# UNIT 14 CHEMICAL EQUILIBRIA

## Structure

## 14.1 INTRODUCTION

Three important aspects of a chemical reaction must be studied for a complete understanding of the subject. These are : (i) whether a chemical reaction is feasible at all (the feasibility of the reactions has already been dealt with in Unit 9 of this course) (ii) if the reaction is feasible, at what stage does it stop, and (iii) how fast or slow does the reaction occur. This last aspect we shall be studying under the heading of chemical kinetics in Unit 18. The present unit describes the second aspect of a chemical reaction i.e. upto what stage does a reaction proceed.

We have already defined, in general, the reversible and irreversible processes in Unit 9. However, for chemical reactions, the two processes can be defined as follows. Irreversible reactions are said to go to completion, implying thereby that the reaction proceeds until at least one of the reactants is completely used up. On the other hand, all those reactions which appear not to proceed beyond a certain stage after sometime even when the reactants are still available, are reversible reactions. They have only reached an equilibrium state. The present unit discusses the meaning of this state of equilibrium and how the equilibrium composition of the reactants and products are correlated with change in Gibb's free energy. It also explains the effects of different factors on chemical equilibrium.

### Objectives

After studying this unit, you should be able to :

- describe chemical equilibrium,
- differentiate between reversible and irreversible reactions,
- derive an expression for equilibrium constant in terms of Gibb's free energy,
- express the equilibrium constant in different ways and apply it to different systems, and
- predict the shift in equilibrium position with the changes in the concentration, temperature or pressure of the system.

## 14.2 REVERSIBLE AND IRREVERSIBLE REACTIONS

In general, chemical reactions can be divided into two types — reversible and irreversible. The reversible reactions are those in which the products can combine back to form the reactants. However, in the irreversible reactions, the same reactants cannot be formed back from the products under normal set of experimental conditions. For the study of equilibrium, we are mainly concerned with reversible reactions. The idea of reversibility of chemical reactions was first realised by Berthollet in 1799. He was trying to explain the cause for substantial amount of deposits of sodium carbonate around some salt lakes of Egypt. He proposed that these deposits are formed due to high concentration of sodium chloride in lake water which reacted with the carbonates present on the shores. Normally, in a laboratory experiment, we find that calcium carbonate is precipitated by the reaction of sodium carbonate with calcium chloride as represented by the equation :

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

What Berthollet proposed was indeed a reverse reaction of the above and the cause for reversibility was in some way connected to the high concentration of dissolved sodium chloride.

Thus, we realise that a chemical reaction such as given above can proceed in both the 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 (or a sign of equality between reactants and products) emphasising the fact that it is a reversible reaction :

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

Further, experimental studies by Gilles and coworkers on the reaction between acetic acid and ethyl alcohol giving ester and water, showed that the amount of ester formed varied with the initial concentrations of the reactants at a fixed temperature and pressure.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

In 1864, Guldberg and Wagge showed experimentally that there exists an equilibrium between the reactants and products in a chemical reaction and that this equilibrium can be reached from either direction (starting either from reactants or the products). Furthermore, the relation between the concentrations of the reactants and the products can be expressed by a simple mathematical expression. Let us consider two reactions to clarify these points.

van't Hoff, in 1877, studied the hydrolysis of ethyl acetate.

$$\underset{\text{Ester}}{CH_3COOC_2H_5} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Acid}}{CH_3COOH} + \underset{\text{Alcohol}}{C_2H_5OH}$$

He observed that the ratio of the product of concentrations of the **products** to the product of concentrations of the **reactants** is always constant at equilibrium and is independent of the initial concentrations of the ester. Expressed mathematically,

$$K = \frac{c_{C_2H_5OH} \times c_{CH_3COOH}}{c_{CH_3COOC_2H_5} \times c_{H_2O}}$$

where '*c*' represents concentration of a species which is written as subscript.

The constant, *K*, in the above expression has a fixed value for a particular reaction at a constant temperature and pressure and is a measure of the extent of reaction. A large value of *K* means numerator is greater than the denominator. This indicates the presence of a larger concentration of products as compared to the concentration of reactants at equilibrium.

Consider another example of the reaction involving hydrogen, iodine and hydrogen iodide, all in the gaseous state. If hydrogen and iodine are kept together in a closed vessel at 723 K, they react chemically to give hydrogen iodide. However, if pure hydrogen iodide is taken in a closed vessel and heated to the same temperature of 723 K, it decomposes to give hydrogen and iodine.

Equilibrium is said to be reached if there is no further change in the concentration of reactants and products with respect to time.

The true state of affairs is that, in both cases, after a sufficiently long time, you would find all the three species, hydrogen, iodine and hydrogen iodide—present in the container. At this stage, we say that an equilibrium has been reached between the reactants and the products as shown by the equation, $H_2 + I_2 = 2HI$. Furthermore, at equilibrium, there exists a definite relationship between the concentrations of hydrogen iodide, hydrogen and iodine.

This state of chemical equilibrium can be viewed from a different point of view. The reaction between the two reactants, A and B, to give products, C and D, can be represented as follows :

$$A + B \rightleftharpoons C + D$$

Initially, there are only A and B present but as the reaction proceeds, some amount of C and D are formed. Once the products C and D are formed, they can also react to give A and B, if the reaction is reversible. Since, the concentration of C and D are small in the beginning, it seems logical that the rate of the reverse reaction, $C + D \longrightarrow A + B$, should also be less than the rate of the forward reaction, $A + B \longrightarrow C + D$. However, as the reaction proceeds, more and more of C and D are produced. Consequently, the rate of the reverse reaction would also increase. Ultimately, a situation would be reached when the rate of the reverse reaction would be exactly equal to that of the forward reaction. Since, these are reactions in opposite directions, there is no change in composition with time and it seems as if the reaction has stopped. We then say that the reacting system is in the equilibrium state. Actually the reactions in both directions do take place but rates of forward and reverse reactions are equal. It is said that a state of dynamic equilibrium has been reached. At this stage, no further change in the concentrations of the products and reactants will take place.

Based on such observations, Guldberg and Wagge gave a quantitative formulation known as the law of mass action. This law gives the relationship between equilibrium concentrations of all the substances taking part in a chemical reaction at equilibrium. Instead of just stating this law, we shall derive this relationship with the help of basic principles of thermodynamics.

## 14.3 DERIVATION OF GENERAL EXPRESSION FOR CHEMICAL EQUILIBRIUM

Even before derivation of equilibrium expression is attempted, we must recapitulate the following conventions in thermodynamics.

1) Any system, to which substances are added or from which they are taken away or in which a chemical reaction takes place, is called an open system.
2) A chemical reaction involving a number of substances is represented by

$$\sum_i \nu_i A_i = 0$$

Where $A_i$ represents a chemical substance at the temperature and pressure of the reaction, and $\nu_i$ is called the stoichiometric coefficient of $A_i$.

$\nu$ values are positive for the products and negative for the reactants. This relationship can be explained using the following example :

$$H_2(g) + \frac{1}{2}\, O_2(g) = H_2O(l)$$

can be written as

$$(1)\ H_2O - (1)\ H_2 - \left(\frac{1}{2}\right)O_2 = 0$$

and the values of $\nu$'s are :

$$\nu_{H_2O} = 1,\ \nu_{H_2} = -1, \text{ and } \nu_{O_2} = -\frac{1}{2}$$

Again, note that $\nu$ is positive for the products, and negative for the reactants.

Let us now consider an open system represented by a general reaction :

$$aA + bB + cC \ldots \rightleftharpoons pP + qQ + rR \ldots \qquad \ldots (14.1)$$

The change in Gibb's free energy, $dG$, for the reaction is given by Eqs. 9.21, 9.23, 9.68 and 9.69.

$$dG = Vdp - SdT + \sum_i \mu_i dn_i \qquad \ldots (14.2)$$

The symbol $\sum_i$ stands for summation of terms; the terms are obtained by giving different values to i.

As per Eq. 9.68 given in Sec. 9.10 of Unit 9 of this course,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,N} dT + \left(\frac{\partial G}{\partial p}\right)_{T,N} dp + \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1} dn_2$$

Using Eqs. 9.21, 9.23 and 9.69, this expression can be written as,
$dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2$
Eq. 14.2 is a generalised form of the above equation.

where $dn_i$ = change in the amount of any particular substance, 'i' and $\mu_i$ = chemical potential of that substance; all other symbols carry their usual meaning. At constant temperature and pressure, Eq. 14.2 reduces to :

$$dG_{T,P} = \sum_i \mu_i\, dn_i \qquad \ldots (14.3)$$

The change in the amount of any substance '$dn_i$' can be more conveniently expressed in terms of another quantity $\xi_i$ (pronounced as "xi") which is a measure of the extent of the reaction. For example, $\xi = 0$ for a substance 'i' means that it has not reacted at all; $\xi = 1$ means whole amount of 'i' has reacted and so on. For any reversible reaction the value of $\xi$ should be between zero and unity.

Let us now derive an expression to specify the variation of free energy with respect to the extent of reaction. The number of moles ($n_i$) of a particular substance i present at different times, as a reaction proceeds, can be expressed by the relation :

$$n_i = n_i^{\circ} + \nu_i \xi \qquad \text{... (14.4)}$$

where $n_i$ is the number of moles of the substance i present before the reaction starts, $\nu_i$ is the stoichiometric coefficient of the same substance in the balanced chemical equation (with a proper sign) and $\xi$ is the extent of the reaction. Note that $n_i^{\circ}$ and $\nu_i$ are constants for a substance while $n_i$ varies as $\xi$ changes. The change in $n_i$ can be obtained by differentiating Eq. 14.4 as,

$$dn_i = \nu_i d\xi \qquad \text{... (14.5)}$$

(since $n_i^{\circ}$ and $\nu_i$ are constants)

Combining Eqs. 14.3 and 14.5, we get,

$$dG_{T,p} = \sum_i^n \mu_i \nu_i d\xi$$

$$\text{Hence, } \left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_i \mu_i \nu_i \qquad \text{... (14.6)}$$

From your study of Unit 9, you can understand that Eq.14.6 represents Gibb's free energy change of the reaction ($\Delta_r G_{T,p}$) at constant temperature and pressure.

In Unit 9, you have studied that $\Delta_r G_{T,p}$ is equal to the sum of the Gibb's free energy of the products minus the sum of the Gibb's free energy of the reactants.

$$\text{i.e., } \left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_i \mu_i \nu_i = \Delta_r G_{T,p} \qquad \text{... (14.7)}$$

Let us apply Eq. 14.7 to two reactions. First, let us consider the formation of water discussed in this section.

$$H_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons H_2O(l)$$

$\Delta_r G_{T,p}$ for the formation of water is given by

$$\Delta_r G_{T,p} = \mu_{H_2O} - \mu_{H_2} - \frac{1}{2} \mu_{O_2}$$

The $\nu_i$ values of $H_2O$, $H_2$ and $O_2$ are 1, $-1$ and $-\frac{1}{2}$, respectively.

As a second example, let us consider the formation of ammonia.

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

For this reaction,

$$\Delta_r G_{T,p} = 2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2}$$

Again, note that the $\nu_i$ values of $NH_3$, $N_2$ and $H_2$ are 2, $-1$ and $-3$, respectively.

A chemical reaction will tend to proceed in a direction of decreasing free energy. At equilibrium, the reaction does not proceed in either direction, implying thereby that there would be an increase in Gibb's free energy of the system if the reaction proceeds in either direction. Hence, the Gibb's free energy of the system will be minimum at equilibrium.

From sec. 9.8 of Unit 9, we know that the Gibb's free energy of the system will be minimum at equilibrium at constant temperature and pressure (see Fig. 14.1). Hence, the derivative of the Gibb's free energy function with respect to the extent of the reaction, which is the slope of the curve in Fig. 14.1, is equal to zero at equilibrium at constant temperature and pressure. In other words,

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p,eq} = \sum_i \mu_i \nu_i = \Delta_r G_{T,p} = 0 \qquad \text{... (14.8)}$$

where 'eq' stands for equilibrium condition.

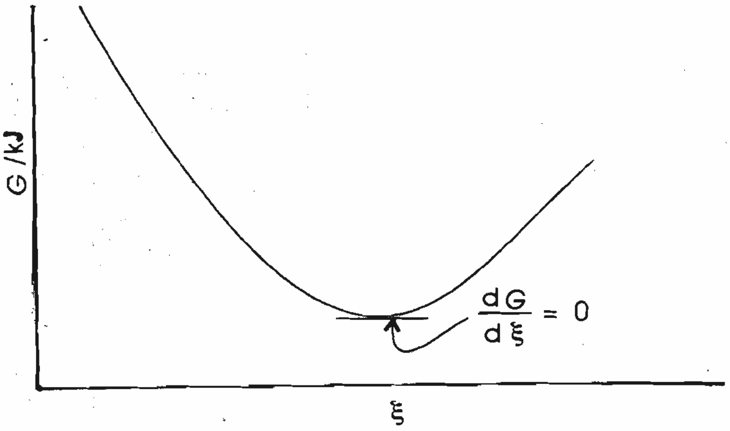

Fig. 14.1 : Change of Gibb's Free Energy and the extent of chemical reaction.

Equation 14.8 is a general expression which is applicable to any reversible chemical reaction under equilibrium conditions at constant temperature and pressure. The equation simply means that the sum of the chemical potentials of the products and reactants is equal to zero at equilibrium.

Equation 14.8 would be most useful if we could express the chemical potential in terms of some experimentally determinable or known quantities. There are a number of ways to express chemical potentials. The next section discusses the substitution for chemical potential in terms of partial pressure, mole fraction and concentration for ideal gas mixtures at equilibrium.

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

**SAQ 1**

For the formation reaction of nitric oxide from nitrogen and oxygen gases, find the value of $\nu$ for each of the reactants and products.

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## 14.4 CHEMICAL EQUILIBRIUM IN IDEAL GAS MIXTURES

Let us derive an expression for the equilibrium constant in terms of partial pressures for a reaction between ideal gases.

### 14.4.1 Equilibrium Constant Expression in Terms of Partial Pressure

Consider a general reaction

$$aA + bB + ... \rightleftharpoons lL + mM + ... \qquad ... (14.9)$$

At constant temperature ($dT = 0$) and pressure ($dp = 0$), the free energy change for the above reaction ($\Delta_r G_{T,p}$) is obtained by using Eq. 14.7.

$$\Delta_r G_{T,p} = (l\mu_L + m\mu_M + ...) - (a\mu_A + b\mu_B + ...) \qquad ... (14.10)$$

where $\mu_L$, $\mu_M$, $\mu_A$, $\mu_B$, ..., etc., are the chemical potentials of the products and reactants; and $l$, $m$, $(-a)$, $(-b)$, ..., etc., are $\nu_i$ values. Remember that the products (such as L and M) have positive $\nu_i$ values and the reactants (such as A and B) have negative $\nu_i$ values; because of this, there is a negative sign between the two terms on the right hand side of Eq. 14.10.

The Chemical potential, $\mu_i$, of an ideal gas 'i' in a gaseous mixture is given by Eq. 9.83 of Unit 9.

$$\mu_i(p_i) = \mu_i^\circ(p) + RT \ln p_i \qquad \text{... (14.11)}$$

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

Using Eq. 14.11 in Eq. 14.10,

$$\begin{aligned}\Delta_r G_{T,p} = {} & [l(\mu_L^\circ(p) + RT \ln p_L) + m(\mu_M^\circ(p) + RT \ln p_M) + \ldots] - \\ & - [a(\mu_A^\circ(p) + RT \ln p_A) + b(\mu_B^\circ(p) + RT \ln p_B) + \ldots]\end{aligned} \qquad \text{... (14.12)}$$

$$\Delta_r G_{T,p} = [(l\mu_L^\circ(p) + m\mu_M^\circ(p) + \ldots) - (a\mu_A^\circ(p) + b\mu_B^\circ(p) + \ldots)] + RT \ln \frac{p_L^l\, p_M^m \ldots}{p_A^a\, p_B^b \ldots} \qquad \text{... (14.13)}$$

Note that in the transformation of Eq. 14.12 to Eq. 14.13, we have used the relation :

$lRT \ln p_L = RT \ln p_L^l$; i.e., a coefficient ($l$) of a logarithmic term ($RT \ln p_L$) is taken inside the logarithmic term as a power.

$$\text{But } (l\mu_L^\circ(p) + m\mu_M^\circ(p) + \ldots) - (a\mu_A^\circ(p) + b\mu_B^\circ(p) + \ldots) = \Delta_r G_{T,p}^\circ \qquad \text{... (14.14)}$$

where $\Delta_r G_{T,p}^\circ$ is the standard free energy change of the reaction at constant temperature and pressure.

Using Eqs. 14.13 and 14.14, we can write

$$\Delta_r G_{T,p} = \Delta_r G_{T,p}^\circ + RT \ln \frac{p_L^l\, p_M^m \ldots}{p_A^a\, p_B^b \ldots} \qquad \text{...(14.15)}$$

Let us now assume that the above system is under equilibrium. Using Eqs. 14.8 and 14.15, we can write that at equilibrium,

$$\Delta_r G_{T,p} = \Delta_r G_{T,p}^\circ + RT \ln \left[\frac{p_L^l\, p_M^m \ldots}{p_A^a\, p_B^b \ldots}\right]_{eq} = 0$$

It is quite interesting to note that Eq. 14.17 relates equilibrium constant of a reaction to the change in standard free energy that takes place during a reaction. In Unit 9, you have studied the method of calculation of $\Delta_r G^\circ$ from the free energies of formation of the reactants and products; once $\Delta_r G^\circ$ is known at a particular temperature. $K_p$ can be calculated using Eq. 14.17. In Unit 17 on Electrochemical cells, you will study the electrochemical method of calculating the equilibrium constant.

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

$$\text{i.e., } \Delta_r G_{T,p}^\circ = -RT \ln \left[\frac{p_L^l\, p_M^m \ldots}{p_A^a\, p_B^b \ldots}\right]_{eq} \qquad \text{... (14.16)}$$

$$\text{or } \Delta_r G_{T,p}^\circ = -RT \ln K_p = -2.303\, RT \log K_p \qquad \text{... (14.17)}$$

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

$$K_p = \frac{p_L^l\, p_M^m \ldots}{p_A^a\, p_B^b \ldots} \text{ at equilibrium} \qquad \text{... (14.18)}$$

$$= \frac{\text{Multiplication of } (p_i)^{\nu_i} \text{ terms of the products}}{\text{Multiplication of } (p_i)^{-\nu_i} \text{ terms of the reactants}} \text{ at equilibrium}$$

where $p_L, p_M, p_A, p_B, \ldots$, etc., are the partial pressures of L, M, A, B, ..., etc., at equilibrium. In subsequent sections, we leave out the subscript ‘eq’ while referring to equilibrium partial pressures. Eq. 14.18 can also be written as,

$$K_p = p_L^l \cdot p_M^m \ldots p_A^{-a} \cdot p_B^{-b} \ldots \qquad \text{... (14.19)}$$

where $p_L, p_M, p_A, p_B, \ldots$, etc., are the equilibrium partial pressures and $l$, $m$, $(-a)$, $(-b)$ ..., etc., are the respective $\nu_i$ values of L, M, A, B, ..., etc. Eq. 14.19 can also be represented as,

$$K_p = \prod_i p_i^{\nu_i} \qquad \text{... (14.20)}$$

Note that $\nu_i$ written as power is positive for the product, $NH_3$, whereas it is negative for $N_2$ and $H_2$, these two being reactants.

where the symbol $\prod_i$ represents the multiplication of different $p_i^{\nu_i}$ terms given in Eq. 14.19. Again, from Eqs. 14.18 to 14.20, we can see that the dimensions of $K_p$ will depend upon the $\nu_i$ values of the reactants and products. This particular aspect will be clear when you study the examples worked out in this unit.

Some authors prefer to give $K_p$ as a dimensionless quantity by dividing $p_i$ by $p^\circ$ where $p^\circ = 1 \text{ bar} = 10^5$ Pa. To represent $K_p$ as a dimensionless quantity, Eq. 14.20 is modified as,

$$K_p = \prod_i \left(\frac{p_i}{p^\circ}\right)^{\nu_i} \qquad \text{... (14.21)}$$

Let us apply Eq. 14.19 to ammonia synthesis reaction.

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

$$K_p = (p_{NH_3})^2\ (p_{N_2})^{-1} \cdot (p_{H_2})^{-3}$$

$$\text{or } K_p = \frac{p^2_{NH_3}}{p_{N_2}\ \ p^3_{H_2}}$$

Since the partial pressures are expressed in Pa unit, $K_p$ for ammonia synthesis has the unit $Pa^{-2}$. If $K_p$ for ammonia synthesis is to be dimensionless, then $K_p$ expression is to be written following 14.21 as,

$$K_p = \frac{p^2_{NH_3}(p^\circ)^2}{p_{N_2} \cdot p^3_{H_2}}$$

Let us illustrate the use of Eq. 14.19 with an example.

**Example 1**

Suppose that, in an experiment 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,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Calculate the value for the equilibrium constant, $K_p$.

**Solution**

At the given temperature, $K_p$ is given by the expression

$$K_p = p^2_{SO_3} \cdot p^{-2}_{SO_2} \cdot p^{-1}_{O_2}$$

$$\text{or } K_p = \frac{p^2_{SO_3}}{p^2_{SO_2} \cdot p_{O_2}} = \frac{(3.58 \times 10^4\ \text{Pa})^2}{(3.42 \times 10^4\ \text{Pa})^2 \times (3.13 \times 10^4\ \text{Pa})}$$

$$= 3.50 \times 10^{-4}\ \text{Pa}^{-1}$$

Note that the unit of $K_p$ as per Eq. 14.19 is given by $(\text{Pa})^{\Sigma\nu_i}$. In the reaction discussed in Example 1, $\Sigma\nu_i = 2 - 2 - 1 = -1$ Hence, the unit of $K_p$ is $\text{Pa}^{-1}$.

Try the following SAQ now.

**SAQ 2**

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

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

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).

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## 14.4.2 Equilibrium Constant Expression in Terms of Mole Fraction

Since Dalton's law tells us that partial pressure of a gas is equal to the mole fraction times the total pressure, Eq. 14.19 can be written as,

$$K_p = (x_L p_t)^l\ (x_M p_t)^m \ldots (x_A p_t)^{-a}\ (x_B p_t)^{-b}$$

$$K_p = \prod_i (x_i\, p_t)^{\nu_i} \qquad \ldots (14.22)$$

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

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

$p_i = p_t \cdot x_i$

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

**Example 2**

Consider the reaction,

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

If a mixture of $NO_2$, and $N_2O_4$ at equilibrium has a total pressure of $1.5 \times 10^5$ Pa, calculate the fraction of $N_2O_4$ that has dissociated at 303 K. $K_p$ for the reaction is $1.4 \times 10^4$ Pa at 303 K.

**Solution**

Suppose that $\xi$ is the fraction of the amount of $N_2O_4$ which has dissociated at equilibrium or it represents the extent of the reaction. Then, $1-\xi$ is the fraction of the amount of $N_2O_4$

remaining at equilibrium and is proportional to the actual number of moles of $N_2O_4$ present at equilibrium.

From the balanced reaction, it is seen that for each mole of $N_2O_4$ decomposed, there are two moles of $NO_2$ produced. Therefore, at equilibrium, $2\xi$ will be proportional to the actual number of moles of $NO_2$ produced.

The total number of moles at equilibrium would then be proportional to $1-\xi+2\xi$ or $1+\xi$.

The mole fractions of the two gases at equilibrium can be written as,

$x_{N_2O_4} = \dfrac{1-\xi}{1+\xi}$ and $x_{NO_2} = \dfrac{2\xi}{1+\xi}$ where $x$ denotes mole fraction.

Using Eq. 14.22, $K_p = (x_{NO_2} \cdot p_t)^2 \cdot (x_{N_2O_4} \cdot p_t)^{-1}$

i.e., $K_p = \dfrac{(x_{NO_2} \cdot p_t)^2}{(x_{N_2O_4} \cdot p_t)}$

Substituting for $x_{NO_2}$ and $x_{N_2O_4}$ we get,

$$K_p = \frac{\left(\dfrac{2\xi}{1+\xi} \cdot p_t\right)^2}{\dfrac{1-\xi}{1+\xi} \cdot p_t}$$

or $K_p = \dfrac{4\xi^2}{(1-\xi)(1+\xi)} p_t = \dfrac{4\xi^2}{1-\xi^2} \cdot p_t$

Substituting the given values, we get,

$1.4 \times 10^4 \text{ Pa} = \dfrac{4\xi^2}{1-\xi^2} \times 1.5 \times 10^5 \text{ Pa}$

or $\dfrac{1-\xi^2}{\xi^2} = \dfrac{1.5}{0.14} \times 4$

or $\dfrac{1}{\xi^2} = 1 + \dfrac{1.5 \times 4}{0.14}$

or $\xi^2 = 0.023$

$\xi = 0.15$

The fraction of $N_2O_4$ dissociated is thus calculated to be 0.15.

**Example 3**

Consider the reaction,

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

where initially 1 mol of CO and 2 mol of $H_2$ were mixed together. Derive an expression for the equilibrium constant, $K_p$, in terms of the extent of the reaction, $\xi$ and the total pressure, $p_t$.

**Solution**

If the extent of the reaction at equilibrium is represented by $\xi$ then we have,

| | $CO(g)$ | $+ 2H_2(g)$ | $\rightleftharpoons CH_3OH(g)$ |
|---|---|---|---|
| Moles at equilibrium | $1-\xi$ | $2-2\xi$ | $\xi$ |
| Mole fraction at equilibrium | $\dfrac{1-\xi}{3-2\xi}$ | $\dfrac{2-2\xi}{3-2\xi}$ | $\dfrac{\xi}{3-2\xi}$ |

Using Eq. 14.22, $K_p = (x_{CH_3OH} \cdot p_t)^1 \cdot (x_{CO} \cdot p_t)^{-1} \cdot (x_{H_2} \cdot p_t)^{-2}$

i.e., $K_p = \dfrac{(x_{CH_3OH} \cdot p_t)}{(x_{CO} \cdot p_t)(x_{H_2} \cdot p_t)^2}$

Hence,

$$K_p = \frac{\left(\frac{\xi}{3-2\xi} \cdot p_t\right)}{\left(\frac{1-\xi}{3-2\xi} \cdot p_t\right)\left(\frac{2-2\xi}{3-2\xi} \cdot p_t\right)^2}$$

$$= \frac{(3-2\xi)^2\,\xi}{(1-\xi)\,(2-2\xi)^2 \,.\, p_t^2}$$

You should be able to do the following SAQ, if you have understood the above examples.

**SAQ 3**

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.

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### 14.4.3 Equilibrium Constant Expression in Terms of Concentration

We know that for an ideal gas,

$$p_i = \frac{n_i RT}{V} = c_i RT$$

where $c_i$ represents molar concentration of a gaseous substance 'i'; other symbols have their usual meaning. Hence we can express Eq. 14.19 in terms of concentrations.

$$K_p = (c_L RT)^l\,(c_M RT)^m \ldots (c_A RT)^{-a}\,(c_B RT)^{-b}$$

$$= \frac{(c_L RT)^l\,(c_M RT)^m \ldots}{(c_A RT)^a\,(c_B RT)^b \ldots} \qquad \ldots (14.23)$$

i.e., $K_p = \prod_i (c_i RT)^{\nu_i}$ ... (14.24)

Eqs. 14.18 and 14.26 are the mathematical expressions of the law of mass action.

Where $\nu_i$ represents the stoichiometric coefficient (along with proper sign) in the chemical equation.

Eq. 14.23 can be written as,

$$K_p = \frac{c_L^l\, c_M^m \ldots}{c_A^a\, c_B^b \ldots}(RT)^{(l+m+\ldots)-(a+b+\ldots)}$$

$$= \frac{c_L^l\, c_M^m \ldots}{c_A^a\, c_B^b \ldots}(RT)^{\Sigma \nu_i}$$

i.e., $K_p = K_c\,(RT)^{\Sigma \nu_i}$ ... (14.25)

where $K_c$ is defined by,

$$= \frac{c_L^l\, c_M^m \ldots}{c_A^a\, c_B^b \ldots} = \frac{\text{Multiplication of } (c_i)^{\nu_i} \text{ terms of the products}}{\text{Multiplication of } (c_i)^{-\nu_i} \text{ terms of the reactants}} \qquad \ldots (14.26)$$

i.e., $K_c = \prod_i (c_i)^{\nu_i}$ ... (14.27)

Eq. 14.25 holds good for reactions between ideal gases.

The dimensions of $K_c$ depend of the $\nu_i$ values of the reactants and the products. In case $K_c$ is to be expressed as a dimensionless quantity, $c_i$ in Eq. 14.27 is to be replaced by $c_i/c_o$ where $c_o$ is the standard concentration and is equal to 1 mol dm$^{-3}$.

i.e., $K_c = \prod_i \left(\frac{c_i}{c_o}\right)^{\nu_i}$ ... (14.28)

It is important to note that $K_p$ and $K_c$ are functions of temperature; we shall discuss this aspect in Sec. 14.7.

Let us study an application of Eq. 14.26.

**Example 4**

Calculate the equilibrium concentrations of all the species at 613 K for the reaction,

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

if the initial concentrations of the three gases is 0.15 M each and $K_c = 0.800$ M at 613 K. The volume of the vessel is 1 dm$^3$.

The unit, mol dm$^{-3}$, is for denoting molarity and is represented by the letter, M.

Note that concentration in

$$\text{molarity} = \frac{\text{Number of moles}}{\text{Volume in dm}^3}$$

The unit of $K_c$ as per Eq. 14.26 is given by $(M)^{\Sigma\nu_i}$. In Example 4, $\Sigma\nu_i = 1 + 1 - 1 = 1$. Hence, the unit of $K_c$ in this example is M.

**Solution**

Suppose that $x$ mol of $PCl_5$ has decomposed at equilibrium. Since volume is 1 dm$^3$, the concentration expressed in molarity is equal to the number of moles of a particular substance.

| | $PCl_5$ | $PCl_3$ | $Cl_2$ |
|---|---|---|---|
| Equilibrium concentration/M | $0.15 - x$ | $0.15 + x$ | $0.15 + x$ |

Using Eq. 14.26, we get

$$K_c = \frac{c_{PCl_3} \cdot c_{Cl_2}}{c_{PCl_5}}$$

Substituting the given values, we get,

$$0.800\ \text{M} = \frac{(0.15 + x) \cdot (0.15 + x)}{(0.15 - x)}\ \text{M}$$

or $0.800\ (0.15 - x) = (0.15 + x)^2$

or $x^2 + 1.1\ x - 0.0975 = 0$

The solution of a quadratic equation of the form $ax^2 + bx + c = 0$ is given by

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

Using the principle of solution of standard quadratic equation, we get,

$x = 0.082$ M or

or $-1.183$ M

We take $x = 0.082$ M, since the second root of the quadratic equation gives the concentrations of $PCl_3$ and $Cl_2$ as (0.15 M − 1.83 M =) − 1.033 M which is impossible. Hence, the equilibrium concentrations are :

$[PCl_5] = (0.15 - 0.082)\ \text{M} = 0.068\ \text{M}$

and $[PCl_3] = [Cl_2] = 0.15 + 0.082 = 0.232\ \text{M}$

Square brackets are used to denote the concentration of a species. For example, $[PCl_5]$ is to be read as : concentration of $PCl_5$

We can verify the answer by substituting the values for concentrations in evaluating $K_c$.

Based on the above discussion, answer the following SAQ.

**SAQ 4**

How are $K_p$ and $K_c$ related to each other for a reaction between ideal gases?

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## 14.5 DETERMINATION OF EQUILIBRIUM CONSTANTS

It is now clear from the above examples that if the initial concentrations and the extent of the reaction are known, equilibrium constants can be calculated. In fact, if we want to make use of any of the equations derived in the previous two sections, we must be sure that the equilibrium has indeed been reached. The following two criteria confirm the presence of equilibrium condition :

1) The value of equilibrium constant should be same when the equilibrium is approached from either side.
2) The value of equilibrium constant should be same when the concentrations of the reacting substances are varied greatly.

Once it is established that an equilibrium has been reached, the next step is to find out the equilibrium concentration of at least one of the reactants or products in order to calculate the extent of the reaction. This can be achieved either by chemical analysis or by measurement of some physical property. The difficulty with the chemical analysis is that the concentration will change during the course of the analysis. Hence, only when the reaction can be stopped at equilibrium by some means (like sudden cooling), can this method be used. Physical methods are more convenient since they do not require stopping of the reaction. The physical properties commonly used for this purpose are density, refractive index, electrical conductivity, light absorption etc.

## 14.6 APPLICATIONS OF EQUILIBRIUM STUDIES

The law of mass action, as represented by Eqs. 14.18 to 14.28, finds many useful applications in chemical calculations like finding out the amounts of products formed at equilibrium or change in free energy of the system etc. We have already seen a few examples of the application of these equations; however, to simplify, we shall categorise the problems into three subsections, namely, homogeneous systems, heterogeneous systems and liquid solutions.

### 14.6.1 Homogeneous Systems

When all the reactants and products are present in the same phase (i.e., gaseous or liquid) we call it a homogeneous system. Let us consider a few examples :

**Example 5**

At 298 K, it was found that $K_p = 7.13$, for the reaction :

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

What is $\Delta_r G°$ for the reaction?

**Solution**

It is worth noting that $K_p$ is given as a dimensionless quantity as per Eq. 14.21.

Using Eq. 14.17, $\Delta_r G° = -RT \ln K_p$

$$= -2.303\, RT \log K_p$$

Substituting the values of $R$, $T$ and $K_p$ in the above equation, we get,

$$\Delta_r G° = (-2.303 \times 8.314 \times 298 \log 7.13)\ \text{J mol}^{-1} = -4.868\ \text{kJ mol}^{-1}$$

In Example 5, the term inside the log factor is greater than 1; hence the calculation is done as in the case of Example 3 of Unit 6 of this course.

**Calculation of $K_p$ from $\Delta_r G°$**

If $\Delta_r G°$ is a negative quantity, then log $K_p$ is a positive quantity. If we assume log $K_p$ to be equal to $x$, then $K_p$ can be calculated as follows :

$\log K_p = x$; hence

$K_p = 10^x =$ Antilog of $x$.

If $\Delta_r G°$ is a positive quantity, then log $K_p$ is a negative quantity. If we assume log $K_p$ to be equal to $-x$, then $K_p$ can be calculated as follows :

$\log K_p = -x$;. hence $\log \dfrac{1}{K_p} = x$

$\dfrac{1}{K_p} = 10^x =$ Antilog of $x$

or $K_p = \dfrac{1}{\text{Antilog of } x}$

Example 6 is worked out using this principle.

**Example 6**

What is the value of $K_p$ for the ammonia synthesis reaction at 500 K as represented by,

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

if $\Delta_r G° = 4.833$ kJ mol$^{-1}$?

**Solution**

$$\Delta_r G° = 4833\ \text{J mol}^{-1} = -(2.303 \times 8.314 \times 500 \log K_p)\ \text{J mol}^{-1}$$

Substituting the given values, we get, $\log K_p = \dfrac{-4833}{2.303 \times 8.314 \times 500} = -0.5048$

$$\therefore\ \log \frac{1}{K_p} = 0.5048;\ \frac{1}{K_p} = 10^{0.5048}$$

$$= \text{Antilog of } 0.5048 = 3.197$$

hence, $K_p = \dfrac{1}{3.197} = 0.3128$

**Example 7**

Hydrogen and iodine react at 699 K according to the equation,

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

If 1.00 mol of $H_2$ and 1.00 mol of $I_2$ are placed in a 1.00 dm$^3$ flask and allowed to react, what mass of hydrogen iodide will be present at equilibrium? At 699 K, $K = 55.3$.

**Solution**

First thing you should notice in this case is that the equilibrium constant is written with a symbol $K$ and not as $K_p$ or $K_c$ since the total number of moles of the products are equal to those of the reactants (i.e., $\Sigma\nu_i = 0$); so, $K_p$ must be equal to $K_c$ (see Eq. 14.25). Hence, we can write, $K = K_c = 55.3$.

Using Eq. 14.26, $55.3 = \dfrac{c^2_{HI}}{c_{H_2} \cdot c_{I_2}}$

If $\xi$ represents the extent of the reaction, the equilibrium concentrations can be written as, $c_{HI} = 2\xi$, $c_{H_2} = 1 - \xi$ and $c_{I_2} = 1 - \xi$; note that the amount of each material is equal to its concentration since volume is 1 $dm^3$. Substituting these values in the above equation, we get,

$$55.3 = \frac{(2\xi)^2}{(1-\xi)(1-\xi)}$$

or $\xi = 0.731$ or 1.269; the value, 1.269, is rejected since the value of $\xi$ cannot be greater than one.

Hence, the amount of HI at equilibrium $= 2\xi$ or $2 \times 0.731 = 1.46$ mol; the mass of HI at equilibrium $= 1.46 \times 0.128$ kg $= 0.188$ kg.

### 14.6.2 Heterogeneous Systems

Chemical reactions may also involve reactants or products in different phases. The most common examples are found where solids and gases are present together at equilibrium. Recall that at standard pressure of 1 bar, the activity of pure solid is unity. Hence, in writing the expression for equilibrium constant the activity or partial pressure terms for solids can be eliminated. Thus, for the reaction,

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

as per Eq. (14.19), $K_p = p^1_{CaO}\, p^1_{CO_2}\, p^{-1}_{CaCO_3} = p_{CO_2}$ [since $p_{CaO} = p_{CaCO_3} = 1$]

Again for the reaction,

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

as per Eq. 14.19, $K_p = \dfrac{p_{CO} \cdot p_{H_2}}{p_{H_2O}}$ since $p_C = 1$, carbon being in the solid form.

Let us illustrate the heterogeneous systems with another example.

**Example 8**

$NH_4HS(s)$ evaporates in an evacuated container at 298 K according to the equation.

$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

Find the pressure of each gas at equilibrium if $K_p = 1.10 \times 10^9 Pa^2$ at 298 K.

**Solution**

We can write for the above reaction,
using Eq. 14.19, $K_p = p_{NH_3} \cdot p_{H_2S}$ (since $p_{NH_4HS} = 1$)
Since the two gases produced in the reaction are in equimolar quantities,

$p_{NH_3} = p_{H_2S}$

or $K_p = p^2_{NH_3} = 1.10 \times 10^9$ $Pa^2$

$p_{NH_3} = p_{H_2S} = 3.32 \times 10^4$ Pa.

