

UNIT 5

Conductance-I |

Structure

5.1	Introduction	Concentration Dependence of Molar Conductivity
	Expected Learning Outcomes	
5.2	Electrolytic Conductance	Kohlrausch's Law of Independent Migration of Ions
5.3	Conductivity and Its Measurement	5.6 Summary
	Measurement of Conductivity	5.7 Terminal Questions
5.4	Molar Conductivity	5.8 Answers
5.5	Concentration Dependence of Conductivity and Molar Conductivity	

5.1 INTRODUCTION

You would recall from BCHCT-133 course that while discussing about ionic equilibrium we introduced the concept of electrolytes and non-electrolytes. The electrolytes were defined to be the substances whose aqueous solutions are electrically conducting in nature. The conduction in such systems is called electrolytic conduction and forms the subject matter of this and the next unit. We would begin the unit by explaining the mechanism of electrolytic conduction and contrast it with that of the metallic conduction which you have learnt in your earlier classes. Then, we would introduce the concept of conductivity and outline its significance. In this context, we would differentiate between conductance and conductivity and establish a relationship between them. We would then discuss different factors affecting conductivity of electrolytic solutions. Thereafter, we would describe the principle of measurement of conductance of electrolytic solutions.

This will be followed by an introduction to the concept of molar conductivity and its significance. We would then discuss the concentration dependence of conductivity and molar conductivity of electrolytic solutions. Herein, we would outline the difference between the behaviour of solutions of weak and strong electrolytes and explain the reasons for the same. In this context, we would introduce the concept of limiting molar conductivities and state the Kohlrausch's law of independent migration of ions and discuss its applications.

In the next unit we would take up the concept of ionic mobility, transference numbers and their determination along with various applications of conductivity measurements.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define electrolytic and metallic conduction;
- ❖ describe the mechanism of conduction in metallic and electrolytic conductors;
- ❖ define and differentiate between the terms; conductance and conductivity of a solution of an electrolyte;
- ❖ list and explain the factors affecting conductivity of electrolytic solutions;
- ❖ describe the method of measurement of conductivity of electrolytic solutions;
- ❖ establish a relationship between conductance and conductivity of a solution;
- ❖ define molar conductivity and explain its significance;
- ❖ discuss the concentration dependence of conductivity and molar conductivity;
- ❖ state Kohlrausch's law of independent migration of ions and give its significance; and
- ❖ solve problems based on conductivity, molar conductivity and Kohlrausch's law of independent migration of ions.

5.2 ELECTROLYTIC CONDUCTANCE

In order to learn about electrolytic conduction, let us take up a simple experiment, which you might have learnt, in your earlier classes also. We take a solution of common salt (NaCl) in water and set up the apparatus as given in the Fig. (5.1). What will happen when we press the switch? Yes, the bulb would glow due to the conduction of current by the salt solution.

You have learnt about electrolytes and non-electrolytes in Unit 7 of the BCHCT-133 course. It will be advisable if you could review the same before continuing.

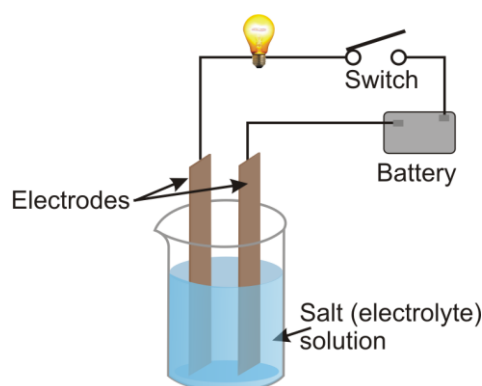


Fig. 5.1: A schematic diagram of experimental set up to demonstrate electrolytic conductance.

Let us learn about the processes involved in this experiment. When we press the switch, the electrons are pushed out of the negative terminal of the battery and these travel to the electrode through the wire. Then, in the solution the current is carried by ions from one electrode to the other; then again, the electrons are carried by the wire to the positive terminal of the battery through the bulb. The passage of electrons (current) through the bulb makes it glow.

A battery provides the electromotive force that pushes electrons out of the negative terminal and pulls electrons into the positive terminal.

You may note that in this simple experiment there are two different mechanisms by which the electrical conduction takes place. These are *metallic conduction* (when the electrons move through the metallic wire) and *electrolytic conduction* (when the current is carried through the solution by ions). In order to understand metallic conduction, we need to recall the electron sea model according to which a metallic solid can be viewed as a fixed array of positively charged metal ions, arranged as a solid lattice. These positively charged ions are surrounded by a sea of mobile electrons, provided by the valence electrons of the atoms, Fig. (5.2 (a)).

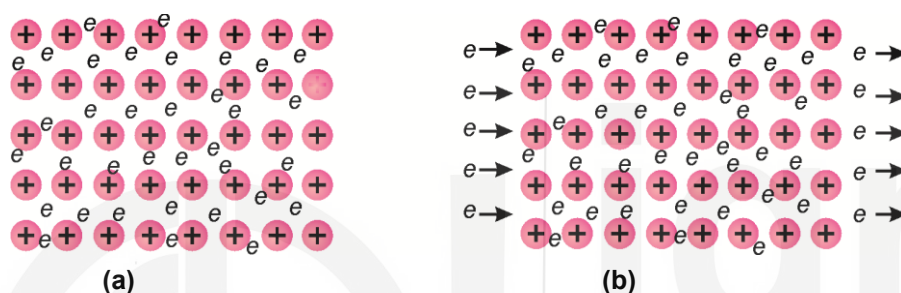


Fig. 5.2: A schematic diagram of a) electron sea model of metal and b) illustration of metallic conduction.

When an electrical field is applied across the metal wire, the electrons move through the lattice of positive ions in response to an applied electric field. A certain number of electrons enter the metal at one end and an equal number of electrons come out of the other end, Fig. (5.2 (b)). In this process of moving through the lattice of positive ions the electrons are scattered away from their straight-line motion due to collisions amongst them as well as with the positive ions. At higher temperature, the electrons move faster, and the positive ions also vibrate more around their mean position. Therefore, the number of collisions between the electrons and ions increase. Consequently, the mobility of the electrons and hence the metallic conductance decreases with an increase in temperature.

On the other hand, in case of aqueous solution of NaCl, the dissolved salt dissociates into Na^+ and Cl^- ions. The Na^+ ions are attracted to the negative electrode, and the Cl^- ions to the positive electrode, Fig (5.3).

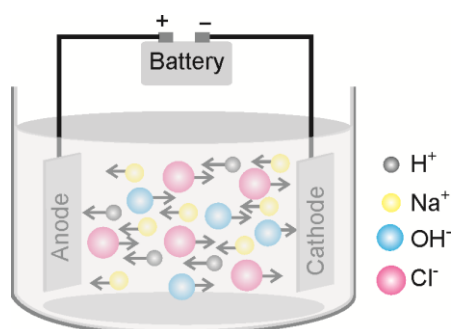


Fig. 5.3: A schematic diagram showing the movement of different ions towards the opposite electrodes in an aqueous solution of NaCl.

In addition, the ions obtained from the autoprotection (autoionisation) of water also move towards opposite electrodes, however as pointed out before, their concentration is too small. The movement of ions generates an electric current equivalent to the flow of electrons along the metal wire.

It is important to note that in case of ionic solutions the passage of current is accompanied by transport of positive and negative ions. In other words, the passage of current involves not only transfer of electricity (charge) from one electrode to the other, but also a transport of matter from one part of the solution to the another. Further, the positive and negative ions have different capacities to carry current i.e., they carry different amounts of current. As a consequence, some kind of a concentration gradient develops in the solution. We will talk more about it later.

When the ions carrying current through the bulk of the solution reach the electrode, they undergo chemical reactions called **electrode reactions**. These reactions are quite characteristic and depend on the nature of the electrolyte and the electrodes. We would take up such reactions in the next unit. For now, we can say that the electrolytic conduction is much more complex than the metallic conduction. Contrary to metallic conduction, the electrolytic conduction increases with increase in temperature. It is due to a greater dissociation of electrolyte and higher mobility of ions at higher temperature.

