibrium concentration or pressure of reactants, temperature, and use of catalyst are studied. The production of ammonia by Haber process, using dinitrogen and dihydrogen is an important reaction, because it is used in the industrial production of several tons of artificial fertilizers. Hence, the study of factors affecting such reactions becomes essential.

Equilibrium constant is independent of initial concentration of reactant but, if change is carried out in concentration or pressure, there is an effect on equilibrium, the equilibrium tries to nullify this effect. Reaction can be endothermic or exothermic. Hence the heat absorbed or evolved, functions like that of the reactant and its effect is on equilibrium which tries to nullify the effect. Le Chatelier studied the effect of concentration and temperature and his presentation is called Le Chatelier's principle whose statement can be written as below :

"If from the factors determining the equilibrium state, any one factor is changed, there will be such a change in the system that the effect will be nullified or made negligible so that the value of equilibrium constant at that temperature will remain constant." This principle

can be applied to both physical and chemical equilibrium.

We shall study in detail the factors like (1) change in concentration (2) change in pressure (3) addition of inert gases (4) change in temperature and (5) use of catalyst affecting the equilibrium.

(1) Effect of change in concentration : If we add or remove the reactant or the product from the reaction in equilibrium, its effect on equilibrium according to Le Chatelier's principle will be as follows :

(a) If the concentration of reactant or product is increased by addition of reactant or product, the reaction will occur in such a way that the increase in concentration will be taken for use i.e. the increase in concentration of reactant, the concentration of product will increase and if concentration of product is increased the reaction will result in the direction of increase in concentration of the reactant.

(b) If the concentration of reactant or product is decreased by removing reactant or product, the reaction will occur in such a way that product or reactant will be established again.
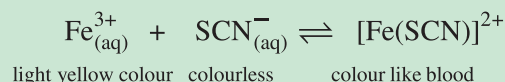
Hence, if any change in concentration of reactant or product is carried out then the equilibrium will try to make this effect minimum and equilibrium will be established accordingly. If we take this as an example, in the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3$, if concentration of reactants dinitrogen or dihydrogen is increased, the reaction will proceed towards right hand side and the product ammonia obtained will be more. If the concentration of dinitrogen or dihydrogen is decreased, the reaction will proceed towards left hand side and reactants of dinitrogen or dihydrogen will be obtained back i.e. production of ammonia will decrease. Here, it is necessary to remember that 1 mole dinitrogen combines with 3 moles of dihydrogen in this reaction and forms 2 moles of ammonia. Hence, increase in concentration of dihydrogen rather than dinitrogen, will give more product. We take another example of heterogeneous equilibrium. If solid $CaCO_{3(s)}$ is heated in closed vessel, the following decomposition reaction will occcur.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

Hence, if more $CaO_{(s)}$ is to be obtained then, the $CO_{2(g)}$ formed in the reaction should be removed because $CO_{2(g)}$, gas can combine with solid $CaO_{(s)}$ and carry out reverse reaction then proportion of product will decrease. Hence, by removing $CO_{2(g)}$ from the reaction vessel, more $CaO_{(s)}$ can be obtained.

Activity : Let us think about one example from ionic equilibrium $Fe^{3+}_{(aq)}$ ion reacts with $SCN^{-}_{(aq)}$ ion and forms $[Fe(SCN)]^{2+}_{(aq)}$ ion.

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}$$
light yellow colour   colourless   colour like blood

In this reaction, if concentration of reactant is increased by addition of $Fe^{3+}_{(aq)}$ or $SCN^{-}_{(aq)}$ ion, then more $[Fe(SCN)]^{2+}_{(aq)}$ will be formed and so the red colour will become more dark. If concentration of product is increased by addition of $[Fe(SCN)]^{2+}_{(aq)}$, then concentration of $[Fe(SCN)]^{2+}_{(aq)}$ will decrease and the darkness of red colour will decrease because the reaction will move towards reactant.

This is given as an experiment for demonstration in practical book. Hence, it can be carried out as the activity.

(2) Effect of change of pressure : The change in pressure can be carried out by increasing or decreasing the concentration of the gas or respectively decreasing or increasing the volume of the vessel. By carrying out this type of change, there will be change in proportions of gaseous reactants or products or total products. Le Chatelier's principle can also be applied to such reactions. In heterogeneous equilibrium if we do not take into consideration the effect of pressure on solid or liquid substances in equilibrium, it can work because their volumes and concentration are independent of change of pressure. Let us take the following example.

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$$
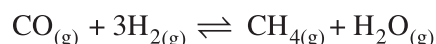
In this reaction 1 mole of reactant $CO_{(g)}$ reacts with three moles of reactant $H_{2(g)}$ and forms 1 mole product $CH_{4(g)}$ and 1 mole product $H_2O_{(g)}$. Thus, 2 moles product is obtained from 4 moles of reactants. Hence, there is decrease in number of moles during reaction.

Suppose, the pressure on the closed vessel in which the reaction is carried out at constant temperature and the volume of equilibrium mixture is made half, then what will happen? Total pressure will be double because

PV = constant. the concentrations or pressures of reactants or products are increased. Hence, according to Le Chatelier's principle, the equilibrium will try to attain the original state. As pressure is doubled and 2 moles of products are obtained and 4 moles of reactants, there is decrease in number of moles and the reaction will go in forward direction i.e. more product will be obtained.

As a reverse of this, if in reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ the number of moles of product increases (from 0 to 1). If pressure is increased by addition of $CO_{2(g)}$, then, the reaction will become reverse reaction and will decrease the product.

(3) Addition of inert gas : If the volume of the system is kept constant and inert gas not taking part in the reaction is added, then there will be no effect on equilibrium. As inert gas does not react with reactant or product, their partial pressure will not change and as a result there will not be any effect on equilibrium. As seen earlier that K_c which depends on Q_c, there is no change on it.

(4) Effect of temperature : The value of equilibrium constant is associated with temperature i.e. the value of equilibrium is constant at constant temperature. If temperature changes its value also changes. Reactions can be of two types (1) Exothermic and (2) Endothermic. With the change in temperature, there is a change in absorbed or evolved heat. In exothermic reaction when heat is absorbed it works as a reactant. In exothermic reaction when heat is evolved, it works as a product. Hence, it can be said that the equilibrium constant increases with increase in temperature in endothermic reaction; equilibrium constant decreases with increase in temperature in exothermic reaction. Especially, let us make it clear that the increase or decrease in temperature affects the rate of reaction. Let us think about reaction of production of $NH_{3(g)}$.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H = -92.38$ kJmol^{-1}
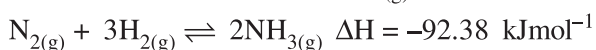
ΔH means change in enthalpy which is the difference in total enthalpies of products and reactants. Its positive value indicates endothermic reaction and negative value indicates exothermic reaction. Hence, the above reaction is exothermic. As seen earlier that increase in temperature is not favourable for exothermic reaction because

reaction will go in reverse direction and will decrease the product. Hence, decrease in temperature is advantageous to obtain more product but by decreasing the temperature the rate of reaction decreases. Hence, more time is required for completion of the reaction.

Hence, as a compromise, at the lowest possible temperature and at the highest possible pressure, catalyst is used. Hence, more possible product is obtained in less possible time. This type of state is called optimization state.

Activity : The effect of temperature on equilibrium can be studied by following reaction.

$$2NO_{2(g)} \underset{+\Delta}{\overset{-\Delta}{\rightleftharpoons}} N_2O_{4(g)} \qquad \Delta H = -ve$$
Brown coloar   Colourless
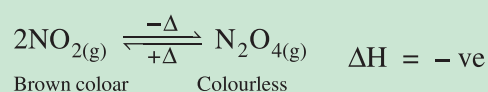
This reaction is exothermic and so the effect of decrease in temperature can be studied using ice and the effect increase in temperature can be studied by keeping the flask in a hot water vessel. For this activity, perform the experiment according to the experiment for demonstration given in a practical book and obtain conclusion regarding effect of temperature.

(5) Effect of catalyst : The use of suitable catalyst always helps to increase the rate of reaction, viz. iron powder is used as the catalyst in the production of ammonia by Haber's process. Use of catalyst is associated with chemical kinetics because it affects the rate of reaction. The function of catalyst is to decrease the energy of activation. Hence, the reaction easily moves forward towards product. During this reaction, the energy of activation decreases but has no effect on equilibrium constant, that is, more proportion of product cannot be obtained. Let us examine the case of reaction of ammonia gas obtained by combination of dinitrogen gas and dihydrogen gas with the halp of Haber's process.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H = -92.38$ kJmol^{-1}
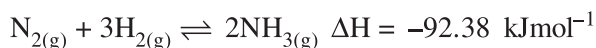
In the above reaction, total 2 moles product are obtained from total 4 moles of reactants. Hence, according to Le Chatelier's principle, increase in pressure is advantageous to get more ammonia but for the reactions occurring in closed vessel and so the pressure has to be kept limited. In addition, this reaction is exothermic and so according to Le Chatelier's principle, the decrease in temperature is advantageous but decrease in

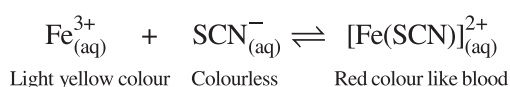temperature affects the rate of reaction. Hence, more time is required for completion of the reaction, which is not economically advantageous in industry. Hence, temperature is also to be restricted. By making compromise with these two and using catalyst whereby the energy of activation is decreased and increasing rate of reaction, more possible product is obtained in less time. Hence, Haber used iron powder as catalyst in the production reaction of ammonia and satisfactory results were obtained. In the production of ammonia, the values of optimum pressure and temperature are 200 bar and 773 K temperature respectively and iron powder is used as catalyst. If the value of equilibrium constant of the reaction K_c is very low then the use of catalyst is not fruitful or helpful.