### 14.6.3 Liquid Solutions

So far we have discussed the reactions which take place in gaseous state or those involving gaseous and solid phases. But the majority of reactions are carried out in liquid solutions.

For example, you have already seen hydrolysis of an ester which can be written as :

Ester + Water $\rightleftharpoons$ Acid + Alcohol

Let us arrive at an expression useful in calculating the equilibrium constants of such reactions.

In an ideal solution, the concentration of each component can be conveniently expressed in terms of molarity. We can use Eq. 14.26 to express $K_c$ of a general reaction (given below) which takes place in a liquid solution; of course, the solution has to exhibit ideal behaviour.

$$aA + bB + \ldots \rightleftharpoons pr + qQ + \ldots$$

In this reaction, A, B, ... etc., and P, Q, ... etc., are the reactants and products; *a, b,* ... etc., and *p, q* ... etc., are the stoichiometric coefficients.

Similar to Eq. 14.26, we can write $K_c$ for the above reaction as,

$$K_c = \frac{c_P^p \cdot c_Q^q \ldots}{c_A^a \cdot c_B^b \ldots} \qquad \ldots (14.29)$$

$$K_c = \frac{m_P^p \cdot m_Q^q \ldots}{m_A^a \cdot m_B^b \ldots} = \frac{[P]^p[Q]^q}{[A]^a[B]^b} \qquad \ldots (14.30)$$

where $m_p$, $m_q$, ... etc., are the molarities of substances. In Eq. 14.30, the square brackets denote the concentrations of the species within the brackets.

Eqs. 14.29 and 14.30 can be applied to the solutions showing ideal behaviour. Similarly even in the case of gas phase reactions, equations such as 14.19 or 14.26 can be used only if the reactants and products are ideal gases. In case of deviation from ideal behaviour, whether it is a gas phase or a liquid phase reaction, activities of the substances must be used in the place of partial pressures or concentrations. But the equilibrium constant expressions become more complicated in such cases and we do not discuss them in this course.

Let us work out an example showing the use of Eq. 14.30.

**Example 9**

Calculate the equilibrium constant for the reaction,

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

at 298 K if 1.00 mol of acetic acid and 1.00 mol of ethyl alcohol are mixed together. At the equilibrium point, the amount of water is 0.333 mol.

**Solution**

The concentrations of substances are given below assuming the total volume to be $V$ dm$^3$:

| | $[CH_3COOC_2H_5]$ | $[H_2O]$ | $[CH_3COOH]$ | $[C_2H_5OH]$ |
|---|---|---|---|---|
| Concentration at equilibrium (in mol dm$^{-3}$) | $0.333/V$ | $0.333/V$ | $(1-0.333)/V$ | $(1-0.333)/V$ |

$$K_c = \frac{(0.667/V)\,(0.667/V)}{(0.333/V)\,(0.333/V)} = 4.01$$

Note that $K_c$ is a dimensionless quantity since $\sum \nu_i$ for this reaction is equal to zero. In cases such as this, volume need not be known as it cancels out in the final expression. If in any reaction $\sum_i \nu_i$ is not equal to zero, the final expression would contain volume term and $K_c$ will have suitable dimensions.

**SAQ 5**

For the reaction,

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

assuming that the reaction has attained equilibrium, calculate the concentration of water at 298 K for a mixture with

$[CH_3COOC_2H_5] = 2.0$ M
$[CH_3COOH] = 0.10$ M and
$[C_2H_5OH] = 0.50$ M
$K$ for this reaction is 4.01 at 298 K.

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## 14.7 EFFECT OF TEMPERATURE ON CHEMICAL EQUILIBRIUM

The equilibrium constant, $K$, of a reversible chemical reaction is a constant at a given temperature; but it varies with temperature. Let us derive an expression useful in bringing out the relationship between the equilibrium constant and temperature.

From Eq. 14.17, we get,

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

$$\text{or } \ln K_p = \frac{-\Delta_r G^\circ}{RT}$$

Differentiating this expression with respect to temperature,

$$\text{or } \frac{d \ln K_p}{dT} = -\frac{1}{R}\frac{d}{dT}\left(\frac{\Delta_r G^\circ}{T}\right) \qquad \text{... (14.31)}$$

Using Eq. 9.45 we can write

$$\frac{d}{dT}\left(\frac{\Delta_r G^\circ}{T}\right) = -\frac{\Delta_r H^\circ}{T^2} \qquad \text{... (14.32)}$$

Combining Eqs. 14.31 and 14.32, we get,

$$\frac{d \ln K_p}{dT} = \frac{\Delta_r H^\circ}{RT^2} \qquad \text{... (14.33)}$$

Eq. 14.33 tells us that equilibrium constant varies with temperature and depends on the standard enthalpy of the reaction.

Assuming that the standard enthalpy change ($\Delta_r H^\circ$) of the reaction remains constant over a small range of temperature; the above equation on integration between limits $K_{p_1}$, $K_{p_2}$, and $T_1$, $T_2$ gives,

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

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

$$\text{or } \log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta_r H^\circ}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{\Delta_r H^\circ (T_2 - T_1)}{2.303\,RT_1\,T_2} \qquad \text{... (14.34)}$$

Eq. 14.34 correlates the equilibrium constant values $K_{p_1}$ and $K_{p_2}$ (expressed in terms of partial pressures) at two different temperatures $T_1$ and $T_2$ to the standard enthalpy of reaction.

According to Eq. 14.25, which is applicable for ideal gases,

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

Using this equation and Eq. 14.33, it is possible to relate $K_c$ values to the respective temperatures as,

$$\log \frac{K_{c_2}}{K_{c_1}} = \frac{\Delta_r U^\circ (T_2 - T_1)}{2.303\,RT_1T_2} \qquad \text{...(14.35)}$$

where $K_{c_1}$ and $K_{c_2}$ are the equilibrium constants (in terms of concentrations) at temperatures $T_1$ and $T_2$ and $\Delta_r U^\circ$ is the standard internal energy change of the reaction. Since reactions are generally carried out at constant pressure, Eq. 14.34 is of greater importance for us. Eq. 14.35 is known as van't Hoff's isochore.

**Example 10**

The equilibrium constant for the reaction

$$H_2(g) + S(s) \rightleftharpoons H_2S(g)$$

is 18.5 at 925 K and 9.25 at 1000 K, respectively. Calculate the standard enthalpy of the reaction. Also calculate $\Delta_r G^\circ$ and $\Delta_r S^\circ$ at 925 K.

**Solution**

Substituting the given values in Eq. 14.34, we get,

$$\log \frac{K_{1000}}{K_{925}} = \frac{\Delta_r H^\circ}{(2.303 \times 8.314)}\left(\frac{1}{925} - \frac{1}{1000}\right)$$

$$\text{or } \log \frac{9.25}{18.5} = \frac{\Delta_r H^\circ}{2.303 \times 8.314}\left(\frac{75}{925 \times 1000}\right)$$

hence $\Delta_r H^\circ = -71.1 \text{ kJ mol}^{-1}$

Using Eq. 14.17, $\Delta_r G^\circ = -2.303 \times 8.314 \times 925 \log 18.5 = -22.4 \text{ kJ mol}^{-1}$

Rearranging Eq. 9.15 of Unit 9, $\Delta_r S^\circ = \dfrac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \dfrac{(-71100 + 22400)\text{ J}}{925\text{ K}}$

$$= -52.6 \text{ J K}^{-1}\text{ mol}^{-1}$$

**SAQ 6**

**For the dissociation of mercuric oxide, $K_p$ values are 0.0196 and 0.1794 at 693 K and 723 K, respectively. Calculate the standard enthalpy of the reaction.**

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## 14.8 LE CHATELIER'S PRINCIPLE AND CHEMICAL EQUILIBRIA

The equilibrium expressions derived in Secs. 14.3 to 14.7 are very useful to perform numerical computations of various kinds as we have already seen with different examples given. However, often one is more interested in predicting qualitatively the results of a change brought about by external forces on the system under equilibrium. For instance, if pressure, temperature or volume is changed for a system under equilibrium, what would be its effect, if any, on the equilibrium itself? Of course, we can find out the effect of such factors on the system under equilibrium with the help of expressions such as, Eq. 14.17 or Eq. 14.34. However, it is much more easily predicted with the help of Le Chatelier's principle.

**Le Chatelier's principle can be stated as follows :**
If a stress is applied to any system under equilibrium, the system would tend to shift in such a way so as to neutralise the effect of that stress (if possible).

The stress for a chemical reaction could be in the form of a change in pressure, temperature or concentration at equilibrium. According to the above principle then, the equilibrium would shift in such a direction so that the effect of these changes is neutralised. We shall consider the effect of each one of these factors on equilibrium separately.

### 14.8.1 Effect of Change of Concentration

Let us consider the reaction,

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

which has attained equilibrium. Now, if we add some $H_2$ to the equilibrium mixture, it will obviously upset the equilibrium. According to Le Chatelier's principle, the equilibrium would shift in such a way so as to oppose the effect of this excess $H_2$. It can do so by using up this excess $H_2$ to react with more $I_2$ to give more of HI. We describe this process by saying that the final position of equilibrium has shifted to the right of the equation. In this final state of equilibrium, then, more amount of HI is formed as compared to earlier equilibrium state. Just the opposite would be the fate of the reaction if, instead of $H_2$, some HI is added to the system under equilibrium. In short, by changing the concentration at equilibrium, the reaction will move forward or in the reverse direction so that the equilibrium constant has the same value.

### 14.8.2 Effect of Change of Pressure

If we consider the above reaction again and suppose that the pressure of the system is increased—perhaps by reducing the volume of the container—the system should react in such a way so as to reduce the effect of the increase in pressure. However, there is no way by which this can be achieved. The forward reaction or the reverse reaction will not be favoured by pressure change since the total number of moles of the reactants is the same as the total number of moles of the products.

However, the situation changes if we consider the synthesis of ammonia :

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

If the pressure of the system is increased at the equilibrium as was done in the previous example, the effect of this increase could be eliminated by the formation of more ammonia. This becomes obvious if you realise that the total number of moles of the reactants is four as compared to the moles of product which is two. Four moles will exert greater pressure than two moles; so, if the system wants to reduce the extra pressure, it can do so by moving in the forward direction. On the other hand, if we decrease the external pressure on the system, more of ammonia will decompose to give nitrogen and hydrogen. Thus, if we want to produce ammonia industrially, it is preferable to carry out the reaction at high pressures.

Comparing the two reactions given above, we can conclude that changes in pressure at equilibrium will affect the amounts of products formed for only those reactions where the total number of moles of reactants are different from the total number of moles of products.

### 14.8.3 Effect of Change of Temperature

Consider once again the synthesis of ammonia from nitrogen and hydrogen which is an exothermic reaction. If the temperature of the system is increased at equilibrium, Le Chatelier's principle tells us that the system should react in such a way so as to neutralise this effect. Let us see how this is possible. We know that the formation of ammonia is an exothermic reaction and, therefore, the reverse reaction of decomposition of ammonia will be endothermic. Thus, the excess heat supplied by raising the temperature of the system can be absorbed by the system if the reaction goes more towards left. This will increase the amounts of $N_2$ and $H_2$ and decrease the amount of $NH_3$ at equilibrium. We can generalise this observation by saying that by raising the temperature of a system undergoing exothermic reaction, we will decrease the amount of the products and increase the amount of the reactants. Just the opposite will be true for all endothermic reactions.

The effect of these factors gains special importance for the production of a substance on large scale. In any industrial production of a substance it is imperative to know the optimum conditions of temperature, pressure and concentrations in order to get the maximum yield at a minimum cost. For instance, in the production of ammonia we know from Le Chatelier's principle that high pressure and high concentration of $N_2$ and $H_2$ will favour the reaction. Similarly, the above principle also predicts that the reaction would be more favourable at low temperatures since it is exothermic. However, we cannot carry out the reaction at a very low temperature since another factor comes into the picture. That is, the rate of the reaction becomes too slow at lower temperatures. Hence, the reaction is performed at pressures of several megapascals and temperatures between 650 and 750 K.

You should be able to do the following SAQs which are based on the above discussion.

**SAQ 7**

Consider the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. How would the equilibrium be affected by,

i) the addition of $Cl_2$ and
ii) decrease in the volume of the container?

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**SAQ 8**

If $\Delta H^\circ = 41$ kJ mol$^{-1}$ for the reaction,

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

what will be the effect of increase of temperature on the equilibrium?

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## 14.9 SUMMARY

In this unit we have discussed the meaning of chemical equilibrium. A general expression for the equilibrium constant was derived from the basic principles of thermodynamics. Different forms of the general expression were then utilised in understanding the equilibria of homogeneous and heterogeneous systems. We then learnt Le Chatelier's principle and its use in predicting the shift in the position of equilibrium by the changes brought about in concentration, temperature and pressure of the system.

## 14.10 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) At 1000 K for the equilibria,
   i) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\qquad K_p = 4.0 \times 10^3$ Pa
   ii) $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ $\qquad K'_p = 2.0 \times 10^5$ Pa

   Solid C, CaO and $CaCO_3$ are mixed and allowed to attain equilibrium at 1000 K. What is the pressure of CO?

3) Show that for the reaction,
   $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$
   the equilibrium constant, $K_p$, is given by

$$K_p = \frac{\xi^3 p_t}{(2+\xi)(1-\xi)^2}$$

   where the symbols have their usual meaning.

4. In a 10.0 dm$^3$ mixture of $H_2$, $I_2$ and HI at equilibrium at 698 K, there are 0.100 mol of $H_2$, 0.100 mol of $I_2$ and 0.740 mol of HI. If 0.500 mol of HI are now added to this system, what will be the concentrations of $H_2$, $I_2$ and HI, once equilibrium has been reestablished?

5. At a certain temperature, $K_c = 7.5$ m$^3$ mol$^{-1}$ for the reaction,
   $2NO_2(g) \rightleftharpoons N_2O_4(g)$
   i) If 2.0 mol of $NO_2$ are placed in a 2.0 dm$^3$ container and allowed to react, what will be the concentrations of $NO_2$ and $N_2O_4$ at equilibrium?
   ii) What will be the equilibrium concentration, if the volume of the container is doubled?

6. Find the $\nu$ value of the reactants and the products in the following cases :
   i) $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$
   ii) $2CH_4(g) \rightleftharpoons C_2H_6(g) + H_2(g)$

7. If $K_p > 1$ for a reaction, comment on the sign of standard free energy change of the reaction.

8. At 298.15 K, the standard free energies of formation of $CH_3COOH(aq)$, $CH_3COO^-(aq)$ and $H^+(aq)$ are $-396.6$, $-369.4$ and 0 kJ mol$^{-1}$, respectively. Using this data, calculate the equilibrium constant for the dissociation of acetic acid at 298.15 K.

9. For the reaction,
   $N_2O_4(g) \rightleftharpoons 2NO_2(g)$,
   $K_p$ is $1.4 \times 10^4$ Pa at 303 K. Find $K_c$ at this temperature.

## 14.11 ANSWERS

### Self Assessment Questions

1) The formation of nitric oxide can be represented by the equation,

   $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

   $\nu$ values are as follows : $\nu_{NO} = 2$; $\nu_{N_2} = -1$ and $\nu_{O_2} = -1$.

2) Let us denote the equilibrium constant for the two equations as $K'_p$ and $K_p$.

$$K'_p = \frac{p_{NH_3}}{p_{N_2}^{1/2} \cdot p_{H_2}^{3/2}}$$

and

$$K_p = \frac{p_{NH_3}^2}{p_{N_2} \cdot p_{H_2}^3}$$

hence,

$$K_p = (K'_p)^2$$

Remember that generally the equilibrium constant value is obtained from the balanced chemical equation representing the reactants in their normal state of existence.

3) i) $K_p = \dfrac{p_{NO_2}^2}{p_{NO}^2 \cdot p_{O_2}}$

ii) Let us assume that 2 mol of NO and 1 mol of $O_2$ are mixed together initially. Let the total pressure be $p_t$.
Let $\xi$ be the fraction of number of moles of $O_2$ which has reacted at equilibrium.

Total Number of moles
$= (2-2\xi)+(1-\xi)+(2\xi)$
$= (3-\xi)$

| | NO | $O_2$ | $NO_2$ |
|---|---|---|---|
| Hence, number of moles at equilibrium | $2-2\xi$ | $1-\xi$ | $2\xi$ |
| Mole fraction at equilibrium | $\dfrac{2-2\xi}{3-\xi}$ | $\dfrac{1-\xi}{3-\xi}$ | $\dfrac{2\xi}{3-\xi}$ |

$$K_p = 4\xi^2(3-\xi)/(2-2\xi)^2(1-\xi)\,p_t$$

4) $K_p = (RT)^{\Sigma\nu_i}\ K_c$ [see Eq. 14.25]
where $\Sigma\nu_i$ = {Sum of the stoichiometric coefficients of the products} − {sum of the stoichiometric coefficients of the reactants}

5) Substituting the given values in Eq. 14.29, we get,

$$4.01 = \frac{(2.0)\,(x)}{(0.10)\,(0.50)}$$

$$x = \frac{4.01 \times 0.050}{2.0} = 0.10\ \text{M}$$

Hence, the concentration of water at equilibrium is 0.10 M.

6) Using Eq. 14.34, we get,

$$\Delta_r H^\circ = \frac{2.303 \times 8.314 \times 693 \times 723}{30} \log \frac{0.1794}{0.0196}\ \text{J mol}^{-1}$$

$$= 308\ \text{kJ mol}^{-1}$$

7) The equilibrium expression for the reaction,

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

can be written as,

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

When,

i) $Cl_2$ is added, $[PCl_5]$ must increase in order to keep the $K_c$ value constant; i.e., some $Cl_2$ will combine with $PCl_3$ to give more of $PCl_5$. Hence, the equilibrium will shift towards left.

ii) volume of the container is decreased, the pressure will increase. According to Le Chatelier's principle, the equilibrium would shift in such a direction so as to neutralise or reduce this increase. Since the total number of moles on the L.H.S. is less than in R.H.S., the equilibrium has to shift towards left in order to bring about pressure decrease.

8) For endothermic reactions, the increase in temperature will move the equilibrium in the forward direction according to Le Chatelier's principle explained in Sec. 14.8.

## Terminal Questions

1) Let the initial concentration of A be $a$ mol dm$^{-3}$;
then, the initial concentration of B $= 1.5a$ mol dm$^{-3}$.
In the beginning, C and D were not present. Suppose that at equilibrium, $x$ mol dm$^{-3}$ of A has reacted. The equilibrium concentration will be then,
$[A] = (a - x)$ mol dm$^{-3}$
$[B] = (1.5a - 2x)$ mol dm$^{-3}$
$[C] = 2x$ mol dm$^{-3}$
$[D] = x$ mol dm$^{-3}$.
But it is given that at equilibrium, the concentrations of A and D are equal; hence,

$$(a - x) = x$$

$$\text{or } x = \frac{a}{2}$$

$$\therefore\ [A] = \left(a - \frac{a}{2}\right) \text{mol dm}^{-3} = \frac{a}{2} \text{ mol dm}^{-3};\ [C] = a \text{ mol dm}^{-3}$$

$$[B] = \left(1.5a - 2 \cdot \frac{a}{2}\right) \text{mol dm}^{-3} = 0.5a \text{ mol dm}^{-3};\ [D] = \frac{a}{2} \text{ mol dm}^{-3}$$

The equilibrium constant is given by the expression;

$$K_c = \frac{[C]^2[D]}{[A]\,[B]^2} = \frac{[C]^2}{[B]^2} \text{ since } [A] = [D]$$

Substituting the values for [C] and [B], we get,

$$K_c = \frac{(a)^2}{(0.5a)^2} = 4;\ K_c \text{ is dimensionless, since } \Sigma \nu_i = 0$$

2) For the two reactions (i) and (ii), the equilibrium constants can be expressed as,

$$K_p = p_{CO_2}$$

$$K'_p = \frac{p^2_{CO}}{p_{CO_2}}$$

For the overall reaction; $CaCO_3\,(s) + C(s) \rightleftharpoons CaO(s) + 2CO(g)$, let the equilibrium constant be $K''_p$.

$$K''_p = p^2_{CO}$$

$$\text{or } K''_p = K'_p \times p_{CO_2}$$

$$K''_p = K'_p \times K_p$$

Substituting the given values, we get,

$$K''_p = 4.0 \times 10^3 \text{ Pa} \times 2.0 \times 10^5 \text{ Pa}$$
$$= 8.0 \times 10^8 \text{ Pa}^2.$$

$$\therefore\ p_{CO} = \sqrt{K''_p} = \sqrt{8.0 \times 10^8 \text{ Pa}^2}$$
$$= 2.8 \times 10^4 \text{ Pa.}$$

3) At equilibrium, the concentration will be given by,

$$\begin{array}{llll} 2H_2S(g) & \rightleftharpoons 2H_2(g) & + S_2(g) & \\ 2(1-\xi) & 2\xi & \xi & \end{array}$$

Total moles $=$
$2 - 2\xi + 2\xi + \xi = 2 + \xi$

The corresponding mole fractions will be,

$$\frac{2(1-\xi)}{2+\xi} \qquad \frac{2\xi}{2+\xi} \qquad \frac{\xi}{2+\xi}$$

The partial pressures of each substance can be obtained by multiplying the mole fraction by total pressure, $p_t$. Substituting the proper values in the equilibrium equation,

$$K_p = \frac{p_{S_2} \times p^2_{H_2}}{p^2_{H_2S}}$$

$$= \frac{\left\{\left(\frac{\xi}{2+\xi}\right)p_t\right\}\left\{\left(\frac{2\xi}{2+\xi}\right)p_t\right\}^2}{\left\{\left(\frac{2(1-\xi)}{(2+\xi)}\right)p_t\right\}^2}$$

$$\text{or } K_p = \frac{\xi^2 p_t}{(2+\xi)(1-\xi)^2}$$

4) For the reaction,

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

equilibrium concentrations can be written as,

$$[HI] = \frac{0.740}{10.0}\ \text{mol dm}^{-3} \qquad \text{(since the volume of the container is 10.0 dm}^3\text{)}$$

$$[I_2] = \frac{0.100}{10.0}\ \text{mol dm}^{-3}$$

$$[H_2] = \frac{0.100}{10.0}\ \text{mol dm}^{-3}$$

Substituting the values in the equilibrium constant expression,

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.0740)^2}{(0.0100)\,.\,(0.0100)}$$

$$= \frac{5.48 \times 10^{-3}}{1.00 \times 10^{-4}} = 54.8$$

Due to the addition of 0.500 mol of HI at equilibrium, the concentration of HI would become (0.074 mol dm$^{-3}$ + 0.05 mol dm$^{-3}$ = ) 0.124 mol dm$^{-3}$. The equilibrium will shift in such a direction so as to reduce the excess of added HI; that is, some more $H_2$ and $I_2$ will be formed. Suppose this amount is $x$ mol dm$^{-3}$ for each of these ($H_2$ and $I_2$) gases, then the new equilibrium concentrations would be,

$[H_2] = (0.0100 + x)$ mol dm$^{-3}$
$[I_2] = (0.0100 + x)$ mol dm$^{-3}$
$[HI] = (0.124 - 2x)$ mol dm$^{-3}$

Substituting the values in equilibrium expression, we get,

$$54.8 = \frac{(0.124 - 2x)^2}{(0.0100 + x)\,(0.0100 + x)}$$

$$\text{or } 7.40 = \frac{(0.124 - 2x)}{(0.0100 + x)}$$

$$0.0740 + 7.40\,x = (0.124 - 2x)$$

$$\text{or } 9.40\,x = 0.050$$

$$x = 5.3 \times 10^{-3}$$

Hence, $[H_2] = (0.01 + 0.0053)$ M = 0.0153 M = $[I_2]$
and $[HI] = 0.113$ M.

5) i) Initial concentration of $NO_2 = \dfrac{2.0 \text{ mol}}{2.0 \text{ dm}^3} = 1.0$ mol dm$^{-3}$ = 1.0 M

Suppose that at equilibrium, $x$ mol dm$^{-3}$ of $N_2O_4$ is formed. Then,

$[NO_2] = (1 - 2x)$ M; $[N_2O_4] = x$ M

Substituting in the equilibrium constant expression, we get,

$$7.5\ \text{m}^3\ \text{mol}^{-1} = \frac{x \text{ mol m}^{-3}}{(1-2x)^2\,(\text{mol m}^{-3})^2}$$

$$\text{or } 7.5 + 30x^2 - 31x = 0$$

$$\text{or } x = \frac{31 \pm \sqrt{(31)^2 - 120 \times 7.5}}{60}$$

$$x = \frac{31 \pm 7.8}{60} = 0.39 \text{ or } 0.65$$

If $x = 0.65$ value is considered, then
$[NO_2]$ at equilibrium = $(1 - 2x)$ M
= $(1 - 1.30)$ M
= $-0.30$ M

This is meaningless and hence is discarded.

M stands for mol dm

We consider only the value, $x = 0.39$, since the second root of the equation has no physical significance.

$[NO_2] = (1 - 2 \times 0.39)$ M = $(1 - 0.78)$ M = 0.22 M
$[N_2O_4] = 0.39$ M.

ii) When the volume of the container is doubled, initial concentration of $NO_2 = \frac{2.0 \text{ mol}}{4.0 \text{ dm}^3} = 0.5 \text{ mol dm}^{-3} = 0.5 \text{ M}$

Following the same procedure as before, we get,

$$7.5 \text{ M}^{-1} = \frac{x \text{ M}}{(0.5-2x)^2 \text{ M}^2}$$

$7.5(0.25 + 4x^2 - 2x) = x$
$1.875 + 30x^2 - 15x = x$
$30x^2 - 16x + 1.875 = 0$
$x = 0.17$ or $0.36$; only the value $x = 0.17$ is considered since the other value has no physical significance.
Hence at equilibrium, $[NO_2] = (0.5 - 2x) \text{ M} = (0.5 - 0.34) \text{ M} = 0.16 \text{ M}$
$[N_2O_4] = x \text{ M} = 0.17 \text{ M}$.

6) i) $\nu_{C_2H_5OH} = +1$, $\nu_{C_2H_4} = -1$, and $\nu_{H_2O} = -1$,
ii) $\nu_{C_2H_6} = +1$, $\nu_{H_2} = +1$ and $\nu_{CH_4} = -2$

7) If $K_p > 1$, $\Delta_rG^\circ$ is a negative quantity and the reaction is feasible.

8) The dissociation of acetic acid can be represented by the equation,

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

$\Delta_rG^\circ$ = (sum of standard free energies of formation of $CH_3COO^-$ and $H^+$ ions) − (standard free energy of formation of acetic acid)
$= [(-369.4 + 0) - (-396.6)] \text{ kJ mol}^{-1}$
$= 27.2 \text{ kJ mol}^{-1}$

Let us represent the equilibrium constant for the dissociation of acetic acid as $K_a$.

$$\log K_a = \frac{-\Delta_rG^\circ}{2.303\,RT}$$

$$= \frac{-27.2 \times 1000 \text{ J mol}^{-1}}{2.303 \times 8.314 \times 298.15 \text{ J mol}^{-1}}$$

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

9) For the reaction

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

$\Sigma\, \nu_i = +2 - 1 = +1$

According to Eq. 14.25,

$$K_c = K_p(RT)^{-\Sigma \nu_i}$$

$$= K_p(RT)^{-1}$$

$$= \frac{1.4 \times 10^4 \text{ Pa}}{8.314 \times 303 \text{ J mol}^{-1}}$$

$$= 5.56 \text{ mol m}^{-3}$$

# UNIT 15 IONIC EQUILIBRIA

## Structure

## 15.1 INTRODUCTION

We have seen in Unit 14 that for any reversible reaction in a solution, the law of mass action can be applied and the equilibrium constant can be expressed in terms of concentrations of various reactants and products. In this unit we are going to find out how the equilibrium expression can be applied to solve the problems regarding solutions of electrolytes. Solutions as you know consist of a solvent and at least one solute. Since majority of the reactions are carried out in water as a solvent, we shall consider the equilibria in aqueous solutions only. For simplicity we shall study these equilibria in several steps. First we shall apply the equilibrium expression to the solute system where the solute dissociates in water but is not affected otherwise by water. Next we shall consider the equilibrium of water dissociation itself. Finally, those cases will be studied where the two equilibria have to be considered together. These studies find wide applications in the fields of analytical, industrial and biochemistry.

### Objectives

After studying this unit, you should be able to :

- define acids and bases on the basis of different concepts,
- write the equilibrium constant expressions for the dissociation of weak acids, weak bases and water,
- define pH scale,
- state the effect of the addition of a substance containing common ion on the dissociation of acids and bases,
- explain the meaning of buffer solutions and their applications,
- state the meaning of hydrolysis and calculate hydrolysis constant,
- find the relationship between solubility and solubility product for different salts, and
- state its application in precipitation reactions.

## 15.2 ELECTROLYTES AND NONELECTROLYTES : ACIDS, BASES AND SALTS

In this unit, we shall confine our discussion to the solutions of electrolytes. It then becomes necessary that we must first know what are electrolytes and nonelectrolytes. If we put two charged electrodes in pure water, a very small amount of electric current will flow. However, if we add a small quantity of common salt (NaCl) to water, current flows easily; the reason being that the salt dissociates in water into its constituent ions—sodium ions and and chloride ions. Sodium ions which are positively charged will move towards negatively charged electrode and chloride ions will move towards the positively charged electrode. Thus current is carried by these ions in solution. All those substances which on dissolution in water conduct electricity are known as electrolytes; the familiar examples are acids, bases or salts. On the other hand, all those substances which when dissolved in water do not conduct electricity are called nonelectrolytes.

A substance may not necessarily ionise completely in solution. It may ionise to a small extent. We thus further classify qualitatively electrolytes into two groups. All those substances which dissociate almost completely are known as strong electrolytes and the substances which dissociate to a small extent in solution are called weak electrolytes. Most of the acids like acetic acid, oxalic acid, sulphurous acid etc. and a few salts like lead acetate and mercuric chloride are all weak electrolytes. On the other hand, most of the salts and a few acids such as perchloric, nitric, hydrochloric, sulphuric etc. fall in the category of strong electrolytes.

Most of our discussions will be confined to equilibria involving weak acids and weak bases. Presently acids and bases are being defined in many different ways. The application of equilibrium expression remains the same in whatever way one defines these acids and bases; yet, it is advisable to have a clear understanding of these different concepts of acids and bases.

### 15.2.1 Arrhenius Concept of Acids and Bases

Arrhenius defined acid as a compound which when dissolved in water gives hydrogen ion and a base, as a compound, which dissociates in water to yield hydroxyl ion. When an acid reacts with a base, it gives salt and water and the process is known as neutralisation reaction. Following examples should make the definition quite obvious :

Acids : $HNO_3 \longrightarrow H^+ + NO_3^-$

$HI \longrightarrow H^+ + I^-$

Bases : $NaOH \longrightarrow Na^+ + OH^-$

$KOH \longrightarrow K^+ + OH^-$

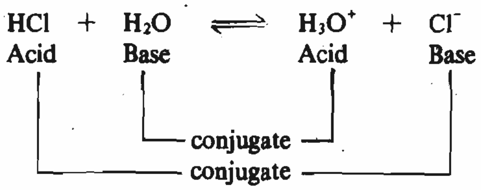
Neutralisation : $\underset{\text{(Acid)}}{H^+ + Cl^-} + \underset{\text{(Base)}}{Na^+ + OH^-} \longrightarrow \underset{\text{(Water)}}{H_2O} + \underset{\text{(Salt)}}{Na^+ + Cl^-}$

This is the most common and frequently used concept. However, there are two main limitations in this concept. First, it does not take into account the role of the solvent in the process. Secondly, there are many substances which do not contain hydrogen ion or hydroxyl ions but behave like acids or bases in their reactions. For examples, ammonia, $NH_3$, behaves like a typical base in reacting with an acid but does not contain hydroxyl ions. Similarly, $BF_3$ molecule does not contain hydrogen ions but does act as an acid towards a base like ammonia in the reaction :

$BF_3 + NH_3 \longrightarrow BF_3 : NH_3$

### 15.2.2 Lowry-Brφnsted Concept of Acids and Bases

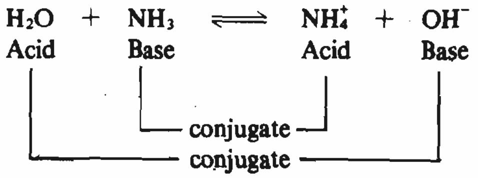
In 1923, two chemists, Lowry and Brφnsted, proposed a wider definition of acids and bases. They defined an acid as any substance (molecule or ion) which can act as a proton donor and a base as a substance which can accept a proton. Since a proton cannot exist free in any solvent, it is always found associated with a conjugate base. Thus, any two substances related by the gain or loss of $H^+$ ion are known as conjugate acid-base pair. For example, HCl is an acid which has a conjugate base, $Cl^-$ ion. Every acid HA has a conjugate base $A^-$ formed by the loss of a proton and every base $A^-$ has a conjugate acid formed when the base accepts a proton. Let us look at the reaction of HCl with water :



Here, water molecule acts as a base (proton acceptor) towards the acid, HCl (proton donor), producing conjugate acid and base, respectively as $H_3O^+$ and $Cl^-$. It can be represented in another way as,

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

'$\text{Acid}_1$' and '$\text{Base}_1$' form a conjugate pair just like '$\text{Acid}_2$' and '$\text{Base}_2$'. Let us consider another case :



In this case $H_2O$ is acting as an acid and $NH_3$ as a base. Thus, we see that water acts as an acid in one case and a base in another. Further, a stronger base will snatch away the proton associated with a weaker base. Thus, water molecule acts as a stronger base than chloride ion to produce a stronger acid ($H_3O^+$) and a weaker base, $Cl^-$ ion. Table 15.1 gives a list of a few examples of **Brønsted** acids and bases.

**Table 15.1 : Brønsted Acids and their Conjugate Bases**

| Acid | Base | Acid | Base |
|---|---|---|---|
| $H_3O^+$ | $H_2O$ | $HSO_4^-$ | $SO_4^{2-}$ |
| $H_2O$ | $OH^-$ | $CH_3COOH$ | $CH_3COO^-$ |
| HCl | $Cl^-$ | $NH_4^+$ | $NH_3$ |
| $H_2SO_4$ | $HSO_4^-$ | $NH_3$ | $NH_2^-$ |

Two main advantages of this concept are quite obvious. First, any substance which can accept a proton is defined as a base and therefore, it does not have to contain hydroxyl ion to be classified as a base. The obvious example is the above reaction where $NH_3$ having no $OH^-$ acts as a base towards water. On the other hand, a compound containing a proton can behave like an acid only in the presence of an acceptor. For example, HCl gas cannot behave like an acid unless there is a base like water present to accept the proton. The second advantage is that the acid strength depends on the solvent. Hence, an acid which behaves like a strong acid in water may act as a weak acid in another solvent depending upon the proton accepting ability of the latter. For example $HClO_4$, HBr, $HNO_3$ etc. are all strong acids in water as shown below :

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$
$$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^-$$
$$HBr + H_2O \longrightarrow H_3O^+ + Br^-$$

These reactions indicate that the equilibrium is shifted almost completely to the right side as their dissociation in water is complete; hence single arrows have been used. Under these conditions, therefore, we cannot differentiate as to which is stronger and which is weaker amongst them. The reason is obvious since water is a strong base for all these acids. Water reduces the strength of all these acids to the same level and these are all called strong acids in water. However, the situation will change if we dissolve all these acids in another solvent which is a weaker base than water, for instance, formic acid. The order of strength found with this base is : perchloric acid > nitric acid > hydrobromic acid. At first the statement sounds ridiculous since we are calling formic acid a base, but a careful examination will clarify this confusion. There is no doubt that formic acid has a proton which can be given off to water;

therefore it is classified as an acid. But, it can also accept a proton from a stronger acid and can thus behave like a base towards a strong acid, as shown by the following reaction :

$$HCOOH + H_2SO_4 \rightleftharpoons HSO_4^- + HCOOH_2^+$$

Thus, Brønsted definition of acids and bases is much wider than Arrhenius concept.

### 15.2.3 Lewis Acids and Bases

There are a number of reactions which resemble acid-base neutralisation reactions but where protons are not involved. Obviously, Arrhenius or Brønsted concepts cannot be utilised for such reactions. Lewis defined acids and bases in a different fashion which has a wider application. According to Lewis, an acid is an electron pair acceptor and a base is an electron pair donor. In other words, any substance which can accept a pair of electrons is an acid and a substance which donates a pair of electrons is a base. A few examples of Lewis acid-base reactions are :

$$BF_3 + NH_3 \rightleftharpoons BF_3NH_3$$
$$H^+ + NH_3 \rightleftharpoons NH_4^+$$
$$H^+ + OH^- \rightleftharpoons H_2O$$

Though for the sake of simplicity, we write $H^+$ ion in equation, free $H^+$ ion cannot exist in solution. It is always associated with solvent molecules. In aqueous solution we represent it by $H_3O^+$ but it has been shown that it exists as $H_9O_4^+$.

Metal ions in complexes accept electron pairs and act as Lewis acids.

Brønsted bases like $OH^-$ or $NH_3$ in the above reactions are also Lewis bases because they react with proton by donating electrons; but Lewis acid is not necessarily **Brønsted** acid since Brønsted acid must contain a proton which can be transferred to a base whereas Lewis acid does not have such a condition.

In our discussions, we shall be primarily concerned with aqueous solutions which involve proton transfer and therefore, Lewis concepts are not of so much use in the present context. However, for the sake of completeness and the wide application of Lewis concept, this has been included here.

**SAQ 1**

Explain with example, the difference between Lewis and Brønsted acids.

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## 15.3 IONIC EQUILIBRIA IN WEAK ACIDS AND BASES

Even in dilute solutions, weak electrolytes are dissociated to a very small extent and are never completely dissociated. Thus, for weak acids and bases, the ions produced on dissociation are in equilibrium with the undissociated molecules in solution and the law of mass action can be applied to such an equilibrium. For simplicity, we shall make use of Eq. 14.30 (refer to the Unit 14 on Chemical Equilibria). The equilibrium constants for the dissociation of acids and bases are expressed by the symbols $K_a$ and $K_b$, respectively. These equilibrium constants, $K_a$ and $K_b$, are called dissociation constants of acids and bases.