Having learnt the mechanisms of metallic and electrolytic conduction let us learn about expressing conductivity and its measurement. However, before that answer the following simple question

SAQ 1

Name the species responsible for carrying current in metallic and electrolytic conductors.

5.3 CONDUCTIVITY AND ITS MEASUREMENT

According to Ohm's law, the current flowing through the conductor is directly proportional to the difference in potential and inversely proportional to the resistance.

You would have learnt about Ohm's law in your school physics class. This law relates the quantity of current flowing through a metallic conductor with the potential applied across it and the resistance offered by it. According to this law, the strength of an electric current flowing through a conductor, i.e., the quantity of electricity flowing per second through the conductor equals the ratio of difference in potential applied across the conductor and the resistance offered by the conductor to the flow of current. This law is valid provided the temperature and other physical conditions remain unchanged. Mathematically, we can write

$$I = \frac{V}{R} \quad \dots(5.1)$$

For a uniform conductor the resistance, R (in Ω) is directly proportional to its length, l (m), and inversely proportional to the area of its cross-section, A (m^2). That is, we can write

$$R \propto \frac{l}{A} \Rightarrow R = \rho \frac{l}{A} \quad \dots(5.2)$$

Where, ρ is the constant of proportionality and is called **resistivity** (or specific resistance) of the conductor. If we have a conductor of unit length and a unit area of cross section ($l=1\text{m}$ and $A=1\text{m}^2$) then

$$\rho = R(\Omega) \frac{1\text{m}^2}{1\text{m}} = (\Omega\text{m}) \quad \dots(5.3)$$

This means that the resistivity is the resistance offered by conductor of unit length and unit cross-section area. The SI unit of resistivity is ohm meter (Ωm) though we commonly use ohm centimeter (Ωcm) where the area and the length of the conductor are in cm^2 and cm , respectively.

However, we are interested in conductance of the electrolytic solution. It is important to note that the solutions containing electrolytes also obey Ohm's law like metallic conductors. It is obvious that a solution of electrolyte that offers lesser resistance to the flow of current would allow more current to pass through it i.e., would be a better conductor. Thus, we can say that the conductance would be reciprocal of the resistance. The conductance is denoted as G and has SI unit, seimens, S (or Ω^{-1} or mho (now obsolete)). The measured conductance for a solution of electrolyte depends on the distance (l) between the electrodes and the surface area (A) of each electrode. It is the conductance due to all the ions present between the two electrodes in the solution. We can write,

$$G = \frac{1}{R} = \frac{1}{\rho} \times \frac{A}{l} = \kappa \times \frac{A}{l} \Rightarrow G = \kappa \times \frac{A}{l} \quad \dots(5.4)$$

Rearranging, we get

$$\kappa = G(\text{S}) \frac{l(\text{m})}{A(\text{m}^2)} = \text{Sm}^{-1} \quad \dots(5.5)$$

The reciprocal of resistivity, ρ is called **conductivity** (or specific conductance) and is denoted as kappa, κ . The conductivity is an intrinsic property of the solution and can be visualised as the conductance of the electrolytic solution present in a unit cube, Fig. 5.4 (a). The SI units of conductivity is siemens m^{-1} (Sm^{-1} or $\Omega^{-1}\text{m}^{-1}$) and would be the conductance of the electrolytic solution present in a cube formed by two electrodes having area of 1m^2 each and separated by 1 meter.

However, for practical purposes we use electrodes of area 1cm^2 and the distance between them as 1cm . In such a situation the conductivity would be the conductance of the electrolytic solution present in a cube having a volume of 1cm^3 , Fig. (5.4 (b)), and its units would be seimen cm^{-1} (Scm^{-1} or $\Omega^{-1}\text{cm}^{-1}$).

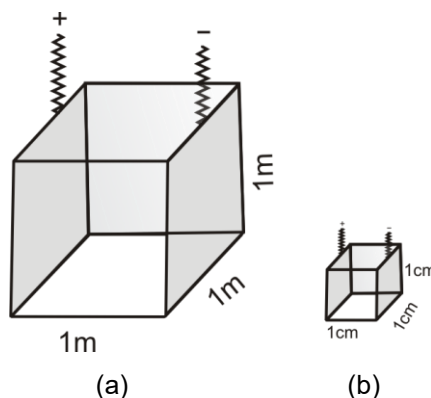
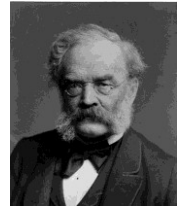


Fig. 5.4: A schematic representation of conductivity a) in SI units b) in commonly used units.

$$R = \rho \frac{l}{A}$$

$$\rho = R \frac{l}{A}$$



(Werner Von Siemens)

The unit of electrical conductance, seimens is named after Werner von Siemens—a German electrical engineer, inventor, and industrialist.

$$\text{Sm}^{-1} = 10^{-2} \text{Scm}^{-1}$$

The SI units of conductivity can be related to common units as

$$\text{Sm}^{-1} = \frac{\text{S}}{\text{m}} = \frac{\text{S}}{100\text{cm}} = 10^{-2} \text{Scm}^{-1} \quad \dots(5.6)$$

In order to understand the physical meaning of conductivity, let's consider a cubic conductor having side = 1cm. Now if we apply a potential of 1V across the conductor, then according to the Ohm's law, the current (in ampere) flowing through the conductor would be $I = \frac{V}{R} = \frac{1}{R}$. Thus, the *conductivity is the amount of current flowing through a conductor having a volume of 1cm³ when a potential of 1V is applied across it.*

You would recall about autoprotection of water from your earlier studies. It is a consequence of amphoteric nature of water. You know that a sample of pure water has $1 \times 10^{-7} \text{M}$ each of hydronium ions and hydroxide ions. These ions impart extremely low conductivity ($\sim 3.5 \times 10^{-5} \text{S m}^{-1}$) to the pure sample of water. Therefore, the pure water is said to be practically non-conducting. However, when we add an electrolyte to water it dissociates or ionises and provides its own ions in the solution, thereby, increasing the number of ions in the solution. As a consequence, the resistance of the solution decreases and the measured current or conductance increases. Thus, we can say that the conductance of a solution is related to the concentration of ions in it.

If a substance can behave as an acid as well as a base, it is said to be **amphoteric** in nature.

In addition to the concentration of the electrolyte, the conductivity of electrolytic solutions also depends on the following factors

- the nature of the electrolyte;
- the dielectric constant of the solvent;
- interionic interactions;
- viscosity of the solvent;
- size of the ions and their solvation; and
- temperature

Let us discuss these factors briefly

The nature of the electrolyte: different electrolytes dissociate / ionise to different extent in solution. As a consequence, for a given molar concentration, the aqueous solution of the strong electrolyte like NaCl will contain more ions than that of a weak electrolyte like acetic acid. As a result, the solutions of strong electrolytes generally have a higher conductivity than those of the weak electrolytes.

The dielectric constant of the solvent: the ionisation of an electrolyte depends on the nature of the solvent. In solvents of low dielectric constant the electrostatic forces between opposite ions is large and the electrolyte is not dissociated completely, thereby, providing fewer ions. Hence the solution shows smaller conductance. On the other hand, a solvent with higher dielectric constant is more ionising and the electrolyte provides more ions and hence higher conductivity. A given electrolyte may be a strong electrolyte in one solvent due to large dissociation but may behave as weak electrolyte in other solvent due to low degree of dissociation.

Interionic interactions: in a solution of an electrolyte there are forces of interaction between the oppositely charged ions of the electrolyte. These are called solute–solute interactions. In dilute solutions, as the constituent ions are far apart, the forces of attraction between them are negligible. As a consequence the ions are free to move and the conductivity is high. On the other hand, in concentrated solutions the forces of interaction are strong. Therefore, the mobility of the ions falls and the conductivity of the solution decreases.

Viscosity of the solvent: the viscosity of the solvent is a measure of solvent–solvent interactions; higher the interaction greater the viscosity. In a solution of the electrolyte, the ions have to move through the solvent and their mobility and hence conductivity would depend on the viscosity of the solvent. If the solvent viscosity is higher the mobility of ions would be low and hence the conductivity would also be low.

