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THE PEOPLE'S
UNIVERSITY

Indira Gandhi National
Open University
School of Sciences

BCHCT-133
CHEMICAL ENERGETICS, EQUILIBRIA AND FUNCTIONAL GROUP ORGANIC CHEMISTRY-I

Block

2

CHEMICAL AND IONIC EQUILIBRIUM

CHEMICAL AND IONIC EQUILIBRIUM

In the previous block on 'Chemical Energetics' you have learnt about the basic aspects of energetics, the laws of thermodynamics, their significance and applications. In this block we would take up chemical and ionic equilibria. Here, we shall apply the principles of thermodynamics to the study of chemical equilibria and its application to equilibria involving ionic systems.

This block contains five units. Unit 5 and 6 deal with chemical equilibria whereas Unit 7 to 9 cover ionic equilibria. In Unit 5, we shall discuss the main features of chemical equilibrium and will derive the expressions for equilibrium constants using thermodynamics. We shall also discuss about the relation between different types of equilibrium constants. In Unit 6, we shall explain Le Chatelier's principle and discuss its applications.

In Unit 7 we will deal with ionisation equilibrium of weak electrolytes, its characterisation, theories of acids & bases and the concept of pH. In Unit 8 we will take up the equilibria in the aqueous solutions of weak acids/bases, polyprotic acids and mixtures of weak acids/bases with salts containing common ions i.e., buffer solutions. The equilibria in aqueous solutions of different types of salts in water would be dealt in Unit 9. It would cover the hydrolysis of salts and the solubility equilibrium of sparingly soluble salts and its applications.

Objectives

After studying this block, you should able to:

- explain chemical equilibrium;
- derive an expression for equilibrium constant in terms of Gibbs energy;
- express the equilibrium constant in different ways;
- state Le Chatelier's principle and explain its applications;
- define and differentiate between electrolytes and non-electrolytes;
- describe different theories of acids and bases; and discuss their merits and demerits;
- define pH and calculate the same for aqueous solutions of strong acids and bases;
- explain the ionisation of weak acids and bases and calculate the pH of their solutions;
- describe the stepwise ionisation of diprotic and polyprotic acids and write expressions for the respective ionisation constants;
- relate the strengths of acids and bases with their molecular structure;
- explain the effect of common ions on the equilibria of weak acids and bases;
- define buffer solutions, explain their mode of action and calculate their pH; and
- define and explain buffer capacity.

UNIT 5

CHEMICAL EQUILIBRIUM –I

Structure

5.1 INTRODUCTION

Many times, the chemists find that the reaction which they are studying does not go to completion. The concentrations of the reactants and products become somewhat constant. Well, at this point, there seems to be a balance between the opposing reactions and the system is said to be in a condition of equilibrium. We have already dealt in the previous block with the feasibility of the reactions. In this unit we are going to deal with the question, upto what stage does a chemical reaction proceed?

Previously you have learnt that chemical reactions are of two types - irreversible and reversible. The irreversible reactions are those which go to completion. This means that the reaction goes on and on until at least one of the reactants is completely used up. Such reaction proceed in only one direction under a given set of conditions. Whereas those reactions which appear not to proceed beyond a certain stage after sometime even though the reactants are not completely used up are called reversible reactions. They have only reached an equilibrium state. Such reaction can occur in forward as well as backward directions under the same set of conditions. In this unit you will understand the meaning of this state of equilibrium and learn how the equilibrium composition of the reactants and products are correlated with change in Gibbs energy.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ differentiate between reversible and irreversible reactions;
- ❖ explain chemical equilibrium;
- ❖ derive an expression for equilibrium constant in terms of Gibbs energy; and
- ❖ express the equilibrium constant in different ways.

5.2 REVERSIBLE AND IRREVERSIBLE REACTIONS

In general, chemical reactions can be divided into two types- reversible and irreversible. Those reactions in which the products can combine back to form the reactants are called reversible reactions. Under usual experimental conditions the irreversible reactions are those where the same reactants cannot be formed back from the products. In this unit, whenever we are referring to reactions in equilibrium, we are referring to reversible reactions.

Now let me narrate to you a short story: Napoleon Bonaparte was the one who helped discover reversible reactions. He brought the concept of reaction reversibility to chemistry. The famous French chemist Claude Louis Berthollet (1748-1822) was appointed as a scientific advisor to him and was taken with him on the most far-flung of his campaigns, even to Egypt in 1798. In Egypt, Berthollet recognized deposits of sodium carbonate around the edges of some of the salt lakes found there. He knew the following reaction

$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 \downarrow + 2NaCl$$

which was known to proceed to completion in the laboratory. Thus he understood that, Na_2CO_3 must have been formed by the reverse of this process brought about by the very high concentration of salt in the slowly-evaporating waters.

Thus it was realized that a chemical reaction such as given above can proceed in both directions – from left to right or vice-versa – depending on the experimental conditions. Each such reaction is usually written containing two half-arrows pointing in opposite directions emphasizing the fact that it is a reversible reaction:

$$Na_2CO_3 + CaCl_2 \rightleftharpoons CaCO_3 \downarrow + 2NaCl$$

This led Berthollet to question the belief of the time that a reaction could only proceed in a single direction. His famous textbook "*Essai de statique chimique*" (1803) presented his speculations on chemical affinity and his discovery that an excess of the product of a reaction could drive it in the reverse direction.

5.3 CHEMICAL EQUILIBRIUM – A DYNAMIC EQUILIBRIUM

Let us start this unit by recalling when is a chemical reaction said to be in equilibrium. As reaction takes place between the reactants, the products are formed and thereby they form a mixture where they are in dynamic equilibrium. As the chemical equilibrium involves a balance between opposite reactions, it is often called dynamic equilibrium. To denote this, a double arrow ($\rightleftharpoons$) is used between reactants and products.

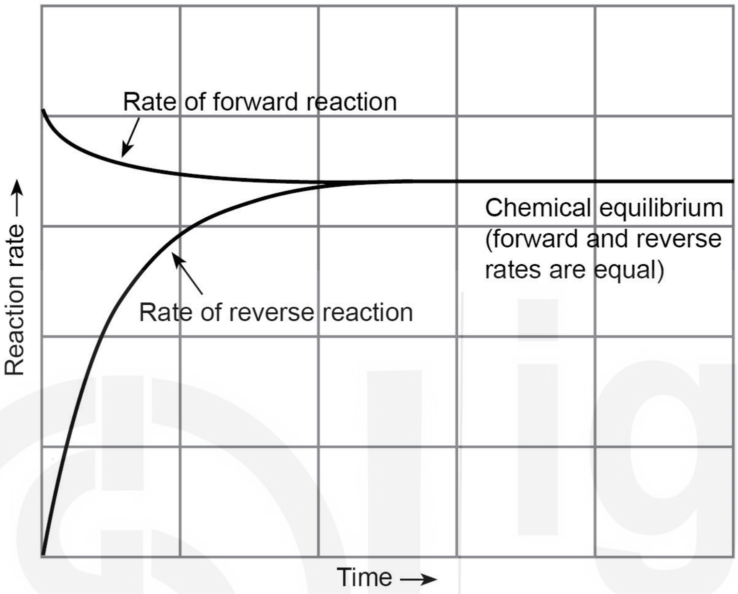


Fig. 5.1: Equilibrium as a dynamic state.

In the above Fig. 5.1 it is shown that, as the reaction reaches the state of equilibrium, reactants form products and products form reactants. This results in a mixture of reactants and products at this stage. At this stage, why you should study this state of equilibrium? Well, it would help us to calculate to what extent the reaction will proceed, the amount of the products formed and the reactants remaining. In the industry, these studies have helped. Industrial processes of importance which are reactions in chemical equilibrium, have been carried out in suitable low-cost conditions so that maximum yield of the desired product can be achieved.

Equi in the word equilibrium means equal. It refers to equal rates of forward and reverse reactions, not to equal quantities or concentrations of the substances involved. The librium part of the word comes from libra, meaning ‘balance’. Chemical equilibrium is an equal balance between two reaction rates.

You should note that in such cases where dynamic equilibrium is established, both the forward and reverse reactions occur at the same rate, or speed. You consider any of the components of the chemical reaction as reactants or products. So you see, a chemical reaction can be written in either way. The same may be explained with the following example.

The two equations $H_2 + I_2 \rightarrow 2\,HI$ "synthesis of hydrogen iodide", as well as $2\,HI \rightarrow H_2 + I_2$ "dissociation of hydrogen iodide" represent the same chemical reaction system in which the roles of the components are reversed, *and both yield the same mixture of components when the equilibrium is reached.* This is the core concept of chemical equilibrium.

Fig. 5.2 a) and b) below show how the concentrations of the three components of this chemical reaction change with time.

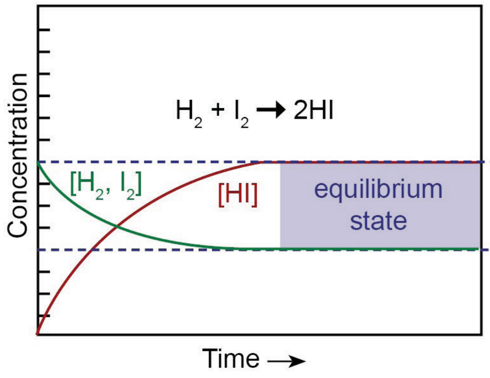


Fig. 5.2 (a)

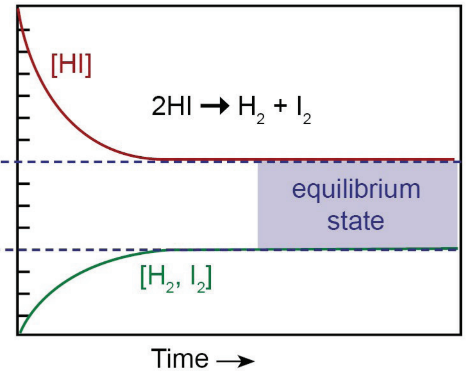


Fig. 5.2 (b)

It does not matter if you start from the left with an equimolar mixture of H_2 and I_2 or you start with a pure sample of hydrogen iodide (Fig. 5.2 b, using twice the initial concentration of HI to keep the number of atoms the same), you will see that whenever equilibrium will be attained (equilibrium state marked on the right) the composition will be the same. So you see that the equilibrium composition does not depend on the direction from which it is approached. Chemical equilibrium is the state reached by a reaction mixture when the rates of forward and reverse reactions have become equal.

For any reaction involving only gases or species in solution (generally aqueous) in which '*α*' moles of substance A react with *b* moles of substance B to give *c* moles of substance C and *d* moles of substance D:

$$\alpha A + bB \ldots\ldots \rightleftharpoons cC + dD$$

the following holds when equilibrium is established:

$$K_c = \frac{[C]^c_{eqm}\ [D]^d_{eqm}}{[A]^\alpha_{eqm}\ [B]^b_{eqm}} \qquad \ldots(5.1)$$

where $[A]_{eqm}$ is the concentration of substance A at equilibrium (mol/L), similarly for substances B, C and D. K_c is called the **equilibrium constant** for the reaction. For a particular reaction, K_c is independent of the initial concentrations, i.e. any combination of concentration of A, B, C and D can be reacted together, yet the same value of K_c is obtained within experimental error. When the respective equilibrium concentrations are inserted into Eq. 5.1 we get the value of K_c. K_c is also called $K_{equilibrium}$ or simply K.

You may note that the products always appear on the numerator of the expression and the reactants always appear on the denominator. As can be seen from Eq. 5.1, a large value of K_c means that the reaction proceeds extensively from left to right – it may be so large in a particular example that the reaction can be considered to go to completion, e.g., the reaction between an aqueous solution of copper (II) sulphate and iron filings. Conversely a small value of K_c means that very little reaction occurs from left to right.

For reactions that are not at equilibrium, we can write a similar expression called the reaction quotient Q. The reaction quotient (Q) measures the relative amounts of products and reactants present during a reaction at a particular point in time. With the help of the reaction quotient you can figure out which direction a reaction would proceed, if you are given the concentrations of the reactants and the products. So you can say that if:

- $Q < K$: there is a net conversion of reactants into products as the forward reaction dominates.
- $Q > K$: a net conversion of products into reactants takes place as the reverse reaction dominates.
- $Q = K$ the reaction is in equilibrium: no net change in the composition of the reaction mixture occurs over time.

Table 5.1: Comparison of *Q* and *K* Values

Value of Q	What It Means
$Q < K$	Reaction proceeds in forward direction
$Q = K$	Reaction is at equilibrium ($\rightleftharpoons$)
$Q > K$	Reaction proceeds in reverse direction

The reaction quotient is denoted as Q_c when the concentrations of the reactants and the products are given. Q_c becomes equal to K_c at equilibrium.

The equation for Q_c may be written by multiplying the concentrations for the species of the products and dividing by the concentrations of the reactants. The concentration is raised to the power of the respective stoichiometric coefficients. Q_c therefore is:

$$Q_C = \frac{[C]^c\ [D]^d}{[A]^\alpha\ [B]^b} \qquad \ldots(5.2)$$

The Q_c value can be compared to the equilibrium constant, K_c, to determine the direction of the reaction that is taking place. The main difference between K_c and Q_c is that K_c describes a reaction that is at equilibrium, whereas Q_c describes a reaction that is not at equilibrium.

SAQ 1

Can you point out the similarities and dissimilarities of the plot in the Fig. 5.2 (a) and 5.2 (b)?

SAQ 2

Why chemical equilibrium is called a ‘dynamic process’?

5.4 GIBBS ENERGY CHANGE IN A CHEMICAL REACTION

In the Unit 4, you have learnt about Gibbs energy. In this section, you will learn about the details of Gibbs energy so that you can arrive at a relationship of it and chemical equilibrium.

In the following Fig. 5.3, Gibbs energy is plotted against the extent of the reaction.

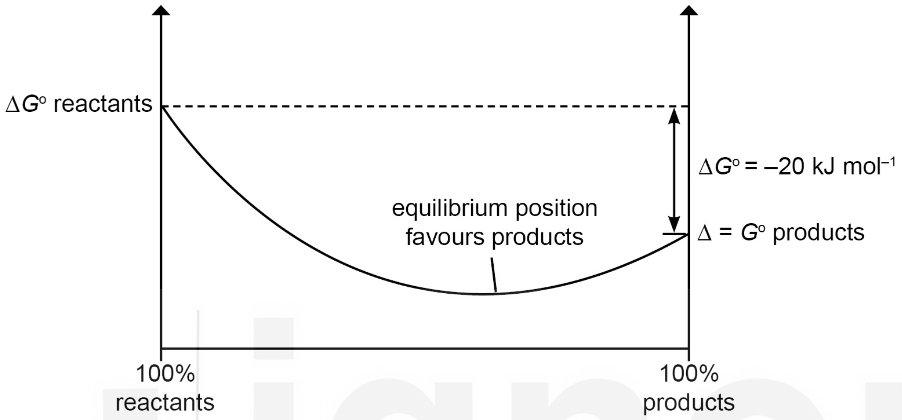


Fig. 5.3: Gibbs energy diagram.

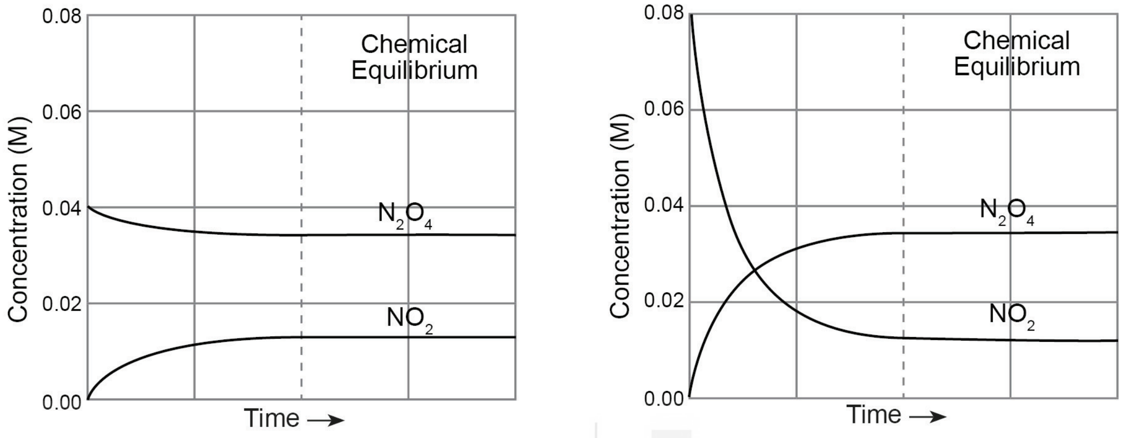
The minimum of the plot in the variations of Gibbs energy as a function of the extent of the reaction (that is how far the reaction has proceeded towards completion), corresponds to the equilibrium composition. This is the way you can find out the equilibrium composition from the minimum of the above plot. Thus, at constant temperature and pressure, the direction of a spontaneous reaction is towards lower values of the Gibbs energy, *G*.

In the previous unit we learnt how to use the values of ΔG so as to understand whether or not a particular chemical reaction or physical change would be spontaneous under specified conditions. Even if a chemical reaction is spontaneous, it necessarily does not convert all of its reactants to products. So, even if you can say whether a reaction is spontaneous or not, it is not much of use, unless you can also determine just how far the reaction will proceed towards completion. The relationship between ΔG^0 and the equilibrium constant for the reaction in question can be utilized to determine such things.

Let us study the following chemical reaction:

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

Equilibrium in this system can be approached from either direction. The question which should arise in your mind now is why does this happen? Now, let us start from the beginning of the above reaction, where we have pure $N_2O_4(g)$ and then slowly let the reaction attain equilibrium. As the reaction proceeds, $NO_2(g)$ molecules start to form, and they mix spontaneously with the remaining $N_2O_4(g)$ molecules so that the reaction mixture is homogeneous at all times. In such cases of spontaneous mixing, always there is an associated negative Gibbs energy which is denoted as $\Delta_{mix}G$. The value of this is negative at all possible reaction mixture compositions. This signifies that, at any possible reaction mixture composition, the two gases N_2O_4 and NO_2 always mix spontaneously. Thus we can now say that, the total Gibbs energy change for the system is the sum of the Gibbs energy change for the chemical reaction and the Gibbs energy change of mixing.



(a) (b)

Fig. 5.4: Initial and equilibrium concentrations. Change in the concentrations of N_2O_4 and NO_2 (b) only NO_2 is present initially.

In experiment (a) concentration of NO_2 increases as concentration of N_2O_4 decreases. In experiment (b), concentration of N_2O_4 increases as concentration of NO_2 decreases. In both experiments, a state of chemical equilibrium is reached when the concentrations level off at constant values: $[N_2O_4] = 0.0337$ M; $[NO_2] = 0.0125$ M. The experiments show that it is a reversible reaction and moves in the direction to achieve and maintain an equilibrium state.

In the Fig. 5.4, rates of the forward and reverse reactions for decomposition of N_2O_4 to NO_2 has been shown. From the plots it is clear that as N_2O_4 is consumed, the rate of the forward reaction decreases; as NO_2 is formed, the rate of the reverse reaction increases. When the two rates become equal, an equilibrium state is attained and there are no further changes in concentrations. At equilibrium, the rates of the forward and reverse reactions are equal.

If the $NO_2(g)$ molecules formed in the reaction would not have mixed with the $N_2O_4(g)$ molecules, then the free energy diagram would simply be a straight line joining G^0 (N_2O_4, g) and $G^0(NO_2, g)$ similar to that shown on the Fig. 5.5. However, when we add the contribution from $\Delta_{mix}G$, we always find that a minimum exists in the Gibbs energy curve. The question is what will be the position of the minimum? Now, that mainly depends on the sign and magnitude of ΔG^0, the standard Gibbs energy change for the reaction. You must be remembering from the previous unit that $\Delta G = 0$ at equilibrium.

Consider the plot (given in Fig. 5.5) of Gibbs energy, *G,* versus the number of moles of product (NO_2) formed, which gives the extent of the reaction. On the left side we have pure reactants. On the right side we have pure products.

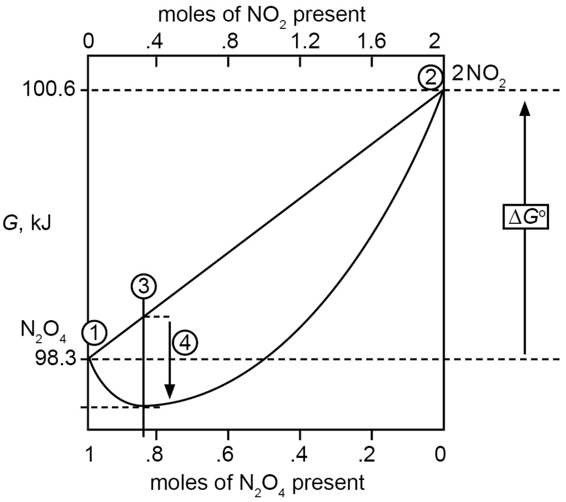


Fig. 5.5: Gibbs energy diagram of N_2O_4.

At this stage, you can study the plot given in Fig. 5.5. The Gibbs energy of 1 mole of N_2O_4 (1) is smaller than that of 2 moles of NO_2 (2) by 2.3 kJ; thus $\Delta G^\circ = +2.3$ kJ for the complete transformation of reactants into products. The straight diagonal line shows the Gibbs energy of all possible compositions if the two gases were prevented from mixing. The curved line shows the Gibbs energy of the actual reaction mixture. This passes through a minimum at (3) where 0.814 mol of N_2O_4 are in equilibrium with 0.372 mol of NO_2. The difference (4) corresponds to the Gibbs energy of mixing of reactants and products which always results in an equilibrium mixture whose Gibbs energy is lower than that of either pure reactants or pure products. So some amount of reaction will occur even though ΔG° for the process is positive. From either direction of the curve if you would try to approach the minimum, ΔG for any small change in composition of the reaction mixture starts becoming less negative, until, when you reach the minimum, ΔG for any infinitesimally small change in composition of the reaction mixture becomes zero. Here, the system is at equilibrium. In other words, the value of ΔG for this, and any other reaction, can be found out from the slope of the Gibbs energy diagram. Here you should remember one important point, that is, when the system has a composition corresponding to the minimum in the Gibbs energy diagram, ΔG for any change in composition is positive, thus no change in composition occurs.

5.4.1 Distinction between ΔG and ΔG^0

If you closely observe the Fig. 5.5, then you can see that ΔG^0 for the reaction $N_2O_4(g) \rightarrow 2NO_2(g)$ is positive. At this point you may have this question in mind that, why does the reaction proceed in the forward direction at all. In order to get an answer to this, you must remember that ΔG^0 is the Gibbs energy change for the conversion of reactants in their standard state to products in their standard state. In this case, the standard state is the pure gases at p^o (standard pressure). A sample of $N_2O_4(g)$ at p^o reacts to give some $NO_2(g)$. But, the pressure of $NO_2(g)$ at equilibrium is much less than p^o so $N_2O_4(g)$ becomes the dominant species in the equilibrium mixture. Next, let us take the example of vapourisation of water, for which ΔG^0 is +8.6 kJ mol^{-1} at 25.0°C. It is well known that water evaporates spontaneously at 25.0 °C. What would happen if the value of ΔG^0 would be positive? It would definitely mean that the partial pressure of water would never reach p^o under these conditions when the system would be at equilibrium. Then what would happen when there is a negative value of ΔG^0? All this means that the predominant species at equilibrium would be the products, and also there would be some reactants in the equilibrium mixture. So you can see that from the sign of ΔG^0 one can say about the composition of the reaction mixture at equilibrium. Another point to be remembered is that ΔG^0 is not a criterion for spontaneity except in the very rare case when the reaction is carried out under standard conditions. You should never forget that the sign of ΔG indicates whether a particular change in composition of the reaction mixture would be spontaneous.

The point 1 in Fig. 5.5 which is 98.3 kJ represents the standard Gibbs energy of the reactants [G^o (reactants)]. The point 2 in Fig. 5.5 which is 100.6 kJ which represents the standard Gibbs energy of the products [G^o (products)]. The difference between G^o (products) and G^o (reactants) is the standard Gibbs energy change, ΔG^0.

$$\Delta G^0 = G^o\,(\text{products}) - G^o\,(\text{reactants})$$

If $\Delta G^0 < 0$, equilibrium shifts to the right, towards products, $K > 1$

If $\Delta G^0 > 0$, equilibrium shifts to the left, towards reactants, $K < 1$

Wherever the ΔG^0 value for a reaction is too large, 20 kJ or more, and if it is positive, then the reaction may not be observed at room temperature. But you will see that when the reaction after some time under the same conditions achieves completion, then ΔG^0 is both large and negative. Thus, if you inspect the size and sign of ΔG^0, you will be able to predict whether the spontaneous reaction observed actually occurs.

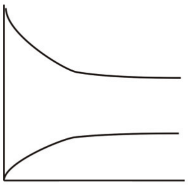
SAQ 3

Label each graph with the correct description:

a) The forward and reverse rates as equilibrium is approached.

b) The overall rate as equilibrium is approached.

c) The reactant and product concentrations as equilibrium is approached (two graphs)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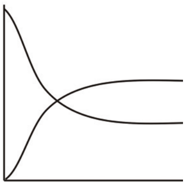
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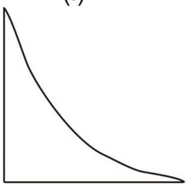
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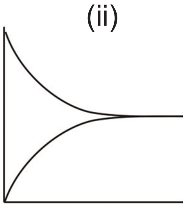

(iv)

5.5 CHEMICAL EQUILIBRIUM IN IDEAL GAS MIXTURES: THERMODYNAMIC DERIVATION OF LAW OF CHEMICAL EQUILIBRIUM

If we start with a general reaction

$$\alpha A + bB\ldots.. \rightleftharpoons cC + dD \qquad \ldots(5.3)$$

where the reactants A and B form the products C and D. α, b, c and d are their stoichiometric coefficients respectively.

The Chemical potential, μ_i is the change in the Gibbs energy per mole of substance "i" added at constant concentration. The Chemical potential, μ_i of an ideal gas; 'i' in a gaseous mixture is given by

Stoichiometric coefficients: is the number written in front of atoms, ions and molecules in a chemical reaction to balance the number of each element on both the reactant and product sides of the equation.

$$\mu_i(p) = \mu_i^0(p) + RT \ln p_i \qquad \ldots(5.4)$$

where $\mu_i°(p)$ is the chemical potential of i in the standard state and p_i is its partial pressure.

In earlier units you have studied that the change in Gibbs energy, dG is given by

$$dG = Vdp - SdT \qquad \ldots(5.5)$$

Again, for the given reaction,

Gibbs energy of the products = $c\mu_C + d\mu_D + \ldots.$

Gibbs energy of the reactants = $\alpha\mu_A + b\mu_B + \ldots.$

where μ terms stand for the chemical potential of various substances.

If the values of chemical potential as defined by Eq. 5.4, are substituted for the values of Gibbs energy of products and reactants, then the differences in Gibbs energy, ΔG is given by the following derivation:

R is the ideal gas constant and in SI unit it's value is 8.314 $JK^{-1}mol^{-1}$.

At constant temperature ($dT = 0$) and pressure ($dp = 0$), the Gibbs energy change for the above reaction $(\Delta G_{T,P})$ is obtained by using Eq. 5.4 and 5.5.

$$\Delta G_{T,P} = (c\mu_C + d\mu_D + \ldots) - (\alpha\mu_A + b\mu_B + \ldots) \qquad \ldots(5.6)$$

where μ_C, μ_D, μ_A, μ_B, …., etc. are the chemical potentials of the products and reactants; and α, b, c and d are the stoichiometric coefficients.

Using Eq. 5.4 in Eq.5.6 we get,

$$\Delta G_{T,P} = [c(\mu_C^o(p) + RT \ln p_C) + d(\mu_D^o(p) + RT \ln p_D) + \ldots]$$

$$-[\alpha(\mu_A^o(p) + RT \ln p_A) + b(\mu_B^o(p) + RT \ln p_B) + \ldots] \qquad \ldots(5.7)$$

$$\Delta G_{T,P} = [c(\mu_C^o(p) + d(\mu_D^o(p) + \ldots) - \alpha(\mu_A^o(p) + b(\mu_B^o(p) + \ldots)]$$

$$+RT \ln\left[\frac{p_C^c \,.\, p_{D\ldots}^d}{p_A^\alpha \,.\, p_{B\ldots}^b}\right] \qquad \ldots(5.8)$$

Note that in the transformation of Eq. 5.7 to Eq. 5.8, we have used the relation:

$$cRT\ \ln p_{\mathrm{C}} = RT\ \ln p_{\mathrm{C}}^{c}$$

i.e. a coefficient (c) of a logarithmic term ($RT \ln p_{\mathrm{C}}$) is taken inside the logarithmic term as a power.

But

$$[c(\mu_{\mathrm{C}}^{\mathrm{o}}(p)+d(\mu_{\mathrm{D}}^{\mathrm{o}}(p)]-[\alpha(\mu_{\mathrm{A}}^{\mathrm{o}}(p)+b(\mu_{\mathrm{B}}^{\mathrm{o}}(p)+...]=\Delta G^{\circ}{}_{T,P} \qquad ...(5.9)$$

Where $\Delta G_{T,P}$ is the standard Gibbs energy change of the reaction at constant temperature and pressure.

Using Eqs. 5.8 and 5.9, we can write

$$\Delta G_{T,P} = \Delta G^{\circ}{}_{T,P} + RT \ln\left[\frac{p_{\mathrm{C}}^{c}\,.\,p_{\mathrm{D}...}^{d}}{p_{\mathrm{A}}^{\alpha}\,.\,p_{\mathrm{B}...}^{b}}\right] \qquad ...(5.10)$$

Let us now assume that the above system is under equilibrium. Using Eqs. 5.9 and 5.10 , we can write that at equilibrium,

$$\Delta G_{T,P} = \Delta G^{\circ}{}_{T,P} + RT\ \ln\left[\frac{p_{\mathrm{C}}^{c}\,.\,p_{\mathrm{D}...}^{d}}{p_{\mathrm{A}}^{\alpha}\,.\,p_{\mathrm{B}...}^{b}}\right]_{\mathrm{eq}} = 0 \qquad ...(5.11)$$

The subscript ‘eq’ stands for equilibrium values of partial pressures.

i.e. $$\Delta G^{\circ}{}_{T,P} = -RT\ \ln\left[\frac{p_{\mathrm{C}}^{c}\,.\,p_{\mathrm{D}...}^{d}}{p_{\mathrm{A}}^{\alpha}\,.\,p_{\mathrm{B}...}^{b}}\right]_{\mathrm{eq}} \qquad ...(5.12)$$

or $$\Delta G^{\circ}{}_{T,P} = -RT\ \ln K_{\mathrm{p}} = -2.303\ RT\ \log K_{\mathrm{p}} \qquad ...(5.13)$$

Where K_{p} is the equilibrium constant in terms of partial pressures.

Now let us look at the following problems which are given as examples.

Example 5.1:

a) In a reversible reaction which reaches equilibrium, when will $\Delta G°$ be equal to zero?

Solution

$\Delta G° = -\ RT \ln K$

If $K = 1$, $\ln K = 0$ and $\Delta G° = 0$, i.e. $\Delta G°$ will be zero when K is unity.

b) When will $\Delta G°$ be negative for an equilibrium reaction?

Solution

$\Delta G° = -\ RT \ln K$ (at equilibrium)

Since RT is positive, $\Delta G°$ will be negative only when $\ln K$ is positive; $\ln K$ will be positive quantity only when the value of K is greater than unity.

c) When will $\Delta G°$ be positive?

Solution

If you follow the statements made in b), then you will obviously be able to conclude that $\Delta G°$ will be positive only when K is less than unity.

d) Estimate K at 300 K when $\Delta G°$ is 1350 cal mol^{-1}.

Solution

SI unit of energy is joule (J) and 1 calories is equal to 4.1858 Joule.

$$\Delta G°_{300} = -R \times 300 \ln K$$

$$\ln K = -\Delta G°_{300}/R \times 300$$

$$\log K = -(1350 \times 4.1858)/(8.314 \times 300 \times 2.303) = -0.9837$$

or $K = 0.1038$

Try the following SAQs which is based on the above discussion.

SAQ 4

At 298.15 K, the $\Delta G°$ for the dissociation of acetic acid,

$CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + H^+(aq)$

is 27.2 kJ mol^{-1}. Calculate the equilibrium constant for the above reaction.

5.6 EQUILIBRIUM CONSTANTS – K_p, K_c, K_x

In this section we are going to study the equilibrium constants for reactions which are not only studied in gaseous system but may be in solutions also. So here you must remember a very important point. For such case, the K is to be expressed in the appropriate concentration units. The symbols K_p, K_c, K_x are generally used to signify that the equilibrium constant expression contains partial pressures, molar concentrations or mole fractions respectively.

5.6.1 K_p

For reactions involving gases, it is convenient to express concentration of any gas at any given temperature in terms of its partial pressure.

To define equilibrium constant in terms of the partial pressures of the reactants and products, you should consider the general gaseous reaction,

$$\alpha A + bB \ldots \rightleftharpoons cC + dD + \ldots \qquad \ldots(5.14)$$

Where p_A, p_B, p_C, p_D, …, etc., are the partial pressures of A, B, C, D, …, etc., at equilibrium and α, b, c and d are their stoichiometric coefficients, the equilibrium constant may be written as,

$$K_p = \frac{p_C^c \cdot p_{D\ldots}^d}{p_A^\alpha \cdot p_{B\ldots}^b} \qquad \ldots(5.15)$$

where K_p is the equilibrium constant in terms of partial pressure and is a constant at a given temperature. It should be noticed that Eq. (5.15) is valid for a system involving ideal gases.

So at equilibrium,

$$\Delta G^\circ_{T,P} = -RT \ln K_p = -2.303\, RT \log K_p \qquad \ldots(5.16)$$

where K_p is the equilibrium constant in terms of partial pressures. The relationship is known as van't Hoff isotherm.

Eq. 5.15 can also be written as,

$$K_p = p_C^c \cdot p_{D\ldots}^d \; p_A^{-\alpha} \cdot p_{B\ldots}^{-b} \qquad \ldots(5.17)$$

Again, from Eqs. 5.15 to 5.17, we can see that the dimensions of K_p will depend upon the stoichiometric coefficients of the reactants and products. This particular aspect will be clear when you study the examples worked out in this unit.

Let us illustrate the use of Eq. 5.15 with an example.

Example 5.2: Suppose that, in an experiment $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ at 1000 K, it is found that

$p_{SO_2} = 3.42 \times 10^4$ Pa, $p_{O_2} = 3.13 \times 10^4$ Pa and

$p_{SO_3} = 3.58 \times 10^4$ Pa for the reaction.

Calculate the value for the equilibrium constant K_p.

Solution: At the given temperature, K_p is given by the expression

$$K_p = (p_{SO_3})^2 \cdot (p_{SO_2})^{-2} (p_{O_2})^{-1}$$

or

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 \cdot (p_{O_2})}$$

$$= \frac{(3.58 \times 10^4 \text{ Pa})^2}{(3.42 \times 10^4 \text{ Pa})^2 \times (3.13 \times 10^4 \text{ Pa})} = 0.35 \times 10^{-4} \text{ Pa}^{-1}$$

Try the following SAQ now.

SAQ 5

Suppose that we write the ammonia synthesis reaction in two different ways:

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

Would you expect any difference in the expression for K_p in the two cases? (Usually, K_p values are calculated using equations of the type (ii) which have integral stoichiometric coefficients).

5.6.2 K_c

The constant K_c is known as the *equilibrium constant* of the particular reaction and gives the ratio of the concentrations of the products to the concentrations of the reactants. The subscript c indicates that the equilibrium condition is expressed in terms of the concentration units, i.e., moles per litre of the various species.

K_c is thus given by the expression,

$$= \frac{c_{C}^{c} \, . \, c_{D\ldots}^{d}}{c_{A}^{\alpha} \; c_{B\ldots}^{b}} \qquad \ldots(5.18)$$

where c is the molar concentration.

5.6.3 K_x

K_x is defined by,

$$= \frac{x_{C}^{c} \, . \, x_{D\ldots}^{d}}{x_{A}^{\alpha} \; x_{B\ldots}^{b}} \qquad \ldots(5.19)$$

where, x_i = mole fraction of the species i.

Since Dalton's law tells us that partial pressure of a gas is equal to the mole fraction times the total pressure, we can write $p_i = x_i p_t$, where p_i is the partial pressure of the i^{th} species. So, Eq. 5.19 can be written as,

$$K_x = (x_C p_t)^c \; . \; (x_D p_t)^d \ldots (x_A p_t)^{-\alpha} \, (x_B p_t)^{-b} \qquad \ldots(5.20)$$

where, x_i = mole fraction of the species i, and p_t = total pressure

---

SAQ 6

Express the equilibrium constant K_p for the reaction,

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

In terms of (i) partial pressures and (ii) mole fractions of the gaseous species.

According to Dalton's law of partial pressure, partial pressure (p_i) of an ideal gas, i, is given by,

$p_i = p_t \, x_i$

where p_t is the total pressure, and x_i is the mole fraction of the gas in a gaseous mixture.

5.7 RELATION BETWEEN – K_p, K_x, K_c

5.7.1 Relation between K_p and K_c

The values of K_p and K_c for a given reaction is not same. The relationship between these constants can be obtained at a particular temperature when we are dealing with ideal gases. For any ideal gas, the pressure is given by

$$P = \left(\frac{n}{V}\right) RT \qquad \ldots(5.21)$$

where V is the volume occupied by n moles of gas at temperature T.

You must be knowing that $\frac{n}{V}$ is nothing else but the molar concentration c, therefore

$$p_i = \frac{n_i RT}{\mathrm{V}} = \mathrm{c}_i RT \qquad \text{...(5.22)}$$

where c_i is the molar concentration of the i^{th} species.

Substituting this value of P in Eq. 5.15 we get,

$$K_\mathrm{p} = \frac{(\mathrm{c_C}RT)^c \,.\, (\mathrm{c_D}RT)^d \ldots}{(\mathrm{c_A}RT)^\alpha \, (\mathrm{c_B}RT)^b \ldots}$$

$$= \frac{\mathrm{c_C^c} \,.\, \mathrm{c_D^d} \cdots}{\mathrm{c_A^\alpha} \, \mathrm{c_B^b} \cdots} (RT)^{(c+d+\ldots)-(\alpha+b+\ldots)} \qquad \text{...(5.23)}$$

Now, $$K_\mathrm{c} = \frac{\mathrm{c_C^c} \,.\, \mathrm{c_D^d} \cdots}{\mathrm{c_A^\alpha} \, \mathrm{c_B^b} \cdots}$$

Thus, $$K_\mathrm{p} = K_\mathrm{c} (RT)^{\Delta n} \qquad \text{...(5.24)}$$

where Δn = number of moles of gaseous products - number of moles of gaseous reactants

If $\Delta n = 0$, then number of moles of reactants is the same as the number of moles of products in gaseous phase.