### 15.3.1 Weak Acids

If HA represents any weak acid, we can write the dissociation reaction as,

$$HA \rightleftharpoons H^+ + A^- \qquad \text{... (15.1)}$$

We have omitted writing $H_2O$ in Eq. 15.1 for the simple reason that the concentration of water remains constant even upto very high concentration of the salt.

and the corresponding dissociation constant expression as,

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (15.2)$$

If the initial concentration of the acid is $c_0$ and $\alpha$ is the degree of dissociation, then the equilibrium concentrations would be,

| | $HA \rightleftharpoons$ | $H^+$ + | $A^-$ |
|---|---|---|---|
| Initial concentration | $c_0$ | | |
| Equilibrium concentration | $(1-\alpha)c_0$ | $\alpha c_0$ | $\alpha c_0$ |

Substituting these values in Eq. 15.2, we get,

$$K_a = \frac{(\alpha c_0)(\alpha c_0)}{(1-\alpha)\, c_0}$$

$$\text{or } K_a = \frac{\alpha^2 c_0}{1-\alpha} \qquad \text{... (15.3)}$$

Application of Eq. 15.3 can be seen from the following examples.

**Example 1**

At 298 K, a 0.100 M solution of acetic acid is 1.34% ionised. Calculate the ionisation constant of acetic acid.

$K_a$ and $K_b$ are usually expressed as dimensionless quantities.

**Solution**

Since $\alpha = 0.0134$, $[H^+] = \alpha c_0 = 0.0134 \times 0.100$ M
$= 0.00134$ M $= [CH_3COO^-]$;
also $[CH_3COOH] = (1 - 0.0134) \times 0.100$ M $= 0.09866$ M

$$\therefore K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(0.00134)^2}{0.09866}$$

or $K_a = 1.82 \times 10^{-5}$

**Example 2**

Calculate the concentration of $H^+$ ions in a solution of 1.0 M acetic acid at 298 K ($K_a = 1.8 \times 10^{-5}$).

**Solution**

As per Eq. 15.1, we can write,

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

Equilibrium concentration $c_0(1-\alpha)$ $\quad c_0\alpha \quad c_0\alpha$

Initial concentration of acetic acid, $c_0 = 1.0$ M.

$\therefore [H^+] = c_0\alpha$ M
$= \alpha$ M

The value of $\alpha$ can be found out by substituting $K_a$ and $c_0$ values in Eq. 15.3.

For a monobasic acid like acetic acid, $[H^+] = [\text{acid}] \times$ degree of dissociation

The simplification, $K_a = \alpha^2 c_0$ is valid only when, $\alpha$ is small compared to 1 and may be neglected when subtracted from 1.

$$1.8 \times 10^{-5} = \frac{\alpha^2}{1-\alpha}$$

Solving for $\alpha$, we get a value of $4.2 \times 10^{-3}$; the other value being negative, has no physical significance.

Hence, $[H^+]$ in 1 M acetic acid $= \alpha$ M
$= 4.2 \times 10^{-3}$ M

Eq. 15.3 can be simplified further if the degree of dissociation is very small, i.e., if $\alpha << 1$, then $K_a = \alpha^2 c_0$

Multiplying both sides by $c_0$, we get,

$K_a . c_0 = \alpha^2 c_0^2$

or $c_0\alpha = \sqrt{K_a c_0}$

$$\text{or } [H^+] = \sqrt{K_a c_0} \qquad (15.4)$$

Remember that in deriving Eq. 15.4, we have made two assumptions. First that the degree of dissociation is much smaller than unity and secondly that water which has been used as a solvent has no effect on the equilibrium of the acid.

### 15.3.2 Weak Bases

For a weak base, BOH, we can write the equations as,

$$BOH \rightleftharpoons B^+ + OH^- \qquad \text{... (15.5)}$$

$$\text{and } K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \text{... (15.6)}$$

If $c_0$ is the initial concentration of the base and $\alpha$ is the degree of dissociation, then,

$$K_b = \frac{(\alpha c_0)(\alpha c_0)}{(1-\alpha)\, c_0} = \frac{\alpha^2 c_0}{1-\alpha} \qquad \text{... (15.7)}$$

$$\text{Also, } [OH^-] = \alpha c_0 = \sqrt{K_b c_0} \text{ if } \alpha << 1 \qquad \text{... (15.8)}$$

### 15.3.3 Polyprotic Acids

Those acids which contain more than one hydrogen atom per molecule and can release proton in more than one step are called polyprotic acids. Each ionisation step is associated with an equilibrium constant.

Consider the case of phosphoric acid which is a triprotic acid. It is also called a tribasic acid implying thereby that each mole of the acid can neutralise three moles of a base. The dissociation reactions are written as.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad \ldots (15.9)$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad \ldots (15.10)$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad \ldots (15.11)$$

Each of these steps of dissociation is connected with an equilibrium constant which can be represented by,

$$K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \qquad \ldots (15.12)$$

$$K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \qquad \ldots (15.13)$$

and

$$K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \qquad \ldots (15.14)$$

The actual values for the three equilibrium constants have been found to be $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$ and $K_3 = 1.0 \times 10^{-12}$ which follow a decreasing order. This is to be expected since an undissociated molecule, $H_3PO_4$, can lose its proton more easily than the negatively charged $H_2PO_4^-$ ion, which is turn, can give off its proton more easily than a double-negatively charged $HPO_4^{2-}$ ion. Hence, in a solution of phosphoric acid the predominant species will be $H_3PO_4$, $H^+$ and $H_2PO_4^-$ with lesser amounts of $HPO_4^{2-}$ and still less of $PO_4^{3-}$.

Another common example is $H_2SO_4$ which dissociates as,

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-; \quad K_1 = \frac{[H^+][HSO_4^-]}{[H_2SO_4]} = 1.0 \times 10^3$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}; \quad K_2 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 1.3 \times 10^{-2}$$

As a test of the understanding of the above concepts, answer the following SAQ.

**SAQ 2**

Calculate the concentration of $OH^-$ ions in a solution of 1.0 M $NH_4OH$ at 298 K ($K_b = 1.8 \times 10^{-5}$).

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## 15.4 IONIC PRODUCT OF WATER

Water is the most commonly used solvent and it is amphoteric in character. The dissociation of water can be represented as,

An amphoteric substance can act both as an acid and as a base.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \ldots (15.15)$$

$$\text{or } 2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad \ldots (15.16)$$

Although Eqs. 15.15 and 15.16 are representations of the same equilibrium, Eq. 15.16 is a better representation in the sense that a free proton having a high charge density and extremely small size is incapable of free existence in solution and, therefore, gets attached to a molecule of water. However, since our calculations on equilibrium constant will not be different in case of either representation, for simplicity sake, we represent the water equilibrium by Eq. 15.15 and the equilibrium constant is written as,

$$K = \frac{[H^+][OH^-]}{[H_2O]} \quad \text{... (15.17)}$$

$$\text{or } K[H_2O] = [H^+][OH^-] \quad \text{... (15.18)}$$

Mass of 1 $dm^3$ of water at 298 K is found to be 0.998 kg. Mass of 1 mole of $H_2O$ is 0.018 kg. Hence, the number of moles of $H_2O$ present in 0.998 kg or 1 $dm^3$ is

$$55.4 \left( \simeq \frac{0.998 \text{ kg}}{0.018 \text{ kg}} \right)$$

which is called the molarity of water.

In pure water the concentration of $H_2O$ molecules is approximately 55.4 M and since the dissociation of $H_2O$ is negligibly small in comparison with its concentration, we can safely assume that the concentration of $H_2O$ at equilibrium is a constant quantity. Thus, $K[H_2O]$ in Eq. 15.18 can be replaced by a new constant, $K_w$, known as the ionic product of water. Thus,

$$K_w = [H^+][OH^-] \quad \text{... (15.19)}$$

Experimental determination gives a value of $1.0 \times 10^{-14}$ for $K_w$ at 298 K. Hence,

$$1.0 \times 10^{-14} = [H^+][OH^-] \quad \text{... (15.20)}$$

Since the amount of $H^+$ and $OH^-$ produced by the dissociation of pure water is equal, concentration of each ion in solution is given by,

$$[H^+] = [OH^-] = 1.0 \times 10^{-17} \quad \text{... (15.21)}$$

$$\text{or } [H^+] = \sqrt{K_w} \text{ (in pure water)} \quad \text{... (15.22)}$$

In the next section, we shall discuss pH scale which is convenient in expressing the $H^+$ ion concentration of solutions. Like any equilibrium constant, $K_w$ also depends on temperature.

## 15.5 pH SCALE

Consider the equilibrium of water as given by Eq. 15.17,

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

Suppose that we add a small quantity of an acid to water, thereby increasing the concentration of $H^+$ ions at equilibrium. The equilibrium will immediately shift back to oppose the effect of this increase by the combination of the added $H^+$ ions with some $OH^-$ ions to form undissociated water till Eq. 15.15 is satisfied. Once the equilibrium is reestablished, the concentration of the hydrogen ion will be more than the concentration of the hydroxyl ion in solution. Hence, at 298 K, whenever the concentration of hydrogen ion in water is greater than $1.0 \times 10^{-7}$ M, we call the solution to be acidic and whenever it is less than $1.0 \times 10^{-7}$ M, we call it a basic solution. Instead of expressing these small concentrations as negative powers of 10, we can state them more conveniently and as a small number by expressing them in terms of their negative logarithm. Hence, instead of writing $H^+$ ion concentration as $1.0 \times 10^{-7}$ M we write it as $-\log [1.0 \times 10^{-7}]$ or simply 7. This number we denote by a symbol pH (small letter, p followed by capital letter, H). Thus,

$$pH = -\log [H^+] \quad \text{... (15.23)}$$

$$\text{or } [H^+] = 10^{-pH} \quad \text{... (15.24)}$$

where $H^+$ ion concentration is expressed in mol $dm^{-3}$. The concept of negative logarithm can be used for defining the concentration of other ions also. For example, pOH represents the concentration of $OH^-$ ion in solution and pM represents the concentration of the metal ion, M, in solution.

**Example 3**

Find the concentration of $H^+$ ions of a solution for which pH value is 4.5.

**Solution**

Using the equation,
$pH = -\log [H^+]$
we get, $4.5 = -\log [H^+]$

or $\log [H^+] = -4.5$

i.e. $[H^+] = 10^{-4.5}$ M

$$
\begin{aligned}
&= 10^{(-5+0.5)}\ \text{M} && \text{... Step (i)}\\
&= 10^{0.5} \times 10^{-5}\ \text{M} && \text{... Step (ii)}\\
&= 3.2 \times 10^{-5}\ \text{M} && \text{... Step (iii)}
\end{aligned}
$$

Pure water, where $H^+$ ion and $OH^-$ ion concentration are both equal to $1.0 \times 10^{-7}$ (at 298 K), will thus have a pH value of 7. An acidic solution means that the pH should be less than 7 and a basic solution should have pH greater than 7.

To calculate $10^x$, see antilog of $x$.

(i) When $x$ is positive, see antilog straight away.
e.g. (1) $10^{0.5}$ = Antilog of $0.5000 = 3.2$
(2) $10^{2.4}$ = Antilog of $2.4 = 2.5 \times 10^2$

(ii) When $x$ is negative, follow the steps given below :

**Step (i) :** The negative exponent ($x$) is shown as the sum of a negative integer and a positive fraction.

**Step (ii) :** Write the resultant number as a product of two terms.

**Step (iii) :** See the antilog of the positive fraction written as power of 10, and multiply this, by 10 raised to the power of negative integer.

These steps are required since while seeing antilogarithm, the mantissa must be positive, although characteristic may be positive or negative. In the light of the above, see Example 3.

Let us do a few simple calculations to see quantitatively as to what happens to the self-ionisation equilibrium of water when we add a small quantity of a strong acid to it. Consider a solution containing 0.010 mole of HCl in one $dm^3$ of water. The concentration of hydrogen ion due to HCl will be $1.0 \times 10^{-2}$ M. This addition of acid will disturb the water equilibrium and this equilibrium will shift to left so that dissociation of water is suppressed. Thus, the concentration of $H^+$ ions produced by the self-ionisation of water ($\approx 10^{-7}$ M) is negligible in comparison with the $H^+$ ion produced by the added acid ($10^{-2}$ M). Hence, the contribution due to water dissociation can be neglected in such a case and the pH of the solution will be 2. The concentration of $OH^-$ ion will then be given by,

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}\ \text{M}$$

or pOH = 12

We can state this in a different way that, in $10^{-2}$ M acid solution, the concentration of $OH^-$ ion ($10^{-12}$ M in the above example) is less than the concentration of $H^+$ ion ($10^{-2}$ M) and, the product of the two is always constant, and is equal to $1.0 \times 10^{-14}$. This can be expressed as,

$$\text{pH} + \text{pOH} = 14 = -\log K_w \qquad \text{... (15.25)}$$

Thus, in pure water or a dilute solution of an acid or a base, we can express the concentration of $H^+$ or $OH^-$ by simply stating the pH of the solution. We have also studied that the contribution due to self-ionisation of water is negligible in cases of solution of strong acids and bases as well as of moderately concentrated solutions of weak acids and weak bases. However, dealing with very dilute solutions of weak acids and bases, we cannot neglect the contributions due to self-ionisation equilibrium of water.

To sum up, while calculating $[H^+]$ of an acid,

- $[H^+] = [H^+]$ from acid, if [acid] is far greater than $10^{-6}$ M.
- $[H^+] = [H^+]$ from acid + $[H^+]$ from water if [acid] is between $10^{-6}$ and $10^{-8}$ M.
- $[H^+] = [H^+]$ from water if [acid] is far less than $10^{-8}$ M.

You try the following SAQs, based on the above concept of pH.

**SAQ 3**

Calculate the pH of the following solutions :

(a) $1.0 \times 10^{-8}$ M HCl (b) $1.0 \times 10^{-10}$ M HCl
(c) $1.0 \times 10^{-10}$ M NaOH

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## 15.6 COMMON ION EFFECT

Let us consider the dissociation of a weak acid such as acetic acid,

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

the equilibrium constant for which can be represented as,

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \qquad \text{... (15.26)}$$

$$\text{or } H^+ = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} \qquad \text{... (15.27)}$$

Suppose that we add some acetate ions in the form of solid sodium acetate to the above solution. Sodium acetate is added in the solid form so as not to cause any change in the volume of the solution. Sodium acetate being a strong electrolyte will dissociate almost completely to give $Na^+$ ions and $CH_3COO^-$ ions in solution. The acetate ions so added will disturb the equilibrium of acetic acid. The equilibrium will, therefore, shift to left producing more of undissociated acetic acid in order to counteract the effect of added acetate ions according to Le Chatelier's principle. The net result is that the dissociation of the acid has been suppressed by the addition of a common ion (acetate ion in the present case) at equilibrium. Thus any ion which is involved in a chemical equilibrium and comes from two different sources in solution is known as 'common ion' and its effect finds great use in the study of buffer solutions (sec. 15.7) and the solubility of sparingly soluble salts (sec. 15.11).

On the basis of the above discussion, answer the following SAQ.

**SAQ 4**

Addition of $NH_4Cl$ to $NH_4OH$ results in the decrease of $OH^-$ ion concentration. Explain.

## 15.7 BUFFER SOLUTIONS

A careful examination of Eq. 15.27 reveals that the hydrogen ion concentration (or the pH of the solution) shall have a constant value equal to $K_a$ (or p$K_a$), if the concentrations of acetate ions and the undissociated acetic acid become equal to each other. In order to find how this condition can be achieved and what are its uses, let us consider a 1.0 M acetic acid solution for which $K_a = 1.8 \times 10^{-5}$. We can write,

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

$$\text{or } 1.8 \times 10^{-5} = \frac{[H^+]^2}{[CH_3COOH]}$$

since, $[H^+] = [CH_3COO^-]$

Assuming that the amount of acetic acid dissociated is negligible in comparison to the initial concentration of acetic acid (1.0 M), we can write the concentration of undissociated acetic acid as, 1.0 M.

$\therefore\ [H^+]^2 = 1.8 \times 10^{-5} \times 1.0\ M^2$

or $[H^+] = \sqrt{1.8 \times 10^{-5}}\,M = 4.2 \times 10^{-3}\ M$

or pH = 2.38; i.e., the pH of 1.0 M acetic acid is 2.38.

To this solution if we add enough of solid sodium acetate to make it 1.0 M in acetate ion concentration, the dissociation of acetic acid will be further suppressed due to common ion effect. Thus, the concentration of acetate ion arising out of the dissociation of acetic acid is negligible in comparision with that supplied by sodium acetate. Hence, we can assume the concentration of acetate ion in solution to be 1.0 M. Similarly, if the dissociation of acetic acid is negligibly small, the concentration of the undissociated acetic acid, $[CH_3COOH]$, can be taken as 1.0 M. Substituting these values in Eq. 15.26, we get,

$$1.8 \times 10^{-5} = \frac{[H^+][1.0]}{[1.0]} = [H^+]$$

or pH $\doteq$ 4.74; i.e., a solution which has 1.0 M acetic acid and 1.0 M sodium acetate has a pH of 4.74.

A solution containing a weak acid and its conjugate base or a weak base and its conjugate acid is called a buffer solution. It resists the change in pH on addition of acids, bases or on dilution.

Such a solution of a weak acid and its salt or a weak base and its salt is known as buffer solution and it has an advantage of maintaining the pH of the solution almost constant even if small quantities of strong acids or bases are added to it. Let us see why this is so.

Assume that to the above solution of acetic acid and sodium acetate, known as acetate buffer, we add hydrochloric acid such that its concentration in the solution becomes 0.01 M. As a result of this, 0.01 M $H^+$ ions will react with 0.01 M acetate ions to form 0.01 M undissociated acetic acid. Thus, the concentration of the undissociated acetic acid will increase from 1.0 M to 1.01 M. The concentration of acetate ion will correspondingly decrease by 0.01 M and its concentration at equilibrium will be (1.0 M − 0.01 M =) 0.99 M. Substituting these values in Eq. 15.27, we get.

$$[H^+] = \frac{1.8 \times 10^{-5} \times 1.01}{0.99}$$

$$= 1.83 \times 10^{-5}$$

∴ pH = 4.74; hence, we find that by the addition of 0.01 M HCl, there is no change in the pH of the solution.

If the same amount of HCl is added to water, the pH of the solution changes from 7 to 2.

Thus, for any weak acid, HA, in presence of its salt, say, NaA, the following equations can be written :

$$HA \rightleftharpoons H^+ + A^-$$
$$NaA \rightleftharpoons Na^+ + A^-$$

Using Eq. 15.2, we can write,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\text{or } [H^+] = K_a \frac{[HA]}{[A^-]}$$

By taking logarithms on both l.h.s. and r.h.s. of Eq. 15.28,

$$\log [H^+] = \log K_a + \log \frac{[Acid]}{[Salt]}$$

Hence, $-\log [H^+]$

$$= -\log K_a - \log \frac{[Acid]}{[Salt]}$$

$$\text{i.e., } pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

This expression is known as Henderson's equation.

The concentration of $A^-$ is mainly due to the dissociation of the salt and negligible due to the dissociation of the acid. Similarly, the concentration of the undissociated acid is the same as the original concentration, since the amount dissociated is negligible.

Hence we can write, $[A^-] = [salt]$ and $[HA] = [Acid]$

$$\text{or } [H^+] = K_a \frac{[Acid]}{[Salt]} \quad \text{... (15.28)}$$

In the case of a buffer of a weak base and its salt, we can write an equation similar to Eq. 15.28 as,

$$[OH^-] = K_b \frac{[Base]}{[Salt]} \quad \text{... (15.29)}$$

For an effective buffer, the ratio of the concentration of the acid (or base) to the concentration of the salt should be between 1/10 and 10/1. Substituting, these values in Eq. 15.28, we get Eqs. 15.30 and 15.31.

**Case (i) :** $\frac{[Acid]}{[Salt]} = \frac{1}{10}$

Using Eq. 15.28, $[H^+] = K_a \frac{1}{10}$

Taking logarithm, $\log [H^+] = \log K_a + \log 1/10$

$$= \log K_a - 1$$

or $-\log [H^+] = -\log K_a + 1$

$$\text{i.e., } pH = pK_a + 1 \quad \text{... (15.30)}$$

**Case (ii) :** $\frac{[Acid]}{[Salt]} = 10$

Again using Eq. 15.28, $[H^+] = K_a.10$

Following the steps shown in case (i) we get,

$$pH = pK_a - 1 \quad \text{... (15.31)}$$

Thus, pH is held within a range of unity on either side of $pK_a$.

Buffers play an important role in nature. For example, blood contains $H_2CO_3/HCO_3^-$ buffer that maintains the pH at 7.4; in the absence of a buffer, the sudden changes in the pH of blood or other cell fluids could cause severe damage to the system. Another example is that the oceans are maintained at about pH = 8.4 by a complex buffering action involving silicates and bicarbonates. In the absence of buffering action, sea-life could be severely affected.

In industrial processes like electroplating, paper manufacturing, alcohol brewing, leather tanning etc. most of the chemical reactions are pH controlled. Applications of buffers in analytical chemistry are innumerable. You should try the following SAQ which is based on the above discussion.

**SAQ 5**

A solution is prepared by adding $2.05 \times 10^{-3}$ kg anhydrous sodium acetate to 0.10 $dm^3$ of 0.10 M HCl solution. What is the pH of the solution?

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## 15.8 HYDROLYSIS

So far we have considered two equilibria—one, of the dissociation of weak acids and bases and the other one, of the self-ionisation of water—and made an assumption that the water equilibrium does not influence the acid-base equilibria since the dissociation of water is negligibly small. We now treat a situation where water equilibria plays an important role The process in which, water not only acts as a solvent but reacts with the solute, is known as hydrolysis.

Suppose we dissolve sodium acetate in water; this being a strong electrolyte, would dissociate completely providing $Na^+$ ions and $CH_3COO^-$ ions in solution.

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

Acetate ions so produced react immediately with water giving undissociated acetic acid and hydroxyl ions according to the equation,

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \qquad \text{... (15.32)}$$

Since there are free $OH^-$ ions in the solution, it becomes basic.

The question arises as to what happens to the $Na^+$ ions in solution. The answer is that they do not react with water. Let us see why it is so. For the sake of argument, let us imagine that $Na^+$ ions also react with water in the same fashion as acetate ion. Accordingly we can write,

$$Na^+ + H_2O \rightleftharpoons NaOH + H^+$$

However, NaOH so produced, will dissociate almost completely giving $OH^-$ ions.

$$NaOH \longrightarrow Na^+ + OH^-$$

The $OH^-$ and $H^+$ ions would be equal in amount and, these two will produce undissociated water. In other words, $Na^+$ ions will not affect the water equilibrium.

Salts like sodium acetate can be thought of as a product of the reaction between a weak acid, $CH_3COOH$, and a strong base, NaOH.

$$NaOH + CH_3COOH \rightleftharpoons CH_3COONa + H_2O$$

Thus our conclusion would be that the salts of a weak acid and a strong base, when dissolved in water, will produce a basic solution.

Let us consider the case of a salt of a weak base and a strong acid like $NH_4Cl$. Similar to the previous example, in this case only $NH_4^+$ hydrolyses as

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

which produces a weak base and excess of hydrogen ions in solution, thus rendering the solution acidic. Hence, we can say that the salt of a weak base and a strong acid will produce an acidic solution.

In case of salts of a weak acid and a weak base, it is not possible to predict qualitatively whether the solution will be acidic or basic. Consider a salt like ammonium acetate, $CH_3COONH_4$, where both the cation and anion can hydrolyse according to the equations:

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

or $$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

Hydrolysis of one ion gives hydrogen ions, whereas that of the other ion gives hydroxyl ions in solution. Therefore, the pH of the solution will depend on the extent of the hydrolysis of the two ions. If $NH_4^+$ hydrolyses to a greater extent than $CH_3COO^-$ ion, the solution will be acidic and, if the reverse is true, then the solution will be basic. If the extent of hydrolysis is exactly equal, then the solution should be neutral as if no hydrolysis is taking place.

The extent of hydrolysis is given by the equilibrium constant of the hydrolysis reaction which is known as hydrolysis constant. Let us consider the equilibrium represented by Eq. 15.32.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$K = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]\,[H_2O]}$$

Since the concentration of water remains constant, we can write,

$$K_h = K[H_2O] = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} \qquad \text{... (15.33)}$$

where $K_h$ is known as hydrolysis constant.

We can find another expression for $K_h$ using the following equilibria.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-;\ K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]} \qquad \text{... (15.34)}$$

$$\text{and } H_2O \rightleftharpoons H^+ + OH^-;\ K_w = [H^+]\,[OH^-] \qquad \text{... (15.35)}$$

From Eqs. 15.34 and 15.35 we get,

$$\frac{K_w}{K_a} = [H^+]\,[OH^-] \times \frac{[CH_3COOH]}{[H^+]\,[CH_3COO^-]} = \frac{[OH^-]\,[CH_3COOH]}{[CH_3COO^-]} \qquad \text{... (15.36)}$$

Comparing Eqs. (15.33) and (15.36) we can write,

$$K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} = \frac{K_w}{K_a} \qquad \text{... (15.37)}$$

Similarly for the hydrolysis of an ion like $NH_4^+$ which produces a weak base, we can write,

$$K_h = \frac{K_w}{K_b} \qquad \text{... (15.38)}$$

Also, it is possible to show that for the hydrolysis of a salt of a weak acid and weak base,

$$K_h = \frac{K_w}{K_a K_b} \qquad \text{... (15.39)}$$

Thus, we notice that the hydrolysis constant is directly related to $K_a$ or $K_b$ of the weak acid or weak base produced.

Let us now find out the relationship between the hydrolysis constant and the degree of hydrolysis for the reaction given by Eq. 15.32. Suppose that the concentration of sodium acetate is $c_0$ and its degree of hydrolysis is '$\alpha$'. The equilibrium concentrations of $OH^-$ and $CH_3COOH$ will each be $c_0\alpha$ and that of $CH_3COO^-$ will be $(1-\alpha)\,c_0$.

$$\begin{array}{lccc} & CH_3COO^- + H_2O & \rightleftharpoons & CH_3COOH + OH^- \\ \text{Equilibrium concentration} & (1-\alpha)\,c_0 & & c_0\alpha \quad\quad c_0\alpha \end{array}$$

Substituting these values in Eq. 15.33, we get,

$$K_h = \frac{(c_0\alpha)\,(c_0\alpha)}{(1-\alpha)\,c_0} = \frac{c_0\alpha^2}{(1-\alpha)} \qquad \text{... (15.40)}$$

If the degree of hydrolysis is small in comparison to unity, we can write,

$$K_h = c_0\alpha^2 \qquad \text{... (15.41)}$$

or $c_0 \,.\, K_h = (c_0\alpha)^2$

or $c_0\alpha = \sqrt{K_h c_0}$

$$\text{or } [OH^-] = \sqrt{K_h c_0} \qquad \text{... (15.42)}$$

$$\text{or } [OH^-] = \sqrt{\frac{K_w}{K_a} c_0}, \text{ Since } K_h = \frac{K_w}{K_a} \qquad \text{... (15.43)}$$

hence,

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{\sqrt{\frac{K_w}{K_a} c_0}} = \left(\frac{K_a K_w}{c_0}\right)^{1/2} \qquad \text{... (15.44)}$$

Taking logarithms and multiplying by $-1$, we get,

$$\text{or } -\log[H^+] = -\frac{1}{2}\log\left(\frac{K_a K_w}{c_0}\right)$$

$$\left[\text{Since } \frac{1}{2}\log\left(\frac{K_a K_w}{c_0}\right) = \frac{1}{2}\log K_a + \frac{1}{2}\log K_w - \frac{1}{2}\log c_0\right]$$

$$-\log[H^+] = -\frac{1}{2}\log K_a - \frac{1}{2}\log K_w + \frac{1}{2}\log c_0$$

$$\text{or } pH = \frac{1}{2} pK_a + \frac{1}{2} pK_w + \frac{1}{2}\log c_0 \qquad \text{... (15.45)}$$

**Example 4**

In 0.10 M solution of sodium acetate, calculate

i) $K_h$

ii) the degree of hydrolysis $(\alpha)$

iii) $[OH^-]$

iv) pH at 298 K.

At 298 K, $K_w = 1.0 \times 10^{-14}$ and $K_a$ for acetic acid $= 1.8 \times 10^{-5}$

**Solution**

i) Using Eq. 15.37, $K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

ii) Using Eq. 15.41, $\alpha = \sqrt{\frac{K_h}{c_0}}$

$$= \sqrt{5.6 \times 10^{-9}}$$
$$= 7.5 \times 10^{-5}$$

iii) Using Eq. 15.42, $[OH^-] = \sqrt{K_h c_0}$

$$= \sqrt{5.6 \times 10^{-11}}$$
$$= 7.5 \times 10^{-6} \text{ M}$$

iv) $pK_a = -\log_{10} 1.8 \times 10^{-5} = 4.74$

$pK_w = 14$

$\log c_0 = \log 0.10 = -1.0$

Using Eq. 15.45, $pH = (\frac{1}{2} \times 4.74) + (\frac{1}{2} \times 14) + (\frac{1}{2} \times (-1.0)) = 8.87$

Hence, $K_h$, $\alpha$ and pH values of a solution of the salt of a weak acid and strong base like sodium acetate can be calculated once $c_0$, $K_a$ and $K_w$ values are known at a particular temperature.

Now that we have seen the importance of pH in the study of ionic equilibria, we shall turn our attention to a group of compounds for which colour depends on the pH of the solution. They are called indicators and are frequently used in the experimental studies of ionic equilibria. Before proceeding to the next section, answer the following SAQ which is similar to the derivation of Eq. 15.45.

**SAQ 6**

Show that for the hydrolysis of a salt of a strong acid and a weak base, the pH of the solution is given by

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c_0$$

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## 15.9 INDICATORS

There are a number of organic substances (dyes) for which the colour depends on the concentration of hydrogen ion in solution. To put it simply, the pH of the solution governs the colour of the dye. For example, phenolphthalein is an organic compound and it shows a pink colour in basic medium but becomes colourless in acid medium. Such substances are either weak acids or weak bases and when dissolved in water, their dissociated form acquires a colour different from that of the undissociated form. If the concentration of the undissociated form is more in solution we see one colour; on the other hand, if the concentration of the dissociated form is more, we see another colour. The concentration of the dissociated or undissociated form depends on the pH of the solution. Further the dissociation of the indicator is so small that it does not affect the pH of the solution. The equilibrium of an indicator which is a weak acid can be represented by,

$$HIn \rightleftharpoons H^+ + In^- \qquad \text{... (15.46)}$$

Colour I Colour II

when HIn is the undissociated form of the indicator and $In^-$ is the dissociated form. These two forms have different colours I and II, respectively. The pH of the solution determines the ratio of [HIn] to $[In^-]$ in the solution. We can write the equilibrium constant expression for the reaction corresponding to Eq. 15.46 as,

$$K = \frac{[H^+][In^-]}{[HIn]}$$

$$\text{or } \frac{[HIn]}{[In^-]} = \frac{[H^+]}{K} \qquad \text{... (15.47)}$$

The human eye can detect the change in colour if the ratio of the two forms of indicator ranges between 0.1 to 10. Thus, in order to use the indicator effectively in this region, we should have a solution for which $H^+$ ion concentration is very near to K value of the indicator. It is for this reason that we use different indicators for different systems. The list of some common indicators and the pH ranges in which these are useful are given in Table 15.2.

**Table 15.2 : pH Range of Indicators**

| Indicator | Acid | Alkaline | pH range |
|---|---|---|---|
| Litmus | Red | Blue | 5.0 – 8.0 |
| Phenolphthalein | Colourless | Pink | 8.3 – 10.0 |
| Methyl Orange | Red | Yellow | 2.1 – 4.4 |
| Methyl Red | Red | Yellow | 4.2 – 6.3 |
| Bromothymol Blue | Yellow | Blue | 6.0 – 7.6 |

The maximum use of indicators is found in the titrations of acids and bases in analytical chemistry.

## 15.10 SOLUBILITY AND SOLUBILITY PRODUCT

In Unit 10 you have studied regarding solubility and saturated solutions. One of the most useful applications of chemical equilibria studies is on sparingly or slightly soluble salts like AgCl, $CaF_2$, $Ag_2CO_3$, $BaCrO_4$ etc. We shall first derive a relationship between solubility of a salt and a quantity called solubility product. Then we shall study the applications of this relationship to different systems. Let us consider a salt with a general formula $A_xB_y$, where $x$

and $y$ are the number of moles of ions A and B, respectively present in one mole of the salt.

e.g., i) for AgCl, $x = 1, y = 1$.
ii) for $Ag_2CrO_4$, $x = 2, y = 1$.
iii) for $CaF_2$, $x = 1, y = 2$.

In a saturated solution, there will an equilibrium between the sparingly soluble solid $A_xB_Y$ and its ions A and B in solution which can be expressed as given in Eq. 15.48. For the sake of simplicity, we are omitting letters such as *s, aq,* etc., in all such equilibria.

$$A_xB_y \rightleftharpoons xA + yB \qquad \text{... (15.48)}$$

If the solubility is $1 \times 10^{-5}$ mol $dm^{-3}$ or less, the salt is described as sparingly soluble or insoluble.

Water is not included in Eq. 15.48, because it is neither used up nor produced in the reaction.

For the present moment, we shall neglect counting $y^+$ charges on the cation A and, $x^-$ charges on the anion B. The equilibrium constant for the reaction given by Eq. 15.48 can be written as,

$$K = \frac{[A]^x[B]^y}{[A_xB_y]} \qquad \text{... (15.49)}$$

$[A_xB_y]$ represents the concentration of the solid $A_xB_y$; this quantity is constant. Hence, we can introduce a new constant $K_{sp}$ in place of $K[A_xB_y]$, which is known as solubility product constant or simply solubility product. Thus Eq. 15.49 can be written as

$$K_{sp} = [A]^x[B]^y \qquad (15.50)$$

Expressed in words, Eq. 15.50 says that the solubility product of a saturated solution of a salt is equal to the product of the concentration of ions raised to suitable powers.

Let $S$ mol $dm^{-3}$ be the solubility of the salt. Then the corresponding concentrations of cation and anion are $xS$ mol $dm^{-3}$ and $yS$ mol $dm^{-3}$, respectively. Substituting these values of concentration in Eq. 15.50 we get,

$$K_{sp} = (xS)^x (yS)^y$$

$$\text{or } K_{sp} = x^x \,.\, y^y \,.\, S^{x+y} \qquad \text{... (15.51)}$$

Conductance method for the determination of the solubility of a sparingly soluble salt has been discussed in Unit 16 of this block. The determination of $K_{sp}$ based on emf measurements is discussed in Unit 17.

Let us apply Eq. 15.51 to the sparingly soluble salts such as AgCl, $CaF_2$ and $Ag_2CO_3$.

In case of AgCl, $x = 1, y = 1$.

Hence, Eq. 15.51 gives

$$K_{sp} = S^2 \qquad \text{... (15.52)}$$

Let us examine an alternate method also.

The equilibria between solid AgCl and its ions can be represented as

$$AgCl \rightleftharpoons Ag^+ + Cl^- \qquad \text{... (15.53)}$$

For this reaction, $K = \frac{[Ag^+]\,[Cl^-]}{[AgCl]}$

or $K[AgCl] = [Ag^+]\,[Cl^-]$
or $K_{sp} = [Ag^+]\,[Cl^-]$ ... (15.54)

If the solubility of AgCl is S mol $dm^{-3}$, then the concentration of $Ag^+$ and $Cl^-$ ions in solution will each be equal to $S$ mol $dm^{-3}$. Substitution in Eq. 15.54 gives, $K_{sp} = S\,.\,S = S^2$.

**Example 5**
At 298 K, the solubility of silver chloride is $1.37 \times 10^{-5}$ M. Calculate its solubility product.

**Solution**
Using Eq. 15.52, $K_{sp} = S^2 = (1.37 \times 10^{-5})^2 = 1.88 \times 10^{-10}$

In case of $CaF_2$, $x = 1, y = 2$; substituting these values in Eq. 15.51 we get,
$K_{sp} = 1.2^2.S^{(1+2)}$
$K_{sp} = 4S^3$ ... (15.55)

Just like the previous case, the alternative method would be to write the equilibrium between solid $CaF_2$ and its ions as :

$$CaF_2 \rightleftharpoons Ca^{2} + 2F^- \qquad \text{... (15.56)}$$

and for this reaction, $K_{sp} = \frac{[Ca^{2+}][F^-]^2}{[CaF_2]}$

or $K_{sp}[CaF_2] = [Ca^{2+}][F^-]^2$

or $K_{sp} = [Ca^{2+}][F^-]^2$ ... (15.57)

If $S$ is the solubility of $CaF_2$, then

$[Ca^{2+}] = S$, and $[F^-] = 2S$

substituting these values in Eq. 15.57 we get,

$K_{sp} = S(2S)^2$

or $K_{sp} = 4S^3$

which is the same as we got in Eq. 15.55. As yet another example, let us consider the equilibrium,

$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$

where, $K_{sp} = [Ag^+]^2[CO_3^{2-}]$

If $S$ is the solubility of $Ag_2CO_3$, then $[Ag^+] = 2S$ and $[CO_3^{2-}] = S$.

Substituting the proper values, once again we get,

$K_{sp} = 4S^3$

We can get the same result by substituting, $x = 2$ and $y = 1$ in Eq. 15.51.

Finally, let us consider the equilibrium :

$Fe_2S_3 \rightleftharpoons 2Fe^{3+} + 3S^{2-}$

where $x = 2$ and $y = 3$, If $S$ is the solubility of $Fe_2S_3$, then,

$K_{sp} = 2^2.3^3.S^{2+3}$

or $K_{sp} = 4.27.S^5$

or $K_{sp} = 108\ S^5$

Using the above ideas, answer the following SAQ.

**SAQ 7**

At 298 K, the solubility product of Bi $(OH)_3$ is $4.0 \times 10^{-31}$. Calculate its solubility.

## 15.11 COMMON ION EFFECT AND THE SOLUBILITY OF A SPARINGLY SOLUBLE SALT

For AgCl, $K_{sp} = S^2$ and $[Ag^+] = [Cl^-] = S$, only if both the ions originate from the dissolution of AgCl in a solvent.