4.13 Ionic Equilibrium in Solution

In this unit on equilibrium, we have so far studied the reactions in which molecular reactions are included. Now, the equilibrium that we shall study in this remaining part of the unit will be reactions in which ions are included. In the previous part of this unit, we have studied the chemical equilibrium and now we shall study ionic equilibrium in the remaining part of the unit. There is an experiment on ionic equilibrium in your practical book. When potassium thiocyanate solution is added to ferric nitrate solution blood like red colour can be obtained. This equilibrium reaction can be written in ionic form as below :

$$Fe^{3+}_{(aq)} \ + \ SCN^-_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)}$$

Light yellow colour   Colourless   Red colour like blood

If we write the equilibrium constant, K_c for the reaction by expressing concentrations of ions, then $K_c = \dfrac{[Fe(SCN)]^{2+}}{[Fe^{3+}][SCN^-]}$. As the concentration of ions are expressed in mollit^{-1} or molarity, equilibrium constant is expressed as K_c. Ions are mostly present in aqueous solutions.

You know that electric current can pass through the aqueous solution of sodium chloride and if we increase the concentration of sodium chloride, conductivity increases. When electric current is passed through water, negligible electric current is passed through it. In aqueous solution the electric current is conducted by ions. Hence, it can be said that in aqueous solution of sodium chloride the ions are present in the solution. On the basis of this Michael Faraday classified

substances into two sections (1) electrolyte and non-electrolyte. In the above example, sodium chloride is an electrolyte because it conducts electricity and gets decomposed by electricity while pure water does not get decomposed by electricity and so it is a non-electrolyte.

Afterwards, it was found that electrolytes can be divided into two parts, viz. some compounds are in the form of ions obtained by complete ionisation of the compound and so their ionisation is almost 100%. e.g. solution of NaCl. Some compounds possess incomplete ionisation i.e. the number of ions in their aqueous solution is less (about 2 to 3%). The conduction of current in aqueous solutions, depend on the number of ions and so it can be said that substances like sodium chloride are completely ionised and so they are called strong electroleytes but substances like water are incompletely ionised and so they are called weak electrolytes. Examples are mentioned in the following Table 4.2.

Table 4.2

Type of Electrolyte	Examples
(1) Strong electrolyte	Aqueous solutions of HCl, NaOH, KCl, NaCl, etc.
(2) Weak electrolyte	Aqueous solutions of CH_3COOH, NH_4OH, CH_3NH_2 etc.

As strong electrolytes are completely ionised, the reaction takes place in forward direction and so equilibrium is not possible but weak electroytes are incompletely ionised and so the reaction occurs both in forward and reverse reactions so that equilibrium becomes possible. Thus, the study of equilibrium constant, factors affecting equilibrium can only be applied to weak electrolytes.

4.14 Acid, Base and Salt

We come in contact with acid, base and salt in our everyday life. In the stomach of a human being about 1.2 to 1.5 litres per day HCl is secreted. In addition, lemon juice, tamarind water etc. are acids. Bases like NaOH and KOH are used in preparation of soap. We also use salts like washing soda, baking soda and salt. Washing soda can be classified as weak base and acetic acid in vinegar as weak acid.

Most of the acids are sour in taste. Word 'Acidus' is there for sour in taste in Latin language. The word Acid is derived from it.
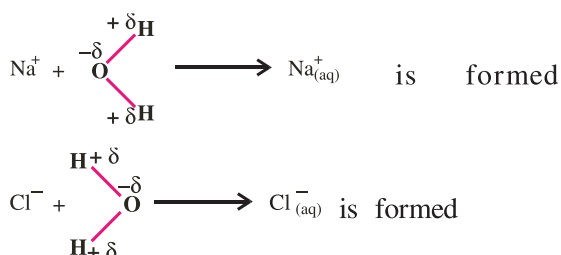
4.14.1 Definition of Acid and Base :

Earlier you have already studied about acids and bases and accordingly their definitions can be given as follows :

Acid means such a substance which is (1) Sour in taste (2) turns wet blue litmus paper red (3) forms salt and water by reacting with base (4) In certain circumstances produces hydrogen gas by reacting with metals. Similarly, base means such a substance which is (1) Bitter in taste (2) turns wet red litmus blue (3) froms salt and water by reaction with acid.

The above definitions have been derived from the properties of the acids and bases. Hence, they are called 'Operational' definitions. Their limitation is that they cannot explain why acids are sour and bases are bitter. Hence, operational definitions are called old definitions. The modern definitions used at present are called 'Conceptual' definitions in which Arrhenius, Bronsted-Lowry and Lewis definitions of acid and bese are included which we shall study later on.

In the unit of solid state, you have studied that Na^+ and Cl^- ions are present in solid NaCl. Even then they do not conduct electricity because each Na^+ ion is surrounded by Cl^- ions and each Cl^- ion is surrounded by Na^+ ions. i.e. the ions remain fixed and so are not available free for conduction of electricity but its aqueous solution or in its molten state conducts elecricity because the ions move apart from each other and become capable of conducting electricity. The reason for conduction of electricity in aqueous solution is due to the nature of water as polar solvent. Water can be expressed as $_{+\delta}\overset{-\delta}{\underset{H \quad H}{O}}_{+\delta}$ on oxygen partial negative charge and on hydrogen partial positive charge are present. Na^+ from NaCl, gets attracted towards negatively charged oxygen $O^{\delta-}$ and Cl^- ion gets attracted towards the positively charged $H^{+\delta}$ in H_2O. Hence,

$$Na^+ + \overset{+\delta H}{\underset{+\delta H}{O^{-\delta}}} \longrightarrow Na^+_{(aq)} \quad \text{is} \quad \text{formed}$$

$$Cl^- + \overset{H^{+\delta}}{\underset{H+\delta}{O^{-\delta}}} \longrightarrow Cl^-_{(aq)} \quad \text{is formed}$$

which try to separate from each other. Hence, conduction of electricity takes place.
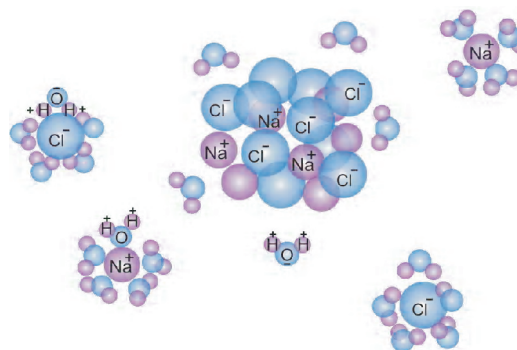
Fig. 4.2 Dissolution of sodium chloride in water

Na^+ and Cl^- ions are stabilised by their hydration with polar water molecules.

Hydrogen chloride and acetic acid are polar covalent compounds. When dissolved in water hydrogen chloride (HCl) is completely ionised viz. $HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$ but acetic acid (CH_3COOH) gets incompletely ionised viz.

$$CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

This type of reaction with water is called hydration reaction and for solvents other than water it is called 'Solvation'. Let us, understand the difference between two terms (1) Dissociation and (2) Ionisation. In dissociation, the positive ion and the negative ion present in the original substance are separated showing dissociation, viz.,

$$Na^+Cl^-_{(s)} + H_2O_{(l)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$
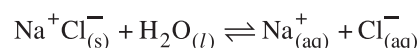
but in ionisation original substance is changed into ion form in aqueous solution. viz.

$$CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$
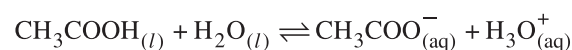
At this stage, we can consider both the terms having same meaning. (Note) : Thermal dissociation can be there, viz.,

$$NH_4Cl_{(s)} \overset{\Delta}{\rightleftharpoons} NH_{3(g)} + HCl_{(g)} \quad \text{and ions}$$

are not obtained, only dissociate. The thermal ionisation is not known.

Arrhenius Concept about Acid and Base : According to Arrhenius concept, substances which dissociate in water and give hydrogen ion (H^+) are called acids and substances which dissociate in water and give hydroxyl ions (OH^-) are called bases e.g.

(1) $HCl_{(g)} \xrightarrow{+H_2O} H^+ + Cl^-$ Acid

(2) $NaOH_{(s)} \xrightarrow{+H_2O} Na^+ + OH^-$ Base
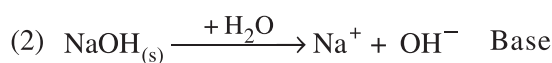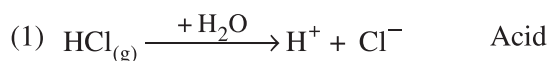
The limitations of this concept are as follows :

(i)   Proton (H^+) is highly unstable.

(ii) It can not exist independently.

(iii) It immediately combines with molecules of solvent water and gives H_3O^+ ions. Its addition in certain bases OH^- is not present even then they show properties of base, viz., NH_3. Similarly compounds like BF_3 do not possess H^+, even then they act as acid.

(iv) This concept can only be applied to aqueous solutions because salt like NH_4Cl reacts as acid in solvent like liquid NH_3. Hence, it is difficult to accept Arrtenius concept as the universal one, because ionisation is given importance. (In addition it is necessry to know that ionic radius of H^+ ion is about 10^{-15} meter and so it is very small in size.) Hence, it easily gets combined with molecules of water and forms H_3O^+ ion which is called hydronium ion. One estimate is that H^+ can be combined with four molecules of water showing. $H^+ + 4H_2O \rightarrow H_9O_4^+$ ion.