Then, $K_\mathrm{p} = K_\mathrm{c}$

5.7.2 Relation between K_p and K_x

You have already derived the relation for K_p in Eq. 5.12 to 5.15. Now in this section let us start with the relation in Eq. 5.15:

$$K_\mathrm{p} = \left[\frac{p_\mathrm{C}^c \,.\, p_\mathrm{D}^d \cdots}{p_\mathrm{A}^\alpha \,.\, p_\mathrm{B}^b \cdots} \right]$$

Now, you know that, in a gaseous mixture, the partial pressure of the component A, p_A, its mole fraction, x_A, and the total pressure P are related as

$$p_\mathrm{A} = x_\mathrm{A} P \qquad \text{...(5.25)}$$

Similarly $p_\mathrm{B} = x_\mathrm{B} P$; $p_\mathrm{C} = x_\mathrm{C} P$ and $p_\mathrm{D} = x_\mathrm{D} P$

Substituting the values in Eq.5.15, we get

$$K_\mathrm{p} = \frac{(x_\mathrm{C} P)^c \,.\, (x_\mathrm{D} P)^d \ldots}{(x_\mathrm{A} P)^\alpha \,.\, (x_\mathrm{B} P)^b \ldots}$$

$$= \frac{(x_\mathrm{C})^c \,.\, (x_\mathrm{D})^d \ldots}{(x_\mathrm{A})^\alpha \,.\, (x_\mathrm{B})^b \ldots} (P)^{(c+d+\ldots)-(\alpha+b+\ldots)} \qquad \text{...(5.26)}$$

In Eq. 5.26

$$\frac{(x_C)^c \, . \, (x_D)^d \ldots}{(x_A)^\alpha \, . \, (x_B)^b \ldots} = K_x$$

So, you can say that,

$$K_p = K_x (P)^{(c+d+\ldots)-(\alpha+b+\ldots)} = K_x (P)^{\Delta n} \qquad \ldots(5.27)$$

You should note here that K_c and K_p depend on temperature, but K_x depends on total pressure and temperature.

With the help of the following example you will be able to understand clearly the relation between K_p and K_x.

Example 5.3:

Now, with the help of this example you will understand, how the equilibrium constant depends on the form of the chemical equation:

The equilibrium between hydrogen, nitrogen, and ammonia can be written in the more than one way:

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

(ii) $1/2N_2(g) + 3/2H_2(g) \rightleftharpoons NH_3(g)$

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

If the value of equilibrium constant for the first reaction is given as 0.19 at 532°C.

Write the equilibrium constant expression and calculate its value for the other two reactions at the same temperature.

The strategy that you should follow is:

First, corresponding to each equation write the equilibrium constant expression, then examine the concentration terms to determine the relationship between equilibrium expressions. Then utilize these relationships to calculate the relationships between equilibrium constants.

Solution

The expressions for the equilibrium constants are:

$$K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.19$$

$$K_2 = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$$

$$K_3 = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

If you look at the concentration terms in the expressions for K_1 and K_2 then you will see that,

$$K_2 = \left\{ \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} \right\}$$

$$K_1 = (K_2)^2$$

Now, check this equation by squaring each term in the equilibrium constant expression for K_2 and then verify that $(K_2)^2$ is equal to K_1. So you can say,

$$(K_2)^2 = K_1 = 0.19$$

To calculate K_2, take the square root:

$$K_2 = 0.44$$

Thus, we can say that when the stoichiometry is halved, the new K is the square root (1/2 power) of the old K.

The third equation is the reverse of the first, so the new K_3 is the old K_1 raised to the –1 power.

$$K_3 = (K_1)^{-1} = \frac{1}{K_1} = \frac{1}{0.19}$$

$$K_3 = 5.3$$

Thus you can see that the values of K have been validated and provide equivalent information. Each value of K thus can be applied to a specific form of equation.

Example 5.4:

Consider the equilibrium

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

If the numerical value of K_p is 0.68 at 458 K, calculate K_c.

Methodology to be followed: Compute Δn from the chemical equation, then use the relationship $K_p = K_c(RT)^{\Delta n}$ to solve K_c. ($R = 8.314\ JK^{-1}mol^{-1}$ and temperature in Kelvin).

Solution : You should first calculate Δn. There are 2 mol of gas on the product side of the chemical equation, and there is 1 mol of gaseous reactant, so Δn is +1 in this case. From $K_p = K_c(RT)^{\Delta n}$, you can say

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

After substituting the numerical values for K_p, R, T and Δn in the equation,

$$K_c = \frac{0.68}{(8.314 \times 458)^{+1}}$$

$$K_c = 1.79 \times 10^{-4}$$

SAQ 7

K_p for the formation of 2 mol ammonia from nitrogen and hydrogen is 2.8×10^{-9} at 298 K. Calculate K_c for

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

SAQ 8

For the reactions given below, calculate K_p from K_c.

(i) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 1.7 \times 10^{-3}$ at 2300K

(ii) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ $K_c = 3.2 \times 10^{81}$ at 25 °C

5.8 SUMMARY

In this unit, we have discussed the meaning of reversible and irreversible reactions as well as chemical equilibrium. A general expression for the equilibrium constant was derived from the basic principles of thermodynamics. The various types of equilibrium constants K_p, K_c and K_x as well as their relation were also discussed.

5.9 TERMINAL QUESTIONS

1. In a reaction $A + 2B \rightleftharpoons 2C + D$, A and B are taken in a closed vessel at 300 K. The initial concentration of B is 1.5 times that of A. At equilibrium, the concentration of A and D are equal. Calculate the equilibrium constant at 300 K.

2. Write an equilibrium constant expression for each chemical equation:

   a) $4NO_2(g) + O_2(g) + 2H_2O(g) \rightleftharpoons 4HNO_3(g)$

   b) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

3. The balanced equation for conversion of oxygen to ozone has a very small value of K_c.

   $3O_2(g) \rightleftharpoons 2O_3(g)$ $K_c = 6.25 \times 10^{-58}$

   a) What is the value of K_c if the equation is written as?

   $3/2O_2(g) \rightleftharpoons O_3(g)$

   b) What is the value of K_c for the conversion of ozone to oxygen?

   $2O_3(g) \rightleftharpoons 3O_2(g)$

4. In the equilibrium mixture of three ideal gases A, B, C, $A(g) \rightleftharpoons B(g) + C(g)$ obtained by dissociation of A to the extent of 20% at a total pressure of 1.0 atm, what are the partial pressures of A, B and C?

5. Calculate the equilibrium constant of a reaction at 300 K if ΔG^0 at this temperature for the reaction is 29.29 kJ mol^{-1}.

6. If an equilibrium is product-favoured, is its equilibrium constant large or small with respect to 1? Explain.

5.10 ANSWERS

Self-Assessment Questions

1. Similarities: final (equilibrium) concentrations of the components are the same in the two cases.

   Dissimilarities:

   In a) the concentration of product is zero initially

   In b) the concentration of reactant is zero initially.

2. Chemical equilibrium is the state reached by a reaction mixture when the rates of forward and reverse reactions have become equal. If the reaction is studied it can be seen that there is no net change, although the forward and reverse reactions continue. Since both the forward and the reverse reactions are continuing so the equilibrium is a 'dynamic' process.

3. a) (i)

   b) (iii)

   c) (ii) and (iv)

4. $\log K = -\Delta G^\circ / 2.303\,RT$

   $$= -27.2 \times 1000\,\text{Jmol}^{-1} / (2.303 \times 8.314 \times 298.15\,\text{Jmol}^{-1})$$

   $K = 1.72 \times 10^{-5}$

5. No there would be no differences in the expressions in the two cases.

6. (i) $K_\text{p} = \left[\dfrac{p^2_{\text{NO}_2}}{p^2_{\text{NO}} \cdot p_{\text{O}_{2\ldots\ldots}}}\right]$

   $$K_\text{x} = \frac{x^2_{\text{NO}_2}}{x^2_{\text{NO}} x_{\text{O}_2}}$$

7. $K_\text{c} = 1.7 \times 10^{-2}$

8. (i) $K_\text{p} = K_\text{c}\,(RT)^{\Delta n} = 1.7 \times 10^{-3}\,(RT)^0 = 1.7 \times 10^{-3}$

   (ii) $K_\text{p} = K_\text{c}(RT)^{\Delta n} = 3.2 \times 10^{81}(RT)^{-1} = 3.2 \times 10^{81}(8.314 \times 298)^{-1}$

   $= 1.29 \times 10^{78}$

Terminal Questions

1. A + 2B = 2C + D

	A	2B	2C	D
Initial	a	$1.5a$	0	0
Equilibrium	a-x	$1.5a$ -$2x$	$2x$	x

Now, $a - x = x$, so $a = 2x$

$$1.5a - 2x = 3x - 2x = x$$

So,

$$K = \frac{[C]^2[D]}{[A][B]^2} = \frac{\left(\frac{2x}{V}\right)^2\left(\frac{x}{V}\right)}{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)^2} = 4$$

2. a) $K_c = \dfrac{[HNO_3]^4_{eqm}}{[NO_2]^4_{eqm}[O_2]_{eqm}\ [H_2O]^2_{eqm}}$

b) $K_c = \dfrac{[CO]_{eqm}[H_2]^3_{eqm}}{[CH_4]_{eqm}[H_2O]_{eqm}}$

3. a) When the stoichiometric coefficients are changed by multiplying by the factor half on both sides:

$$K_{c_{1/2}} = \frac{[O_3]_{eqm}}{[O_2]^{3/2}_{eqm}} = \left[\frac{[O_3]^2_{eqm}}{[O_2]^3_{eqm}}\right]^{1/2} = (K_c)^{1/2}$$

$$= (6.25 \times 10^{-58})^{1/2}$$
$$= 2.5 \times 10^{-29}$$

b) For the reverse reaction the equilibrium constant becomes the inverse of the original one, that is 1.6×10^{57}.

4. Let us take one mole of A to start with. Since 20% of A is dissociated, the equilibrium amounts of A, B, C according to the reaction A $\rightleftharpoons$ B + C will be $n_A = 1 - 0.2 = 0.8$ mole; $n_B = 0.2$ mole and $n_C = 0.2$ mole

Total number of moles $N = n_A + n_B + n_C = 0.8 + 0.2 + 0.2 = 1.2$

$\therefore$ Mole fractions of A, B, C at equilibrium are:

$$x_A = \frac{0.8}{1.2};\ x_B = \frac{0.2}{1.2};\ x_C = \frac{0.2}{1.2}$$

Total pressure P (from the data) = 1 atm.

and Partial pressure p = Total pressure × mole fraction

$\therefore$ Partial pressure of A, $p_A = \dfrac{0.8}{1.2} \times 1.0 = 0.667\,\text{atm.}$

Similarly $p_B = \frac{0.2}{1.2} \times 1.0 = 0.167$ atm.

and $p_C = \frac{0.2}{1.2} \times 1.0 = 0.167$ atm.

5. Substituting the values of

$\Delta G^\circ = 29.29 \times 10^3 \text{ Jmol}^{-1} = 29290 \text{ Jmol}^{-1}$;

T = 300 K

R = 8.314 JK^{-1} mol^{-1} in the equation

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

we get

$29290 = -8.314 \times 300 \times 2.303 \ \log \ K$

$$\Rightarrow \ \log K = -\frac{29290}{8.314 \times 300 \times 2.303} = -5.0991$$

Whence $\Rightarrow \ K = 7.96 \times 10^{-6}$.

6. Equilibrium constants are used to predict whether a reaction will favour the products or the reactants. If $K > 1$, the reaction will be product-favoured.

UNIT 6

CHEMICAL EQUILIBRIUM –II

Structure

6.1 INTRODUCTION

Often, the chemist is in a situation, when he/she has to predict what will be the effect on the equilibrium of a chemical system when there is a change in the conditions. It has been seen that the equilibrium mixture responds to this change by shifting to a new equilibrium position, however, the equilibrium constant remains the same.

We have already dealt in the previous unit the reversible and irreversible reactions and Gibbs energy change in a chemical reaction. Also we have dealt in details the equilibrium constants- K_p, K_c and K_x and the relation between them.

In this unit we are going to deal with the applications of equilibrium studies in both homogeneous and heterogeneous systems. Also we are going to discuss the Le Chatelier's Principle. Thereupon we are going to discuss the effect of change of concentration, or pressure, or temperature as well as the addition of inert gas or catalyst on the equilibrium.

Expected Learning Outcomes

After studying this unit, you should be able to:

- describe the applications of equilibrium studies;

- state Le Chatelier's Principle;
- explain the effect of change in concentration, pressure, temperature to the chemical equilibrium;
- Predict the response of an equilibrium system to changes in conditions by applying Le Chatelier's principle;
- explain the effect of addition of inert gas to the chemical equilibrium; and
- describe the effect of a catalyst on a chemical equilibrium.

6.2 APPLICATIONS OF EQUILIBRIUM STUDIES

Let us start this unit by understanding how to apply the equilibrium studies in real life situations.

6.2.1 Determining Equilibrium Constants

At this stage, you must be aware that, whenever you have to determine the value of an equilibrium constant, you have to know the equilibrium concentrations of all of the concentrations that appear in the equilibrium constant expression. With the help of these values K_c is obtained.

Thus whenever you will be calculating equilibrium constants, at first you should make a table, which would show (i) initial conditions, (ii) changes that take place when a reaction occurs, (iii) final (equilibrium) conditions. Let us understand this with the help of the following examples.

Example 6.1: Determining an equilibrium constant value

Consider the colourless gas dinitrogen tetraoxide, $N_2O_4(g)$. When heated it dissociates to form red-brown $NO_2(g)$ according to the equation

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

a) b)

Fig. 6.1: a) The formation of brown NO_2 in the boiling water increases.
b) The ice cold container, which contains more molecules of colourless N_2O_4, so its colour is lighter.

For example, let us take that 2.00 mol $N_2O_4(g)$ is placed into an empty 5.00 L flask and heated to 407 K. Almost immediately a dark red-brown colour appears. So it indicates that the colourless gas N_2O_4 has been transformed into red-brown NO_2 (Fig. 6.1a). By measuring the intensity of colour, it can be determined that the concentration of NO_2 at equilibrium is 0.525 mol/L. To use this information to calculate the equilibrium constant, follow these steps:

1. Firstly, you should write down the balanced equation for the reaction for which you are going to calculate the equilibrium constant of the reaction. From it derive the equilibrium constant expression. The balanced equation and equilibrium constant expressions are

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad \ldots(6.1)$$

2. Next you must enter the values of initial concentration, change in concentration, and equilibrium concentration for each substance included in the equilibrium constant expression in a proper table. Now, if you can check the data: we have the number of moles of $N_2O_4(g)$ and the volume of the flask. Now let us calculate the initial concentration of $N_2O_4(g)$ as (conc. N_2O_4) = 2.00 mol/5.00 L = 0.400 mol/L. In the initial condition, as there was no NO_2, the initial concentration of NO_2 is zero. After the reaction took place and equilibrium was reached, the equilibrium concentration of NO_2 was measured as 0.525 mol/L. The reaction table looks like this:

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial concentration (mol/L)	0.400		0
Change as reaction occurs (mol/L)	----		----
Equilibrium concentration (mol/L)	----		0.525

3. Now, let us take the change in concentration of one substance to be *x*. Use the stoichiometric coefficients in the balanced equilibrium equation to calculate the other changes in terms of *x*. As the reaction proceeds from left to right, the concentrations of reactants decrease. So the change in concentration of a reactant should be negative and the change in concentration of a product should be positive. In this problem, you have been given both initial and equilibrium concentrations of NO_2. So let us take *x* to be the change in concentration of NO_2 which is not known.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial concentration (mol/L)	0.400		0
Change as reaction occurs (mol/L)	---		x
Equilibrium concentration (mol/L)	---		0.525

Next, we use the mole ratio from the balanced equation to find the change in concentration of N_2O_4 in terms of *x*.

$$\Delta(\text{conc.}N_2O_4) = \frac{x\ \text{mol}\ NO_2\ \text{formed}}{\text{L}}\, x\, \frac{1\ \text{mol}\ N_2O_4\ \text{formed}}{2\ \text{mol}\ NO_2\ \text{formed}}$$

$$= \frac{1}{2}x\ \text{mol}\ N_2O_4\ \text{reacted}/\text{L}$$

The sign of the change in concentration of N_2O_4 is negative, because the concentration of N_2O_4 decreases. The table becomes

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial concentration (mol/L)	0.400		0
Change as reaction occurs (mol/L)	$-½\, x$		x
Equilibrium concentration (mol/L)	-		0.525

4. Now, you take the values of initial concentrations and the changes in concentrations and calculate the equilibrium concentrations in terms of x and enter them in the table. The concentration of N_2O_4 at equilibrium, $[N_2O_4]$, is thereby the sum of the initial 0.40 mol/L of N_2O_4 and the change due to reaction $-½x$ mol/L; that is, $[N_2O_4]_{eqm} = (0.40 - ½x)$ mol/L. In the same way, the equilibrium concentration of NO_2 (which is already known to be 0.525 mol/L) is $0 + x$, and the table becomes

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial concentration (mol/L)	0.400		0
Change as reaction occurs (mol/L)	$-½\, x$		x
Equilibrium concentration (mol/L)	$0.400 - ½\, x$		$0.525 \quad = 0 + x$

5. Use the simplest possible equation to solve for x. Then use x to calculate the unknown you were asked to find. (Usually the unknown is K_c or a concentration.) In this case, the simplest equation to solve for x is the last entry in the table, $0.525 = 0 + x$, and it is easy to see that $x = 0.525$. Calculate $[N_2O_4] = (0.400 - ½x)$ mol/L = $(0.400 - ½ \times 0.525)$ mol/L = 0.138 mol/L. The problem stated that $[NO_2] = 0.525$ mol/L, so K_c is given by

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.525\,\text{mol/L})^2}{(0.138\,\text{mol/L})} = 2.00\ (\text{at } 407\,\text{K})$$

6. In this case the equilibrium concentration of product is larger than the concentration of reactant. So you should have a value greater than 1.

Example 6.2: Determining an equilibrium constant value

Consider the gas phase reaction

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

Let the above reactants of initial concentrations of each 0.0175 mol/L be heated to 425°C. What happens after some time? Well, concentrations of H_2 and I_2 decrease whereas the concentration of HI increases. At equilibrium $[HI] = 0.0276$ mol/L. Use this experimental information to calculate the equilibrium constant.

Answer: $K_c = 56$

Solution

The above information is to be used and the six steps to be followed.

1. Write the balanced equation and equilibrium constant expression.

$$H_2(g)+I_2(g) \rightleftharpoons 2HI(g) \qquad K_c=\frac{[HI]^2}{[H_2]\,[I_2]} \qquad \ldots(6.2)$$

2. Next, enter the known information in a proper table.

3. Represent changes in concentration in terms of *x*.

   You should enter *x* in the third column, because both initial and equilibrium concentrations of HI are known. So, easily you can calculate *x*. Next, derive the rest of the concentration changes in terms of *x*. If the concentration of HI increases by a given quantity, the mole ratios say that the concentrations of H_2 and I_2 must decrease only half as much:

$$\frac{x\,\text{mol HI produced}}{\text{L}}\times\frac{1\,\text{mol}\,H_2\,\text{consumed}}{2\,\text{mol}\,H_2\,\text{produced}}$$

$$=\frac{1}{2}x\,\text{mol/L}\,H_2\,\text{consumed}$$

   Because the coefficients of H_2 and I_2 are equal, each of their concentrations decreases by ½ *x* mol/L. The entries in the table for change in concentration of H_2 and I_2 are negative, because their concentrations decrease.

4. Calculate equilibrium concentrations and enter them in the table.

	$H_2(g)$	+ $I_2(g)$	$\rightleftharpoons$ 2 $HI(g)$
Initial concentration (mol/L)	0.0175	0.0175	0
Change as reaction occurs (mol/L)	$-\frac{1}{2}x$	$-\frac{1}{2}x$	x
Equilibrium concentration (mol/L)	$0.0175-\frac{1}{2}x$	$0.0175-\frac{1}{2}x$	$0.0276 = 0 + x$

5. Now let us solve equations to find the value of *x*. The last row and column in the table contains 0.0276 = 0 + *x*, which gives *x* = 0.0276. Substitute this value into the other two equations in the last row of the table to get the equilibrium concentrations, and substitute them into the equilibrium constant expression:

$$K_c=\frac{[HI]^2}{[H_2]\,[I_2]}=\frac{(0.0276)^2}{\left(0.0175-\left[\frac{1}{2}\times 0.0276\right]\right)\left(0.0175-\left[\frac{1}{2}\times 0.0276\right]\right)}$$

$$=\frac{(0.0276)^2}{(0.0037)(0.0037)}\ (\text{at } 424^\circ\text{C}) \quad =55.6$$

   Is the answer correct? You see, here the equilibrium constant is greater than 1, so there should be more products than reactants when equilibrium is reached. The equilibrium concentration of the product (0.0276 mol/L) is larger than those of the reactants (0.0037 mol/L each).

Experimentally determined equilibrium constants for a few reactions are given in Table 6.1. These reactions occur to widely differing extents, as shown by the wide range of K_c values.

Table 6.1: Selected Equilibrium Constants at 25°C

Reaction	K_c	K_p
$\frac{1}{8} S_8(s) + O_2(g) \rightleftharpoons SO_2(g)$	4.2×10^{52}	4.2×10^{52}
$2\ H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$	3.2×10^{81}	1.3×10^{80}
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	3.5×10^{8}	5.8×10^{5}
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	4.5×10^{-31}	4.5×10^{-31}
	1.7×10^{-3} (at 2300 K)	
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	2.5×10^{1}	2.5×10^{1}
$2NO_2(g) \rightleftharpoons N_2O_4(g)$	1.7×10^{2}	7.0
$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$	2.0×10^{-28}	1.25×10^{-25}
Cis-2-butene(g) ⇌ *trans*-2-butene (g)	3.2	3.2
Weak acids and bases		
Formic acid $HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) +$ $HCOO^-(aq)$	1.8×10^{-4}	------
Acetic acid $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) +$ $CH_3COO^-(aq)$	1.8×10^{-5}	-------
Carbonic acid $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) +$ $HCO_3^-(aq)$	4.2×10^{-7}	-------
Ammonia (weak base) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$	1.8×10^{-5}	-------
Very slightly soluble solids		-------
$CaCO_3(s) \rightleftharpoons Ca^+(aq) + CO_3^{2-}(aq)$	3.8×10^{-9}	-------
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.8×10^{-10}	-------
$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$	1.5×10^{-16}	-------

6.2.2 The Significance of the Value of Equilibrium Constant

The value of the equilibrium constant gives us the information how far the reaction has proceeded when the equilibrium has been achieved. Also, it can be used to calculate how much product will be present at equilibrium. There are three important cases to consider.

Case 1

The symbol >> means "much greater than".

K_c >> 1: In this case, reaction is strongly product-favoured; you should understand that the concentrations of products are much greater than concentrations of reactants under equilibrium conditions.

Whenever it is a large value of K_c, most reactants have been converted to products when equilibrium has been achieved. That is, the products are strongly favoured over the reactants. An example is the reaction of NO(*g*) with $O_3(g)$, which is one way that ozone is destroyed in the stratosphere.

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

$$K_c = \frac{[NO_2]\,[O_2]}{[NO]\,[O_3]} = 6 \times 10^{34} \quad \text{(at 25°C)} \qquad \ldots(6.3)$$

The reaction goes to completion only when equilibrium has been reached. If reaction is slow this could take a lot of time.

The very large value of K_c tells us that if 1 mole each of NO and O_3 are mixed in a flask at 25°C and allowed to come to equilibrium, $[NO_2][O_2] >> [NO][O_3]$. So, only NO_2 and O_2 will be found in the flask. For practical purposes, this reaction goes to completion, and it would not be necessary to use the equilibrium constant to calculate the quantities of products that would be obtained.

Case 2

The symbol << means "much less than".

K_c<< 1: Reaction is strongly reactant-favoured; concentrations of reactants are greater than concentrations of products under equilibrium conditions.

On the other hand, an extremely small K_c means that when equilibrium has been achieved, very little of the reactants have been transformed into products. The reactants are favoured over the products at equilibrium. An example is

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

$$K_c = \frac{[O_3]^2}{[O_2]^3} = 6.25 \times 10^{-58} \quad \text{(at 25°C)}$$

So you can say that, $[O_3]^2 << [O_2]^3$ and if O_2 is placed in a flask at 25°C, very little O_3 will be found when equilibrium is achieved. There will be no change in the concentration of O_2. We would write "N.R." and say that no reaction occurs.

Case 3

$K_c \cong 1$: Equilibrium mixture contains significant concentrations of reactants and products; calculations are needed to determine equilibrium concentrations.

Whenever K_c is neither extremely large nor extremely small, the equilibrium constant must be used to calculate how far, a reaction proceeds toward products. In contrast with the reactions in Case 1 and Case 2, dissociation of dinitrogen tetraoxide has neither a very large nor a very small equilibrium constant. At 391K the value is 1.00, which means that significant concentrations of both N_2O_4 and NO_2 are present at equilibrium.

$$K_c = 1.00 \frac{[NO_2]^2}{[N_2O_4]}$$

So $$[NO_2]^2 = [N_2O_4] \qquad \text{(at 391 K)} \qquad \ldots(6.4)$$

If the concentrations of N_2O_4 and NO_2 at equilibrium are both 1.0 mol/L, then the ratio of $[NO_2]^2/[N_2O_4]$ does equal the K_c value of 1.00 at 391 K. Can you say what would happen if the concentrations were much smaller? Would they still be equal? You can verify this by using Eq.6.4. Let us take the value of the equilibrium concentration of NO_2 to be 0.01, then the concentration of N_2O_4 must be $(0.01)^2$, which equals 0.0001. Thus, even though $K_c = 1.00$, the concentration of one substance can be much larger than the concentration of the other. This happens because there is a squared term in the numerator of the equilibrium constant expression and a term to a different power (the first power) in the denominator. So you see, whenever the total of the exponents in the numerator is not the same as the total in the denominator, it will not be possible for you to confirm which concentration will be more, that of the reactants or the products, unless and until you do a calculation.

On the other hand, if the total of the exponents is the same, then if $K_c > 1$, products predominate over reactants, and if $K_c < 1$, reactants predominate over products. Example,

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad K_c = \frac{[H_2]\,[I_2]}{[HI]^2} = 0.040 \quad \text{(at 25°C)}$$

At this stage, a question may arise in your mind, are reactant - favoured systems in which small quantities of products form are important? Well, in many cases they are. Examples include the acids and bases listed in Table 6.1.

For acetic acid, the acidic ingredient in vinegar, the reaction is

$$CH_3COOH(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq)$$

$$K_c = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \quad \text{(at 25°C)}$$

The value of K_c for acetic acid is small, and under equilibrium conditions the concentrations of the products (acetate ions and hydronium ions) are much smaller than the concentration of the reactant (acetic acid molecules). So you see that acetic acid is a weak acid.

Now you see, the equilibrium reactions are similar and the equilibrium constant expressions all have the same form for formic acid, acetic acid, and carbonic acid:

$$K_c = \frac{[H_3O^+]\,[\text{anion}^-]}{[\text{acid}]}$$

where anion$^-$ is $HCOO^-$, CH_3COO^-, or HCO_3^-, and acid is HCOOH, CH_3COOH, or H_2CO_3. From data in Table 6.1, we can say that formic acid is stronger (has a larger K_c value) than acetic acid and of the three acids carbonic acid is the weakest. So you see, since the pattern of the equilibrium constant is the same for these reactions, you can quantitatively compare the extent to which the reaction is product-favoured.

If the forward reaction has a large tendency to occur, then the reverse reaction has little tendency to occur. This means that the equilibrium constant for the reverse of a strongly product-favoured reaction will be extremely small. Table 6.1 shows that combustion of hydrogen to form water vapour has an enormous equilibrium constant (3.2×10^{81}). This reaction is strongly product-favoured. We say that it goes to completion.

The reverse reaction, decomposition of water to its elements, is strongly reactant-favoured, as indicated by the very small value of K_c.

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

$$K_c = \frac{[H_2]^2\,[O_2]}{[H_2O]^2} = 3.1 \times 10^{-82} \quad \text{(at 25°C)}$$

SAQ 1

Use equilibrium constants (Table 6.1) to predict which of the reactions given below will be product-favoured at 25 °C. Place all of the reactions in order from most reactant-favoured to least reactant-favoured.

a) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

b) $HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+ + HCOO^-(aq)$

c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

6.2.3 Using Equilibrium Constants

Because equilibrium constants have numeric values, you would be able to predict quantitatively the direction of a reaction.

Predicting the Direction of a Reaction

Let us start with a mixture of 50.00 mmol $NO_2(g)$ and 100.00 mmol $N_2O_4(g)$ at 25°C in a container with a volume of 10 L. Will you be able to say whether it is in equilibrium? Otherwise, in which direction will it react to achieve equilibrium? In such cases you should use the reaction quotient, Q_c, which has the same mathematical form as the equilibrium constant expression but is a ratio of actual concentrations in the mixture, instead of equilibrium concentrations.

You know that,

- If Q_c is equal to K_c then the reaction is at equilibrium. The concentrations will not change.
- If Q_c is less than K_c then the concentrations of products are not as large as they would be at equilibrium. The forward reaction will occur and the products will form till equilibrium is reached.
- If Q_c is greater than K_c, then the product concentrations are bigger than they would be at equilibrium. The reverse reaction will proceed from right to left and reactants will form till equilibrium is reached.

For the reaction

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad K_c = \frac{[N_2O_4]}{[NO_2]^2} = 1.7 \times 10^2 \text{ (at } 25°C)$$

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{(100.00 \times 10^{-3}\ \text{mol}/10\text{L})}{(50.00 \times 10^{-3}\ \text{mol}/10\text{L})^2}$$

$$= \frac{1.0 \times 10^{-2}}{(5.0 \times 10^{-3})^2} = 4.0 \times 10^2$$

In the above example, Q_c is greater than K_c, so, in order to attain equilibrium, some N_2O_4 will react to form NO_2. As the reverse reaction takes place, Q_c becomes smaller and eventually becomes equal to K_c.

Example 6.3:

Predicting direction of reaction

Consider the equilibrium of the reaction used to generate hydrogen gas industrially.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad K_c = 0.94 \text{ at } 25\ °C$$

If 1.0 mole CH_4, 1.0 mole H_2O, 2.0 mole H_2, and 0.50 mole CO are mixed in a 10.0 L container at 25 °C, will the concentration of H_2O be greater or less than 0.10 mol/L when equilibrium is reached?

Answer: Less than 0.10 mol/L

Solution

Calculate the initial concentration of each gas and thus evaluate Q_c. Then compare Q_c with K_c.

$$[CH_4] = \frac{1.0\,\text{mol}}{10.0\,\text{L}} = 0.10\,\text{mol/L} \qquad [H_2] = \frac{2.0\,\text{mol}}{10.0\,\text{L}} = 0.20\,\text{mol/L}$$

$$[H_2O] = \frac{1.0\,\text{mol}}{10.0\,\text{L}} = 0.10\,\text{mol/L} \qquad [CO] = \frac{0.50\,\text{mol}}{10.0\,\text{L}} = 0.050\,\text{mol/L}$$

Because the units are defined by the equilibrium constant expression, leave them out.

$$Q_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]} = \frac{(0.050)\,(0.20)^3}{(0.10)\,(0.10)} = 0.040$$

which is much smaller than 0.94, the value of K_c. Because $Q_c < K_c$, the forward reaction, i.e. a reaction of CH_4 with H_2O to form CO and H_2, will occur until the equilibrium concentrations are reached. The initial concentration of H_2O was 0.10 mol/L; when H_2O reacts with CH_4, the H_2O concentration decreases.

Now we shall discuss how to draw qualitative conclusions without actual calculations. Because all concentrations are fractions, multiplying concentrations will give smaller fractions. The concentrations are of the order 10^{-1}, but the numerator has concentration to the fourth power and the denominator to the second power overall. This means that Q_c would be much less than 1 and the reaction will occur in forward direction before equilibrium is reached. Therefore, the concentration of H_2O would decrease and become less than 0.10 mol/L.

So we can say if the value of Q_c is much smaller than the value of K_c, the reaction will move to the forward direction. Similarly, when the value of Q_c is much larger than that of K_c, the reaction will move in the reverse direction.

SAQ 2

For the equilibrium

$$2SO_2\,(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad K_c = 245 \text{ (at 1000K)}$$

The equilibrium concentrations are $[SO_2] = 0.102$, $[O_2] = 0.0132$, and $[SO_3] = 0.184$. Suppose that the concentration of SO_2 is suddenly doubled. Calculate Q_c and use it to show that the forward reaction would take place to reach a new equilibrium.

6.3 LE CHATELIER'S PRINCIPLE

Whenever there is a slight disturbance in the system at equilibrium either by a change in the temperature or the concentration of reactants or products, the system will react in response to the change. In this section, we will discuss how changes in these factors influence the composition of the equilibrium mixture and the value of the equilibrium constant.

Whenever there is a change in the concentration or the partial pressures of any of the reactants or products, the composition of a system at equilibrium changes. Henri Louis Le Chatelier (1850-1936) was the first one to describe qualitatively how these changes influence a chemical reaction at equilibrium.

Le Chatelier's principle can be written as: Any change to a chemical reaction at equilibrium causes the reaction to proceed in the direction that reduces the effect of the change.

Whenever there is a change in concentration, pressure, or temperature, the concerned reaction proceeds in the direction that reduces the impact of the change. Let us take the following example of the formation of ammonia:

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

Now, can you predict what would happen if you added hydrogen, to the equilibrium mixture of nitrogen, hydrogen, and ammonia? Le Chatelier's principle predicts that a reaction will occur to reduce the change. In this case concentration changed, because the concentration of hydrogen increased, so the system proceeds in that direction to decrease the concentration of hydrogen (and nitrogen) concentration by forming more ammonia. Whereas, if the hydrogen would be removed, the system would proceed in the direction where it forms more hydrogen (and nitrogen).

The Le Chatelier's principle is utilised by the chemists to improve the yield of reaction. Suppose there is a way of removing ammonia as soon as it forms, then the reaction will continue until either the nitrogen or the hydrogen is all used up. Now, how do you remove ammonia? It is seen that ammonia can easily be liquefied at modest pressure, whereas nitrogen and hydrogen cannot be. A reactor can be designed to operate at a moderate pressure and separate the liquid from the gases. Whenever the liquid ammonia is removed, the system thereby produces more. The process continues to produce ammonia until the nitrogen or hydrogen is consumed.

Efficient production of ammonia is an important issue because ammonia is an important industrial product, with uses ranging from fertilizer to rocket fuels.

Now we will discuss the effects of change of concentration, or pressure, or temperature, as well as the addition of inert gas or catalyst on the equilibrium.

6.3.1 Effect of Change of Concentration

In order to understand the concepts in a better way, let us take the following examples.

Example 6.4: You all must be knowing that the Bhopal plant made phosgene, $COCl_2$, on-site. The reaction of carbon monoxide and chlorine to form phosgene, like any equilibrium system, shows the effects of changes in concentration.

$$Cl_2(g) + CO(g) \rightleftharpoons COCl_2(g)$$

Can you say what will be the direction of reaction if carbon monoxide is added?

The first way we might look at the problem is to use Le Chatelier's principle and state that the reaction will proceed to consume some of the added carbon monoxide. Because carbon monoxide is a reactant, the reaction will form some additional product in response to this change.

$$Cl_2(g) + CO(g) \xRightarrow{\rightleftharpoons} COCl_2(g)$$

The symbol $\xRightarrow{\rightleftharpoons}$ is generally used to indicate that the reaction proceeds to the right, to use up added carbon monoxide, but the equilibrium constant does not change.

We can also arrive at a solution to the problem by seeing how an increase in the concentration of [CO] changes Q_c. Let us start with the equilibrium constant expression from the chemical equation.

$$K_{eq} = \frac{[COCl_2]}{[CO]\ [Cl_2]}$$

K_{eq} is calculated from the concentrations of all the species at equilibrium. If carbon monoxide is added to the equilibrium mixture, then Q_c is smaller than K_{eq} and the reaction proceeds towards the right, to form more phosgene and use up some of the added CO.

Now, with the help of Example 5, you will understand how a system responds when the equilibrium concentrations are disturbed.

Example 6.5: How do you predict the direction of a reaction when the system is disturbed?

In which direction does the reaction proceed when sulphur dioxide is added to an equilibrium mixture of oxygen, sulphur dioxide, and sulphur trioxide?

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

Note: This you should solve with the help of Le Chatelier's principle.

Solution: If the concentration of SO_2 increases, then the reaction will proceed in the direction that decrease the concentration of the added substance. SO_3 will form as SO_2 is consumed.

$$SO_2(g) + \frac{1}{2}O_2(g) \xRightarrow{\rightleftharpoons} SO_3(g)$$

An alternative to applying Le Chatelier's principle involves comparing Q_c and $K_{eq.}$ The equilibrium constant expression is

$$K_{eq} = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$$

If SO_2 is added to the system, Q_c becomes smaller than K_c and the reaction proceeds to the right.

Answer: To the right, to produce more SO_3.

6.3.2 Effect of Change of Pressure

Changes in the partial pressures of gases have the same effects as change in concentration, because pressure is just another measure of concentration. So you can change partial pressures of the reacting species by adding (or removing) either the reactants or products. Also, it can be done by changing the volume of the reaction vessel. In the following example, you will see the effect of changing the volume of the container.

Example 6.6:

How the equilibrium system responds to change in volume?

Some PCl_5 is placed in a 10.0 L reaction cylinder. The temperature is increased to 500 K, and the following reaction reaches equilibrium.

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

Now, let us investigate a situation where increase in the external pressure decreases the volume to 1.0 L. You must keep the temperature constant at 500 K.

Note

Le Chatelier's principle should be utilised. The system will proceed in that direction where the effect of the change is minimized.

Solution

As there is a reduction in the volume, the concentrations (partial pressures) of the species increase. Why is it so? It is because the same numbers of moles are now in a smaller volume. The system responds to reduce the effect of this change by decreasing the number of moles of gases. We look at the chemical equation and see that the reactant side of the equation has 1 mole gas (PCl_5), but the product side has 2 moles of gases PCl_3 and Cl_2.

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

1 mole gas on reactant side ⇌ 2 moles of gas on product side.

In this case, if you Increase the external pressure, there will be a decrease in the volume of the system, so the reaction will proceed in the direction which will reduce the number of moles of gases. So here, if you decrease the volume, more reactants will be formed.

SAQ 3

Ammonia is formed by the reaction of nitrogen and hydrogen, all in the gas phase ($N_2 + 3H_2 \rightleftharpoons 2NH_3$). After the system reaches equilibrium, the volume of the container is decreased. In which direction does the reaction proceed?

Table 6.1: Relationship between Change in Number of Moles of Gases in a Reaction and Response of the System to Changes in Volume and Pressure

Example	Δn_g	Decrease in Volume (or increase in external pressure) favours formation of	Increase in Volume (or decrease in external pressure) favours formation of
$CaCO_3(s) + 3C(s) \rightleftharpoons CaC_2(s) + CO(g)$	+1	Reactants	Products
$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2} O_2(g)$	+0.5		
$CO_2(g) + NaOH(s) \rightleftharpoons NaHCO_3(s)$	-1	Products	Reactants
$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$	-1		
$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$	-1		
$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$	0	No effect	No effect
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	0		

6.3.3 Effect of Change of Temperature

Le Chatelier's principle also predicts how a change in the temperature affects an equilibrium system. Heat is a "product" in an exothermic reaction, so if you add heat, the reaction will move to the left to consume the added heat. As a result more reactants form, and product is consumed. Heating an endothermic reaction causes the system to form additional products. Thus, if you change the temperature of a reaction, the value of K_{eq} changes.

The influence of temperature can be seen by studying the formation of sulphur trioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -198 \text{ kJ}$$

The formation of sulphur trioxide is an exothermic reaction; when heated, the system forms additional reactants as a reaction occurs to consume the added heat.

Increasing the temperature of an exothermic reaction decreases K_{eq}, so more reactants form.

When this reaction is studied at laboratory temperatures, this exothermic reaction proceeds towards the formation of SO_3. At high temperatures, such as those found in a furnace, the equilibrium constant becomes much less than 1 and sulphur trioxide decomposes to sulphur dioxide and oxygen.