Size of ions and their solvation: the speed with which ions move in an electrolytic solution under the influence of applied electric field is inversely proportional to the mass and the size of the ions. A smaller ion would move faster than a larger one, however, we need to be careful here because smaller ions with high charge density may be heavily solvated and as a consequence may have a larger effective size than a large ion that is bigger but is not solvated much.

Temperature: the conductance of a solution generally increases with an increase in temperature. The rise in conductance with temperature is due to the decrease in the viscosity of the solution which leads to an increase in the speed of the ions. Secondly, in case of a weak electrolyte, the extent of ionisation also increases with temperature thus increasing the number of ions and hence higher conductivity.

Having learnt about conductivity and the factors affecting it let us now learn how do we measure conductivity. However, before that answer the following simple question to assess your understanding of conductivity.

SAQ 2

Define conductivity and give the relationship between conductance and conductivity of an electrolytic solution.

5.3.1 Measurement of Conductivity

As discussed above, the conductance is the reciprocal of resistance. Therefore, the conductance and hence the conductivity of an electrolytic solution can be determined by measuring its resistance. You have learnt about measurement of resistance of a wire by using a potentiometer based on Wheatstone bridge, in your school physics class. However, there are two limitations of using this method for measuring the resistance of ionic solutions. First limitation is that if we pass direct current (DC) through the solution, this would cause electrolysis and the composition of the solution would change. In some cases, there may be liberation of gases on the electrodes. This leads to errors in the measurement. Secondly, it is not possible to connect a solution of

unknown resistance to the bridge like a metallic wire. So, the question comes up is that, “how do we measure the resistance and hence the conductance of the given electrolytic solution?”

The first limitation is taken care of by using alternating current (usually a frequency of 500-2000 Hz is supplied) as suggested by Kohlrausch. As a result of the reversal of the direction of the symmetrical current about a thousand times per second, the effects of each pulse of the current is completely neutralised by the next. The second issue is resolved by using a specially designed device called **conductivity cell**. The solution whose conductance is to be determined is taken in the conductivity cell; in fact, the cell is dipped in the solution and the resistance of the solution contained between the two electrodes of the conductivity cell is measured by using Kohlrausch conductance bridge based on the principle of Wheatstone bridge. Let us briefly describe the set up for measuring the resistance (and hence conductance) of an electrolytic solution.

The setup of the apparatus is schematically given in Fig. (5.5). Here R_3 and R_4 are two fixed resistances, R_1 is a variable resistance and fourth arm of the Wheatstone bridge is the conductivity cell whose resistance needs to be measured, this unknown resistance is indicated as R_2 . The a.c. power to the Wheatstone bridge is provided by an oscillator in the audio frequency range. As the frequency of the alternating current is within the range of human ear a set of headphones (or some other electronic device) is used as the detector for the null point (you would recall that in measuring the resistance of a wire using dc, a galvanometer is used for this purpose).

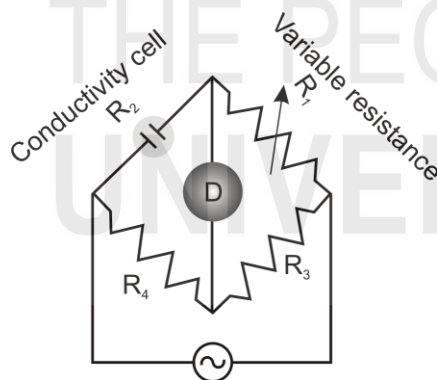


Fig. 5.5: A schematic diagram of the set up used for the measurement of resistance of an electrolytic solution.

The variable resistance is changed to achieve null (balance) state. The passage of the current through the detector (earphones) produces a buzzing sound which decreases as we get closer and closer to the balance stage. It becomes minimum at the balance point. At this stage, the unknown resistance, R_2 is given by the following expression.

$$R_2 = R_1 \frac{R_4}{R_3} \quad \dots(5.7)$$

Conductivity cell

The simplest kind of conductivity cell consists of two platinum electrodes fused in a glass or in an unbreakable epoxy body. In fact, the conductivity cells come

in different shapes and sizes, Fig. (5.6). The platinum electrodes are electrochemically coated with chloroplatinic acid. This imparts a rough finish to the electrode and is called **platinum black**. This rough finish increases the surface area of measurement and improves the response of the electrode. These electrodes are separated by a distance ' l ' and have a surface area equal to ' A '. Thus, in a typical measurement the resistance of the solution confined between these electrodes is measured. For solutions having high conductivity values the conductivity cells with large distance between the electrodes are employed. Some commonly used conductivity cells are shown in Fig. 5.6.

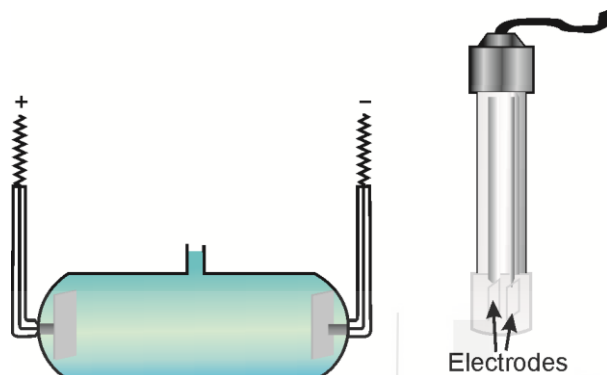


Fig. 5.6: A schematic diagram showing different types of conductivity cells.

From Eq. (5.4) we can find the relationship between conductance and conductivity as

$$\frac{1}{R} = G = \kappa \frac{A}{l} \quad \dots(5.8)$$

On rearranging we get,

$$\kappa = \frac{1}{R} \frac{l}{A} = G \frac{l}{A} \quad \dots(5.9)$$

In a conductivity cell the electrodes have a constant surface area and their position is fixed, i.e., they have a constant distance of separation. Thus, the ratio of distance between the electrodes to the area of the electrode is constant for a conductivity cell. It is called **cell constant** and its SI unit is m^{-1} however practical unit of cell constant is cm^{-1} because the typical surface areas and the distance between the electrodes of conductivity cells is quite small and are expressed in cm^2 and cm respectively. So we can rewrite the Eq. (5.9) as

$$\text{Conductivity} = \frac{1}{\text{resistance}} \times \text{cell constant} = \text{conductance} \times \text{cell constant} \quad (5.10)$$

This implies that to determine conductivity of a solution we need to measure its resistance, take its reciprocal to obtain conductance and then multiply conductance with the cell constant. We have learnt above to measure resistance of a solution so we can easily get the value of conductance. However, for getting conductivity we need the value of cell constant. Now the question comes up is that how do we determine the cell constant?

Determination of cell constant

In a typical laboratory conductivity cell, the surface area of the electrode is of the order of $1\text{--}2 \text{ cm}^2$ and the distance between them is around 1 cm . If these

values are known, we can in principle calculate the cell constant. However, it is not possible to measure these values accurately, so we use an indirect method of determining the cell constant. For this, we take a solution of known conductivity (determined by some other method) and use the given conductivity cell to measure its resistance and hence the conductance. This can then be used to determine the cell constant. Generally standard solutions of KCl with known conductivity values are used for the purpose. Let us understand it with the help of an example.

It is difficult to obtain cell constant from the geometrical dimensions of the cell. It is, therefore, calculated indirectly by measuring the resistance of a standard solution of known conductivity.

Example 5.1: The resistance of a standard solution of 0.1 M KCl at 25°C taken in a conductivity cell was found to be 72 Ω. If the conductivity of 0.1 M KCl solution at 298 K is given to be 0.01290 S cm⁻¹ calculate the cell constant.

Solution: As given above,

$$\text{Conductivity} = \frac{1}{\text{resistance}} \times \text{cell constant}$$

Rearranging, we get

$$\text{cell constant} = \text{conductivity} \times \text{Resistance}$$

Substituting the values

$$\text{Cell constant} = 0.01290 \text{ S cm}^{-1} \times 72 \Omega$$

$$\text{Cell constant} = 0.93 \text{ cm}^{-1} \text{ (You know that } \Omega = \text{S}^{-1}\text{)}$$

Thus, the cell constant = 0.93 cm⁻¹.

Having learnt about the determination of cell constant, let's take another example for the determination of conductivity of an electrolyte.