Concept of Bronsted - Lowry for Acid and Base : Danish chemist Bronsted and English chemist Lowry presented the concept of acid and base. They made H^+ (Proton) as a base. According to their concept, the substance which gives a proton or donates a proton is called the acid and the substance which receives a proton or accepts a proton is called the base. Thus, acid is a proton donor and base is a proton acceptor. Let us take the dissociation reaction of hydrogen chloride in water.

$$\overset{\text{Base}}{\downarrow} \quad \overset{\text{Acid}}{\downarrow}$$
$$HCl_{(g)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$
$$\underset{\text{Acid}}{\uparrow} \qquad\qquad\qquad \underset{\text{Base}}{\uparrow}$$

Similarly,

$$\overset{\text{Acid}}{\downarrow} \qquad\qquad \overset{\text{Base}}{\downarrow}$$
$$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$
$$\underset{\text{Base}}{\uparrow} \qquad\qquad\qquad \underset{\text{Acid}}{\uparrow}$$

We shall understand in detail the first from the above reactions :
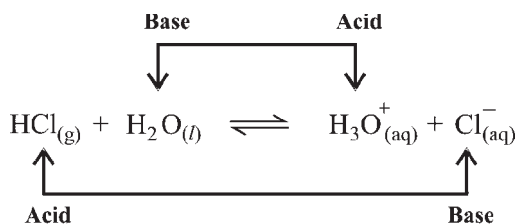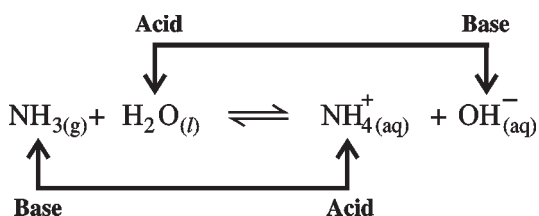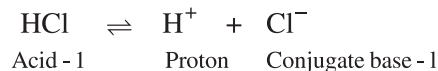
$$\underset{\text{Acid - 1}}{HCl} \rightleftharpoons \underset{\text{Proton}}{H^+} + \underset{\text{Conjugate base - 1}}{Cl^-}$$

As it gives proton, HCI is an acid

$$\underset{\text{Base - 2}}{H_2O} + \underset{\text{Proton}}{H^+} \rightleftharpoons \underset{\text{Conjugate acids - 2}}{H_3O^+}$$
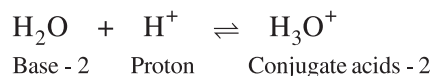
As it accepts a proton, H_2O is a base.

Total reaction :

$$\underset{\text{Acid - 1}}{HCl} + \underset{\text{Base - 2}}{H_2O} \rightleftharpoons \underset{\text{Acid - 2}}{H_3O^+_{(aq)}} + \underset{\text{Base - 1}}{Cl^-_{(aq)}}$$
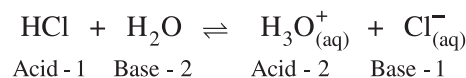
In the above reaction giving-taking of proton is not shown. Hence, it can be said that only transfer of proton takes place, it is not obtained free. Every acid will lose proton and so its conjugate base will be formed and every base will accept a proton and so its conjugate acid will be formed. Hence, this concept is known as proton transfer or conjugate acid-base concept.

We have earlier seen in limitations of Arrhenius concept that OH^- is not present in NH_3 even then it acts as a base but according Bronsted - Lowry concept it can be explained.

$$\underset{\text{Base - 1}}{NH_3} + \underset{\text{Acid - 2}}{H_2O} \rightleftharpoons \underset{\text{Acid - 1}}{NH_4^+{}_{(aq)}} + \underset{\text{Base - 2}}{OH^-_{(aq)}}$$
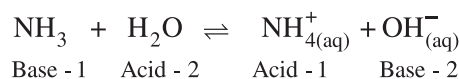
In the reaction, base NH_3 accepts a proton and forms conjugate acid NH_4^+ ion and acid H_2O loses proton and forms conjugate base OH^-.

Thus the concept of Bronsted - Lowry is found to be more applicable and acceptable than Arrhenius concept. Even then its limitations are also known. The difficulties are observed in the study of reactions in organic chemistry and complex salts. BF_3 has no proton even then it acts as an acid. Hence, the third concept has come in to existence, which is known as Lewis acid-base concept. Proton is given importance in Bronsted-Lowry concept.

Lewis Concept of Acid and Base : Lewis, in presenting this concept, in 1923, mentioned that acid means a substance which can accept a pair of electrons and base means a substance which can donate a pair of electrons. Thus, instead of the concepts of proton, ionisation, conjugate acid or base, he made electrons associated with all reactions and substances and

its arrangement as the base of the concept. As seen earlier BF_3 can be said an acid or not and NH_3 can be said a base or not can be solved by this concept. It will be clear from the following reaction :

| Acid | Base | Salt |

Thus, BF_3 accepts the pair of electron and so it is acid and NH_3 donates a pair of electron, so it is base. Electron deficient substances or ions like $AlCl_3$, Co^{3+}, Mg^{2+}, will act as acid and substances like H_2O, NH_3, OH^-, F^- will act as base. They are respectively called Lewis acid and Lewis base.

Activity : Study the above concepts and then give reason for the following statement. Discuss it with your teacher also. "All Bronsted-Lowry acids can be Lewis acids but all Lewis acids are not Bronsted-Lowry acid." Make a list of such acids and bases.

4.15 Ionisation of Acid and Base

Arrhenius concept of acid and base is useful in understanding ionisation of acid and base in most of the chemical and biochemical reaction, ionisation is there in aqueous medium. Acids like $HClO_4$, HCl, HNO_3, HBr, H_2SO_4, are called strong acids because they are completely ionised in aqueous solutions. Similarly bases like NaOH, KOH, $Ba(OH)_2$ are strong bases because they are completely ionised in aqueous medium. The magnitude of ionisation determines the strength of acid or base. According to Bronsted - Lowry, the magnitude of accepting or donating a proton delides the strong or weak (HA) acid or base.

Let us take the following example :

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Thus, in above dissociation, equilibrium is attained and equilibrium is dynamic, that is the transfer of proton in forward and reverse reaction takes place continuously. If above reaction is more in forward reaction, then strength of acid will be more and if in reverse reaction, the strength of acid will be less and so their

respective conjugate base will be weak and strong respectively. e.g. The conjugate bases of strong acids HCl, H_2SO_4, HNO_3 etc. namely Cl^-, SO_4^{2-} and NO_3^- will be weak bases. In the same way the conjugate acids of strong bases NaOH, KOH etc, namely Na^+ and K^+ etc. will be weak acids. Weak acid or base may not ionise completely and so equilibrium is obtained. Indicator like phenolphthalein is colourless in presence of acid and shows pink colour in presence of base.

4.16 Ionic Product of Water

Water is an amphoteric oxide when acid is added to it; it accepts the proton and act as base and when base is added to it, it donates a proton and acts as acid. When reaction between two molecules of water takes place, one molecule donates proton and other molecule receives proton and shows conjugate acid-base reaction.

$$\underset{\text{Acid - 1}}{H_2O_{(l)}} + \underset{\text{Base - 2}}{H_2O_{(l)}} \rightleftharpoons \underset{\substack{\text{Conjugate} \\ \text{acid - 2}}}{H_3O^+_{(aq)}} + \underset{\substack{\text{Conjugate} \\ \text{base - 2}}}{OH^-_{(aq)}}$$

If we express the equilibrium constant of the above reaction them.

$$K_a = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$$

where K_a is the dissociation constant of acid. There is no significant change in concentration of water (55.5M) because H_2O is a weak acid (possesses about 10^{-7}M H^+). Thus, if H_2O is considered constant,

$$K_a \times [H_2O]^2 = [H_3O^+][OH^-] = K_w$$

where K_w is ionic product of water. Water is neutral and so $[H_3O^+]$ and $[OH^-]$ in it are 10^{-7} M. Hence, $K_w = [H_3O^+][OH^-] = (10^{-7})(10^{-7}) = 10^{-14}$ which is constant and equilibrium constant remains constant at constant temperature; so the value of K_w will be constant at constant temperature, viz., the value of K_w is 1×10^{-14} at 298 K. If we find the ratio of concentrations of dissociated and undissociated water, $10^{-7}/55.5 = 1.8 \times 10^{-9}$ equilibrium remain on left hand side, i.e. the number of undissociated molecules or its concentration will be more.

From the above study, three possibilities arise :

(i) $[H_3O^+] > [OH^-]$ i.e. concentration of $[H_3O^+]$ is more in solution and so solution is acidic.

(ii) $[H_3O^+] < [OH^-]$ i.e. concentration of $[OH^-]$ is more in solution and so solution is basic.

(iii) $[H_3O^+] = [OH^-]$ i.e. concentration of both $[H_3O^+]$ and $[OH^-]$ are equal and so solution will remain neutral.

4.17 pH Scale

If we express the concentration of hydronium ion $[H_3O^+]$ in molarity then values like 10^{-12} to 10^{-2} are possible. It is difficult to express these values on simple graph paper. Hence, scientist Sorensen found a scale which is called pH scale. According to him pH = $-\log_{10}[H_3O^+]$. The values 10^{-12} to 10^{-2} shown above can be converted to +12 to +2 if calculated on the basis of this relation and plotting of graph can be easy. The definition of pH can be given like this, "pH of a solution is the negative logarithm to the base 10, of the molar concentration of hydrogen or hydronium ion". According to thermodynamics, activity is more proper word instead of concentration but in dilute solutions activity and concentration can be considered to be the same. Now as seen earlier a solution containing 10^{-7}M $[H_3O^+]$ and $[OH^-]$ is neutral. Hence,

pH = $-\log_{10}[H_3O^+]$ = $-\log_{10}10^{-7}$M = 7 and for acidic solution $[H_3O^+] > 10^{-7}$M, pH < 7 Similarly, for basic solution $[H_3O^+] < 10^{-7}$M, Hence, pH > 7. Therefore, it can be written as :

pH < 7 Acidic solution

pH > 7 Basic solution

pH = 7 Neutral solution

As seen above,

K_w = $[H_3O^+][OH^-]$

Putting the values, $K_w = (10^{-7})(10^{-7}) = 10^{-14}$

and $-\log K_w = -\log(10^{-14})$

$\therefore$ pK_w = 14

$\therefore$ pH + pOH = pK_w = 14

Temperature affects the values of pH, pOH, pK_w. The above discussion can be shown in the following table :

Concent-ration (M)	Acidic	Neutral	Basic
$[H_3O^+]$	more than10^{-7}	10^{-7}	less than10^{-7}
$[OH^-]$	less than10^{-7}	10^{-7}	more than10^{-7}
pH	less than7	7	more than 7
pOH	more than7	7	less than 7

pH paper, litmus paper or universal indicator can be used to test whether the solution is acidic or basic but the exact values of pH can be determined with the help of instrument called pH meter.

Example 11 : In one drink, the concentration of hydrogen ion is found to be 4×10^{-3}. What will be the value of its pH ? Also calculate the value of pOH.

Solution :

pH = $-\log_{10}[H_3O^+]$

= $-\log_{10}(4 \times 10^{-3})$ = $-(0.6021 - 3.0)$

= + 2.3979 $\approx$ 2.4

pK_w = pH + pOH

$\therefore$ 14 = 2.4 + pOH

$\therefore$ pOH = 11.6

Example 12 : Calculate pH and pOH of solution containing 0.03M NaOH.