So you see, that these results match with that of Le Chatelier's principle. The numerical value of K_{eq} changes with temperatures, so it is important to specify the temperature when describing a system at equilibrium.

Example 6.7: Influence of temperature changes on equilibrium

How does an increase in temperature influence each of the following equilibria?

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H = +52\,kJ$

(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ$

Solution

(a) The reaction is endothermic, so, if you increase the temperature, the equilibrium shifts toward products. The equilibrium constant increases as the temperature is increased, so more products form.

(b) The reaction is exothermic, so if you increase the temperature, the equilibrium shifts toward reactants. The equilibrium constant decreases with increasing temperature, so more reactants form.

SAQ 4

For the formation of phosgene ΔH is -108 kJ

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

In which direction does the system react if temperature is increased?

6.3.4 Effect of Addition of Inert Gas

You may come across situations when an inert or a non-reactive gas is added to a reaction container. In most cases they do not react or affect the partial pressures of the reactants or products. So the pressures of materials other than the reactants or products have no effect on the equilibrium due to addition of such material. For example, the SO_3-SO_2 equilibrium when studied in the presence or absence of other gases, the results are the same as long as the other gases do not participate in the reaction.

Now let us discuss the effect of addition of inert gas on the equilibrium constant. There are two cases on which equilibrium depends. These are:

(1) **Addition of an inert gas at constant volume:** When an inert gas is added to the system in equilibrium at constant volume, then the total pressure will increase. But the partial pressures of gaseous reactants and of the products will not change and the equilibrium will not change. Hence, when an inert gas is added to the system in equilibrium at constant volume there will be no effect on the equilibrium.

(2) **Addition of an inert gas at constant pressure:**
When an inert gas is added to the system in equilibrium at constant pressure, then the total volume will increase. Hence, the partial pressure of gaseous products will decrease. Therefore, the equilibrium will shift towards the direction in which there is increase in number of moles of gases. For example: Consider the following reaction in equilibrium:

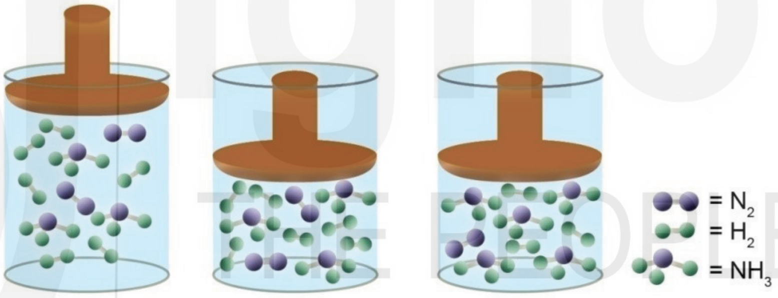
$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

The addition of an inert gas at constant pressure to the above reaction will shift the equilibrium towards the forward direction because the number of moles of gaseous products is more than the number of moles of the gaseous reactants.

6.3.5 Effect of Addition of Catalyst

It must be known to you that catalysts only speed up the rate of a reaction, but addition of catalyst makes no difference to the position of equilibrium. Can you say why is it so? It is because a catalyst speeds up the forward and reverse reaction to the same extent. Because adding a catalyst doesn't affect the relative rates of the two reactions, it can't affect the position of equilibrium. Then why do the chemists use a catalyst? Well the reason is, for a dynamic equilibrium to be set up, the rates of the forward reaction and the reverse reaction have to become equal. Now, this doesn't happen instantly. For a very slow reaction, it could take years! A catalyst speeds up the rate at which a reaction reaches dynamic equilibrium.

Also remember that catalysts are compounds that accelerate the progress of a reaction without being consumed. Common examples of catalysts include acid catalysts and enzymes. Reactions proceed faster through a lower-energy transition state with the help of catalysts. The energy of the transition state, which is the rate-limiting step, is lowered by catalysts. Thus there is reduction in the necessary energy of activation to allow a reaction to proceed and, in the case of a reversible reaction, reach equilibrium more rapidly.



(a) (b) (c)

Fig. 6.2: Qualitative effect of pressure and volume on the equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. (a) A mixture of gaseous N_2, H_2, and NH_3 at equilibrium. (b) When the pressure is increased by decreasing the volume, the mixture is no longer at equilibrium ($Q_c < K_c$). (c) Reaction occurs from left to right, decreasing the total number of gaseous molecules until equilibrium is re-established ($Q_c = K_c$).

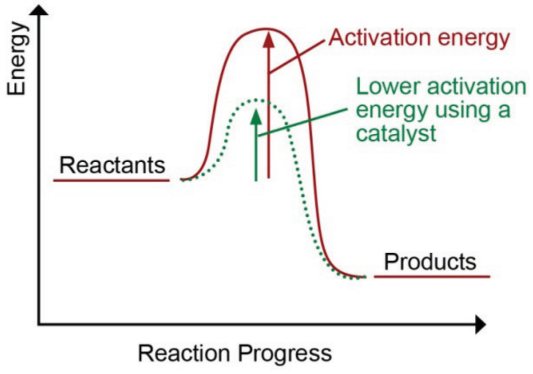


Fig. 6.3: Lowering of the energy of the transition state with catalyst.

Example 6.8:

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

In which direction, toward reactants or toward products, does the reaction shift if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift toward products to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

SAQ 5

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

Can you say which direction the reaction will shift if the equilibrium is stressed by the following change?

i. Br_2 is removed.

ii. $COBr_2$ is added.

SAQ 6

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60\text{ kJ}$$

6.4 SUMMARY

In this unit, we have discussed the applications of equilibrium studies and Le Chatelier's Principle. The effect of change in concentration, pressure, temperature to the chemical equilibrium have also been discussed in detail. Also in this unit, clues have been given as to how to predict the response of an equilibrium system to changes in conditions by applying Le Chatelier's principle. Also discussions have been carried out to understand the effect of addition of inert gas to the chemical equilibrium as well as evaluate the effect of a catalyst on a chemical equilibrium.

6.5 TERMINAL QUESTIONS

1. State Le Chatelier's principle.
2. Given this equilibrium, predict the direction of shift of equilibrium for each stress.

   $H_2(g) + I_2(s) + 53\text{ kJ} \rightleftharpoons 2HI(g)$

   a) decreased temperature
   b) increased pressure
   c) removal of HI
3. Given this equilibrium, predict the direction of shift of equilibrium for each stress.

   $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 196\text{ kJ}$

   a) removal of SO_3
   b) addition of O_2
   c) decreased temperature
4. Given this equilibrium, predict the direction of shift of equilibrium for each stress listed.

   $CO_2(g) + C(s) + 171\text{ kJ} \rightleftharpoons 2CO(g)$

   a) addition of CO
   b) increased pressure
   c) addition of a catalyst
5. The synthesis of NH_3 uses this chemical reaction.

   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92\text{ kJ}$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of NH_3.
6. The synthesis of $CaCO_3$ uses this chemical reaction.

   $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + 180\text{ kJ}$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of $CaCO_3$.

6.6 ANSWERS

Self-Assessment Questions

1. The order from most reactant-favoured to least reactant-favoured is (a), (b), (c). First, find out the form of the equilibrium constant expressions of all the reactions. If they have similar ones then the smaller the equilibrium constant is, the less product-favoured (more reactant-favoured) the reaction is. The equilibrium constant expressions are all of the same form because $H_2O(l)$ does not appear in the expressions for (a) and (b). The equilibrium constants for reactions (a) and (b) are 1.8×10^{-5} and

1.8×10^{-4}, respectively. The equilibrium constant for reaction (c) is not given in Table 6.1, but K_c for the reverse reaction is given as 1.7×10^2. Because the reaction is reversed, it is necessary to take the reciprocal which gives an equilibrium constant for reaction (c) of 5.8×10^{-3}. Therefore the most reactant-favoured reaction (smallest K_c) is (a), the next smallest K_c is for reaction (b), and the largest K_c is for reaction (c), which is the least reactant-favoured. So the answer is all reactions are reactant-favoured.

2. $$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.184\times2)^2}{(0.102)^2(0.0132)} = 986.10$$

   Which is much larger than 245, the value of K_c. Thus the product concentrations are bigger than that at equilibrium. So in order to attain equilibrium, some SO_3 will form SO_2. As the reverse reaction takes place, Q_c becomes smaller until it becomes equal to K_c.

3. The system produces additional NH_3. The numbers of moles of gas on the reactant and product sides of the chemical equation are to be checked. If there are any liquids or solids then consider their volume negligible compared with that occupied by gases. If a reaction has the same number of moles of gas on both sides, then changes in volume or pressure do not cause any net reaction. We define Δn_g as the change in the number of moles of gases (number of moles of product gases – number of moles of reactant gases) and can arrive at some qualitative conclusions, shown in Table 6.1.

4. The reaction shifts to the left, forming more CO and Cl_2. If the temperature is increased then the left (reactant) side is favoured, since the reverse reaction is endothermic.

5. i. toward reactants

   ii. toward reactants

6. Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts back toward reactants.

Terminal Questions

1. When an equilibrium is stressed, the equilibrium shifts to minimize that stress.

2. a) towards reactants b) no effect c)towards products

3. a) towards products b) towards products c) towards products

4. a) towards reactants b) towards reactants c) no effect

5. increased pressure, decreased temperature, removal of NH_3

6. increased pressure, decreased temperature, addition of CO_2

UNIT 7

IONIC EQUILIBRIUM-I

Structure

7.1 INTRODUCTION

In the previous two units of this block you have learnt about general aspects of Chemical Equilibrium in terms of its types, significance, representation and factors affecting it etc. As you know that a large number of the reactions in the general chemistry laboratory are carried out in aqueous solutions and many of these contain ionic species. The equilibrium in such systems containing ionic species is referred to as Ionic Equilibrium and is the topic of this and the next two units. We would apply the concepts learnt in the previous two units to the systems having ionic species.

We would begin the unit by taking up the nature of aqueous solutions in terms of their electrical conductivity based on the nature of the solute. In this context you would learn about electrolytes, their types and the factors affecting their behaviour. We would also talk about the ionisation equilibrium of weak electrolytes, its characterisation in terms of ionisation constant, and Ostwald's dilution law. This would be followed by a review of different theories of acids and bases, as these constitute a significant class of substances showing ionic equilibrium. Herein, we would take up different theories and learn about their merits and demerits. Towards the end of the unit, we would take up the discussion on autoprotolysis-an important property of water. In this context we would define ionic product of water and discuss its significance. We would then define the concept of pH and take up some examples for the calculation of pH value of solutions of strong acids and bases.

In the next unit, you would learn about equilibria in the aqueous solutions of weak acids/bases, polyprotic acids and mixtures of weak acids/bases with salts containing common ions.

Expected Learning Outcomes

After studying this unit, you should be able to:

- define and differentiate between electrolytes and non-electrolytes;
- define degree of ionisation of a weak electrolyte and discuss the factors affecting it;
- state and explain Ostwald's dilution law;
- describe different theories of acids and bases;
- state the merits and limitations of different theories of acids and bases;
- define conjugate acid-base pairs and identify them in an acid-base equilibrium;
- define ionic product of water and explain its significance; and
- define pH and calculate the same for aqueous solutions of strong acids and bases.

7.2 ELECTROLYTES AND NON-ELECTROLYTES

You must be aware that one should not operate electrical equipment with wet hands or while standing in water. Have you ever thought that why are we advised so? This is due to the conducting nature of water from tap, river or pond or so. As a consequence of conducting nature of water, the electric current may flow from the electrical appliance to the human body and the person operating the electrical appliance with wet hands may get electrocuted. Now, the question is what makes water conducting? In fact, the pure water is practically non-conducting; it is the presence of the ionic species in the water that makes it conducting. Let us learn about the behaviour of aqueous solutions that contain ionic species.

An electrolyte is a substance that dissolves in water to give an electrically conducting solution

A wide variety of aqueous solutions are electrically conducting in nature. The conducting nature of the solution is determined by the nature of the solute dissolved in water. For example, suppose we take two beakers containing say 100 cm^3 of distilled water each and to one of these beakers we add 2 g of sugar whereas to the second beaker we add 2 g of sodium chloride. The solution of sugar in water is found to be non-conducting whereas that of sodium chloride is observed to be conducting. The solutes whose aqueous solutions conduct electricity are called **electrolytes** and the ones whose aqueous solutions do not conduct electricity are called **non-electrolytes.** Swedish Chemist Svante′ Arrhenius explained the conductivity of aqueous solutions in terms of the *ionic theory of solutions*. He proposed that certain substances when dissolved in water produce freely moving ions, which are responsible for conducting nature of aqueous solutions.

Let us analyse the example given above. To begin with, a sample of water consists of a large number of water molecules, which are polar but electrically neutral and are extensively hydrogen bonded. The water molecules do not carry any net electric charge, so when they move no overall electric charge is carried and for all practical purposes water is non-conducting. However, when a substance like sodium chloride dissolves in water, the crystal lattice of sodium chloride is broken and sodium ions and chloride ions are released in the solution. These ions move under the influence of an electric field towards the oppositely charged electrodes. Each ion carries a certain quantity of charge and contributes towards electrical conductivity. On the other hand, when we dissolve sugar in water, the intermolecular interactions between the sugar molecules are broken and *neutral* sugar molecules are released in the solution. As the sugar molecules do not carry any charge and when they move no charge is carried and as a result the solution is non-conducting

7.2.1 Strong and Weak Electrolytes

Let's take our argument further and raise a question that, "are the solutions of all electrolytes equally conducting?" To answer this question, let's once again take two beakers. In one of these we take 0.01 M solution of sodium chloride whereas in the other we take 0.01 M solution of acetic acid. Both of these are electrolytes i.e., their solutions conduct electricity but it is found that their equimolar solutions conduct electricity to different extents. The aqueous solution of acetic acid is poorly conducting whereas that of sodium chloride is highly conducting. How do we explain this?

You would recall from above, that Arrhenius explained the electrical conductivity of aqueous solutions in terms of presence of ions in the solution. As both the solutions taken in the example given above, have same molar concentration we expect similar number of ions in solutions and hence similar conductivities. The difference in their electrical conductivities is due to the fact that in case of sodium chloride, the electrolyte is completely dissociated into its ions whereas in case of acetic acid only a few ions are generated in the solution due to the ionisation. An aqueous solution of acetic acid consists mainly of unionised acetic acid molecules and only some acetate ions and hydrogen ions generated by ionisation of a few acetic acid molecules depending on its concentration. The electrolytes like NaCl, which completely dissociate in aqueous solutions, are called **strong electrolytes** whereas the ones which are partially ionised are called **weak electrolytes.** The generation of ions in the two cases can be represented as

$$\mathrm{NaCl(aq)} \rightarrow \mathrm{Na^{+}(aq) + Cl^{-}(aq)} \quad \text{[Dissociation]} \quad \ldots(7.1)$$

$$\mathrm{CH_3COOH(aq)} \rightleftharpoons \mathrm{CH_3COO^{-}(aq) + H^{+}(aq)} \quad \text{[Ionisation]} \quad \ldots(7.2)$$

You may have noticed that we have used two terms viz., dissociation and ionisation in our discussion above. Though these are used interchangeably we need to understand the difference between them. When the electrolyte is ionic i.e., consists of ions as in NaCl crystal we use the term **dissociation** to convey that the ions in the crystal are *dissociated* from each other and are released in the solution. On the other hand, if the electrolyte is a molecular species as in acetic acid we use the term **ionisation** to convey that the molecular electrolyte *ionises* to produce ions in the solution. *In one case the **ions are already there** and get dissociated whereas in the other case the **ions are generated in solution.***

An ionic compound produces ions in aqueous solution by dissociation whereas a molecular compound produces ions in solution by ionisation.

Let's take one more example. Let's again take two beakers containing 0.01 M solutions of magnesium chloride and ammonia respectively. We find that the solution of magnesium chloride is highly conducting whereas that of ammonia has relatively much lower electrical conductivity. This indicates that while ionic compound, magnesium chloride is a strong electrolyte; molecular ammonia is an example of a weak electrolyte. The process of generation of ions in the two cases can be represented as

$$MgCl_2(aq) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq) \qquad \ldots(7.3)$$

$$NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad \ldots(7.4)$$

On the basis of the examples of electrolytes taken above, we may conclude that *generally molecular compounds are either nonelectrolytes (cf. sugar) or weak electrolytes (cf. acetic acid) whereas ionic compounds (cf. NaCl and* $MgCl_2$*) are strong electrolytes.* However, there are exceptions, for example if we dissolve a molecular compound, HCl (g) in water we get a highly conducting solution. Hydrogen chloride gas is dissolved in water; it gives HCl (aq), which is a strong electrolyte that ionises completely in solution to produces hydrogen ions and chloride ions.

Generally molecular compounds are either nonelectrolytes or weak electrolytes whereas ionic compounds are strong electrolytes.

$$HCl(g) \rightarrow HCl(aq) \rightarrow H^+(aq) + Cl^-(aq) \qquad \ldots(7.5)$$

You may note that in case of acetic acid and ammonia we used double arrow to indicate partial ionisation and equilibrium between ionised and unionised species whereas in case of hydrochloric acid we have used a single arrow to convey that there is complete ionisation.

7.2.2 Degree of Ionisation

Let's move on and raise another question, "Will two weak electrolytes have same electrical conductivity?" To find answer, we take 0.001 M solutions of acetic acid and chloroacetic acid in two different beakers and measure their electrical conductivities. We find that the electrical conductivity of chloroacetic acid is much more than that of acetic acid. A calculation, about which you would learn in the next unit, shows that in case of 0.001 M chloroacetic acid there are approximately 8.8 times more ions than in a solution of acetic acid of same concentration. It means that chloroacetic acid is more ionised than acetic acid and hence has more electrical conductivity.

The extent of ionisation of a weak electrolyte is quantified or expressed in terms of **degree of ionisation** (also called as **degree of dissociation**). It is indicated by a symbol 'α' and refers to the fraction of molecules of the weak electrolyte that give ions in solution. In other words, it may be seen as the ratio of the number of ionised electrolyte molecules to the total number of the electrolyte molecules dissolved in water.

Degree of ionisation

$$= \frac{\text{Number of molecules of electrolyte ionised}}{\text{Total number of molecules of electrolyte dissolved}} \qquad \ldots(7.6)$$

Sometimes the extent of ionisation is expressed as percentage ionisation. It is obtained by multiplying the degree of ionisation by 100.

Percentage ionisation

$$= \frac{\text{Number of molecules of electrolyte ionised}}{\text{Total number of molecules of electrolyte dissolved}} \text{x100 \%} \quad \ldots(7.7)$$

Let's learn about the factors affecting the degree of ionisation of weak electrolytes.

7.2.3 Factors Affecting Degree of Ionisation of Weak Electrolytes

The strong electrolytes by definition are fully ionised in solution i.e., their degree of ionisation is 1. However, the degree of ionisation of a weak electrolyte is much less than 1 and depends on a number of factors as discussed below.

i) **Nature of solvent:** the nature of solvent is an important factor that determines the degree of ionisation of an electrolyte. A solvent of high dielectric constant has higher ionising power and is favorable for the ionisation of the electrolyte. Water with highest dielectric constant is the best ionising solvent available.

ii) **Temperature**: the degree of ionisation increases with an increase in the temperature of the solution. That means at higher temperature there is higher ionisation of the weak electrolyte. This can be understood in terms of the effect of temperature on ionisation equilibrium constant about which you would learn later.

iii) **Presence of common ions**: the degree of ionisation of weak electrolytes is affected by the presence of a strong electrolyte having an ion common to the ions obtained from ionisation of the electrolyte. This can be rationalised in terms of the effect of addition of a common ion (product) to a reaction at equilibrium (Le- Chatelier's principle). For example, the solubility of sparingly soluble AgCl decreases further in presence of NaCl that provides common Cl^- ions.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad \ldots(7.8)$$

$$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq) \qquad \ldots(7.9)$$

The Cl^- ions obtained from the ionisation of NaCl shift the solubility equilibrium of AgCl in the backward direction and decrease the solubility of AgCl. You would learn about it in details in Unit 9.

iv) **Dilution**: the degree of ionisation of a weak electrolyte increases with dilution. In order to understand the effect of dilution we need to learn about ionisation constant and the Ostwald's dilution law, which we would take up in the next section.

However, before proceeding further, answer the following simple question to assess your learning.

SAQ 1

Explain the difference between dissociation and ionisation with the help of suitable examples.

7.3 IONISATION CONSTANT AND OSTWALD'S DILUTION LAW

You have learnt that a weak electrolyte is partially ionised in aqueous solutions and there is equilibrium between the ionised and unionised species. In order to understand the process, let us take a weak molecular electrolyte, AB that ionises to give A^+ and B^- ions. To begin with, some molecules of AB ionise to give the ions, which is followed by recombination of some of the ions to give back unionised molecular electrolyte. The process continues till there is equilibrium between the unionised electrolyte and the ions. The ionisation equilibrium can be represented as

$$AB(aq) \rightleftharpoons A^+(aq) + B^-(aq) \qquad \ldots(7.10)$$

At a given temperature, the relative proportions of ionised and unionised forms of the electrolyte (AB) remain fixed at equilibrium with unionised AB molecules being the predominant species. The equilibrium can be characterised in terms of the equilibrium constant as given below.

$$K = \frac{[A^+]\,[B^-]}{[AB]} \qquad \ldots(7.11)$$

As the equilibrium constant characterises an ionisation (or dissociation) reaction it is called **ionisation (or dissociation) constant.** The magnitude of ionisation constant depends on the degree or extent of ionisation of the electrolyte; higher the ionisation, higher is the magnitude of ionisation constant.

7.3.1 Ostwald's Dilution Law

In the process of studying the chemical affinities of acids and bases Wilhelm Ostwald applied (in1888) the law of mass action to the ionisation of weak acids, and developed a simple mathematical relationship between the degree of dissociation (α), the concentration (c), and the equilibrium constant (K) for the dissociation of weak acids. This relationship is known as the **Ostwald's dilution law** and is valid for weak electrolytes. The relationship can be derived as follows.

Let us consider a weak electrolyte, AB that ionizes partially to give A^+ and B^- ions and the equilibrium between ionised and unionised species in the solution can be represented as

$$AB(aq) \rightleftharpoons A^+(aq) + B^-(aq) \qquad \ldots(7.12)$$

If we begin with c mol dm^{-3} of the electrolyte and assume that the degree of ionisation (or dissociation) is 'α' then the concentration of various species in the solution in the beginning and at the equilibrium can be represented as

	$AB(aq) \rightleftharpoons$	$A^+(aq)$ +	$B^-(aq)$
Initial concentration	c	0	0
Change due to ionisation	$-c\alpha$	$c\alpha$	$c\alpha$
Equilibrium concentration	$c(1-\alpha)$	$c\alpha$	$c\alpha$

The equilibrium constant for the reaction can be written as

$$K = \frac{[A^+][B^-]}{[AB]} \qquad \ldots(7.13)$$

Substituting the concentrations of various species at equilibrium in the equilibrium constant expression Eq. (7.13), we get

$$K = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)} \qquad \ldots(7.14)$$

Since, for weak electrolytes, $\alpha <<< 1$, we can ignore α in the denominator and write

$$K = c\alpha^2 \qquad \ldots(7.15)$$

Rearranging and solving, we get,

$$\alpha = \sqrt{\frac{K}{c}} \qquad \ldots(7.16)$$

As $c \alpha \frac{1}{V}$ where V is the volume of the solution containing a certain amount of solute; V, increases with dilution,

We can write,

$$\alpha = \sqrt{KV} = K'\sqrt{V} = \frac{K'}{\sqrt{c}} \quad \therefore K' = \sqrt{K} \qquad \ldots(7.17)$$

This is the mathematical expression for **Ostwald's dilution law** and implies that, *"The degree of ionisation of a weak electrolyte is directly proportional to the square root of dilution or inversely proportional to the square root of the concentration"*

The Ostwald dilution law can be experimentally verified by determining the degree of ionisation for a weak electrolyte at different dilutions using conductance measurements. The degree of ionisation is determined as a ratio of the conductance of the electrolyte at a given dilution to its conductance at infinite dilution.

$$\alpha = \frac{\lambda_V}{\lambda_\infty} \qquad \text{…(7.18)}$$

Where, λ_V and λ_∞ are the equivalent conductances at dilution V and infinite dilution respectively. You may note here that this law is not valid for strong electrolytes because the *strong electrolytes ionise completely at all dilutions.*To assess whether you have understood Ostwald's law, solve the following question.

Strong electrolytes ionise completely at all dilutions

SAQ 2

State and explain Ostwald's dilution law.

7.4 THEORIES OF ACIDS AND BASES: A REVIEW

In your earlier classes you must have studied about acids and bases. You may also be aware that there are different theories of acids and bases. As we are going to take up the equilibria involving acids and bases in aqueous solutions, it is worthwhile to recall the basic theories of acids and bases.

7.4.1 Arrhenius Theory

It is the earliest and most commonly used theory of acids and bases. It was proposed by Svante′ Arrhenius in1884 while explaining the electrical properties of solutions of electrolytes. Prior to 1884, it was believed that the passage of electrical current through the solutions of some substances generates charged species called ions that are responsible for the electrical conductivity of the solutions. Contrary to this belief, Arrhenius proposed that the passage of electrical current is not essential for the conducting properties of solutions of electrolytes; these substances when dissolved in water dissociate into ions and conduct electricity. Acids and bases are examples of such substances. Arrhenius defined an acid as a substance that produces hydrogen ions (H^+) by dissociating in aqueous solution. According to Arrhenius, the dissociation reaction for an acid, HA can be represented as

$$\mathrm{HA} \rightarrow \mathrm{H^+} + \mathrm{A^-} \qquad \text{…(7.19)}$$

Where A^- refers to the anion of the acid. Similarly, an acid HX would dissociate as

$$\mathrm{HX} \rightarrow \mathrm{H^+} + \mathrm{X^-} \qquad \text{…(7.20)}$$

Modern investigations reveal that the hydrogen ion may bind with as many as four water molecules and exist as $H_9O_4^+$ (aq)

Arrhenius was awarded the 1903 Nobel Prize in Chemistry, "*in recognition of the extraordinary services he has rendered to the advancement of Chemistry by his electrolytic theory of dissociation*."

The generation of H^+ ion in all acid solutions explains the similarity of the properties of all acids. Hydrochloric acid, HCl is an example of an Arrhenius acid whose dissociation can be represented as

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq) \qquad \ldots(7.21)$$

It is however, worthwhile to note here that the hydrogen ions so produced in aqueous solutions cannot exist independently; these combine with the water molecules in the solution. It is due to the fact that the hydrogen ions are very small in size (~10^{-15} m) and each hydrogen ion carries one unit of positive charge. The consequent high charge density (charge / size) makes it impossible for the H^+ ion to exist free in a polar solvent like water. Therefore, it binds itself to a water molecule and forms H_3O^+ ion called **hydronium ion** (or oxonium ion or the hydroxonium ion) as given below.

$$H^+(aq) + H_2O(l) \rightarrow H_3O^+(aq) \qquad \ldots(7.22)$$

The ionisation of HCl in water may then be represented as

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \qquad \ldots(7.23)$$

Therefore, according to the modern view of the Arrhenius concept an acid may also be defined as a substance that, when dissolved in water, produces hydronium ions, H_3O^+ (aq). It is worthwhile to make a mention of another class of molecules that increase the concentration of hydronium ions on being dissolved in water. These ionise to generate hydronium ion, e.g., acetic acid. The ionisation of acetic acid can be represented as

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \qquad \ldots(7.24)$$

Such acids are called as **weak acids**. You would learn in details about weak acids in the next unit. On the other hand, according to Arrhenius, a base is defined as a substance that produces a hydroxide ion (OH^-) on dissociation in aqueous solutions.

$$MOH(aq) \rightarrow M^+(aq) + OH^-(aq) \qquad \ldots(7.25)$$

Where M^+ refers to the cation of the base. Sodium hydroxide is a common example of an Arrhenius base, dissociating as,

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq) \qquad \ldots(7.26)$$

Similar to weak acids, certain molecules behave as weak bases and produce hydroxide ions on ionisation. For example, the ionisation of a weak base, ammonium hydroxide can be represented as

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad \ldots(7.27)$$

The neutralisation reaction between a strong acid (say HCl) and a strong base (say NaOH) can be represented as

$$HCl(aq) + NaOH(aq) \rightarrow H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \qquad \ldots(7.28)$$

$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O$ ...(7.29)

Cancelling common terms in Eq.(7.29) we get

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \ldots(7.30)$$

As can be seen above, Eq. (7.29), the Na^+ and Cl^- ions do not participate in the neutralisation reaction. Such ions are called as **spectator ions**. Thus, the neutralisation reaction between a strong acid and a strong base, according to Arrhenius theory, is basically the reaction between a hydrogen ion and a hydroxide ion to give a molecule of water. Thus, we see that the Arrhenius theory is quite simple and explains the acid- base behaviour of substances to a good extent. However it has a few limitations like:

- It is applicable for aqueous solutions only.
- It does not explain the acidic behaviour of some substances that lack hydrogen (e.g., $AlCl_3$, SO_3, N_2O_5) or the basic character of substances that lack OH (e.g., NH_3, Na_2O, Na_2CO_3).

7.4.2 Brønsted and Lowry Theory

In 1923, Danish Chemist Johannes N. Brønsted and British Chemist Thomas M. Lowry independently addressed one of the limitations of Arrhenius theory and came up with a theory having wider applicability. According to them, an acid is defined as a species that can donate or transfer a proton (H^+) to another species, and a base is defined as a substance that can accept a proton from other species. The acid-base reactions then become just *proton-transfer* reactions *between* the donor and the acceptor; there is no requirement of water as the solvent. Thus, according to this theory, molecule or ion capable of donating or transferring a proton is an acid, while any molecule or ion that can accept a proton is a base. In other words, the definition applies to protonic systems. Let's take some examples

An acid contains at least one ionisable H atom, and a base contains an atom with a lone pair of electrons where the proton can bind.

The reaction between ammonia (NH_3) and hydrogen fluoride (HF) in gaseous phase can be written as

$$NH_3 + HF \rightarrow NH_4^+ + F^- \qquad \ldots(7.31)$$

Here, HF acts as an acid (as it donates or transfers a proton) and NH_3 acts as a base (as it accepts a proton). You may note in this example that there is no role of a solvent. However, the theory is applicable for aqueous systems also. Let's take the same example in aqueous medium. The reaction between ammonia and HF in aqueous medium can be written as

$$NH_3(aq) + HF(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq) + F^-(aq) \qquad \ldots(7.32)$$

$$NH_3(aq) + H_3O^+(aq) + F^-(aq) \rightarrow NH_4^+(aq) + F^-(aq) + H_2O(l) \qquad \ldots(7.33)$$

Omitting F^- ions on both sides in Eq. (7.33) we get

$$NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) + H_2O(l) \qquad \ldots(7.34)$$

This reaction explains the basic nature of ammonia in terms of it accepting a proton from hydronium ion, which was formed by donation of a proton by HF to H_2O. Thus, in this reaction *the solvent (water) plays the role of a mediator in the transfer of proton from HF to ammonia.* It takes a proton from HF to form hydronium ion Eq. (7.32) and then transfers the same to ammonia molecule to form ammonium ion Eq. (7.34). Further, you may note that according to Brønsted-Lowry theory, in any acid-base equilibrium both forward and reverse reactions involve proton transfers. Let us consider the reaction of NH_3 with H_2O.

A conjugate acid-base pair consists of two species in an acid-base reaction, one acid and one base, that differ by the gain or loss of a proton.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad \ldots(7.35)$$

Here, in the forward reaction NH_3 behaves as a base as it accepts the proton and H_2O is acting as an acid by transferring its proton to ammonia molecule. In the reverse reaction NH_4^+ ion acts as the acid and OH^- ion behaves as a base. When an acid (H_2O here) donates or transfers its proton to another species the remaining part of the acid becomes a base (OH^-here) and is called **conjugate base** of the acid. Similarly, when a base (NH_3 here) accepts a proton from another species it becomes an acid (NH_4^+ here) and is called **conjugate acid** of the base. The species NH_4^+ and NH_3 [or H_2O and OH^-] form a **conjugate acid-base pair** and is indicated by a diagonal line e.g., NH_4^+/NH_3. The acid in such a pair is called conjugate acid of the base, whereas the base is the conjugate base of acid.

It is important to note that, in the equilibrium reaction, the members of each conjugate acid-base pair are designated by the same numerical subscript as shown below.

$$\underset{\text{acid}_1}{H_2O(l)} + \underset{\text{base}_2}{NH_3(aq)} \rightleftharpoons \underset{\text{acid}_2}{NH_4^+(aq)} + \underset{\text{base}_1}{OH^-(aq)} \qquad \ldots(7.36)$$

The position of the equilibrium is determined by the relative strengths of the acids and bases involved in the reaction. Let us take the example of ionisation of hydrogen fluoride in water to understand it. The equilibrium can be given as

$$\underset{\text{acid}_1}{HF(aq)} + \underset{\text{base}_2}{H_2O(l)} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{F^-(aq)} \qquad \ldots(7.37)$$

In this case, the H^+ ions obtained from the ionisation of HF molecule can be accepted either by F^- ions or by H_2O molecules. If the water molecules accept the proton, the reaction goes in the forward direction. On the other hand if F^- ions take the proton it makes the reaction go to left. It is experimentally found that the equilibrium is slightly towards the left; this indicates that the F^- ion is a stronger base than H_2O. Let's take another example, say dissolution of HCl in water.

$$\underset{\text{acid}_1}{HCl(aq)} + \underset{\text{base}_2}{H_2O(l)} \rightarrow \underset{\text{acid}_2}{H_3O^+(aq)} + \underset{\text{base}_1}{Cl^-(aq)} \qquad \ldots(7.38)$$

In this case, the hydrogen ions produced from the ionisation of HCl can be accepted either by H_2O molecules or by Cl^- ions. As we know that HCl is completely ionised in dilute aqueous solution i.e., the reaction goes to completion in the forward direction. This means that Cl^- ion is a much weaker base than H_2O. What do we infer from these two examples?

Yes, you are right. We can infer that *in a conjugate acid-base pair a weaker acid has a stronger conjugate base whereas a stronger acid has a weaker conjugate base.*

In a conjugate acid-base pair a weaker acid has a stronger conjugate base whereas a stronger acid has a weaker conjugate base.

As indicated above, according to the Brønsted and Lowry concept an acid contains at least one ionizable H atom, and a base contains an atom with a lone pair of electrons onto which a proton can bind. In case the substance has an ionisable proton as well as a lone pair of electrons, it may behave either as an acid or as a base, depending on the other species in reaction. Water (H_2O) is an interesting molecule with these features; let us look at the following two examples

$$\underset{\text{acid}_1}{H_2O(l)} + \underset{\text{base}_2}{CO_3^{2-}(aq)} \rightleftharpoons \underset{\text{acid}_2}{HCO_3^-(aq)} + \underset{\text{base}_1}{OH^-(aq)} \qquad \ldots(7.39)$$

$$\underset{\text{acid}_1}{CH_3COOH(aq)} + \underset{\text{base}_2}{H_2O(l)} \rightleftharpoons \underset{\text{base}_1}{CH_3COO^-(aq)} + \underset{\text{acid}_2}{H_3O^+(aq)} \qquad \ldots(7.40)$$

You may note here that in the first case H_2O is acting as an acid by donating a proton whereas in the second case it behaves as a base by accepting the proton. Such a substance that can behave as an acid as well as a base is called an **amphoteric substance**.

Similar to the Brønsted- Lowry concept involving proton transfer, another concept was proposed by German Chemist Hermann Lux in 1939 which was extended by H. Flood around 1947. It involved transfer of oxide ion in the acid- base reactions. According to **Lux-Flood definition** *an acid is defined as substance that is an oxide acceptor and base is an oxide donor.* This definition covers non-protonic systems, for example,

$$H_2O + CaO \rightleftharpoons Ca^+ + 2OH^- \qquad \ldots(7.41)$$

$$H_2O + SiO_2 \rightleftharpoons 2H^+ + SiO_3^{2-} \qquad \ldots(7.42)$$

Here, CaO donates oxide therefore, it is a basic oxide whereas SiO_2 is an oxide acceptor and hence it is an acidic oxide.

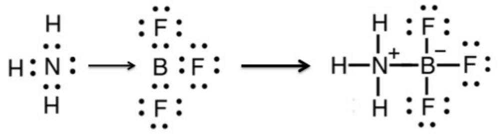
According to Lux-Flood definition an acid is defined as substance that is an oxide acceptor and base is an oxide donor.

You would have realized that the Brønsted- Lowry concept has a wider applicability than the Arrhenius concept, as it does not depend on the nature of solvent. However, even Brønsted-Lowry theory has a limitation that it is applicable for protonic systems only as it emphasizes the involvement of a proton. Further still, there are substances whose acid-base behaviour cannot be explained either by Arrhenius or Brønsted-Lowry theories. For example, $AlCl_3$ that does not contain a hydrogen atom but behave as an acid or Na_2CO_3, which neither has OH nor accepts a proton but behaves as a base.

7.4.3 Lewis Theory

In 1923 G. N. Lewis proposed a yet another theory of acids and bases that has even broader applicability. It does not limit to systems involving H^+ or OH^- ions but extends even to the reactions in gases and in solids. He defined an acid as a species (an atom, molecule or an ion) that can form a covalent bond by accepting an electron pair from another species, and a base as a species that can form a covalent bond by donating an electron pair to another species. Such acids and bases are called **Lewis acids and bases**. Lewis acids are species with vacant orbitals that can accommodate the electron pairs and Lewis bases are species that have lone-pair of electrons available for sharing. Let us take an example

$$NH_3 + BF_3 \rightarrow NH_3 \rightarrow BF_3 \qquad \ldots(7.43)$$



Lewis base Lewis acid

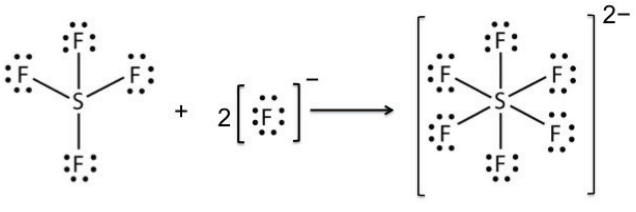
In this case the lone pair is donated by ammonia (base) and is accepted by electron deficient molecule BF_3 (acid). This reaction can be seen as a molecule with incomplete octet (BF_3) accepting a lone pair of electrons and completing its octet. In the following reaction, SO_3 is the Lewis acid that accepts the electron pair provided by oxide ion, and completes the octet of electrons on sulphur atom.

$$O^{2-} + SO_3 \rightarrow SO_4^{2-} \qquad \ldots(7.44)$$

Lewis base Lewis acid

Sometimes a molecule or an ion may expand its octet to accept an electron pair. For example, in the reaction between SiF_4 and F^- ions to give SiF_6, SiF_4 (Lewis acid) accepts two lone pairs of electrons from two F^- ions (Lewis bases) to give SiF_6^{2-}**.** Here, silicon expands its octet to accommodate six fluoride ions. You may note here that in SiF_6^{2-} silicon atom has twelve electrons around it.

$$SIF_4 + 2F^- \rightarrow SiF_6^{2-} \qquad \ldots(7.45)$$



Lewis acid Lewis base

The product of a Lewis acid– Lewis base reaction is called an **adduct** (or addition compound). You know that a covalent bond formed by the donation of a pair of electrons by an electron rich species to an electron deficient species is called a coordinate covalent bond. Thus, in an adduct the two species are linked by a **coordinate bond**. Having recalled different acid-base theories, why don't you test your understanding by solving the following simple self assessment questions?