Example 5.2: The resistance of a conductivity cell containing 0.1M KCl solution was found to be 100 Ω. If the resistance of the same cell when filled with an electrolytic solution is observed to be 220 Ω, calculate the conductivity of the given solution. The conductivity of 0.1 M KCl solution is given as 1.29 S m⁻¹.

Solution: In this problem we are given three data viz., the conductivity and resistance of 0.1 M KCl and the resistance of the given solution. We need to determine the conductivity of the given solution.

Approach: We would first use the data on 0.1 M KCl as in example 5.1 to determine the value of cell constant and then use it to determine the conductivity of the given solution.

Given: Conductivity (0.1 M KCl) = 1.29 Sm⁻¹ = 0.0129 S cm⁻¹

Resistance (0.1 M KCl) = 100 Ω = 100 S⁻¹

From example 5.1, cell constant = conductivity × resistance

Substituting the given values for KCl, we get

$$\text{Cell constant} = 0.01290 \text{ S cm}^{-1} \times 100 \text{ S}^{-1} = 1.29 \text{ cm}^{-1}$$

$$\begin{aligned} 1 \text{ m}^{-1} &= \frac{1}{\text{m}} \\ &= \frac{1}{100 \text{ cm}} \\ &= 0.01 \text{ cm}^{-1} \end{aligned}$$

Now, for the given solution, resistance = $220 \Omega = 220 \text{ S}^{-1}$

From Eq. (5.10), we know

$$\text{conductivity} = \frac{1}{\text{resistance}} \times \text{cell constant}$$

Substituting the value of resistance for the given solution and the value of the cell constant, we get

$$\text{conductivity} = \frac{1}{220 \text{ S}^{-1}} \times 1.29 \text{ cm}^{-1} = 0.00586 \text{ S cm}^{-1}$$

Thus, the conductivity of the given solution would be $0.00586 \text{ S cm}^{-1}$.

Having learnt about conductivity and its measurement let us introduce the concept of molar conductivity. However, before that answer the following simple questions to assess your understanding of measurement of conductivity.

SAQ 3

The resistance of a conductivity cell containing 0.001 M KCl solution measured at 298 K was found to be 1500Ω . If the conductivity of 0.001 M KCl solution at same temperature is $1.46 \times 10^{-4} \text{ S cm}^{-1}$ calculate the cell constant for the conductivity cell used.

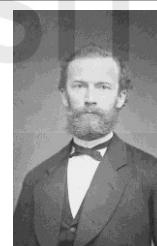
SAQ 4

The resistance of 0.01 M solution of KCl taken in a conductivity cell having two electrodes having an area of 1.8 cm^2 each and at a distance of 0.9 cm was found to be 2800Ω . Calculate the conductivity of 0.01 M solution of KCl.

5.4 MOLAR CONDUCTIVITY

If we wish to compare the conduction behaviour of different electrolytic solutions, we find that conductivity, as discussed above, is not a suitable quantity. This is so because at a given temperature the solutions of different electrolytes in a given solvent may differ in terms of the charge, size and concentration of the ions produced; and mobility of the ions—the ease with which the ions move under the applied potential gradient. Therefore, we need a property that is characteristic of the electrolyte and is independent of the concentration of the solution. In other words, in order to compare the conduction behavior of different electrolytes, we should compare their conductivities in solutions having same concentration in a given solvent at a given temperature. Such a quantity was defined by German physicist Kohlrausch; he introduced the concept of equivalent conductivity, denoted as Λ (lambda) that represented the conductance by all the ions produced by one equivalent of the electrolyte in the solution. This can be visualised as the conductance per equivalent concentration.

However, now a days we use the term called **molar conductivity**. It is denoted by Λ_m and represents the conductance by all the ions produced by one mole of the electrolyte in the given solution. It may be defined as *the conductance of a volume of solution containing the ions obtained from one mole of a dissolved electrolyte when placed between two parallel electrodes*



F. W. Georg
Kohlrausch
(1840-1910)

For uni- univalent electrolytes the equivalent conductivity and molar conductivity values are identical because 1 mole and 1 g equivalent of the electrolyte would be same.

which are at a unit distance and are large enough to contain the whole solution between them.

To visualise molar conductivity, we can imagine two parallel electrodes that are separated by 1 m and are so large that the solution enclosed between them contains all the ions produced by 1 mole of the electrolyte. If the concentration of the solution is 1 mol m^{-3} , the volume of hypothetical molar conductivity cell would be 1 m^3 and the electrodes would have an area of 1 m^2 each. On the other hand, if the concentration is 2 mol m^{-3} , the volume of hypothetical molar conductivity cell would be 0.5 m^3 ; for a concentration 0.1 mol m^{-3} the volume will be 10 m^3 . In general, if the concentration is $c \text{ mol m}^{-3}$, the volume containing all the ions from one mole of the electrolyte would be $\frac{1}{c} \text{ m}^3$. That is, higher the concentration, lower the volume and vice-versa. Therefore, the molar conductivity can be obtained by multiplying the conductivity by a factor $1/c$ or V , the volume of solution containing 1 mol of the electrolyte. Thus, we can mathematically write molar conductivity as conductivity divided by molar concentration of the solution i.e.,

$$\Lambda_m = \frac{\kappa}{c} = \kappa \times V \quad \dots(5.11)$$

Here κ is the conductivity, c is the concentration (in mol m^{-3}) of the electrolyte, V is the volume (in m^3) of solution containing 1 mole of the electrolyte and Λ_m , the molar conductivity of the electrolyte. As the SI unit of conductivity is S m^{-1} , we can derive the SI unit of molar conductivity defined above as

$$\Lambda_m = \frac{\kappa (\text{S m}^{-1})}{c (\text{mol m}^{-3})} = \text{S m}^2 \text{ mol}^{-1} \quad \dots(5.12)$$

However, as you would have realised by now that the conductivity cells used in the laboratory have much smaller dimensions. Also, the concentrations are expressed in mol dm^{-3} . Thus, there is a need to redefine molar conductivity in terms of commonly used units. In such a case, to visualise molar conductivity, we can imagine two parallel electrodes that are separated by a distance of 1 cm and are so large that the solution enclosed between them contains all the ions produced by 1 mole of the electrolyte. If the concentration of the solution is 1 mol dm^{-3} , the volume of hypothetical conductivity cell having 1 mole of the electrolyte would be 1 dm^3 . On the other hand, if the concentration is $c \text{ mol dm}^{-3}$ the volume containing all the ions from one mole of the electrolyte would be $\frac{1}{c} \text{ dm}^3$. A schematic representation of the relationship between conductivity and molar conductivity is given in Fig. (5.7). Here the volume of the solution contained between two large plates (electrodes) is 1 dm^3 .

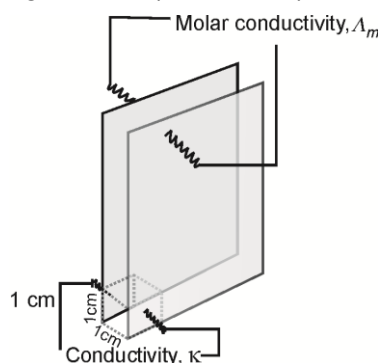


Fig. 5.7: A schematic representation of the relationship between molar conductivity and conductivity.

The molar conductivity once again would be defined by Eq. (5.11), but its expression would get modified and the units will also be different as shown below.

$$\Lambda_m = \frac{\kappa (\text{S cm}^{-1})}{c (\text{mol dm}^{-3})} = \frac{\kappa (\text{S cm}^{-1}) 1000 \text{ cm}^3 \text{ dm}^{-3}}{c (\text{mol dm}^{-3})} = \frac{1000 \kappa}{c} \text{ S cm}^2 \text{ mol}^{-1} \quad \dots(5.13)$$

$$\Lambda_m = \frac{1000 \kappa}{c} \text{ S cm}^2 \text{ mol}^{-1} \quad \dots(5.14)$$

Remember, the concentration in this expression is in mol dm^{-3} . Let us take up an example to learn about the importance of expression given in Eq. (5.14)

Example 5.3: The conductivity of a 0.1 M aqueous solution of acetic acid is found to be $5.3 \times 10^{-4} \text{ S cm}^{-1}$. Calculate the molar conductivity of acetic acid at the given concentration.