Solution :

NaOH is a base so; $[OH^-]$ = 0.03M

Now, pOH = $-\log_{10}[OH^-]$

= $-\log_{10}(0.03)$

= $-(-2.000 + 0.4771)$

= + 1.5229 $\approx$ 1.52

Now, pK_w = pH + pOH

$\therefore \ 14 = pH + 1.52$

$\therefore \ pH = 12.48$

Solution 13 : 0.1 ml 0.001M HCl solution is diluted with water to make 10 litres. Calculate pH of the dilute solution.

Solution : According to

$$N_1V_1 = N_2V_2$$

$$0.1 \times 0.001 = 10000 \times x$$

$$\therefore \ x = \frac{0.1 \times 0.001}{10000}$$

$$\therefore \ x = 10^{-8}M$$

Now, $pH = -\log_{10}[H_3O^+]$

$$= -\log_{10} (10^{-8})$$

$$\therefore \ pH = 8$$

If the pH of solution is 8, solution must be basic but we have diluted HCl, so it is wrong. The principle says that when concentration of HCl becomes 10^{-8}M, the concentration of $[H_3O^+]$ of water is 10^{-7}M and so it cannot be neglected. It should be taken into calculation. Hence,

$[H_3O^+]$ in solution = concentration of HCl + concentration of $[H_3O^+]$ ion in water.

$$= 10^{-8} + 10^{-7} = 1.1 \times 10^{-7}$$

$$\therefore \ pH = -\log_{10}[H_3O^+]$$

$$= -\log_{10}(1.1 \times 10^{-7}) = 6.98$$

This value is acceptable because it is less than 7 and solution is acidic.

Thus, in solutions of acids having very low concentration, the concentration of $[H_3O^+] = 10^{-7}$M cannot be neglected. It should be taken in calculation so that correct pH can be obtained.

4.18 Ionisation Constant of Weak Acid and Weak Base

4.18.1 Ionisation Constant of Weak Acid (K_a) :
In aqueous solution of weak monobasic acid HA, there is a partial ionisation and so the equilibrium is obtained as below :

$$HA_{(aq)} + H_2O_{(l)} \ \rightleftharpoons \ H_3O^+_{(aq)} + A^-_{(aq)}$$
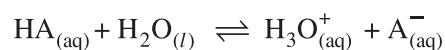
Suppose the initial concentration of weak acid (HA) is C mollit^{-1} and degree of ionisation is α, then following can be written :

Reaction :

$$HA_{(aq)} + H_2O_{(l)} \ \rightleftharpoons \ H_3O^+_{(aq)} + A^-_{(aq)}$$
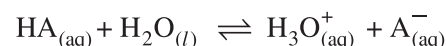
Initial concentration(M)	C	0	0
Degree of ionisation(α)	$1-\alpha$	α	α
Concentration at equilibrium(M)	$(1-\alpha)C$	αC	αC

Equilibrium constant $K_e = \dfrac{[H_3O^+] \ [A^-]}{[HA] \ [H_2O]}$

$$= \frac{(\alpha C) \ (\alpha C)}{(1 - \alpha)C \ [H_2O]} \ \ ..... \ 4.21$$

But $[H_2O]$ is accepted as constant and so

$$K_e \ [H_2O] = \frac{(\alpha C) \ (\alpha C)}{(1 - \alpha)C}$$

$$= \frac{\alpha^2 C}{(1 - \alpha)} = K_a \ \ ....4.22$$

where K_a is the ionisation constant or dissociation constant of the acid HA. (At this stage we consider both the terms same) Hence, for any weak monobasic acid, following can be written

$$K_a = \frac{[H_3O^+] \ [A^-]}{[HA]} \ \ ....4.23$$

The unit of K_a will be mollit^{-1}.

As the values of K_a depend on $[H_3^+O]$ the values of K_a will be different for different $[H_3O^+]$. Lesser the value of K_a, weaker will be the acid. The value of K_a will be constant at definite temperature. In table 4.3 the values of ionisation constants of some weak acids are given.

Table 4.3

The Ionisation Constants (K_a) of some weak acids at 298K

Acid	K_a
Hydrofluoric acid (HF)	3.5×10^{-4}
Nitrous acid (HNO$_2$)	4.5×10^{-4}
Formic acid (HCOOH)	1.8×10^{-4}
Acetic acid (CH$_3$COOH)	1.74×10^{-5}
Benzoic acid (C$_6$H$_5$COOH)	6.5×10^{-5}
Hypochlorus acid (HClO)	3.0×10^{-8}
Hydrocyanic acid (HCN)	4.9×10^{-10}
Phenol (C$_6$H$_5$OH)	1.3×10^{-10}

According to the relations seen earlier,

$$pH = -\log_{10}[H_3O^+]$$

$$pOH = -\log_{10}[OH^-]$$

Similarly, $pK_a = -\log_{10}[K_a]$

$p_{A^-} = -\log_{10}[A^-]$ can be written.

where $[A^-]$ is the concentration of negative ion.

It is apparent from above relations that if the values of initial concentration $[H_3O^+]$ and K_a are known, then at equilibrium, $[H_3O^+]$ concentration can be determined and pH can be calculated.

Suppose, if we take 0.1M CH$_3$COOH as weak acid HA and its ionisation constant K_a as 1.74×10^{-5} at 298 K, temperature then $[H_3O^+]$, [CH$_3$COOH], pH, pOH, pK_w etc. at equilibrium can be calculated.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$
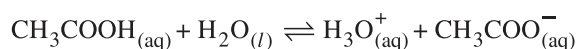
$$K_e = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]} \quad \text{and}$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

If we take α as the degree of ionisation of weak CH$_3$COOH then

$$K_a = \frac{(0.1 \times \alpha)(0.1 \times \alpha)}{0.1(1-\alpha)}$$

$$K_a = \frac{(0.1)^2 \alpha^2}{(1-\alpha)(0.1)}$$

$$K_a = \frac{(0.1)\alpha^2}{(1-\alpha)}$$

The value of K_a is given as 1.74×10^{-5} and so,

$$\frac{(0.1)\alpha^2}{(1-\alpha)} = 1.74 \times 10^{-5}$$

The value of α being very small (0.02 to 0.03); $(1-\alpha)$ can be written as ≈ 1

$$\therefore \ 0.1 \times \alpha^2 = 1.74 \times 10^{-5}$$

$$\therefore \ \alpha^2 = \frac{1.74 \times 10^{-5}}{0.1} = 1.74 \times 10^{-4}$$

$$\therefore \ \alpha = \sqrt{1.74 \times 10^{-4}} = 1.32 \times 10^{-2}$$

Now, $[H_3O^+] = \alpha C = 1.32 \times 10^{-2} \times 0.1$

$$= 1.32 \times 10^{-2} M$$

$$\therefore \ pH = -\log_{10}[H_3O^+]$$

$$= -\log_{10}(1.32 \times 10^{-2}) = 2.88$$

In the same way $CH_3COO^- = 2.88$

The amount of undissociated CH$_3$COOH will be $(1-(1.32 \times 10^{-3}) \times 0.1)$.

According to $(1-\alpha)C$.

$$= (1 - 1.32 \times 10^{-2}) \times 0.1$$

$$= 0.09668M$$

Though the solution is acidic, if we want to know concentration of OH$^-$, it is possible.

$$pH + pOH = pK_w$$

$$2.88 + pOH = 14$$

$$\therefore \ pOH = 11.12$$

$$\therefore \ -\log_{10}[OH^-] = 11.12$$

$$\therefore \ \log_{10}[OH^-] = -11.12 = -12.00 + 0.88$$

$$\therefore \ [OH^-] = \text{antilog} \ -12.00 + 0.88$$

$$= 7.586 \times 10^{-12} \ M$$

Activity : The pH of 0.1M monobasic weak acid HA is 4.40. Calculate the values of $[H_3O^+]$, $[A^-]$, $[HA]$, K_a, pK_a in the solution at equilibrium.
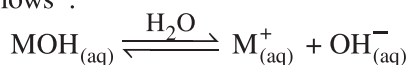
Solution : Use the above method and try to calculate the values and verify that they are as follows :

$[H_3O^+] = [A^-] = 4.0 \times 10^{-5}M$

$[HA] \approx 0.1M$

$K_a = 1.6 \times 10^{-8}$, $pK_a = 7.80$

4.18.2 Ionisation Constant (K_b) of Weak Base :

The ionisation of monoacidic weak base MOH will take place in aqueous solution as follows :

$$MOH_{(aq)} \xrightleftharpoons{H_2O} M^+_{(aq)} + OH^-_{(aq)}$$

As base is weak, incomplete ionisation will occur and so equilibrium will be obtain and it can be expressed as below :

$$K_e = \frac{[M^+][OH^-]}{[MOH][H_2O]} \quad ....4.24 \text{ and}$$

$$K_e \times [H_2O] = \frac{[M^+][OH^-]}{[MOH]} = K_b \quad ....4.25$$

where K_b is the ionisation or dissociation constant of monoacidic weak base. If we know the initial concentration of weak base and its degree of ionisation, we can calculate the value of K_b as we have studied earlier. $[M^+] = [OH^-]$. Let us study with the following example.

Example 14 : Calculate the values of $[NH_4^+]$, $[OH^-]$, pOH, pH of 0.1M NH_4OH solution at equilibrium. The ionisation constant of NH_4OH is 1.8×10^{-5}

Solution : NH_4OH is a weak base, so it can be written in the same manner as the earlier one.

Reaction :

$$NH_4OH_{(aq)} \xrightleftharpoons{H_2O} NH^+_{4(aq)} + OH^-_{(aq)}$$
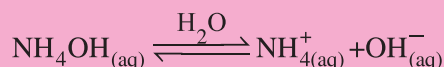
Initial concentration (M)   0.1   0   0

Degree of ionisation $(1-\alpha)$ α α

Concentration at equilibrium (M) $(1-\alpha)C$ αC αC

But $C = 0.1$

At equilibrium M $(1-\alpha)\times 0.1$ $\alpha \times 0.1$ $\alpha \times 0.1$

$$K_b = \frac{(\alpha C)(\alpha C)}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha}$$

But $K_b = 1.8 \times 10^{-5}$ is given and the value of α being very small $(1-\alpha)$ can be taken nearly equal to 1.