SAQ 3

The species in the first column of the table given below act as acids. Write the corresponding conjugate bases in the second column.

Acid species	Conjugate base
HPO_4^{2-}	
HOCl	
PH_4^+	

SAQ 4

Identify the conjugate acid-base pairs in the following chemical reactions

(a) $SO_3^{2-} + NH_4^+ \rightleftharpoons HSO_3^- + NH_3$

(b) $HS^- + CN^- \rightleftharpoons S^{2-} + HCN$

(c) $F^- + HSO_4^- \rightleftharpoons HF + SO_4^{2-}$

7.5 IONIC PRODUCT OF WATER, K_w

Pure water is generally considered to be a nonelectrolyte due to its negligibly small electrical conductivity. However, it does have a *non-zero* conductivity that indicates towards the presence of ions in pure water. Where do these ions come from? In order to answer this question; we recall an important property of water, viz., its amphoteric nature i.e., water can act as a weak acid as well as a weak base. In a sample of water a small number of water molecules donate a proton (thus acting as an acid), which is accepted by equal number of other water molecules (acting as bases) as shown below

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \ldots(7.46)$$

As a consequence, a small concentration of H_3O^+ ions and OH^- ions is formed in a sample of water and this process is called **autoprotolysis (or autoionisation) of water**. The autoprotolysis of water indicates that water acts as an amphoteric substance even in the absence of any other substance. The equilibrium given in Eq. (7.46) is characterised by an equilibrium constant whose expression can be written as

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \qquad \ldots(7.47)$$

As the degree of ionisation of water is very small i.e., very few water molecules are ionised, the concentration of H_2O remains unchanged (constant). The Eq. (7.47) can be rearranged to define a new constant K_w, as

$$K_{eq} x [H_2O]^2 = [H_3O^+][OH^-] = K_w \qquad \ldots(7.48)$$

This constant, $\boldsymbol{K_w}$, is called the **ionic-product constant** of water. As defined, K_w is the product of the molar concentrations of H_3O^+ and OH^- ions in pure water sample at a given temperature. The value of K_w has been experimentally determined from the measurement of electrical conductivity of highly purified samples of distilled water at different temperatures and at 298 K its value has been found to be 1.0×10^{-14} mol^2 dm^{-6}. Using K_w we can find the concentrations of H_3O^+ and OH^- ions in water. As the autoprotolysis of water molecules give equal number of ions of each type, the concentrations of these ions is equal, we may, therefore, write

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2 = 1.0 \times 1.0^{-14} \text{ mol}^2 \text{ dm}^{-6} \qquad \ldots(7.49)$$

$$\Rightarrow \quad [H_3O^+] = 1.0 \times 1.0^{-7} \text{ mol dm}^{-3} \qquad \ldots(7.50)$$

Thus, in pure water and in neutral aqueous solutions at 298 K

$$[H_3O^+] = [OH^-] = 1.0 \times 1.0^{-7} \text{ mol dm}^{-3} \qquad \ldots(7.51)$$

In acidic solutions this equality is disturbed and there are more hydronium ions than the hydroxide ions. Similarly, in basic solutions there would be an excess of OH^- ions. You must note here that hydronium ions and hydroxide ions are present in all aqueous solutions, and they are always in equilibrium with water molecules. *The autoprotolysis equilibrium discussed above applies to all aqueous solutions and the ionic-product equation holds for water.*

7.5.1 pH Scale

The concentration of H_3O^+ and OH^- ions in the aqueous solutions of acids and bases vary over a very wide range depending on the amount of acid or base added to water to get the solution. In order to quantitatively express the concentration of these ions especially in dilute solutions (< 0.01 M) we need to use negative powers of 10 and it is quite inconvenient to handle these numbers. In 1909 a Danish botanist S.P.L. Sorensen, while working on brewing of beer, proposed a practical scale called **pH scale** for expressing the concentration or 'potential' of H^+ ions in aqueous solutions. He defined pH as the negative logarithm (to the base 10) of the molar concentration of hydrogen (we now use hydronium) ions in solution. That is,

$$\text{pH} = -\log_{10}[H^+] \quad \text{or} \quad -\log_{10}[H_3O^+] \qquad \ldots(7.52)$$

The letter p was derived from the German word 'Potenz' meaning power and the term in the square bracket represented the molar concentration of hydrogen ions. For example, if we have an aqueous solution in which the concentration of hydrogen ions is 1.0×10^{-3} M, its pH can be calculated to be

$$\text{pH} = -\log_{10}[1 \times 10^{-3}] = -[-3] = 3$$

The basic logic of the scale was that by taking logarithm the numbers expressed as negative powers of 10, representing concentration of hydrogen ions, become simple negative numbers (e.g., $\log_{10} 10^{-3} = -3$), which are relatively easier to handle. However, to make it even better, the expression was multiplied by −1 so that the concentration of hydrogen ions in aqueous solutions of acids and bases could be expressed in terms of simple positive numbers.

As stated above, Eq. (7.51); in pure water and in neutral solutions at 298 K, the concentration of hydronium ions would be 1.0×10^{-7} mol dm^{-3}, which gives a pH value of 7.0.

$$\text{pH} = -\log_{10}[1 \times 10^{-7}] = -[-7] = 7$$

For acidic solutions the concentration of hydronium ions would be greater than 1.0×10^{-7} mol dm^{-3}, which would give a pH of less than 7. On the other hand, in case of the basic solutions in which the concentration of hydronium ions would be less than 1.0×10^{-7} mol dm^{-3} the pH would be more than 7. You may note here that the way pH is defined there is an inverse relationship between the concentration of hydrogen ions in the solution and its pH. Higher the concentration, lower the pH and vice-versa.

Aqueous solutions at 298 K

Neutral solutions:
pH=7.0

Acidic solutions:
pH < 7.0

Basic solutions:
pH >7.0

You should further note here that pH is not a physical property like pressure or volume it is merely a way of representing the concentration (which is a physical quantity) of hydronium ions in aqueous solutions. Secondly, you should also take note of the fact that like all equilibrium constants the value of K_w also depends on temperature and the value of 1.0×10^{-14} is at 298 K. At higher or lower temperatures than 298 K the value of K_w will be different. Accordingly, the concentration of hydronium ions in a water sample would be different. Say at 323 K where the value of $K_w = 5.47 \times 10^{-14}$ mol^2 dm^{-6}, the concentration of hydronium ions in water would be would be 2.34×10^{-7} mol dm^{-3}. This corresponds to a pH of 6.63. This means that pure water or a neutral aqueous solution would have a pH of 6.63 at 323 K.

A number of similar terms have been defined using the p notation, which means, 'the *negative logarithm of*'. The important and relevant ones are:

$$\text{pOH} = -\log_{10}[\text{OH}^-] \qquad \ldots(7.53)$$

$$\text{p}K_\text{w} = -\log_{10} K_\text{w} \qquad \ldots(7.54)$$

$$\text{p}K_\text{a} = -\log_{10} K_\text{a} \qquad \ldots(7.55)$$

$$\text{p}K_\text{b} = -\log_{10} K_\text{b} \qquad \ldots(7.56)$$

Of these the first two terms you can recognise and understand. You would learn about the other two in the next unit when we will deal with weak acids and bases. There is an important relationship between pH, pOH and pK_w. Let's workout the relationship by recalling the following expression:

$$K_\text{w} = [\text{H}_3\text{O}^+][\text{OH}^-] \qquad \ldots(7.48)$$

Taking logs and multiplying by –1 on both sides, we get

$$-\log K_\text{w} = -\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-] \qquad \ldots(7.57)$$

$$\Rightarrow \quad \text{p}K_\text{w} = \text{pH} + \text{pOH} \qquad \ldots(7.58)$$

As you know that at 298 K the value of $K_w = 1.0 \times 10^{-14}$ which, gives the value of pK_w to be 14. Substituting it in Eq. (7.58) we get the following important expression (valid at 298 K)

$$\text{pH} + \text{pOH} = 14 \qquad \dots(7.59)$$

This means that if we know the value of pH of a given solution at 298 K we can find its pOH value and vice versa by using the Eq. (7.59).

7.5.2 Calculation of pH

Let us take up some examples to learn about calculating pH values for aqueous solutions of strong acids and bases using the equations given above. Let's begin by calculating the pH value for 0.001 M aqueous solution of HCl. As you are aware, HCl is a strong acid so it would ionise completely in solution and we can write.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \qquad \dots(7.37)$$

As we have 0.001 M HCl it will provide 0.001 M hydronium ions on complete ionisation. So the concentration of H_3O^+ ions would be = 1.0×10^{-3} mol dm^{-3} which can be used to calculate the pH. However, before attempting the calculation let us also consider the other source of hydronium ions in the solution i.e., autoprotolysis of water

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \dots(7.46)$$

If we assume the temperature to be 298 K then autoprotolysis of water is expected to provide 1.0×10^{-7} mol dm^{-3} of hydronium ions. This number is much smaller (1/10,000) than 1.0×10^{-3} mol dm^{-3} obtained from ionisation of HCl. This gets even smaller due to common ion effect because according to Le-Chatelier principle the hydronium ions obtained from the ionisation of HCl cause the autoprotolysis equilibrium to shift to the left and decrease the concentration of hydronium ions obtained from autoprotolysis of water.

If the concentration of a species from a minor source happens to be less than or equal to 5% of the concentration from a major source, then it can be ignored without causing appreciable change in the calculated value.

In absence of HCl, $[H_3O^+]_{water}$ from autoprotolysis = 1.0×10^{-7} M

In presence of HCl, $[H_3O^+]_{water}$ from autoprotolysis = $<<1.0 \times 10^{-7}$ M

As the concentration of hydronium ions obtained from autoprotolysis of water is much smaller than that obtained from ionisation of HCl it can be ignored and we can calculate the pH based on the concentration of hydronium ions obtained from ionisation of HCl only. That is

$$\text{pH} = -\log_{10}[1 \times 10^{-3}] = -[-3] = 3$$

Let's go further and calculate the pH of a solution of HCl obtained by diluting the above solution 100 times i.e., it has a concentration $= \dfrac{1x10^{-3}}{100} = 1x10^{-5}$ M

Proceeding as before we get:

Concentration of hydronium ions from ionisation of HCl = 1.0×10^{-5} M

Concentration of hydronium ions from autoprotolysis of water = $<1.0 \times 10^{-7}$ M

As the concentration of hydronium ions from autoprotolysis of water is less than 1% of that obtained from dissociation of HCl, we can again ignore it and calculate the pH based on the concentration of hydronium ions obtained from ionisation of HCl only. That is

$$pH = -\log_{10}[1\times10^{-5}] \quad = \quad -[-5] = 5$$

Now, if we go still further and dilute the HCl solution in question by another 100 times then what would be the pH? Will it be 7.0 as the concentration of HCl would be 1.0×10^{-7} M? Let's analyse. Proceeding as before, we get:

Concentration of hydronium ions from ionisation of HCl = 1.0×10^{-7} M

Concentration of hydronium ions from autoprotolysis of water ~1.0×10^{-7} M

Now since the concentration of hydronium ions from two sources are comparable we cannot ignore the hydronium ions obtained from autoprotolysis of water. We need to work out the total concentration of hydronium ions. As HCl is a strong electrolyte so we are sure about the concentration of hydronium ions from complete ionisation of HCl = 1.0×10^{-7} M. However, in order to calculate the amount of hydronium ions from autoprotolysis of water we need to solve the autoprotolysis equilibrium applying the common ion effect as shown below. We assume that the concentration of hydronium ions obtained from autoprotolysis of water = x

	$H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^+(aq)$	$+ \; OH^-(aq)$
Concentration of ions from autoprotolysis of water	x	x
Concentration of H_3O^+ ions from ionisation of HCl	1.0×10^{-7}	0
Total H_3O^+ ion concentration	$[x + (1.0 \times 10^{-7})]$	x

Assuming the temperature to be 298 K, the following equation must hold for the aqueous solution.

$$[H_3O^+][OH^-] = 1.0\times10^{-14}\ mol^2\ dm^{-6} \qquad \ldots(7.49)$$

Substituting the values from the table we get

$$[x+(1.0\times10^{-7})](x) = 1.0\times10^{-14}$$

On simplification we get a quadratic equation as follows,

$$x^2+(1.0\times10^{-7})(x)-(1.0\times10^{-14})=0$$

$$\Rightarrow \qquad x^2+(1\times10^{-7})x-(1\times10^{-14})=0$$

As you know that for a quadratic equation, $ax^2 + bx + c = 0$, the value of x can be obtained by the following expression

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

So for our equation,

$$x = \frac{-10^{-7} \pm [(10^{-7})^2 + (4 \times 1 \times 10^{-14})]^{1/2}}{2}$$

$$= \frac{-10^{-7} \pm [5 \times 10^{-14}]^{1/2}}{2}$$

$$= \frac{-10^{-7} \pm [2.24 \times 10^{-7}]}{2}$$

$$= \frac{1.24 \times 10^{-7}}{2} = 6.2 \times 10^{-8}\ \text{M} \qquad \text{(Ignoring the negative root)}$$

The total concentration of hydronium ions in the solution = Hydronium ions from ionisation of HCl + hydronium ions from autoprotolysis of water

$$= (1.0 \times 10^{-7}) + (6.2 \times 10^{-8})$$

$$= 1.62 \times 10^{-7}\ \text{M}$$

$$\Rightarrow \text{pH} = -\log_{10}[1.62 \times 10^{-7}] = -[-6.79] = 6.79$$

Having learnt about the calculation of pH values of the solution of an acid (hydrochloric acid) at different concentrations, let us learn about the calculation of pH of a solution of a base by taking an example.

Example 7.1: Calculate the pH of 0.010 M aqueous solution of NaOH at 298 K.

Solution: Since NaOH is a strong base; it will fully ionise in the solution to give Na^+ and OH^- ions as given below

$$\text{NaOH(aq)} \rightarrow \text{Na}^+\text{(aq)} + \text{OH}^-\text{(aq)}$$

The concentration of hydroxide ions would be

$$[\text{OH}^-] = 1.0 \times 10^{-2}\ \text{mol dm}^{-3}$$

From Eq. 7.48 we know that,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\Rightarrow \qquad [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

Substituting the values at 298 K,

$$\Rightarrow \qquad [\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-14}\text{mol}^2\text{dm}^{-6}}{1.00 \times 10^{-2}\text{mol dm}^{-3}}$$

$$= 1.00 \times 10^{-12}\ \text{mol dm}^{-3}$$

$$\text{pH} = -\log(1.00\times 10^{-12}) = -(-12) = 12$$

Alternatively, we can first use the concentration of hydroxide ions to find pOH and then use Eq. (7.59) to find out the value of pH, i.e.,

$$\text{pOH} = -\log(1.00\times 10^{-2}) = -(-2) = 2$$

$$\text{pH} = \text{p}K_\text{w} - \text{pOH} = 14 - 2 = 12$$

Thus the pH of the solution would be 12.

Having learnt about the calculation of pH for aqueous solutions of acids and bases, solve the following SAQs to gauge your understanding of these.

SAQ 5

Calculate the pH of 2×10^{-3} M aqueous solution of hydrochloric acid.

SAQ 6

What would be the pH of the resulting solution if 100 cm^3 of 2×10^{-3} M hydrochloric acid solution is mixed with 150 cm^3 of 2×10^{-3} M solution of sodium hydroxide at 298 K?

7.6 SUMMARY

In this introductory unit on ionic equilibrium we started by discussing the nature of aqueous solutions in terms of their electrical conductivity based on the nature of the solute. Herein, we introduced the concept of an electrolyte and defined it to be a substance, which when dissolved in water gives an electrically conducting solution. The electrolytes, which completely dissociate or ionise in aqueous solutions are called strong electrolytes and are highly conducting. On the other hand, the electrolytes that are partially ionised are called weak electrolytes and their solutions have low electrical conductivity. We also discussed the factors affecting the ionisation of weak electrolytes. These happen to be the nature of solvent, temperature, presence of common ions and dilution. The variation of degree of ionisation of weak electrolytes with concentration was expressed in terms of Ostwald's dilution law. According to this law "The degree of ionisation of a weak electrolyte in a solution is directly proportional to square root of dilution".

After the discussion on electrolytes, their types and the factors affecting their behaviour we reviewed different concepts of acids and bases. We started by recalling Arrhenius concept, according to which an acid is defined as a species that generates a hydrogen ion in water and a base as the species that provides hydroxide ions in water. Though a simple concept, it has limited applicability as it is valid only for aqueous solutions and does not include species that do not have a hydrogen or OH. On the other hand, in Brønsted and Lowry concept the acids and bases are defined in terms of transfer of protons. The species transferring the proton is called an acid and the one accepting it is called a base. According to Brønsted-Lowry concept in any acid-base equilibrium both forward and reverse reactions involve proton transfers. The species on either side of the equilibrium are related as conjugated acid-base pairs. A stronger acid has a weaker conjugate base and vice versa. The Lewis concept, which we discussed later, describes acid-base behavior in terms of donation/ acceptance of a lone pair of electron from one species to another; the donor being a base and the acceptor an acid.

We then discussed about the consequences of the amphoteric nature of water. It was stated that in a sample of pure water some molecules donate a H^+ ion whereas an equal number of others accepts the same. This leads to the formation of hydronium and hydroxide ions and the process is called autoprotolysis of water. The product of the concentrations of hydronium ions and hydroxide ions in an aqueous solution is called ionic product constant of water and has a unique value at a given temperature. Using autoprotolysis of water we introduced the concept of pH which is a scale used for expressing the concentrations of H^+ ions in aqueous solutions. The pH is defined as the negative logarithm (to the base 10) of the molar concentration of hydrogen (or hydronium) ions in solution. We also explained the procedure to calculate the pH of aqueous solutions of strong acids and bases with the help of examples.

7.7 TERMINAL QUESTIONS

1. Define an electrolyte and differentiate between weak and strong electrolytes.

2. List different factors that affect the ionisation of weak electrolytes.

3. Outline the drawbacks of Arrhenius theory of acids and bases.

4. In the following reactions, label each species as an acid or a base. Also identify the conjugate acid-base pairs in these reactions.

   a. $HSO_4^-(aq) + NH_3(aq) \rightleftharpoons SO_4^{2-}(aq) + NH_4^+(aq)$

   b. $HPO_4^{2-}(aq) + NH_4^+(aq) \rightleftharpoons H_2PO_4^-(aq) + NH_3(aq)$

5. In a conjugate acid-base pair a stronger conjugate acid has a weaker conjugate base and vice-versa. Explain with the help of suitable examples.

6. What is an amphoteric substance? With the help of suitable examples show that water is an amphoteric substance.

7. In the following reactions, identify the Lewis acid and Lewis base.

   a. $SnCl_4 + 2Cl^- \rightarrow SnCl_6^{2-}$

   b. $BBr_3 + :AsH_3 \rightarrow BBr_3 \leftarrow AsH_3$

8. What is pH? Calculate the pH of a solution of hydrochloric acid having a concentration of 2×10^{-5} M.

9. Calculate the pH of a solution prepared by mixing 100 cm^3 of 0.001 M HCl and 300 cm^3 of 0.020 M NaOH at 298 K.

7.8 ANSWERS

Self-Assessment Questions

1. Ionisation and dissociation are closely related processes associated with the dissolution of electrolyte in water to make a solution. These are often used interchangeably; however, there is a minor difference. When an ionic electrolyte e.g., NaCl which consists of ions packed in a crystal lattice is dissolved, the ions dissociate from one another and go into solution. Such a process is called dissociation. On the other hand, when we dissolve a molecular electrolyte e.g., acetic acid, the electrolyte molecules ionise and produce ions in solution. Such a process is called ionisation. Thus, in dissociation the ions already present in the electrolyte become free in solution whereas in ionisation the ions are formed from molecular electrolyte under the influence of the solvent.

2. According to Ostwald's dilution law, "The degree of ionisation of a weak electrolyte is directly proportional to the square root of dilution". For a weak electrolyte, the degree of ionisation (α), the concentration (c), and the equilibrium constant (K) are related as $\alpha = \sqrt{K/c}$.

   As the concentration of a solution containing certain amount of electrolyte is related inversely with the volume of the solution containing one mole of the solute (dilution) we can write $\alpha = \sqrt{KV}$. Thus, as the volume (V) of the solution containing a given amount of weak electrolyte increases the degree of ionisation of the electrolyte increases.

3. The conjugate bases of given acids are as under:

Acid species	**Conjugate base**
HPO_4^{2-}	PO_4^{3-}
HOCl	ClO^-
PH_4^+	PH_3

4. The conjugate acid-base pairs in given reactions are as under:

   a. $SO_3^{2-} + NH_4^+ \rightleftharpoons HSO_3^- + NH_3$

   Conjugate acid/base pairs: NH_4^+/NH_3 and HSO_3^-/SO_3^{2-}

   b. $HS^- + CN^- \rightleftharpoons S^{2-} + HCN$

   Conjugate acid/base pairs: HCN/CN^- and HS^-/S^{2-}

c. $F^- + HSO_4^- \rightleftharpoons HF + SO_4^{2-}$

Conjugate acid/base pairs: HSO_4^- / SO_4^{2-} and HF / F^-

5. HCl is a strong acid so it would ionise completely in solution and we can write.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

As we have 2×10^{-3} M HCl, the concentration of H_3O^+ ions would be $= 2.0 \times 10^{-3}$ mol dm^{-3}. In addition to this we would have about 1×10^{-7} mol dm^{-3} of hydronium ions from autoprotolysis of water. Since this number is negligibly small as compared to the concentration of hydronium ions obtained from ionisation of HCl, we calculate the pH by using the concentration of hydronium ions obtained only from hydrochloric acid i.e., 2.0×10^{-3} M

Therefore, pH = $-\log_{10} [2 \times 10^{-3}] = -[-2.70] = 2.70$

6. When we add 150 cm^3 of 2×10^{-3} M sodium hydroxide solution to 100 cm^3 of 2×10^{-3} M hydrochloric acid solution all the hydrochloric acid would be neutralised by 100 cm^3 of NaOH and there will be an excess of 50 cm^3 of 2×10^{-3} M sodium hydroxide that will be present in a total volume of 250 cm^3. Therefore, we can calculate the final concentration of sodium hydroxide using the formula $M_1V_1 = M_2V_2$.

$$M_2 = \frac{M_1V_1}{V_2}$$

Substituting the values,

$$M_2 = \frac{0.002 \times 50}{250} = 0.0004 \text{ M}$$

Since NaOH is a strong base it is fully ionised to give Na^+ and OH^- ions, i.e., the concentration of hydroxide ions would be

$$\rightarrow \quad [OH^-] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$$

we know that,

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

$$\Rightarrow \quad [H_3O^+] = \frac{K_w}{[OH^-]}$$

Substituting the values at 298 K,

$$\Rightarrow \quad [H_3O^+] = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{4.00 \times 10^{-4} \text{ mol dm}^{-3}}$$

$$= 2.50 \times 10^{-9} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log (2.50 \times 10^{-9}) = -(-8.60) = 8.60$$

Thus, the pH of the given solution would be 8.60

Terminal Questions

1. An electrolyte may be defined as a substance which when dissolved in water gives an electrically conducting solution. The electrolytes which completely dissociate or ionise in aqueous solutions e.g., sodium chloride are called strong electrolytes and have high electrical conductivity. On the other hand, the electrolytes that are partially ionised, e.g., acetic acid are called weak electrolytes and have low electrical conductivity.

2. The following factors affect the degree of ionisation of weak electrolytes:
   - i. Nature of solvent
   - ii. Temperature
   - iii. Presence of common ions
   - iv. Dilution

3. The following are some of the limitations of Arrhenius theory of acids and bases:
   - It is applicable for aqueous solutions only and does not explain the acid-base behaviour in non-aqueous solvents or in gaseous systems.
   - It does not explain the acidic behaviour of substances that lack hydrogen e.g., $AlCl_3$ or the basic character of substances that lack OH e.g., NH_3.

4. The acids and bases and the conjugate acid-base pairs in given reactions are as under:

   a. $$\underset{\text{acid}_1}{HSO_4^-} + \underset{\text{base}_2}{NH_3} \rightleftharpoons \underset{\text{base}_1}{SO_4^{2-}} + \underset{\text{acid}_2}{NH_4^+}$$

   The conjugate acid-base pairs are HSO_4^- / SO_4^{2-} and NH_4^+ / NH_3

   b. $$\underset{\text{base}_1}{HPO_4^{2-}} + \underset{\text{acid}_2}{NH_4^+} \rightleftharpoons \underset{\text{acid}_1}{H_2PO_4^-} + \underset{\text{base}_2}{NH_3}$$

   The conjugate acid-base pairs are $H_2PO_4^- / HPO_4^{2-}$ and NH_4^+ / NH_3

5. In Brønsted and Lowry concept the acids and bases are defined in terms of transfer of protons. For example, when we dissolve ammonia in water, the following equilibrium is established.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Here ammonia accepts a proton from water and acts as a base whereas water acts as an acid in the forward reaction. In the reverse reaction ammonium ion donates a proton to hydroxide ion and acts as an acid; the hydroxide ions act as a base. Here, NH_4^+ ions and NH_3 constitute a conjugate acid-base pair. Similarly, H_2O and OH^- ions form a conjugate acid-base pair.

As the reaction proceeds to a good extent in the forward direction we can say that water is a stronger acid than ammonium ion. There are two bases in the reaction (NH_3 and OH^-). The reaction proceeding in the forward direction means that the proton donated by water is accepted by ammonia in preference to hydroxide ion. That is ammonia is a stronger base than hydroxide ion. Thus, we can say that the conjugate base (OH^-) of a stronger acid (H_2O) is a weaker base. Similarly, the conjugate acid (NH_4^+) of a stronger base (NH_3) is a weaker acid.

6. A substance that can behave as an acid or as a base depending on other substance in the reaction is called an amphoteric substance. Water is a common example of amphoteric substances. In the following reaction

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

Water acts as an acid by donating a proton to carbonate ions. On the other hand, in the reaction given below, water acts as a base by accepting a proton from chloroacetic acid.

$$ClCH_2COOH(aq) + H_2O(l) \rightleftharpoons ClCH_2COO^-(aq) + H_3O^+(aq)$$

7. a. In this reaction $SnCl_4$ is the acid whereas Cl^- ions act as base.

   b. In this reaction BBr_3 is the acid whereas $:AsH_3$ acts as base.

8. It is a scale for expressing the concentrations of H^+ ions in aqueous solutions. It is defined as the negative logarithm (to the base 10) of the molar concentration of hydrogen (or hydronium) ions in solution. That is,

$$pH = -\log_{10}[H^+] \text{ or } = -\log[H_3O^+]$$

HCl is a strong acid so it would ionise completely in solution and we can write.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

As we have 2×10^{-5} M HCl it will provide 2×10^{-5} M hydronium ions on complete ionisation i.e., the concentration of H_3O^+ ions in the solution $= 2.0 \times 10^{-5}$ mol dm^{-3}. In addition to this we would have about 1×10^{-7} mol dm^{-3} of hydronium ions from autoprotolysis of water. However, due to common ion effect of the hydronium ions obtained from ionisation of HCl the autoprotolysis of water gets suppressed and the concentration of hydronium ions from this source gets further reduced.

Under these conditions, the concentration of hydronium ions from autoprotolysis of water is negligibly small as compared to the hydronium ions obtained from ionisation of hydrochloric acid. So we calculate the pH of the solution by using the concentration of hydronium ion obtained from ionisation of HCl only i.e., $= 2.0 \times 10^{-5}$

Therefore, $pH = -\log[2 \times 10^{-5}] = -[-4.70] = 4.70$

9. The given solution has hydrochloric acid as well as sodium hydroxide so the two would neutralise each other. We need to find out the final composition of the solution before calculating the pH. To begin with, we can calculate the amounts of HCl and NaOH individually.

   HCl has a concentration of 0.01 M which means its has 0.01 moles of HCl in 1000 cm^3 or 0.01 / 1000 = 1×10^{-5} moles of HCl per cm^3 of the solution

   As the volume of HCl is 100 cm^3 so there are $100 \times 1 \times 10^{-5}$ moles = 1×10^{-3} moles of HCl = 0.001 moles of HCl in the solution.

   Similarly, we can calculate the number of moles of NaOH in the solution to be

   $$= \frac{0.02}{1000} \times 300 = 0.006 \text{ moles}$$

   Of these, 0.006 moles of NaOH, 0.001 moles would be used to neutralise all the HCl and there will be an excess of 0.006-0.001 = 0.005 moles of NaOH. Now, these 0.005 moles are present in a total volume of 400 cm^3

   $$\Rightarrow \text{ Concentration of NaOH} = \frac{0.005}{400} \times 1000 = 0.0125\text{M} = 1.25 \times 10^{-2}\text{ M}$$

   Since NaOH is a strong base it is fully ionised to give Na^+ and OH^- ions.

   $$\text{NaOH(aq)} \rightarrow \text{Na}^+\text{(aq)} + \text{OH}^-\text{(aq)}$$

   $$\Rightarrow \quad [\text{OH}^-] = 1.25 \times 10^{-2} \text{ mol dm}^{-3}$$

   we know that $K_w = [H_3O^+][OH^-]$

   $$\Rightarrow \quad [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

   Substituting the values at 298 K,

   $$\Rightarrow [\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-14} \text{mol}^2 \text{dm}^{-6}}{1.25 \times 10^{-2} \text{moldm}^{-3}} = 8.0 \times 10^{-13} \text{moldm}^{-3}$$

   $$\text{pH} = -\log[8.0 \times 10^{-13}] = -[-12.1] = 12.1$$

   Thus, the pH of the given solution would be 12.1.

UNIT 8

IONIC EQUILIBRIUM-II

Structure

8.1 INTRODUCTION

In the previous unit you have learnt about the introductory aspects of ionic equilibrium i.e., the equilibria involving ionic species. We began with electrolytes, their types, their ionisation behavior and factors affecting their ionisation behaviour. This was followed by a review of different theories of acids and bases and an important aspect of aqueous solutions viz., autoprotolysis of water. The autoprotolysis of water was then used to define ionic product of water. After discussing its significance we introduced the concept of pH and we also took up calculation of pH for aqueous solutions of strong acids, bases and their mixtures.

In the present unit we would continue our discussion on ionic equilibrium and take up the ionisation of weak acids and bases, the quantitative characterisation of their ionisation equilibria and calculation of pH values of solutions of weak acids and bases. This would be followed by the discussion on ionisation behaviour of diprotic and polyprotic acids, the corresponding ionisation constants and their significance. We would then take up the relationship between the strengths of acids and bases and their molecular structure. Thereafter, the effect of common ions on the ionisation equilibria of weak acids and bases would be taken up leading tothe introduction of concept of buffer solutions. We would explain buffer action and derive an expression to calculate the pH of buffer solutions and calculate the pH values of some common buffer systems. In the end we would discuss about buffer capacity.

In the next unit we would continue our discussion on ionic equilibria and take up the equilibria in aqueous solutions of different types of salts wherein we would talk about hydrolysis of salts and characterisation of the corresponding equilibria. The next unit would also cover the solubility equilibrium of sparingly soluble salts and its applications.

Expected Learning Outcomes

After studying this unit, you should be able to:

- explain the ionisation of weak acids and bases and write down the expressions for the corresponding ionisation constants;
- state the significance of the magnitude of ionisation constants of weak acids and bases;
- calculate the pH of solutions of weak acids and bases;
- describe the stepwise ionisation of diprotic and polyprotic acids and write expressions for the respective ionisation constants;
- calculate the concentration of different species in a solution of a triprotic or polyprotic acid;
- relate the strengths of acids and bases with their molecular structure;
- explain the effect of common ions on the ionisation equilibria of weak acids and bases;
- define buffer solutions and give examples of some common buffer systems;
- explain buffer action with the help of suitable examples;
- derive Henderson-Hasselbalch equation for calculating the pH of a buffer solution;
- calculate the pH values of the solutions of some common buffer systems; and
- explain the meaning of buffer capacity and state the factors that affect the buffer capacity.

8.2 IONISATION CONSTANTS OF WEAK ACIDS AND BASES

You would recall from the previous unit that according to the Arrhenius theory, weak acids and weak bases are the ones which do not ionise completely in aqueous solutions and there exists equilibrium between the ionised and unionised species in the solution. For example, for a weak acid HA, and for a weak base BOH, we can write the ionisation equilibria as

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad \ldots(8.1)$$

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq) \qquad \ldots(8.2)$$

On the other hand, according to the Brønsted and Lowry theory the equilibrium in an aqueous solution of weak acid HA can be given as under:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad \ldots(8.3)$$

The acid HA reacts with water to produce hydronium ion and the conjugate base, A^-. The ionisation equilibrium concerning a weak base, B according to the Brønsted and Lowry theory can be given as under:

$$B + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq) \qquad \ldots(8.4)$$

The process of ionisation of a weak acid (or weak base) in aqueous solution is called **acid (or base) ionisation** and the equilibrium given above is called **acid (or base) ionisation equilibrium**. This equilibrium is characterised by a constant called **ionisation equilibrium constant** or simply **ionisation constant**. Let us derive the expression for the ionisation constant for a weak acid.

As stated before, ionisation and dissociation are used interchangeably therefore; acid ionisation is also called acid dissociation. Similarly, acid ionisation constant is also called acid dissociation constant.

8.2.1 Ionisation Constant for a Weak Acid

As given above, the ionisation equilibrium for a weak acid, HA can be written as

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad \ldots(8.3)$$

In order to derive an expression for the ionisation constant characterising this equilibrium, let us take *c* mol dm^{-3} solution of the weak acid, HA and assume that the degree of ionisation at this concentration is α. The initial and equilibrium concentrations of different species in the solution would be as:

Concentration / mol dm^{-3}	$HA(aq) + H_2O(l)$	$\rightleftharpoons$ $H_3O^+(aq)$	+ $A^-(aq)$
Initial	c	0	0
Change due to ionisation	$-c\alpha$	$c\alpha$	$c\alpha$
At equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

The equilibrium constant for the ionisation equilibrium can be written as

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \ldots(8.5)$$

Here, the subscript 'a' in the symbol for equilibrium constant indicates acid. Also note that the concentration of water does not appear in the equilibrium constant expression, as it does not change and is included in K_a.

Substituting the concentrations of different species at equilibrium in the expression we get,

$$K_a = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \Rightarrow K_a = \frac{c\alpha^2}{(1-\alpha)} \qquad \ldots(8.6)$$

The value of K_a is indicative of the strength of the acid, higher the value, stronger the acid. As you can note that the ionisation constant is directly proportional to the square of the degree of ionisation, which means that a higher value refers to higher degree of ionisation. This in turn means that the acid would produce more hydronium ions in solution i.e., the acid is stronger. The ionisation constant values for some common weak acids at 298K are given in Table 8.1

Higher the K_a, higher the ionisation and hence stronger the acid

Table 8.1: Ionisation constants for some weak acids at 298 K

Name of the weak acid	**Molecular formula**	**Ionisation constant, K_a**
Chloroacetic acid	$ClCH_2COOH$	1.4×10^{-3}
Hydrofluoric acid	HF	7.1×10^{-4}
Formic acid	$HCOOH$	1.7×10^{-4}
Benzoic acid	C_6H_5COOH	6.5×10^{-5}
Acetic acid	CH_3COOH	1.8×10^{-5}
Hydrocyanic acid	HCN	4.9×10^{-10}

You would recall from the Ostwald's dilution law discussed in the previous unit that the degree of ionisation depends on the dilution (or concentration) of the electrolyte. As weak acids are weak electrolytes, these would also ionise to different extent as a function of concentration. We can use ionisation constant to determine the degree of ionisation of the weak acid in a solution, which in turn can be used to calculate the pH of a solution of the weak acid. Let us take up an example

Example 8.1: Calculate the degree of ionisation and the pH of a 0.1 M aqueous solution of acetic acid at 298K.
[Given, K_a (CH_3COOH) = 1.8×10^{-5}at 298K]

Solution: The equilibrium reaction for the ionisation of acetic acid, can be given as under:

$$CH_3COOH\ (aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq) \quad \ldots(8.4)$$

If the degree of ionisation of acetic acid in this solution is taken as α, the initial and equilibrium concentrations of various species in the solution would be:

Concentration/ mol dm^{-3}	CH_3COOH (aq) +	H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	CH_3COO^-(aq)
Initial	0.1		0	0
Change due to ionisation	-0.1α		0.1α	0.1α
At equilibrium	$0.1\,(1-\alpha)$		0.1α	0.1α

We can write the expression for K_a as:

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

Substituting the equilibrium concentrations of different species from the table, we get

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

Assuming that α, is small as compared to 1, we can ignore it in the denominator; we get, $K_a = 0.1\alpha^2$

On rearranging it gives,

$$\alpha = \sqrt{\frac{K_a}{0.1}}$$

Substituting the values of K_a,

$$\alpha = \sqrt{\frac{1.8\times10^{-5}}{0.1}} = \sqrt{1.8\times10^{-4}} = 0.0134$$

➔ Degree of ionisation of acetic acid in 0.1 M solution = 0.0134

Percentage ionisation = Degree of ionisation × 100 = 0.0134 × 100 = 1.34 %

This means that at a concentration of 0.1 M, 1.34 % of the molecules of acetic acid are ionised; it translates to 134 molecules per 10000 molecules. Let us now calculate the value of pH for the solution

From the table above, we see that the concentration of hydronium ions, $[H_3O^+]$ at equilibrium = $0.1\times\alpha = 0.1 \times 0.0134 = 1.34 \times 10^{-3}$ M. This can be used to calculate the pH as follows:

$$➔ \quad pH = -\log\,[H_3O^+] = -\log\,[1.34\times10^{-3}]$$

$$pH = -(-2.87) = 2.87$$

Thus, the pH of the 0.1 M aqueous solution of acetic acid would be 2.87

Having learnt to compute the pH of a given solution of weak acid using its K_a value, let us take another example to calculate the K_a value of a weak acid using the pH of its given solution.

Example 8.2: A 0.10 M aqueous solution of acrylic acid-a weak acid used in manufacture of plastics has a pH of 2.63. Calculate the value of K_a for acrylic acid?

Solution: The ionisation equilibrium of acrylic acid can be given as under:

$$HAcry(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Acry^-(aq)$$

If the degree of ionisation of acrylic acid in this solution is taken as α, the initial and equilibrium concentrations of various species would be

Concentration/ mol dm^{-3}	HAcry (aq) + H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	Acry$^-$ (aq)
Initial	0.10	0	0
Change due to ionisation	– 0.10 α	0.10 α	0.10 α
At equilibrium	0.10 (1 $-\alpha$)	0.10 α	0.10 α

As per the table given above, the concentration of hydronium ion at equilibrium would be 0.10α. We are given the pH of the solution as 2.63, which can be used to calculate the concentration of hydronium ions. Equating the two we can get the value of α which can then be used to calculate the value of K_a. Let's proceed by computing the concentration of hydronium ions first

We know that $\text{pH} = -\log_{10}[H_3O^+] \Rightarrow [H_3O^+] = \text{antilog}(-\text{pH})$

$$\Rightarrow \quad [H_3O^+] = \text{antilog}(-2.63) = 2.34 \times 10^{-3}\ \text{M}$$

Equating the expression for equilibrium concentration of hydronium ions with this calculated value:

$$\Rightarrow \quad 0.10\ \alpha = 2.34 \times 10^{-3}$$

we get $\alpha = 2.34 \times 10^{-2}$

We know that the K_a for a weak acid whose *c* molar solution has degree of ionisation α, is given by the following expression.

$$\Rightarrow \quad K_a = \frac{c\alpha^2}{(1-\alpha)} \qquad \text{...(8.6)}$$

Substituting the values of *c* and α

$$\Rightarrow \quad K_a = \frac{0.1 \times (2.34 \times 10^{-2})^2}{(1-0.0234)}$$

$$\Rightarrow \quad K_a = \frac{0.1 \times 5.48 \times 10^{-4}}{0.9766}$$

$$\Rightarrow \quad K_a = \frac{0.1 \times 5.48 \times 10^{-4}}{0.9766} = 5.61 \times 10^{-5}$$

The K_a value for the acrylic acid is found to be = 5.61×10^{-5}

8.2.2 Ionisation Constant for a Weak Base

Let's now take up the ionisation equilibrium for a weak base, B and derive an expression for its ionisation constant. As per Brønsted and Lowry theory, the ionisation of the weak base, B in aqueous solution can be written as

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq) \qquad \ldots(8.7)$$

If we start with *c* mol dm^{-3} of the weak base and assume that the degree of ionisation at this concentration is α, the initial and equilibrium concentrations of different species in the solution would be as follows

Concentration / mol dm^{-3}	$B(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$BH^+(aq)$ +	$OH^-(aq)$
Initial	c	0	0
Change due to ionisation	$-c\alpha$	$c\alpha$	$c\alpha$
At equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

The equilibrium constant for the ionisation equilibrium for the weak base, B can be written as

$$K_b = \frac{[BH^+][OH^-]}{[B]} \qquad \ldots(8.8)$$

Here, the subscript b in the symbol for equilibrium constant indicates base. Also note that the concentration of water does not appear in the equilibrium expression as its concentration remains constant and is included in K_b.