We have already seen that the solubility of AgCl in pure water is $1.37 \times 10^{-5}$ M and its $K_{sp}$ is equal to $1.88 \times 10^{-10}$. Let us now proceed to find out what will happen to the solubility of AgCl if it is dissolved in a solution containing $Ag^+$ ions. A qualitative answer to this question can be easily found on the basis of Le Chatelier principle. When the concentration of $Ag^+$ ion is increased, the equilibrium described by Eq. 15.53 will shift towards left forming more of solid AgCl in order to oppose the effect of the increase in concentration of $Ag^+$ ion. Thus there will be a decrease in the solubility of AgCl in presence of a common ion such as $Ag^+$ as compared to that in pure water. Let us arrive at expressions useful in calculating the solubility of salts in presence of common ions.

There are two assumptions :

(i) sparingly soluble salts in solutions are completely dissociated

(ii) all strong electrolytes are completely dissociated in solution.

**Solubility of silver chloride in presence of silver nitrate**

Assume that silver chloride is dissolved in a solution containing $c$ mol dm$^{-3}$ of $AgNO_3$. In solution, then, there will be $Ag^+$, $Cl^-$ and $NO_3^-$ ions present. The $Cl^-$ ions in solution are provided by the dissolution of AgCl in water only. However, there are two sources for the presence of $Ag^+$ ions in solution, one is from the dissolution of AgCl and the other from $AgNO_3$. A solution of $c$ molar concentration of $AgNO_3$ will provide $c$ mol dm$^{-3}$ of $Ag^+$ ions in the solution. Assuming this contribution to be much larger in comparison with $Ag^+$ ion concentration due to dissolved AgCl, we can write,

$[Ag^+] = c$

Substituting this value in Eq. 15.54, we get

$K_{sp} = c[Cl^-]$

$$\text{or } [Cl^-] = \frac{1.88 \times 10^{-10}}{c} \quad \text{... (15.58)}$$

The chloride ion concentration must be equal to the number of moles of AgCl dissolved in 1 dm$^3$ of solution (or equal to its solubility). Hence,

$$S = \frac{1.88 \times 10^{-10}}{c} \quad \text{... (15.59)}$$

**Example 6**

Find the solubility of AgCl in 1 M $AgNO_3$ solution and compare with its solubility in water.

**Solution**

The solubility of AgCl($s$) in presence of 1 M $AgNO_3$($c$ = 1 M) can be calculated using Eq. 15.59.

$$S = \frac{1.88 \times 10^{-10}}{1} = 1.88 \times 10^{-10}$$

Hence the solubility of AgCl in presence of 1 M $AgNO_3$ is $1.88 \times 10^{-10}$ M. You can see that, as compared to the solubility of AgCl in water ($1.37 \times 10^{-5}$ M), its solubility in presence of 1 M $AgNO_3$ is $10^5$ times less.

**Example 7**

Find the solubility of $CaF_2$ in

i) water ii) 0.10 M NaF iii) 0.10 M $Ca(NO_3)_2$ ($K_{sp} = 4.0 \times 10^{-11}$)

**Solution**

i) Let us assume that the solubility of $CaF_2$ in water is $S$. Since 1 mol $CaF_2$ can give 1 mole of $Ca^{2+}$ ion and 2 mole of $F^-$ ion in solution, we can write the concentrations of $Ca^{2+}$ and $F^-$ ions as follows :

$[Ca^{2+}] = S$ and $[F^-] = 2S$

Hence,

$$K_{sp} = [Ca^{2+}][F^-]^2$$

$$\text{or } 4.0 \times 10^{-11} = S(2S)^2 = 4S^3$$

$$\therefore\ S = (1.0 \times 10^{-11})^{1/3} = (10 \times 10^{-12})^{1/3} = 2.2 \times 10^{-4}\ \text{M (approximated to two places)}$$

Note that while taking cube root, $1.0 \times 10^{-11}$ is changed into $10 \times 10^{-12}$. It is easier to take the cube root, if the power of 10 is **exactly divisible** by 3 (i.e., the remainder is zero). You can see that $-12$ is exactly divisible by 3 but not $-11$.

Hence the solubility of $CaF_2$ in pure water is $2.2 \times 10^{-4}$ M.

ii) In 0.10 M NaF

In presence of NaF, the solubility of $CaF_2 = [Ca^{2+}] = \dfrac{K_{sp}}{[F^-]^2}$

Total $[F^-] = [F^-]$ from $CaF_2 + [F^-]$ from NaF.

Since $[F^-]$ from NaF is much larger than $[F^-]$ supplied by $CaF_2$, the total fluoride ion concentration is equal to the NaF concentration which is 0.10 M. Substituting the proper values we get,

$$[Ca^{2+}] = \frac{4.0 \times 10^{-11}}{(0.10)^2} = 4.0 \times 10^{-9}\ \text{M}$$

Hence, the solubility of $CaF_2$ in 0.10 M NaF is $4.0 \times 10^{-9}$ M.

iii) in 0.10 M $Ca(NO_3)_2$

First we have to find $[F^-]$

$$[F^-]^2 = \frac{K_{sp}}{[Ca^{2+}]} \text{ or } [F^-] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]}}$$

Substituting the given values, we get,

$$[F^-] = \sqrt{\frac{4.0 \times 10^{-11}}{0.10}}\ \text{M} = 2.0 \times 10^{-5}\ \text{M.}$$

Since each mole of $CaF_2$ produces 2 mole $F^-$ ions in solution, the solubility of $CaF_2$ will be equal to one half the concentration of the fluoride ion in solution or $1.0 \times 10^{-5}$ M.

When dealing with problems of this nature, two important points must be remembered.

First, if the solubility of a salt like $CaF_2$ is given as $S$, then the concentration of $Ca^{2+}$ ion would be S but the concentration of fluoride ion, would be $2S$. This is so because each mole of $CaF_2$ which goes in solution gives 1 mole of $Ca^{2+}$ and 2 mole of fluoride ions. The second point which is a source of common confusion and where error can arise is in writing the concentration of one ion in terms of the concentration of the other. For example, the concentration of fluoride ion in a saturated solution of $CaF_2$ can be expressed as,

$[F^-] = 2[Ca^{2+}]$

but not, $[Ca^{2+}] = 2[F^-]$

No doubt when 1 mole of $CaF_2$ goes into slution, it will yield 1 mole of $Ca^{2+}$ ions and 2 mole of fluoride ions, but to find the equivalence, we must write,

$2 \times$ (number of moles of $Ca^{2+}$ ions) = Number of moles of fluoride ions.

or $2[Ca^{2+}] = [F^-]$

Now that we have seen how the presence of a common ion affects the equilibrium of a sparingly soluble salt, we come to the following conclusions regarding the solubility of a sparingly soluble salt.

Here the word 'suitable powers' stands for the number of ions present per formula unit. For example in $Ca_3(PO_4)_2$, the 'suitable power' for $Ca^{2+}$ is 3 and for $PO_4^{3-}$, it is 2.

i) In a saturated solution, $K_{sp}$ = Ionic product

ii) When the product of the concentration of ions raised to suitable powers (i.e., the ionic product) is less than the solubility product value, the concentration of the ions can be increased by dissolving more of the salt. Hence, for an unsaturated solution
$K_{sp} >$ Ionic product

iii) When the concentration of either ion in solution is increased by the addition of a soluble salt containing a common ion, the ionic product increases. Hence, the equilibrium of the sparingly soluble salt is shifted such that it is precipitated. In other words, precipitation will occur when
Ionic product $> K_{sp}$

Let us see the applications of these generalisations with the help of a few examples.

**Example 8**

Show that it is impossible to prepare a solution of chromium hydroxide, $Cr(OH)_3$, having 0.1 M concentration of $Cr^{3+}$ ions at pH = 7; $K_{sp}$ for $Cr(OH)_3 = 6.3 \times 10^{-31}$.

**Solution**

When the ionic product of $Cr(OH)_3$ is equal to its solubility product, the solution will be saturated. That will indicate the state of maximum concentration of $Cr^{3+}$ ions in solution. Thus in a saturated solution,

Solubility product = Ionic Product = $[Cr^{3+}][OH^-]^3$
Substituting the given values we get,

$$6.3 \times 10^{-31} = [Cr^{3+}](1.0 \times 10^{-7})^3$$

$$\therefore\ [Cr^{3+}] = \frac{6.3 \times 10^{-31}}{1.0 \times 10^{-21}} \text{ M (since at neutral pH, } [OH^-] = 1.0 \times 10^{-7} \text{ M)}$$

Hence, at pH = 7, the maximum concentration of $Cr^{3+}$ ions in solution would be $6.3 \times 10^{-10}$ M and it is impossible to prepare a solution having 0.1 M concentration of $Cr^{3+}$ ions at this pH.

An important fact that emerges from this example is that the precipitation or solubility of a hydroxide compound is directly related to $OH^-$ ion concentration or the pH of the solution. It is not only true for the solubility of metallic hydroxides as in the above example, but also for many other cases where $OH^-$ ion is produced due to hydrolysis. For instance, consider the equilibrium of $CaF_2$ once again. The $K_{sp}$ for $CaF_2$ is $4.0 \times 10^{-11}$ and the solubility is $2.2 \times 10^{-4}$ M. The fluoride ions present in the solution through the dissolution of $CaF_2$ could further react with water, though to a small extent, according to the equation,

$$F^- + H_2O \rightleftharpoons HF + OH^-$$

If some $H^+$ ions in the form of an acid are added to the above solution, these will react with the free $OH^-$ ions and the equilibrium will shift to the right. This will reduce the concentration of $F^-$ ions in solution; so, more of $CaF_2$ will dissolve

Many a times two or more ions are separated from a mixture by means of a technique called selective precipitation. As an example, let us assume that from a solution containing $Ag^+$, $Ni^{2+}$ and $Cu^{2+}$ ions, $Ag^+$ ions are to be separated from the other two. This can be achieved by the addition of a substance which will produce a silver salt for which $K_{sp}$ is much low. Thus, the addition of a calculated amount of chloride ion will cause the ionic product of the sparingly soluble AgCl exceed its $K_{sp}$ value; hence, AgCl is precipitated. Under this condition, $NiCl_2$ and $CuCl_2$ remain in solution since their $K_{sp}$ values are larger than their ionic product values. The precipitated solid AgCl can be separated by filtration.

In qualitative analysis of salts, a number of metal ions are precipitated as sulphides using hydrogen sulphide. However, some of these ions are precipitated in acid medium and some others in basic medium. The overall dissociation reaction of $H_2S$ can be represented as

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

The equilibrium constant for this reaction is $1.3 \times 10^{-21}$ and the concentration of $H_2S$ in a saturated solution is 0.1 M. Substituting these values in the equilibrium constant expression, we get,

$$1.3 \times 10^{-21} = \frac{(H^+)^2\,(S^{2-})}{0.1}$$

$$\text{or } [S^{2-}] = \frac{1.3 \times 10^{-22}}{[H^+]^2}$$

When $H_2S$ is passed through a solution which is basic ($pH > 7$). $H^+$ ions obtained from $H_2S$ dissociation is consumed due to the formation of undissociated water. This results in increased dissociation of $H_2S$ and hence, higher concentration of $S^{2-}$ ion.

Thus the sulphide ion concentration can be controlled by the adjustment of the pH of the solution. The metallic sulphides which have low $K_{sp}$ values can be precipitated with rather small concentrations of sulphide ions in solution. This is achieved if the solution is acidic. The metallic sulphides which have higher $K_{sp}$ values need higher concentration of sulphide ions for their precipitation and a higher pH ($pH > 7$) of the solution is to be maintained.

As an example, let us consider a solution of $pH = 3$, which contains 0.010 M each of $Mn^{2+}$ and $Cu^{2+}$ ions at $pH = 3$. Let us pass $H_2S$ through this solution such that $[H_2S] = 0.1$ M. At this pH, the concentration of sulphide ion would be,

$$[S^{2-}] = \frac{1.3 \times 10^{-22}}{(1.0 \times 10^{-3})^2} = 1.3 \times 10^{-16} \text{ (since } [H^+] = 1.3 \times 10^{-3} \text{ M at pH} = 3)$$

and therefore,

$$[Cu^{2+}]\,[S^{2-}] = (1.0 \times 10^{-2})\,(1.3 \times 10^{-16})$$
$$= 1.3 \times 10^{-18}$$

The $K_{sp}$ for $CuS = 6.3 \times 10^{-36}$. Since, we find that the ionic product (I.P.) > $K_{sp}$, CuS will precipitate from the solution. However, $K_{sp}$ for MnS is $3 \times 10^{-13}$ which is much greater than its I.P. ($1.3 \times 10^{-18}$ M); hence MnS remains in solution. After separation of CuS, we can increase the pH of the solution, thereby increasing the concentration of sulphide ion to the limit such that MnS also precipitates out. It is this combined use of the selective precipitation technique and proper control of pH which are the guiding principles in the qualitative analysis of the salts. Try the following SAQ.

**SAQ 8**

The solubility product of magnesium hydroxide, $Mg(OH_2)$, is $1.8 \times 10^{-11}$. What is the pH of a saturated solution of $Mg(OH)_2$?

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## 15.12 SUMMARY

The basic definitions of acids and bases as given by Arrhenius, Lowry-Brønsted and Lewis have been discussed, Strong acids and bases are supposed to dissociate almost completely in water whereas weak acids and bases are not. Equilibrium conditions have been applied to weak acids and weak bases to determine the dissociation constants of these acids and bases in terms of concentrations

A solution containing a weak acid (or a weak base) and its salt is defined as a buffer solution. The effect of common ion in the form of a salt affects the dissociation equilibrium of weak acids (or weak bases) so that the pH of the solution remains constant. The pH of these solutions changes very little by the addition of small amounts of strong acids and bases.

Some salts of strong acid and weak base, weak acid and strong base or weak acid and weak base undergo hydrolysis. The pH of the solution depends on the dissociation constants, $K_a$ and $K_b$.

Indicators are weak acids or bases that exhibit different colours in dissociated and undissociated forms. Different indicators change their colour in different pH regions. Hence, the use of a particular indicator for a titration is guided by the range of pH change near the equivalence point.

In case of a sparingly soluble salt, the product of the concentration of ions in a saturated solution raised to their appropriate powers is known as solubility product. The wider differences in the solubility product values of different salts are made use of in analytical chemistry for their separation.

## 15.13 TERMINAL QUESTIONS

1) Calculate the change in pH that occurs when $1.0 \times 10^{-3}$ kg of sodium fluoride is added to 0.0025 dm$^3$ of 0.10 M HF(*aq*). $K_a$ for HF $= 7.2 \times 10^{-4}$.

2) Calculate the H$^+$ ion concentration of a solution that is 0.050 M in acetic acid and 0.10 M in sodium acetate. Calculate H$^+$ ion concentration when concentrated HCl is added to this solution such that [HCl] $= 1.0 \times 10^{-3}$ M. Assume that there is not much change in volume.
($K_a$ for acetic acid $= 1.8 \times 10^{-5}$)

3) Calculate the concentration of $Cl_3CCOOH$, $Cl_3CCOO^-$ and H$^+$ in a 0.25 M solution of trichloroacetic acid.
($K_a$ for $Cl_3CCOOH = 0.22$)
**Hint** : Note that $K_a$ is not much low.

4) Calculate the molarity of HCN solution that is 0.010% ionised at equilibrium.
($K_a$ for HCN $= 6.0 \times 10^{-10}$)
**Hint** : Note that $K_a$ is very much low.

5) What is the molarity of an aqueous ammonia solution for which OH$^-$ ion concentration is $1.0 \times 10^{-3}$ M? $K_b = 1.8 \times 10^{-5}$.

6) Calculate the solubility of
   i) $PbCl_2$ and
   ii) $Ag_2CrO_4$ at 298 K in mol dm$^{-3}$
   $K_{sp}$ for the two salts are $1.6 \times 10^{-5}$ and $9.0 \times 10^{-2}$, respectively.

## 15.14 ANSWERS

**Self Assessment Questions**

1) Any substance that can accept a pair of electrons is called Lewis acid whereas a Brφnsted acid is defined as any substance which acts as a proton donor. Typical examples of the two classes are given below :
Lewis Acid : H$^+$, $BF_3$, any metal ion in coordination compounds.
Brφnsted Acid : HCl, $HNO_3$, $H_2SO_4$ etc.

2) The equation for the dissociation of $NH_4OH$ is,

$$\begin{array}{ccc} NH_4OH & \rightleftharpoons & NH_4^+ + OH^- \\ c_0(1-\alpha) & & c_0\alpha \quad c_0\alpha \end{array}$$

where $c_0$ = Initial concentration of ammonium hydroxide solution
$\alpha$ = Degree of dissociation of ammonium hydroxide

Proceeding as per subsec. 15.3.2, we can write, $K_b = \frac{\alpha^2 c_0}{1-\alpha}$

By substituting the values of $K_b$ and $c_0$, we get $\alpha = 4.2 \times 10^{-3}$.
Hence, $[OH^-] = \alpha c_0 = 4.2 \times 10^{-3}$ M
Alternatively, since $NH_4OH$ is a weak base,

Using Eq. 15.8, $[OH^-] = \sqrt{K_b c_0}$

$$= \sqrt{1.8 \times 10^{-5}}$$
$$= \sqrt{18 \times 10^{-6}}$$
$$= 4.2 \times 10^{-3} M$$

3) a) We have to consider $[H^+]$ from both the sources, namely from the dissociation of HCl and water.
Let $H^+$ concentration as also $OH^-$ concentration due to dissociation of water be $x$.
Since $[HCl] = 1.0 \times 10^{-8}$ M,
total $[H^+] = (x + 1.8 \times 10^{-8})$ M
But $[H^+]\,[OH^-] = K_w = 1.0 \times 10^{-14}$
i.e., $(x + 1.0 \times 10^{-8})\,(x) = 1.8 \times 10^{-14}$
Solving for $x$, we get, $x = 9.5 \times 10^{-8}$
$\therefore\ [H^+] = (9.5 \times 10^{-8} + 1.0 \times 10^{-8})\ M = 1.05 \times 10^{-7}$ M
$pH = -\log_{10}(1.05 \times 10^{-7}) = 6.98$
Note that pH of $1.0 \times 10^{-8}$ M HCl is in the acidic range (<7).

b) Concentration of $H^+$ provided by $HCl = 1.0 \times 10^{-10}$ M
Concentration of $H^+$ due to $H_2O = 1.0 \times 10^{-7}$ M.
Since the $[H^+]$ ion due to the dissociation of water molecule is much greater than the hydrogen ions provided by HCl, the concentration of $H^+$ ions due to HCl can be neglected in comparison with that from water. Thus, we can write,

$[H^+] = 1.0 \times 10^{-7}$ M and pH = 7.

c) As in the above case $(OH^-)$ from water is far greater than $(OH^-)$ from NaOH.
Hence $[OH^-] = [OH^-]$ from water $\simeq 10^{-7}$ M

Hence $(H^+) = \frac{K_w}{(OH^-)} = 10^{-7}$ M and pH = 7.

4) Ammonium chloride, being a strong electrolyte, dissociates almost completely to give $NH_4^+$ ions and $Cl^-$ ions. The $NH_4^+$ ions so produced suppresses the dissociation of the weak electrolyte, $NH_4OH$, due to common ion effect.

5) Moles of sodium acetate added $= \frac{\text{Mass}}{\text{Molar mass}} = \frac{2.05 \times 10^{-3}\ \text{kg}}{0.082\ \text{kg mol}^{-1}} = 0.025$ mol

Moles of HCl in solution $= 0.10\ \text{mol dm}^{-3} \times 0.10\ \text{dm}^3 = 0.010$ mol
Since HCl and $CH_3COONa$ react in the ratio of 1 : 1 as per equation,

$CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$,

0.010 mol HCl will react with 0.010 mol $CH_3COONa$ to give 0.010 mol $CH_3COOH$.
Hence, moles of $CH_3COONa$ remaining in solution after reaction

$= (0.025 - 0.010)$ mol
$= 0.015$ mol
$[CH_3COONa]$ in solution after the reaction

$$= \frac{0.015\ \text{mol}}{0.10\ \text{dm}^3} = 0.15\ M$$

[Acid] = Acetic acid concentration = $[CH_3COONa]$ reacted

$$= \frac{0.010\ \text{mol}}{0.10\ \text{dm}^3} = 0.10\ M$$

Substituting the proper values in Eq. 15.28, we get,

$$[H^+] = \frac{K_a\,[\text{acid}]}{[\text{salt}]} = \frac{1.8 \times 10^{-5} \times 0.10}{0.15}\ M$$

$$= 1.2 \times 10^{-5}\ M$$

$\therefore\ pH = -\log(1.2 \times 10^{-5}) = 4.9$

6) Consider a salt of a weak base and a strong acid, BX. Let $c_0$ be the initial concentration of the salt BX and $\alpha$ be the degree of hydrolysis. The cation $B^+$ hydrolyses as follows :

$$\begin{array}{lccccccc} & B^+ & + & H_2O & \rightleftharpoons & BOH & + & H^+ \\ \text{Equilibrium concentration} & c_0(1-\alpha) & & & & c_0\alpha & & c_0\alpha \end{array}$$

The hydrolysis constant, $K_h$, can be expressed as,

$$K_h = \frac{(c_0\alpha)^2}{(1-\alpha)\,c_0} = \frac{\alpha^2 c_0}{(1-\alpha)}$$

If $\alpha << 1$ then,

$K_h c_0 = (c_0\alpha)^2$

or $c_0\alpha = (K_h c_0)^{1/2}$

We also know that

$$K_h = \frac{K_w}{K_b}$$

Hence, $[H^+] = \left(\frac{K_w c_0}{K_b}\right)^{1/2}$

$$-\log [H^+] = -\frac{1}{2}[\log K_w + \log c_0 - \log K_b]$$

or $\mathrm{pH} = \frac{1}{2}\,pK_w - \frac{1}{2}\log c_0 - \frac{1}{2}\,pK_b$

7) For $Bi(OH)_3$, $x = 1, y = 3$

Using Eq. 15.51, $K_{sp} = 1^1.3^3.S^{1+3}$

$= 27\,S^4$

Since $K_{sp} = 4.0 \times 10^{-31}$,

$$S^4 = \frac{4.0 \times 10^{-31}}{27}$$

$$\therefore\; S = \left(\frac{4.0 \times 10^{-31}}{27}\right)^{1/4}$$

$= (0.148 \times 10^{-31})^{1/4}$

$= (1.48 \times 10^{-32})^{1/4}$

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

Hence the solubility of $Bi(OH)_3$ is $1.1 \times 10^{-8}$ mol dm$^3$.

8) From Eq. 15.51

$K_{sp} = 1^1.2^2.S^{2+1} = 4S^3$

$$S = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{1.8 \times 10^{-11}}{4}\right)^{1/4}$$

$= (4.5 \times 10^{-12})^{1/3}$

$= 1.7 \times 10^{-4}$ mol dm$^{-3}$

$[OH^-] = 2S = 3.4 \times 10^{-4}$ mol dm$^{-3}$

$$[H^+] = \frac{10^{-14}}{3.4 \times 10^{-4}} = 2.9 \times 10^{-11}$$

$\mathrm{pH} = 10.5$

**Terminal Questions**

1) pH of 0.10 HF can be calculated by using the equation,

$[H^+] = \sqrt{c_0 K_a}$

or $-\log [H^+] = -\frac{1}{2}(\log c_0 + \log K_a) = -\frac{1}{2}(\log 0.1 + \log 7.2 \times 10^{-4})$

$= -\frac{1}{2}(-1.0 - 3.14)$

$\mathrm{pH} = 2.07$

0.0010 kg of NaF $= \frac{0.0010}{0.042}$ mol of NaF $= 0.0238$ mol

$$\therefore \text{ Concentration of NaF} = \frac{0.0238 \text{ mol}}{2.5 \times 10^{-3} \text{ dm}^{-3}} = 9.5 \text{ M}$$

Substituting the proper values in the equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]},$$

$$\text{pH} = -\log K_a + \log \frac{9.5}{0.1}$$

$$= 3.14 + 1.98 = 5.12$$

2) i) Using Eq. 15.28,

$$[\text{H}^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$= 1.8 \times 10^{-5} \times \frac{0.050}{0.10} = 9.0 \times 10^{-6} \text{ M}$$

ii) Again using Eq. 15.28,

$$[\text{H}^+] = 1.8 \times 10^{-5} \times \frac{(0.050 + 0.001)}{(0.10 - 0.001)}$$

$$= 9.3 \times 10^{-6} \text{ M}$$

3) Since $K_a$ for trichloroacetic acid is not much low, $\alpha$ will not be much low. Thus we use Eq. 15.3 only.

Dissociation of the acid can be written as

$$Cl_3CCOOH \longrightarrow H^+ + Cl_3CCOO^-$$

$$0.25\,(1-\alpha) \quad 0.25\,\alpha \quad 0.25\,\alpha$$

where $\alpha$ is the degree of dissociation of the acid. Hence,

$$K_a = \frac{c_0 \alpha^2}{1-\alpha}$$

$$0.22 = 0.25 \frac{\alpha^2}{1-\alpha}$$

or $0.25\,\alpha^2 = 0.22 - 0.22\,\alpha$

or $0.25\,\alpha^2 + 0.22\,\alpha - 0.22 = 0$

$$\alpha = \frac{-0.22 \pm \sqrt{(0.22)^2 + 4 \times 0.22 \times 0.25}}{2 \times 0.25}$$

$= 0.60$ (leaving the negative value)

Hence, $[H^+] = [Cl_3CCOO^-] = 0.25\,\alpha = 0.25 \times 0.60 = 0.15$ M

and $[Cl_3CCOOH] = c_0(1-\alpha) = 0.25 \times 0.4 = 0.10$ M

4) Since $K_a$ is much low, $\alpha$ can also be expected to be much low. Hence we can write following subsec. 15.3.1,

$K_a = \alpha^2 c_0$

Since $\alpha = 0.010\% = 1.0 \times 10^{-4}$

$$\text{or } c_0 = \frac{K_a}{\alpha^2} = \frac{6.0 \times 10^{-10}}{1.0 \times 10^{-8}} \text{ M} = 6.0 \times 10^{-2} \text{ M}$$

Hence the molarity of HCN solution is $6.0 \times 10^{-2}$ M.

5) Since $NH_4OH$ solution is a weak base, we can use Eq. 15.8.

Hence $[OH^-] = \sqrt{K_b c_0}$

$$c_0 = \frac{[OH^-]^2}{K_b}$$

$$= \frac{1.0 \times 10^{-6}}{1.8 \times 10^{-5}}$$

$$= 5.6 \times 10^{-2}$$

Hence the molarity of ammonia solution is $5.6 \times 10^{-2}$ M.

6) i) Solubility of $PbCl_2 = \left(\frac{1.6 \times 10^{-5}}{4}\right)^{1/3} = (4.0 \times 10^{-6})^{1/3} = 0.016 \text{ mol dm}^{-3}$

ii) Solubility of $Ag_2CrO_4 = \left(\frac{9.0 \times 10^{-2}}{4}\right)^{1/3} = (22.5 \times 10^{-3})^{1/3} = 0.28 \text{ mol dm}^{-3}$.

# UNIT 16 ELECTROLYTIC CONDUCTANCE OF SOLUTIONS

## Structure

## 16.1 INTRODUCTION

We have already seen in Unit 15 that an electrolyte on dissolution in water dissociates to give positive and negative ions which may carry single or multiple charges. For example, when sodium chloride is dissolved in water, the sodium ions, $Na^+$, and chloride ions, $Cl^-$ are formed and get dispersed throughout the solution homogeneously. These ions are responsible for the passage of current through sodium chloride solution. In order to find the amount of current carried by these ions and the changes brought about by the passage of current through a solution, we should learn more about the nature and properties of the solvent. For instance, depending on the nature of the solvent, there are many kinds of interactions possible in an electrolyte solution. Two of these are ion-dipole and ion-ion interactions. We shall study a few possible interactions which influence the passage of current through aqueous solution, since water is a commonly used solvent. We shall then look into some of the useful applications of conductance studies. In the next unit, we shall study the designing and the applications of electrochemical cells.

### Objectives

After going through this unit, you should be able to :

- describe the nature of ions in solution and the possible interactions among them,
- state Faraday's law of electrolysis and apply the same to a few systems,
- define specific and molar conductance of a solution,
- describe the dependence of conductance on concentration,
- state Kohlrausch's law of independent mobility of ions,
- state the applications of conductance measurements,
- explain the conductance method for titrations, and
- describe the method of determination of ionic product of water, dissociation constant of weak acids and weak bases and solubility of sparingly soluble salts.

## 16.2 INTERACTIONS IN SOLUTIONS

**Since water is the most commonly used solvent, our studies are mainly confined to reactions in water. It is desirable that we refresh our memory about the nature and structure of water. The structure of water has been dealt with in Units 3 and 6 of Atoms and Molecules course, in**

Unit 9 of Inorganic Chemistry course and in Unit 3 of this course. Based on a number of physico-chemical studies, the water molecule may be represented as shown in Fig. 16.1.

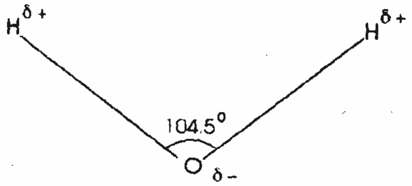

Fig. 16.1 : Structure of water molecule.

It is a bent molecule, H—O—H bond angle being approximately 104.5°. It shows polar character due to a large difference in the electronegativities of oxygen and hydrogen atoms. It thus has a permanent dipole moment. We should, therefore, expect water molecules to interact with each other. This kind of interaction between permanent dipoles is called dipole-dipole interaction. Due to this interaction, there is net force of attraction between the molecules. In addition, there will be hydrogen bonds present between oxygen atom of one molecule and hydrogen atoms of other molecules. When a salt is dissolved in water, it will produce ions in solution. As a result, there will be additional interactions between ions and water as well as between the ions themselves. We shall now consider such interactions in detail.

**Ion-Solvent Interaction**

An ion in solution will create an electrical field around it and solvent molecules with dipole moment will strongly interact with the field due to the ion. The water molecules will thus orient themselves in such a way that the dipoles lie along the field direction in order to minimise the energy of the system. The negative end of the water dipole will point towards the cation and the reverse will be true for the anion. Thus, each ion will be surrounded by a number of water molecules. Of course, generally, this number will depend on the size and charge of the ion and the nature of the solvent molecules. These ions are then called 'solvated ions'; in case of water, they are known as hydrated ions. The ion-solvent interaction is strong enough to hold a certain fixed number of solvent molecules (called coordination number) around a particular ion; however, the interaction is not so strong as to always produce different chemical species in solution. Whenever the interaction is strong enough to give different product, we define it as solvolysis and, in case of water, it is called hydrolysis. Solvent molecules so held by the central ion are known to form the first solvation shell. The first hydration shell for most of the cations usually contains either four or six molecules of water. For example, $Cr^{3+}$ or $Ni^{2+}$ is present as $[Cr(H_2O)_6]^{3+}$ or $[Ni(H_2O)_6]^{2+}$ in aqueous solution. The solvent structure far away from the ion differs little from the bulk structure of the solvent. In between these two extremes, there is a region of solvent structure where solvent molecules are under the influence of two forces, one from the ions present in the solution and the other due to intermolecular forces of the solvent. The solvent molecules in this region are consequently oriented randomly. To sum up, we can say that an electrolyte on dissolution in a solvent produces solvated ions. There is an inner or a primary solvent shell in which the solvent molecules are bound through the strong ion-dipole interaction. There is an outer or secondary solvent layer where molecules are not aligned in any particular fashion either by the field of the ion or by the forces that act in bulk solvent. The solvation number of an ion is defined as the mean number of solvent molecules in the primary solvation shell.

Coulomb's law states that the force of attraction between two oppositely charged particles is directly proportional to the product of the charges and inversely proportional to the square of the distance between them. Mathematically it is expressed as :

$$F \propto \frac{q_1 \cdot q_2}{r^2}$$

where $q_1$ and $q_2$ are the charges on the two particles, $r$ is the distance between them and $F$ is the force of attraction.

**Ion-Ion Interactions**

Any two ions present in a solution will interact with each other. Like charges will repel each other whereas unlike charges will attract each other. The electrostatic forces between any two ions is governed by Coulomb's law. Thus a sodium ion in a solution of sodium chloride will be repelled by other sodium ions in its vicinity but it will be attracted by chloride ions. However in solutions, a well-ordered structure as found in the solids—where each ion is surrounded by a definite number of oppositely charged species at a fixed distance—is not possible. In solutions, the thermal motion will not leave the ions at fixed positions. The net result is that at any given moment on an average, there will be an atmosphere of excess of negative ions around each positive ion and the reverse will be true for the negative ion as shown in Fig. 16.2

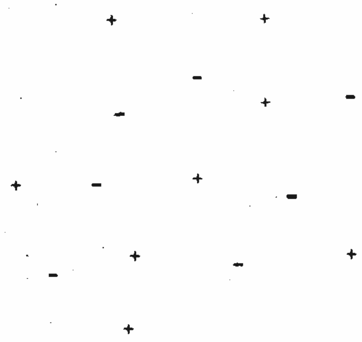

Fig. 16.2 : Atmosphere of oppositely charged ions around each cation and anion.

The measure of the electrostatic interaction is given by a term called, ionic strength, $I$. The ionic strength depends on the concentration of the ions present and the charge carried by the ions. It is given by the expression,

$$I = \frac{1}{2} \sum_i m_i z_i^2 \qquad ..... (16.1)$$

where $m_i$ is the molal concentration of ion 'i' in solution and $z_i$ is the charge associated with the same ion.

In the case of a dilute solution (of density, $d$), its molarity ($c_i$) is related to its molality ($m_i$) as per Eq. 16.2.

$$c_i = m_i d \qquad ..... (16.2)$$

Substituting the value of $m_i$ from Eq. 16.2 into Eq. 16.1 we get,

$$I \simeq \frac{1}{2d} \sum_i c_i z_i^2 \qquad ..... (16.3)$$

Eq. 16.3 indicates that the electrostatic interaction between any two ions in solution is directly proportional to concentration of the solution. This has been experimentally verified in terms of a quantity called ion-atmosphere radius. It is defined as the effective radius at which the atmosphere of opposite charges is situated around an ion. The radii of ion-atmosphere around sodium ion in $1.0 \times 10^{-2}$ M, $1.0 \times 10^{-4}$ M and $1.0 \times 10^{-6}$ M sodium chloride solutions have been calculated to be in the ratio of 1:10:100. Thus, we see that ion-atmosphere radius increases with dilution. Hence, it can be concluded that at very low concentrations or at infinite dilution, an ion would be free from inter-ionic interactions. The concepts developed so far form the basis for the theory of ionic solutions as given by Debye and Hückel. However, our immediate concern is to study the effects of passage of current through an electrolyte solution but not the theory of electrolytic conductance. Next four sections are devoted to these studies only.

## 16.3 FARADAY'S LAWS OF ELECTROLYSIS

A process in which a chemical change is brought about by the passage of current through a solution is called electrolysis. The apparatus in which electrolysis is carried out is known as electrolytic cell. Consider a solution of an electrolyte into which two metal plates are dipped. The metal plates do not chemically react with the solution. On connecting the plates to the two terminals of a battery, a current starts flowing through the solution due to movement of ions in solution. The negatively charged plate is called cathode and the positively charged plate is known as anode. The ions which move towards cathode and anode are known as cations and anions, respectively. The combined name for the two plates is electrodes. As the ions reach the two electrodes, a chemical reaction takes place at each electrode; oxidation at the anode and reduction at the cathode. Suppose that an electric current is passed through a solution of copper sulphate into which two copper electrodes are dipped. Then the following reactions occur at the electrodes:

At the anode : $Cu \longrightarrow Cu^{2+} + 2e^-$ (oxidation)
At the cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$ (reduction)

For simplicity we have represented the net reaction at the anode as oxidation of Cu to $Cu^{2+}$. However, the anodic reaction may be a complicated one involving sulphate ions.

The battery pushes electrons to one electrode and takes away from the other. In other words, electrons are transferred between the electrodes and ions. The current in the solution is due to migration of ions. Suppose that a current ($I$) is passed through an electrolyte solution for a time $t$. Then the quantity of electric current ($q$) passed is given by the product of current and time.

$$q = I \, . \, t \qquad \text{..... (16.4)}$$

The units of quantity of electricity, current and time are coulomb (C), ampere (A) and second (s), respectively. Hence,

1 C = 1 A s

An electrolytic cell designed to measure the quantity of electric current that has passed through the solution is called a coulometer (see Example 1). For example, a silver coulometer uses platinum electrodes and a solution of silver nitrate as an electrolyte. On electrolysis the following reaction occurs at the cathode and silver gets deposited.

$$Ag^+ + e^- \longrightarrow Ag \qquad \text{..... (16.5)}$$

By measuring the increase in mass of the cathode, one can calculate the quantity of electric current that has passed during electrolysis. To understand the calculations involving coulometer, we must study Faraday's laws of electrolysis.

In 1813, Faraday made certain useful observations on the decomposition of electrolyte solutions by the passage of electric current. These are known as Faraday's laws of electrolysis and are stated below :

1) The mass ($w$) of a product formed at an electrode is directly proportional to the quantity of electricity ($q$) passed i.e.

   $$w \propto q \qquad \text{..... (16.6)}$$

2) The masses of different products (say $w_1$ and $w_2$ for two substances 1 and 2) formed at the electrodes by the passage of the same quantity of electricity are directly proportional to their equivalent weights. Thus the quantity of electricity that has passed through the electrolytic cell can be measured by the extent of the chemical reaction which has taken place in a cell or vice-versa.

Before seeing the usefulness of these laws, let us explain the term **faraday**. The quantity of electricity carried by 1 mole of electrons is called **faraday** and given the symbol, $F$. The charge on one electron is $1.602 \times 10^{-19}$ C. Hence, the charge on one mole of electrons would be $1.602 \times 10^{-19} \times 6.022 \times 10^{23}$ C or 96489 C. It is usual to approximate one faraday as being equal to 96500 C.

Consider an electrode reaction :

$$X^{n+} + ne^- \longrightarrow X$$

The quantity of electricity required for the deposition of 1 mole of X will be equal to $n$F, where $n$ is the number of moles of electrons required for the reaction. Let $M$ be the mass of 1 mole atoms of an element X. Therefore, for the deposition of $M$ kg (or 1 mole) of the element, we require nF or $n \times 96500$ C of electricity. It can also be expressed as follows :

$n \times 96500$ C of electricity deposits $M$ kg (or 1 mole) of an element. Hence, $q$ coulomb of electricity deposits $\dfrac{M \, . \, q}{n \, . \, 96500}$ kg of the element.

$$\text{or } w = \frac{M \, . \, q}{n \, . \, 96500} \text{ kg} \qquad \text{..... (16.7)}$$

where $w$ = mass of an element deposited by the passage of $q$ coulomb of current.