$K_b = \alpha^2 C$

$\therefore 1.8 \times 10^{-5} = \alpha^2 C = \alpha^2 \times 0.1$

$\therefore \alpha^2 = \dfrac{1.8 \times 10^{-5}}{0.1} = 1.8 \times 10^{-4}$

$\therefore \alpha = \sqrt{1.8 \times 10^{-4}} = 1.34 \times 10^{-2}$

$[NH_4^+] = [OH^-]$

$\alpha C = 1.34 \times 10^{-2} \times 0.1$

$= 1.34 \times 10^{-3}M$

$pOH = -\log_{10}[OH^-]$

$= -\log_{10}(1.34 \times 10^{-3}) \approx 2.87$

$pH + pOH = 14$

$\therefore pH = 14 - pOH$

$= 14 - 2.87 = 11.13$

In table 4.4 the values of ionisation constants of some monoacidic bases at 298 K are given.

**Table 4.4 The Ionisation Constants (K_b) of some weak bases at 298 K**

Base	K_b
Ammonium hydroxide (NH_4OH)	1.77×10^{-5}
Methyl amine (CH_3NH_2)	4.4×10^{-5}
Dimethyl amine ($(CH_3)_2NH$)	5.4×10^{-5}
Trimethyl amine ($(CH_3)_3N$)	6.45×10^{-5}
Aniline ($C_6H_5NH_2$)	4.27×10^{-10}
Urea (NH_2CONH_2)	1.3×10^{-14}

Activity : Calculate the following example by the method as shown earlier and compare the answers with the given values.

Example 15 : The ionisation constant of dimethyl amine $[(CH_3)_2NH]$ is 5.4×10^{-4}. If the initial concentration of dimethyl amine is 0.02 M, calculate $[OH^-]$, $[(CH_3)_2NH]$, $[H_3O^+]$, pH and pOH in solution at equilibrium.

Solution :

Reaction :

$$(CH_3)_2NH_{(aq)} + H_2O_{(l)} \rightleftharpoons (CH_3)_2NH^+_{2(aq)} + OH^-_{(aq)}$$
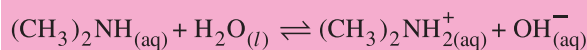
The following values will be obtained by calculation, compare them :

$$[OH^-] = [(CH_3)_2NH^+_2] = 3.28 \times 10^{-4} M$$

$$[H_3O^+] = 3.0 \times 10^{-9}M$$

$$pOH = 3.48, \ pH = 10.52$$

Relation between K_a and K_b : As seen earlier the values of K_a and K_b show the strength of acid and base respectively. In reference to conjugate acid base, every acid has conjugate base and every base has conjugate acid; viz.

$$\underset{\text{Acid - 1}}{NH^+_{4(aq)}} + \underset{\text{Base - 2}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Base - 1}}{NH_{3(aq)}} + \underset{\text{Acid - 2}}{H_3O^+_{(aq)}}$$
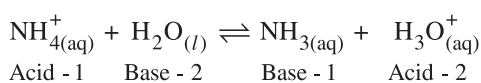
The value of K_a for the reaction will be

$$K_a = \frac{[H_3O^+][NH_3]}{[NH^+_4]} \ \ ....4.25$$

$$= 5.6 \times 10^{-10}$$

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$
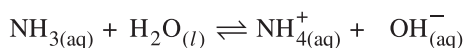
$$K_b = \frac{[NH^+_4][OH^-]}{[NH_3]} \ \ ....4.26$$

The value of this K_b is found to be 1.8×10^{-5}. On adding the above reactions,

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + NH_{3(aq)}$$

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + NH^+_{4(aq)}$$

$$\overline{}$$

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$
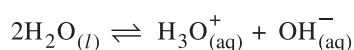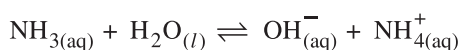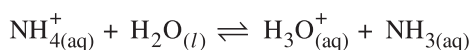
and $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ 4.27

K_w is ionic product of water, K_a is ionisation constant of NH^+_4 acid and K_b is the ionisation constant of base NH_3.

$$\therefore \ K_a \times K_b =$$

$$\left[[H_3O^+][NH_3]\Big/[NH^+_4]\right] \times \left[[NH^+_4][OH^-]\Big/[NH_3]\right]$$

$$........4.28$$

$$= \ [H_3O^+][OH^-] = K_w \ \ \ \ ....4.29$$

$$\therefore \ K_a \times K_b = 5.6 \times 10^{-10} \times 1.8 \times 10^{-5}$$

$$= 1.008 \times 10^{-14} \approx 1.0 \times 10^{-14} = K_w.$$

Hence, it can be concluded that the constant for the net reaction is the product of the equilibrium constants of two or more reactions involved in it.

$$\therefore \ K_{net} = K_1 \times K_2 \times K_3 \ \ \ \ .... 4.30$$

If we know ionisation constant of conjugate acid or base, then the ionisation constant of their conjugate base or acid can be known with the help of K_w viz. The ionisation constant of CH_3COOH is $K_a = 1.7 \times 10^{-5}$ so the ionisation constant of its conjugate base CH_3COO^- ion will be $K_b = \dfrac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.75 \times 10^{-10}$

$$\text{or } pK_a + pk_b = 14 \ \ \ \ .... 4.31$$

$$\therefore \ pk_b = 14 - pK_a \ \ \ \ \ \text{or}$$

$$- \log K_b = 14 + \log K_a \ \ \ \ .... 4.32$$

and from the value of $- \log K_b$, the value of K_b can be calculated.

Example 16 : The dissociation constant of formic acid (HCOOH) is 1.8×10^{-4}. What will be the value of dissociation constant of conjugate base formate ion $(HCOO^-)$?
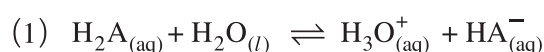
Solution :

$$K_a = 1.8 \times 10^{-4} \ \text{ and } \ K_w = 1.0 \times 10^{-14}$$
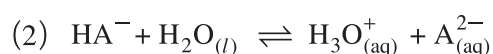
$$K_a \times K_b = K_w$$

$$\therefore \ K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.5 \times 10^{-9}$$

Dissociation constants of dibasic or polybasic (diprotic or polyprotic) acids : Sulphuric acid, oxalic acid etc. are dibasic acids and phosphoric acid, citric acid are tribasic acids. Their dissociation constants are two K_{a_1} and K_{a_2} for dibasic and three K_{a_1}, K_{a_2} and K_{a_3} for tribasic acids respectively. Suppose, dibasic weak acid is expressed as H_2A, then its dissociation will occur in the following two steps and corresponding K_{a_1} and K_{a_2} will be obtained. For tribasic acid dissociation will occur in three steps and corresponding K_{a_1}, K_{a_2} and K_{a_3} will be obtained.

(1) $H_2A_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HA^-_{(aq)}$

$$K_{a_1} = \frac{[H_3O^+][HA^-]}{[H_2A]} \quad ....4.33$$

(2) $HA^- + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^{2-}_{(aq)}$

$$K_{a_2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} \quad ....4.34$$

4.18.3 Factors Affecting Strength of Acid : From the study of dissociation constant, pH value etc., it is found that their values are different. The reason for this is that $[H_3O^+]$ available can be more or less. What may be the reason for this? If the acid is strong, its value of K_a will be high and the value of pH will be low. The dissociation of acid will depend on strength of acid and the polarity of H–A bond. As the strength of H–A bond decreases, the energy required for breaking that bond will decrease and HA will be stronger. When difference between electronegativities of A and B will increase, apparently ionisation will occur and will be easy to break the structure of the bond. Hence, acidity will increase.

On comparing the elements of the same group of periodic table, the strength of H–A bond will be more important factor than polar nature. As we go down in the group the size of A will increase and so strength of H–A bond will decrease and hence acid strength will increase.
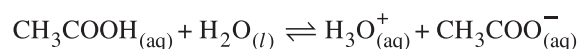
Increase in Size
→
HF << HCl << HBr << HI
→
Increase in acid strength
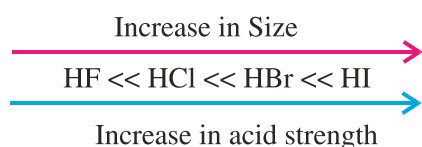
For this reason, H_2S is stronger acid than H_2O, but if we discuss the elements in the same period of periodic table, the polarity of H–A bond will determine the strength of acid. As the electronegativity of A increases, the strength of acid will increase.
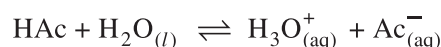
Increase in electronegativity
→
CH_4 << NH_3 << H_2O << HF
→
Increase in acid strength
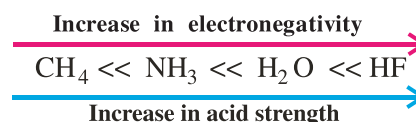
4.18.4 Effect of common ion on ionisation constant of weak acid and base : Let us take the example of weak acid, acetic acid (CH_3COOH)

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

OR

$$HAc + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Ac^-_{(aq)}$$

where HAc and Ac^- are the short forms of CH_3COOH and CH_3COO^- ion.

$$K_a = \frac{[H_3O^+][Ac^-]}{[HAc]} \quad ....4.35$$

Suppose we add salt CH_3COONa or HCl, to the solution of HAc in equilibrium, then what will happen ? As studied earlier in chemical equilibrium if HCl is added, $[H_3O^+]$ will increase and if CH_3COONa is added, $[Ac^-]$ will increase. Hence, according to Le Chatelier's principle, the equilibrium will make negligible change and will keep the same value of equilibrium constant. This means that the equilibrium will be shifted towards left and concentration of HAc will increase i.e. the amount of undissociated acid will increase and there will be decrease in $[H_3O^+]$ and hence, there will be increase in pH. By addition of HCl due to increase in $[H_3O^+]$ similar result will be obtained. This effect is known as effect of common ion effect on dissociation constant of acid.