Substituting the concentrations of different species from the table in the base ionisation constant expression we get,

$$K_b = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \qquad K_b = \frac{c\alpha^2}{(1-\alpha)} \qquad \ldots(8.9)$$

The value of K_b is indicative of the strength of the base. As ionisation constant is directly proportional to the square of the degree of ionisation, a higher value of ionisation constant refers to higher degree of ionisation or a stronger base. The ionisation constant values of some common weak bases at 298K are given in Table 8.2.

Table 8.2: Ionisation constants for some weak bases at 298 K

Name of the weak base	**Molecular formula**	**Ionisation constant, K_b**
Diethylamine	$(CH_3CH_2)_2NH$	6.9×10^{-4}
Dimethylamine	$(CH_3)_2NH$	5.1×10^{-4}
Ethylamine	$CH_3CH_2NH_2$	4.3×10^{-4}
Methylamine	CH_3NH_2	4.4×10^{-4}
Ammonia	NH_3	1.8×10^{-5}
Hydroxylamine	NH_2OH	1.1×10^{-8}
Aniline	$C_6H_5NH_2$	4.2×10^{-10}

As in the case of weak acids discussed above, we can use ionisation constant of a weak base to determine the degree of ionisation of the weak base, which in turn can be used to calculate the pH of a solution of a weak base. Let us take up an example

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Example 8.3: Calculate the degree of ionisation and the pH of a 0.1 M solution of methylamine, CH_3NH_2 at 298 K.
[Given, K_b (CH_3NH_2) = 4.4×10^{-4}]

Solution: The ionisation equilibrium of methylamine in water, can be given as under:

$$CH_3NH_2\,(aq) + H_2O\,(l) \rightleftharpoons CH_3NH_3^+\,(aq) + OH^-\,(aq)$$

If the degree of ionisation of methylamine in the 0.1 M solution is taken as α, the initial and equilibrium concentrations of various species in the solution would be

Concentration / mol dm^{-3}	CH_3NH_2 (aq) + H_2O (l) $\rightleftharpoons$	$CH_3NH_3^+$(aq) +	OH^-(aq)
Initial	0.1	0	0
Change due to ionisation	$-0.1\,\alpha$	$0.1\,\alpha$	$0.1\,\alpha$
At equilibrium	$0.1\,(1-\alpha)$	$0.1\,\alpha$	$0.1\,\alpha$

We can recall the expression for K_b, Eq. (8.9)

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

Assuming that α, is small as compared to 1, we can ignore it in the denominator of Eq. (8.9), we get $K_b = c\alpha^2$

Which gives $\alpha = \sqrt{\frac{K_b}{c}}$

Substituting the values of K_b and c we get,

$$\alpha = \sqrt{\frac{4.4 \times 10^{-4}}{0.1}} = \sqrt{4.4 \times 10^{-3}} = 0.066$$

Degree of ionisation of methylamine in 0.1 M aqueous solution = 0.066

Percentage ionisation = degree of ionisation × 100 = 0.066 × 100 = 6.6 %

This means that at a concentration of 0.1 M, 6.6 % of the molecules of methylamine are ionised. As the value of degree of ionisation (0.066) is more than 5% of the initial concentration, our assumption of it being small and neglecting it is not valid. So we cannot ignore it. We go back to Eq. (8.9), we had

$$\Rightarrow \qquad K_b = \frac{c\alpha^2}{(1-\alpha)} \qquad \ldots(8.9)$$

Substituting the values of K_b and c, we get

$$\Rightarrow 4.4\times10^{-4} = \frac{0.1\alpha^2}{(1-\alpha)}$$

On simplification,

$$\Rightarrow (4.4\times10^{-4}) - (4.4\times10^{-4})\alpha = 0.1\alpha^2$$

On rearranging,

$$\Rightarrow 0.1\alpha^2 + (4.4\times10^{-4})\alpha - (4.4\times10^{-4}) = 0$$

We need to solve the above quadratic equation to get the value of the degree of ionisation, α. As you know that for a quadratic equation, $ax^2 + bx + c = 0$, the value of x can be obtained by the following expression

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

In the present case we can write

$$\alpha = \frac{-(4.4\times10^{-4}) \pm \sqrt{(4.4\times10^{-4})^2 - 4\times0.1\times(4.4\times10^{-4})}}{2\times0.1}$$

Solving we get,

$$\alpha = \frac{-(4.4\times10^{-4}) \pm \sqrt{(1.936\times10^{-7}) + (1.76\times10^{-4})}}{0.2}$$

$$\alpha = \frac{-(4.4\times10^{-4}) \pm \sqrt{1.76\times10^{-4}}}{0.2}$$

$$\alpha = \frac{-(4.4\times10^{-4}) \pm 1.327\times10^{-2}}{0.2} = \frac{1.28\times10^{-2}}{0.2} = 6.4\times10^{-2}$$

$$\alpha = 6.4\times10^{-2} \quad \text{(ignoring the negative root)}$$

From the table above, we see that the concentration of hydroxide ions, $[OH^-]$ at equilibrium = $0.1\times\alpha = 0.1 \times 0.064 = 0.0064 = 6.4 \times 10^{-3}$ M

$$pOH = -\log[OH^-] = -\log[6.4\times10^{-3}]$$

$$pOH = -(-2.19) = 2.19$$

we know that at 298 K,

$$pH = 14 - pOH$$

$$\Rightarrow \quad pH = 14 - 2.19 = 11.81$$

Having learnt about the ionisation of weak acids and bases and characterisation of their equilibria in terms of the respective ionisation constants it is time we take up the ionisation behaviour of diprotic and polyprotic acids. These acids can generate or donate two or more protons in solution. However, before moving ahead answer the following self-assessment questions to gauge your understanding of ionisation of weak acids and bases.

SAQ 1

Give the expression relating the ionisation constant of a weak acid with its degree of ionisation and discuss the significance of the magnitude of ionisation constant.

SAQ 2

Morphine is an alkaloid found naturally in a number of plants and animals and is used as a medicine to relieve pain. It is a weak base having $K_b = 1.6 \times 10^{-6}$. Calculate the pH of 0.01 M aqueous solution of morphine at 298 K.

8.3 IONISATION OF DIPROTIC AND POLYPROTIC ACIDS

The weak acids discussed above had only one ionisable hydrogen atom i.e., they generate only one hydrogen ion in aqueous solution even if they may have more than one hydrogen atom. On the other hand, a number of acids have two or more than two ionisable hydrogen atoms. Accordingly, these are called diprotic or polyprotic acids. The acids containing three ionisable hydrogen atoms are sometimes called triprotic acids. These acids ionise in a stepwise manner; i.e., they sequentially lose one hydrogen ion at a time. To begin with let us learn about the ionisation of a diprotic acid.

8.3.1 Ionisation of Diprotic Acids

In order to understand the ionisation behaviour of diprotic acids we take the example of carbonic acid, H_2CO_3. The successive ionisation equilibria for H_2CO_3 can be given as

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq); \quad K_{a1} \qquad \ldots(8.10)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq); \quad K_{a2} \qquad \ldots(8.11)$$

Where, K_{a1} and K_{a2} are the ionisation constants of the first and the second stage of ionisation respectively. The expressions for the ionisation constants and their experimental values at 298 K are

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = 4.3 \times 10^{-7} \qquad \ldots(8.12)$$

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = 4.8 \times 10^{-11} \qquad \ldots(8.13)$$

You may note here that the first ionisation constant, K_{a1} is about 10,000 times larger than the second ionisation constant, K_{a2}. In general, the successive ionisation constants for di and polyprotic acids get smaller and smaller. Can you think of a reason for the same? The reason is quite simple, in case of first ionisation the proton is getting lost from a neutral species or we may say that it is removed from a species with one unit of negative charge. On the other hand, in case of second ionisation, we need to remove a proton from a species with two units of negative charge which is relatively difficult. In general in successive ionisations a proton is removed from more and more negatively charged species.

8.3.2 Ionisation of Triprotic Acids

As the name suggests, triprotic acids have three ionisable protons that ionise successively. The ionisation equilibria corresponding to the successive ionisation of a triprotic acid, for example, H_3PO_4 can be given as

$$H_3PO_4\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + H_2PO_4^-(aq); \quad K_{a1} \qquad \ldots(8.14)$$

$$H_2PO_4^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq); \quad K_{a2} \qquad \ldots(8.15)$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq); \quad K_{a3} \qquad \ldots(8.16)$$

Where, $K_{a1,}$ K_{a2} and K_{a3} are the ionisation constants of the first, second and the third stage of ionisation respectively. The expressions for the ionisation constants and their experimental values at 298 K are

$$K_{a1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]}; \quad = 7.1\times10^{-3} \qquad \ldots(8.17)$$

$$K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} \quad = 6.3\times10^{-8} \qquad \ldots(8.18)$$

$$K_{a3} = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^{2-}]} \quad = 4.2\times10^{-13} \qquad \ldots(8.19)$$

Here again you may note that the successive ionisation constants get smaller and smaller. In order to get an insight into the equilibria involved in di- and polyprotic acids it is worthwhile to calculate the concentration of various species in an aqueous solution of such acids. We take the example of 1.0 M solution of phosphoric acid.

Example 8.4: Calculate the concentrations of the following species in a 1.0 M aqueous solution of phosphoric acid

$$[H_2PO_4^-], [HPO_4^{2-}], [PO_4^{3-}] \text{ and } [H_3O^+]$$

The values of successive equilibrium constants are given as

$$K_{a1} = 7.1\times10^{-3};\ K_{a2} = 6.3\times10^{-8}; \quad \text{and} \quad K_{a3} = 4.2\times10^{-13}$$

Solution: To begin with we assume that in the first stage of ionisation phosphoric acid behaves as a weak acid and the corresponding equilibrium reaction can be given as;

$$H_3PO_4\,(aq) + H_2O(l) \rightleftharpoons H_3O^+\,(aq) \;+\; H_2PO_4^-(aq)$$

The initial and equilibrium concentrations of different species in the solution would be as follows

Concentration mol dm^{-3}	$H_3PO_4\,(aq) + H_2O(l) \rightleftharpoons$	$H_3O^+\,(aq)$ +	$H_2PO_4^-(aq)$
Initial	1.0	0	0
Change due to ionisation	$-\alpha$	α	α
At equilibrium	$1-\alpha$	α	α

The equilibrium constant for the ionisation reaction is given as

$$K_{a1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} \qquad \text{… (8.17)}$$

We recall the relationship between K_a and α for a weak acid; Eq. (8.6)

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \qquad \text{… (8.6)}$$

Substituting the value of K_a and c in the ionisation constant expression, we get,

$$7.1\times10^{-3} = \frac{(\alpha^2)}{(1-\alpha)}$$

If we assume the first ionisation of phosphoric acid to be like a weak acid, and ignore α in the denominator of the above expression, we get

$$\alpha^2 = 7.1\times10^{-3} \;\Rightarrow\; \alpha = 0.0843$$

The value of α comes to be 0.0843 (i.e., 8.43%), which is more than 5% of the initial concentration. Thus, our assumption is not valid and we cannot ignore α. Going back to Eq. (8.6)

$$7.1\times10^{-3} \Rightarrow \frac{(\alpha^2)}{(1-\alpha)}$$

Simplifying and rearranging, we get

$$\alpha^2 + (7.1\times10^{-3})\alpha - (7.1\times10^{-3}) = 0$$

So we need to solve the following quadratic equation to get the value of α.

$$\alpha^2 + 0.0071\,\alpha - 0.0071 = 0$$

Recall that for a quadratic equation $ax^2 + bx + c = 0$, the value of the root, x can be obtained by the following equation.

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

So for our equation,

$$\Rightarrow \ \alpha = \frac{-(0.0071) \pm \sqrt{(0.0071)^2 - 4 \times 1 \times (-0.0071)}}{2}$$

$$\Rightarrow \quad \alpha = \frac{-(0.0071) \pm \sqrt{(0.0000504) + (0.0284)}}{2}$$

$$\Rightarrow \quad \alpha = \frac{-(0.0071) \pm \sqrt{(0.0284504)}}{2}$$

$$\Rightarrow \quad \alpha = \frac{-(0.0071) \pm 0.1687}{2} = \frac{0.1616}{2} = 0.0808$$

Thus, solving the equation gives the value of α as 0.0808. This infact gives the concentrations of $[H_2PO_4^-]$, as well as that of $[H_3O^+]$. (See the equilibrium concentrations in the above table)

$$\Rightarrow \quad [H_3O^+] = [H_2PO_4^-] = \alpha = 0.0808 = 8.08 \times 10^{-2}\ \text{M}$$

The consideration of second stage of ionisation would help us get the concentration of $[HPO_4^{2-}]$. The ionisation equilibrium for the second stage of the ionisation would be

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) \ + \ HPO_4^{2-}(aq)$$

The initial and equilibrium concentrations of different species in the solution would be as follows

Concentration/mol dm^{-3}	$H_2PO_4^-(aq) + H_2O\ (l) \rightleftharpoons$	$H_3O^+(aq)$	+ HPO_4^{2-} (aq)
Initial	0.0808	0.0808	0
Change due to ionisation	$-\alpha$	+ α	+ α
At equilibrium	0.0808$-\alpha$	0.0808+ α	α

The equilibrium constant for the ionisation reaction is given as

$$K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} \qquad \text{…(8.18)}$$

Substituting the equilibrium concentrations from the table in the equilibrium constant expression, we get

$$\frac{[0.0808 + \alpha]\,[\alpha]}{[0.0808 - \alpha]} = 6.3 \times 10^{-8}$$

Assuming α to be negligible as compared to the initial concentration (0.0808 M) we get

$$\frac{[0.0808][\alpha]}{[0.0808]} = 6.3\times10^{-8} \Rightarrow \alpha = 6.3\times10^{-8}$$

So the concentration of HPO_4^{2-} ions would be = 6.3×10^{-8} M which is equal to the second ionisation constant.

You may note here that the concentration (6.3×10^{-8} M) of hydronium ions produced in this stage of ionisation is much less than that produced in the first stage (0.0808 M). This means that practically all the hydronium ions present in the solution are obtained from the first stage of ionisation. This is a general feature of ionisation of most of the di- and polyprotic acids.

We would now consider the third stage of ionisation of phosphoric acid.

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

The initial and equilibrium concentrations of different species in the solution would be as follows

Concentration/mol dm^{-3}	HPO_4^{2-} (aq)+ H_2O (l) ⇌	H_3O^+(aq) +	PO_4^{3-} (aq)
Initial	6.3×10^{-8}	0.0808	0
Change due to ionisation	$-\alpha$	$+\alpha$	$+\alpha$
At equilibrium	$6.3\times10^{-8}-\alpha$	$0.0808+\alpha$	α

The equilibrium constant for the ionisation reaction is given as

$$K_{a3} = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^{2-}]} \qquad \ldots(8.19)$$

Substituting the equilibrium concentrations from the table in the equilibrium constant expression, we get

$$\frac{[\alpha]\,[0.0808+\alpha]}{[6.3\times10^{-8}-\alpha]} = 4.2\times10^{-13}$$

Assuming the value of α to be negligible as compared to 6.3×10^{-8} (and obviously to 0.0808 M), we get

$$\frac{[\alpha]\,[0.0808]}{[6.3\times10^{-8}]} = 4.2\times10^{-13}$$

Solving, we get

$$\Rightarrow \quad \alpha = \frac{4.2\times10^{-13}\times6.3\times10^{-8}}{0.0808} = 3.27\times10^{-19}$$

Therefore, the concentration of phosphate ions in the solution would be 3.27×10^{-19} M. Thus, the concentrations of different ions in the 1.0 M solution of phosphoric acid would be

$[H_2PO_4^-] = 8.08 \times 10^{-2} M$ $[HPO_4^{2-}] = 6.3 \times 10^{-8} M$

$[PO_4^{3-}] = 3.27 \times 10^{-19} M$ $[H_3O^+] = 8.08 \times 10^{-2} M$

From the example given above, you can take note of a few important aspects of ionisation of polyprotic acids

i) A large amount of the polyprotic acid remains unionized, (in this example; 1.0–0.0808 = 0.9192 M i.e., about 92%).

ii) The concentrations of mono-negative ion of the polyprotic acid and the hydronium ions can be obtained by considering just the first stage of ionisation only. These are the only ions whose concentrations are significant and further ionisations do not alter these concentrations significantly.

iii) The concentration of di-negative ion of the polyprotic acid equals the ionisation constant of second stage

Assess your understanding of ionisation of di- and polyprotic acids by answering the following questions.

SAQ 3

Write down the equilibrium reactions for the successive ionisation of oxalic acid ($H_2C_2O_4$)-a diprotic acid. Also give the expressions for the ionisation constants for the reactions.

SAQ 4

Calculate the concentrations of the following species in a 1.0 M aqueous solution of carbonic acid, H_2CO_3.[Given $K_{a1} = 4.4\times10^{-7}$ and $K_{a2} = 4.7\times10^{-11}$]

$[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$ and $[H_3O^+]$

8.4 STRENGTHS OF ACIDS AND BASES

We have discussed a number of theories of acids and bases and have talked about strong and weak acids and bases. Have you ever thought what makes an acid (say HCl) strong and a closely related molecule (HF) a weak acid? The strength of an acid or a base depends on a number of factors, like the temperature, nature of solvent, and the molecular structure. In order to understand or determine the relative strengths of acids and bases as a function of their molecular structure, we keep the temperature and the nature of solvent the same and rationalise the relative strength in terms of the molecular structure. Let's make an attempt to understand the relative strengths of acids as a function of their molecular structure. We would take different classes of molecules.

Strengths of Hydrohalic Acids

You have learnt that one of the requirements for a molecule to behave, as an acid is that it is able to lose or donate a proton. The ease of the process determines its strength as an acid, easier the process stronger the acid. This in turn depends on the strength of the bond between acidic proton and other atoms of the molecule. Let's take a simple case of binary hydrohalic acids of HX type that ionise as

Bond	Bond enthalpy
H−F	568.2
H−Cl	431.9
H−Br	366.1
H−I	298.3

$$HX \rightarrow H^+ + X^- \qquad \ldots(8.20)$$

There are two factors that determine the extent of this reaction. The first being the strength of the H−X bond and the second the polarity of the bond. You would recall from your earlier understanding of periodic properties of elements, that when we go down a group of elements in the periodic table, the size of atom X increases, and the strength of H−X bond decreases. This, in turn means that it becomes easier to break the bond and make H^+ available and hence from bond strength considerations the strength of the acid increases down the group. Now let's take up the second factor, i.e., the polarity of the bond. As you know that the polarity of a bond depends on the difference in the electronegativities of the bonded atoms. The electronegativities of the elements decrease down the group. The electronegativity of hydrogen is 2.1, so the difference in electronegativities of the bonded atoms in halogen acids decreases down the group. As the polarity decreases, so is the tendency to lose a proton. In other words, from polarity considerations, the acidity should decrease down the group. Thus, there are two opposing factors: one (bond strength) increasing the strength of acid and the second (polarity) decreasing the strength of the acid as we move down the group. However, it has been experimentally found that the order of acidity of different hydrohalic acids varies as

Element	Electro-negativity
Fluorine	4
Chlorine	3
Bromine	2.8
Iodine	2.5

H−F << H−Cl < H−Br < H−I

This means that HI is a strong acid whereas HF is a weak acid. This trend indicates that bond enthalpy is more significant factor than bond polarity in determining the acid strength of binary hydrohalic acids

Strengths of Oxoacids

You would recall from your earlier studies that an oxoacid contains a hydrogen atom attached to an oxygen atom, which, in turn, is attached to another atom Y. The structure of an oxoacid can be represented as

−Y−O−H

Oxoacids and oxyacids are synonymous and are used interchangeably

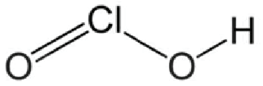
Where, the atom Y is bonded to other atom(s) in the molecule. Since in all oxoacids the acidic H atom is bonded to an oxygen atom, the bond strength is not a distinguishing factor in determining their relative acidity. It is the charge (electrons) on the oxygen atom or the polarity of the O−H bond that is important. This means that the presence of any group that can withdraw electrons from oxygen atom would make the removal of hydrogen ion easier.

Element	Electro-negativity
Hydrogen	2.1
Oxygen	3.5
Chlorine	3.0
Bromine	2.8

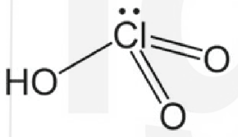
Let's take the example of two simple oxoacids viz., HOCl and HOBr. As the chlorine atom is more electronegative than bromine, it would make oxygen atom relatively more positive in HOCl than that in HOBr. The electronegativity of oxygen is 3.5 whereas that for chlorine and bromine is 3.0 and 2.8 respectively. Due to the difference in the electronegativities of oxygen and chlorine/bromine oxygen pulls electrons from both of them but to a lesser extent from chlorine than from bromine. This would make the O−H bond more polar, which means it will be easier for the hydrogen ion to be removed in case of HOCl. That is, it will be the stronger of the two acids. This is substantiated by the experimental data also as the acid dissociation constants for HOCl and HOBr are 2.9×10^{-8} and 2.3×10^{-9} respectively i.e., HOCl is about 12 times stronger than HOBr.

In some of the oxoacids, the atom Y is attached to a number of oxygen atoms. In such cases the number of such oxygen atoms determines the strength of the oxoacid. Higher the number of oxygen atoms stronger is the acid. Let's understand it by taking the example of oxoacids of chlorine. The structures of oxoacids of chlorine are as under

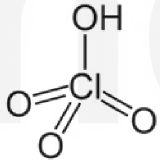
Hypochlorous acid



Chlorous acid



Chloric acid



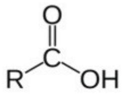
Perchloric acid

As the number of oxygen atoms attached to the chlorine atom increases, these pull electrons away from the chlorine atom and make it more and more positive. This in turn makes the removal of hydrogen ion easier by decreasing the electron density at the oxygen atom. Experimentally also the acidic strength of these oxoacids is found to vary as

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

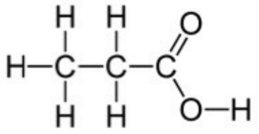
We have so far discussed about the relative strength of inorganic acids. Let's learn about the factors determining the strengths of carboxylic acids.

Strengths of Carboxylic Acids

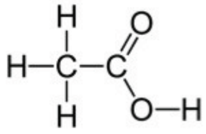


Carboxylic acid

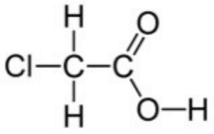
You know that carboxylic acids are organic acids containing –COOH functional group. Different carboxylic acids differ in terms of the structure and nature of R group. Let us take three closely related carboxylic acids viz., ethanoic acid (acetic acid), 2-chloroethanoic acid and propanoic acid whose structures are given below



propanoic acid



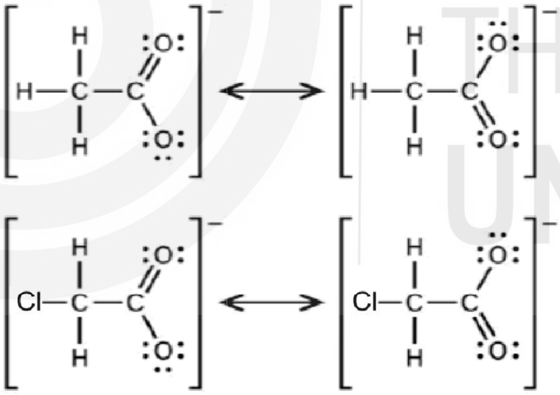
ethanoic acid



2-chloroethanoic acid

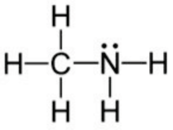
In this example we take ethanoic acid as representative carboxylic acid and the other two molecules as its derivatives so as to understand the effect of structure of R group. Ethanoic acid is a weak acid characterised by its acid dissociation constant of 1.8×10^{-5}. In case of 2-chloroethanoic acid highly electronegative chlorine atom withdraws electrons from carbon atom to which it is attached. This in turn pulls electrons from the carbon atom of the carboxylic group thereby making the O−H bond more polar and the strength of the acid increases, $K_a = 1.4 \times 10^{-3}$. 2-chloroethanoic acid is about seventy seven times stronger than ethanoic acid. On the other hand, propanoic acid may be considered as a derivative of ethanoic acid in which a methyl group replaces one of the hydrogen atoms of the methyl group attached to carbon atom of carboxylic acid group. As you are aware, the methyl group is electron-donating group, it would increase the electron density at the carbon atom to which it is attached. This in turn donates electrons to the carbon atom of the carboxylic group thereby making the O−H bond lesser polar and the strength of the acid decreases, $K_a = 1.4 \times 10^{-5}$. As the electron donating effect of methyl group is much weaker than the electron withdrawing effect of chlorine atom, propanoic is only slightly weaker than ethanoic acid.

In addition to the electron withdrawing or electron donating effects of the substituents, the stability of the anion formed as a consequence of ionisation of the acid is also an important factor. 2-chloroethanoiate ion obtained from the ionisation of 2-chloroethanoic acid is more resonance stabilised than the ethanoate ion obtained from the ionisation of ethanoic acid. The chlorine atom pulls the electrons from the carboxylate ion and stabilises the structure.

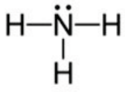


Strengths of Simple Bases

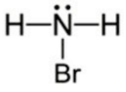
Having learnt about the relative acidities of different types of acids let's take up the basicity of simple amines. You know that ammonia is basic as it can donate its lone pair (present on nitrogen atom). Once again we take three closely related molecules, viz., ammonia, bromamine and methylamine whose structure are given below to understand the relationship between molecular structure and basicity.



methylamine



ammonia



bromamine

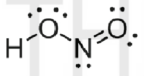
In ammonia, there is a lone pair of electrons available on the nitrogen atom. In addition the N atom pulls electrons from the three hydrogen atoms due to the difference in electronegativities. This accumulates negative charge on the nitrogen atom and N atom can easily donate its lone pair of electrons, thus making ammonia basic (K_b=1.82 ×10^{-5}). In case of bromamine, one of the hydrogen atoms of ammonia is replaced by a bromine atom. As the electronegativity of Br (2.8) is higher than that of H (2.1), the nitrogen atom is not able to pull electrons from it as effectively as was with H atom. As a consequence, the negative charge accumulation on nitrogen atom decreases. This leads to a relatively lower ease of donating lone pair of electrons by nitrogen and hence the basicity decreases. In other words, bromamine is a weaker base than ammonia. On the other hand, in case of methylamine, the methyl group beingelectron-donating group increases the availability of lone pair on the nitrogen atom. This makes methylamine a stronger base than ammonia. Thus, the order of basicity of these molecules should be

Methylamine > ammonia > bromamine

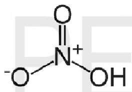
The experimental values of base dissociation constants, K_b's for methylamine, ammonia and bromamine being 4.17 ×10^{-4}, 1.82 ×10^{-5} and 2.45 ×10^{-8} respectively support the above given order of basicity.

SAQ 5

The structures of nitrous and nitric acids are given as under.



nitrous acid



nitric acid

Which of these acids would be stronger and why?

8.5 COMMON ION EFFECT

In Unit 6 you have learnt about Le-Chatelier principle that deals with the effect of different factors on the systems under equilibrium. As weak acids and bases also exhibit systems in equilibrium we expect these equilibria also to be affected by such factors. Here we would consider the effect of adding a solute, having an ion common with the weak acid or base, to an aqueous solution of weak acid or base as the case may be. To begin with, let's consider a weak acid HA that ionises as

$$HA\,(aq) \rightleftharpoons H^{+}\,(aq) + A^{-}\,(aq) \qquad \ldots(8.1)$$

What will happen if to an aqueous solution of acid HA we add a solution of a salt NaA? NaA being a strong electrolyte will dissociate completely into the ions as follows

$$NaA\,(aq) \rightarrow Na^{+}\,(aq) + A^{-}\,(aq) \qquad \ldots(8.20)$$

The A^- ions provided by the salt appear on the product side of the above equilibrium, Eq.(8.1) so according to Le-Chatelier principle they will make the equilibrium shift to the left. We say that the common ions have suppressed the ionisation of the weak acid or in other words, the degree of ionisation of weak acid would decrease. Let us take an example to understand the effect of common ions on the ionisation equilibrium of a weak acid

The shift in equilibrium of a weak acid / base caused by the addition of a salt having an ion in common with the weak acid /base is called **common ion effect.**

Example 8.5: An aqueous solution contains 0.1 M each of acetic acid and sodium acetate. Calculate the degree of ionisation of acetic acid and the pH of the solution. Compare your results with the ones obtained in example 8.1.

Solution: The equilibrium for the ionisation of acetic acid, can be given as under:

$$CH_3COOH\,(aq) + H_2O(l) \rightleftharpoons H_3O^+\,(aq) + CH_3COO^-\,(aq)$$

The salt sodium acetate would dissociate as

$$CH_3COONa\,(aq) \rightarrow Na^+\,(aq) + CH_3COO^-\,(aq)$$

If the degree of ionisation of acetic acid in this solution is taken as α, the initial and equilibrium concentrations of various species in the solution would be

Concentration / mol dm^{-3}	CH_3COOH (aq)+ H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	CH_3COO^-(aq)
Initial	0.1	0	0
Change due to ionisation of acetic acid	-0.1α	0.1α	0.1α
Change due to dissociation of sodium acetate	0	0	0.1
At equilibrium	$0.1\,(1-\alpha)$	0.1α	$0.1\,(1+\alpha)$

We can write the expression for acid ionisation constant of acetic acid as

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

Substituting the equilibrium concentrations of different species from the table above, in the equilibrium constant expression, we get

$$K_a = \frac{[0.1\alpha][0.1(1+\alpha)]}{[0.1(1-\alpha]}$$

As acetic acid is a weak acid and its degree of ionisation which is already low is further suppressed by the presence of acetate ions (the common ion) we can reasonably assume that

$$\alpha << 1;\ \text{and}\ (1-\alpha) \sim 1;\ \text{also}\ (1+\alpha) \sim 1$$

Under these conditions we write

$$K_a = \frac{[0.1\alpha][0.1]}{[0.1]} = [0.1\alpha]$$

Substituting the value of the acid ionisation constant, K_a

$$1.8 \times 10^{-5} = [0.1\,\alpha] \Rightarrow \alpha = 1.8 \times 10^{-4}$$

So the degree of ionisation of acetic acid in the given solution = 0.00018.

Percentage ionisation = degree of ionisation × 100 = 0.00018 × 100 = 0.018 %

Recall that in example 8.1 we computed the degree of ionisation of 0.1 M acetic acid (without any salt) to be = 0.0134 or 1.34%. Thus, the addition of 0.1 M sodium acetate has drastically reduced the degree of ionisation of acetic acid [from 1.34 % to 0.018 %]. You can note here that the presence of common ions have decreased the extent of ionisation by as much as 74 times.

Let's now calculate the pH. As per the table, the concentration of hydronium ions at equilibrium = 0.1α

➔ $[H_3O^+]_{\text{equilibrium}} = 0.1 \times \alpha = 0.1 \times 0.00018 = 1.8 \times 10^{-5}$

we know that

$$pH = -\log\,[H_3O^+]$$

Substituting the value of $[H_3O^+]$,

$$pH = -\log\,[1.8 \times 10^{-5}]$$

$$pH = -(-4.74) = 4.74$$

Once again recalling from example 8.1, the pH of 0.1 M acetic acid (without any salt) was computed to be 2.87; the addition of 0.1 M sodium acetate has **increased** the pH **from 2.87 to 4.75.**

Similarly, we can deal with the aqueous solutions of weak bases containing a salt having a common ion. In such cases also the degree of ionisation would decrease. What do you think would be the effect on pH of the solution of a weak base? Will it increase or decrease? Write your response here before proceeding further.

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The decrease in the degree of ionisation of a weak base means that the concentration of hydroxyl ions would decrease which implies that the concentration of hydronium ions would increase. Therefore the pH of an aqueous solution of weak base would **decrease** on adding a salt having a common ion. Let us take up an important type of solutions that exploit the change in pH of a weak acid or a base on adding a salt containing common ions.

8.6 BUFFER SOLUTIONS

If we repeat the calculations given in example 8.5 for a solution containing 0.1 M acetic acid and 0.2 M sodium acetate we find that the degree of ionisation further decreases to 0.00009 and the pH increases to 5.04. This indicates that the pH of aqueous solutions of weak acids or bases can be controlled by adding suitable amounts of a salt containing common ion. The aqueous solutions containing weak acids or weak bases and a salt of common ion are quite important as these act as buffer solutions. *A buffer solution is defined as a solution that resists the change in its pH on adding small volumes of strong acid / base or on dilution.* The buffer solutions containing weak acid and its salt are called **acidic buffer solutions** e.g. acetic acid and sodium acetate, $CH_3COOH + CH_3COONa$. On the other hand, the buffer solutions containing weak base and its salt are called **basic buffer solutions** e.g. a buffer containing a mixture of ammonium hydroxide and ammonium chloride; $NH_4OH + NH_4Cl$. Let us learn about the way a buffer solution perform its function.

8.6.1 Buffer Action

In order to understand the action of a buffer solution we take the example of a common acidic buffer viz., acetic acid –sodium acetate buffer. As stated above it consist of a mixture of acetic acid and sodium acetate. The ionisation of acetic acid and dissociation of sodium acetate can be given as

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \qquad \ldots(8.21)$$

$$CH_3COONa(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq) \qquad \ldots(8.22)$$

You may recall from example 8.5 that in a mixture of acetic acid and sodium acetate the degree of ionisation of acetic acid decreased from an initial low value. This means that at equilibrium very few of the acetic acid molecules are ionised. In other words, for all practical purposes the concentration of acetic acid molecules in the solution is equal to the concentration of acetic acid taken initially. Similarly, sodium acetate being a salt gets fully dissociated and provides an equivalent amount of acetate ions. In addition to these, a negligibly small number of acetate ions are obtained from ionisation of acetic acid. In other words, for all practical purposes the concentration of acetate ions in the solution is equal to the concentration of sodium acetate taken initially. On the other hand, the concentration of hydronium ions is much smaller as compared to the concentrations of acetic acid and sodium acetate. Thus, you can see that a buffer system contains a conjugate acid-base pair (acetic acid -acetate ion here) and the concentrations of these two are quite high as compared to that of the hydronium ions. The conjugate acid and base constituting the buffer are called **acid reserve** and the **base reserve** respectively. These provide 'buffering' against the added base and acid respectively. Let's see their mode of action.

A buffer system contains a conjugate acid- base pair and the concentrations of these two are quite high as compared to that of the hydronium ions.

If we add a small amount of a strong acid such as HCl to a buffer solution containing acetic acid and sodium acetate, the added H_3O^+ ions would react with an equivalent amount of the base reserve in the buffer i.e., CH_3COO^- ions to generate undissociated acetic acid. The reaction can be given as

$$CH_3COO^-(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l) \qquad \ldots(8.23)$$

Some of the acetic acid molecules so obtained would dissociate back, but the number would be too small to be significant. The net effect would be that the concentration of acetic acid would increase slightly where as that of acetate ions (base reserve) would decrease slightly. The concentration of hydronium ions and thus the pH of the solution would not change significantly as the added hydronium ions are consumed by reaction with acetate ions.

Similarly, when small amounts of a strong base like NaOH is added, the hydroxyl ions produced by it would react with an equivalent amount of hydronium ions and neutralise them to produce water as per the following reaction

$$OH^-(aq) + H_3O^+(aq) \rightarrow H_2O(l) \qquad \ldots(8.24)$$

Some of the hydronium ions present in the solution get consumed in the process. In order to compensate for that some of the acetic acid molecules (acid reserve) ionise to provide hydronium ions and maintain the equilibrium. However, these would generate some additional acetate ions roughly equal to the amount of added hydronium ions. The net effect would be that the concentration of acetic acid would decrease slightly whereas that of acetate ions would increase slightly; but the concentration of hydronium ions and thus the pH of the solution would not change significantly.

You may note here that the added acid or the base only cause minor changes in the concentrations of the weak acid and the salt constituting the buffer solution. On the other hand, the concentration of the hydronium ions and thus the pH does not change significantly. Let us derive a mathematical expression for determining the pH of a buffer solution.

8.6.2 Henderson-Hasselbalch Equation

The Henderson-Hasselbalch equation relates the pH of a given buffer solution to the concentrations of its components viz. weak acid / base and the salt containing common ion. In order to derive this expression we again take the example of acetic acid-sodium acetate buffer. As given above, the acetic acid ionises in water and the following equilibrium is established

$$CH_3COOH\ (aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \qquad \ldots(8.21)$$

The equilibrium is characterised by the following acid ionisation constant

$$K_a = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]} \qquad \ldots(8.25)$$

The ionisation constant expression can be rearranged to give,

$$[H_3O^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} \qquad \ldots(8.26)$$

As discussed above, for all practical purposes, the concentration of undissociated acetic acid in the buffer solution can be taken as initial acid concentration [Acid], and the concentration of acetate ions equals the total sodium acetate concentration, i.e., [Salt]. In the light of this the Eq. (8.26) may be rewritten as

$$[\mathrm{H_3O^+}] = K_\mathrm{a} \times \frac{[\mathrm{Acid}]}{[\mathrm{Salt}]} \qquad \ldots(8.27)$$

You may note here that K_a is a constant so the concentration of hydronium ions depends directly on the ratio of acid to salt concentrations; higher the ratio more the hydronium ion concentration.

Taking log on the both sides of Eq. (8,27) we get,

$$\log[\mathrm{H_3O^+}] = \log K_\mathrm{a} + \log\frac{[\mathrm{Acid}]}{[\mathrm{Salt}]} \qquad \ldots(8.28)$$

multiplying throughout by (–1) gives

$$-\log[\mathrm{H_3O^+}] = -\log K_\mathrm{a} - \log\frac{[\mathrm{Acid}]}{[\mathrm{Salt}]} \qquad \ldots(8.29)$$

$$\Rightarrow \quad \mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{Salt}]}{[\mathrm{Acid}]} \;\because \mathrm{pH} = -\log[\mathrm{H_3O^+}];\; \mathrm{p}K_a = -\log K_\mathrm{a} \qquad \ldots(8.30)$$

This is known as **Henderson-Hasselbalch equation** for an acidic buffer. We can derive a similar expression for a basic buffer (e.g., ammonium hydroxide and ammonium chloride). The expression for a basic buffer would be

$$\Rightarrow \quad \mathrm{pOH} = \mathrm{p}K_\mathrm{b} + \log\frac{[\mathrm{Salt}]}{[\mathrm{Base}]} \qquad \ldots(8.31)$$

These equations are very handy in calculating the pH values of common buffer solutions. Let's take up some simple examples to see the application of these equations.