Substituting the value of $q$ from Eq. 16.4 into Eq. 16.7 we get

$$w = \frac{M \, . \, I \, . \, t}{n \, . \, 96500} \qquad \text{..... (16.8)}$$

This equation is useful in calculating the mass of an element deposited by the passage of known quantity of current. Let us make use of Eq. 16.8 in solving some problems.

*n* is equal to the charge on an ion.

**Example 1**

A current of $5.0 \times 10^{-3}$ A is passed for 100 minutes through a silver coulometer. Calculate the mass of silver deposited on the cathode. Atomic mass of Ag = 107.9 (or M = 0.1079 kg mol$^{-1}$).

**Solution**

Substituting the given values in Eq. 16.8 we get,

$$w = \frac{0.1079 \text{ kg mol}^{-1} \times 5.0 \times 10^{-3} \text{ A} \times (100 \times 60) \text{ s}}{1 \times 96500 \text{ C mol}^{-1}} \quad (n = 1, \text{ since 1 mole of } Ag^{+} \text{ ions needs 1 mole of electrons})$$

$$w = 3.4 \times 10^{-5} \text{ kg}$$

**Example 2**

Two electrolytic cells, one containing silver nitrate solution and the other copper sulphate solution as electrolytes were connected in series. A steady current of 1.50 A was passed through them until 0.00145 kg of silver was deposited at the cathode of the first cell. How long did the current flow? What mass of copper was deposited in the second cell?

**Solution**

1 C = 1 A s

Let $t$ second be the time for which the current flowed through the cells.
For the deposition of Ag,
$n = 1, I = 1.50$ A, $w = 0.00145$ kg, $M = 0.1079$ kg mol$^{-1}$
Rearranging Eq. 16.8 and substituting the given values we get,

$$t = \frac{w\, n\, 96500}{M\, I}$$

$$t = \frac{0.00145 \text{ kg} \times 1 \times 96500 \text{ A s mol}^{-1}}{0.1079 \text{ kg mol}^{-1} \times 1.50 \text{ A}} = 865 \text{ s}$$

Since the electrolytic cells containing $AgNO_3$ and $CuSO_4$ are connected in series, same quantity of current is passed through both the cells. Hence, for the deposition of Cu, we have, $I = 1.50$ A and $t = 865$ s. But $n = 2$ in the electrolysis of $CuSO_4$ solution, since

$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

Further, mass of one mole atoms of Cu = 0.06354 kg.

Substituting these values in Eq. 16.8 we get,

$$\left.\text{mass of copper deposited}\right\} = \frac{0.06354 \text{ kg mol}^{-1} \times 1.50 \text{ A} \times 865 \text{ s}}{2 \times 96500 \text{ C mol}^{-1}} = 4.27 \times 10^{-4} \text{ kg}$$

You should now be able to apply the laws of electrolysis in solving the following SAQs.

**SAQ 1**

If a 5 A current is passed through an electrolytic cell containing moltern magnesium chloride, how long would it take to prepare a mole of magnesium metal?

[ **Hint** : $Mg^{2+} + 2e^{-} \longrightarrow Mg$ ]

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**SAQ 2**

1 dm$^3$ of a solution of 2.0 M $CuSO_4$ is electrolysed using platinum electrodes by passing 4.50 A current for 9000 s.

Calculate

i) the mass of Cu deposited, and
ii) the amount of $Cu^{2+}$ in the solution at the end of the electrolysis.

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## 16.4 ELECTROLYTIC CONDUCTANCE

We shall now turn our attention to a property of the electrolyte solution, called, conductivity. The electrical resistance ($R$) of a sample is directly proportional to its length ($l$) and inversely proportional to its cross-sectional area ($A$). It can be expressed as,

$$R \propto \frac{l}{A}$$

$$\text{or } R = \rho \cdot \frac{l}{A} \qquad \text{..... (16.9)}$$

The proportionality constant, $\rho$, is known as its electrical resistivity. The unit of resistance is ohm ($\Omega$) while the unit of resistivity is ohm metre ($\Omega$ m). The electrical conductance is defined as the inverse of electrical resistance. Similarly, conductivity or specific conductance ($\kappa$) of a material is defined as the reciprocal of its electrical resistivity. Hence, Eq. 16.9 can be written as

$$R = \frac{1}{\kappa} \cdot \frac{l}{A} \qquad \text{..... (16.10)}$$

$$\text{or } \kappa = \frac{l}{AR} \qquad \text{..... (16.11)}$$

Since the resistance is expressed in ohm, the reciprocal ohm ($\Omega^{-1}$) was earlier used as the unit for conductance. However, in SI system; the unit for conductance is 'siemens' and, given the symbol 'S'. Hence, the unit for conductivity will be S $m^{-1}$. (1 S = 1 $\Omega^{-1}$).

For the measurement of electrical resistance ($R_x$) of a sample, we use a set-up known as Wheatstone bridge. It consists of two wires $R_1$, $R_2$, of known resistance values, and a third resistance, $R_s$, the value of which can be adjusted. These are all connected to a battery source, E, as shown in Fig. 16.3. $R_s$ is adjusted until points a and b are exactly at the same potential. This can be tested by momentarily connecting a sensitive ammeter (A) between a and b. If the two points are exactly at the same potential, there will be no deflection in the ammeter.

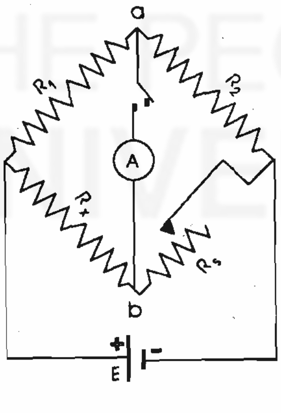

Fig. 16.3 : Wheatstone bridge.

Under these conditions, the following relation will hold good :

$$\frac{R_1}{R_2} = \frac{R_x}{R_s}$$

$$\text{or } R_x = \frac{R_s \cdot R_1}{R_2} \qquad \text{..... (16.12)}$$

For finding the resistance of a solution ($R_{cell}$), we make slight alterations in the Wheatstone bridge described above. Instead of a battery, we use an alternating current source to prevent electrolysis. The electrolysis that occurs when current passes in one direction is reversed when it passes in the other direction. The direction of current changes so rapidly that the build-up of charge at the electrode is not possible

Finally, instead of an ammeter, we use an alternating current detector as shown in Fig. 16.4.

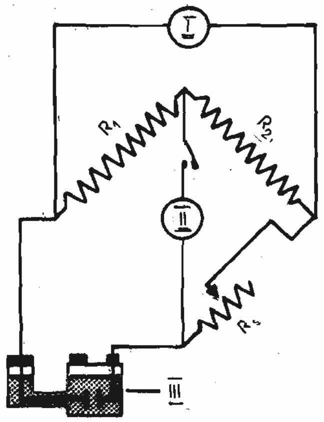

**Fig. 16.4 : Wheatstone bridge where electrolytic cell occupies one arm of the bridge :**
**I) AC source of frequency;**
**II) Alternating current detector;**
**III) Test cell ($R_{Cell}$)**

At the balance point,

$$R_{cell} = R_s \left( \frac{R_1}{R_2} \right) \qquad \text{..... (16.13)}$$

The relationship between specific conductance and resistance is given by Eq. 16.11 as

$$\kappa = \frac{l}{A} \cdot \frac{1}{R}$$

$$\text{or } \kappa = k_{cell} \, \frac{1}{R} \qquad \text{..... (16.14)}$$

Nowadays, conductivity bridges facilitate direct reading of the resistance and conductance values, without having to use Eq. 16.13. In CHE-03(L) laboratory course, experiments involving conductivity bridges have been included.

where $k_{cell}$ is the cell constant representing $\frac{l}{A}$ ratio; it is a constant as far the same cell is used for measurements. Since the conductivities of certain standard solutions have been carefully measured, we could use such a solution in a cell and measure its resistance. Thus knowing $\kappa$ and $R$, we can calculate the value of $k_{cell}$ the cell constant. Once $k_{cell}$ is determined, we can use the same cell for the measurement of conductivity of other electrolyte solutions. Using these ideas, work out the following SAQ.

**SAQ 3**

A conductance cell filled with 0.020 M KCl has a resistance of 195.96 Ω at 298 K. When filled with a 0.050 M $AgNO_3$ solution, it has a resistance of 94.2 Ω. The specific conductance of 0.020 M KCl is $0.2768 \text{ S m}^{-1}$. What is the specific conductance of 0.050 M $AgNO_3$ solution?

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## 16.5 MOLAR AND EQUIVALENT CONDUCTANCE

In order to compare the conductivities of different electrolytes, we must use the same concentration. It is because the conductivity of the solution depends on the number of ions present. Therefore, instead of specific conductance, we use molar conductivity, $\Lambda_m$, which is the conductivity per unit molar concentration and is given by the expression :

$$\Lambda_m = \frac{\kappa}{c} \qquad \text{..... (16.15)}$$

where $c$ is in mol $m^{-3}$ units. The molar conductivity is usually expressed in $\text{S m}^2 \text{ mol}^{-1}$ or $\text{S cm}^2 \text{ mol}^{-1}$. It may be remembered that, $\text{S m}^2 \text{ mol}^{-1} = 10000 \text{ S cm}^2 \text{ mol}^{-1}$.

It might be thought that $\Lambda_m$ should be a quantity independent of concentration. However, it is an experimental fact that $\Lambda_m$ for NaCl, KBr. etc. in aqueous solution does vary with concentration. This is due to the ionic interactions which change with concentration. This, in turn, affects the conductivity, $\kappa$.

If we plot the molar conductivities of a large number of electrolytes against the concentrations we find that these fall into two distinct categories. In one class of electrolytes, there is a small increase in molar conductivities with the decrease in concentration. Such electrolytes are called 'strong electrolytes'. Since these electrolytes dissociate almost completely even in concentrated solution, the number of ions do not change much with concentration. The conductivity should not vary much since it is directly related to the number of ions present in solution. The minor changes observed are due to interionic interactions. The second class of compounds, known as 'weak electrolytes', are those where ionisation is incomplete. The ionisation will increase with dilution, and hence, the molar conductivity increases with dilution. Thus the conductivity is directly proportional to the degree of dissociation of a weak electrolyte.

It is to be remembered that $c$ in Eq. 16.15 is to be expressed in mol $m^{-3}$ units. If the concentration is given in terms of molarity (mol $dm^{-3}$), then the following conversion is to be carried out :

$c(\text{mol m}^{-3}) = \text{Molarity} \times 1000$ ... (16.16)

Earlier, equivalent conductivity ($\Lambda_{eq}$), which is given by the following expression, was in use.

$$\Lambda_{eq} = \frac{1000\kappa}{c'}$$

where $c'$ is the concentration expressed in terms of normality of the solution.

However, IUPAC recommends the use of molar conductivity only.

**Example 3**

At 298 K, the resistance of $2.00 \times 10^{-2}$ M KCl is 195.96 Ω and that of $2.50 \times 10^{-3}$ M $K_2SO_4$ is 775.19 Ω. The specific conductance ($\kappa$) of $2.00 \times 10^{-2}$ M KCl at 298 K is 0.2768 S $m^{-1}$. Calculate molar conductivity of $K_2SO_4$ solution.

**Solution**

First we have to find out the cell constant. From Eq. 16.14

$$k_{cell} = \kappa \times R$$

Substituting the given values for $2.00 \times 10^{-2}$ M KCl, we get,

$$k_{cell} = 0.2768 \text{ S m}^{-1} \times 195.96\ \Omega$$
$$= 54.24 \text{ m}^{-1}.$$

Next, we have to calculate the $\kappa$ of $K_2SO_4$ solution.

$$\kappa = \frac{k_{cell}}{R} = \frac{54.24 \text{ m}^{-1}}{775.19\ \Omega}$$
$$= 0.06997 \text{ S m}^{-1}.$$

The concentration of $K_2SO_4$ is given in molarity. Hence, its concentration in mol $m^{-3}$ units may be obtained by using Eq. 16.16.

$$c = 1000 \times 2.50 \times 10^{-3} \text{ mol m}^{-3}$$
$$= 2.50 \text{ mol m}^{-3}$$

We can calculate $\Lambda_m$ using Eq. 16.15,

$$\Lambda_m = \frac{\kappa}{c} = \frac{0.06997}{2.50} \text{ S m}^2 \text{ mol}^{-1}.$$
$$= 0.028 \text{ S m}^2 \text{ mol}^{-1}.$$

## 16.6 MOLAR CONDUCTANCE AT INFINITE DILUTION

We have already seen that the molar conductance of an electrolyte increases with decreasing concentrations as is apparent from the values given in Table 16.1.

**Table 16.1 : Molar Conductance at 298 K**

| Concentration | $\Lambda_m$/S $m^2$ $mol^{-1}$ | | | |
|---|---|---|---|---|
| M | HCl | KCl | $CH_3COOH$ | $AgNO_3$ |
| 1.000 | 0.03328 | 0.01119 | — | — |
| 0.100 | 0.03913 | 0.01289 | 0.00052 | 0.01091 |
| 0.010 | 0.04120 | 0.01413 | 0.00162 | 0.01248 |
| 0.001 | 0.04214 | 0.01469 | 0.00486 | 0.01305 |
| 0.0005 | 0.04227 | 0.01478 | 0.01350 | 0.01314 |

Many of the books tabulate $\Lambda_m$ in terms of S $cm^2$ $mol^{-1}$.

Moreover, as a consequence of interionic interactions, every ion in solution has a diffused ionic atmosphere of opposite charges. The motion of an ion under the influence of an electric field would be least affected by the interionic forces when the solution is very dilute. Indeed the value of molar conductance extrapolated to zero concentration should be independent of interionic interactions. It is called limiting molar conductivity or molar conductance at infinite dilution and given the symbol, $\Lambda_m^0$. Kohlrausch gave an empirical formula on the basis of his experimental results, which connects the molar conductivites with concentration, for strong electrolyte:

$$\Lambda_m = \Lambda_m^0 - A c_r^{1/2} \qquad \text{..... (16.17)}$$

Where $A$ is constant; its value depends on the nature of the electrolyte rather than on the identity of the specific ions. For example, electrolytes of the type KCl, NaOH, NaCl etc. have the same value of $A$ whereas $BaCl_2$ $CuSO_4$ etc, have a different value.

**Kohlrausch's Law of the Independent Migration of Ions**

On the basis of conductivity measurements on a series of strong electrolytes, Kohlrausch discovered that the molar conductance at infinite dilution is the sum of the contributions from each ion. It is known as the law of independent migration (or mobility) of ions. This law can be expressed as :

$$\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0 \qquad \text{..... (16.18)}$$

where $\nu_+$ and $\nu_-$ are numbers of cations and anions per formula unit, respectively and $\lambda_+^0$ and $\lambda_-^0$ are the corresponding molar conductivities of the ions at infinite dilution. For example, Table 16.2 gives $\Lambda_m^0$ values for a number of salts. If you compare the values for any pair of salts having a common ion, it always shows a constant difference between $\Lambda_m^0$ values. These values can be explained if we assume that $\Lambda_m^0$ is the sum of two terms, one arising due to cation and the other due to anion. Thus the first set of values gives the difference due to the different contributions of $K^+$ and $Na^+$, the second due to $K^+$ and $Li^+$ and the third due to $Cl^-$ and $NO_3^-$.

**Table 16.2 : $\Lambda_m^0$ values for Some Electrolytes**

| Electrolyte | $\Lambda_m^0$ S m$^2$ mol$^{-1}$ | Electrolyte | $\Lambda_m^0$ S m$^2$ mol$^{-1}$ | Electrolyte | $\Lambda_m^0$ S m$^2$ mol$^{-1}$ |
|---|---|---|---|---|---|
| KCl | 0.01498 | KOH | 0.02715 | $KNO_3$ | 0.01450 |
| NaCl | 0.01264 | NaOH | 0.02481 | $NaNO_3$ | 0.01216 |
| Difference | 0.00234 | | 0.00234 | | 0.00234 |
| KCl | 0.01498 | $KNO_3$ | 0.01450 | $KClO_4$ | 0.01400 |
| LiCl | 0.01150 | $LiNO_3$ | 0.01101 | $LiClO_4$ | 0.01051 |
| Difference | 0.00348 | | 0.00349 | | 0.00349 |
| LiCl | 0.01150 | KCl | 0.01498 | NaCl | 0.01264 |
| $LiNO_3$ | 0.01101 | $KNO_3$ | 0.01450 | $NaNO_3$ | 0.01216 |
| Difference | 0.00049 | | 0.00048 | | 0.00048 |

**Ostwald's Dilution Law**

In the case of weak electrolytes, it is not possible to obtain the limiting molar conductance value, $\Lambda_m^0$, by extrapolation of molar conductance value to zero concentration since there is a large increase in molar conductance and the experimental measurements become unreliable. This can be seen from the values given for acetic acid in Table 16.1. For weak electrolytes, Ostwald derived a relationship between the molar conductivity and the limiting molar conductance. This relationship is known as Ostwald's dilution law.

The molar conductivity of weak electrolyte can be expressed as the product of degree of ionisation of the electrolyte and its limiting molar conductance:

$$\Lambda_m = \alpha \, . \, \Lambda_m^0 \qquad \text{..... (16.19)}$$

where $\alpha$ is the degree of ionisation.

If $c$ is the molar concentration of the electrolyte, we can express the ionisation of a weak electrolyte as follows :

$$\begin{array}{ccccc} MA & \rightleftharpoons & M^+ & + & A^- \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

$$\text{So, } K = \frac{[\mathrm{M}^+][\mathrm{A}^-]}{[\mathrm{MA}]} = \frac{(\alpha c)(\alpha c)}{(1-\alpha)c} = \frac{\alpha^2 c}{1-\alpha} \qquad \text{..... (16.20)}$$

Eq. 16.20 can be rearranged as

$$\frac{1-\alpha}{\alpha^2 c} = \frac{1}{K}$$

$$\text{or } \frac{1-\alpha}{\alpha} = \frac{\alpha c}{K} \text{ (multiplying both sides of the equation by } \alpha c\text{)}$$

$$\text{or } \frac{1}{\alpha} - 1 = \frac{\alpha c}{K}$$

$$\text{or } \frac{1}{\alpha} = 1 + \frac{\alpha c}{K} \qquad \text{..... (16.21)}$$

But from Eq. 16.19, we know that

$$\frac{1}{\alpha} = \frac{\Lambda_m^0}{\Lambda_m}$$

Substituting the value of $\frac{1}{\alpha}$ in Eq. 16.21, we get

$$\frac{\Lambda_m^0}{\Lambda_m} = 1 + \frac{c}{K} \cdot \frac{\Lambda_m}{\Lambda_m^0}$$

Dividing throughout by $\Lambda_m^0$ we get,

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{c\,\Lambda_m}{K\,(\Lambda_m^0)^2} \qquad \text{..... (16.22)}$$

It is found that for concentrations higher than 0.1 mol dm$^{-3}$, Ostwald's law is not followed strictly. We can use Kohlrausch's law of independent mobility of ions to calculate indirectly $\Lambda_m^0$ value for weak electrolytes as illustrated by the following example :

$$\Lambda_m^0(\mathrm{CH_3COOH}) = \Lambda_m^0(\mathrm{CH_3COONa}) + \Lambda_m^0(\mathrm{HCl}) - \Lambda_m^0(\mathrm{NaCl})$$

Notice that all the terms on the right hand side are for strong electrolytes and are known; thus, we can calculate the value for the weak electrolyte, $CH_3COOH$, as shown below :

The values of molar conductance at infinite dilution for sodium acetate, hydrochloric acid and sodium chloride are 0.009101, 0.04261 and 0.01264 S m$^2$ mol$^{-1}$, respectively.

$$\begin{aligned}\text{Hence, } \Lambda_m^0(\mathrm{CH_3COOH}) &= [(0.009101 + 0.04261) - 0.01264]\ \mathrm{S\ m^2\ mol^{-1}} \\ &= 0.03907\ \mathrm{S\ m^2\ mol^{-1}}.\end{aligned}$$

## 16.7 IONIC MOBILITIES AND TRANSPORT NUMBER

**Potential gradient is the voltage drop for unit length. Its unit is V m$^{-1}$. Ionic mobility ($u$) can be defined as the velocity of an ion under unit potential gradient.**

**Unit of ionic mobility**

$$= \frac{\text{Unit of velocity}}{\text{Unit of potential gradient}}$$

$$= \frac{\mathrm{m\ s^{-1}}}{\mathrm{V\ m^{-1}}} = \mathrm{m^2\ V^{-1}\ s^{-1}}$$

**Transport number of an ion indicates the fraction of the total current carried by it.**

$$t_+ + t_- = 1$$

**If the total quantity of electricity is $q$ while the transport numbers of cation and anion are $t_+$ and $t_-$, then,**

$$\left.\begin{array}{l}\text{quantity of electricity}\\ \text{carried by cation } (q_+)\end{array}\right\} = t_+ q = t_+ It \text{ and}$$

$$\left.\begin{array}{l}\text{quantity of electricity}\\ \text{carried by anion } (q_-)\end{array}\right\} = t_- q = t_- It$$

**The above is true only if two ions are present in the solution.**

The next question which arises in this connection is why should there be a difference between the values of limiting molar conductivities of similarly charged ions, if these ions are just acting as carriers of electric charges only?

The answer lies in the fact that different ions have different mobilities in solution. The mobility of an ion in solution is mainly dependent upon the size of the hydrated ion. The ionic mobility is defined as the velocity with which an ion would move under a potential gradient of 1 V m$^{-1}$ in a solution. It provides a link between theoretical and measurable quantities. For instance, ionic mobility, ($u$) is related to molar ionic conductivity by the following equations :

$$\lambda_+^0 = z_+ u_+ F \ \textit{and}\ \lambda_0^0 = z_- u_- F \qquad \text{..... (16.23)}$$

where $z_+$ and $z_-$ are the valency of the ions, $u_+$ and $u_-$ represent the ionic mobilities and $F$ is the faraday. In the above equation, if one of the two quantities, $\lambda$ or $u$, is known, the other can be calculated.

To find the values of $\lambda_+^0$ or $\lambda_-^0$ we define yet another quantity, called transport of transference number of an ion indicated by the symbol $t_+$ or $t_-$. It is defined as the fraction of the total current carried by an ionic species and can be expressed mathematically as,

$$t_+^0 = \frac{\lambda_+^0}{\Lambda_m^0} \text{ and } t_-^0 = \frac{\lambda_-^0}{\Lambda_m^0} \qquad \text{..... (16.24)}$$

The transport number and the limiting molar conductance are measurable quantities. Hence, the molar ionic conductivity value can be calculated from Eq. 16.24. Finally, once the molar ionic conductivity value is obtained, we can then make use of Eq. 16.23 to calculate the ionic mobility.

$t_+$ and $t_-$ stand for transport numbers of the ions at any given concentration, whereas $t_+^0$ and $t_-^0$ are the transport numbers at infinite dilution. The methods of determination of $t_+$ and $t_-$ are discussed in the next section. The transport numbers measured at low concentrations are exptrapolated to zero concentration to obtain $t_+^0$ and $t_-^0$.

From the definitions, we know that,

$$S = \frac{1}{\Omega} \text{ and } C = A\,s$$

$$\frac{S}{C} = \frac{1}{\Omega\,A\,s} = \frac{1}{V\,s}$$

since 1 V = 1 Ω A

(emf = Resistance × current as per ohm's law)

**Example 4**

Calculate the ionic mobility of the cation in an infinitely dilute solution of KBr at 298 K. Given that the transport number of $K^+$ is 0.48 and the molar conductance of KBr at infinite dilution is $1.52 \times 10^{-2}$ S m$^2$ mol$^{-1}$.

**Solution**

From Eq. 16.24 we can write

$$t_+^0 = \frac{\lambda_+^0}{\Lambda_m^0}$$

or $\lambda_+^0 = t_+^0\,\Lambda_m^0$

Substituting the value $\lambda_+^0$ in Eq. 16.23 we get,

$$t_+^0\,\Lambda_m^0 = z_+\,u_+\,F$$

Hence,

$$u_+ = \frac{t_+^0\,\Lambda_m^0}{z_+\,F}$$

Substituting the given values in the above equation we get,

$$u_+ = \frac{0.48 \times 1.52 \times 10^{-2}\ \text{S m}^2\ \text{mol}^{-1}}{1 \times 96500\ \text{C mol}^{-1}} = 7.6 \times 10^{-8}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}$$

We shall now look into the methods of determination of transport number.

## 16.8 DETERMINATION OF TRANSPORT NUMBER

There are mainly two methods for the determination of transport number. Let us discuss Hittorf method first.

**Hittorf Method**

An electrolytic cell of the type shown in Fig. 16.5 is divided into three compartments. Each one has a stop-cock at the bottom so that the solution can be drained from any compartment for analysis. It is connected in series with a sensitive ammeter (M), silver coulometer (C) and a battery (E). K is the connecting key.

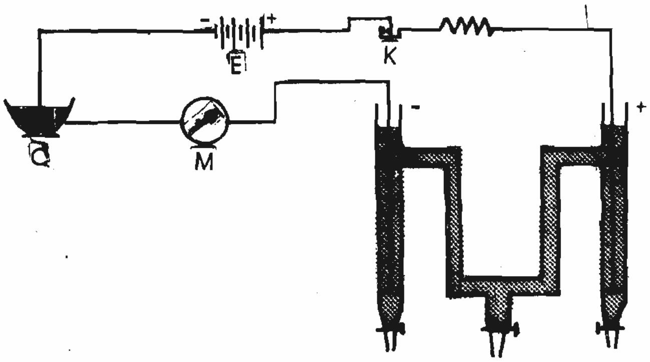

Fig. 16.5 : Transport number determination by Hittorf method.

The cell is filled with the electrolyte solution of known concentration. A known amount of electricity (≈ $I\,t$) is passed through the cell, where $I$ is the current and $t$ is the time interval. At the end of electrolysis, a known volume of the electrolyte is drained out from the cathode compartment and analysed to find the concentration of the electrolyte. Knowing the initial amount of the electrolyte and its amout at the end of electrolysis, we can find the change in its amount. At the same time, by determining the amount of silver deposited in the coulometer, the exact quantity of electricity passed can be accurately determined. Let us see how transport number is calculated from these measurements.

From Eq. 16.7, the number of moles of cations discharged at the cathode by the passage of $I$ ampere current for $t$ second, is given by

$$\text{Number of moles of cations discharged} = \frac{\text{Mass of the element deposited}}{\text{Mass of one mol atoms of the element}}$$

$$= \frac{w}{M} = \frac{q}{nF}$$

If $z_+$ is the electrovalency of the cation of the element, then $n = z_+$.

$$\text{Hence, the number of moles of cations discharged} = \frac{w}{M} = \frac{It}{z_+F} \qquad \text{..... (16.25)}$$

Quantity of electricity carried by the cations $\Big\} = q_+ = t_+It$;

Hence, the number of moles of cations moving into the cathode compartment as per Eq. 16.7

$$= \frac{w}{M} = \frac{q_+}{z_+F} = \frac{t_+It}{z_+F}$$

At the same time, when these cations are getting discharged, some cations from the middle compartment will move into the cathode compartment to keep the solution in the cathode compartment electrically neutral. Just the opposite reaction will take place in the anode compartment. Now the moles of cations that move into the cathode compartment would be $t_+\left(\frac{It}{z_+F}\right)$. Due to this, there would be a change in the amount of the electrolyte in the cathode compartment; this change can be calculated as shown below:

Change in the amount of the electrolyte around the cathode = (Moles of cations entering into the cathode compartment) − (moles of cations discharged at the cathode)

$$= t_+\frac{It}{z_+F} - \frac{It}{z_+F} = (t_+ - 1)\frac{It}{z_+F} \qquad \text{..... (16.26)}$$

Note that the r.h.s. of Eq. 16.26 is a negative quantity since $t_+$ is less than 1 and $(t_+ - 1)$ is a negative quantity. The physical significance of Eq. 16.26 is that the change in the amount of the electrolyte around the cathode is negative. In other words, there is a decrease in the amount of the electrolyte (as a result of electrolysis) around the cathode.

This change in the amount of the electrolyte can be found out after stopping the current and draining out a known volume of the solution from the cathode compartment for chemical analysis. At the same time, $q$ can be calculated by knowing the difference in masses of the cathode in the coulometer before and after passing current. Thus, one can find the value of transport number.

Note that the amount of a substance

$$= \frac{\text{Mass of the substance}}{\text{Its molar mass}}$$

Also, molar mass of HCl = 0.0365 kg mol$^{-1}$

**Example 5**

A solution of HCl was electrolysed between Pt electrodes in a Hittorf cell. The analysis of the solution from the cathode compartment before and after the electrolysis indicated the masses of HCl as $1.82 \times 10^{-4}$ kg and $1.67 \times 10^{-4}$ kg. The silver deposited at the cathode of the coulometer in the same circuit was $2.52 \times 10^{-4}$ kg. Calculate the transport number of both the ions.

**Solution**

According to Eq. 16.26, change in the amount of HCl around the cathode,

$$(t_+ - 1)\frac{It}{z_+F} = \frac{(1.67 \times 10^{-4} - 1.82 \times 10^{-4})\ \text{kg}}{0.0365\ \text{kg mol}^{-1}}$$

$$(t_+ - 1)\left(\frac{It}{z_+F}\right) = -\frac{0.15 \times 10^{-4}\ \text{kg}}{0.0365\ \text{kg mol}^{-1}} = -4.1 \times 10^{-4}\ \text{mol}$$

But as per Eq. 16.25

$$\text{number of moles of cations discharged} = \frac{It}{z_+F} = \frac{2.52 \times 10^{-4}\ \text{kg}}{0.108\ \text{kg mol}^{-1}}$$

$$= 23.33 \times 10^{-4}\ \text{mol}$$

Hence,

$(t_+ - 1)(23.33 \times 10^{-4}) = -4.1 \times 10^{-4}$

$t_+ - 1 = -0.18$

$t_+ = 1 - 0.18 = 0.82$ and $t_- = 1 - 0.82 = 0.18$.

### Moving Boundary Method

Suppose that the transference number of the cation, $M^{z+}$, of a salt MA is to be determined. A solution of MA is introduced into a tube with known uniform bore, where it forms an upper layer over a solution of another electrolyte $M_1A$, having a common anion, A. The two electrolytes are so chosen such that the mobility of $M^{z+}$ is much greater than $M_1^{z+}$ and the two solutions form a sharp boundary between them (Fig. 16.6).

Fig. 16.6 : Apparatus for moving boundary method

I) Cathode;

II) boundary after passing the current for time $t$;

III) initial boundary;

IV) anode.

The boundary can be observed by the use of any physical property. For instance the difference in the refractive index of the two electrolytes can be utilised. When a current $I$ is passed through the cell for a time $t$, the boundary will move. $M_1^{z+}$ will neither be able to overtake $M^{z+}$

nor lag behind it; therefore the boundary between the electrolytes will be preserved. Suppose that the boundary moves a distance $x$ and the concentration of the electrolyte MA is $c$. If the cross-section area of the tube is $a$, than $xa = V$, where $V$ is the volume of the column of electrolyte between the boundaries before and after the experiment. Hence, the number of moles of electrolyte in this volume will be equal to $Vc$. Each mole of cation $M^{z+}$ carries a charge, $z_+F$. Thus, the charge carried by $Vc$ mole of the cation is $Vcz_+F$; but, the total quantity of charge supplied is $It$.

Hence,

$$\text{Transport number, } t_+ = \frac{\text{Charge carried by cation}}{\text{Total charge}}$$

$$= \frac{Vcz_+F}{It} = \frac{xacz_+F}{It} \qquad \text{..... (16.27)}$$

**SAQ 4**

In a moving boundary experiment with 0.020 M NaCl solution, a current of 0.0016 A moved the boundary through a distance of 0.060 m in 2070 s. The radius of the tube is $1.884 \times 10^{-3}$ m. Calculate the transport number of both the ions.

**Hints** : 1) The tube is cylindrical and its cross-sectional area $(a) = \pi \times (\text{radius})^2$

2) Concentration $(c)$ = Molarity $\times 10^3$
[ since $1\ \text{dm}^{-3} = 10^3\ \text{m}^{-3}$ ]

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## 16.9 APPLICATIONS OF CONDUCTIVITY MEASUREMENTS

The conductance measurements on electrolyte solutions can provide a lot of useful information. We have already seen that we can divide the electrolytes into strong and weak categories on the basis of the magnitude of molar conductance. This classification helps us in understanding the behaviour of different substances in solution. Further, these measurements can lead us to evaluate the degree of ionisation and the ionisation constants for weak electrolytes. We can also determine the solubility of sparingly soluble salts. Finally, the conductance experiments can be performed to find the equivalence points in acid-base or precipitation titrations. Let us see how it is actually done in each case.

**Determination of the Ionic Product of Water**

We can determine both the degree of dissociation and the ionic product of water using conductivity measurements. For this purpose, conductivity water is prepared by repeated distillation of water containing a small quantity of NaOH and $KMnO_4$. Experimentally determined value for conductivity on such samples of distilled water is

$$\kappa(H_2O) = 5.50 \times 10^{-6}\ \text{S m}^{-1}$$

To find out the molar conductance, we must know the concentration of water since from Eq. 16.15,

$$\Lambda_m = \frac{\kappa}{c}$$

$$\text{But the concentration } (c) \text{ of water} = \frac{\text{Amount of water}}{\text{Volume}}$$

$$= \frac{\text{Mass of water}}{\text{Molar mass of water}} \times \frac{1}{\text{Volume}}$$

$$= \frac{1\ \text{kg}}{0.018\ \text{kg mol}^{-1}} \times \frac{1}{10^{-3}\ \text{m}^3}$$

$$c = 5.56 \times 10^4\ \text{mol m}^{-3}.$$

The concentration of water is calculated using the fact that 1 $dm^3$ (i.e., $10^{-3}\ m^3$) of water has a mass of 1 kg. Also the molar mass of water is 0.018 kg $mol^{-1}$.

Substituting the values of $\kappa$ and $c$ we get,

$$\Lambda_m = \frac{5.50 \times 10^{-6}}{5.56 \times 10^{4}} \text{ S m}^2 \text{ mol}^{-1}$$

$$\Lambda_m = 9.90 \times 10^{-11} \text{ S m}^2 \text{ mol}^{-1}$$

The molar conductance at infinite dilution, $\Lambda_m^0$, can be calculated on the basis of law of independent mobility of ions. In the present case, since water dissociates to a small extent into $H^+$ and $OH^-$ ions we can write,

$$\Lambda_m^0 (H_2O) = \lambda^0 (H^+) + \lambda^0 (OH^-)$$

The values of $\lambda^0(H^+)$ and $\lambda^0 (OH^-)$, as determined experimentally are, $3.498 \times 10^{-2}$ S m² mol$^{-1}$ and $1.980 \times 10^{-2}$ S m² mol$^{-1}$, respectively. Hence,

$$\begin{aligned}\Lambda_m^0 &= (3.498 + 1.980) \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1} \\ &= 5.478 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}\end{aligned}$$

From Eq. 16.19, we know that

$$\Lambda_m = \alpha \, \Lambda_m^0$$

$$\text{or } \alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

where $\alpha$ is the degree of dissociation of water.

Substituting the proper values obtained above, we get

$$\begin{aligned}\alpha &= \frac{9.90 \times 10^{-11} \text{ S m}^2 \text{ mol}^{-1}}{5.478 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}} \\ &= 1.81 \times 10^{-9}\end{aligned}$$

Thus, the degree of dissociation of water is found to be $1.81 \times 10^{-9}$.

Further, we have already learnt in Unit 15 of this block that the ionic product of water is given by the equation :

$$K_w = [\,H^+\,][\,OH^-\,] = (c\alpha)\,(c\alpha) = \alpha^2 c^2 \qquad \text{..... (16.28)}$$

Substituting $c$ and $\alpha$ values in this equation, we get

$$\begin{aligned}K_w &= (1.81 \times 10^{-9})^2 \,(5.56 \times 10^4 \text{ mol m}^{-3})^2 \\ &= 1.01 \times 10^{-8} \text{ mol}^2 \text{ m}^{-6} \\ &= 1.01 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}\end{aligned}$$

1m = 10 dm

$(1 \text{ m})^{-6} = (10 \text{ dm})^{-6}$

$= 10^{-6} \text{ dm}^{-6}$

Hence, $1.01 \times 10^{-8} \text{ m}^{-6}$

$= 1.01 \times 10^{-8} \times 10^{-6} \text{ dm}^{-6}$

$= 1.01 \times 10^{-14} \text{ dm}^{-6}$

Also $1.01 \times 10^{-8} \text{ mol}^2 \text{ m}^{-6}$

$= 1.01 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

Thus we see that the degree of dissociation and the ionic product of water can be calculated.

**Dissociation Constant of a Weak Acid**

We have learnt in Unit 15 of this block that the dissociation of a weak acid can be represented as,

$$\begin{array}{ccccc} HA & \rightleftharpoons & H^+ & + & A^- \\ c\,(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

where the symbols have their usual meaning. The dissociation constant is written as

$$K_a = \frac{\alpha^2 c}{(1-\alpha)} \qquad \text{..... (16.29)}$$

From Eq. 16.19 we know,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

Hence, Eq. 16.29 can be written as

$$K_a = \frac{(\Lambda_m/\Lambda_m^0)^2\, c}{\left(1 - \dfrac{\Lambda_m}{\Lambda_m^0}\right)} = \frac{\Lambda_m^2\, c}{\Lambda_m^0 (\Lambda_m^0 - \Lambda_m)} \qquad \text{..... (16.30)}$$

Following the steps shown in Example 3, we can calculate the molar conductance of a weak acid at any given concentration, if its resistance is known. The molar conductance at infinite dilution, $\Lambda_m^0$, can be calculated from the principle of independent migration of ions. Thus for HA we can write

$$\Lambda_m^0 (HA) = \lambda^0(H^+) + \lambda^0(A^-) \qquad \text{..... (16.31)}$$

$\lambda^0$ values for most of the common ions have been determined and given in Table 16.3.

It is thus possible to calculate the dissociation constant of a weak acid or any other weak electrolyte.