In the same way, in the case of ionisation of weak base NH_3, if we increase $[NH_4^+]$ by adding salt like NH_4Cl then, according to Le Chatelier's principle, as $[NH_4^+]$ increases the equilibrium will shift towards left and hence, undissociated NH_3 will increase, i.e. $[OH^-]$ will decrease. As a result, pH will decrease. We can prove these two effects by following examples.

Example 17 : What will be the change in pH of 0.1M CH_3COOH acid if 0.1M CH_3COONa is added to its solution? pK_a of CH_3COOH = 4.74

Solution : Firstly in absence of common ion (CH_3COO^-), for weak acid

$$[H_3O^+] = \sqrt{K_a \cdot C}$$

pK_a = 4.74

$\therefore - \log K_a$ = 4.74

$\therefore \log K_a = -4.74 = \overline{5} + 0.26$

K_a = Antilog $(\overline{5} - 0.26)$

$\therefore K_a = 1.8 \times 10^{-5}$

$\therefore [H_3O^+] = \sqrt{K_a \cdot C_o}$

$= \sqrt{1.8 \times 10^{-5} \times 10^{-1}}$

$= \sqrt{1.8 \times 10^{-6}} = 1.3416 \times 10^{-3}$

$\therefore$ pH $= -\log_{10}[H_3O^+]$

$= -\log_{10}(1.3416 \times 10^{-3}) = 2.87$

Now, if 0.1M CH_3COONa is added, then,

$$K_a = \frac{[H_3O^+][Ac^-]}{[HAc]}$$

$$K_a = \frac{[H_3O^+][0.1]}{[0.1]} \qquad ....4.36$$

$[Ac^-]$ = Ac^- available from CH_3COONa and Ac^- from dissociation of HAc. But concentration of Ac^- available from dissociation of HAc can be neglected in comparison to Ac^- (0.1M)

available from CH_3COONa. Hence, $Ac^- = 0.1M$ can be taken.

$\therefore [H_3O^+] = 1.8 \times 10^{-5}$

$\therefore -\log_{10}[H_3O^+]$ = pH

$= -\log_{10}(1.8 \times 10^{-5}) = 4.81$

Hence, it can be proved that the dissociation of acid decreases due to effect of common ion and so $[H_3O^+]$ decreases and so pH increases.

Example 18 : What will be the change in pH of 0.1M weak base NH_4OH if 0.1M NH_4Cl is added to the solution? K_b for NH_4OH = 1.77×10^{-5}

Solution : As mentioned above calculate on the basis of method of determination of ionisation constant. Compare the values obtained with the following values.

pH of 0.1M NH_4OH in absence of NH_4Cl = 11.13, pH of 0.1M NH_4OH in presence of NH_4Cl = 9.25. Thus, this example shows that the pH of a solution of weak base decreases due to effect of common ion.

4.19 Hydrolysis of Salt and pH of Their Solutions

Salt is obtained by combination of acid and base in definite proportion. When the salt is dissolved in water, ionisation occurs. The following types of salts are obtained depending on acid or base being strong or weak.
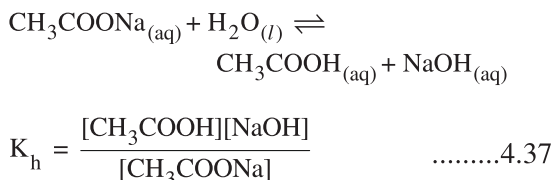
Acid	Base	Salt	Property	Example
(1) Strong	Strong	Neutral	Neutral	$NaOH + HCl \rightarrow NaCl + H_2O$
(2) Strong	Weak	Acidic	Acidic	$HCl + NH_4OH \rightleftharpoons NH_4Cl + H_2O$
(3) Weak	Strong	Basic	Basic	$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$
(4) Weak	Weak	Neutral or Acidic or Basic	Neutral or Acidic or Basic	$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$ $HCOOH + NH_4OH \rightleftharpoons HCOONH_4 + H_2O$ $C_6H_5COOH + NH_4OH \rightleftharpoons C_6H_5COONH_4 + H_2O$

Salt formed from strong base and strong acid is neutral and so its pH is 7.0. e.g. NaCl. But if salt is formed from strong acid and weak base, it will be acidic and pH of its aqueous solution will be less than 7 e.g. NH_4Cl. Similarly
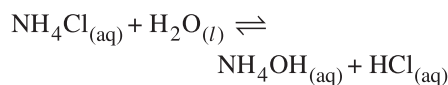
salt formed from weak acid and strong base is basic and its pH in aqueous solution will be more than 7, e.g. CH_3COONa. The reason is that salt reacts with water and undergoes hydrolysis reaction.

Hydrolysis reaction is an equilibrium reaction and so its corresponding equilibrium constant can be calculated which is known as hydrolysis constant (K_h). It can be determined with the help of the example of weak acid and strong base e.g. CH_3COONa
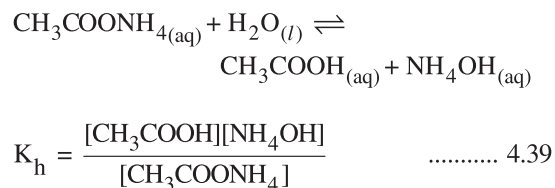
(1) For salt of weak and strong base,

$$CH_3COONa_{(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$CH_3COOH_{(aq)} + NaOH_{(aq)}$$

$$K_h = \frac{[CH_3COOH][NaOH]}{[CH_3COONa]} \qquad ....4.37$$

(2) For salt of strong acid and weak base (e.g. NH_4Cl)

$$NH_4Cl_{(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$NH_4OH_{(aq)} + HCl_{(aq)}$$

$$K_h = \frac{[NH_4OH][HCl]}{[NH_4Cl]} \qquad (4.38)$$

(3) For salt of weak acid and weak base(e.g. CH_3COONH_4),

$$CH_3COONH_{4(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$CH_3COOH_{(aq)} + NH_4OH_{(aq)}$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COONH_4]} \qquad .... 4.39$$

Earlier you have studied about K_a and K_b. The equation of K_h can be obtained from them as shown below :

Salt	Hydrolysis constant	PH of solution
Strong acid weak base	$K_h = K_w/K_b = \dfrac{[H_3O^+]^2}{C_O}$	< 7
Weak acid strong base	$K_h = K_w/K_a = \dfrac{[OH^-]}{C_O}$	> 7
Weak acid weak base	$K_h = K_w/K_a \cdot K_b = \dfrac{[H_3O^+][OH^-]}{C_O}$	= 7

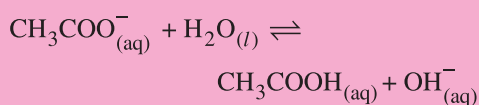where C_o is the initial concentration of salt.

Thus, from the nature of the salt pH of its aqueous solution can be calculated.

Example 19 : Calculate pH of 0.1M sodium acetate (CH_3COONa) solution. K_a of $CH_3COOH = 1.8 \times 10^{-5}$ $K_w = 1.0 \times 10^{-14}$

Solution :

$$CH_3COONa_{(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$CH_3COOH_{(aq)} + NaOH_{(aq)}$$

OR

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$CH_3COOH_{(aq)} + OH^-_{(aq)}$$
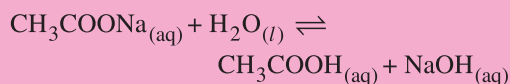
$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

But $K_h = \dfrac{[OH^-]^2}{C_o}$

$$\therefore 5.5 \times 10^{-10} = \frac{[OH^-]^2}{0.1}$$

$$\therefore [OH^-]^2 = 5.5 \times 10^{-10} \times 0.1$$
$$= 5.5 \times 10^{-11}$$

$$\therefore [OH^-]^2 = \sqrt{5.5 \times 10^{-11}}$$
$$= 7.4 \times 10^{-6}$$

Now, $pOH = -\log_{10}[OH^-]$
$$= -\log_{10}(7.4 \times 10^{-6}) = 5.13$$
$pH = 14 - pOH$
$$\therefore pH = 14 - 5.13 = 8.87$$

4.20 Buffer Solutions

The pH of the fluids like blood in our body and urine is almost constant. If there is change in this pH, it affects biochemical reaction in the body. The pH of chemical and biochemical reactions in our body are constant, viz. the pH of human saliva is 6.4. In addition,

hydrochloric acid is present in human stomach which helps in digestion. The pH of cosmetics are also kept constant. Hence, the question arises that how pH in any solution can be kept constant. Such solutions are called buffer solutions. Its definition can be given as below :

"The solution which resists the change in pH carried out by addition of acid or base in small proportion to them or are being diluted, and the values of their pH remain constant are called buffer solutions". Buffer solutions can be acidic or basic. If pK_a of weak acid and pK_b of weak base are known, buffer solutions of known pH can be prepared. Buffer solutions can be of three types as follows :

(i) Acidic buffer solution : Acidic buffer solution can be prepared by mixture of weak acid and its salt with strong base.

(ii) Basic buffer solution : Basic buffer solution can be prepared by mixture of weak base and its salt with strong acid.

(iii) Neutral buffer solution : Neutral buffer solution can be prepared by neutralisation of weak acid and weak base. These types of buffer solutions are shown below :

Type	Substances	Value of pH
Acidic	$CH_3COOH + CH_3COONa$	< 7
Basic	$NH_4OH + NH_4Cl$	> 7
Neutral	$CH_3COOH + NH_4OH$	≈ 7

Buffer solution of known pH can be prepared by using the following Henderson-Hasselbalch equation.

For acidic solution,

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} \qquad ....4.40$$

where [acid] is concentration a weak acid and its dissociation constant is K_a and [salt] is concentration of the salt of this weak acid with strong base. For an acidic buffer solution, it can be written as

$$pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

Similarly, for basic buffer solution e.g. $NH_4OH + NH_4Cl$ can be written that,

$$pH = pK_b + \log \frac{[NH_4Cl]}{[NH_4OH]}$$

Such buffer solutions can be used in chemical and biochemical reactions and esepcially in analytical chemistry. In human body buffer solutions containing $[HCO_3^-]$ and $[CO_3^{2-}]$ as well as $[H_2PO_4^-]$ and $[HPO_4^{2-}]$ are present.