Example 8.6: Calculate the pH of a buffer solution containing 0.1 M acetic acid and 0.5 M sodium acetate.
[Given: K_a (acetic acid) = 1.8×10^{-5}]

Solution: As per the Henderson-Hasselbalch equation the pH of an acidic buffer solution is given by the following expression

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{Salt}]}{[\mathrm{Acid}]} \qquad \ldots(8.30)$$

First let's compute the value of pK_a

$$\mathrm{p}K_\mathrm{a} = -\log K_\mathrm{a} = -\log[1.8\times10^{-5}] = -[-4.74] = 4.74$$

Given: [acetic acid] = 0.1 M and [sodium acetate] = 0.5 M

Substituting in the Eq. (8.30) we get

$$\mathrm{pH} = 4.74 + \log\frac{[0.5]}{[0.1]} = 4.74 + \log 5 = 4.74 + 0.6990 = 5.44$$

Thus, the pH of the given buffer solution would be 5.44

Example 8.7: Calculate the pH of a buffer solution containing 0.1 M ammonium hydroxide and 0.2 M ammonium chloride at 298 K. [Given: K_b (ammonium hydroxide) = 1.8×10^{-5}]

Solution: As per the Henderson-Hasselbalch equation the pOH of a basic buffer solution is given by the following expression

$$\Rightarrow \quad \text{pOH} = \text{p}K_b + \log\frac{[\text{Salt}]}{[\text{Base}]} \qquad \ldots(8.31)$$

First let's compute the value of pK_b

$$\text{p}K_b = -\log K_b = -\log[1.8\times10^{-5}] = -[-4.74] = 4.74$$

Given: [ammonium hydroxide] = 0.1 M and [ammonium chloride] = 0.2 M

Substituting the values in the Eq. (8.31), we get

$$\text{pOH} = 4.74 + \log\frac{[0.2]}{[0.1]} = 4.74 + \log 2 = 4.74 + 0.3010 = 5.04$$

You know that at 298 K, pH + pOH =14

$$\Rightarrow \quad \text{pH} = 14.0 - 5.04 = 8.96$$

Thus, the pH of the given buffer solution would be 8.96

Example 8.8: Calculate the pH of a buffer solution prepared by mixing 40 cm^3 of 0.1 M acetic acid and 60 cm^3 of 0.5 M sodium acetate. [Given: K_a (acetic acid) = 1.8×10^{-5}]

Solution: As in example 8.6 the pH can be obtained by using Henderson-Hasselbalch equation, viz.,

$$\Rightarrow \quad \text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} \qquad \ldots(8.30)$$

We have already calculated the pK_a value for acetic acid to be 4.74.

Now we need to calculate the concentrations of acetic acid and sodium acetate in the buffer solution. We are given that 40 cm^3 of acetic acid and 60 cm^3 of sodium acetate are mixed, which makes the total volume of the solution to be 100 cm^3. The concentrations of acetic acid and sodium acetate in the buffer can be obtained by using dilution equation viz., $M_1V_1 = M_2V_2$

$$\text{Concentration of acetic acid in the buffer} = M_2 = \frac{M_1V_1}{V_2} = \frac{0.1\times40}{100} = 0.04\,\text{M}$$

$$\text{Concentration of sodium acetate in the buffer} = M_2 = \frac{M_1V_1}{V_2} = \frac{0.5\times60}{100} = 0.30\,\text{M}$$

Substituting the values in the Henderson-Hasselbalch equation we get,

$$\Rightarrow \quad \text{pH} = 4.74 + \log\frac{[0.30]}{[0.04]} = 4.74 + \log 7.5 = 4.74 + 0.875 = 5.62$$

Thus, the pH of the given buffer solution would be 5.62

8.6.3 Buffer Capacity

It is important to know that all the buffer solutions of a given buffer system are not equally effective. The effectiveness of a given buffer is expressed in terms of a term called **buffer capacity** and refers to its ability to resist pH change on adding small volumes of an acid or a base solution. It can also be visualised as the tolerance of the buffer towards the addition of acid/base solution. The buffer capacity of a given buffer depends on the absolute concentrations of the acid and base reserves as well as their relative amounts.

A buffer containing higher concentration of weak acid/base and the salt has a higher capacity to resist change in pH value. This means adding a certain amount of strong acid or base to a buffer containing higher concentration of buffer components would show lesser change in pH as compared to a buffer containing lower concentrations of the constituents. A buffer containing 0.5 M each of acetic acid and sodium acetate has a higher buffer capacity than that containing 0.1M each of the components. You may note that to begin with, both the buffers would have same pH value.

According to IUPAC, buffer capacity is defined as, "The capacity of a solution to resist changes in pH on the addition of strong acid or strong base which may be expressed numerically as the number of moles of strong acid or strong base required to change the pH by one unit when added to one litre of the specified buffer solution".

You would recall from the buffer action discussed in Section 8. 2 that addition of small amounts of strong acid / base to a buffer slightly alters the amounts of the components of the buffer. Also, the pH of the buffer depends on the ratio of the buffer components; Eq. (8.30) and Eq. (8.31). For a buffer having similar concentrations of acid / base and its salt the change in their ratio on adding small volumes of strong acid / base is much less than that for a buffer having different concentrations of acid / base and its salt. Therefore, a buffer containing similar concentration of its components has a higher buffer capacity than the buffers containing different concentrations of the buffer components. In conclusion we can say that the buffers containing higher absolute concentrations of its components and the ones containing similar concentrations of its components have a better ability to resist the change in pH on addition of small volumes of strong acid/base solutions.

SAQ 6

Calculate the pH of a buffer solution prepared by mixing 100 cm^3 of 0.3 M acetic acid with 200 cm^3 of 0.6 M solution of sodium acetate.[Given: K_a (acetic acid= 1.8×10^{-5})]

SAQ 7

Which of the following buffer solutions would have the highest buffer capacity?

a) Buffer containing 1.0 M acetic acid and 0.1 M sodium acetate

b) Buffer containing 1.0 M acetic acid and 1.0 M sodium acetate

c) Buffer containing 0.1 M acetic acid and 0.1 M sodium acetate

d) Buffer containing 0.5 M acetic acid and 1.0 M sodium acetate

Justify your answer.

8.7 SUMMARY

In this unit we continued our discussion on ionic equilibrium and started by taking up the ionisation equilibria associated with the ionisation of weak acids and weak bases. In this context we talked about degree of ionisation of weak acids and bases and the way to express the ionisation constants characterising the respective ionisation equilibria. As the magnitude of ionisation equilibrium constant or just ionisation constant is proportional to the degree of ionisation, it conveys about the strength of the acid / base; higher the magnitude of ionisation constant, stronger the acid / base. We also explained the logic and procedure to calculate the pH of a solution of a weak acid or base using the value of ionisation constant or calculating ionisation constant using the pH of the solution.

The discussion on the ionisation of weak acids and bases was followed by a discussion on the ionisation equilibria and the corresponding ionisation constants for diprotic and polyprotic acids. In this process you learnt that diprotic and polyprotic acids undergo sequential ionisation wherein each time one of the ionisable protons gets ionised. The ionisation constant of the first stage of ionisation has a relatively higher magnitude and the successive ionisation constants get smaller and smaller. We also explained the procedure to calculate the concentration of all the species present in an aqueous solution of a triprotic acid.

The addition of a salt containing an ion common with the weak acid or a weak base suppresses its ionisation and thus decreases its degree of ionisation. You have learnt that by changing the amount of salt containing a common ion added to a solution of a weak acid/base we can control the extent of ionisation of the weak acid/base and thus can control its pH. This fact is used in buffer solutions, which may be defined as the solutions that resist the change in their pH on addition of small volumes of solutions of strong acids or strong bases or on dilution. A buffer solution typically contains a weak acid or a weak base and a salt having an ion common with the acid/base. We explained the way buffers perform their function and also derived expressions to compute the pH value of a buffer solution and used the same to calculate the pH of some buffer solutions.

Towards the end, we discussed about buffer capacity-the ability of a buffer to resist change in pH. We stated that buffer solutions containing higher absolute concentrations of the acid/base and salt have higher buffer capacity and also that the buffers in which the concentration of the constituents is similar have better buffer capacity.

8.8 TERMINAL QUESTIONS

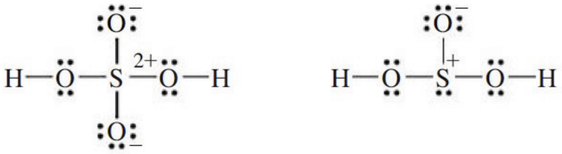
1. Define ionisation constant. What is the significance of ionisation constant of a weak base?
2. Formic acid (HCOOH) is a weak acid. Write the ionisation equilibrium reaction for formic acid in water and also give expression for the corresponding ionisation constant.

3. How would the degree of ionisation of a weak acid change with dilution of its solution? Explain

4. Dimethylamine, $(CH_3)_2NH$, is a weak base having $K_b = 5.1 \times 10^{-4}$. Calculate the pH of a 0.2 M aqueous solution of dimethylamine at 298 K.

5. The pH of an aqueous solution of lactic acid, $CH_3CH(OH)COOH$-a weak acid, was found to be 2.7. Calculate the concentration of the solution if K_a (lactic acid) = 1.4×10^{-4}.

6. The Lewis structures of sulphuric and sulphurous acids are given below. Predict which one of these would be a stronger acid on the basis of given structures.



Sulphuric acid Sulphurous acid

7. Adipic acid, $HOOC(CH_2)_4COOH$ is a diprotic acid with the acid dissociation constants as $K_{a1} = 3.9 \times 10^{-5}$ and $K_{a2} = 3.9 \times 10^{-6}$. Calculate the concentrations of all the ionic species present in 0.1 M aqueous solution of adipic acid.

8. Explain the effect of common ions on the ionisation equilibrium of weak acids with the help of a suitable example.

9. Define buffer solutions. Write the expression for the pH of a basic buffer solution.

10. Calculate the pH values for the following buffer solutions containing:

    i) 1.5 M acetic acid and 1.5 M sodium acetate

    ii) 0.15 M acetic acid and 0.15 M sodium acetate

    Which of these buffer solutions would have a higher buffer capacity?

8.9 ANSWERS

Self-Assessment Questions

1. The degree of ionisation (α) and the ionisation constant (K_a) for a weak acid are related as:

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

According to the relation given above, a higher ionisation constant implies a higher degree of ionisation. Thus, the magnitude of ionisation constant of a weak acid is a measure of the strength of the acid; higher the value stronger the acid.

2. The ionisation of morphine can be represented as

$$C_{17}H_{19}O_3N + H_2O(l) \rightleftharpoons C_{17}H_{19}O_3NH^+(aq) + OH^-(aq)$$

If we assume that the degree of ionisation of the solution at given concentration is α, the initial and equilibrium concentrations of different species in the solution would be as follows:

Concentration/ mol dm^{-3}	$C_{17}H_{19}O_3N(aq) + H_2O(l) \rightleftharpoons$	$C_{17}H_{19}O_3NH^+(aq)$ +	$OH^-(aq)$
Initial	0.01	0	0
Change due to ionisation	-0.01α	0.01α	0.01α
At equilibrium	$0.01(1-\alpha)$	0.01α	0.01α

We can write the expression for K_b as, $K_b = \frac{c\alpha^2}{(1-\alpha)}$

$$K_b = \frac{0.01\alpha^2}{(1-\alpha)}$$

Assuming that for weak base the degree of ionisation, α, is small as compared to 1, we can ignore it in the denominator, we get $K_b = 0.01\alpha^2$

Which gives, $\alpha = \sqrt{\frac{K_b}{0.01}}$

Substituting the value of the equilibrium constant,

$$\alpha = \sqrt{\frac{1.6 \times 10^{-6}}{0.01}} = \sqrt{1.6 \times 10^{-4}} = 0.0126$$

Degree of ionisation = 0.0126 ➔ Percentage ionisation = 1.26%

As the value of degree of ionisation is less than 5%, our assumption is justified.

From the table above, we see that the concentration of hydroxide ions, $[OH^-]$ at equilibrium = $0.01 \times \alpha$

➔ $[OH^-] = 0.01 \times 0.0126 = 0.000126 = 1.26 \times 10^{-4}$ M

$$pOH = -\log[OH^-] = -\log[1.26 \times 10^{-4}]$$

$$pOH = -(-3.90) = 3.90$$

we know that at 298 K, pH + pOH = 14

pH = 14 – pOH

➔ $pH = 14 - 3.90 = 10.10$

Thus, the pH of 0.01 M solution of morphine would be 10.10.

3. The equilibrium reactions for the successive ionisation of oxalic acid are as under:

$$H_2C_2O_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HC_2O_4^-(aq)$$

$$HC_2O_4^-(aq.) \; + \; H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2O_4^{2-}(aq)$$

The corresponding equilibrium constant expressions are:

$$K_{a1} = \frac{[HC_2O_4^-]\,[H_3O^+]}{[H_2C_2O_4]} \quad \text{and} \quad K_{a2} = \frac{[C_2O_4^{2-}]\,[H_3O^+]}{[HC_2O_4^-]}$$

4. The equilibrium reaction for the first stage of ionisation of carbonic acid can be given as;

$$H_2CO_3(aq) \; + \; H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

If α is the degree of ionisation of the carbonic acid at the given concentration, the initial and equilibrium concentrations of different species in the solution would be as follows

Concentration/ mol dm^{-3}	$H_2CO_3(aq) + H_2O\ (l) \rightleftharpoons$	$H_3O^+(aq)$ +	$HCO_3^-(aq)$
Initial	1.0	0	0
Change due to ionisation	$-\alpha$	α	α
At equilibrium	$1-\alpha$	α	α

The equilibrium constant for the ionisation reaction is given as

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$$

Substituting the value of the ionisation constant and the equilibrium concentrations from the table above in the equilibrium constant expression, we get

$$4.4 \times 10^{-7} = \frac{[\alpha][\alpha]}{[1-\alpha]} \Rightarrow \frac{[\alpha^2]}{[1-\alpha]}$$

Since it is assumed to be a weak acid, ignoring α in the denominator we get,

$$\alpha^2 = 4.4 \times 10^{-7} \Rightarrow \alpha = 0.00066$$

As the value of α is about 0.07% so our assumption is valid and we get the concentrations of bicarbonate and hydronium ions as

$$[HCO_3^-] = [H_3O^+] = c\alpha$$

Substituting the values

$$\Rightarrow \quad [HCO_3^-] = [H_3O^+] = 1\times 6.6\times 10^{-4} = 6.6\times 10^{-4} M$$

The equilibrium equation for the second stage of ionisation of carbonic acid can be given as;

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

Assuming α to be the degree of ionisation, the initial and equilibrium concentrations of different species in the solution would be as follows

Concentration/ mol dm^{-3}	HCO_3^- (aq) + H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	CO_3^{2-}(aq)
Initial	6.6×10^{-4}	6.6×10^{-4}	0
Change due to ionisation	$-6.6 \times 10^{-4}\alpha$	$6.6 \times 10^{-4}\alpha$	$6.6 \times 10^{-4}\alpha$
At equilibrium	$6.6 \times 10^{-4}(1-\alpha)$	$6.6 \times 10^{-4}(1+\alpha)$	$6.6 \times 10^{-4}\alpha$

The equilibrium constant expression for second stage of ionisation

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$$

Substituting the equilibrium concentrations from the table in the equilibrium constant expression, we get

$$\frac{[6.6\times 10^{-4}(1+\alpha)]\,[6.6\times 10^{-4}\alpha)]}{[6.6\times 10^{-4}(1-\alpha)]} = 4.7\times 10^{-11}$$

Since the second stage ionisation is like that of a weak acid, we can assume α to be negligible as compared to 1 in the numerator and denominator, we get

$$[6.6\times 10^{-4}\alpha)] = 4.7\times 10^{-11}$$

$$\alpha = \frac{4.7\times 10^{-11}}{6.6\times 10^{-4}} = 7.1\times 10^{-8}$$

$$\Rightarrow \quad \alpha = 7.1\times 10^{-8}$$

As the value of α is quite small as compared to the initial concentration of bicarbonate ions (6.6×10^{-4} M) our ignoring it is justified.

From the table above, the concentration of CO_3^{2-} ions= $6.6 \times 10^{-4}\alpha$

$$\Rightarrow [CO_3^{2-}] = 6.6\times 10^{-4}\times 7.1\times 10^{-8} = 4.7\times 10^{-11} M$$

So the concentration of CO_3^{2-} ions would be = 4.7×10^{-11} M

The concentration of H_2CO_3 would be equal to the initial concentration (1.0 M) minus the degree of ionisation of first stage i.e.,

1.0 –0.00066 = 0.99934 M

So the concentrations of different species in the 1.0 M solution of carbonic acid would be

$$[HCO_3^-] = 6.6 \times 10^{-4} M \qquad [H_3O^+] = 6.6 \times 10^{-4} M$$

$$[CO_3^{2-}] = 4.7 \times 10^{-11} M \qquad [H_2CO_3^-] = 0.99934 M$$

5. In case of nitric acid there are two oxygen atoms attached to the nitrogen atom, whereas nitrous acid has only one. Due to higher electronegativity, these would withdraw electrons from nitrogen atom and make the OH bond polar leading to greater tendency to lose proton. As there are two such oxygen atoms in nitric acid, the effect would be more pronounced in it and nitric acid would be stronger than nitrous acid.

6. According to the Henderson-Hasselbalch equation the pH of the acetic acid-sodium acetate buffer would be given as

$$\Rightarrow \quad pH = pK_a + \log \frac{[\text{Sodium acetate}]}{[\text{Acetic acid}]}$$

First let's compute the value of pK_a

$$pK_a = -\log K_a = -\log[1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

The concentrations of sodium acetate and acetic acid in the buffer mixture can be calculated by using dilution formula.

The total volume of the solution = 100 cm^3+ 200 cm^3= 300 cm^3.

Concentration of acetic acid in the buffer solution

$$M_2 = \frac{M_1V_1}{V_2} = \frac{0.3 \times 100}{300} = 0.10 \text{ M}$$

Concentration of sodium acetate in the buffer solution

$$M_2 = \frac{M_1V_1}{V_2} = \frac{0.6 \times 200}{300} = 0.40 \text{ M}$$

The pH can be calculated using Henderson-Hasselbalch equation, viz.,

$$\Rightarrow \quad pH = pK_a + \log \frac{[\text{Sodium acetate}]}{[\text{Acetic acid}]}$$

Substituting the values in the equation we get,

$$\Rightarrow \quad pH = 4.74 + \log \frac{[0.40]}{[0.10]} = 4.74 + \log 4$$

$$= 4.74 + 0.602 = 5.34$$

Thus the pH of the given buffer solution would be **5.34**

7. b) As this buffer has the maximum absolute concentrations of the components of the buffer and also the two concentrations are equal.

Terminal Questions

1. The ionisation constant refers to the equilibrium constant for the ionisation reaction of a weak acid or a weak base. The ionisation constant for a weak base is a measure of the extent of its ionisation. Higher the value of the ionisation constant greater the ionisation and thus stronger the base

2. The equilibrium reaction for the ionisation of formic acid, can be given as under:

$$\text{HCOOH (aq)} + H_2O(l) \rightleftharpoons H_3O^+ \text{(aq)} + \text{HCOO}^- \text{(aq)}$$

The ionisation constant expression for ionisation of formic acid would be

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

3. The degree of ionisation of a weak acid increases with dilution. In order to understand the variation of degree of ionisation with dilution we write the expression relating the ionisation constant and degree of ionisation for a weak acid as

$$K_a = c\alpha^2$$

As the concentration varies inversely with volume of the solution containing unit amount of the solute, we write, $c=1/V$. Substituting in the above equation we get,

$$K_a = \frac{1}{V}\alpha^2$$

If dilution increases, the value of $1/V$ decreases and to keep K_a constant, the degree of ionisation increases. Thus the degree of ionisation increases with dilution.

4. The equilibrium reaction for the ionisation of dimethylamine in water, can be given as under:

$$(CH_3)_2NH \text{ (aq)} + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+\text{(aq)} + OH^-\text{(aq)}$$

If the degree of ionisation of dimethylamine in this solution is α, the initial and equilibrium concentrations of various species in the solution would be

Concentration/ mol dm^{-3}	$(CH_3)_2NH$ (aq) + H_2O (l) $\rightleftharpoons$	$(CH_3)_2NH_2^+$(aq) +	OH^-(aq)
Initial	0.1	0	0
Change due to ionisation	-0.1α	0.1α	0.1α
At equilibrium	$0.1(1-\alpha)$	0.1α	0.1α

We can write the following expression relating the base ionisation constant and degree of ionisation.

$$K_b = \frac{c\alpha^2}{(1-\alpha)} \Rightarrow K_b = \frac{0.1\alpha^2}{(1-\alpha)}$$

Assuming that for the weak base α, is small as compared to 1, we can ignore it in the denominator, we get

$$K_b = 0.1\alpha^2 \quad \Rightarrow \quad \alpha = \sqrt{\frac{K_b}{0.1}}$$

Substituting the values of K_b,

$$\alpha = \sqrt{\frac{5.1\times10^{-4}}{0.1}} = \sqrt{5.1\times10^{-3}} = 0.072$$

Degree of ionisation, $\alpha = 0.072$

The value of degree of ionisation (0.072) is more than 5% of the initial concentration, so our assumption of it being small and neglecting it is not valid. So going back to the expression for K_b, we had

$$\Rightarrow \; K_b = \frac{0.1\alpha^2}{(1-\alpha)}$$

Substituting the value of ionisation constant again,

$$\Rightarrow \; 5.1\times10^{-4} = \frac{0.1\alpha^2}{(1-\alpha)}$$

Simplifying and rearranging, we get

$$(5.1\times10^{-4}) - (5.1\times10^{-4})\alpha = 0.1\alpha^2$$

$$\Rightarrow 0.1\alpha^2 + (5.1\times10^{-4})\alpha - (5.1\times10^{-4}) = 0$$

We need to solve the above quadratic equation to get the degree of dissociation. You may recall that for a quadratic equation, $ax^2 + bx + c = 0$, the value of x can be obtained by the following equation

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

In case of our quadratic equation, we get

$$\Rightarrow \; \alpha = \frac{-(5.1\times10^{-4}) \pm \sqrt{(5.1\times10^{-4})^2 - 4\times0.1\times(-5.1\times10^{-4})}}{2\times0.1}$$

$$\Rightarrow \alpha = \frac{-(5.1\times10^{-4}) \pm \sqrt{(2.60\times10^{-7}) + (2.04\times10^{-4})}}{0.2}$$

$$\Rightarrow \; \alpha = \frac{-(5.1\times10^{-4}) \pm \sqrt{2.04\times10^{-4}}}{0.2}$$

$$\Rightarrow \alpha = \frac{-(5.1\times10^{-4}) \pm 1.43\times10^{-2}}{0.2} = \frac{1.38\times10^{-2}}{0.2} = 6.9\times10^{-2}$$

$$\alpha = 6.9\times10^{-2}$$

From the table above, we see that the concentration of hydroxide ions, $[OH^-]$ at equilibrium = $0.1\times \alpha = 0.1 \times 0.069 = 0.0069 = 6.9 \times 10^{-3}$ M

We know that

$$pOH = -\log[OH^-]$$

Substituting the value of $[OH^-]$

$$pOH = -\log\,[6.9\times10^{-3}]$$

$$pOH = -(-2.16) = 2.16$$

You know that at 298 K, pH + pOH = 14

$$pH = 14 - pOH$$

$$\Rightarrow \quad pH = 14 - 2.16 = 11.84$$

5. The equilibrium reaction for the ionisation of the weak acid-lactic acid, $CH_3CH(OH)COOH$, can be given as under:

$$CH_3CH(OH)COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CH(OH)COO^-(aq)$$

If the degree of ionisation of *c* mol dm^{-3} solution of lactic acid is assumed to be α, the initial and equilibrium concentrations of various species in the solution would be

Concentration / mol dm^{-3}	$CH_3CH(OH)COOH(aq) + H_2O(l) \rightleftharpoons$	$H_3O^+(aq)+$	$CH_3CH(OH)COO^-(aq)$
Initial	c	0	0
Change due to ionisation	$-c\alpha$	$c\alpha$	$c\alpha$
At equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

The equilibrium constant for the ionisation reaction of lactic acid can be written as

$$K_a = \frac{[H_3O^+][CH_3CH(OH)COO^-]}{[CH_3CH(OH)COOH]}$$

Substituting the concentrations of different species at equilibrium in the expression we get,

$$K_a = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \quad \Rightarrow \quad cK_a = \frac{c^2\alpha^2}{(1-\alpha)}$$

As lactic acid is a weak acid, we can ignore α in the denominator, we get

$$cK_a = c^2\alpha^2$$

From the table above we see that $c\alpha$ is equal to the concentration of hydronium ions. Substituting,

$$cK_a = [H_3O^+]^2$$

$$c = \sqrt{\frac{[H_3O^+]^2}{K_a}}$$

So we can calculate the concentration of hydronium ions from the given value of pH and substitute the same in the above expression to get the concentration of the solution.

Let's now calculate the concentration of hydronium ions:

We know that pH= $-\log_{10}[H_3O^+]$ ➔ $[H_3O^+]$ = antilog (–pH)

➔ $[H_3O^+]$ = antilog (–3.7) = 2.0×10^{-4}M

We know that,

$$c = \sqrt{\frac{[H_3O^+]^2}{K_a}}$$

Substituting the values of hydronium ion concentration and of K_a, we get

$$\Rightarrow \quad c = \sqrt{\frac{[2\times10^{-4}]^2}{1.4\times10^{-7}}} = \sqrt{\frac{4\times10^{-8}}{1.4\times10^{-7}}} = \sqrt{0.286} = 0.5345\,\text{M}$$

Thus, the concentration of the given solution of lactic acid is found to be 0.5345 M

6. In case of sulphuric acid, there are two oxygen atoms attached to the sulphur besides the hydroxyl group whereas there is only one such oxygen atom in sulphurous acid. These oxygen atoms would withdraw electrons from sulphur atom due to their higher electronegativity. This in turn would make the OH bond more polar leading to its greater tendency to lose proton. Due to two such oxygen atoms the hydroxyl groups would be more polar in sulphuric acid than that in sulphurous acid. Therefore, of the given two acids, sulphuric acid would be stronger.

7. The equilibrium reaction for the first stage of ionisation of adipic acid can be given as;

$$(CH_2)_4(COOH)_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HOOC(CH_2)_4(COO)^-(aq)$$

If α is the degree of ionisation of adipic acid in the given solution, the initial and equilibrium concentrations of different species in 0.1 M solution of adipic acid would be as follows

Concentration/ mol dm^{-3}	$(CH_2)_4(COOH)_2(aq)+H_2O(l) \rightleftharpoons H_3O^+(aq)+HOOC(CH_2)_4(COO)^-(aq)$		
Initial	0.1	0	0
Change due to ionisation	-0.1α	0.1α	0.1α
At equilibrium	$0.1(1-\alpha)$	0.1α	0.1α

The equilibrium constant for the reaction would be

$$K_{a1} = \frac{[HOOC(CH_2)_4COO^-][H_3O^+]}{[HOOC(CH_2)_4COOH]}$$

Substituting the equilibrium concentrations from the table in the equilibrium constant expression, we get

$$K_{a1} = \frac{[0.1\alpha][0.1\alpha]}{0.1\,[1-\alpha]} = \frac{[0.1\alpha^2]}{[1-\alpha]}$$

Substituting the value of K_a,

$$3.9\times10^{-5} = \frac{[0.1\alpha^2]}{[1-\alpha]}$$

As adipic acid is a weak acid, therefore, ignoring α in the denominator we get,

$$0.1\alpha^2 = 3.9\times10^{-5} \Rightarrow \alpha = 0.00197$$

As the value of α is about 0.2% our assumption is valid. From the table we can write,

$$\rightarrow [HOOC\,(CH_2)_4COO^-] = [H_3O^+] = c\alpha = 0.1\times0.00197 = 1.97\times10^{-4}$$

Now, the equation for the second stage of ionisation of adipic acid can be given as;

$$HOOC(CH_2)_4(COO)^-(aq)+H_2O(l) \rightleftharpoons H_3O^+(aq)+ (CH_2)_4(COO^-)_2(aq)$$

Again, assuming α to be the degree of ionisation, the initial and equilibrium concentrations of different species would be as follows

Concentration/ mol dm^{-3}	$HOOC(CH_2)_4(COO)^-(aq)+ H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) +(CH_2)_4(COO^-)_2\ (aq)$		
Initial	1.97×10^{-4}	1.97×10^{-4}	0
Change due to ionisation	$-1.97\times10^{-4}\alpha$	$1.97\times10^{-4}\alpha$	$1.97\times10^{-4}\alpha$
At equilibrium	$1.97\times10^{-4}(1-\alpha)$	$1.97\times10^{-4}(1+\alpha)$	$1.97\times10^{-4}\alpha$

The equilibrium constant expression for second stage of ionisation of adipic acid would be

$$K_{a2} = \frac{[(CH_2)_4(COO^-)_2][H_3O^+]}{[HOOC(CH_2)_4COO^-]}$$

Substituting the equilibrium concentrations from the table in the equilibrium constant expression, we get

$$\frac{[1.97\times10^{-4}(1+\alpha)][1.97\times10^{-4}\alpha]}{[1.97\times10^{-4}(1-\alpha)]} = 3.9\times10^{-6}$$

For the weak acid, assuming α to be negligible as compared to 1 in the numerator and denominator, we get

$$[1.97\times10^{-4}\alpha] = 3.9\times10^{-6}$$

$$\alpha = \frac{3.9\times10^{-6}}{1.97\times10^{-4}} = 1.98\times10^{-2}$$

$$\Rightarrow \quad \alpha = 1.98\times10^{-2}$$

From table, the concentration of $(CH_2)_4(COO^-)_2$ ions would be

$= 1.97\times10^{-4}\,\alpha$ M

Substituting the value for α,

$= 1.97 \times 10^{-4} \times 1.98 \times 10^{-2}$ M

$= 3.9 \times 10^{-6}$ M

The concentration of undissociated adipic acid would be equal to the initial concentration (0.1 M) minus the concentration of hydronium ions i.e., 1.97×10^{-4}

$$0.10 - (1.97\times10^{-4}) = 0.0998$$

So the concentrations of different species in the 0.1 M solution of adipic acid would be

$$[HOOC(CH_2)_4COO^-] = [H_3O^+] = 1.97\times10^{-4}\,M$$

$$[(CH_2)_4(COO^-)_2] = 3.90\times10^{-6}\,M$$

$$[(CH_2)_4(COOH)_2] = 9.98\times10^{-2}\,M$$

8. The presence of common ions in an aqueous solution of a weak acid decreases the degree of ionisation of the weak acid. Let us understand with the help of the ionisation of formic acid (0.1 M) and the effect of addition of sodium formate (0.2 M) to it. K_a (HCOOH) = 1.7×10^{-4}.

   The equilibrium reaction for the ionisation of formic acid, can be given as under:

$$\text{HCOOH (aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{HCOO}^-\text{(aq)}$$

From example 8.1, the degree of ionisation of a weak acid is given as

$$\alpha = \sqrt{\frac{K_a}{c}}$$

Substituting the values of K_a and c we get, $\alpha = \sqrt{\frac{1.7\times10^{-4}}{0.1}} = 0.0041$

Thus, the degree of ionisation of formic acid in 0.1 M solution = 0.0041

We generally add solid salt so that there is no dilution

Now if we add sodium formate to the solution such that its concentration in solution is 0.2 M.

The salt sodium formate would dissociates as

$$\text{HCOONa (aq)} \rightarrow \text{Na}^+\text{(aq)} + \text{HCOO}^-\text{(aq)}$$

If the degree of ionisation of formic acid in this solution of formic acid and sodium formate is α, then the initial and equilibrium concentrations of various species in the solution would be

Concentration/mol dm^{-3}	HCOOH (aq)+ H_2O (l) $\rightleftharpoons$	H_3O^+(aq)	+ $HCOO^-$(aq.)
Initial	0.1	0	0
Change due to ionisation of formic acid	-0.1α	0.1α	0.1α
Change due to dissociation of sodium formate	0	0	0.2
At equilibrium	$0.1(1-\alpha)$	0.1α	$0.2(1+0.5\alpha)$

We can write the expression for acid ionisation constant of formic acid as

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

Substituting the equilibrium concentrations of different species from the table, we get

$$K_a = \frac{[0.1\alpha][0.2(1+0.5\alpha)]}{[0.1(1-\alpha)]}$$

As formic acid is a weak acid and its degree of ionisation is further suppressed by the presence of formate ions (the common ion) we can reasonably assume that

$\alpha << 1$; and $(1-\alpha) \sim 1$; also $(1 + 0.5\alpha) \sim 1$

Under these conditions we can write

$$K_a = \frac{[0.1\alpha][0.2]}{[0.1]} = [0.2\alpha]$$

Substituting the value of the acid ionisation constant, K_a

$$1.7 \times 10^{-4} = [0.2\alpha] \Rightarrow \alpha = 8.5 \times 10^{-4}$$

So the degree of ionisation of formic acid in the given solution = 0.00085.

➔ The degree of ionisation of formic acid decreased from 0.0041 to 0.00085 due to the common ions provided by sodium formate.

9. A buffer solution can be defined as a solution that resists change in its pH on addition of small volumes of solutions of strong acids or bases or on slight dilution. A basic buffer solution consists of a weak base and a salt having an ion common with the weak base. The pH of a basic buffer solution is given by the following expression.

$$\Rightarrow \text{pOH} = \text{p}K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

Where [salt] refers to the concentration of the salt and [base] represents the concentration of weak base in the solution. pK_b is the negative log of the base ionisation constant K_b.

10. The pH of these solutions can be calculated by using Henderson-Hasselbalch equation,

$$\Rightarrow \text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

First let's compute the value of pK_a

$$\text{p}K_a = -\log K_a = -\log[1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

i) substituting the values we get

$$\Rightarrow \quad \text{pH} = 4.74 + \log\frac{[1.5]}{[1.5]} = 4.74 + 0 = 4.74$$

ii) $$\Rightarrow \quad \text{pH} = 4.74 + \log\frac{[0.15]}{[0.15]} = 4.74 + 0 = 4.74$$

Both of the buffer solutions would have same pH value of 4.74. However, the buffer (i) having the higher concentrations of acid and the salt (1.5 M) would have a higher buffer capacity

UNIT 9

IONIC EQUILIBRIUM-III

Structure

9.1 INTRODUCTION

In the previous two units on ionic equilibrium you have learnt about the nature of electrolytes, theories of acids and bases, concept of pH, behaviour of weak acids and bases including diprotic and polyprotic acids, common ion effect and buffer solutions. You have also learnt about calculating the pH of aqueous solutions of acids, bases and buffer solutions. In this last unit of the block we would continue our discussion on ionic equilibrium and would take up the hydrolysis of different types of salts and solubility equilibria of sparingly soluble salts.

In the context of hydrolysis of salts we would discuss the meaning of hydrolysis and define the term, 'degree of hydrolysis'. This would then be used to qualitatively predict the acid-base nature of the salt solutions. Thereafter, the hydrolysis equilibrium would be characterised in terms of hydrolysis constant and will be related to the acid/ base ionisation constants of the conjugate acid/base of the ions getting hydrolysed. We would also work out the expressions for calculating the pH of the aqueous solutions of different types of salts.

The discussion on hydrolysis of salts would be followed by the equilibria associated with the solubility of sparingly soluble salts. In this context we would introduce the concept of solubility product constant and relate it to the solubility for different types of salts. The effect of common ions and of the solution pH on the solubility equilibrium and hence the solubility would also be taken up. Towards the end of the unit we would take up important qualitative and quantitative applications of solubility product principle.

In the next block of this course you would learn about preparation of aromatic compounds.

Expected Learning Outcomes

After studying this unit, you should be able to:

- explain the hydrolysis behaviour of different types of salts;
- differentiate between the hydrolysis behaviour of acidic, basic and neutral salts;
- predict whether an aqueous solution of a given salt would be acidic, basic or neutral;
- define degree of hydrolysis and hydrolysis constant, and derive a relationship between them;
- derive expressions for calculating the pH of aqueous solutions of different types of salts;
- calculate the pH of aqueous solutions of different types of salts;
- define solubility and express the solubility equilibrium of sparingly soluble salts in terms of suitable expressions;
- derive the relationship between solubility and solubility product constant for salts of AB, AB_2, A_2B and A_2B_3 types;
- explain the effect of common ion on solubility equilibrium of sparingly soluble salts;
- discuss the effect of pH on the solubility of sparingly soluble salts; and
- discuss some quantitative and qualitative applications of solubility product principle.

9.2 SALT HYDROLYSIS

As you are aware, that salts are produced as a result of neutralisation reaction between an acid and a base. What would be the acid-base nature of the aqueous solutions prepared from these salts? Will they be acidic, basic or neutral? Let's check!

Let's take 100 cm^3 of distilled water each in three beakers labelled as 1,2 and 3 and add 0.5 g of sodium chloride to beaker labelled as 1, 0.5 g of sodium acetate to beaker labelled as 2 and 0.5 g of ammonium chloride to beaker labelled as 3. If we measure the pH of the resulting solutions at 298 K, we find that the solution of sodium chloride has a pH of 7.0; the pH of ammonium chloride is in acidic range whereas that of sodium acetate solution is found to be in basic range. The question comes up is "why do different salt solutions have different acid-base behaviour?" To understand this let's analyse the behaviour of the ions produced when these salts are dissolved in water.

Dissolution of Sodium Chloride

On dissolving sodium chloride in water, the water molecules hydrate the ions in the lattice of the salt and as a result of the energy released in the process the ions dissociate from the lattice and are released in the solution. The overall process can be given as

$$NaCl(s) + H_2O(l) \rightarrow Na^+(aq) + Cl^-(aq) \qquad \ldots(9.1)$$

The ions so produced (Na^+ and Cl^-) do not react with water and move freely in solution.

$$Na^+(aq) + H_2O(l) \rightarrow \text{No reaction} \qquad \ldots(9.2)$$

$$Cl^-(aq) + H_2O(l) \rightarrow \text{No reaction} \qquad \ldots(9.3)$$

Let's learn why don't these ions react with water? You would recall the ionisation of hydrochloric acid in water is given as

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \qquad \ldots(9.4)$$

Here, water molecules accept a proton from HCl and form hydronium ions. As hydrochloric acid is a strong acid, the reaction goes to completion in the forward direction i.e., there is no backward reaction. You may note that in this reaction, there are two bases viz., H_2O and Cl^- ions. Since the reaction does not go in backward direction i.e., here the chloride ions do not accept a hydrogen ion to form HCl; we can say that Cl^- ion (anion of strong acid, HCl) is much weaker a base than H_2O and does not react with it. That explains the reaction in Eq. (9.3). Similarly, we can consider the ionisation of NaOH which can be shown as

The anion of a strong acid is a much weaker base than H_2O and does not react with water.

$$NaOH(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) \qquad \ldots(9.5)$$

Here again the reaction goes to completion in the forward direction. This implies that sodium ions (cations of a strong base) are much weaker an acid than water and do not react with it. As both (Na^+ and Cl^-) the ions do not react with water the solution is neutral as it contains equal number of hydronium and hydroxide ions from autoprotolysis of water. Such salts are called **neutral salts.**

Dissolution of Sodium Acetate

On dissolution of sodium acetate in water the ions in the lattice are hydrated and are dissociated from the lattice due to the energy released during their hydration. The overall process can be given as

$$CH_3COONa(s) + H_2O(l) \rightarrow Na^+(aq) + CH_3COO^-(aq) \qquad \ldots(9.6)$$

The reactions of ions (Na^+ and CH_3COO^-) so produced with water are as under

$Na^+(aq) + H_2O(l) \rightarrow$ No reaction …(9.2)

$$\underset{\text{Base}_1}{CH_3COO^-(aq)} + \underset{\text{Acid}_2}{H_2O(l)} \rightleftharpoons \underset{\text{Acid}_1}{CH_3COOH(aq)} + \underset{\text{Base}_2}{OH^-(aq)} \quad \text{…(9.7)}$$

Here, the acetate ions accept hydrogen ion from water and act as a base as per Brønsted-Lowry concept. In other words, the anion (CH_3COO^-) of weak acid (CH_3COOH) acts as a stronger base as compared to water. Secondly, as before, the cation (Na^+) of a strong base (NaOH) does not react with water. As the reaction produces OH^- ions, the resulting solution is basic and the pH is more than 7 at 298 K. Such salts are called **basic salts**.