**Table 16.3 : Ion Conductances at Infinite Dilution at 298 K**

| Ion | $10^4 \times \lambda_+^0/\text{S m}^2\text{ mol}^{-1}$ | Ion | $10^4 \times \lambda_-^0/\text{S m}^2\text{ mol}^{-1}$ |
|---|---|---|---|
| $H^+$ | 349.8 | $OH^-$ | 198.0 |
| $K^+$ | 73.52 | $Cl^-$ | 76.34 |
| $Na^+$ | 50.11 | $NO_3^-$ | 71.46 |
| $Ag^+$ | 61.9 | $CH_3COO^-$ | 40.9 |
| $NH_4^+$ | 73.6 | $Br^-$ | 78.14 |

Let us consider an example for the determination of dissociation constant of a weak acid.

**Example 6**
Calculate the dissociation constant for acetic acid at 298 K if 0.040 M solution of the acid has a molar conductance of $8.59 \times 10^{-4}\text{ S m}^2\text{ mol}^{-1}$.

**Solution**
The principle of independent migration of ions gives

$$\Lambda_m^0 = \lambda^0(H^+) + \lambda^0(CH_3COO^-)$$

Substituting the proper values from Table 16.3 gives,

$$\Lambda_m^0 = (349.8 + 40.9) \times 10^{-4}\text{ S m}^2\text{ mol}^{-1}$$
$$= 390.7 \times 10^{-4}\text{ S m}^2\text{ mol}^{-1}$$

From Eq. 16.30, we get

$$K_a = \frac{\Lambda_m^2\, c}{\Lambda_m^0(\Lambda_m^0 - \Lambda_m)}$$

or

$$K_a = \frac{(8.59 \times 10^{-4}\text{ S m}^2\text{ mol}^{-1})^2 \times 0.040\text{ mol dm}^{-3}}{(390.7 \times 10^{-4}\text{ S m}^2\text{ mol}^{-1})(390.7 \times 10^{-4} - 8.59 \times 10^{-4})\text{ S m}^2\text{ mol}^{-1}}$$

$$K_a = 1.98 \times 10^{-5}\text{ mol dm}^{-3}$$

Note that concentration is expressed in mol dm$^{-3}$ units while calculating $K_a$ or any equilibrium constant values (as per Unit. 14).

The value so obtained is in close agreement with the accepted standard value of $1.8 \times 10^{-5}$.

**Determination of Solubility of a Sparingly Soluble Salt**
The solubility of a sparingly soluble salt can be determined using conductance method. By finding $\Lambda_m$ and $\kappa$ values of the salt and substituting the same in the rearranged form of Eq. 16.15, the concentration, $c$, of a sparingly soluble salt in its solution can be calculated:

$$c = \frac{\kappa(\text{salt})}{\Lambda_m(\text{salt})} \qquad \text{..... (16.32)}$$

It is to be noted that $\kappa$(salt) is the conductivity of the salt alone and is given by the equation,

$$\kappa(\text{salt}) = \kappa(\text{solution}) - \kappa(\text{water}) \qquad \text{..... (16.33)}$$

Hence, $\kappa$ (salt) is calculated by subtracting $\kappa$ (water) from $\kappa$ (solution), which are both determined experimentally.

Further, we know that the sparingly soluble salts are at extremely low concentrations even in a saturated solution. Hence, the molar conductivity of a saturated solution of a sparingly soluble salt can be assumed to be equal to the molar conductivity at infinite dilution.

$$\Lambda_m(\text{salt}) = \Lambda_m^0(\text{salt}) \qquad \text{..... (16.34)}$$

or using Eq. 16.18,

$$\Lambda_m^0(\text{salt}) = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0 \qquad \text{..... (16.35)}$$

where $\nu_+$ and $\nu_-$ are the numbers of cations and anions per formula unit of the salt.

Combining Eqs. 16.32, 16.33 and 16.35, we get

$$c = \frac{\kappa(\text{solution}) - \kappa(\text{water})}{\nu_+ \lambda_+^0 + \nu_- \lambda_-^0} \qquad \text{..... (16.36)}$$

Substituting the values of quantities in Eq. 16.36, the concentration of the sparingly soluble salt in its saturated solution can be determined.

**Example 7**

Specific conductances ($\kappa$) at 298 K of a saturated solution of AgCl and of water used for dissolving the salt are $2.850 \times 10^{-4}$ S $m^{-1}$ and $5.50 \times 10^{-6}$ S $m^{-1}$, respectively. The ionic conductances at infinite dilution for $Ag^+$ and $Cl^-$ ions are $61.9 \times 10^{-4}$ S $m^2$ $mol^{-1}$ and $76.34 \times 10^{-4}$S $m^2$ $mol^{-1}$ Calculate the solubility of AgCl in kg $m^{-3}$.

**Solution**

Substituting the given values in Eq. 16.36, we get,

$$c = \frac{(2.850 - 0.055) \times 10^{-4}\ \text{S m}^{-1}}{(61.9 + 76.34) \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}} \quad (\text{since } \nu_+ = \nu_- = 1)$$

$$= \frac{2.795 \times 10^{-4}\ \text{S m}^{-1}}{138.24 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}}$$

$$= 2.022 \times 10^{-2}\ \text{mol m}^{-3}$$

$$= 2.022 \times 10^{-2} \times 0.143\ \text{kg m}^{-3} (\text{since molar mass of AgCl} = 0.143\ \text{kg mol}^{-1})$$

$$= 2.89 \times 10^{-3}\ \text{kg m}^{-3}$$

**Conductometric Titrations**

Acid-base or precipitation titrations can be performed with the help of conductivity measurements. In acid-base titrations, three different situations can arise:

a) titration between a strong acid and a strong base
b) titration of a weak acid with a strong base and
c) titration of a weak acid with a weak base.

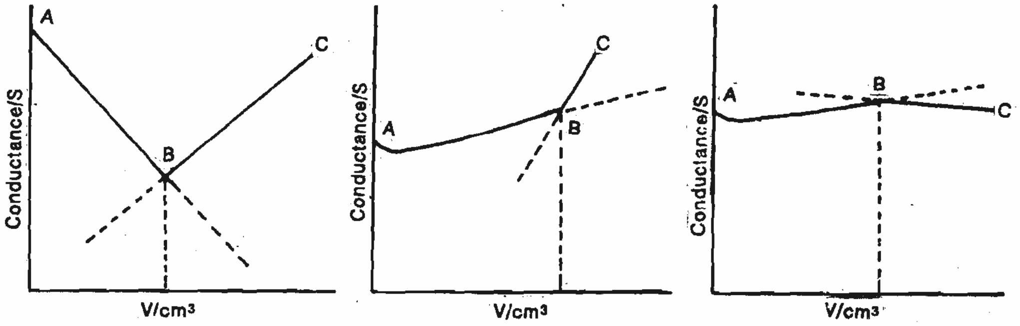
Let us consider each one of them separately.

i) Suppose we titrate a strong acid, say, HCl, with a strong base, NaOH:

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

Actually, the addition of NaOH results in replacing $H^+$ ions by $Na^+$ ions in solution as shown by the above equation. The ionic conductance of $H^+$ is more than that of $Na^+$ ion. As a result, the conductivity of the solution will decrease with the addition of NaOH. At the equivalence point, the conductivity will have the lowest value since all the $H^+$ ions have been replaced by $Na^+$ ions in solution. After the equivalence point, addition of NaOH will produce excess of $Na^+$ ions as well as fast moving $OH^-$ ions. Again there will be a rise in the conductivity of the solution. A typical plot of conductance ($1/R$) against the volume of the base ($V$) added for a strong acid-strong base titration is shown in Fig. 16.7 a. The decrease in conductance before the equivalence point is much sharper than the increase after the equivalence point. The reason is that $H^+$ ions are far more mobile than $OH^-$ ions. The equivalence point, B, is obtained by the intersection of the two lines. AB and BC.

ii) In the case of titration between a weak acid and a strong base, we get a titration curve as shown in Fig. 16.7 b.



(a) (b) (c)

Fig. 16.7 : a) Conductometric titration of a strong acid with a strong base;
b) conductometric titration of a weak acid with a strong base;
c) conductometric titration of a weak acid and a weak base.

Initially the conductance will be low, since the dissociation of a weak acid is low and smaller number of $H^+$ ions is produced. On addition of NaOH, $H^+$ ions combine with $OH^-$ ions to produce water; but, at the same time, some fresh $H^+$ ions are produced in the solution. As soon as $H^+$ ions are removed in the form of water, the equilibrium

$$HA \rightleftharpoons H^+ + A^-$$

will shift to the right. In addition to these $H^+$ ions, we will also have some $Na^+$ ions in solution. The net result is that there is a slight increase in conductivity. This trend will be seen till the equivalence point is reached. However, after the equivalence point, there will be a sudden increase in the conductivity due to the presence of $Na^+$ ions and $OH^-$ ions. Since NaOH is a strong electrolyte, it dissociates completely in solution. So even a small excess will produce enough of fast moving $OH^-$ ions. The equivalence point in this case may not be very sharp; but the extrapolation of the curves before and after the equivalence point will cut at a point which will be the equivalence point.

iii) When the titration between a weak acid and a weak base is carried out (Fig. 16.7 c), the initial nature of the titration curve obtained will be similar to that found in (ii). This means the conductivity will slowly increase before the equivalence point. After the equivalence point, further addition of a base will not make much of a difference in the conductivity since the base itself is very weak, having low dissociation constant value.

**Conductometric Titration of a Precipitation Reaction**

Let us consider a typical precipitation reaction between the solutions of NaCl and $AgNO_3$ which is expressed as,

$$Na^+ + Cl^- \xrightarrow{AgNO_3} AgCl + Na^+ + NO_3^-$$

Initially we have $Na^+$ ions and $Cl^-$ ions in solution. The slow addition of $AgNO_3$ gives solid AgCl and $Na^+$ and $NO_3^-$ ions in solution. Thus as the titration proceeds, we are replacing $Cl^-$ ions by $NO_3^-$ ions in solution. Since there is not much of a difference in the conductance of $Cl^-$ ions and $NO_3^-$, this part of the curve (AB) in Fig. 16.8 remains almost horizontal, without much of a change in the slope, After the equivalence point, B, there will be a continuous increase in the conductance with the addition of $AgNO_3$. This is so because each addition of $AgNO_3$ will give more $Ag^+$ and $NO_3^-$ ions which would increase the conductance.

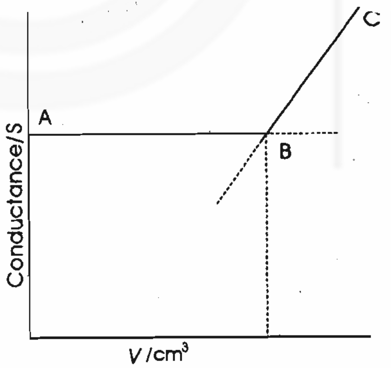


Fig. 16.8 : Conductance against volume plot for precipitation titration.

## 16.10 SUMMARY

In the present unit, we have discussed the behaviour of electrolytes in solution under the influence of an electric field. Since the ions produced by the dissolution of an electrolyte are charged particles, these are bound to interact with each other. However, these interactions will not be as strong as in solid state due to the thermal motion of the ions. At the same time, the ions will interact with polar molecules of the solvent, water.

After explaining the nature of these interactions, we then analysed in brief as to what happens to these solutions at the electrodes when we pass an electric current through them. This has been summed-up in the two laws of Faraday.

Different ions, even when they carry same charge, will move at different rates under the influence of an electric potential. The mobility of an ion is defined in terms of a quantity known as transport number. Two common methods for the experimental determination of transport number have been discussed.

The utility of conductance studies has been discussed in the determination of the dissociation constant of a weak electrolyte and the solubility of sparingly soluble salts. The conductance methods of acid-base and precipitation titrations have been discussed.

## 16.11 TERMINAL QUESTIONS

1) The specific conductance at 298 K of a saturated solution of $BaSO_4$ is $4.580 \times 10^{-4}$ S $m^{-1}$ and that of water is $5.50 \times 10^{-6}$ S $m^{-1}$. The molar conductance at infinite dilution of $BaSO_4$ is $2.86 \times 10^{-2}$ S $m^2$ $mol^{-1}$. What is the solubility of $BaSO_4$ at 298 K?

2) 1000 C of electricity is passed through a NaOH solution in an electrolysis apparatus. Calculate the volume of hydrogen and oxygen liberated at S.T.P.

3) A moving boundary experiment is carried out with 0.100 M solution of HCl at 298 K. Sodium ions are caused to follow the hydrogen ions. The cross-sectional area of the tube is $3.0 \times 10^{-5}$ $m^2$. With 3.0 milliampere current, the boundary moves $3.08 \times 10^{-2}$ m in an hour. Calculate the transport number of the hydrogen ion.

4) Calculate the time required to discharge all the $Cr^{3+}$ ions from 500 $cm^3$ of 0.270 M $Cr_2(SO_4)_3$ by a current of 3.00 A.

5) The limiting molar conductivities of KCl, $KNO_3$, and $AgNO_3$ are

   $1.499 \times 10^{-2}$ S $m^2$ $mol^{-1}$
   $1.450 \times 10^{-2}$ S $m^2$ $mol^{-1}$, and
   $1.334 \times 10^{-2}$ S $m^2$ $mol^{-1}$, respectively.

   What is the limiting molar conductivity of AgCl at this temperature?

6) A solution of $AgNO_3$ was electrolysed with silver electrodes. $1.74 \times 10^{-4}$ kg silver was deposited on the cathode. If the transport number of $Ag^+$ ion is 0.37, calculate the decrease in the amount of $AgNO_3$ around the cathode compartment.

## 16.12 ANSWERS

**Self Assessment Questions**

1) To reduce each $Mg^{2+}$ ion to magnesium metal, two electrons are required,

   $Mg^{2+} + 2e^- \longrightarrow Mg$

   Hence $n = 2$

   Rearranging Eq. 16.8, we get, $t = \dfrac{96500\, nw}{IM}$

   Since 1 mol magnesium is to be prepared, $\dfrac{w}{M} = 1$ mol.

   Also, $I = 5$ A

   Hence $t = \dfrac{96500 \times 2 \times 1}{5}\, s = 38600\, s.$

2) i) To reduce each $Cu^{2+}$ ion to copper metal, two electrons are required.

   $Cu^{2+} + 2e^- \longrightarrow Cu$

   Hence $n = 2$

   According to Eq. 16.8, $w = \dfrac{MIt}{96500n}$

   Substituting for $M$, $I$, $t$ and $n$ we get,

   $w = \dfrac{0.06354 \times 4.50 \times 9000}{96500 \times 2}$ kg [ since $M = 0.06354$ kg $mol^{-1}$ ]

   $w = 1.33 \times 10^{-2}$ kg.

ii) Amount of Cu deposited $= \dfrac{w}{M} = 0.21$ mol

Amount of Cu initially present = 2.0 mol
(since 1 $dm^3$ of 2.0 M solution contains 2.0 mol of copper)
Amount of Cu at the end of the electrolysis = (2.0 − 0.21) mol
= 1.79 mol

This must also be equal to the amount of $Cu^{2+}$ ions present in the solution at the end of electrolysis.

3) Substituting the given values for 0.020 M KCl in Eq. 16.14, we get,

$$\kappa = k_{cell} \times \frac{1}{R}$$

$$0.2768\ S\ m^{-1} = k_{cell} \times \frac{1}{195.96\ \Omega}$$

$$k_{cell} = 0.2768 \times 195.96\ m^{-1}$$

Using this value of $k_{cell}$ for 0.050 M $AgNO_3$ solution in Eq. 16.14 we get

$$\kappa(AgNO_3) = 0.2768 \times 195.96\ m^{-1} \times \frac{1}{94.2\ \Omega}$$

$$= 0.576\ S\ m^{-1}.$$

4) According to Eq. 16.27,

transport number, $t_+ = \dfrac{x\,a\,c\,z_+\,F}{It}$

where the symbols have their usual meaning.
Substituting the given values we get,

$$t(Na^+) = \frac{0.060\ m \times 3.14 \times (1.884 \times 10^{-3}\ m)^2 \times (0.020 \times 10^3\ mol\ m^{-3}) \times (1 \times 96500\ C\ mol^{-1})}{0.0016\ A \times 2070 s}$$

$= 0.39$

Hence, $t(Cl^-) = (1 - t(Na^+)) = 0.61$

i) $A = \pi r^2 = 3.14 \times (1.884 \times 10^{-3}\ m)^2$

ii) concentration in mol $m^{-3}$ units
= Molarity × $10^3$

iii) $z_+ = 1$

**Terminal Questions**

1) According to Eq. 16.36,

$$c = \frac{\kappa(solution) - \kappa(water)}{\nu_+ \lambda^0_+ + \nu_- \lambda^0_-}$$

but $\nu_+ \lambda^0_+ + \nu_- \lambda^0_- = \Lambda^0_m$(salt) according to Eq. 16.35. Hence, combining the two equations we get,

$$\frac{\kappa(solution) - \kappa(water)}{\Lambda^0_m(salt)}$$

Substituting the given values we get,

$$c = \frac{(4.580 \times 10^{-4} - 0.0550 \times 10^{-4})\ S\ m^{-1}}{(2.86 \times 10^{-2})\ S\ m^2\ mol^{-1}}$$

$$= 1.58 \times 10^{-2}\ mol\ m^{-3}.$$

2) According to the equations,

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ and $4\ OH^- \rightleftharpoons 2H_2O + O_2 + 4e^-$, we find that for the production of 1 mole each of $H_2$ and $O_2$, we require 2 and 4 faradays of electricity respectively.

Hence $n = 2$ for the production of hydrogen, whereas for the production of oxygen, $n = 4$.

Using Eq. 16.7, the amount of hydrogen produced,

$$n^{H_2} = \frac{w}{M} = \frac{q}{nF}$$

Also as per gas law, volume of hydrogen,

$$V_{H_2} = \frac{n_{H_2} RT}{p} [\text{ At STP, } p = 1.013 \times 10^5\ Pa,\ T = 273.15\ K\ ]$$

using the above two expressions,

$$V_{H_2} = \frac{qRT}{nFp}$$

$$= \frac{1000\ \text{C} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 273.15\ \text{K}}{2 \times 96500\ \text{C mol}^{-1} \times 1.0132 \times 10^{5}\ \text{Pa}}$$

$$= 1.162 \times 10^{-4}\ \text{m}^3$$

Similarly, $V_{O_2} = \frac{qRT}{nFp}$ [ Note that $n = 4$ in the case of oxygen evolution ]

$$= 5.81 \times 10^{-5}\ \text{m}^3$$

3) $t_+ = \frac{x\, a\, c\, z_+ F}{It}$ (as per Eq. 16.27)

$$= \frac{3.08 \times 10^{-2}\ \text{m} \times 3.0 \times 10^{-5}\ \text{m}^2 \times 0.100 \times 10^{3}\ \text{mol m}^{-3} \times 1 \times 96500\ \text{C mol}^{-1}}{3.0 \times 10^{-3}\ \text{A} \times 1 \times 60 \times 60\ \text{s}}$$

$= 0.83.$

4) 1000 cm$^3$ of 1 M $Cr_2(SO_4)_3$ solution contains 2 mol of $Cr^{3+}$ ions. Amount of $Cr^{3+}$ in the given solution ($n_{Cr^{3+}}$)

$$= \frac{500\ \text{cm}^3}{1000\ \text{cm}^3} \times \frac{0.270\ \text{M}}{1\ \text{M}} \times 2\ \text{mol}$$

$= 0.270$ mol

From the following equation,

$$Cr^{3+} + 3e^- \rightleftharpoons Cr$$

we find that for producing each mole of Cr, we require 3F of electricity (i.e., $n = 3$)

From Eq. 16.7

$$n_{Cr^{3+}} = 0.270\ \text{mol} = \frac{w}{M} = \frac{q}{nF} = \frac{It}{nF} = \frac{(3.00\ \text{A})\ t}{(3 \times 96500)\ \text{C mol}^{-1}}$$

$$t = \frac{0.270 \times 3 \times 96500}{3.00}\ \text{s} = 2.61 \times 10^{4}\ \text{s}.$$

5) We can write

$$\Lambda_m^0\,(AgCl) = \Lambda_m^0\,(AgNO_3) + \Lambda_m^0\,(KCl) - \Lambda_m^0\,(KNO_3)$$

Substituting the given values we get,

$$\Lambda_m^0\,(AgCl) = (1.334 + 1.499 - 1.450) \times 10^{-2}\ \text{S m}^2\ \text{mol}^{-1}$$
$$= 1.383 \times 10^{-2}\ \text{S m}^2\ \text{mol}^{-1}$$

6) As per Eq. 16.25,
number of moles of $Ag^+$ ions discharged

$$= \frac{It}{z_+F} = \frac{w}{M} = \frac{1.74 \times 10^{-4}\ \text{kg}}{0.108\ \text{kg mol}^{-1}} = 0.0016\ \text{mol}$$

As per Eq. 16.26, change in the amount of $AgNO_3$ around the cathode compartment $= (t_+ - 1)\frac{It}{z_+F}$

$= (-0.63) \times (0.0016)$ mol
$= -0.0010$ mol

Hence, the decrease in the amount of $AgNO_3$ around the cathode compartment = 0.0010 mol.

# UNIT 17 ELECTROCHEMICAL CELLS

## Structure

## 17.1 INTRODUCTION

In Unit 16, we have seen that on passing electric current through an electrolyte solution, a chemical reaction takes place. In other words, an electric current can cause a chemical reaction to take place under suitable conditions. Is the reverse process also possible? Or by means of a chemical reaction, can we produce electricity? The answer is yes and in both the processes, we make use of a group of reactions where electron transfer takes place.

In an electrolytic cell, a chemical reaction takes place by passing electricity through an electrolyte in a fused state or in solution. On the other hand, when an electrochemical cell is used to generate electricity by the use of a chemical reaction, it is called a galvanic or voltaic cell. In this unit, we shall mainly study different types of galvanic cells, the electrodes used and their effect on the voltage generated. We shall also look at the relationship between the free energy change for the reaction and the electrical potential generated by the cell. Common practical cells will also be discussed as well as the applications of emf measurements. Finally there will be a discussion on the applications of electrolytic cells also.

### Objectives

After reading this unit, you should be able to :

- explain the terms used in electrochemistry such as anode, cathode, oxidation, reduction and emf,
- calculate the cell potential for a given cell,
- correlate the electrical energy generated by the cell with the free energy change for the cell reaction,
- correlate the dependence of the cell potential on the temperature and the concentration of the electrolytes,
- describe the characteristics and the half-cell reactions of various kinds of electrodes used,
- differentiate between primary and secondary cells,
- list different types of dry cells in common use, and
- describe the use of electrolytic cells.

## 17.2 GALVANIC OR VOLTAIC CELLS

Let us recapitulate the definitions of the terms, oxidation and reduction. Oxidation is the loss or release of electrons. Reduction is the gain or addition of electrons. These two processes are illustrated below :

**Oxidation**

$A \longrightarrow A^{n+} + ne^-$

**Reduction**

$B + me^- \longrightarrow B^{m-}$

Usually oxidation and reduction reactions take place together. Such reactions are also called **redox reactions.**

Electrochemical cells make use of spontaneous oxidation-reduction reactions to produce electricity. These cells are known as galvanic or voltaic cells in recognition of the work by Italian scientists, Galvani and Volta. Let us explain the functioning of a volatic cell.

In any spontaneous redox reaction, the two processes,

$A \longrightarrow A^+ + e^-$ (oxidation)

$B + e^- \longrightarrow B^-$ (reduction)

take place without doing any useful work, if we just mix them together. The energy released by such a reaction is in the form of heat. However, if we devise a means of performing oxidation and reduction in separate compartments rather than mixing the two together, we can force the electrons to flow from oxidation to reduction compartment through an external wire, thus producing current. Part of the energy of the reaction is thus converted into electrical work. Let us take the example of the most common and familiar galvanic cell, known as Daniell cell. It consists of a container divided into two compartments by a porous plug. The function of the porous plug is not to allow the free mixing of the electrolyte solutions in the two compartments but to allow the flow of ions. In one compartment, a strip of zinc metal is immersed in a solution of zinc sulphate whereas, the other compartment holds a solution of copper sulphate with a copper strip immersed in the solution. The two metal strips henceforth called the electrodes, are connected to an ammeter through copper wires as shown in Fig. 17.1. The moment the two electrodes are connected, a current starts flowing as shown by the deflection in the ammeter. As the current flows through the circuit, zinc strip dissolves while copper deposits at the other electrode.

When zinc metal goes into solution as $Zn^{2+}$ ion, it leaves behind an excess of electrons on the zinc electrode; hence this electrode is assigned a negative charge as shown in Fig. 17.1. On the other hand, the electrons from copper electrode are picked up by the copper ions in solution thereby resulting in a positive charge on the cathode.

Metals in their normal mode of existence are assigned an oxidation state of zero.

In a galvanic cell, cathode is assigned a positive sign and the anode, a negative sign. However, in an electrolytic cell, these electrodes acquire charges opposite to the above. However, in both the cases, oxidation takes place at anode and reduction takes place at cathode.

It is commonly said that the current flows from positive electrode to the negative in the circuit; however, the flow of electrons in the connecting wire is from the negative electrode (anode) to the positive electrode (cathode) in the galvanic cell.

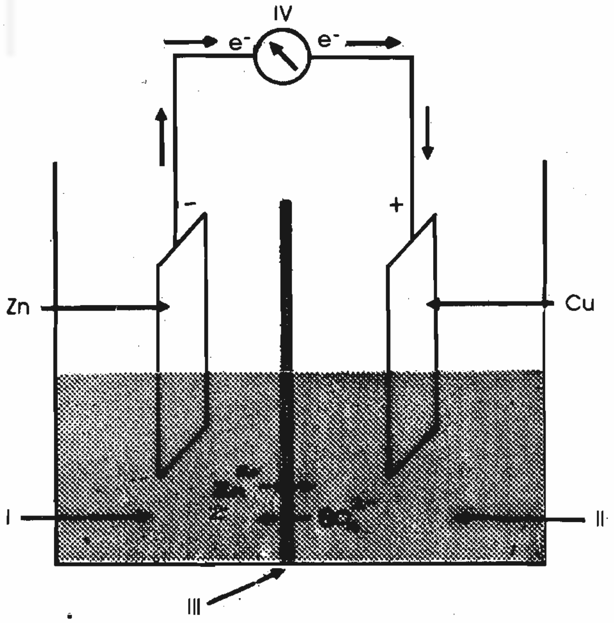


Fig. 17.1 : Daniell Cell :

I) $ZnSO_4$ solution; II) $CuSO_4$ solution; III) porous plug; IV) ammeter

The overall reaction in Daniell cell can be represented as

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$

whereas the reactions taking place in the two compartments known as half-cell reactions can be written as :

$Zn \rightleftharpoons Zn^{2+} + 2e^-$ ...... oxidation
and $Cu^{2+} + 2e^- \rightleftharpoons Cu$ ...... reduction

The capacity to do electrical work by a cell is called the cell potential.

There is always an equilibrium between the atoms in the electrode and the ions present in the solution as represented by the above equations. The electrode at which oxidation takes place is called anode; it is at a lower potential than the cathode at which reduction takes place. Zinc metal dissolves as $Zn^{2+}$ ion leaving behind an excess of electrons at this electrode. Thus anode gets negatively charged and attains relatively lower potential. On the other hand, ions in solution around the cathode withdraw electrons from it causing it to become positively charged and attain relatively higher potential. By convention, we regard the current through the connecting wire to flow from positive to negative, that is from cathode to anode in the present context. However, we should not forget that the flow of electrons in the wire is in the opposite direction, that is, from zinc to copper. However, in an electrolytic cell, the situation will be just the opposite. The anode would acquire a positive charge and the cathode, a negative charge. In order to avoid any confusion, we shall always refer to an electrode, where oxidation takes place, as anode, and the electrode, where reduction takes place, as cathode, irrespective of whether the cell is galvanic or electrolytic.

**SAQ 1**
How do we define anode and cathode? What sign — positive or negative — would you assign to anode and cathode in (a) a galvanic cell (b) an electrolytic cell?

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## 17.3 EXPERIMENTAL MEASUREMENT OF EMF

The capacity to do electrical work by a cell is called the cell potential. It is expressed in volt (V). We could use a voltmeter to measure the cell potential. However, this would not give us the correct value of cell potential. The reason is that the cell potential is dependent upon the concentration of the electrolyte which would change if we allow the current to flow in the circuit through the voltmeter. Hence, we must measure the potential difference between the two half-cells when the cell is held at almost constant composition and no current is flowing.

The potential difference of a cell when no current is drawn out and when the cell is operating reversibly is called the emf (electromotive force) of the cell. The measurement of the emf can be done by using a potentiometer. More recently emf is found with the help of an electronic digital voltmeter which draws negligible current.

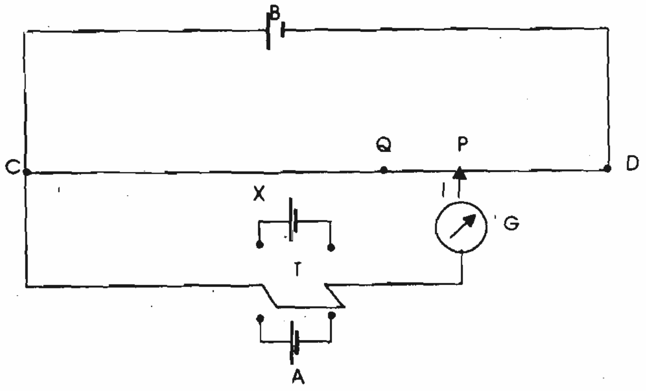

**Fig. 17.2 : Potentiometric measurement of emf of a cell.**

Fig. 17.2 shows a simple set-up to measure the emf of a cell. The potentiometer consists of a wire of uniform cross-section and high resistance. This wire is stretched between two terminals, C and D. It is connected to a storage battery, B. The terminal C is connected to a sliding point I which can be moved from C to D. In between C and D, there is a double throw-switch T and a galvanometer G. The function of the switch is to bring either a standard (weston) cell, A, or the test cell X (for which emf is to be determined) in the circuit. First, we connect A in the circuit and move I to such a position P that there is no deflection in the galvanometer. The exact length of the wire from C to P is recorded. Let us suppose this length is $l_1$. Next by means of the switch T, we remove A but bring cell X in the circuit. The emf of A and X may not be the same, hence on replacement of A by X, the galvanometer will show a deflection. We move the contact point to such a position Q that there is again no deflection in the galvanometer. Measure the length of the wire $l_2$, from C to Q. Under the conditions of no deflection, the drop in potential of the battery B across the slide wire is balanced by the emf of the cell (A or X). Hence, we can write,

$$\frac{\text{emf of X}}{\text{emf of A}} = \frac{\text{Drop in potential from C to Q } (E_2)}{\text{Drop in potential from C to P } (E_1)} = \frac{\text{Resistance due to wire length CQ}}{\text{Resistance due to wire length CP}} = \frac{l_2}{l_1}$$

$$\frac{E_2}{E_1} = \frac{l_2}{l_1}$$

$$\text{In general, } E_2 = E_1 . \frac{l_2}{l_1} \qquad \text{..... (17.1)}$$

where $E_2$ and $E_1$ are the emf values of the test cell and the standard cell, respectively.

We make use of a standard cell in the procedure described above for the standardisation of a potentiometer. We describe here, Weston cadmium cell, which is a commonly used standard cell.

**Weston Cell**

The most commonly used standard cell is called Weston cell. Its voltage remains constant for a long period of time and is reproducible. The change in voltage with temperature is also small. Due to these advantages, Weston cell is widely used as a standard cell. The basic cell reaction can be represented as

$$Cd + Hg_2SO_4 \rightleftharpoons CdSO_4 + 2Hg$$

It is prepared in the form of a H—shaped container as shown in Fig. 17.3

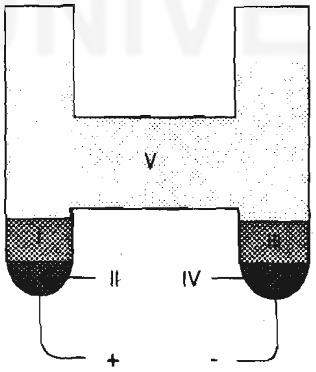

**Fig. 17.3 : Weston cell : I) Paste of Hg and $Hg_2SO_4$ II) Mercury III) $3CdSO_4 . 8H_2O$ crystals IV) Cd (Hg) (V) Saturated $CdSO_4$ solution**

In one arm of the container, mercurous sulphate — mercury paste is in contact with mercury. In the other arm, some crystals of cadmium sulphate are dropped over the surface of cadmium amalgam (12.5%). The container is then filled with a saturated solution of cadmium sulphate. The cell produces an emf of 1.01845 V at 293 K.

## 17.4 STANDARD ELECTRODE POTENTIAL

Consider a strip of zinc metal immersed into an aqueous solution of zinc sulphate at constant temperature and pressure. Both metal and the solution contain zinc ions which can be transferred between the two phases. If some zinc ions from the metal enter into the solution, there would be a net negative charge on the electrode due to the excess of electrons left behind. On the other hand, zinc ions already in solution attract electrons from the electrode and the resulting zinc atoms would stick to the surface of the electrode. This process will leave a positive charge on the electrode. In a short time, however, the rate of escape and of return of zinc ions become equal and an equilibrium is established as expressed by

$$Zn^{2+} + 2e \rightleftharpoons Zn$$

Depending upon whether the equilibrium lies towards left or right, the net charge on the electrode will arise.

Thus we see that there will be a potential difference developed at the junction of the metal and the solution. However, the potential difference between the two phases cannot be readily measured. Therefore, instead of measuring the electrode potentials, we usually measure the total cell potential. The cell potential can be written as the sum of the two electrode potentials neglecting other effects which contribute to the potential difference between the phases. Thus,

$$E_{cell} = E_{cathode} + E_{anode} \qquad \text{..... (17.2)}$$

The total cell potential is a measure of the driving force of a chemical reaction whereas $E_{cathode}$ and $E_{anode}$ are representative of oxidising and reducing capabilities of the concerned reactants, respectively. Hence, in order to obtain a large cell potential, we must use a strong oxidising agent along with a strong reducing agent. Now the question arises as to how do we decide which is a better oxidising agent and which is a better reducing agent. To determine the comparative oxidising or reducing capacity of any substance, we must use some standard against which all other electrode potentials are measured. We shall now explain the necessity of having such a standard.

Let us consider an example, say Daniell cell, the standard cell potential of which is 1.1 V. It just tells us that zinc is a better reducing agent than copper since zinc gets oxidised to $Zn^{2+}$ ion and it reduces $Cu^{2+}$ ions to metallic copper. However, it will not tell us whether a third substance, say, Fe is a better reducing agent than zinc or copper. In order to get some idea regarding the relative oxidising and reducing abilities of different substances, we must measure the cell potentials keeping one half-cell the same in every case. This is necessary since we cannot measure directly the potential of a half-cell. It is like saying that for a reducing agent to give off its electrons, surely you must have an oxidising agent to accept that electron. It cannot function as an oxidising agent on its own without the presence of a reducing agent. Further, for comparing the reducing powers of different substances, we must use the same oxidising agent. The standard against which all other potentials are measured is a hydrogen electrode. We now describe a standard hydrogen electrode.

The chemical reaction taking place at the hydrogen electrode is given by the equation :

$$2H^+ + 2e^- \longrightarrow H_2$$

The electrode potential for the standard hydrogen electrode is arbitrarily assigned a value of zero. Fig. 17.4 shows a standard hydrogen electrode where hydrogen gas is bubbled through a glass hood (*B*) over the surface of Pt electrode (*A*) at a pressure of 1 bar ($\simeq$ 1 atm). The electrode is immersed in an acid in which [ $H_3O^+$ ] = 1 M. The whole set-up is kept at 298 K.

Recent redefinition of the standard state for the pressure of the gas is 1 bar. But 1 bar is not much different from 1 atm. Therefore, we specify the pressure in terms of atm only.

$1 \times 10^5$ Pa = 1 bar = 0.987 atm

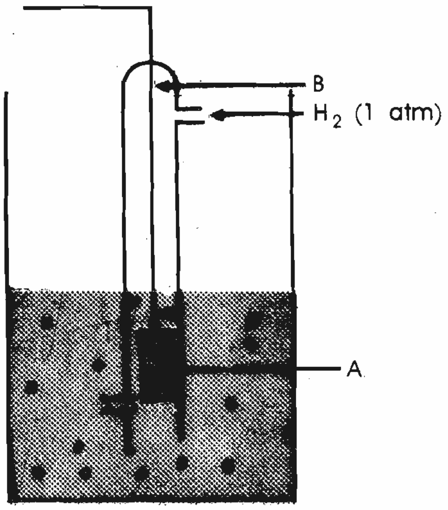

Fig. 17.4 : Standard hydrogen electrode.

In view of the confusion that existed in literature regarding the sign convention in reporting the standard state half-cell potentials ($E°$), IUPAC has set down the following rules in this regard:

1) All electrode reactions are written as reduction reactions.
2) All reactions that produce better reducing agents than hydrogen are given a negative reduction potential value.
3) The most negative reduction potential values are written at the top of the table of standard reduction potentials (Table 17.1).

**Table 17.1 : The Standard Reduction Potentials ($E°$) for Some Half-Cell Reactions**

| Half-cell reactions | $E°$/V |
|---|---|
| $Li^+ + e^- \longrightarrow Li$ | − 3.05 |
| $K^+ + e^- \longrightarrow K$ | − 2.93 |
| $Ca^{2+} + 2e^- \longrightarrow Ca$ | − 2.87 |
| $Mg^{2+} + 2e^- \longrightarrow Mg$ | − 2.36 |
| $Al^{3+} + 3e^- \longrightarrow Al$ | − 1.66 |
| $Zn^{2+} + 2e^- \longrightarrow Zn$ | − 0.76 |
| $Fe^{2+} + 2e^- \longrightarrow Fe$ | − 0.44 |
| $Sn^{2+} + 2e^- \longrightarrow Sn$ | − 0.14 |
| $Pb^{2+} + 2e^- \longrightarrow Pb$ | − 0.13 |
| $Fe^{3+} + 3e^- \longrightarrow Fe$ | − 0.04 |
| $2H^+ + 2e^- \longrightarrow H_2$ | 0.00 |
| $Cu^{2+} + 2e^- \longrightarrow Cu$ | + 0.34 |
| $Cu^+ + e^- \longrightarrow Cu$ | + 0.52 |
| $I_2 + 2e^- \longrightarrow 2I^-$ | + 0.54 |
| $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ | + 0.59 |
| $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ | + 0.77 |
| $Ag^+ + e^- \longrightarrow Ag$ | + 0.80 |
| $Br_2 + 2e^- \longrightarrow 2Br^-$ | + 1.09 |
| $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ | + 1.33 |
| $Cl_2 + 2e^- \longrightarrow 2Cl^-$ | + 1.36 |
| $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ | + 1.49 |
| $F_2 + 2H^+ + 2e^- \longrightarrow 2HF$ | + 3.03 |

Standard reduction potential indicates the willingness of a species to be reduced under standard conditions. Larger the reduction potential, greater is the ease with which a particular species can be reduced; in other words, it is a powerful oxidising agent. This is so because, in an oxidation—reduction reaction, an oxidising agent gets reduced and a reducing agent gets oxidised.