4.21 Solubility Product of Sparingly Soluble Salts

We have studied earlier that ionic substances like NaOH are highly soluble in water. It absorbs moisture from the air and dissolves. While covalent compounds like LiF are less soluble in water and non-ionic compounds like CdS are almost insoluble in water. Hence, substances can be divided into three types :

Type 1 : Soluble : The substances whose solubility in water is more than 0.1M. e.g. NaCl, HCl, NaOH

Type 2 : Insoluble : The substances whose solubility is very less in water. e.g. CdS, PbS

Type : 3 Sparingly soluble : The substances whose solubility is less than 0.01M. e.g. AgCl, $BaSO_4$, $PbSO_4$

The basis of solubility is on the lattice enthalpy and hydration enthalpy of the substance. If hydration enthalpy is more than lattice enthalpy, the substance will be soluble in water. The second thing is that polar substance dissolves in polar solvents and non-polar substance dissolves in non-polar solvents. e.g. Polar substance like NaCl is soluble in polar solvent like water and nonpolar substance like naphthalene can dissolve in non-polar solvent like benzene.

Sparingly soluble substances are soluble in less proportion and so possess equilibrium and whatever substance is dissolved, it completely gets ionised. We shall study the equilibrium constant of sparingly soluble salt and effect of common ion on its solubility.

Solubility Product Constant of Sparingly Soluble Salt : Suppose, if we dissolve sparingly soluble substance like AgCl in water and prepare its saturated solution, then following reaction will occur and equilibrium will be established.

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

Equilibrium constant $K_e = \dfrac{[Ag^+][Cl^-]}{[AgCl]}$ 4.41

For pure solid substance, its concentration is its density and density remains constant at constant temperature, so concentration can be considered constant. Hence,

$$K_e \cdot [AgCl_{(s)}] = [Ag^+][Cl^-] = K_{sp} \qquad ....4.42$$

where K_{sp} is the solubility product constant of sparingly soluble salt AgCl which is also expressed only as solubility product. Now, if we determine concentration of Ag^+ and Cl^- ions, then solubility product can be obtained. At 298 K, the solubility of AgCl is found to be 1.3×10^{-5} M

Hence, $[Ag^+] = [Cl^-] = 1.3 \times 10^{-5}$ M

$\therefore K_{sp} = [Ag^+][Cl^-]$

$\qquad = (1.3 \times 10^{-5})(1.3 \times 10^{-5})$

$\qquad = (1.69 \times 10^{-10})(mollit^{-1})^2$ or M^2

If solubility is to be determined in grams, it can be obtained by multiplying with molecular mass.

Example 20 : The concentration of $Mg(OH)_2$ in its saturated solution is found to be 8.2×10^{-4} gramlitre^{-1} at 298 K temperature. Calculate K_{sp} of $Mg(OH)_2$. The molecular mass of $Mg(OH)_2$ is 58.0 grammole^{-1}.

Solution : Concentration of $Mg(OH)_2$ is 8.2×10^{-4} grammole^{-1}

Solubility of $Mg(OH)_2$ in mol lit^{-1}

$\dfrac{8.2 \times 10^{-4}}{58} = 1.41 \times 10^{-5}$ M

Now, $Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$
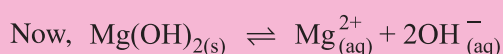
Hence, $[Mg^{2+}] = 1.41 \times 10^{-5}$ M but

$[OH^-] = 2 \times 1.41 \times 10^{-5}$ M

so, according to $K_{sp} = [Mg^{2+}][OH^-]^2$

$K_{sp} = (1.41 \times 10^{-5})(2 \times 1.41 \times 10^{-5})^2$

$\qquad = 1.076 \times 10^{-14}$ M^3

The types of sparingly soluble salts and the formula of calculation of the values of Ksp are as follows :

Type	Example	Formula for K_{sp} and unit
1 : 1	AgCl	$K_{sp} = S^2$ M^2
1 : 2	CaF_2	$K_{sp} = 4S^3$ M^3
2 : 2	$BaSO_4$	$K_{sp} = S^2$ M^2
2 : 1	$Mg(OH)_2$	$K_{sp} = 4S^3$ M^3

where S = solubility in mollit^{-1} or M.

If solubility is given in grams and volume is given in mililitres, the solubility in gramlitre^{-1} or M can be obtained.

Activity : Mention the formula and units of solubility products of the following substances AgBr, $PbSO_4$, $Al(OH)_3$, Bi_2S_3 and $Zr_3(PO_4)_2$.

Utility of Solubility Product :

(1) If the values of solubility products are known, the solubilities of the substances in the solutions can be compared.

(2) Whether precipitation of soluble substance into insoluble substance will take place or not can also be determined, viz. we want to know whether precipitates of AgCl will be obtained or not by addition of solution of NaCl to a solution of $AgNO_3$. For this get $[Ag^+]$ in M from the solution of $AgNO_3$ and $[Cl^-]$ in M from the solution of added NaCl. Multiply them. Mention this product or multiplication as I_p and compare its value with the value of its K_{sp}. Three possibilities are there. according to which precipitatres of sparingly soluble salt can be obtained or not can be predicted.

(i) $I_p > K_{sp}$ Precipitates of sparingly soluble salt will be obtained or precipitation will occur.

(ii) $I_p < K_{sp}$ Precipitates of sparingly soluble salt will not be obtained or precipitation will not occur.

(iii) $I_p = K_{sp}$ Shows equilibrium, Hence precipitation will not occur but solution will remain in saturated state.

4.22 Effect of Common Ion on Solubility of Sparingly Soluble Salt

The sparingly soluble salt that has dissolved in solution that is completely dissociated and so it is in ionic form. Hence, it is a strong electrolyte. Earlier, in chemical equilibrium, effect of concentration, application of Le Chatelier's principle etc. have been studied. Solubility product is ionic equilibrium and the effect of concentration can be studied. As it is equilibrium constant, it will depend on temperature, but its value will be constant at constant temperature.

What will happen if we add soluble ionic substance like KCl in the solution of a sparing soluble salt like AgCl?

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$
$$KCl_{(s)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$
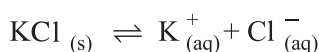
The Cl⁻ from AgCl in equilibrium and Cl⁻ ion obtained by complete ionisation of KCl, the concentration of Cl⁻ will increase. Hence, according to Le Chatelier's principle, the equilibrium will shift towards left side so as to nullify the effect of Cl⁻ i.e. more AgCl will be formed. In other words, there will be decrease in solubility of AgCl. Hence, it can be said that because of the effect of common ion on sparingly soluble salt its solubility decreases and sparingly soluble salt precipitates more.

Now, $K_{sp} = 4S^3$ ∴ $1.8 \times 10^{-11} = 4S^3$

∴ $S = \sqrt[3]{\dfrac{1.8 \times 10^{-11}}{4}} = 1.65 \times 10^{-4}$ M.

Thus, solubility of $Mg(OH)_2$ in water in absence of NaOH will be 1.65×10^{-4} M.

Now, concentration of OH⁻ in presence of 0.1 M NaOH will be equal to concentration of OH⁻ available from complete ionisation of NaOH and concentration of OH⁻ available from ionisation of $Mg(OH)_2$ but the solubility of $Mg(OH)_2$ is less and so concentration of OH⁻ available from its ionisation can be neglected in comparison to 0.1 M OH⁻ from NaOH. Hence, for

$K_{sp} = [Mg^{2+}] [OH^-]^2$

$1.8 \times 10^{-11} = [S] (2 \times 0.1)^2$

∴ $[S] = \dfrac{1.8 \times 10^{-11}}{4 \times 10^{-2}}$

$= 0.45 \times 10^{-9} = 4.5 \times 10^{-10}$ M

Thus, the solubility of sparingly soluble salt $Mg(OH)_2$ decreases from 1.65×10^{-4} M to 4.5×10^{-10} M in presence of common OH⁻ ion. Thus, solubility of sparingly soluble salt decreases in presence of common ion.

The use of effect of common ion can be made to separate one ion from the other in presence of other ion in qualitative analysis. It can also be used for decrease in solubility of the components in the mixture. In qualitative analysis, the solubility products of sulphides of metal ions of second group are less in comparison to solubility products of sulphides of metal ions of III B group ions, therefore, HCl is added before adding H_2S water to test the second group ions.

$$H_2S_{(aq)} \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$
$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
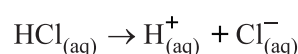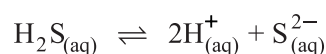
The common ion available from HCl creates common ion effect on the equilibrium and decreases concentration of S^{2-} ions. Hence, the sulphides of the ions included in second group can only be precipitated because their solubility

products are less. In the same way, for precipitation of ions of group III A ammonium chloride (in excess) is added along with NH_4OH. The concentration of OH^- available from ionisation of NH_4OH gets decreased due to common ion effect due to NH_4^+ available from NH_4Cl. Hence, the hydroxides of the ions of III A group only will be precipitated because the values of solubility products of the hydroxides of III A group are low. Above this, if HCI gas is passed through saturated solution of NaCI, NaCI becomes insoluble and separates as precipitates due to the common ion effect of Cl^- ions.

It is necessary to note that under certain situations the solubility increases instead of decreasing. The solubility of salt like phosphate increases when acid is added to their solutions or pH of the solution decreases. The reason for this is that, phosphate ion combines with H^+ available from acid and converts into acid by accepting proton. Hence, solubility of phosphate salt increases.

SUMMARY

It is said that equilibrium is established when number of molecules moving from liquid state to vapour state and number of molecules moving from vapour state to liquid state are same and it is dynamic. Equilibrium is established in both physical and chemical types of reactions. At this point of time the rates of forward and reverse reactions become equal. Equilibrium constant K_c is expressed as the ratio of the multiplication of concentration of products to the multiplication of concentration of reactants; concentration of each can be expressed as power of their stoichiometric coefficient.