Solution: We know from Eq. (5.14) that the molar conductivity of a c molar solution is given by the following expression in which κ is the conductivity of the solution in S cm^{-1} .

$$\Lambda_m = \kappa \frac{1000}{c}$$

We are given, $\kappa = 5.3 \times 10^{-4} \text{ S cm}^{-1}$ and $c = 0.1 \text{ M} = 0.1 \text{ mol dm}^{-3}$

Substituting the values, we get

$$\Lambda_m = 5.3 \times 10^{-4} \times \frac{1000}{0.1} = 5.3 \text{ S cm}^2 \text{ mol}^{-1}$$

Thus, the molar conductivity of acetic acid solution would be $5.3 \text{ S cm}^2 \text{ mol}^{-1}$

Let us take one more example

Example 5.4: In a conductivity cell, the two platinum electrodes, each having an area of 3 cm^2 are 1.5 cm apart. The resistance of a 0.05 M solution of a salt is found to be 50Ω . Calculate the molar conductivity of the solution.

Solution: Here, we need to find molar conductivity, which we know is given by the following expression (where concentration is in mol dm^{-3} and κ in S cm^{-1})

$$\Lambda_m = \frac{1000 \kappa}{c} \text{ S cm}^2 \text{ mol}^{-1}$$

We know the concentration, so we need to find the conductivity which according to Eq.(5.9) is given as

$$\kappa = \frac{1}{R} \frac{\ell}{A}$$

Substituting the values, we get

$$\kappa = \frac{1}{50 \text{ S}^{-1}} \frac{1.5 \text{ cm}}{3.0 \text{ cm}^2} = 0.01 \text{ S cm}^{-1}$$

Substituting the value of conductivity and concentration in the expression for molar conductivity we get,

You may note that while using the eq. 5.14, we take κ in terms of S cm^{-1} and c in mol dm^{-3} (or molar concentration), the resulting molar conductivity is obtained in the units of $\text{S cm}^2 \text{ mol}^{-1}$

$$\Lambda_m = \frac{1000 \times 0.01}{0.05} = 200 \text{ S cm}^2 \text{ mol}^{-1}$$

Alternatively, we could first find cell constant, then conductivity and finally molar conductivity. Thus, the molar conductivity of the given solution would be $200 \text{ S cm}^2 \text{ mol}^{-1}$

Having learnt about the concept of molar conductivity, its physical significance and relationship with conductivity and concentration we need to talk about conductivity water, the water used in preparing solutions for conductivity determinations. However, before that answer the following simple questions to assess your learning.

SAQ 5

The resistance of $6.25 \times 10^{-2} \text{ M}$ solution of chloroacetic acid when measured using a conductivity cell of cell constant 0.6 cm^{-1} was found to be 180Ω . Calculate molar conductivity of chloroacetic acid at this concentration

SAQ 6

The resistance of 0.02 M KCl solution at 298 K was found to be 250Ω . If the conductivity of 0.02 M KCl is $0.277 \Omega \text{ m}^{-1}$, calculate the distance between the electrodes of the conductivity cell if they had a surface area of 2 cm^2 each.

Conductivity water

As you know, the conductivity of an electrolytic solution depends on all the ions present in the solution irrespective of their source. In a measurement of conductivity of a given solution of a particular electrolyte, the trace amount of impurity present in the water used for preparing the solution would affect the measured conductance. It is, therefore, important that the water used for preparing the solution is free from all types of ions as far as possible. Such water can be obtained by repeated distillation of water and is called **conductivity water**. The conductivity of such water is about $10^{-7} \text{ S cm}^{-1}$. In precise measurements of conductivity, the conductance of the water used for preparing the solution is measured separately and is subtracted from the observed conductance of the solution. Let us take up an example to understand it.

Example 5.5: A conductivity cell having a cell constant of 0.3 cm^{-1} when filled with 0.01 M solution of acetic acid gave a resistance of 1982Ω . The water used for preparing the solution had a conductivity of $7.0 \times 10^{-6} \text{ S cm}^{-1}$. Calculate the molar conductivity of 0.01 M acetic acid solution.

Solution: From Eq. (5.10), we know that

$$\text{conductivity} = \frac{1}{\text{resistance}} \times \text{cell constant}$$

We are given, resistance = 1982Ω = 1982 S^{-1} and cell constant = 0.3 cm^{-1}

Substituting the values, we get

Conductivity of 0.01 M acetic acid

$$= \frac{1}{1982 \text{ S}^{-1}} \times 0.3 \text{ cm}^{-1} = 1.51 \times 10^{-4} \text{ S cm}^{-1}$$

This conductivity is due to the ions obtained from acetic acid as well as contributed by water used for preparing the solution. So, we need to subtract the contribution from water.

The conductivity due to acetic acid alone

$$= (1.51 \times 10^{-4} - 7.0 \times 10^{-6}) \text{ S cm}^{-1} = 1.44 \times 10^{-4} \text{ S cm}^{-1}$$

$$\text{Now we know that molar conductivity} = \Lambda_m = \frac{1000 \kappa}{c} \text{ S cm}^2 \text{ mol}^{-1}$$

Substituting the values of conductivity and concentration, we get

$$= \Lambda_m = \frac{1000 \times 1.44 \times 10^{-4}}{0.01} = 1.44 \text{ S cm}^2 \text{ mol}^{-1}$$

Thus, the molar conductivity of 0.01 M solution of acetic acid is calculated to be $14.4 \text{ S cm}^2 \text{ mol}^{-1}$

Having learnt about conductance, conductivity, molar conductivity, and their interrelationships along with their determination let us now take up the concentration dependence of conductivity and molar conductivity.

5.5 CONCENTRATION DEPENDENCE OF CONDUCTIVITY AND MOLAR CONDUCTIVITY

Conductivity and molar conductivity of a solution, both vary with change in the concentration of the solution. You would recall from above that the conductivity refers to the conductance due to all the ions contained in a unit volume of the solution. As on decreasing the concentration of the solution the number of ions in the unit volume of the solution would decrease therefore the conductivity of an electrolytic solution would decrease with decrease in the concentration. This decrease in conductivity is observed both for weak as well as strong electrolytes however, the nature of change is different in the two cases. A schematic diagram showing the concentration dependence of conductivity of a weak and a strong electrolyte is given in Fig. (5.8)

The conductivity of an electrolytic solution at any given concentration is the conductance of unit volume of solution kept between two electrodes with unit area of cross section and at a distance of unit length.

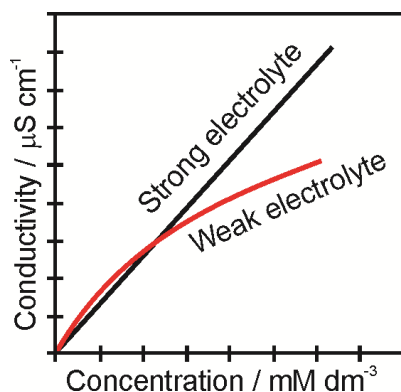


Fig. 5.8: A schematic diagram showing the concentration dependence of conductivity for a strong and a weak electrolyte.

The strong electrolytes by definition are completely ionised practically at all concentrations. So, a decrease in concentration simply decreases the number of ions and hence the decrease in conductivity. On the other hand, in case of

weak electrolytes at moderate concentrations the extent of ionisation is quite small. You would recall from the course BCHCT-133 that according to Ostwald's dilution law, the degree of ionisation of a weak electrolyte increases on dilution. Thus, in case of weak electrolytes there are two factors which are operative. First, the decrease in concentration decreases the number of ions in the unit volume (as in case of strong electrolytes) and second with dilution the degree of ionisation increases thereby increasing the number of ions in the unit volume. One of these factors decreases the number of ions in the unit volume while the other one increases them. However, the decrease in concentration of ions due to decrease in concentration is much more than the increase in concentration of ions due to increase in ionisation. Therefore, the conductivity of the solution of a weak electrolyte decreases on dilution. However, the decrease in conductivity of weak electrolyte is gradual whereas that for a strong electrolyte is sharp as shown in the Fig. (5.8).