These $E°$ values represent the driving force or spontaneity of the reactions under standard conditions. For example, the reaction,

$F_2 + 2H^+ + 2e^- \longrightarrow 2HF$

has a strong tendency to go in the forward direction since it has a high positive potential value, whereas, the reaction,

$Li^+ + e^- \longrightarrow Li$

has the least tendency to go in the forward direction; rather, it has strong tendency to go in the reverse direction. These observations are in accordance with our basic knowledge of chemistry. Fluorine shows a strong tendency to become fluoride ion; thus, fluorine should act as a powerful oxidising agent. The same reasoning tells us that lithium metal should act as a strong reducing agent. These conclusions are borne out by experimental results. Now that we have a set of values for the standard half-cell potentials, we can use them to calculate the standard cell potential for any cell.

$E°_{anode} = - E°$ and $E°_{cathode} = E°$, where $E°$ is the standard reduction potential as per Table 17.1

There are, however, a few points to be kept in mind before we set out to calculate the standard cell potentials.

- Since the cell potentials are a measure of the tendency of a particular reaction to go in a particular direction, these potentials are cited in volt and not as volt per mole.
- The calculation of the standard cell potential from the standard potentials of the two half-cells will not be affected by the stoichiometric coefficients used to balance the overall reaction.

- You must remember that Table 17.1 gives the standard reduction potentials for some half-cell reactions. But at the anode, a particular species gets oxidised. In order to get the standard potential for the oxidation reaction at the anode, the sign of the standard reduction potential for that reaction must be reversed.
  i.e., $E^\circ_{\text{anode}} = -E^\circ$ as per Table 17.1.

  For example, let us calculate the standard cell potential for the reaction :

  $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$

  for which the half-cell reactions and corresponding potentials are given below :

  $Cu \longrightarrow Cu^{2+} + 2e \qquad E^\circ_{\text{anode}} = -E^\circ_{Cu^{2+}/Cu} = -0.34\ V$
  $Ag^+ + e \longrightarrow Ag \qquad E^\circ_{\text{cathode}} = E^\circ_{Ag^+/Ag} = 0.80\ V$

  we shall not multiply the $Ag^+/Ag$ cell potential by two which is a number used to balance the overall reaction. Secondly, we must keep in mind that in the overall reaction, copper metal is getting oxidised to $Cu^{2+}$ ion. Hence, when we are adding the cathodic and anodic potentials to find the total cell potential, we must reverse the sign of the potential for $Cu^{2+}/Cu$ couple.

An alternative method to arrive at the cell potential value is as follows:

$E^\circ_{\text{cell}} = [\,E^\circ_{\text{reduction}}$ (r.h.s. electrode) $]$
$-\ [\,E^\circ_{\text{reduction}}$ (l.h.s. electrode) $]$
$= [0.080 - (+0.34)]\ V = 0.46\ V$

If the sign of $E^\circ_{\text{cell}}$ is negative, then anode and cathode are interchanged. Note that r.h.s. and l.h.s. stand for right hand side and left hand side, respectively.

  Thus the standard cell potential for the reaction would be

  $$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{anode}} + E^\circ_{\text{cathode}} \\ &= -E^\circ_{Cu^{2+}/Cu} + E^\circ_{Ag^+/Ag} \\ &= [(-0.34) + (0.80)]\ V \\ &= 0.46\ V \end{aligned}$$

  A positive $E^\circ_{\text{cell}}$ value indicates that the reaction is spontaneous under standard conditions.

  But, if any reaction is written in such a way that on calculation, the cell potential has a negative sign, it should be inferred that the reaction is non-spotaneous. For example, under standard conditions,

  $2Fe^{3+} + 2Cl^- \longrightarrow 2Fe^{2+} + Cl_2 \qquad E^\circ_{\text{cell}} = -0.59\ V$

  is not a spontaneous reaction. On the other hand, the following reaction is spontaneous :

  $2Fe^{2+} + Cl_2 \longrightarrow 2Fe^{3+} + 2Cl^- \qquad E^\circ_{\text{cell}} = +0.59\ V$

  And the above is the cell reaction that takes place when a galvanic cell is designed using $Fe^{2+}$, $Fe^{3+}$ and $Cl^-$, $Cl_2$ as reacting species.

**SAQ 2**
Predict which of the following reactions will be spontaneous with the help of standard potential values :

i) $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$
ii) $Cu + 2H^+ \longrightarrow Cu^{2+} + H_2$
iii) $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

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## 17.5 ELECTROCHEMICAL CELL REPRESENTATION AND CELL REACTION

An abbreviated way of representing the Daniell cell is

$Zn \mid Zn^{2+}(c_1) \parallel Cu^{2+}(c_2) \mid Cu$

The anodic reaction is always written on the left and, the cathodic reaction on the right. Also by convention, within the half-cell, the reactants are written before the products. A single vertical line is used to indicate a phase boundary and, a double vertical line represents the elimination of potential at the junction of two electrolyte solutions. Finally, the concentrations of aqueous solutions may be written in parenthesis after the symbol of the ions. The line notation, therefore, corresponds to the direction of the flow of electrons.

In the Daniell cell, when electrons from the anode travel through the wire, it will create an excess of positive charge ($Zn^{2+}$) around the electrode. Simultaneously, excess negative charge ($SO_4^{2-}$) will accumulate around cathode. To maintain electroneutrality in both the cells and the continuous flow of electric current, the negative ions ($Cl^-$ or $NO_3^-$) from the salt bridge would flow into the anode compartment and the positive ions ($K^+$) will move into the cathode compartment. Since the sizes of $K^+$ and $Cl^-$ or $NO_3^-$ ions are almost equal, their speeds will also be equal.

Many a times, instead of separating the two solutions by means of a porous plug, the two separate half-cells are connected by means of a salt-bridge. It consists of a U-tube filled with a saturated solution of a strong electrolyte such as KCl, $NH_4NO_3$ etc. The two ends of the U-tube are plugged by cotton-wool or the whole solution is set in agar-agar gel to prevent the free flow of KCl into the two cells. (see Fig. 17.5).

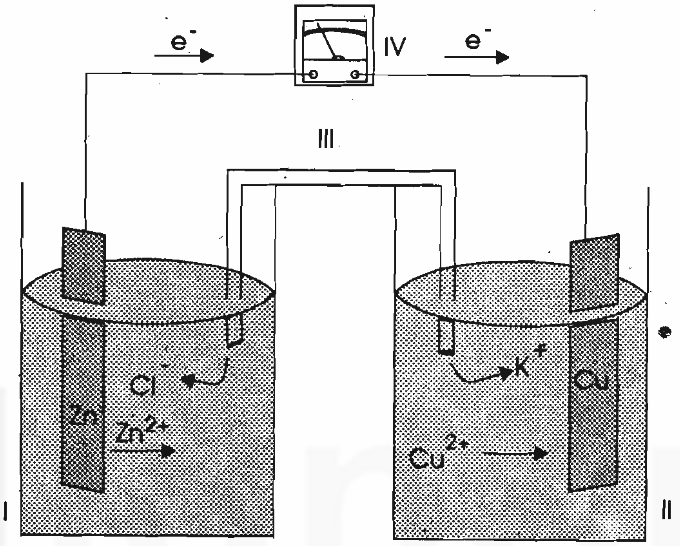

**Fig. 17.5 : Daniell cell with salt bridge:**
**I) anodic compartment**
**II) cathodic compartment**
**III) salt bridge**
**IV) voltmeter.**

When we draw current from the cell, the negatively charged $Cl^-$ ion will flow out from the salt-bridge to neutralise the excess of positive charge due to production of $Zn^{2+}$ ion in the anode compartment. Similarly $K^+$ ion will flow into the other compartment to neutralise the excess of sulphate ions. Thus the electroneutrality of the solution in the two compartments is maintained.

**Cell construction from cell reaction**

Now we shall discuss the steps involved in constructing a cell from a given chemical reaction:

Step (i) : From the given chemical equation, write the balanced ionic equation.

Step (ii) : Separate this ionic equation into two parts, one in which oxidation takes place and, another, in which reduction takes place. Balance each part using electrons. Sometimes $H^+$, $OH^-$ or $H_2O$ also may have to be added to either side of the equation for proper balancing.

Step (iii) : The oxidation part must appear on the left side of the cell. The reduction part must appear on the right side of the cell. Usually electrons and $H_2O$ are not indicated in the representation of the cell. Also stoichiometric numbers must not appear in the representation.

Step (iv) : The electrodes are shown at the extreme left and right positions. These are shown distinctly separated from the corresponding electrolytes by means of single vertical lines. In case of gas electrodes and many redox systems (which we shall study in detail in Sec. 17.8), inert electrodes such as Pt wire or carbon rod are used for electrical contact.

Step (v) : A pair of vertical lines or a dotted line must be used to show the barrier between the left side and right side parts. Two vertical lines indicate the use of a salt bridge and a dotted line shows a porous barrier.

Step (vi) : It is usual to represent the pressure of the gases, the concentration of the electrolytes and the physical state of the electrodes within parenthesis.

**Example 1**

Using the above steps, let us try to construct a cell for the reaction:

$Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$

Let us assume that the concentrations of $Cu(NO_3)_2$ and $AgNO_3$ are $c_1$ and $c_2$, respectively.

**Solution**

Step (i) : The balanced ionic equation is :

$Cu + 2Ag^+ \text{——} Cu^{2+} + 2Ag$

Note that the $NO_3^-$ ions do not appear on both the sides due to cancellation.

Step (ii) : Oxidation : $Cu \longrightarrow Cu^{2+} + 2e^-$

Reduction : $2Ag^+ + 2e^- \longrightarrow 2Ag$

| Step (iii) : | Left side | Right side |
|---|---|---|
| | $Cu, Cu^{2+}$ | $Ag^+, Ag$ |

Step (iv) : $Cu \mid Cu(NO_3)_2\ AgNO_3 \mid Ag$

Step (v) : $Cu \mid Cu(NO_3)_2 \mid\mid AgNO_3 \mid Ag$

We assume that there is a salt bridge between the two parts.

Step (vi) : $Cu(s) \mid Cu(NO_3)_2\,(c_1) \mid\mid AgNO_3\,(c_2) \mid Ag\,(s)$

**Example 2**

As another example, let us construct a cell in which the following reaction takes place:

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

Let us assume that the concentrations of $ZnSO_4$ and $H_2SO_4$ are $c_1$ and $c_2$, and the pressure of hydrogen gas is $p_1$.

**Solution**

Step (i) : The balanced ionic equation is :

$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Note that $SO_4^{2-}$ ions do not appear in this equation.

Step (ii) : Oxidation :

$Zn \longrightarrow Zn^{2+} + 2e^-$

Reduction :

$2H^+ + 2e^- \longrightarrow H_2$

| Step (iii) : | Left side | Right side |
|---|---|---|
| | $Zn, Zn^{2+}$ | $H^+, H_2$ |

Step (iv) : $Zn \mid ZnSO_4 \qquad H_2SO_4 \mid H_2 \mid Pt$

Note that in the right side, Pt is used for electrical contact.

Step (v) : $Zn \mid ZnSO_4 \mid\mid H_2SO_4 \mid H_2 \mid Pt$

Step (vi) : $Zn\,(s) \mid ZnSO_4\,(c_1) \mid\mid H_2SO_4(c_2) \mid H_2\,(g, p_1) \mid Pt\,(s)$

So far we studied the method of arriving at a cell from cell reaction. Now we shall study the steps involved in writing the cell reaction, once the cell is known.

**Steps for writing the cell reaction for a galvanic cell**

i) Write the half-cell reaction corresponding to oxidation taking place at the anode.

ii) Similarly write the half-cell reaction for the reduction taking place at the cathode.

iii) Combine the above two half-cell reactions so that the number of electrons released at the anode is equal to the number of electrons used at the cathode.

Alternatively, the following steps can be used for writing the cell reaction for a galvanic cell.

(i) Write **reduction reactions** at both the electrodes

(ii) Write the equations so that both electrodes use the same number of electrons.

(iii) The overall reaction is the oxidation reaction on the l.h.s. electrode and the reduction reaction on r.h.s. electrode. By subtracting the l.h.s. reduction reaction from the r.h.s. reduction reaction, this is obtained.

**Example 3**

Let us illustrate the above steps using the following example:

Let us consider the cell,

$Al\,(s) \mid Al^{3+}\,(c_1) \mid\mid Cu^{2+}\,(c_2) \mid Cu\,(s)$

**Solution**

Step (i) : **Oxidation at the anode**

$$\mathrm{Al} \longrightarrow \mathrm{Al}^{3+} + 3e^- \qquad \text{..... (1)}$$

Step (ii) : **Reduction at the cathode**

$$\mathrm{Cu}^{2+} + 2e^- \longrightarrow \mathrm{Cu} \qquad \text{..... (2)}$$

Step (iii) : Before combining Eqs. (1) and (2), we have to multiply (1) by 2 and (2) by 3 so that six mole electrons (same number of electrons) are exchanged between the two electrodes.

Hence, (1) X 2 gives,

$$2\mathrm{Al} \longrightarrow 2\mathrm{Al}^{3+} + 6e^- \qquad \text{..... (3)}$$

(2) × 3 gives,

$$3\mathrm{Cu}^{2+} + 6e^- \longrightarrow 3\mathrm{Cu} \qquad \text{..... (4)}$$

Adding (3) and (4), we get

$$2\mathrm{Al} + 3\mathrm{Cu}^{2+} \longrightarrow 2\mathrm{Al}^{3+} + 3\mathrm{Cu} \qquad \text{..... (5)}$$

Using the above steps, Example 3 can be worked out as follows :

Step (i) :

L.h.s. electrode:

$\mathrm{Al}^{3+} + 3e^- \longrightarrow \mathrm{Al}$

R.h.s. electrode:

$\mathrm{Cu}^{2+} + 2e^- \longrightarrow \mathrm{Cu}$

Step (ii) :

For both the electrodes, write the equations involving same number of electrons.

$2\mathrm{Al}^{3+} + 6e^- \longrightarrow 2\mathrm{Al}$

$3\mathrm{Cu}^{2+} + 6e^- \longrightarrow 3\mathrm{Cu}$

Step (iii) :

Cell reaction = (Reduction reaction at the r.h.s. electrode) − (Reduction reaction at the l.h.s. electrode)

$3\mathrm{Cu}^{2+} + 6e^- - 2\mathrm{Al}^{3+} - 6e^- \longrightarrow 3\mathrm{Cu} - 2\mathrm{Al}$

i.e., $2\mathrm{Al} + 3\mathrm{Cu}^{2+} \longrightarrow 2\mathrm{Al}^{3+} + 3\mathrm{Cu}$

Using the principles explained above, answer the following SAQ.

**SAQ 3**

Draw a diagram of a Galvanic cell where the following reaction takes place:

$$2\mathrm{Al} + 3\mathrm{ZnSO_4} \longrightarrow \mathrm{Al_2(SO_4)_3} + 3\mathrm{Zn}$$

Label the electrodes and indicate the flow of electrons in the cell. Assume that the concentrations of $\mathrm{Al_2(SO_4)_3}$ and $\mathrm{ZnSO_4}$ solutions are $c_1$ and $c_2$, respectively.
**(Hint :** You may draw this diagram using Fig. 17.5.)

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## 17.6 NERNST EQUATION

It was discussed in Sec. 9.3 of Unit 9 that the decrease in Gibbs free energy ($-\Delta G$) for any reaction would be equal to the maximum useful work ($-W_{\text{net}}$) that can be obtained from the system at constant temperature and pressure. The only kind of work done in an electrochemical cell is the electrical work which can be calculated from Eq. 17.4

Electrical work done by the system $= -W_{\text{net}}$

= Quantity of electricity × cell potential ..... (17.4)

As mentioned in Table 1.3 of Unit 1;

$$\text{Cell potential} = \frac{\text{Electrical energy or work}}{\text{Quantity of charge}} \qquad \text{..... (17.3)}$$

The quantity of electricity carried by 1 mol of electrons is $1F$. Hence the quantity of electricity carried by $n$ mol of electrons is $nF$. If the cell potential is $E$, then Eq. 17.4 can be written as,

$$\text{Electrical work} = -W_{\text{net}} = nFE \qquad \text{..... (17.5)}$$

$$\text{Hence, } -\Delta G = nFE \qquad \text{..... (17.6)}$$

Under standard state conditions,

$$-\Delta G^\circ = nFE^\circ \qquad \text{..... (17.7)}$$

The standard state conditions have been defined in Unit 9 of Block 2 of this course.

For a general reaction of the type,

$$a\mathrm{A} + b\mathrm{B} + \ldots\ldots \rightleftharpoons c\mathrm{C} + d\mathrm{D} + \ldots\ldots$$

We can adopt Eq. 14.15 of Unit 14 of this block and write.

$$\Delta G = \Delta G^\circ + RT \ln Q \qquad \text{..... (17.8)}$$

$$\text{where } Q = \frac{a_{\mathrm{C}}^{c}\, a_{\mathrm{D}}^{d} \ldots.}{a_{\mathrm{A}}^{a}\, a_{\mathrm{B}}^{b} \ldots.} \qquad \text{..... (17.9)}$$

In Eq. 17.9, $a_{\mathrm{C}}$, $a_{\mathrm{D}}$, . . . etc., refer to the activities of the substances.

Substituting the values of $\Delta G$ and $\Delta G^\circ$ from Eqs. 17.6 and 17.7 in Eq. 17.8, we get

$$-nFE = -nFE^\circ + RT \ln Q \qquad \text{..... (17.10)}$$

Dividing throughout by $-\ nF$,

$$E = E^\circ - \frac{RT}{nF} \ln Q \qquad \text{..... (17.11)}$$

$$\text{or } E = E^\circ - \frac{2.303\ RT}{nF} \log Q \qquad \text{..... (17.12)}$$

At 298 K, the numerical value of $\frac{2.303\ RT}{F}$ is 0.059.

Hence, at 298 K,

$$E = E^\circ - \frac{0.059}{n} \log Q \qquad \text{..... (17.13)}$$

Eqs. 17.12 and 17.13 are known as Nernst Equation in honour of Nernst who in 1889 first derived this equation. If activity coefficients are equal to unity, the activities given in Eq. 17.9 can be replaced by concentrations. Then, Eqs. 17.12 and 17.13 can be written as,

$$E = E^\circ - \frac{2.303\ RT}{nF} \log \frac{[\,\mathrm{C}\,]^c [\,\mathrm{D}\,]^d \ldots}{[\,\mathrm{A}\,]^a [\,\mathrm{B}\,]^b \ldots} \qquad \text{..... (17.14)}$$

$$\text{At 298 K, } E = E^\circ - \frac{0.059}{n} \log \frac{[\,\mathrm{C}\,]^c [\,\mathrm{D}\,]^d \ldots}{[\,\mathrm{A}\,]^a [\,\mathrm{B}\,]^b \ldots} \qquad \text{..... (17.15)}$$

Eqs. 17.14 and 17.15 are better known forms of Nernst Equation. Nernst equation brings out the dependence of emf on the concentrations of the substances taking part in the cell reaction.

## 17.7 APPLICATIONS OF NERNST EQUATION

Let us consider some applications of Nernst equation.

**Equilibrium constant of the cell reaction**

We can calculate the equilibrium constant of a given reaction from the standard emf of the cell. For this purpose, we derive Eq. 17.17.

At equilibrium, $\Delta G = 0$ and hence, Eq. 17.8 becomes, $0 = \Delta G^\circ + RT \ln K$ [ At equilibrium, $Q$ is replaced by $K$ ]

$$\text{or } \Delta G^\circ = -\,RT \ln K \qquad \text{..... (17.16)}$$

Combining Eqs. 17.7 and 17.16,

$$-\,nFE^\circ = -\,RT \ln K$$

$$\left.\begin{aligned} &\text{Hence, } E^\circ = \frac{RT}{nF} \ln K \\ &\text{or } E^\circ = \frac{2.303\ RT}{nF} \log K \end{aligned}\right\} \qquad \text{..... (17.17)}$$

Eq. 17.17 is interesting due to the fact that the equilibrium constant of a reaction is related to standard emf of the cell where the reactants and products are in their standard states. Eq. 17.17 can also be written to the following way :

$K = e^{nE^\circ F/RT}$

Hence from $E^\circ$ value, the equilibrium constant can be calculated.

**Example 4**

Calculate the equilibrium constant at 298 K for the cell reaction taking place in the cell,

$\mathrm{Al}(s)\ |\ \mathrm{Al}^{3+}\,(c_1)\ ||\ \mathrm{Cu}^{2+}\,(c_2)\ |\ \mathrm{Cu}\,(s)$

**Solution**

In Example 3, we have arrived at the cell reaction for this cell.

$2\mathrm{Al} + 3\mathrm{Cu}^{2+} \longrightarrow 2\mathrm{Al}^{3+} + 3\mathrm{Cu}$

Also we have mentioned, that six mole electrons are exchanged between the electrodes; i.e., n = 6.

$E^\circ_{\text{cell}} = E^\circ_{\text{anode}} + E^\circ_{\text{cathode}}$

$= (-\ E^\circ_{\mathrm{Al}^{3+}/\mathrm{Al}}) + E^\circ_{\mathrm{Cu}^{2+}/\mathrm{Cu}}$

$= [\,-\,(-\ 1.66) + 0.34\,]$ V

$= 2.0$ V

At 298 K, Eq. 17.17 becomes, $E^\circ = \dfrac{0.059}{n} \log K$

$$\log K = \frac{12.0}{0.059} = 203.390$$

Hence, $K = 2.5 \times 10^{203}$

**Calculation of $E_{cell}$ from the Concentration of Electrolytes**

Consider the half-cell reaction:

$$M^{n+} + ne \longrightarrow M$$

Applying Nernst equation (Eq. 17.12) to the above reaction,

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]} \qquad \text{..... (17.18)}$$

**Since [ M ] = 1, Eq. 17.18 can be utilised to write the equations for the two half-cell reactions for the Daniell cell shown below :**

**Zn (*s*) | ZnSO₄ (*c*₁) || CuSO₄ (*c*₂) | Cu (*s*)**

$$E_{cell} = E_{anode} + E_{cathode} \qquad \text{..... (17.19)}$$

$$= (-E_{Zn^{2+}/Zn}) + E_{Cu^{2+}/Cu} \qquad \text{..... (17.20)}$$

Note that zinc is oxidised in the anode. But $E_{Zn^{2+}/Zn}$ represents the reduction potential of zinc. Hence,

$E_{anode} = -E_{Zn^{2+}/Zn}$

**Using Eq. 17.18**

$$E_{Zn^{2+}/Zn} = E^{\circ}_{Zn^{2+}/Zn} - \frac{2.303\,RT}{2F} \log \frac{1}{[Zn^{2+}]} \qquad \text{..... (17.21)}$$

$$E_{Cu^{2+}/Cu} = E^{\circ}_{Cu^{2+}/Cu} - \frac{2.303\,RT}{2F} \log \frac{1}{[Cu^{2+}]} \qquad \text{..... (17.22)}$$

**Using Eqs. 17.20, 17.21 and 17.22,**

$$E_{cell} = (E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Zn^{2+}/Zn}) - \frac{2.303\,RT}{2F}\left(\log \frac{1}{[Cu^{2+}]} - \log \frac{1}{[Zn^{2+}]}\right)$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303\,RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad \text{..... (17.23)}$$

**Note that** $E^{\circ}_{cell} = -E^{\circ}_{Zn^{2+}/Zn} + E^{\circ}_{Cu^{2+}/Cu}$ ..... **(17.24)**

**Eq. 17.24 could be used to indicate whether a given cell can function as a galvanic cell when the substances are in their standard states; that is, when the concentrations of the electrolytes are equal to 1 M.**

Eq. 17.23 is useful in predicting whether a given cell can function as a galvanic cell when the concentrations of the substances are not equal to 1 M.

**Example 5**

Calculate the cell potential of a Daniell cell at 298 K when the concentrations of $Zn^{2+}$ and $Cu^{2+}$ are 1.5 M and 0.5 M, respectively.

**Solution**

For Daniell cell, $E^{\circ}_{cell} = 1.1$ V and $n = 2$

Also at 298 K, $\dfrac{2.303\,RT}{2} = 0.059$ V

Hence Eq. 17.23 becomes,

$$E_{cell} = (1.1 - \frac{0.059}{2} \log \frac{1.5}{0.5}) \text{ V}$$

$$= (1.1 - \frac{0.059}{2} \times 0.4771) \text{ V}$$

$E_{cell} = 1.09$ V.

The cell reaction for Daniell cell is as follows:

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$

The substances in the l.h.s. are Zn and $Cu^{2+}$; the substances in the r.h.s. are $Zn^{2+}$ and Cu.

We have derived Eqs. 17.23 and 17.24 for Daniell cell. We can write generalised expressions for any electrochemical cell as follows:

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303\,RT}{nF} \log_{10} \frac{\text{Product of concentrations of substances in the r.h.s. raised to suitable powers}}{\text{Product of concentrations of substances in the l.h.s. raised to suitable powers}} \qquad \text{..... (17.25)}$$

In the above expression, $E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$

$n$ = Number of electrons required to balance the oxidation and the reduction reactions

Substances in the r.h.s. = Substances in the right hand side of the cell reaction.
Substances in the l.h.s. = Substances in the left hand side of the cell reaction.

The term 'suitable powers' refers to stoichiometric coefficients in the cell reaction.

### Thermodynamic Quantities from emf Values

We shall now study how $\Delta H$, $\Delta S$, and $\Delta G$ for the cell reaction can be calculated using modified forms of Nernst equation. Eq. 17.6 gives the relationship between $\Delta G$ and $E$ values. Hence, if $E_{cell}$ value is known, $\Delta G$, for the cell reaction can be calculated.

$$-\Delta G = nFE \qquad \text{..... (17.6)}$$

Similarly, the change in entropy accompanying the cell-reaction can also be determined. In Unit 9, we have derived Eq. 9.42 which relates the temperature coefficient of the free energy change at constant pressure, $\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$, to the decrease in entropy ($-\Delta S$).

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -\Delta S \qquad \text{..... (9.42)}$$

By differentiating $\Delta G$ and $E_{cell}$ appearing in Eq. 17.6 with respect to temperature at constant pressure, we can write

$$-\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = nF\left(\frac{\partial E}{\partial T}\right)_p \qquad \text{..... (17.26)}$$

since $n$ and $F$ are constants.

Using Eqs. 9.42 and 17.26, we get,

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p \qquad \text{..... (17.27)}$$

$$\text{i.e., } \Delta S = nF\left[\frac{(E_2 - E_1)}{(T_2 - T_1)}\right]_p \qquad \text{..... (17.28)}$$

In case $E_2$ and $E_1$ (the emfs of the cell at temperatures $T_2$ and $T_1$) are known, $\Delta S$ can be calculated. $\left(\frac{\partial E}{\partial T}\right)_p$ is known as the temperature coefficient of emf at constant pressure.

Again Eq. 9.15 states,

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

$$\text{or } \Delta H = \Delta G + T\Delta S \qquad \text{..... (17.29)}$$

Using Eqs. 17.6, 17.27 and 17.29,

$$\Delta H = -nFE + TnF\left(\frac{\partial E}{\partial T}\right)_p \qquad \text{.... (17.30)}$$

Hence if $E$, $T$ and $\left(\frac{\partial E}{\partial T}\right)_p$ are known, then the enthalpy change accompanying the cell reaction can be calculated.

In the light of above discussion, answer the following SAQs.

### SAQ 4

Calculate the equilibrium constant at 298 K for the following reaction :

$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$

Use the standard potentials given below:

$Zn^{2+} + 2e \longrightarrow Zn \qquad E^\circ = -0.76\ V$
$[Zn(NH_3)_4]^{2+} + 2e \longrightarrow Zn + 4NH_3 \qquad E^\circ = -1.03\ V$

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**SAQ 5**

Write down the equations relating $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ to $E^\circ$ and $\left(\frac{\partial E^\circ}{\partial T}\right)_p$

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## 17.8 TYPES OF ELECTRODES

A large number of electrodes are known and these can be conveniently divided into several categories depending upon the nature of the half-cell reactions. We shall now look at some of the commonly used electrodes.

**Metal-metal ion electrode :** This is the most common type of electrode where a metal is in equilibrium with a solution containing its ions. The half-cell reaction is represented by

$$M^{n+} + ne \longrightarrow M$$

and the potential is given by Eq. 17.18

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{2.303\,RT}{nF} \log \frac{1}{[M^{n+}]} \qquad \text{..... (17.18)}$$

$Cu^{2+}/Cu$, $Zn^{2+}/Zn$, $Ag^{+}/Ag$, $Pb^{2+}/Pb$ etc. are common examples of metal-metal ion electrodes.

**Gas Electrodes :** Hydrogen electrode (Fig. 17.4) is a typical example of this type of electrode where a gas is in equilibrium with its ions in solution. The gas/electrolyte equilibrium takes place on the surface of an inert metal or any other inert conductor. The commonly used inert electrode materials are platinum and carbon.

The electrode potential for the reaction is given below:

$$2H^+ + 2e^- \longrightarrow H_2$$

$$E = E^\circ - \frac{0.059}{n} \log Q \qquad \text{..... (17.13)}$$

Applying Eq. 17.9 to the reduction of $H^+$ ions,

$$Q = \frac{a_{H_2}}{a^2_{H^+}} \qquad \text{..... (17.31)}$$

In case of a solution, the activity can be replaced by concentration, while for a gas, activity can be substituted by its partial pressure.

Thus, $a_{H^+} = [H^+]$ and $a_{H_2} = p_{H_2}$

Using these in Eq. 17.13, we get at 298 K,

$$E_{H^+/H_2} = E^\circ_{H^+/H_2} - \frac{0.059}{2} \log \frac{p_{H_2}}{[H^+]^2} \qquad \text{..... (17.32)}$$

(since $n = 2$)

i.e., $E_{H^+/H_2} = E^\circ_{H^+/H_2} + 0.059 \log [H^+] - \frac{0.059}{2} \log p_{H_2}$

$$E_{H^+/H_2} = -\,0.059\ \text{pH} - \frac{0.059}{2} \log p_{H_2} \qquad \text{..... (17.33)}$$

[ since $E^\circ_{H^+/H_2} = 0$ and $-\log [H^+] = \text{pH}$ ]

If $p_{H_2} = 1$ atm, then $E_{H^+/H_2} = -\,0.059$ pH ..... (17.34)

Hence pH of the solution will decide the electrode potential of a hydrogen electrode, when hydrogen gas pressure is 1 atm. This principle is made use of in Sec. 17.11 for determining the pH of a solution using hydrogen electrode.

**Amalgam Electrode** : Active metals of Group IA and IIA which react with water can be used in amalgam form. The reaction can be represented as :

$$M^{n+} + ne^- \longrightarrow M(Hg)$$

and the electrode potential is written as

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{0.059}{n} \log \frac{[M(Hg)]}{[M^{n+}]} \qquad \text{..... (17.35)}$$

where [ M(Hg) ] indicates the concentration of the metal M dissolved in Hg.

**Metal-Insoluble Salt Electrode** : The typical examples of such electrodes are calomel electrode and silver-silver chloride electrode. These are represented as :

$Hg/Hg_2Cl_2\,(s)$, KCl (*c*) and
$Ag/AgCl\,(s)$, KCl (*c*)

It can be seen from the above half-cells that a metal (Hg or Ag) is in contact with a saturated solution of its sparingly soluble salt ($Hg_2Cl_2$ or AgCl) and another soluble salt (KCl) having common anion ($Cl^-$).

In this connection we discuss the functioning of saturated calomel electrode. The saturated calomel electrode is often used as a reference electrode in place of hydrogen electrode which is inconvenient and difficult to prepare. As a reference electrode, saturated calomel electrode is reversible and has a fixed potential. It can be represented as

$Hg \mid Hg_2Cl_2(s) \mid$ KCl (saturated)

Fig. 17.6 shows a simple construction of saturated calomel electrode (SCE). It consists of mercury in contact with mercurous chloride (calomel) and chloride ions (from saturated KCl). Mercurous chloride is reduced to mercury, when saturated calomel electrode is used as cathode, according to the equation:

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$$

The half-cell potential for saturated calomel electrode is 0.2682 V.

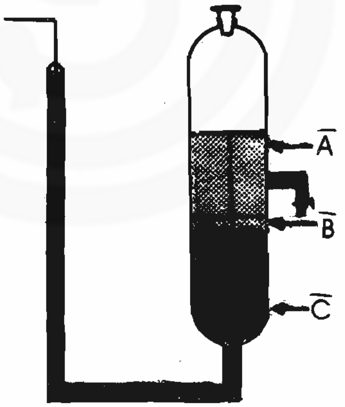

**Fig. 17.6 : Saturated calomel electrode : A) KCl (saturated); B) $Hg_2Cl_2$; C) Hg.**

In the silver-silver chloride electrode, Ag is in equilibrium with Ag ion in solution:

$$Ag^+ + e \rightleftharpoons Ag$$

As the solution is saturated with AgCl, silver ion produced will combine with $Cl^-$ ions to give insoluble AgCl and the electron is transferred to the electrode.

$$AgCl + e^- \longrightarrow Ag + Cl^-$$

The standard half-cell potential is 0.2223 V.

In silver-silver chloride electrode, half-cell reaction can be considered to be one of the following two types. Care must be evinced in choosing proper $E^\circ$ values and expression for $E$ calculation:

i) $Ag^+ + e^- \longrightarrow Ag$
$E^\circ_{Ag^+/Ag} = 0.80$ V and
$E_{Ag^+/Ag} =$

$$\left(0.80 - \frac{2.303\,RT}{F} \log \frac{1}{[Ag^+]}\right) V \qquad \text{..... (17.36)}$$

ii) $AgCl + e^- \longrightarrow Ag + Cl^-$
$E^\circ_{AgCl/Cl^-} = 0.2223$ V and
$E_{AgCl/Cl^-} =$

$$\left(0.2223 - \frac{2.303\,RT}{F} \log [Cl^-]\right) V \qquad \text{..... (17.37)}$$

**Membrane Electrode** : In this type of electrode (Fig. 17.7), a semipermeable membrane (X) separates two solutions containing different concentrations of the salt, MA and is permeable to one of the ions say, $M^+$. This ion will have a tendency to diffuse into a more dilute solution, but the anion, $A^-$, cannot follow and therefore, a difference of potential is set up. This will retard the migration of $M^+$ and after sometime equilibrium will be established. Under these conditions, the standard potential difference is given by

$$E^\circ = \frac{RT}{F} \ln \frac{[M^+]_\alpha}{[M^+]_\beta} \qquad \text{..... (17.38)}$$

**Fig. 17.7 : Membrane electrode.**

where $[\,M^+\,]_\alpha$ and $[\,M^+\,]_\beta$ represent $[\,M^+\,]$ in the two halves of the cell across the membrane. The most useful and common electrode of this kind is a **glass electrode.** This is used for measuring the $H^+$ ion concentration of solutions. Other ion selective electrodes have been developed for measurement of concentrations of $Na^+$, $K^+$ etc.

Glass electrode and quinhydrone electrode (a redox electrode) are discussed in Sec. 17.11.

**Redox Electrodes** : It is usually referred to as a system in which a species exists in solution in two different oxidation states. The electrodes are nonreactive with solution and are just carriers of electrons. A typical example is $Pt/Fe^{3+}, Fe^{2+}$, where platinum electrode is immersed into a solution containing $Fe^{3+}$ and $Fe^{2+}$ ions. The half-cell reaction can be represented by

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

with a potential given by

$$E = E^\circ - \frac{0.059}{1}\log\frac{[\,Fe^{2+}\,]}{[\,Fe^{3+}\,]} \qquad \text{..... (17.39)}$$

**SAQ 6**

The chlorine gas electrode is represented as $Pt(s)\mid Cl_2(p)\mid Cl^-(c)$. Write an expression for its half-cell potential.

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## 17.9 TYPES OF GALVANIC CELLS

As seen in the previous section, there are many kinds of electrodes. All these electrodes may combine in many different ways to give a large number of galvanic cells. Hence, it would be desirable and useful to classify them into two broad groups: (1) chemical cells (2) concentration cells.

### Chemical Cells

Any cell in which the two half-cell reactions use different reactants is called a chemical cell. A typical example is Daniell cell.

Two examples for electrode concentration cells are given below:

i) A cell having amalgams of different concentrations of the same metal as the electrodes.
ii) A cell having hydrogen electrodes, the gas pressures being different.

### Concentration Cells

If the chemical reactions in two half-cells are the same, but the concentrations of the electrolyte solutions or electrode materials are different, then the net reaction is the transfer of species from higher concentration to lower concentration. There is no net chemical reaction in the cell. Such cells are known as concentration cells.

For example, consider a cell consisting of two half-cells at different $Zn^{2+}$ concentrations ($c_1$ and $c_2$).

$$Zn(s)\mid ZnSO_4\,(c_1)\parallel ZnSO_4(c_2)\mid Zn(s)$$

The overall reaction involves the passage of $Zn^{2+}$ from a solution of higher concentration ($c_2$) to that of lower concentration ($c_1$).

**At the anode**

$$Zn \longrightarrow Zn^{2+}\,(c_2) + 2e^-$$

**At the cathode**

$$Zn^{2+}(c_2) + 2e^- \longrightarrow Zn$$

Cell reaction : $Zn^{2+}(c_2) \longrightarrow Zn^{2+}(c_1)$

You must remember that, $E^\circ_{cell}$ for a concentration cell is zero. This can be shown as follows :

$$E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$$

$$= -\,(E^\circ_{Zn^{2+}/Zn}) + (E^\circ_{Zn^{2+}/Zn})$$

Hence, $E^\circ_{cell} = 0$

The emf of the above concentration cell can be calculated using Eq. 17.14.

$$E_{cell} = -\frac{2.303\,RT}{2F}\log\frac{c_1}{c_2} \qquad ..... (17.40)$$

At 298 K, this expression becomes,

$$E_{cell} = \frac{0.059}{2}\log\frac{c_2}{c_1} \qquad ..... (17.41)$$

Although chemical cells and concentration cells can be further classified based on transfer of matter across the two half-cells, we do not discuss these types.