For reaction $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Equilibrium constant has constant value at constant temperature and at this stage macroscopic properties like concentration, pressure, etc become constant. For gaseous reaction K_p is taken instead of K_c and partital pressure of gaseous reactants and products are expressed instead of concentrations. The relation between K_p and K_c is expressed as $K_p = K_c(RT)^{\Delta n_g}$. In which direction reaction will occur (forward or reverse) can be expressed by reaction quotient Q_c which is equal to K_c at equilibrium. Le Chatelier's principle, mentions that if the equilibrium gets disturbed by change in factors like concentration, temperature, pressure etc., then equilibrium will move in the direction whereby the effect has been minimised or made negligible and the value of equilibrium constant will not change. This can be used in industries to know how equilibrium can be obtained by study of changes in factors like concentration, pressure, temperature, inert gas etc. In industries, we can change or control factors accordingly so that reaction shifts from reactants to products (left to right). If catalyst is used, only the rate of required reaction will increase but no change will occur in amounts of reactants or products because the effect on forward and reverse reactions will be the same and so equilibrium constant will not change.

The substances which allow the electric current to pass through their aqueous solutions are called electrolytes. Acid, base and salt are electrolytes because their aqueous solutions conduct electric current. The reason for the conduction of electric current in aqueous solution of electrolyte is the formation of ions due to dissociation or ionisation which conducts electric current. While the weak electrolytes are incompletely dissociated and so the equilibrium is established between its ions and undissociated molecules. This is called ionic equilibrium.

According to Arrhenius ionisation theory, acid is called a substance which gives hydrogen ion (H^+) and base is called a substanec which gives hydroxyl ion (OH^-) on ionisation. According to Bronsted - Lowry theory, acid is defined as a proton donor and base is defined as proton acceptor. Each acid has its conjugate base and each base has its conjugate acid. Hence, it is known as conjugate acid - base or proton - transfer theory. Proton is tranferred between acid and base. Bronsted - Lowry is more general than Arrhenius definition. According to Lewis' definition, acid means a substance which accepts a pair of electrons and base is a substance which donates a pair of electrons. This definition can be applied to organic chemistry, complex compounds chemistry in addition to acid-base. Hence, it is considered universally acceptable. Ionisation constant is also an equilibrium constant. The ionisation constants of weak acid (K_a) and weak base (K_b) can be determined. Concentration of acid can be expressed as $pH = -\log_{10}[H_3O^+]$. Hence, pH scale is determined for acid - base. Similary, concentration of OH^- can be expressed as $pOH = -\log_{10}[OH^-]$, ionisation constant of water as $pK_w = -\log_{10}K_w [H_3O^+]$ and $[OH^-]$ can be calculted by the use of relation $pK_w = pH + pOH$. If pH < 7 solution will be acidic, pH > 7 solution will be basic and pH = 7 solution will be neutral.

Different salts can be obtained by neutralisation of strong or weak acid and strong or weak base. In such salts, acidic, basic and neutral salts are included. When such salts react with water, hydration (hydrolysis) reaction occurs and solution obtained can be acidic, basic or neutral. This is also an equilibrium reaction and so corresponding equilibrium constant for it can be determined. Hydrolysis constant is expressed as K_h. pH or pOH can be calculated from the values of K_a and K_b and the value of K_h characteristic for the particular salt. Some solutions are such whose pH does not change by addition of small amount of acid or base or in case they are being diluted. Such solutions are called buffer solutions which can be acidic, basic or of neutral type. The control of pH is useful in the control of biological reactions in our body and chemical reactions in analytical chemistry, industries etc.

Sparingly soluble salts (whose solubility is less than 0.01M in water) dissolve in water depending on their solubility and equilibrium is established. Hence, equilibrium constant for this can be obtained which is known as solubility product constant or solubility product of the sparingly soluble salt. The study of effect of common ion, acid, etc. on the solubility of sparingly soluble salt can be carried out by application of Le Chatelier's principle. Generally, the solubility of sparingly soluble salt decreases due to effect of common ion. This is used in qualitative analysis. By mixing two solutions, whether precipitates will be obtained or not, can be predicted by comparing concentration product I_p with the solubility product K_{sp}. If $I_p > K_{sp}$ precipitation will occur and if $I_p < K_{sp}$ the precipitation will not occur and if $I_p = K_{sp}$, the precipitation will not occur but solution will remain in saturated state.

EXERCISE

1. **Select the proper choice from the given multiple choices :**

(1) Chemical equilibrium is

(A) Dynamic (B) Steady state

(C) Dynamic or stable state (D) None from the above

(2) The example of homogeneous equilibrium is

(A) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ (B) $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$

(C) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ (D) $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

(3)   Mention Lewis acid from following compounds

   (A) HCl   (B) CH_3OOH (C) H_2O (D) BF_3

(4)   Mention conjugate base of acid $H_2PO_4^-$

   (A) PO_4^{3-} (B) HPO_4^{2-} (C) H_3PO_4 (D) $H_2P_2O_7$

(5)   According to which theory NH_3 cannot be said to be base?

   (A) Bronsted-Lowry   (B) Lewis   (C) Arrhenius   (D) Ionisation

(6)   In a reaction, what is necessary for precipitation?

   (A) $I_p < K_{sp}$ (B) $I_p = K_{sp}$ (C) $I_p > K_{sp}$ (D) $K_{sp} > I_p$

(7)   The solubility of sparingly soluble salt by the effect of common ion

   (A) Decreases   (B) Increases

   (C) Remains constant   (D) Increases very high

(8)   Le Chatelier's principle is applicable to

   (A) Chemical equilibrium only   (B) Ionic equilibrium only

   (C) Both chemical and ionic equilibrium. (D) All of the above

(9)   Ferric chloridc solution will be

   (A) Basic   (B) Neutral   (C) Acidic   (D) Cannot be said

(10) With the use of catalyst, the value of equilibrium constant

   (A) Increases   (B) Decreases

   (C) Remains constant   (D) Increases or Decreases

2.   Answer the following questions in brief :

(1)   Mention the relation between K_p and K_c.

(2)   Describe effect of concentration on chemical equilibrium.

(3)   Write the formula for the ionic product of water.

(4)   Mention the relation between equilibrium constants of forward and reverse reactions.

(5)   Write definitions of acid and base according to Arrhenius theory.

(6)   Write definitions of Lewis acid and base.

(7)   Mention conjugate acid-base theory giving suitable example.

(8) Explain the terms solubility product and ionic product.

(9) Mention the relation amongst hydrolysis constant of the salt, dissociation constant and ionic product of water.

(10) Write three examples of conjugute acid-base and conjugate base-acid.

3. Write answers of the following questions :

(1) Mention the operational and conceptual definitions of acid and base.

(2) Derive the formula for dissociation constant of a weak acid.

(3) Derive the formula for dissociation constant of a weak base.

(4) Obtain the relation between equilibrium constants K_c and K_p.

(5) Derive the formula for the solubility product of sparingly soluble salt CaF_2.

(6) Mention the use of effect of common ion in qualitative analysis.

(7) Giving definition of buffer, explain acidic, basic and neutral buffer, giving suitable examples.

(8) Bronsted-Lowry acid can be a Lewis acid but all Lewis acids cannot be Bronsted-Lowry acid. Explain giving suitable example.

(9) Derive the formula of ionic product of water.

(10) Explain calculation of pH of a solution from dissiociation constant.

4. Calculate the following examples :

(1) Calculate pH and pOH of following solutions.

(a) 0.1 M HCl, 0.1 M H_2SO_4, 0.1 M, HNO_3

(b) 0.1 M NaOH, 0.1 M KOH, 0.1 M, $Ba(OH)_2$

(2) Calculate pH of following solutions.

(a) 3.65 gram HCl in 250 ml solution

(b) 9.80 gram H_2SO_4 in 500 ml solution

(c) 1.6 gram NaOH in 250 ml solution

(d) 11.2 gram KOH in 500 ml solution

(3) Calculate pH of 250 ml solution containing 6 gram acetic acid. Dissociation constant of acetic acid is 1.8×10^{-5}

(4) Calculate pH of 500 ml ammonium hydroxide solution containing 7 gram ammonium hydroxide. Dissociation constant of ammonium hydroxide is 1.8×10^{-5}

(5) The dissociation constant of benzoic acid is 6.5×10^{-5} at 298 K. What will be the pH of its 0.15 M solution and its $[H_3O^+]$ ion concentration ?

(6) The dissociation constant of dimethyl amine is 5.4×10^{-5} at 298 K. What will be the pH of its 0.25 M solution and $[H_3O^+]$ ion concentration ?

(7) To prepare one acidic buffer solution 0.125 M sodium acetate is added to 0.25 M solution of acetic acid. If dissociation constant of acetic acid is 1.8×10^{-5}, what will be the pH of this buffer solution ?

(8) To prepare one basic buffer solution, 0.250 M NH_4Cl is added to a solution of 0.125 M ammonium hydroxide. If dissociation constant of ammonium hydroxide is 1.8×10^{-5}, what will be the pH of this buffer solution ?

(9) 20 ml 0.04 M NaCI solution is added to 10 ml 0.06 M $AgNO_3$ solution. If solubility product of AgCI is 1.8×10^{-10} at 298 K, predict whether precipitation will occur or not ?

(10) 20 ml 0.025 M K_2CrO_4 solution is added to 20 ml 0.05 $BaCl_2$ solution. If solubility product of $BaCrO_4$ is 1.2×10^{-10} at 298 K, predict whether precipitation will occur or not ?

(11) Calculate hydrolysis constant and pH of a solution of 0.1 M sodium acetate. Dissociation constant of acetic acid is 1.8×10^{-5} at 298 K and ionic product of water is 1.04×10^{-14}

(12) Calculate hydrolysis constant and pH of 0.30 M NH_4Cl solution. The dissociation constant and ionic product of water are 1.8×10^{-5} and 1.04×10^{-14} respectively at 298 K.

(13) If 20 ml 0.15 M NaOH solution is added to a 10 ml 0.1 M 10 H_2SO_4 solution, what will be the pH of the resulting mixture ?

(14) If 20 ml 0.15 M HCI solution is added to 10 ml 0.1 M $Ba(OH)_2$ solution, what will be the pH of the resulting mixture ?

(15) If dissociation constant of aniline is 4.27×10^{-10} at 298 K, what will be the dissociation constant of its conjugate acid ? $K_w = 1.04 \times 10^{-14}$.

(16) If dissociation constant of acetic acid is 1.76×10^{-5} at 298 K, what will be dissociation constant of its conjugate base ? $K_w = 1.04 \times 10^{-14}$.