Dissolution of Ammonium Chloride

On dissolution of ammonium chloride in water the ions in the lattice are hydrated and are dissociated from the lattice due to the energy released during their hydration. The overall process can be given as

$NH_4Cl(s) + H_2O(l) \rightarrow NH_4^+(aq) + Cl^-(aq)$ …(9.8)

The reactions of ions (NH_4^+ and Cl^-) so produced with water are as under

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ …(9.9)

$Cl^-(aq) + H_2O(l) \rightarrow$ No reaction …(9.3)

Here, the ammonium ions donate hydrogen ion to water and act as an acid as per Brønsted-Lowry concept. In other words, the cation of a weak base acts as a stronger acid than water. As the reaction produces H_3O^+ ions, the resulting solution is acidic and hence the pH is less than 7 at 298 K. Secondly, as before the anion (Cl^-) of a strong acid (HCl) does not react with water.

In the process of dissolution of a salt in water, the solvent molecules hydrate the ions in the lattice and the energy so released overcomes the lattice energy binding the ions together. As a result the solvated ions dissociate from the lattice and come into the solution as solvated (hydrated here) ions.

In these examples we have seen the behaviour of different ions in aqueous solutions. Of the four ions taken up, we find that two (CH_3COO^- and NH_4^+)of these ions do react with water. This reaction of anions or/and cations produced by the salts with water is called **salt hydrolysis**. You may note here that the anions of weak acids produce the conjugate acid and hydroxide ion whereas the cations of weak bases give the conjugate base and hydronium ion on reaction with water. Accordingly, the resulting solution is basic or acidic respectively. Now the question is that, "What would be the nature of solution obtained by dissolving NH_4NO_2– a salt of a weak acid and a weak base in water?" Write your response here before you move ahead.

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You know that $NH_4NO_2$is formed by neutralization of a weak acid (HNO_2) by a weak base (NH_4OH). Therefore, you are right to think that in this case both, the anion as well the cation produced on dissolution of NH_4NO_2 would undergo hydrolysis. The acid-base nature of this solution would then be determined by the relative amounts of the hydronium and hydroxide ions produced in solution due to their hydrolysis. We would discuss the basis to answer this question in the next subsection.

9.2.1 Hydrolysis Constants and Degree of Hydrolysis

In order to learn about quantitative aspects of the salt hydrolysis, let us take up the equilibrium given in Eq. (9.7). This reaction represents the hydrolysis of acetate ions.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \quad \text{…(9.7)}$$

As the equilibrium in this reaction concerns the *hydrolysis* of an ion it can be called as **hydrolysis equilibrium** and the equilibrium constant characterising it is called **hydrolysis constant,** K_h. The hydrolysis constant expression for the reaction in Eq. (9.7) would be

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad \text{…(9.10)}$$

In this reaction Eq. (9.7)) acetate ion behaves as a weak base and the equilibrium can be seen as for the ionisation of a weak base and the equilibrium constant can be seen as K_b −the ionisation constant for the weak base

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

Let's multiply the numerator and denominator of the Eq. (9.10)by the concentration of hydronium ions, $[H_3O^+]$.

$$K_h = \frac{[CH_3COOH][OH^-][H_3O^+]}{[CH_3COO^-][H_3O^+]} \quad \text{…(9.11)}$$

On reorganising the terms, we get

$$K_h = \left(\frac{[CH_3COOH]}{[CH_3COO^-][H_3O^+]}\right) \times \left([OH^-][H_3O^+]\right) \quad \text{…(9.12)}$$

Don't you find the first and second terms in Eq. (9.12) familiar? Let's recall the ionisation of acetic acid in water and the corresponding ionisation constant

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \quad \text{…(9.13)}$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \quad \text{…(9.14)}$$

You can note that the first term on the right hand side in Eq. (9.12) is the reciprocal of the expression in Eq. (9.14). Further, the second term in the Eq. (9.12) is nothing but the K_w, the ionic product of water. Substituting these into Eq. (9.12) we get an important relation.

$$K_h = \left(\frac{[CH_3COOH]}{[CH_3COO^-][H_3O^+]}\right) \times \left([OH^-][H_3O^+]\right) = \frac{1}{K_a} \times K_w \quad \text{…(9.15)}$$

$$K_h = \frac{K_w}{K_a} \text{ or } K_aK_h = K_w \quad \text{…(9.16)}$$

This implies that the product of K_h of the anion acting as a base and K_a of its conjugate acid equals ionic product of water (K_w).You may take note from Eq.(9.15) that the hydrolysis constant (K_h) of the anion of a salt varies inversely as the ionisation constant K_a of the corresponding conjugate acid. That is, *weaker the acid, greater is the hydrolysis constant of its* anion.

If we replace K_h in Eq. (9.16) by K_b

$$K_aK_b = K_w$$

we can say that for conjugate acid–base pairs the product of acid- and base-ionisation constants in aqueous solution equals the ionic product constant of water.

Similarly, we can consider the hydrolysis equilibrium given in Eq.(9.9) wherein ammonium ions hydrolyse by donating a hydrogen ion(act as a weak acid) to water.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad \ldots(9.9)$$

The expression for hydrolysis constant would be as follows

$$K_h = \frac{[H_3O^+][NH_3]}{[NH_4^+]} \qquad \ldots(9.17)$$

Again by multiplying the numerator and the denominator of the expression by concentration of hydronium ions, $[H_3O^+]$ and reorganising the terms as before, we would get

$$\Rightarrow \qquad K_h = \frac{K_w}{K_b} \qquad \text{or} \qquad K_h K_b = K_w \qquad \ldots(9.18)$$

In this reaction (Eq. 9.9) ammonium on behaves as a weak acid and the equilibrium can be seen as for the ionisation of a weak acid and the equilibrium constant can be seen as K_a −the ionisation constant for the weak acid

$$K_a = \frac{[H_3O^+][NH_3]}{NH_4^+}$$

This implies that the product of K_h of the cation acting as a weak acid and K_b of its conjugate base equals ionic product of water (K_w). Further, the hydrolysis constant (K_h) of the cation of a salt of a weak base varies inversely as the dissociation constant, $K_{b,}$ of the corresponding conjugate base. Having learnt about hydrolysis and its quantitative expression, let us define the term, 'degree of hydrolysis' and develop a relationship between the hydrolysis constant and degree of hydrolysis of an ion.

Degree of Hydrolysis

We can define a parameter called 'degree of hydrolysis' that is similar to the degree of ionisation or degree of dissociation defined in previous unit. This refers to the extent of hydrolysis or *the fraction of the anions of weak acids or cations of weak base in solution that react with water and get hydrolysed*. Like degree of ionisation or dissociation, the degree of hydrolysis is also represented in terms of Greek alphabet α (Some people prefer to use *h* or *x* as a symbol for the degree of hydrolysis; however we would use α). Let us consider the hydrolysis of an anion, $A^-$of the weak acid HA, taken in aqueous solution.

$$A^-(aq)+H_2O(l) \rightleftharpoons HA(aq)+OH^-(aq) \qquad \ldots(9.19)$$

If we take a salt solution containing *c* mol dm^{-3}of the anion, A^- of the weak acid HA, and assume that the degree of hydrolysis of the anion at this concentration is 'α'; then the initial and equilibrium concentrations of different species in the solution would be as follows

Concentration / mol dm^{-3}	$A^-(aq)$ + $H_2O(l) \rightleftharpoons$	HA(aq) +	$OH^-(aq)$
Initial	c	0	0
Change due to hydrolysis	$-c\alpha$	$c\alpha$	$c\alpha$
At equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

The equilibrium constant for the hydrolysis reaction for the anion can be written as

$$K_h = \frac{[HA][OH^-]}{[A^-]} \qquad \ldots(9.20)$$

You may note here that the same expression, Eq. (9.21), would be valid for the hydrolysis of the cation of a weak base.

Substituting the concentrations of different species at equilibrium, from the table above, in Eq. (9.20) we get,

$$K_h = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \Rightarrow K_h = \frac{c\alpha^2}{(1-\alpha)} \qquad \ldots(9.21)$$

Assuming that α, is small as compared to 1, we can ignore it in the denominator of Eq. (9.21), we get

$$K_h = c\alpha^2 \qquad \alpha = \sqrt{\frac{K_h}{c}} \qquad \ldots(9.22)$$

Recall from Eq. (9.16),

$$K_h = \frac{K_w}{K_a} \qquad \ldots(9.16)$$

Substituting it in Eq.(9.22) we get,

$$\alpha = \sqrt{\frac{K_w}{K_a c}} \qquad \ldots(9.23)$$

Thus, knowing the values of K_w, K_a and the concentration of the anion we can calculate its degree of hydrolysis. Similarly we can derive a relationship between the degree of hydrolysis of a cation of a weak base and the ionisation constant of the weak base. The relationship would be

You may derive the relationship given in Eq. (9.24) in the same way.

$$\alpha = \sqrt{\frac{K_w}{K_b c}} \qquad \ldots(9.24)$$

Having learnt about the degree of hydrolysis of ions and their relationship with the acid/base dissociation constants of the conjugate acid/base we can now take up the question raised just before the beginning of the subsection 9.2.1. Recall that we asked for the acid-base nature of solution obtained by dissolving NH_4NO_2 in water. Let's take it as an example now and calculate the degree of hydrolysis of the ions obtained on its dissolution so as to check the acid-base nature of the aqueous solution of NH_4NO_2.

Example 9.1: Determine the acid-base nature of the aqueous solution obtained by dissolving NH_4NO_2 in water to get 0.01 M solution at 298 K.
[Given K_b (NH_4OH) =1.8×10^{-5}; K_a (HNO_2) = 4.5×10^{-4}]

Solution: The dissolution of ammonium nitrite in water involves the hydration of the ions and their dissociation from the lattice. The overall process can be given as

$$NH_4NO_2(s) + H_2O(l) \rightarrow NH_4^+(aq) + NO_2^-(aq) \qquad \ldots(9.25)$$

The reactions of the ions $(NH_4^+$ and $NO_2^-)$ so produced with water are as under

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad \ldots(9.26)$$

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq) \qquad \ldots(9.27)$$

In water ammonia exists as ammonium hydroxide (NH_4OH)

The degree of hydrolysis of ammonium ions would be given by Eq. (9.24)

$$\alpha = \sqrt{\frac{K_w}{K_b c}} \qquad \ldots(9.24)$$

where K_b is the base ionisation constant for the conjugate base (NH_4OH) of ammonium ion. Substituting the values at 298 K, we get

$$\Rightarrow \qquad \alpha = \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 10^{-2}}} = \sqrt{5.55 \times 10^{-8}} = 2.36 \times 10^{-4}$$

On the other hand the degree of hydrolysis of nitrite ions would be given by Eq. (9.23).

$$\alpha = \sqrt{\frac{K_w}{K_a c}} \qquad \ldots(9.23)$$

where K_a is the acid ionisation constant for the conjugate acid HNO_2. Substituting the values at 298 K, we get

$$\Rightarrow \qquad \alpha = \sqrt{\frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4} \times 10^{-2}}} = \sqrt{2.22 \times 10^{-9}} = 4.7 \times 10^{-5}$$

So we see that the degree of hydrolysis of ammonium ions that produce hydronium ions is more than that of nitrite ions which generate hydroxide ions. This means that in the solution the concentration of hydronium ions will be more than that of the hydroxide ions. ***Therefore the solution would be acidic and would have a pH value of less than 7.0 at 298* K.**

We have discussed about the acid-base nature of aqueous solutions of different types of salts on the basis of degree of hydrolysis. We can even work out mathematical equations for calculating the pH of salt solutions. However before we derive these equations solve the following SAQ to assess your understanding of the hydrolysis of salts.

SAQ 1

Define salt hydrolysis and calculate the degree of hydrolysis of benzoate ions in 0.01M aqueous solution of sodium benzoate at 298 K.
[Given: $K_a(C_6H_5COOH) = 6.5 \times 10^{-5}$ at 298 K]

SAQ 2

In the salts listed in the first column of the table given below, write the ion (s) that will be hydrolysed in the column 2 and the acid-base nature of the salt in the column 3 respectively.

Given: K_b (NH_4OH) = 1.8×10^{-5}; K_a (HCOOH) = 1.8×10^{-4};
K_a (C_6H_5COOH) = 6.5×10^{-5}

Salt	Ion (s) that will be hydrolysed	Acid-base nature of the resulting aqueous solution of the salt
HCOONa		
NH_4Br		
$C_6H_5COONH_4$		

9.3 pH OF SALT SOLUTIONS

You have so far learnt that when salts dissolve in water the ions present in the lattice get hydrated and dissociate from the lattice. Thereafter, in some cases the ions react with water molecules to either donate a hydrogen ion to it or accept a hydrogen ion from it and in the process act as an acid or a base. This produces hydronium or hydroxide ions and makes the solution acidic or basic respectively. Let's learn how to calculate the pH of such salt solutions. We would take four cases as:

a) Aqueous solution of salt of a strong acid and a strong base

b) Aqueous solution of salt of a weak acid and a strong base

c) Aqueous solution of salt of a strong acid and weak base

d) Aqueous solution of salt of a weak acid and a weak base

Let's begin with aqueous solution of salt of a strong acid and a strong base.

a) pH of aqueous solution of salt of a strong acid and a strong base

You would recall from above in section 9.2 that when a salt of a strong acid and a strong base e.g., NaCl dissolves in water the resulting ions do not react with water. That is, neither the anion nor the cation gets hydrolysed. In such a case the only source of hydronium and hydroxide ions in the solution is the autoprotolysis of water. As this process generates equal amounts of the hydronium and hydroxide ions so the resulting solution is neutral and has a pH of 7.0 at 298K.

b) pH of aqueous solution of salt of a weak acid and a strong base

Once again, as discussed above in section 9.2 when a salt of a weak acid and a strong base dissolves in water, the resulting cation remains unaffected and it is the anion that gets hydrolysed. For example, in case of dissolution of sodium acetate, the acetate (CH_3COO^-) ions react with water as under and get hydrolysed.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \qquad \ldots(9.6)$$

You have learnt above that if we start with a solution containing c mol dm^{-3} of the anion of the weak acid and assume that the degree of hydrolysis of the anion at this concentration to be α, then the hydrolysis constant is given as

$$K_\text{h} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \qquad \ldots(9.21)$$

and the equilibrium concentration of hydroxide ions obtained from hydrolysis is equal to $c\alpha$. Rearranging Eq. (9.21) and ignoring α in the denominator we get

$$cK_\text{h} = c^2\alpha^2 = [OH^-]^2$$

$$\Rightarrow \quad [OH^-] = \sqrt{cK_\text{h}} \qquad \ldots(9.28)$$

You know that, $[H_3O^+] = \dfrac{K_\text{w}}{[OH^-]}$

Substituting from Eq. (9.28)

$$\Rightarrow \quad [H_3O^+] = \frac{K_\text{w}}{\sqrt{cK_\text{h}}} = \sqrt{\frac{K_\text{w}^2}{cK_\text{h}}} \qquad \ldots(9.29)$$

Further, from Eq. (9.16),

$$\Rightarrow \quad K_\text{h} = \frac{K_\text{w}}{K_\text{a}}$$

Substituting in Eq. (9.29) we get

$$\Rightarrow \quad [H_3O^+] = \sqrt{\frac{K_\text{w}^2}{cK_\text{h}}} = \sqrt{\frac{K_\text{w}^2 K_\text{a}}{cK_\text{w}}} \qquad \ldots(9.30)$$

Simplifying,

$$\Rightarrow \quad [H_3O^+] = \sqrt{\frac{K_\text{w}K_\text{a}}{c}} \qquad \ldots(9.31)$$

Taking logarithm on both sides, we get

$$\log[H_3O^+] = \frac{1}{2}(\log K_\text{w} + \log K_\text{a} - \log c) \qquad \ldots(9.32)$$

Multiplying throughout by –1

$$-\log[H_3O^+] = -\frac{1}{2}\log K_\text{w} - \frac{1}{2}\log K_\text{a} + \frac{1}{2}\log c \qquad \ldots(9.33)$$

$$\text{pH} = \frac{1}{2}\text{p}K_\text{w} + \frac{1}{2}\text{p}K_\text{a} + \frac{1}{2}\log c \qquad \ldots(9.34)$$

We know that at 298 K, $pK_w = 14.0$ at 298K

$$\Rightarrow \quad pH = \frac{1}{2}(14) + \frac{1}{2}pK_a + \frac{1}{2}\log c \qquad \ldots(9.35)$$

$$\Rightarrow \quad pH = 7.0 + \frac{1}{2}pK_a + \frac{1}{2}\log c \qquad \ldots(9.36)$$

This is the desired expression for calculating the pH of an aqueous solution prepared by dissolving a salt of a weak acid with a strong base in water. You may note here that the second term in the Eq. (9.36) is positive and the third term is slightly negative at moderate concentrations; the resulting solution would have a pH>7.0 i.e., the solution would be basic.

You may say that in highly dilute solutions (say $c < 10^{-5}$ M), the third term may become larger then the second term and the pH may become less than 7.0. Here you must remember that at such low concentrations the autoprotolysis of water would become important and the concentration of hydroxyl ions from that could not be neglected and the pH would be close to 7 but the solution would remain basic.

Example 9.2: Calculate the pH of 0.01 M aqueous solution of sodium acetate at 298 K. [Given: K_a (CH_3COOH) =1.8×10^{-5} at 298K]

Solution: As sodium acetate is a salt of a weak acid and a strong base the pH of its aqueous solution would be given by the Eq. (9.36).

$$\Rightarrow \quad pH = 7.0 + \frac{1}{2}pK_a + \frac{1}{2}\log c \qquad \ldots(9.36)$$

Let's first calculate the pK_a for acetic acid (the conjugate acid of the anion)

$$pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = -(-4.74) = 4.74$$

Substituting the values of pK_a and c in Eq. (9.36)

$$\Rightarrow \quad pH = 7.0 + \frac{1}{2}(4.74) + \frac{1}{2}\log(1.0 \times 10^{-2})$$

$$\Rightarrow pH = 7.0 + 2.37 + \frac{1}{2}(-2.0) = 9.37 - 1.0 = 8.37$$

Thus, the pH of 0.01 M aqueous solution of sodium acetate would be 8.37.

c) pH of aqueous solution of salt of a weak base and a strong acid

Recall from Sec. 9.2 that when a salt of a weak base and a strong acid dissolves in water, the resulting anion remains unaffected and it is the cation that gets hydrolysed. For example, in case of dissolution of ammonium chloride, the ammonium (NH_4^+) ions react with water and get hydrolysed as under.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad \ldots(9.9)$$

You have also learnt above that for a c mol dm^{-3}aqueous solution of a cation of the weak base if we assume the degree of hydrolysis to be $\alpha$the hydrolysis constant of the cation is given as

$$K_h = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \qquad \ldots(9.21)$$

and the concentration of the resulting hydronium ions is equal to $c\alpha$.
Rearranging Eq. (9.21) and ignoring α in the denominator we get

$$cK_h = c^2\alpha^2$$

Substituting $c\alpha$ by [H_3O^+]

$$cK_h = [H_3O^+]^2$$

$$\Rightarrow \quad [H_3O^+] = \sqrt{cK_h} \qquad \ldots(9.37)$$

Further, from Eq. (9.18),

$$\Rightarrow \quad K_h = \frac{K_w}{K_b}$$

Substituting in Eq. (9.37), we get

$$\Rightarrow \quad [H_3O^+] = \sqrt{\frac{cK_w}{K_b}} \qquad \ldots(9.38)$$

Taking logarithm on both sides, we get

$$\log[H_3O^+] = \frac{1}{2}\log K_w - \frac{1}{2}\log K_b + \frac{1}{2}\log c \qquad \ldots(9.39)$$

Multiplying throughout by –1

$$-\log[H_3O^+] = -\frac{1}{2}\log K_w + \frac{1}{2}\log K_b - \frac{1}{2}\log c \qquad \ldots(9.40)$$

$$\text{pH} = \frac{1}{2}\text{p}K_w - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log c \qquad \ldots(9.41)$$

We know that, $pK_w(\text{at 298 K}) = 14.0$; substituting in Eq. (9.41)

$$\Rightarrow \quad \text{pH} = 7.0 - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log c \qquad \ldots(9.42)$$

This is the desired expression for the pH of an aqueous solution prepared by dissolving a salt of a weak base with a strong acid in water at 298 K. Remember that this equation is valid only at 298 K. At any other temperature the first term on the right would be different. Let us take an example to see the application of this expression.

Example 9.3: Calculate the pH of 0.001 M aqueous solution of ammonium chloride at 298 K. [Given: K_b (NH_4OH) =1.8×10^{-5}]

Solution: As ammonium chloride is a salt of a weak base with a strong acid its pH would be given by Eq. (9.42)

$$\Rightarrow \qquad \text{pH} = 7.0 - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log c \qquad \ldots(9.42)$$

Let's first calculate the pK_b for ammonium hydroxide (the conjugate base of the cation)

$$\text{p}K_b = -\log K_b = -\log\,[1.8 \times 10^{-5}] = -\,[-\,4.74] = 4.74$$

Substituting the values of pK_b and c in the Eq. (9.42)

$$\Rightarrow \quad \text{pH} = 7.0 - \frac{1}{2}(4.74) - \frac{1}{2}\log(1.0 \times 10^{-3})$$

$$\Rightarrow \quad \text{pH} = 7.0 - 2.37 - \frac{1}{2}(-3.0) = 4.63 + 1.50 = 6.13$$

Thus, the pH of 0.001 M aqueous solution of ammonium chloride at 298 K would be 6.13 i.e., the solution would be acidic.

d) pH of aqueous solution of salt of a weak acid and a weak base

On the basis of what you have learnt so far in this unit you understand that when a salt of a weak acid and a weak base dissolves in water the resulting anion as well as the cation would get hydrolysed. Let us consider a salt BA that dissociates to give the ions B^+ and A^- both of which get hydrolysed. The overall reaction of hydration and dissociation of the salt can be represented as

$$\text{BA(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{B}^+\text{(aq)} + \text{A}^-\text{(aq)} \qquad \ldots(9.43)$$

Here, both the ions would get hydrolysed. Though their concentrations would be same but the degree of their hydrolysis would depend on the magnitude of the ionisation constants of the corresponding conjugate acid/base. In other words, we may say that the pH of the solution would depend on the values of K_a, the acid dissociation constant of the conjugate acid of the anion as well as K_b, the base dissociation constant of the conjugate base of the cation. The exact treatment of the equilibria involved in this case is quite complex and beyond the scope of this course. However we can learn about the resulting expression and analyse the same. The expression for the pH of an aqueous solution prepared by dissolving the salt of a weak acid with a weak base in water at 298 K is as follows.

$$\text{pH} = 7.0 + \frac{1}{2}\text{p}K_a - \frac{1}{2}\text{p}K_b \qquad \ldots(9.44)$$

You may note a few things here. First, as expected the pH depends on the pK_a as well as the pK_b. Secondly, the pH does not depend on the concentration of the salt and thirdly, if the pK_a = pK_b, then the solution would be neutral and at

298 K the pH would be 7.0.In order to see the application of this expression let us take up the problem in the example 9.1 once again.

Example 9.4: Calculate the pH of a 0.01 M aqueous solution ofNH_4NO_2at 298 K. [Given: $K_b(NH_4OH) = 1.8 \times 10^{-5}$; $K_a(HNO_2) = 4.5 \times 10^{-4}$]

Solution: As ammonium nitrite is a salt of a weak acid and a weak base its pH would be given by Eq. (9.44).

$$\text{pH} = 7.0 + \frac{1}{2}\text{p}K_a - \frac{1}{2}\text{p}K_b \qquad \ldots(9.44)$$

We are given: $K_b(NH_4OH) = 1.8 \times 10^{-5}$and $K_a(HNO_2) = 4.5 \times 10^{-4}$, let's first calculate the corresponding pK values

$$\text{p}K_a = -\log K_a = -\log[4.5 \times 10^{-4}] = -[-3.35] = 3.35$$

$$\text{p}K_b = -\log K_b = -\log[1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

Substituting the values in Eq. (9.44)

$$\text{pH} = 7.0 + \frac{1}{2}(3.35) - \frac{1}{2}(4.74) = 6.31$$

Thus, the pH of the 0.01 M aqueous solution of NH_4NO_2 at 298 K would be 6.31.

Recall that in example 9.1 we argued and showed on the basis of degree of hydrolysis that the solution of ammonium nitrite would have an acidic pH. The same is substantiated now on the basis of detailed treatment of the equilibria and we are able even to calculate the pH of the solution.

Having learnt about different aspects of acid-base equilibria of aqueous solutions of different types of salts, solve the following simple questions to assess your understanding.

SAQ 3

100 cm^3 of 0.02 M sodium hydroxide solution is added to 100 cm^3 of 0.02 M solution of acetic acid at 298 K. Calculate the pH of the resulting solution.

[Given: $K_a(CH_3COOH) = 1.8 \times 10^{-5}$]

SAQ 4

Calculate the pH of 0.05 M aqueous solution of ammonium benzoate at 298 K.

[Given: $K_a(C_6H_5COOH) = 6.5 \times 10^{-5}$; $K_b(NH_4OH) = 1.8 \times 10^{-5}$]

9.4 SOLUBILITY EQUILIBRIA

You know that when we dissolve a solute in a solvent to make solution the amount of solute that dissolves in a given amount of solvent depends on the nature of solute, solvent and the temperature. The amount of solute that dissolves in 100 $cm^3$of the solvent at a given temperature is called its **solubility**. Closely related ionic solutes may have widely different solubilities, for example the solubility of NaF is about 4 g at 298 K whereas, we can dissolve about 36 g of sodium chloride in 100 $cm^3$of water at same temperature. As against these reasonably soluble ionic solids we can have some solids that are generally referred to as insoluble. For example, in gravimetric determination of chloride ions we precipitate them from their solution as silver chloride for their quantitative determination expecting all the chloride ions to be precipitated on adding silver ion solution.

However, if we take a dried sample of silver chloride, mix it in water and measure its electrical conductivity, we find that the conductivity is far more than that expected of pure distilled water. It indicates that silver chloride does dissolve in water to some extent and dissociates to provide ions that are responsible for the increase in electrical conductivity of its solution. The solubility of silver chloride is found to be about 1.82×10^{-4}g per 100 cm^3 of water at 298 K and such salts with extremely low solubilities are called sparingly soluble salts. We are going to discuss the equilibria in solutions of such sparingly soluble salts.

9.4.1 Solubility Product Constant

You have learnt above that when a soluble ionic compound like sodium acetate, dissolves in water, it dissociates completely into hydrated ions. The same holds true for the dissolved sparingly soluble salts also. That is, when a sparingly soluble salt MX is added to water an extremely small fraction of it dissolves and generates ions by dissociation. These ions may combine back to give solid salt and more of the salt may dissolve. Over a period of time equilibrium is established between the ions obtained from the dissociation of dissolved salt and the solid salt i.e., we get a saturated solution of the salt along with the undissolved solid salt. Such equilibrium for a salt of MX type in aqueous solution can be represented as

$$MX(s) + H_2O(l) \rightleftharpoons M^+(aq) + X^-(aq) \qquad \ldots(9.45)$$

The corresponding equilibrium constant can be written as

$$K = [M^+]\,[X^-] \qquad \ldots(9.46)$$

As the equilibrium in Eq. (9.45) is a heterogeneous equilibrium the concentration of solid MX and liquid water would not appear in the expression of equilibrium constant; these are included in the value of *K*. Thus, the equilibrium constant is essentially the product of the concentrations of the ions obtained from the dissociation of dissolved sparingly soluble salt and is called as **solubility product constant** or simply the **solubility product** and is denoted as $\boldsymbol{K_{sp}}$.

$$K_{sp} = [M^+][X^-] \quad \ldots(9.47)$$

The magnitude of $K_{sp,}$ at a given temperature depends on the extent to which the solid solute dissolves to give ions in solution. In other words, it depends on the solubility of salt. We would derive a relationship between the K_{sp} and the solubility of the sparingly soluble salt a little later. Let's first learn about the expressions for K_{sp} for different types of salts.

If we dissolve a sparingly soluble salt of say MX_2 type in water the equilibrium can be represented as

$$MX_2(s) + H_2O(l) \rightleftharpoons M^{2+}(aq) + 2X^-(aq) \quad \ldots(9.48)$$

The corresponding expression for K_{sp} would be

$$K_{sp} = [M^{2+}][X^-]^2 \quad \ldots(9.49)$$

As before, the concentration of solid $MX_2$and water would not appear in the expression for $K_{sp.}$ Similarly for salt of MX_3 type dissolved in water the solubility equilibrium and the corresponding expression for K_{sp} would be

$$MX_3(s) + H_2O(l) \rightleftharpoons M^{3+}(aq) + 3X^-(aq);\ K_{sp} = [M^{3+}][X^-]^3 \quad \ldots(9.50)$$

In general for a salt of M_pX_q type dissolved in water the solubility equilibrium and the corresponding expression for K_{sp} would be

$$M_pX_q(s) + H_2O(l) \rightleftharpoons pM^{n+}(aq) + qX^{m-}(aq);\ K_{sp} = [M^{n+}]^p[X^{m-}]^q \quad \ldots(9.51)$$

Thus, the *solubility product constant for a compound is the product of the molar concentrations of the constituent ions in solution, each raised to the power of its stoichiometric coefficient in the solubility equilibrium*.

The values of the solubility product constants of some common sparingly soluble salts at 298 K are given in 9.1.

Table 9.1: The K_{sp} values for some common sparingly soluble salts at 298 K

Salt	K_{sp}	**Salt**	K_{sp}
CuS	6.0×10^{-36}	AgBr	5.0×10^{-13}
$Al(OH)_3$	4.6×10^{-33}	AgCl	1.8×10^{-10}
PbS	2.5×10^{-27}	$BaSO_4$	1.1×10^{-10}
ZnS	1.1×10^{-21}	$CaCO_3$	3.8×10^{-9}
NiS	3.0×10^{-19}	$PbCl_2$	1.6×10^{-5}

Let us learn how to write the solubility equilibrium and expression for K_{sp} for some sparingly soluble salts in the example 9.5.

Example 9.5: Write the solubility equilibrium and expressions for K_{sp} for the following sparingly soluble salts.

i. AgCl ii. MgF_2 iii. CaC_2O_4 iv. $Al_2(SO_4)_3$

Solution: The solubility equilibrium and the expressions for K_{sp} for the given sparingly soluble salts are as under:

i. $AgCl(s) + H_2O(l) \rightleftharpoons Ag^+(aq) + Cl^-(aq);\ K_{sp} = [Ag^+][Cl^-]$

ii. $MgF_2(s) + H_2O(l) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq);\ K_{sp} = [Mg^{2+}][F^-]^2$

iii. $CaC_2O_4(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq);\ K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$

iv. $Al_2(SO_4)_3(s) + H_2O(l) \rightleftharpoons 2Al^{3+}(aq) + 3SO_4^{2-}(aq);\ K_{sp} = [Al^{3+}]^2[SO_4^{2-}]^3$

9.4.2 Solubility and Solubility Product Constant

As stated above, the value of K_{sp} is a measure of the solubility of the sparingly soluble salts; larger the value, the higher the solubility. Let's raise some questions. First, if the K_{sp} values for two sparingly soluble salts are equal, would their solubility also be equal? And secondly, would the solubility of a salt with higher K_{sp} value always be greater than that of lower K_{sp} value?.

The answer to these questions is not 'yes' as we cannot compare the solubilities of different salts merely by comparing their K_{sp} values. It is so because as you would have noticed above, the value of K_{sp} depends on the solubility of the salt as well as on the formula of the salt. Let us learn about the relationship between the K_{sp} and the solubility of the sparingly soluble salts of different types.

Solubility and K_{sp} for MX Type of Salt

Let us take the dissolution of silver chloride (AgCl) in water as an example of sparingly soluble salt of MX type. The solubility equilibrium would be

$$AgCl(s) + H_2O(l) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad \ldots(9.52)$$

The expression for K_{sp} would be

$$K_{sp} = [Ag^+][Cl^-]. \qquad \ldots(9.53)$$

Let's assume that the solubility of AgCl in water at 298 K is '*s*' $moldm^{-3}$. This means that if we take a solid sample of silver chloride and try to dissolve it in water then only '*s*' moles of it would dissolve in 1 dm^3 of distilled water and rest of it would remain as undissolved solid i.e., we would get a saturated solution. The initial and equilibrium concentrations of various ionic species in the solution so obtained would be

Concentration* / mol dm^{-3}	$AgCl(s) \rightleftharpoons Ag^+(aq)$	+ $Cl^-(aq)$
Initial	0	0
Change due to dissociation of AgCl	*s*	*s*
At equilibrium	*s*	*s*

* Note that the concentration of the solid AgCl does not change

Thus, the concentration of both the ions at equilibrium would be '*s*' mol dm^{-3} each. Substituting it in the expression for K_{sp}, Eq. (9.53)we get

$$K_{sp} = (s \text{ mol dm}^{-3})\,(s \text{ mol dm}^{-3}) = s^2 \text{ mol}^2\,\text{dm}^{-6} \qquad \ldots(9.54)$$

$$\Rightarrow \qquad K_{sp} = s^2 \qquad \ldots(9.55)$$

Like all equilibrium constants, K_{sp} is also dimensionless. However, you must remember that solubility in the expression for K_{sp} is in mol dm^{-3}. In some cases you may be provided solubilities in terms of g dm^{-3} or g per 100 cm^3, you must convert them into mol dm^{-3} so as to calculate the K_{sp}. Let's take up an example.

Example 9.6: Silver chloride-a sparingly soluble salt has a solubility of 1.82×10^{-4} g per 100 cm^3at 298 K. Calculate the value of the K_{sp} for AgCl at 298 K.

Solution: As silver chloride is a MX type of salt, the value of K_{sp} would be given by Eq. (9.60) wherein the solubility '*s*' is in mol dm^{-3}. However, we are given the solubility in g per 100 cm^3. Therefore we would first need to convert it to the units of mol dm^{-3}. The approach would be as follows:

Solubility in g per100 cm^3➔Solubility in g dm^{-3}➔Solubility in mol dm^{-3}➔Concentration of Ag^+ and Cl^- ions in mol dm^{-3}➔K_{sp} for AgCl

Given Solubility of AgCl per 100 cm^3= 1.82×10^{-4} g

➔Solubility of AgCl in g per dm^3 can be obtained by multiplying the solubility in g per 100 cm^3 by 10 i.e.,

= 1.82×10^{-4} g × 10 = 1.82×10^{-3}g

➔ Solubility in mol dm^{-3} can be obtained by dividing solubility in g dm^{-3} by the molar mass

$$=> \qquad s = \frac{1.82 \times 10^{-3}}{M}$$

$$➔ \qquad s = \frac{1.82 \times 10^{-3}}{143.32} = 1.26 \times 10^{-5}\,\text{M}$$

Now, as per Eq. (9.55), $K_{sp} = s^2$

Substituting the value of s in the Eq. (9.60)we get,

$$K_{sp} = s^2 = (1.26 \times 10^{-5})^2 = 1.58 \times 10^{-10}$$

Thus, the K_{sp} for AgCl is found to be 1.58×10^{-10}

Solubility and K_{sp} for MX_2 Type of Salt

Let us take the dissolution of calcium fluoride (CaF_2) in water as an example of sparingly soluble salt of MX_2 type. The solubility equilibrium would be

$$CaF_2(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \qquad \ldots(9.56)$$

The expression for K_{sp} would be

$$K_{sp} = [Ca^{2+}]\,[F^-]^2. \qquad \ldots(9.57)$$

Let us assume that the solubility of CaF_2 in water at 298 K is 's' mol dm^{-3}. This means that if we take a solid sample of calcium fluoride and try to dissolve it in water then only 's' moles of it would dissolve in 1 $dm^3$of distilled water and rest of it would remain as undissolved solid i.e., we would get a saturated solution. The initial and equilibrium concentrations of various species in solution would be

Concentration / mol dm^{-3}	CaF_2 (s) + H_2O(l) ⇌	Ca^{2+} (aq) +	$2F^-$ (aq)
Initial		0	0
Change due to dissociation		s	$2s$
At equilibrium		s	$2s$

Thus, the concentration of calcium ions at equilibrium would be 's' mol dm^{-3}whereas that of fluoride ions would be twice this amount i.e., $2s$ mol dm^{-3}. Substituting these equilibrium concentrations in the expression for K_{sp}, Eq. (9.57), we get

$$K_{sp} = (s)(2s)^2 = s \times 4s^2 = 4s^3 \qquad \ldots(9.58)$$

You may once again note here that we are not using any units for K_{sp}. In Example 9.6 you have learnt to calculate the value of K_{sp} by using the solubility of the sparingly soluble salt. You may come across a situation wherein you need to determine the solubility of a sparingly soluble salt by using given value of $K_{sp.}$ Let's learn the same with the help of another example.

Example 9.7: The solubility product for a sparingly soluble salt, calcium fluoride at 298 K is found to be 4.0×10^{-11}. Calculate the solubility of calcium fluoride in g per 100 cm^3at 298 K.

Solution: Calcium fluoride is a MX_2 type of salt and we are provided with the value of K_{sp} for it and we need to calculate the solubility of calcium fluoride in g per 100 cm^3.As per Eq. (9.58), the molar solubility and the K_{sp} for a MX_2 type of salt are related as

$$K_{sp} = 4s^3$$

Determination of solubility is straight forward by rearranging Eq. (9.58) as follows

$$K_{sp} = 4s^3 \;\Rightarrow\; s = \sqrt[3]{\frac{K_{sp}}{4}} \qquad \ldots(9.59)$$

This provides solubility in terms of mol dm^{-3}; however we need to determine it in g per 100 cm^3. Therefore, the approach would be as follows:

Calculate the solubility in mol dm^{-3}➔Solubility in gdm^{-3}➔Solubility in g per 100 cm^3. So we begin by determining the solubility in mol dm^{-3} by using Eq. (9.59) i.e.,

$$s = \sqrt[3]{\frac{K_{sp}}{4}}$$

The calculation of cube root can easily be done with the help of log tables as shown below.

$$s = (1.0 \times 10^{-11})^{\frac{1}{3}}$$

Taking logs

$$\text{Log}\, s = \frac{1}{3}\log\,(1.0 \times 10^{-11})$$

$$= \frac{1}{3}(-11.0) = -3.666$$

$$= \bar{4}.3334$$

Taking antilog

$$s = \text{antilog}\,(0.3334) \times 10^{-4}$$

$$s = 2.15 \times 10^{-4}$$

Substituting the value of K_{sp} we get,

$$s = \sqrt[3]{\frac{4.0 \times 10^{-11}}{4}} = \sqrt[3]{1.0 \times 10^{-11}} = (1.0 \times 10^{-11})^{\frac{1}{3}}$$

$$= 2.15 \times 10^{-4}\ \text{M}$$

In order to convert the molar solubility to solubility in g dm^{-3}, we multiply the molar solubility by molar mass of calcium fluoride i.e.,

Solubility in g dm^{-3}= 2.15×10^{-4} mol dm^{-3}× 78.07 g mol^{-1} = 1.68×10^{-2} g dm^{-3}

The solubility in g per 100 cm^3 would be obtained by dividing solubility in g dm^{-3} by 10 i.e.,

$$\text{Solubility in g per 100 cm}^3 = \frac{1.68 \times 10^{-2}\,\text{g}\,\text{dm}^{-3}}{10} = 1.68 \times 10^{-3}$$

Thus, the solubility of calcium fluoride would be 1.68×10^{-3} g per 100 cm^3.