5.5.1 Concentration Dependence of Molar Conductivity

You would recall from above that the molar conductivity represents the conductance by all the ions produced by one mole of the electrolyte in a given solution. It is defined as the conductance of a volume of solution containing the ions obtained from one mole of a dissolved electrolyte when placed between two parallel electrodes which are at a unit distance and are large enough to contain the whole solution between them. Also, from Eq. (5.11) we can note that molar conductivity is a product of two terms viz., the conductivity, κ and the volume, V of solution containing 1 mole of the electrolyte.

$$\Lambda_m = \kappa \times V \quad \dots(5.11)$$

This implies that we need to consider the effect of change in concentration on both the parameters. We have seen above that $V=1/c$ which means that the volume containing 1 mole of the electrolyte increases with decrease in the concentration. We have also learnt that the conductivity of solution decreases with decrease in concentration for the strong as well as weak electrolytes. So, the two factors viz., conductivity and volume work in opposite direction to change the molar conductivity; volume tends to increase it with decrease in concentration and the conductivity tends to decrease it. However, the volume factor is much stronger, and it can more than compensate the decrease due to decrease in conductivity. Therefore, *the molar conductivity of the strong as well as weak electrolytes increase on dilution*. However, the changes are different in the two cases let us learn about them.

Strong electrolytes

The molar conductivity depends on the concentrations of ions and the speed with which the ions move. As stated above, the degree of ionisation of strong electrolytes is one (100 %) even at moderate concentrations. So, on dilution, there is no significant increase in the number of ions. However, at moderate and high concentrations the inter-ionic interactions are quite strong and therefore the mobility of the ions is slow and hence the conductivity is low. On diluting the solution, these inter-ionic attractions decrease, and the ions are relatively free to move and their mobility and hence the conductivity increases.

In moderate or high concentration of solutions, the increase in molar conductivity with dilution is gradual and in the region of low concentration the molar conductivity increases linearly. At extremely low concentrations ($c \rightarrow 0$) (when the ions are effectively infinitely far apart and do not interact with one another) the molar conductivity becomes maximum. This is called the limiting molar conductivity or molar conductivity at infinite dilution and is denoted as Λ^0 . The variation of molar conductivity with concentration can be given by the following equation.

$$\Lambda = \Lambda^0 - A\sqrt{c} \quad \dots(5.15)$$

Thus, if we plot Λ against square root of concentration ($\sqrt{c}$) for dilute solutions we would get a straight line having a negative slope ($-A$) and an intercept equal to Λ^0 . A schematic diagram showing the variation in the molar conductivity with concentration for some electrolytes is given in Fig. (5.9).

It is observed that the slope of the line (value of A) depends on the type (stoichiometry) of the electrolyte for a given solvent and temperature. The types of strong electrolytes can be understood based on the number of cations and anions produced on their dissociation in the solution. For example, NaCl and KCl are 1:1 electrolyte, whereas CaCl_2 and BaCl_2 are the examples of 2:1 electrolytes. It is important to note that all electrolytes of a given type have the similar value for ' A '.

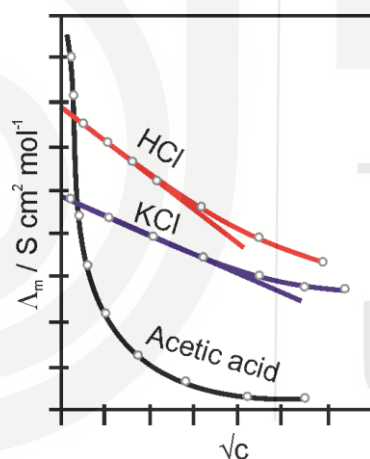


Fig. 5.9: A schematic diagram showing variation in the molar conductivity with $\sqrt{c}$ for some strong and weak electrolytes.

Weak electrolytes

At moderate or high concentrations weak electrolytes have low degree of ionisation and therefore, the number of ions and hence the molar conductivity is low. As the number of ions is small the interionic interactions between the oppositely charged ions are not as significant as those in case of strong electrolytes. Therefore, when a solution of a weak electrolyte like acetic acid is diluted, the degree of ionisation increases as per the Ostwald's law. This leads to an increase in the number of ions in the volume of solution containing 1 mol of the electrolyte leading to an increase in molar conductivity. As there is a significant increase in the degree of ionisation of the weak electrolyte on dilution, the molar conductivity increases sharply.

The increase is quite steep in the region of extremely low concentrations. The limiting molar conductivity in case of weak electrolytes is achieved at

The increase in the molar conductivity on dilution in case of weak electrolytes is due to the increase in the number of ions due to increase in the degree of ionization of the electrolyte, whereas in the case of strong electrolytes, it is due to the weakening of the interionic interactions.

extremely low concentrations where the degree of ionisation becomes 100 %. However, at such a low concentration the conductivity of the solution is so low that it cannot be measured accurately. Also, the molar conductivity versus concentration graph for weak electrolytes does not allow extrapolation to zero concentration. Therefore, in such cases the molar conductivity at infinite dilution is obtained by using Kohlrausch law of independent migration of ions discussed below.

5.5.2 Kohlrausch's Law of Independent Migration of Ions

On the basis of extensive studies of the equivalent conductivity of various strong and weak electrolytes at extremely low concentrations ($c \rightarrow 0$) Kohlrausch observed that the equivalent conductivities at infinite dilution for pairs of electrolytes having a common ion differed by a constant value. As mentioned above, now a days we use molar conductivity in place of equivalent conductivity so the data is given in terms of molar conductivities. For example,

As the data is for 1:1 electrolytes; there will not be any difference between the values of molar conductivities and equivalent conductivities

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{LiCl}) = 34.9 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^0(\text{KNO}_3) - \Lambda_m^0(\text{LiNO}_3) = 34.9 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{KNO}_3) = 4.9 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^0(\text{LiCl}) - \Lambda_m^0(\text{KNO}_3) = 4.9 \text{ S cm}^2 \text{ mol}^{-1}$$

Based on such observations, Kohlrausch proposed that at infinite dilution, where all electrolytes (strong or weak) are completely ionised and the interionic effects do not exist, each ion migrates independently of its co-ion. This is the **Kohlrausch's law** of independent migration of ions.

At infinite dilution, these ions contribute a definite share to the total molar conductivity of the electrolyte. The share depends the nature of the ion and is independent of the counterion in the electrolyte. Under such conditions, the molar conductivity of an electrolyte at infinite dilution can be represented as the sum of molar conductivities of individual ions at infinite dilution. That is for a uni-uni (1:1) electrolyte AB, we can write,

$$\Lambda_m^0(\text{AB}) = \lambda_m^0(\text{A}^+) + \lambda_m^0(\text{B}^-) \quad \dots(5.16)$$

Where $\lambda_m^0(\text{A}^+)$ and $\lambda_m^0(\text{B}^-)$ are the limiting molar conductivities of the A^+ and B^- ions. For other than uni-univalent electrolytes, the molar conductivity can be given by the following expression

$$\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0 \quad \dots(5.17)$$

Where, ν_+ and ν_- are the number of cations and anions generated by the dissociation / ionisation of the electrolyte and λ_+^0 and λ_-^0 are the limiting molar conductivities of the cation and anion respectively. The limiting molar conductivities of some common ions are given in Table 5.1.

Table 5.1: The limiting molar conductivities of some common ions at 298 K

Ion	$\lambda^0 / \text{S cm}^2 \text{mol}^{-1}$	Ion	$\lambda^0 / \text{S cm}^2 \text{mol}^{-1}$
H^+	349.6	OH^-	199.1
Li^+	38.7	F^-	55.4
Na^+	50.1	Cl^-	76.3
K^+	73.5	Br^-	78.1
Ag^+	61.9	CH_3COO^-	40.9
Mg^{2+}	106.0	SO_4^{2-}	160
Ca^{2+}	119.0	PO_4^{3-}	278.4

An important application of Kohlrausch's law of independent migration of ions is that it allows us to calculate the molar conductivity of a weak electrolyte at infinite dilution by suitably adding and subtracting the molar conductivities of appropriate strong electrolytes. For example, the molar conductivity of acetic acid at infinite dilution can be obtained by adding the molar conductivities at infinite dilution for HCl and CH_3COONa and subtracting that of NaCl from the sum as given below.