**SAQ 7**

Calculate the emf of the following concentration cell at 298 K :

$Zn(s) \mid ZnSO_4\,(1\,M) \parallel ZnSO_4\,(2\,M) \mid Zn(s)$

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## 17.10 PRACTICAL CELLS

Most of the galvanic cells described above are primary cells. In such cases, where the cell reaction reaches an equilibrium state, there is no further flow of current and the cell ceases to function. It is then called a 'dead' cell. For the purposes of practical applications, the chemical cells are usually sealed into a container. The more common types are zinc-carbon, silver oxide-zinc, zinc-mercury etc. and they are commonly called dry cells.

There are other kinds of cells which are known as secondary cells or storage batteries. These batteries require initial charging from some other energy source to generate a non-equilibrium state of the reactants. When they are in use to produce electricity, they slowly return to equilibrium state. Such batteries can be recharged and the cycle repeated a number of times. Lead storage and nickel-cadmium cells fall under this category of secondary cells.

Finally, there is the third kind of practical cells known as 'fuel cells' which have found applications in space-crafts etc. Let us now study some of these practical cells. Except the fuel cells, others are used by us in every day life and are available in the market.

**Leclanche Cell** : It is also called zinc-carbon dry cell. This type of cell is commonly used in toys, flash lights etc. It contains a zinc cup which acts as an anode and is filled with a moist paste of ammonium chloride, manganese dioxide, zinc chloride in starch and finely divided carbon. A central carbon rod immersed in the paste acts as a cathode. The whole cell is enclosed in either card board or metal which seals it against the atmosphere as shown in Fig. 17.8. The actual reactions which take place in the cell are quite complicated and not completely understood. However, simplified version of the reactions is given below:

**At the anode**

$Zn \longrightarrow Zn^{2+} + 2e^-$

$Zn^{2+} + 4NH_3 \longrightarrow [\,Zn(NH_3)_4\,]^{2+}$

**At the cathode**

$2MnO_2 + 2NH_4^+ + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$

**Fig. 17.8 : Leclanche cell :**
**I) Graphite cathode;**
**II) Zinc cup anode;**
**III) Moist paste of $NH_4Cl$, $MnO_2$, $ZnCl_2$ and carbon**

This cell produces about 1.5 V but drops to about 0.8 V as the reaction proceeds. This drop is because the reaction products cannot diffuse away from the electrolyte. If such a cell is left unused for a short time, the voltage may rise back again to about 1.3 V. The cell appears to be dead, because large excess of $[\,(Zn(NH_3)_4)\,]Cl_2$ formed crystallises out around the anode. The electrolyte becomes unable to conduct electricity effectively. A little warming of the cell may restore the voltage again due to the diffusion of the complex.

**Alkaline Cells :** These are similar to Leclanche cell except that the electrolyte, ammonium chloride, is replaced by potassium or sodium hydroxide. They can withstand under heavy use, have longer shelf-life and deliver more current. Main reasons for the better performance of alkaline cells are: (i) larger effective area since the anode is made porous and (ii) absence of acid atmosphere; due to the acid atmosphere caused by the presence of $NH_4^+$ ions in Leclanche cell, the electrodes in it get corroded easily.

Due to prolonged storage, these cells slowly get discharged even without putting them to any usage. The period for which a particular cell can retain its voltage is called its shelf-life.

The basic reactions that take place in alkaline cells are given below :

**At the anode**

$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^-$

**At the cathode**

$2MnO_2 + 2H_2O + 2e^- \longrightarrow 2MnO(OH) + 2OH^-$

The cell produces approximately 1.5 V.

**Button-Cells** : These are small button like cells which are used in watches, calculators, cameras etc. The main advantage is the small size and stable voltage of about 1.3 to 1.5 V. Some cells use a mixture of $HgO$, $Zn(OH)_2$ and KOH while others use $Ag_2O$, $Zn(OH)_2$ and KOH. In the mercury cell, the cathode is steel, while in the other cell, it is silver oxide (Fig. 17.9). The anode in both the cases is zinc.

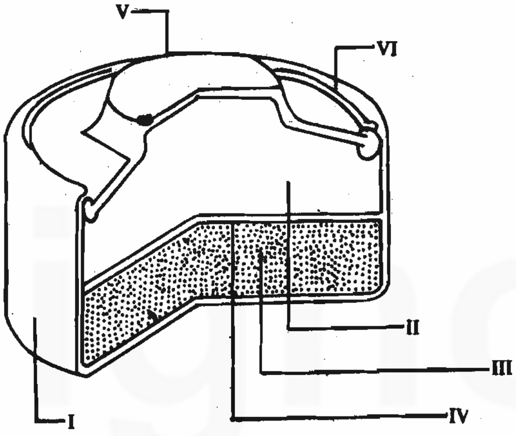

**Fig. 17.9 : Button cell : I) metal cup; II) zinc anode; III) Ag₂O cathode; IV) separator; V) cap over anode; VI) gasket.**

The reactions are given below:

**At the anode**

$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^-$

**At the cathode**

$$\left.\begin{array}{l} Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^- \\ \text{or } HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^- \end{array}\right\}$$

**Emergency Cells :** These batteries are used in life-vests. Initially there is no electrolyte solution present, but when sea water fills in, the reaction starts and lights up a bulb connected to the battery.

For example, for one such battery, the electrode reactions are given below :

**At the anode**

$Mg \longrightarrow Mg^{2+} + 2e^-$

**At the cathode**

$CuCl + e^- \longrightarrow Cu + Cl^-$

**Secondary Cells :** The most common example of this type is the lead storage battery (Fig. 17.10) used in cars etc. It consists of a series of lead plates or preferably lead-antimony alloy plates which are harder than lead plates. These plates are covered with a paste of lead sulphate and are dipped in a solution of dilute $H_2SO_4$ which acts as the electrolyte. They are connected in series, so that the emf of the battery becomes the sum of emfs of all the galvanic cells. The battery is first connected to an outside source of electricity and charged. During charging, reduction takes place on one of the electrodes and $PbSO_4$ is converted into lead and sulphate ions. At the other electrode, oxidation takes place and $PbO_2$ deposits on the plate.

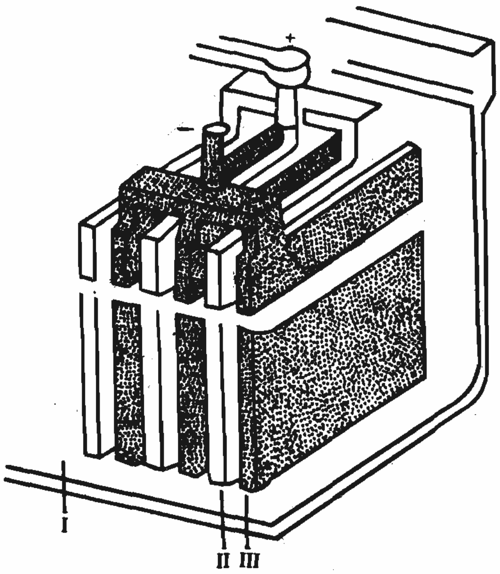

**Fig. 17.10 : One cell of a storage battery showing alternating plates of Pb and $PbO_2$. I) $H_2SO_4$ (electrolyte ); II) $PbO_2$ (cathode); III) Pb (anode).**

During the use or the discharge of the battery, following reactions occur :

**At the anode**

$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

**At the cathode**

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$

The batteries can be charged repeatedly a number of times. If it is left unused for a long time, a slow discharging may take place.

**Fuel Cells :** These cells are ordinary galvanic cells with a difference that reactants are continually supplied from outside and not sealed inside the cell. The reactants are easily available fuels such as hydrogen, methane, oxygen etc. Let us consider one practically useful hydrogen/oxygen fuel cell. The basic reactions at the electrodes are given below :

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ and $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

The overall reaction can be written as, $2H_2 + O_2 \longrightarrow 2H_2O$
with an emf of 1.2 V.

Figure 17.11 shows the basic features of $H_2/O_2$ fuel cell. It consists of two electrodes (usually platinum/carbon) which are porous. Hydrogen and oxygen gases are passed over the

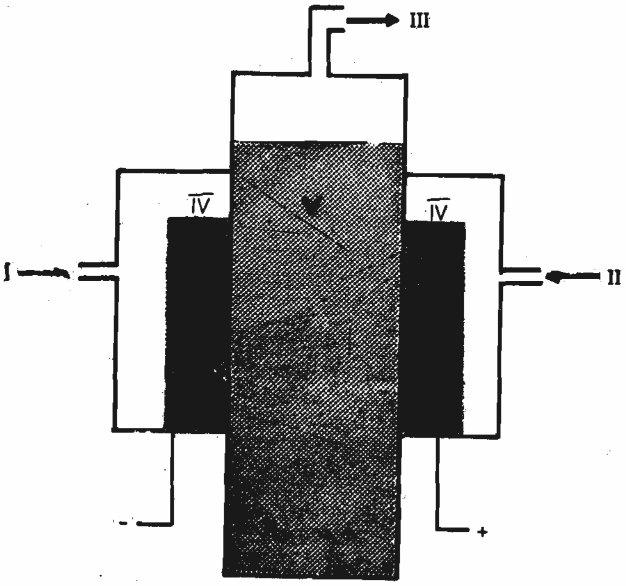

**Fig. 17.11 : Fuel Cell : I) inlet for $H_2$; II) inlet for $O_2$; III) outlet for steam; IV) porous carbon electrodes; V) KOH solution.**

electrodes through which they diffuse into a central compartment. The latter contains KOH at high temperature (473 K) and pressure (30 − 40 atm). The water formed during the reaction evaporates and can be condensed to be used as drinking water. Instead of $H_2$, other anodic materials like $CH_4$, $N_2H_4$ etc., have also been used. It is not advisable to burn $H_2$ and $O_2$ to produce heat which may then be converted into electricity. The reason is that the thermodynamic efficiency of fuel cells is much more than the burning process.

The following SAQ is based on the above information.

**SAQ 8**
**Explain why :**

a) a dry cell comes back to life if left idle for a while.

b) fuel cells are considered better than an electrical power plant using the same fuel.

c) alkaline cells are considered better than Leclanche cell.

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## 17.11 APPLICATIONS OF EMF MEASUREMENTS

The emf measurements on redox reactions can lead to a large amount of useful data. For instance, with the help of emf measurements, we can obtain the overall equilibrium constant of a reaction, solubility product constant for a sparingly soluble salt, pH of a solution, thermodynamic quantities for a reaction or can even perform a redox titration. In each case, we have to devise a suitable cell for the potential measurements. We shall discuss a few common examples to see how it is actually done.

**Determination of Equilibrium Constant**

As we have already studied in Sec. 17.7, if we measure the standard cell potential for a system, we can calculate the equilibrium constant. We know that

$$\log K = \frac{nFE^\circ}{2.303\,RT} = \frac{nE^\circ}{0.059} \text{ (at 298 K)} \qquad \text{..... (17.42)}$$

Note that similar to Ag-AgCl electrode discussed in Sec. 17.8, the half-cell reaction for Pb—$PbSO_4$ electrode can be considered to be one of the following two types :

i) $Pb^2 + 2e^- \longrightarrow Pb$

$E_{Pb^{2+}/Pb} =$

$$E^\circ_{pb^{2+}/pb} - \frac{2.303\,RT}{2F} \log \frac{1}{[Pb^{2+}]} \qquad \text{..... (17.43)}$$

ii) $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$

$E_{PbSO_4/SO_4^{2-}} =$

$$E^\circ_{pbSO_4/SO_4^{2-}} - \frac{2.303\,RT}{2F} \log [SO_4^{2-}] \qquad \text{..... (17.44)}$$

For the present calculation, first type shown above is used as the anode and $Cu^{2+}/Cu$ is used as the cathode.

Hence, $E_{cell} =$

$$E^\circ_{cell} - \frac{0.059}{2} \log_{10} \frac{[Pb^{2+}]}{[Cu^{2+}]} \qquad \text{...... (17.45)}$$

Note that $E^\circ_{cell} = -E^\circ_{pb^{2+}/pb} + E^\circ_{cu^{2+}/cu}$

$= (-(-0.13) + 0.34)$ V
$= 0.47$ V

**Determination of Solubility Product Constant**

Suppose that we want to find the solubility product constant for a sparingly soluble salt, $PbSO_4$. We can set up a cell consisting of $Pb/Pb^{2+}$ as one of the electrodes and $Cu^{2+}/Cu$ as the other. The electrolytes contains $SO_4^{2-}$ ions at 1 M concentration in the two compartments and the concentration of $Cu^{2+}$ ions is also kept at 1 M. The two half-cells are connected through a salt bridge. The cell can be represented as :

$Pb(s) \mid PbSO_4(s) \mid K_2SO_4\ (1\ M) \mid\mid CuSO_4\ (1\ M) \mid Cu(s)$

and the overall reaction can be represented as :

$Pb + Cu^{2+} \longrightarrow Pb^2 + Cu$

In the above cell, since the $Pb^{2+}$ ions are in equilibrium with solid $PbSO_4$, it is a saturated solution. The standard cell potential for the given cell calculated from the standard reduction potentials (Table 17.1) comes out to be 0.47 V. In an experiment, the cell potential for the above cell was found to be 0.70 V. Substituting these values in Eq. 17.45, we get

$$0.70\ V = \left(0.47 - \frac{0.059}{2} \log \frac{[Pb^{2+}]}{(1)}\right) V, \text{ since } [Cu^{2+}] = 1\ M$$

or $[Pb^{2+}] = 1.6 \times 10^{-8}$ M
Since, $K_{sp} = [Pb^{2+}][SO_4^{2-}]$,
$K_{sp}$ for $PbSO_4 = (1.6 \times 10^{-8}) \times 1$ [ since $[SO_4^{2-}] = 1M$ ]
$= 1.6 \times 10^{-8}$

**Potentiometric Titrations :** A large variety of titrations can be performed with the help of emf measurements. Let us consider one such titration where the concentration of an unknown amount of $Fe^{2+}$ ions is to be determined by titrating against a solution of $Ce^{4+}$ ions of known concentration. We shall construct a cell where a known volume of ferrous salt solution is kept in one compartment with an inert Pt electrode and the other half-cell contains calomel electrode as reference. The two are connected as usual by a salt bridge. We keep on measuring the emf. of the cell after each addition of small quantities of $Ce^{4+}$ ions from a burette. At any instant during the titration, we shall have a mixture of $Fe^{2+}/Fe^{3+}$ and emf will be guided by the ratio of the concentrations of $Fe^{2+}$ and $Fe^{3+}$ ions.

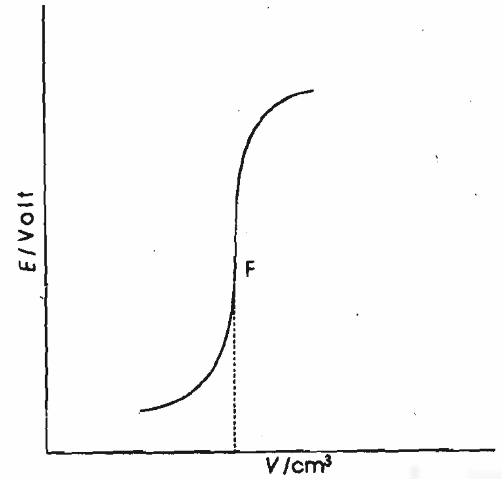

**Fig. 17.12 : A plot of the cell potential ($E$) against the volume ($V$) of $Ce^{4+}$ solution added.**

As more and more of $Ce^{4+}$ is added, more and more $Fe^{3+}$ ion will be produced and lesser will be the concentration of $Fe^{2+}$ ions. The net result will be a gradual increase in the emf till the equivalence point where the greatest change in emf will occur. After the equivalence point, the emf will, however, be governed by the ratio $(Ce^{4+})/(Ce^{3+})$. If we plot a graph of emf ($E$) against volume ($V$) of $Ce^{4+}$ solution, we shall get a curve as shown in Fig. 17.12 from which we can determine the equivalence point (F).

### Determination of pH

While determining pH of a solution, one of the electrodes must be hydrogen electrode or quinhydrone electrode or glass electrode while the other electrode can be calomel or any other electrode.

### Using Hydrogen Electrode

Consider a cell in which a $Cu^{2+}/Cu$ electrode is connected with a $H_2/H^+$ electrode through a salt bridge. The concentration of $Cu^{2+}$ ion is kept at 1 M, the pressure of hydrogen gas at 1 atm and temperature at 298 K.

The cell can be represented as

$Pt(s) \mid H_2(g, 1\ atm) \mid H^+(c) \parallel CuSO_4\ (1\ M) \mid Cu\ (s)$

The overall reaction will be

$Cu^{2+} + H_2 \longrightarrow Cu + 2H^+$

We substitute the given values in Eq. 17.14.

$$E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{2F} \log \frac{[\ H^+\ ]^2}{[\ Cu^{2+}\ ] \cdot p_{H_2}} \qquad \text{..... (17.46)}$$

$$E_{cell} = (0.34 - \frac{0.059}{2} . \log [\ H^+\ ]^2)\ V \quad [\text{ since } [\ Cu^{2+}\ ] = 1\ M \text{ and } p_{H2} = 1\ atm\ ]$$

$$E_{cell} = (0.34 + 0.059\ pH)\ V$$

Thus, by measuring the emf of the cell, we can calculate the hydrogen ion concentration or the pH of the solution.

Generally calomel electrode is used along with hydrogen electrode for determining the pH of a solution.

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{anode} + E^\circ_{cathode} \\ &= - E^\circ_{H^+/H_2} + E^\circ_{Cu^{2+}/Cu} \\ &= - [-(-0) + 0.34]\ V \\ &= 0.34\ V \end{aligned}$$

### Using Quinhydrone Electrode

In Sec. 17.8, we mentioned that an inert metal dipped in a solution containing a mixture of oxidised and reduced forms of a substance constitutes an oxidation-reduction electrode. One such example is 'quinone-hydroquinone electrode', which is commonly-used in analytical chemistry. It is also called quinhydrone electrode. The reaction involves transfer of electrons between the reduced and the oxidised forms as shown by the following equation :

We commonly use the symbol $H_2Q$ for hydroquinone [ $C_6H_4(OH)_2$ ] and Q for quinone [ $C_6H_4O_2$ ].

$$\underset{(Q)}{C_6H_4O_2} + 2H^+ + 2e^- \rightleftharpoons \underset{(H_2Q)}{C_6H_4(OH)_2}$$

Using Eq. 17.14, we can write emf of the electrode as

1 : 1 mixture of quinone and hydroquinone is called quinhydrone.

$$E_{Q/H_2Q} = E^\circ_{Q/H_2Q} - \frac{RT}{2F}\ln\frac{[\,H_2Q\,]}{[\,Q\,][\,H^+\,]^2}$$ (Where $E_{Q/H_2Q}$ is the potential of quinhydrone electrode) ..... (17.47)

At 298 K, $E^\circ = +\,0.6990$; if we take equal amounts of quinone and hydroquinone (i.e., [ Q ] = [ $H_2Q$ ] at 298 K, we can write the above equation as

$$E_{Q/H_2Q} = (0.6990 + \frac{0.059}{2}\log[\,H^+\,]^2)\ \text{V}$$

$$= (0.6990 - 0.059\ \text{pH})\ \text{V} \qquad \text{..... (17.48)}$$

This electrode can be used in conjunction with a saturated calomel electrode to measure the pH of a solution. Let us represent such a cell as follows:

Hg ($l$) | $Hg_2Cl_2$ ($s$) | KCl (saturated) || $H^+$ ($c$) | Q, $H_2Q$ | Pt ($s$)

To measure the pH of a solution, first the emf of the cell ($E_{cell}$) is measured :

$E_{SCE}$ = Potential of the saturated calomel electrode = 0.2682 V

But $E_{cell} = E_{anode} + E_{cathode}$

$$E_{cell} = -\,E_{SCE} + E_{Q/H_2Q}$$

i.e. $E_{cell} = (-\,E_{SCE} + 0.6990 - 0.059\ \text{pH})$ V

$$= (-\,0.2682 + 0.6990 - 0.059\ \text{pH})\ \text{V}$$

$$= (0.4308 - 0.059\ \text{pH})\ \text{V}$$

$$\text{Hence, pH} = \frac{(0.4308 - E_{cell})}{0.059} \qquad \text{..... (17.49)}$$

If $E_{cell}$ is known, pH of the solution can be calculated.

The quinone-hydroquinone electrode is easier to make than a hydrogen electrode and the former attains equilibrium quickly. The main limitation with this electrode is that it cannot be used in alkaline medium.

**Using Glass Electrode**

It has been observed that when a thin membrane of soft glass separates two solutions, a potential is developed across the membrane and the potential depends mainly on the pH of the two solutions. The emf of the electrode is given by

$$E = E^\circ_{glass} - \frac{RT}{nF}\ln[\,H^+\,] \qquad \text{..... (17.50)}$$

It is prepared by dipping an Ag − AgCl electrode in a solution of 0.1 M HCl contained in a thin glass bulb as shown in Fig. 17.13.

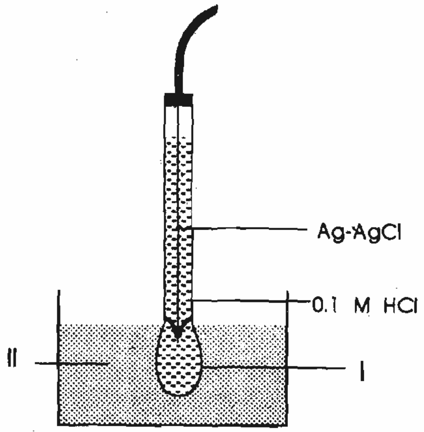

Fig. 17.13 : Glass electrode: I) thin glass membrane; II) $H^+$ ion

Just like quinone-hydroquinone electrode, this is used in conjunction with a saturated calomel electrode and can be represented as

Ag($s$) | AgCl($s$) | HCl (0.1 M) | glass | $H^+$($c$) | | KCl (saturated) | $Hg_2Cl_2$($s$) | Hg($l$)

The pH of the solution can be calculated, once we know the cell potential and the saturated calomel potential as in the case of quinone-hydroquinone electrode. Since we do not know the $E^{\circ}_{glass}$ value, we first find the cell potential for a solution of known hydrogen ion concentration. Then we measure the emf with the solution of unknown pH using the same set-up. The difference in potential between the solutions of known and unknown pH can be written as,

$$E_{known} - E_{unknown} = 2.303\,\frac{RT}{F}\,(pH_{known} - pH_{unknown}) \qquad \text{..... (17.51)}$$

## 17.12 ELECTROLYTIC CELLS

Although we have learnt the laws of electrolysis in Unit 16, we have not studied the electrode reactions in different systems and their practial applications. We shall now discuss some of these points in this section.

When electricity is passed through a fused electrolyte, it causes a change which is otherwise non-spontaneous. As an example, molten sodium chloride on electrolysis leads to the following electrode reactions:

$Na^+ + e^- \longrightarrow Na$

$2Cl^- \longrightarrow Cl_2 + 2e^-$

Thus sodium metal could be collected at the cathode whereas evolution of chlorine gas takes place at the anode. The extent of electrolysis is determined on the basis of Faraday's laws. The situation becomes different if instead of molten sodium chloride, we take an aqueous solution of sodium chloride for electrolysis.

### Electrolysis of Aqueous Sodium Chloride Solution

In this case, the prediction of electrode reaction may not be that easy and straightforward, since there is more than one possibility of electrode reactions. For instance, the following anodic reactions can occur :

$2Cl^- \longrightarrow Cl_2 + 2e^-$

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Similarly, the possible reactions at the cathode are :

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$Na^+ + e^- \longrightarrow Na$

$2H^+ + 2e^- \longrightarrow H_2$

It can be shown on the basis of electrode potentials that the following reactions take place at the two electrodes:

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$2Cl^- \longrightarrow Cl_2 + 2e^-$

As per experimental results also, it is found that $Cl_2$ is evolved at the anode and $H_2$ at the cathode and the overall reaction can be written as :

$2Cl^- + 2H_2O \longrightarrow Cl_2 + H_2 + 2OH^-$

It gives us the information that the oxidation of $Cl^-$ is easier than that of water, whereas water can be reduced much more easily than sodium or hydrogen ions.

**Overvoltage**
In an electrolytic cell, evolution of gases at the electrodes occurs in sufficient amounts only when the applied potential is much higher than the calculated potential for the cell. The difference between the reversible potential and the applied potential is called the overvoltage.

### Electrolysis of Aqueous Sodium Sulphate Solution

In this case, the cathodic reaction is the same as above. The evolution of hydrogen gas takes place. However, at the anode, $SO_4^{2-}$ ions are much more difficult to oxidise than water. Hence, at the anode, evolution of $O_2$ gas takes place. The electrode reactions are :

$4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$ (at the cathode)

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ (at the anode)

and the overall reaction can be written as

$2H_2O \longrightarrow 2H_2 + O_2$

**Corrosion**
The loss of material due to chemical attack is known as corrosion. For example, when a wet surface of iron is exposed to air, rusting or corrosion takes place. Metallic iron gets oxidised and oxygen gets reduced (to $OH^-$ ions).

**Passivity**
In some cases like aluminium metal, aluminium oxide forms a thin surface coating on the metal. Such formation of oxide on the surface stops further reactivity of some metals. In such cases, the metals are said to have become passive.

An experimental observation is that in order to produce appreciable amounts of products, one has to apply much higher cell potential than the calculated value. The additional voltage that must be applied beyond the cell potential is called the overvoltage. It is mainly due to slow attainment of equilibrium at the electrode and depends on the nature and physical state of the electrode, physical state of the substance deposited and number of other factors. We do not intend considering at length some of the irreversible phenomena like overvoltage, corrosion and passivity in this course. Let us now look at some of the applications of electrolysis.

## 17.13 APPLICATIONS OF ELECTROLYSIS

A large number of chemical industries use electrolytic processes to give products in rather pure state. It is used in metallurgy and refining of many metals. Production of many non-metals like halogens etc., as well as a large number of compounds is based on electrolysis. Electroplating is yet another application.

**Metallurgy**
Many a times after performing basic processes of concentrating the ore and roasting it, we end up with the oxides of metal. These have to be reduced to get the metal. In some cases, the reduction of metal oxides is not possible with common reducing agents like carbon etc., which instead of reducing metal oxide to metal, react with carbon to give metal carbides. Active metals like Na, Mg etc., which are usually found in common salt as their ions, are manufactured by electrolysis of molten salt. In the metallurgy of aluminium from bauxite ore, the ore is refined and treated to obtain pure $Al_2O_3$, which is then subjected to electrolysis in molten cryolite to yield aluminium metal.

**Production of Other Chemicals**
Chlorine, which has antibacterial and pesticidal properties and is used in the production of many useful compounds such as polyvinyl chloride etc., is not found free in nature. It is produced electrolytically. Similarly, fluorine is obtained by oxidising fluoride ion electrolytically since the oxidizing power can be increased with the increase in the applied voltage. Production of commercially useful compounds like caustic soda, bleaching powder etc., is also done electrolytically. Many organic compounds are also being synthesised by this process.

**Electroplating**
Electroplating is defined generally as the process of depositing a layer of any metal on an object by electrolysis. The object to be electroplated (either a metal or even plastic) is made the cathode after it is first coated with graphite or some metal (e.g. palladium). Electrolyte is a solution of a salt of the metal to be plated. Usually but not necessarily, the anode is an impure metal to be plated. As an example, consider a solution of copper sulphate in which cathode is a thin strip of pure metal and the anode is a rod of impure copper. As the current is passed and electrolysis progresses, impure copper dissolves and pure copper is deposited on the cathode. Impurities which do not dissolve, such as silver, gold etc., simply fall off to the bottom of the cell. Electroplating besides being decorative, can be very useful in preventing corrosion. Chromium electroplated over steel prevents rusting of iron.

## 17.14 SUMMARY

We began our study with an elementary account of production of electricity with the help of chemical reactions. Then we looked at how the cell potential is measured under standard conditions. We explained the setting up of standard hydrogen electrode, with reference to which, all other potentials are measured. Then we discussed the importance of the table of standard reduction potentials for some selected half-cell reactions. Measurement of cell potential and its relation with the concentrations of the oxidised and the reduced species was developed in the form of Nernst equation. The different applications of Nernst equation were then discussed. Next we briefly looked at different kinds of galvanic cells and some of the commercial cells. We finally discussed some of the applications of emf measurements.

## 17.15 TERMINAL QUESTIONS

1) Explain why copper does not dissolve in hydrochloric acid but dissolves in dilute nitric acid.
**Hints** : Look at the $E^\circ$ values of $Cu^{2+}/Cu$ and $H^+/H_2$. Also $E^\circ_{NO_3^-/NO}$ is 0.96 V; assume that copper dissolves in an acid to form $Cu^{2+}$ ion.

2) With the help of standard reduction potential values, decide
   a) which is a better oxidising agent—$MnO_4^-$ or $Cr_2O_7^{2-}$ and
   b) which is a better reducing agent—$Cl^-$ or $Br^-$?

3) Calculate the cell potential at 298 K for the reaction

   $Al^{3+} + Fe \longrightarrow Al + Fe^{3+}$

   The concentrations of $Al^{3+}$ and $Fe^{3+}$ are 1.2 and 2.5 M.

4) Calculate $E^\circ$ for the cell

   $Zn(s) \mid Zn^{2+}\,(1.0\,M) \parallel H^+\,(1.0\,M) \mid H_2(g, 1\,atm) \mid Pt(s)$

   and then calculate the equilibrium constant for the reaction,

   $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

5) Write an expression for the half-cell potential for the following redox system:

   $Pt(s) \mid Cr_2O_7^{2-}\,(c_1), Cr^{3+}\,(c_2), H^+\,(c_3)$

6) For the following concentration cell, calculate the $H^+$ ion concentration and pH of the solution in the cathodic compartment at 298 K.

   $Pt\,(s) \mid H_2\,(g, 1\,atm) \mid H^+\,(2 \times 10^{-4}\,M) \mid \mid H^+\,(c) \mid H_2\,(g, 1\,atm) \mid Pt\,(s)$

   For this cell, emf is 0.150 V.

7) For Weston cell, emf is 1.018 V at 293 K. Its temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_p$ $= -\,4.00 \times 10^{-5}\,V\,K^{-1}$. Calculate $\Delta G$, $\Delta S$ and $\Delta H$ for the cell reaction of this cell.

## 17.16 ANSWERS

### Self Assessment Questions

1) The electrode, at which oxidation occurs, is called anode, whereas the electrode where reduction takes place, is called cathode.
   a) In galvanic cell, the cathode is given a positive sign and the anode, a negative sign.
   b) In electrolytic cell, the two signs are reversed. The anode is given a positive sign and the cathode is given a negative sign.

2) As explained in Sec. 17.4, if any reaction leads to negative cell potential, that particular reaction will be non-spontaneous. Hence, we have to calculate the cell potentials in each case to know whether a particular reaction is spontaneous or not.

   i) $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$

   $E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$
   $= [-\,(-\,0.44) + 0\,]$ V (since standard potential for $Fe^{2+}/Fe$ is $-$ 0.44 V)
   $= 0.44$ V.

   This reaction is spontaneous.

   ii) $Cu + 2H^+ \longrightarrow Cu^{2+} + H_2$

   $E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$
   $= [-\,(0.34) + 0\,]$ V (since for $Cu^{2+}/Cu$, $E^\circ = +\,0.34$ V)
   $= -\,0.34$ V.

   This reaction is non-spontaneous.

   iii) $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

   $E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$
   $= [-\,(0.54) + 0.77\,]$ V
   $= 0.23$ V. This reaction is spontaneous.

3) Remember in a galvanic cell, the l.h.s. compartment is the one where oxidation takes place, and in the r.h.s. compartment, the reduction takes place. The flow of electrons in the wire is from anode to cathode. The two compartments are separated by a salt bridge. Following these conventions, we can draw the diagram as given in Fig. 17.14.

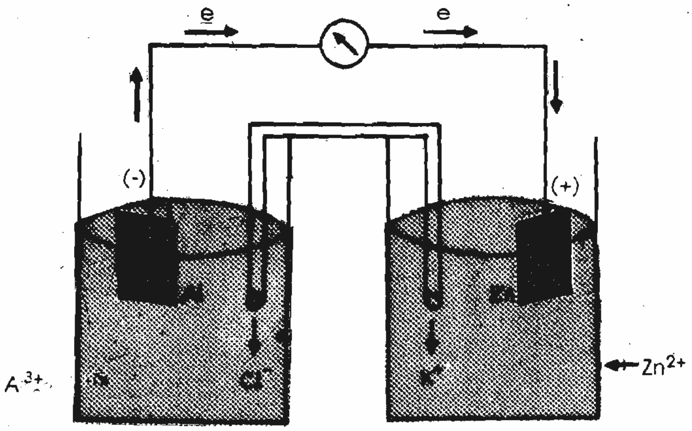

**Fig. 17.14 : Galvanic cell.**

Following the steps given in Sec. 17.5, it is represented as

$Al(s) \mid Al_2(SO_4)_3(c_1) \parallel ZnSO_4(c_2) \mid Zn(s)$

4) From the given values, we can calculate the $E°$ value for the overall reaction as follows :

$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E^\circ_{cathode} = -0.76\ V$

$Zn + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+} + 2e^- \qquad E^\circ_{anode} = -(-1.03)\ V = 1.03\ V$

Combining the two we get,

$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+};\ E^\circ = (1.03 - 0.76)\ V = 0.27\ V$

Note that $n = 2$ for this reaction.

Substituting the values in Eq. 17.42, we get,

$$\log K = n\left(\frac{F}{2.303\ RT}\right)E^\circ$$

$$= 2 \times \frac{1}{0.059\ V} \times 0.27\ V$$

$$= 9.2$$

$$K = 10^{9.2} = 1.6 \times 10^9$$

5) Similar to Eqs. 17.6, 17.28 and 17.30, we can write

$$-\Delta G^\circ = nFE^\circ$$

$$\Delta S^\circ = nF\left[\frac{(E^\circ_2 - E^\circ_1)}{(T_2 - T_1)}\right]_p$$

$$\Delta H^\circ = -nFE^\circ + TnF\left(\frac{\partial E^\circ}{\partial T}\right)_p$$

6) The half-cell reaction is

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$

The half-cell potential can be written as :

$$E_{Cl_2/Cl^-} = E^\circ_{Cl_2/Cl^-} - \frac{0.059}{2}\log\frac{c^2}{p_{Cl_2}}$$

7) Using Eq. 17.41, $E_{cell} = (0.0295 \log 2)\ V$

$= 0.0295 \times 0.3010\ V$

$= 8.88 \times 10^{-3}\ V$

8) a) As the reaction products accumulate near the electrodes, the electrode reactions become slow and may finally stop. After leaving it idle for a while, the products diffuse away and the cell starts functioning again.

b) The fuel cells are considered better since the reactions take place under nearly reversible conditions and the efficiency is higher in producing more useful work.

c) Alkaline dry cell lasts longer because zinc electrode does not corrode easily (due to absence of acidic conditions).

## Terminal Questions

1) The standard reduction potential for

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

is + 0.34 V as compared to standard hydrogen electrode for which potential is 0.0 V. This indicates that copper is a poorer reducing agent than hydrogen. Thus copper would not dissolve in acids unless these contain oxidising anions like $NO_3^-$. Since $E^\circ_{NO_3^-/NO}$ is larger than $E^\circ_{Cu^{2+}/Cu}$, $NO_3^-$ can be reduced by Cu.

2) a) The electrode potentials for the two systems are :

$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V

and $E^\circ_{MnO_4^-/Mn^{2+}} = 1.49$ V

Hence, $MnO_4^-$ is a better oxidising agent than $Cr_2O_7^{2-}$.

b) $E^\circ_{Cl_2/Cl^-} = 1.36$ V and $E^\circ_{Br_2/Br^-} = 1.09$ V

Hence, $Br^-$ is a better reducing agent than $Cl^-$.

3) For the reaction

$$Al^{3+} + Fe \longrightarrow Al + Fe^{3+}$$

We can write.

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Fe^{3+}]}{[Al^{3+}]}$$

$$= -1.62 - \frac{0.059}{3}\log\frac{2.5}{1.2}$$

$$= -1.63 \text{ V}$$

4) $E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$

$= (-(-0.76) + 0)$ V $= 0.76$ V

Using Eq. 17.42, $\log K = \frac{0.76 \times 2}{0.059} = 25.76$

$K = 5.8 \times 10^{25}$

5) The half-cell reaction can be represented by :

$$Cr_2O_7^{2-} + 14\,H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

The half-cell potential is given by

$$E_{Cr_2O_7^{2-}/Cr^{3+}} = E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} - \frac{0.059}{6}\log\frac{c_2^2}{c_1c_3^{14}}$$

6) Following Sec. 17.9, the cell reaction is

$$2H^+\,(c) \longrightarrow 2H^+\,(2 \times 10^{-4}\text{ M})$$

Using Eq. 17.40, $E_{cell} = 0.150 \text{ V} = \left[-\frac{0.059}{2}\log\left(\frac{2\times10^{-4}}{c}\right)^2\right]$ V

$0.150 = 0.059 \log c - 0.059 \log (2 \times 10^{-4})$

$= 0.059 \log c + 0.2182$

$0.059 \log c = -0.0682$

$\log c = -1.16$ and pH $= 1.16$.

$[H^+]$ in the cathode $= c = 6.92 \times 10^{-2}$ M

7) Substituting the given values in Eq. 17.6 we get

$\Delta G = -2 \times 96{,}500 \text{ C} \times 1.018 \text{ V}$

$= -2 \times 96{,}500 \times 1.018$ J

$= -1.964 \times 10^5$ J

Using Eq. 17.28 we get,

$\Delta S = 2 \times 96{,}500 \text{ C} \times (-4.00 \times 10^{-5} \text{ V K}^{-1})$

$= -7.72 \text{ J K}^{-1}$

Also, substitution in Eq. 17.30 gives,

$\Delta H = -2 \times 96{,}500 \text{ C} \times 1.018 \text{ V} + [\,293 \text{ K} \times 2 \times 96{,}500 \text{ C} \times (-4.00 \times 10^{-5} \text{ V K}^{-1})$

$= -1.99 \times 10^5$ J.