As we have worked out the relationship between the solubility and the K_{sp} for MX and MX_2 types of salts we can derive similar relationships for other types of salts. The relationship between the molar solubility and the K_{sp} for different types of salts are given in Table 9.2.

Table 9.2: Relationship between the solubility product constant, K_{sp} and molar solubility, s for different types of sparingly soluble salts

Salt	Salt type	Relationship between K_{sp} and s	
AgCl, $CaSO_4$	MX	$K_{sp} = s^2$	$s = \sqrt{K_{sp}}$
$MgCl_2$, Ag_2CO_3	MX_2 , M_2X	$K_{sp} = 4s^3$	$s = \sqrt[3]{\frac{K_{sp}}{4}}$
$Al(OH)_3$,	MX_3	$K_{sp} = 27s^4$	$s = \sqrt[4]{\frac{K_{sp}}{27}}$
$Al_2(SO_4)_3$,$Ca_3(PO_4)_2$	M_2X_3, M_3X_2	$K_{sp} = 108\ s^5$	$s = \sqrt[5]{\frac{K_{sp}}{108}}$

SAQ 5

Derive a relationship between the solubility and K_{sp} for a sparingly soluble salt of M_2X_3 type having a solubility of s mol dm^{-3}.

9.5 EFFECT OF COMMON ION ON SOLUBILITY EQUILIBRIUM

In Unit 8 you have learnt about the effect of common ion on the ionisation equilibrium of weak acids. Let's learn whether the common ions affect the solubility equilibrium also and if yes, what is the effect? Let us attempt to learn it with the help of an example.

Example 9.8: Calculate the molar solubility of CaF_2 - a sparingly soluble salt in 0.01 M solution of NaF at 298 K and compare the result with the one obtained in example 9.7.[Given: $K_{sp}(CaF_2)= 4.0 \times 10^{-11}$ at 298K]

Solution: In example 9.7 we calculated the solubility of calcium fluoride in water to be: 2.15×10^{-4} M . Let us calculate the same in 0.01 M solution of NaF here.

In order to calculate the solubility in a solution of 0.01 M NaFwe assume that the solubility of CaF_2in this solution is s mol $dm^{-3.}$ The initial and equilibrium concentrations of various species in the solution would be as follows:

Concentration/ mol dm^{-3}	$CaF_2(s) + H_2O(l)$	$\rightleftharpoons$	Ca^{2+} (aq)	+	$2F^-$ (aq)
Initial			0		0
Change due to dissociation of CaF_2			s		$2s$
Change due to dissociation of 0.01 M NaF (a strong electrolyte)			--		0.01
At equilibrium			s		$2s$ + 0.01

The expression for K_{sp} of CaF_2 is: $K_{sp} = [Ca^{2+}]\,[F^-]^2$

Substituting the values of K_{sp} and the equilibrium concentrations from the table in the expression for K_{sp} we get

$$4.0\times10^{-11} = [s][2s+0.01]^2$$

Assuming that the solubility is very low we ignore 2*s* in comparison to 0.01 M and write

$$4.0\times10^{-11} = [s][0.01]^2 \Rightarrow s = 4.0\times10^{-7}\,\text{mol dm}^{-3}$$

As the value of solubility obtained is far less than 0.01 our assumption is valid. Further, we observe that the solubility of the sparingly soluble salt CaF_2has decreased from 2.15×10^{-4} M (in water) to about 4.0×10^{-7} M in presence of 0.01 M sodium fluoride-an electrolyte containing common ion. Thus, the solubility would decrease by about 535 times.

On the basis of example 9.8 we can say that the common ions do affect the solubility equilibria in the same way as any other equilibrium. You may also note that the value of K_{sp} depends only on the temperature, and not on the individual ion concentrations. As we have seen in the example, addition of a salt having common ions shifted the equilibrium to the left however, the value of K_{sp} was maintained.

K_{sp} and Precipitation

We have defined solubility product constant as the product of the concentration of the ions obtained from the dissociation of dissolved sparingly soluble salt. These concentrations are raised to the power equal to their stoichiometric coefficient in the equilibrium expression. It depends on the solubility of the salt and its value is indicative of the same. If we try to think of the solubility equilibrium slightly differently, we find that it also gives an idea about the product of the concentration of ions that can remain in solution. Which means that if the product of the concentration of ions were more than K_{sp} the ions would combine and form solid or in other words they would form a **precipitate**.

It is worthwhile to recall here the concept of reaction quotient, *Q* about which you have learnt in subsection 6.2.3. You would recall that reaction quotient has the same mathematical form as the equilibrium constant expression but uses actual concentrations of different species in the mixture, instead of equilibrium concentrations used in equilibrium constant. In the context of solubility equilibrium we can define an equivalent of reaction quotient as ion-product (or ionic-product), Q_{sp}. For example, the expressions for K_{sp} and Q_{sp} for lead chloride would be

$$K_{sp} = [Pb^{2+}][Cl^-]^2;\, Q_{sp} = [Pb^{2+}]_i[Cl^-]_i^2 \qquad \ldots(9.60)$$

We have to keep in mind that in case of K_{sp} we use equilibrium concentrations and for Q_{sp} the concentrations at any instant (generally initial or at the time of mixing) are used. In order to determine whether ions in a solution will form a precipitate or not we need to compare the values of K_{sp} and Q_{sp}. If,

$Q_{sp} > K_{sp}$; there would be precipitation

$Q_{sp} < K_{sp}$; there would not be any precipitation

$Q_{sp} = K_{sp}$; we would get a saturated solution; still no precipitation

Let's us take an example.

Example 9.9: Will a precipitate of PbI_2 be formed if we add 2 drops of 0.1 M KI solution to 10 cm^3 of a solution containing 0.01M Pb^{2+} ions at 298 K? Assume that the drop volume is 0.05 cm^3 and there is no dilution of lead ion solution on adding KI.
[Given: $K_{sp}(PbI_2) = 7.0 \times 10^{-9}$ at 298K]

Solution: The approach to solve this problem is very straightforward. We need to calculate the concentration of the added iodide ion and compute the value of Q_{sp} for $PbI_2$and compare it with the given value of $K_{sp.}$

The volume of KI added =V_1= 0.05 × 2 = 0.1 cm^3

Concentration of KI =M_1= 0.1 M

Final volume = V_2 = 10.1cm^3

➔ Concentration of I^- ions $= \frac{M_1 \times V_1}{V_2} = \frac{0.1 \times 0.1}{10.1} = 1.0 \times 10^{-3}$M

As there is no dilution of lead ion solution ➔ $[Pb^{2+}]$ = 0.01 M

$$\Rightarrow \quad Q_{sp} = [Pb^{2+}]\,[I^-]^2 = (0.01) \times (0.001)^2 = 1.0 \times 10^{-8}$$

As the value of Q_{sp} (1.0×10^{-8}) is more than K_{sp}(7.0×10^{-9}) for PbI_2there will be precipitation of lead iodide from the solution.

Would the precipitate of PbI_2 be formed if we use just 1 drop of KI in place of two drops? (*Answer: No; Check by calculation.*)

pH and Solubility

Let's raise a question, "Does the solubility of a sparingly soluble salt depend on the pH of the medium?" To answer this we take two examples, first let's consider the dissolution of magnesium hydroxide, Mg $(OH)_2$ –a sparingly soluble metal hydroxide commonly used as an antacid.

$$Mg(OH)_2(s) + H_2O(l) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \qquad \ldots(9.61)$$

In acidic medium, say in stomach, the hydroxide ions obtained from the dissociation of magnesium hydroxide would combine with the hydronium ions in the stomach to give water molecules.

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l) \qquad \ldots(9.62)$$

As the hydroxyl ions get consumed in the process then according to the Le-Chatelier principle the solubility equilibrium Eq. (9.61) for magnesium hydroxide, would shift to right. This implies that more of $Mg(OH)_2$would dissolve to maintain the equilibrium constant i.e., the solubility will increase.

Let's take another example, say of solubility ofCaF_2in a solution of hydrochloric acid. $CaF_2$is a salt of a weak acid HF; the solubility equilibrium in its aqueous solution would be as under.

$$CaF_2(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \qquad \ldots(9.63)$$

The fluoride ions – conjugate base of weak acid (HF) are expected to get hydrolysed in solution as given below

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^- \qquad \ldots(9.53)$$

The added hydrochloric acid (a strong acid), on the other hand would ionise completely to provide hydronium ions.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \qquad \ldots(9.54)$$

The hydronium ions so produced neutralise the hydroxyl ions obtained from hydrolysis. As a consequence the hydrolysis equilibrium of fluoride ions shifts to the right i.e., more fluoride ions are hydrolysed. As the fluoride ions are removed from the equilibrium mixture, more CaF_2 dissolves to maintain the equilibrium. Thus, we see that the solubility of calcium fluoride increases in an acidic solution.

Similarly we can show that in case of a salt of a weak base and strong acid, the cation of the salt would get hydrolysed to give hydronium ions. In such a case the solubility would increase in basic medium because the added hydroxyl ions would neutralize the hydronium ions obtained from the hydrolysis of the cation and shift the equilibrium to the right.

The solubilities of metal hydroxides and salts of weak acids / bases depend on the concentration of hydronium/ hydroxyl ions or the pH of the solution. In such cases the hydronium / hydroxyl ions are not a part of the equilibrium but they alter the equilibrium by consuming or eliminating one of the species from the equilibrium. This in turn affects the solubility equilibrium and hence the solubility.

9.6 APPLICATIONS OF SOLUBILITY PRODUCT PRINCIPLE

The solubility product constant and the effect of common ions and pH on solubility equilibrium find a wide variety of applications in industry and analytical determination. Some of the common applications of the solubility product principle are as under.

- Salting out of soap
- Purification of sodium chloride

- Qualitative determinations in the laboratory
- Quantitative determinations in the laboratory

Let us discuss these one by one.

Salting out of soap

As you know that soaps are generally sodium or potassium salts of higher fatty acids like stearic acid. These are prepared by alkaline hydrolysis (or saponification) of fats and oils, or their fatty acids. In this process, the oil or fat is heated with a concentrated solution of alkali (e.g., NaOH). The higher fatty acids obtained by the hydrolysis of oil or fat are neutralised by alkali to form the soap. Part of the soap precipitates out but a large amount of it stays dissolved in the reaction mixture. For example, the solution equilibrium for sodium stearate is as under

$$C_{17}H_{35}COONa\,(aq) \rightleftharpoons C_{17}H_{35}COO^{-}(aq) + Na^{+}(aq) \qquad \ldots(9.64)$$

In order to recover soap from the solution we exploit the effect of common ion on the equilibrium and add a concentrated solution of sodium chloride (or sometimes crystals of NaCl). This increases the concentration of sodium ions in the reaction mixture and separate the soap out of solution by shifting the equilibrium given in Eq. (9.64) to the left. As the soap comes out of the solution by added salt this process is called as **salting out of soap**.

Purification of sodium chloride

Sodium chloride (common salt) is generally obtained from natural source (sea water) and is contaminated with salts of other metals and other impurities. This needs to be purified before being used. One of the methods of purification of sodium chloride exploits the effect of common ion on the solubility equilibrium. For this purpose a saturated solution of the impure sodium chloride is prepared and filtered to remove impurities. Thereafter a stream of hydrogen chloride gas is passed through the solution. The HCl gas in water is solvated and gets fully ionised to hydronium and chloride ions. As this provides a large concentration of chloride ions the ionic product of sodium and chloride ions (Q_{NaCl}) exceed the solubility product (K_{SP}) of NaCl; thereby pure crystalline salt is obtained. Other salts stay in solution.

Qualitative determinations in the laboratory

You would have learnt and performed qualitative salt analysis in your earlier classes wherein one identifies the cation (s) and anion (s) in the given salt (or a salt mixture). You would recall that in cation analysis the cations are placed in six different groups (I to VI) and we use a specific reagent to check for the presence of cations of a given group. The cations of a given group are then identified by the colour and nature of the precipitate formed. The grouping of cations in this scheme is based on the principles of solubility product, its relationship with the solubility and the effect of common ions and pH on the solubility equilibrium. Let's learn about the separation of the groups in cation analysis.

You would recall that the group reagent for the first group happens to be dil. HCl. This provides chloride ions that precipitate the group I cations as their chlorides.

When we add dil. HCl to the salt solution containing different cations, the Pb^{2+}, Hg_2^{2+} and Ag^+ are precipitated because their chlorides are sparingly soluble and their solubility product is exceeded whereas all other chlorides with higher solubility product stay in solution. The precipitated chlorides are removed by filtration and identified.

The group II cations are precipitated as sulphides. The group reagent for second group is H_2S gas that is passed into the acidic solution obtained as a filtrate after removing the precipitates of the first group cations. H_2S ionises in aqueous solution to provide sulphide ions that precipitate the cations.

$$H_2S(g) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-} \quad \ldots(9.65)$$

$$Cu^{2+}(aq) + S^{2-}(aq) \rightarrow CuS(s) \quad \ldots(9.66)$$

The hydronium ions (from ionisation of HCl) act as a common ion and suppress the ionisation of H_2S,which is a weak diprotic acid. The concentration of sulphides ions becomes very low and as a consequence only those cations are precipitated whose sulphides have low solubility product. For example, CuS with a $K_{sp}= 6.0 \times 10^{-37}$ is precipitated whereas NiS with a $K_{sp}= 1.4 \times 10^{-24}$ stays in solution.

Sometimes, Lead cation can appear in Group II as well because $PbCl_2$ is somewhat soluble (it has moderate solubility product) and therefore it may not be completely precipitated by HCl.

In the third group the ammonium chloride followed by ammonia (or ammonium hydroxide) is used as the group reagent, which is added to the filtrate of second group after boiling off the H_2S. Ammonium hydroxide ionises to provide hydroxide ions that precipitate the cations as hydroxides. These are filtered and analysed.

$$NH_4OH\ (aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad \ldots(9.67)$$

$$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s) \quad \ldots(9.68)$$

Here the added ammonium chloride provide ammonium ions that suppress the ionisation of ammonium hydroxide (ammonia in water) thereby decreasing the concentration of hydroxyl ions. As a consequence only the hydroxides of the third group cations having low value of the K_{sp} get precipitated. For the fourth group we pass H_2S again but the medium is alkaline due to the added ammonia in the third group.

$$H_2S(g) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-} \quad \ldots(9.65)$$

In this medium, the hydroxide ions from ammonium hydroxide react with the hydronium ions obtained from the ionisation of H_2S to produce water and shift the ionisation equilibrium of H_2S in the forward direction thereby increasing the concentration of sulphides ions. As a consequence the cations whose sulphides have high solubility product are also precipitated. Remember that these were not precipitated in the acidic medium of group II.

$$Zn^{2+}(aq) + S^{2-}(aq) \rightarrow ZnS(s) \quad \ldots(9.69)$$

In the fifth group the reagent is ammonium carbonate and the cations are precipitated as their carbonates. The precipitates are filtered and identified. Once the carbonates are precipitated and filtered the filtrate may contain Na^+, K^+ or

NH_4^+ ions. All the salts of these cations are soluble so these are identified with specific tests.

Quantitative determinations in the laboratory

One of the important methods of quantitative determination in the Chemistry laboratory is gravimetric analysis. In this method the ion to be determined is reacted with a suitable reagent so as to quantitatively convert it into a precipitate. This precipitate is then filtered, dried and weighed. The mass of the precipitate so obtained is proportional to the amount of ion being determined. In these determinations, the concepts of solubility product and the factors affecting it are very crucial. Suitable methods could be devised for selective precipitation and determination of an ion from a mixture purely on the basis of solubility product. For example, if we have a mixture of 0.01 M Ag^+ and 0.01 M Pb^{2+} ions in a solution we can selectively precipitate silver ions by controlling the concentration of precipitating chloride ions. The K_{sp} values for AgCl and $PbCl_2$ are 1.8×10^{-10} and 1.7×10^{-5}respectively.Let us calculate the concentration of chloride ions required to precipitate AgCl and $PbCl_2$ respectively.

The K_{sp} for silver chloride, $K_{sp} = [Ag^+][Cl^-]$

Concentration of Ag^+ ions in solution = 0.01 M

Concentration of chloride ions required for precipitation of silver chloride can be calculated by using the fact that the precipitation occurs when ionic product constant (Q_{sp}) is greater than the solubility product constant, i.e.,

$$Q_{sp} > K_{sp};$$

$$[Ag^+][Cl^-] > K_{sp} \Rightarrow [Cl^-] > \frac{K_{sp}}{[Ag^+]}$$

Substituting the values,

$$[Cl^-] > \frac{1.8 \times 10^{-10}}{0.01} = 1.8 \times 10^{-8} \text{ M}$$

Thus, silver chloride would precipitate when the concentration of chloride ions is more than 1.8×10^{-8} M. Similarly, we calculate the concentrations of chloride ions required for precipitating lead chloride

The K_{sp} for lead chloride, $K_{sp} = [Pb^{2+}][Cl^-]^2$

Concentration of Pb^{2+} ions= 0.01 M

Concentration of chloride ions required for precipitation of lead chloride =

$$[Cl^-]^2 > \frac{K_{sp}}{[Pb^{2+}]} = \frac{1.7 \times 10^{-5}}{0.01} = 1.7 \times 10^{-3}$$

Substituting the values,

$$[Cl^-] > \sqrt{1.7 \times 10^{-3} \text{ M}} = 4.12 \times 10^{-2} \text{ M}$$

So you can see that we need a little more than 1.8×10^{-8} M chloride ions for the precipitation of AgCl to take place whereas for $PbCl_2$ to be precipitated we need at least 4.12×10^{-2}M chloride ions. Thus, by suitably controlling the concentration of chloride ions we can selectively precipitate silver ions whereas the lead ions would stay in solution.

SAQ 6

An aqueous solution contains Ba^{2+} and Sr^{2+} ions at a concentration of 10^{-5}M and 10^{-1} M respectively. Which of the ions would precipitate first on adding a solution of potassium chromate dropwise to the mixture? Assume that there is no dilution.

[Given: $K_{sp}(BaCrO_4)= 1.2 \times 10^{-10}$; $K_{sp}(SrCrO_4)= 3.5 \times 10^{-5}$at 298K]

9.7 SUMMARY

In this last unit of the block on Chemical and Ionic Equilibrium we continued our discussion on ionic equilibrium and focused on the hydrolysis of salts in aqueous solutions and the solubility of sparingly soluble salts. In a typical process of dissolution of a salt in water the water molecules hydrate the ions of the salt and as a result of the energy released in the process the ions dissociate from the lattice and are released in the solution. Thereafter, the anions of weak acids and cations of weak bases react with water and get hydrolysed. The hydrolysis of anions of weak acids involves accepting a hydrogenion from water and generating hydroxide ions in solution thus making the solution alkaline. On the other hand, the hydrolysis of cations of weak bases involves donating a hydrogen ion to water and generating hydronium ions in solution thus making the solution acidic. In case of salts of weak acids and weak bases both the ions get hydrolysed and the nature of solution is determined by the ions getting hydrolysed to a greater extent. The ions obtained on dissolution of a salt of a strong acid and a strong base, do not get hydrolysed and their solution is neutral. The hydrolysis equilibrium of an ion is characterised in terms of a hydrolysis constant that is related to the K_a or K_b of the conjugate acid or base of the ion getting hydrolysed and the ionic product of water.

When a sparingly soluble salt is added to water an extremely tiny fraction of it gets dissolved and like any other salt it dissociates into ions that get hydrated. However, most of the salt remains undissolved and equilibrium exists between the solid salt and the ions. This heterogeneous equilibrium is recognised in terms of equilibrium constant called as solubility product constant, K_{sp}. The solubility product of a salt is related to its molar solubility and the relationship depends on the formula of the salt. Further, like any other equilibrium the solubility equilibrium is also affected by the presence of common ions. The solubility equilibrium is suppressed by the presence of common ions and the solubility decreases. In addition to the common ions the pH of the solution also affects the solubility in cases of metal hydroxides and the salts of weak acids and bases. The solubility product and the effect of common ions and pH on solubility equilibrium find a wide variety of applications in industry and analytical determination strategies. Some of the common applications like, salting out of soap, purification of sodium chloride and qualitative &quantitative determinations in the laboratory have also been discussed.

9.8 TERMINAL QUESTIONS

1. Give the equilibrium representing hydrolysis of an anion of a weak acid in aqueous solution and derive a relationship between the hydrolysis constant of the anion and acid dissociation constant of the weak acid.

2. Define degree of hydrolysis. Write down the equilibrium reaction for the hydrolysis of anion in a salt NaA of a weak acid, HA, and calculate the pH of its 0.10 M solution. [Given: K_a(HA)= 1.8×10^{-4} at 298K].

3. Sodium benzoate is used as a food preservative. Calculate the pH of 0.01 M aqueous solution of sodium benzoate at 298 K.
   [Given: K_a(benzoic acid)= 6.5×10^{-5} at 298K].

4. Write the solubility product expressions for the following salts:

   i) $PbCl_2$; ii) Ag_2S; iii) $Al(OH)_3$; iv) NiS; v) $BaCO_3$

5. Calcium oxalate−one of the significant constituents of kidney stones has a solubility of 6.1×10^{-3} g dm^{-3}. Calculate the value for K_{sp} for calcium oxalate.

6. Derive a relationship between the K_{sp} and molar solubility of ammonium carbonate.

7. Calculate the molar solubility of CaF_2 - a sparingly soluble salt in 0.01 M calcium nitrate solution at 298 K. Compare the result with that obtained in example 9.8. [Given: $K_{sp}(CaF_2) = 4.0 \times 10^{-11}$ at 298K]. What inference do you draw?

8. Arrange the following salts of magnesium in the order of increasing solubilities.

   MgF_2,$MgCO_3$, $Mg_3(PO_4)_2$

   [Given: $K_{sp}(MgF_2)= 3.7 \times 10^{-8}$, $K_{sp}(MgCO_3)=3.5 \times 10^{-8}$,
   $K_{sp}(Mg_3(PO_4)_2)=1.0 \times 10^{-25}$at 298K].

9.9 ANSWERS

Self-Assessment Questions

1. Salt hydrolysis refers to the reaction of the ion (s) of the salt with water. The dissolution of sodium benzoate in water involves hydration of the ions followed by their dissociation from the lattice. The overall process can be given as

   $$C_6H_5COONa(s) + H_2O(l) \rightarrow Na^+(aq) + C_6H_5COO^-(aq)$$

   Of these, the sodium ions do not react with water whereas benzoate ions would get hydrolysed and the hydrolysis equilibrium can be given as

   $$C_6H_5COO^-(aq) + H_2O(l) \rightleftharpoons C_6H_5COOH(aq) + OH^-(aq)$$

   The degree of hydrolysis for an anion of a weak acid is given by the following expression, Eq. (9.23)

$$\alpha = \sqrt{\frac{K_w}{K_a c}}$$

where K_a is the acid dissociation constant for the conjugate acid C_6H_5COOH, here. Substituting the values of K_w, K_a, and c at 298 K we get

$$\Rightarrow \quad \alpha = \sqrt{\frac{1.0\times10^{-14}}{6.5\times10^{-5}\times10^{-2}}} = \sqrt{1.54\times10^{-8}} = 1.24\times10^{-4}$$

The degree of hydrolysis of benzoate ions in 0.01 M aqueous solution of sodium benzoate is found to be $= 1.24\times10^{-4}$

2. The details of the ions that will be hydrolysed in the given salts and the acid-base nature of the resulting solutions are as under

Salt	**Ion (s) getting hydrolysed**	**Acid-base nature of the aqueous solution of salt**
HCOONa	$HCOO^-$	Basic
NH_4Br	NH_4^+	Acidic
$C_6H_5COONH_4$	$C_6H_5COO^-$ and NH_4^+	Acidic*

* The degree of hydrolysis is inversely proportional to the square root of the acid/ base dissociation constant of the conjugate acid/ base of the ion getting hydrolysed. As the dissociation constant of ammonium hydroxide is less than that of benzoic acid, ammonium ions would hydrolyse more than benzoate ion. As a consequence the solution would be acidic.

3. To begin with we are dealing with a simple neutralisation reaction between a strong base and a weak acid to generate a salt and water. The reaction can be given as

$$CH_3COOH(aq) + NaOH(aq) \rightleftharpoons CH_3COONa(aq) + H_2O(l)$$

We need to first calculate the amounts of reactants in the solution.

$$\text{Amount of NaOH} = \frac{0.02\ \text{moles}}{1000\ \text{cm}^3}\times 100\ \text{cm}^3 = 0.002\ \text{moles}$$

$$\text{Amount of } CH_3COOH = \frac{0.02\text{moles}}{1000\ \text{cm}^3}\times 100\ \text{cm}^3 = 0.002\text{moles}$$

Thus, 2 millimoles of NaOH are reacting with 2 millimoles of acetic acid. As the acid and base are in equal amounts their neutralisation will generate 2 millimoles of salt (sodium acetate). However this salt will be present in a total volume of 200 cm^3. Thus,

➔ Molar concentration of sodium acetate in solution

$$= \frac{0.002\ \text{moles}}{200\ \text{cm}^3}\times 1000\ \text{cm}^3 = 0.01\,\text{M}$$

As sodium acetate is a salt of weak acid and strong base its anion would get hydrolysed. The pH of such a solution is given by the following expression, Eq. (9.36).

$$\Rightarrow \quad pH = 7.0 + \frac{1}{2}pK_a + \frac{1}{2}\log c \qquad \ldots(9.36)$$

Let's first calculate the pK_a for acetic acid (the conjugate acid of the anion)

$$pK_a = -\log K_a = -\log[1.8\times10^{-5}] = -[-4.74] = 4.74$$

Substituting the values at 298 K in Eq. (9.36).

$$pH = 7.0 + \frac{1}{2}(4.74) + \frac{1}{2}\log(0.01)$$

$$\Rightarrow \quad pH = 7.0 + 2.37 + \frac{1}{2}(-2.0) = 9.37 - 1.0 = 8.37$$

The pH of the resulting solution would be 8.37

4. Ammonium benzoate is a salt of a weak acid and a weak base. The pH of aqueous solution of such a salt is given by Eq. (9.44).

$$pH = 7.0 + \frac{1}{2}pK_a - \frac{1}{2}pK_b \qquad \ldots(9.44)$$

We are given:

$K_b(NH_4OH) = 1.8 \times 10^{-5}$ and $K_a(C_6H_5COOH) = 6.5 \times 10^{-5}$

Let's first calculate the corresponding pK values

$$pK_a = -\log K_a = -\log[6.5\times10^{-5}] = -[-4.19] = 4.19$$

$$pK_b = -\log K_b = -\log[1.8\times10^{-5}] = -[-4.74] = 4.74$$

Substituting the values in Eq. (9.44),

$$pH = 7.0 + \frac{1}{2}(4.19) - \frac{1}{2}(4.74) = 6.73$$

Thus, the pH of the given solution of sodium benzoate would be 6.73

5. For the dissolution of a salt of M_2X_3 type the equilibrium would be

$$M_2X_3(s) \;+\; H_2O(l) \rightleftharpoons 2M^{3+}(aq) + 3X^{2-}(aq)$$

The expression for K_{sp} would be $K_{sp} = [M^{3+}]^2[X^{2-}]^3$.

If we assume that the solubility of the salt in water at 298 K is 's' mol dm^{-3}, the initial and equilibrium concentrations of various species in the solution would be

Concentration/ mol dm^{-3}	$M_2X_3(s) + H_2O(l) \rightleftharpoons$	$2M^{3+}(aq)$ +	$3X^{2-}(aq)$
Initial		0	0
Change due to ionisation		$2s$	$3s$
At equilibrium		$2s$	$3s$

Substituting the equilibrium concentrations in the expression for K_{sp}, we get

$$K_{sp} = (2s)^2(3s)^3 = 4s^2 \times 27s^3 = 108\,s^5$$

$$\Rightarrow \quad K_{sp} = 108\,s^5$$

6. In order to decide the ion precipitating first we need to compute the concentration of potassium chromate required for their respective precipitation and the one requiring lesser amount would precipitate first. Let's calculate the concentrations of precipitating agent required.

The K_{sp} for barium chromate $= K_{sp} = [Ba^{2+}][CrO_4^{2-}]$

Concentration of Ba^{2+} ions= 10^{-6} M

Concentration of chromate ions required for precipitation of barium chromate can be calculated by using the fact that the precipitation occurs when ionic-product is greater than the solubility product, i.e.,

$$Q_{sp} > K_{sp}$$

$$[Ba^{2+}][CrO_4^{2-}] > K_{sp} \qquad [CrO_4^{2-}] > \frac{K_{sp}}{[Ba^{2+}]}$$

Substituting the values,

$$[CrO_4^{2-}] > \frac{1.2\times10^{-10}}{10^{-6}} = 1.2\times10^{-4}\text{ M}$$

Thus, barium chromate would precipitate when the concentration of chromate ions is more than 1.2×10^{-4} M. Similarly, we calculate the concentrations of precipitating agent required for precipitating strontium chromate

The K_{sp} for strontium chromate $= K_{sp} = [Sr^{2+}][CrO_4^{2-}]$

Concentration of Sr^{2+} ions= 10^{-1} M

Concentration of chromate ions required for precipitation of strontium chromate=

$$[CrO_4^{2-}] > \frac{K_{sp}}{[Sr^{2+}]} = \frac{3.5\times10^{-5}}{10^{-1}} = 3.5\times10^{-4}\text{ M}$$

As the concentration of chromate ions required for the precipitation of barium ions is low they will be precipitating first.

Terminal Questions

1. Let us take HA as the weak acid. Its anion, A^- would react with water and get hydrolysed. The equilibrium representing hydrolysis of the anion can be represented as:

$$A^- aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

The expression for hydrolysis constant would be

$$K_h = \frac{[HA][OH^-]}{[A^-]}$$

Multiplying the numerator and denominator of the hydrolysis constant expression by concentration of hydronium ions, $[H_3O^+]$ and reorganising the terms we get,

$$K_h = \frac{[HA][OH^-][H_3O^+]}{[A^-][H_3O^+]}$$

$$K_h = \frac{[HA]}{[A^-][H_3O^+]} \times [OH^-][H_3O^+]$$

$$\Rightarrow K_h = \frac{1}{K_a} \times K_w$$

The relation suggests that the hydrolysis constant of an anion of a weak acid is inversely related to the acid dissociation constant of the weak acid.

2. Degree of hydrolysis may be defined as the fraction of the total ions of a given type that react with water and get hydrolysed. The general reaction for the hydrolysis of anion of the salt NaA, i.e., A^- can be shown as under

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

The pH of an aqueous solution of an anion of a weak acid is given in terms of Eq. (9.36)

$$pH = 7.0 + \frac{1}{2}pK_a + \frac{1}{2}\log c$$

We are given the value of K_a for the weak acid, which can be used to calculate the pK_a value for HA

$$pK_a = -\log K_a = -\log[1.8 \times 10^{-4}] = -[-3.74] = 3.74$$

Substituting the values of K_a and c in Eq. (9.36)

$$\Rightarrow pH = 7.0 + \frac{1}{2}(3.74) + \frac{1}{2}\log(1.0 \times 10^{-1})$$

$$\Rightarrow pH = 7.0 + 1.87 + \frac{1}{2}(-1.00) = 8.87 - 0.50 = 8.37$$

Thus, the pH of the solution would be 8.37.

3. Sodium benzoate is a salt of weak acid (benzoic acid) and a strong base (sodium hydroxide). On dissolution in water, the anion of the salt i.e., benzoate ion would get hydrolysed. The hydrolysis equilibrium can be given as

$$C_6H_5COO^-(aq) + H_2O(l) \rightleftharpoons C_6H_5COOH(aq) + OH^-(aq)$$

The pH of the solution can be calculated by using Eq. (9.36)

$$\text{pH} = 7.0 + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log c$$

We are given the value of K_a for the benzoic acid, which can be used to calculate the pK_a value

$$\text{p}K_a = -\log K_a = -\log[6.51\times 0^{-5}] = -[-4.18] = 4.18$$

Substituting the values of K_a and c in Eq. (9.36)

$$\Rightarrow \text{pH} = 7.0 + \frac{1}{2}(4.18) + \frac{1}{2}\log(1.0\times 10^{-2})$$

$$\Rightarrow \text{pH} = 7.0 + 2.09 + \frac{1}{2}(-2.00) = 9.09 - 1.00 = 8.09$$

The pH of 0.01 M solution of sodium benzoate would be = 8.09

4. The solubility product expressions for the given sparingly soluble salts are as under

    i) $PbCl_2$: $K_{sp} = [Pb^{2+}][Cl^-]^2$

    ii) Ag_2S: $K_{sp} = [Ag^+]^2[S^{2-}]$

    iii) $Al(OH)_3$: $K_{sp} = [Al^{3+}][OH^-]^3$

    iv) NiS: $K_{sp} = [Ni^{2+}][S^{2-}]$

    v) $BaCO_3$: $K_{sp} = [Ba^{2+}][CO_3^{2-}]$

5. The solubility equilibrium for calcium oxalate can be given as

$$CaC_2O_4(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

The expression for K_{sp} would be $K_{sp} = [Ca^{2+}]\,[C_2O_4^{2-}]$

If we assume that the solubility of CaC_2O_4 in water at 298 K is s mol dm^{-3}then initial and equilibrium concentrations of various ionic species in the solution would be

Concentration / mol dm^{-3}	$CaC_2O_4(s)$ + $H_2O(l)$ ⇌	$Ca^{2+}(aq)$	+	$C_2O_4^{2-}(aq)$
Initial		0		0
Change due to ionisation		s		s
At equilibrium		s		s

Substituting the equilibrium concentrations in the expression for K_{sp}, we get

$$K_{sp} = (s)(s) = s^2$$

Where solubility is in mol dm^{-3}, however we are given solubility in g dm^{-3}. To convert it to mol dm^{-3} we need to divide the given solubility by the molar mass of calcium oxalate (128.1 g mol^{-1})

➔ Solubility in mol dm^{-3}=

$$\frac{\text{Solubility in gdm}^{-3}}{\text{Molar mass}} = \frac{6.1\times10^{-3}}{128.1} = 4.76\times10^{-5}\text{M}$$

Substituting in the expression for K_{sp}, we get

$$K_{sp} = s^2 = (4.76\times10^{-5})^2 = 2.27\times10^{-9}$$

The value of K_{sp} for calcium oxalate is found to be = 2.27×10^{-9}

6. The equilibrium reaction for the dissolution of ammonium carbonate ($(NH_4)_2CO_3$) can be given as

$$(NH_4)_2CO_3(s) + H_2O(l) \rightleftharpoons 2NH_4^+(aq) + CO_3^{2-}(aq)$$

The expression for K_{sp} would be $= K_{sp} = [NH_4^+]^2[CO_3^{2-}]$

If we assume that the solubility of $(NH_4)_2CO_3$ in water at 298 K to be s mol dm^{-3} then the initial and equilibrium concentrations of various ionic species in solution would be

Concentrations (mol dm^{-3})	$(NH_4)_2CO_3(s) + H_2O(l) \rightleftharpoons$	$2NH_4^+(aq)$ +	$CO_3^{2-}(aq)$
Initial		0	0
Change due to ionisation		2s	s
At equilibrium		2s	s

Substituting the equilibrium concentrations from the table in the expression for K_{sp}, we get

$$K_{sp} = (2s)^2(s) = 4s^2 \times s = 4s^3$$

This is the desired relationship between the K_{sp} and the molar solubility of ammonium carbonate.

7. In order to calculate the solubility in of CaF_2 in 0.01 M calcium nitrate we assume that the solubility of CaF_2in 0.01 M calcium nitrate is s mol dm$^{-3.}$ The initial and equilibrium concentrations of various ionic species in solution would be as follows:

Concentration / mol dm^{-3}	$CaF_2(s) + H_2O(l) \rightleftharpoons$	$Ca^{2+}(aq)$ +	$2F^-(aq)$
Initial		0	0
Change due to dissociation		s	$2s$
Change due to dissociation of 0.01 M Calcium nitrate (a strong electrolyte)		0.01	--
At equilibrium		s+0.01	$2s$

The expression for K_{sp} of CaF_2 is: $K_{sp} = [Ca^{2+}][F^-]^2$

Substituting the values of K_{sp} and the equilibrium concentrations from the table we get

$$4.0 \times 10^{-11} = [s + 0.01]\,[2s]^2$$

Assuming that the solubility is very low we ignore '*s*' in comparison to 0.01 M and write

$$4.0 \times 10^{-11} = [0.01][2s]^2 \Rightarrow 4s^2 = 4.0 \times 10^{-9} \text{mol dm}^{-3}$$

$$\Rightarrow s^2 = 1.0 \times 10^{-9} \text{mol dm}^{-3} \Rightarrow s = 3.16 \times 10^{-5} \text{mol dm}^{-3}$$

As the value of solubility obtained is far less than 0.01 our assumption is valid.

In example, 9.7 we calculated the solubility of CaF_2 to be 2.15 × 10^{-4}M (in water) which was shown to decrease to about 4.0 × 10^{-7} M in presence 0.01 M sodium fluoride (example 9.8) i.e., about 525 times lesser.

Now we find that in presence of 0.01 M calcium nitrate the solubility has decreased to about 3.16 × 10^{-5}Mwhich is about 7 times lesser than that in water.

This lesser decrease in case of calcium nitrate is due to the fact that in case of fluoride ion as the common ion the effect was significant because K_{sp} expression has second power of fluoride ion concentration whereas it depends on only the first power of concentration of calcium ions so the effect is marginal.

8. In order to arrange these salts in terms of increasing solubilities we need to calculate the solubilities of each of these salts separately.

MgF_2 is a salt of MX_2 type and from Table 9.2 the solubility is related to the K_{sp} as follows

$$s = \sqrt[3]{\frac{K_{sp}}{4}}$$

Substituting the value of K_{sp} we get,

$$s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{3.7\times10^{-8}}{4}} = 2.09\times10^{-3}\,\text{M}$$

$MgCO_3$is a salt of MX type and from Table 9.2 the solubility is related to the K_{sp} as follows

$$s = \sqrt{K_{sp}}$$

Substituting the value of K_{sp} we get,

$$s = \sqrt{3.5\times10^{-8}} = 1.87\times10^{-4}$$

$Mg_3(PO_4)_2$is a salt of M_3X_2 type and from Table 9.2 the solubility is related to the K_{sp} as follows

$$s = \sqrt[5]{\frac{K_{sp}}{108}}$$

Substituting the value of K_{sp} we get,

$$s = \sqrt[5]{\frac{1.0\times10^{-25}}{108}} = 3.91\times10^{-6}\,\text{M}$$

Thus, the order of solubilities of the given salts is

$Mg_3(PO_4)_2 < MgCO_3 < MgF_2$