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl}) \quad \dots(5.18)$$

$$(\lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0) + (\lambda_{\text{Na}^+}^0 + \lambda_{\text{CH}_3\text{COO}^-}^0) - (\lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0) = (\lambda_{\text{H}^+}^0 + \lambda_{\text{CH}_3\text{COO}^-}^0) = \Lambda_m^0(\text{CH}_3\text{COOH})$$

The experimental values of molar conductivities at infinite dilution for HCl, CH_3COONa and NaCl are 425.9, 91.0 and 126.4 $\text{S cm}^2 \text{mol}^{-1}$, respectively. These can be substituted in the above expression to get the molar conductivity of acetic acid at infinite dilution as follows

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = 425.9 + 91.0 - 126.4 = 390.5 \text{ S cm}^2 \text{mol}^{-1} \quad \dots(5.19)$$

Let us calculate the same by using the limiting molar conductivities of the H^+ and CH_3COO^- ions from Table 5.1.

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{CH}_3\text{COO}^-}^0 = 349.6 + 40.9 = 390.5 \text{ S cm}^2 \text{mol}^{-1} \quad \dots(5.20)$$

There is an excellent agreement between the calculated values. Let us now sum up what have we learnt in this unit. However, before that you may solve the following simple question to assess your learning.

SAQ 7

Calculate the molar conductivities of sodium sulphate and calcium phosphate by using the data given in Table 5.1

5.6 SUMMARY

In this unit on conductance, we have basically focused on different aspects of electrolytic conduction. We started the unit by introducing conduction in electrolytic solutions and explained the mechanism of electrolytic conduction in

terms of movement of ions under the influence of applied potential. This was compared with metallic conduction wherein the conduction is due to movement of electrons. Then we introduced the concept of conductance and conductivity of electrolytic solutions and established the relationship between them. The conductivity was defined as the conductance of all the ions present in a unit cube of the electrolytic solution.

Thereafter we discussed different factors affecting conductivity of electrolytic solutions and explained the principle of measurement of conductance of electrolytic solutions. This was followed by an introduction to the concept of molar conductivity which is defined as the conductance of a volume of solution containing the ions obtained from one mole of a dissolved electrolyte when placed between two parallel electrodes which are at a unit distance and are large enough to contain the whole solution between them. Having explained the concept of conductivity we discussed the concentration dependence of conductivity and molar conductivity of electrolytic solutions. In this context the difference in the behaviour of solutions of weak and strong electrolytes was highlighted and explained. This led to the introduction of the concept of limiting molar conductivities and the Kohlrausch's law of independent migration of ions. The rationale for the law and its applications were also taken up.

5.7 TERMINAL QUESTIONS

1. Explain the mechanism of conduction in metallic conductors.
2. List different factors affecting conductivity of an electrolytic solution.
3. Give the relation between the conductance and conductivity of an electrolytic solution measured with a conductivity cell having a cell constant equal to 1.0 cm^{-1} .
4. The resistance of a 0.10 M solution of potassium chloride taken in a conductivity cell at 25°C is found to be 24.96Ω . If at 25°C the conductivity for 0.1 M solution of KCl is $0.011639 \text{ S cm}^{-1}$; calculate the cell constant.
5. Define molar conductivity and give its SI units.
6. The resistance of a 0.01 M solution of acetic acid measured at room temperature with a conductivity cell having a cell constant of 0.40 cm^{-1} was found to be 2770Ω . Calculate the molar conductivity of acetic acid at this concentration.
7. What is conductivity water? Why do we need to use it in the conductance measurement experiments?
8. State Kohlrausch's law of independent migration of ions.
9. The molar conductivities at infinite dilution for hydrochloric acid, sodium monochloroacetate and sodium chloride are observed to be 425.9 , 89.8 and $126.4 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. Calculate the molar conductivity of monochloroacetic acid at infinite dilution.

5.8 ANSWERS

Self Assessment Questions

1. In metallic conductors the current is carried by the electrons whereas in case of electrolytic conductors it is carried by ions.
2. The conductivity of a solution can be defined as the conductance of all the ions in the electrolytic solution present in a unit cube. The conductance, G and conductivity, κ of a solution is related as

$$G = \kappa \times \frac{A}{l}$$

Where A is the surface area of the electrodes and l is the distance between them.

3. We know from Eq. (5.10) that

$$\text{Conductivity} = \frac{1}{\text{resistance}} \times \text{cell constant}$$

Rearranging, we get Cell constant = conductivity $\times$ resistance

Substituting the values, we get,

$$\text{Cell constant} = 1.46 \times 10^{-4} \text{ S cm}^{-1} \times 1500 \text{ S}^{-1} = 0.219 \text{ cm}^{-1}$$

4. We are given the surface area of electrodes and distance between them in the conductivity cell. This can be used to calculate the cell constant

$$\text{Cell constant} = \frac{\text{distance}}{\text{area}} = \frac{0.9 \text{ cm}}{1.8 \text{ cm}^2} = 0.5 \text{ cm}^{-1}$$

We know that Conductivity = $\frac{1}{\text{Resistance}}$ $\times$ cell constant

Substituting the values of resistance and cell constant we get,

$$\text{Conductivity, } \kappa = \frac{1}{2800 \text{ S}^{-1}} \times 0.5 \text{ cm}^{-1} = 1.79 \times 10^{-5} \text{ S cm}^{-1}$$

5. We know that Conductivity = $\frac{1}{\text{Resistance}}$ $\times$ cell constant

Given: Resistance = $180 \Omega = 180 \text{ S}^{-1}$; cell constant = 0.6 cm^{-1}

Substituting the values, we get

$$\kappa = \frac{1}{180 \text{ S}^{-1}} \times 0.6 \text{ cm}^{-1} = 3.33 \times 10^{-3} \text{ S cm}^{-1}$$

Once we know the value of conductivity, we can compute molar conductivity by using the following expression (where concentration is in mol dm^{-3})

$$= \Lambda_m = \frac{1000 \kappa}{c} \text{ S cm}^2 \text{ mol}^{-1}$$

Substituting the values,

$$= \Lambda_m = \frac{1000 \text{ cm}^3 \text{ dm}^{-3} \times 3.33 \times 10^{-3} \text{ S cm}^{-1}}{6.25 \times 10^{-2} \text{ mol dm}^{-3}} = 53.28 \text{ S cm}^2 \text{ mol}^{-1}$$

6. We know that

$$\text{Conductivity} = \frac{1}{\text{resistance}} \times \text{cell constant}$$

Rearranging we get Cell constant = Conductivity $\times$ resistance

Given:

$$\text{Conductivity} = 0.277 \Omega^{-1}\text{m}^{-1} = 0.00277 \text{ S cm}^{-1}; \text{Resistance} = 250 \text{ S}^{-1}$$

Substituting the values,

$$\text{Cell constant} = 0.00277 \text{ S cm}^{-1} \times 250 \text{ S}^{-1} = 0.6925 \text{ cm}^{-1}$$

Now we know that

$$\text{cell constant} = \frac{\text{distance between the electrodes, } \ell}{\text{surface area of electrodes, } A}$$

Rearranging we get,

Distance between the electrodes =

cell constant $\times$ surface area of the electrodes

Substituting the values

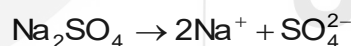
$$\text{Distance between the electrodes} = 0.6925 \text{ cm}^{-1} \times 2 \text{ cm}^2 = 1.385 \text{ cm}$$

7. We know that the molar conductivity at infinite dilution for an electrolyte is given as

$$= \Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$$

Where, ν_+ and ν_- are the number of cations and anions generated by the dissociation / ionisation of the electrolyte and λ_+^0 and λ_-^0 are the limiting molar conductivities of the cation and anion respectively.

To calculate the molar conductivity at infinite dilution for sodium sulphate we write the equation for dissociation of sodium sulphate as



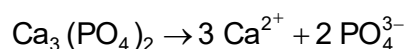
The molar conductivity at infinite dilution would be

$$\Lambda_m^0(\text{Na}_2\text{SO}_4) = 2\lambda_{\text{Na}^+}^0 + \lambda_{\text{SO}_4^{2-}}^0$$

Substituting the values of limiting molar conductivities of the ions from Table 5.1 we get

$$\Lambda_m^0(\text{Na}_2\text{SO}_4) = (2(50.1) + 160) \text{ S cm}^2 \text{ mol}^{-1} = 260.2 \text{ S cm}^2 \text{ mol}^{-1}$$

For calcium phosphate the dissociation of salt would be as



The molar conductivity at infinite dilution would be

$$\Lambda_m^0(\text{Ca}_3(\text{PO}_4)_2) = 3\lambda_{\text{Ca}^{2+}}^0 + 2\lambda_{\text{PO}_4^{3-}}^0$$

Substituting the values of limiting molar conductivities of the ions from Table 5.1 we get

$$\Lambda_m^0(\text{Ca}_3(\text{PO}_4)_2) = (3(119) + 2(278.4)) \text{ S cm}^2 \text{ mol}^{-1} = 913.8 \text{ S cm}^2 \text{ mol}^{-1}$$

Terminal Questions

1. The mechanism of conduction in metallic conductors can be explained in terms of the electron sea model. According to this model a metallic solid can be viewed as a fixed array of positively charged metal ions surrounded by a sea of mobile electrons, provided by the valence electrons of the atoms. When an electrical field is applied across the metal wire, the electrons move through the lattice of positive ions in response to an applied electric field. A certain number of electrons enter the metal at one end and an equal number of electrons come out of the other end.
2. The factors affecting the conductivity of an electrolytic solution are as under:

- the concentration of ions
- the nature of the electrolyte;
- the dielectric constant of the solvent;
- interionic interactions;
- viscosity of the solvent;
- size of the ions and their solvation; and
- temperature

3. The conductivity and conductance of an electrolytic solution are related as

$$\text{Conductivity} = \text{Conductance} \times \text{cell constant}$$

If the value of cell constant = 1.0 cm^{-1} then the magnitude of conductivity will be same as that of measured conductance. However, you must remember that the units of conductance are S^{-1} whereas for conductivity it is $\text{S}^{-1} \text{ cm}^{-1}$.

4. From Eq. (5.10), we know that

$$\text{Conductivity} = \frac{1}{\text{resistance}} \times \text{cell constant}$$

Rearranging, we get

$$\text{Cell constant} = \text{conductivity} \times \text{resistance}$$

Substituting the values, we get,

$$\text{Cell constant} = 0.011639 \text{ S cm}^{-1} \times 24.96 \text{ S}^{-1} = 0.29 \text{ cm}^{-1}$$

5. Molar conductivity is defined as the conductance of a volume of solution containing the ions obtained from one mole of a dissolved electrolyte when placed between two parallel electrodes which are at a unit distance and are large enough to contain the whole solution between them. The SI units of molar conductivity are $\text{S m}^2 \text{ mol}^{-1}$.
6. From Eq. (5.10), we know that

$$\text{Conductivity} = \frac{1}{\text{resistance}} \times \text{cell constant}$$

We are given,

Resistance = $2770 \Omega = 2770 \text{ S}^{-1}$ and Cell constant = 0.40 cm^{-1}

Substituting the values, we get

$$\text{Conductivity} = \frac{1}{2770 \text{ S}^{-1}} \times 0.40 \text{ cm}^{-1} = 1.44 \times 10^{-4} \text{ S cm}^{-1}$$

We know that molar conductivity = $\Lambda_m = \frac{1000 \kappa}{c} \text{ S cm}^2 \text{ mol}^{-1}$

Substituting the values of conductivity and concentration, we get

$$= \Lambda_m = \frac{1000 \text{ cm}^3 \text{ dm}^{-3} \times 1.44 \times 10^{-4} \text{ cm}}{0.01 \text{ mol dm}^{-3}} = 1.44 \text{ S cm}^2 \text{ mol}^{-1}$$

Thus, the molar conductivity of 0.01 M solution of acetic acid is computed to be $14.4 \text{ S cm}^2 \text{ mol}^{-1}$

7. A sample of water that is free from all types of ionic impurities and has negligible conductivity is called conductivity water. It is obtained by repeated distillation of water. It is important to use conductivity water in conductance measurement experiments because the conductivity of the ions contributed by impurities introduce error in the conductivity measurement of a sample.
8. Kohlrausch law states that at infinite dilution, all electrolytes are completely ionised and the interionic effects do not exist, therefore each ion migrates in solution independent of other ions. Under such conditions, the molar conductivity of an electrolyte at infinite dilution can be represented as the sum of molar conductivities of individual ions at infinite dilution.
9. The molar conductivity of a monochloroacetic acid at infinite dilution can be obtained by adding the molar conductivities at infinite dilution for HCl and $\text{ClCH}_2\text{COONa}$ and subtracting that of NaCl from the sum as given below.

$$\Lambda_m^0(\text{ClCH}_2\text{COOH}) = \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{ClCH}_2\text{COONa}) - \Lambda_m^0(\text{NaCl})$$

$$(\Lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0) + (\lambda_{\text{Na}^+}^0 + \lambda_{\text{ClCH}_2\text{COO}^-}^0) - (\lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0) = (\lambda_{\text{H}^+}^0 + \lambda_{\text{ClCH}_2\text{COO}^-}^0)$$

$$= \Lambda_m^0(\text{ClCH}_2\text{COOH})$$

The values of molar conductivities at infinite dilution for HCl, $\text{ClCH}_2\text{COONa}$ and NaCl are given as 425.9, 89.8 and $126.4 \text{ S cm}^2 \text{ mol}^{-1}$, respectively.

Substituting these values in the above expression we get

$$\Lambda_m^0(\text{ClCH}_2\text{COOH}) = 425.9 + 89.8 - 126.4 = 389.3 \text{ S cm}^2 \text{ mol}^{-1}$$

UNIT 6

Conductance-II |

Structure

6.1	Introduction	Determination of Solubility and Solubility Product of Sparingly Soluble Salts
	Expected Learning Outcomes	
6.2	Ionic Mobilities and Transference Number	Determination of Ionic Product of Water
6.3	Determination of Transference Numbers	Determination of Hydrolysis Constant of a Salt
	Hittorf's Method	
	Moving Boundary Method	6.5 Conductometric Titrations
6.4	Applications of Conductivity Measurements	6.6 Summary
	Determination of Ionisation Constant of a Weak acid	6.7 Terminal Questions
		6.8 Answers

6.1 INTRODUCTION

In the previous unit you have learnt about some aspects of electrolytic conduction. You have learnt about basic concepts like conductance, conductivity, and molar conductivity in terms of interrelations between them, their significance, determination, and factors affecting them. In this unit we would continue our learning of electrolytic conduction and take up two main aspects viz., the migration of ions and the application of conductance measurements.

We would begin the unit by discussing migration of ions in an electrolytic solution under the influence of applied potential. In this context we would introduce the concepts of ionic mobility and transference numbers. We would then take up the principle and experimental methods of determination of transference numbers. This will be followed by different applications of conductance measurements. These include determination of: ionisation constant of weak acids, ionic product of water, solubility and solubility product of sparingly soluble salts and degree of hydrolysis and hydrolysis constant for a salt. In addition, we would also take up conductometric titrations as application of conductance measurements.

In the next unit we would take up electrochemical cells in terms of their types, representation and emf etc.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define ionic mobility and outline its significance;
- ❖ list and explain factors affecting ionic mobility;
- ❖ define transference numbers and relate them to ionic mobilities;
- ❖ explain the principles of Hittorf's and moving boundary methods for the determination of transference numbers;
- ❖ describe the procedure of Hittorf's method and moving boundary method for the determination of transference numbers;
- ❖ define indicator electrolyte and list the requirements for an electrolyte to be indicator electrolyte in the moving boundary method;
- ❖ solve problems based on Hittorf's and moving boundary methods;
- ❖ list some important applications of conductivity measurements;
- ❖ explain the conductometric determination of ionisation constant of a weak acid;
- ❖ determine solubility and solubility product of a sparingly soluble salt using conductance measurement data;
- ❖ explain the method of determination of ionic product of water using conductance measurements;
- ❖ state the importance of conductometric titrations; and
- ❖ explain the titration curves for the titration of weak (or strong) acids with a strong base.

6.2 IONIC MOBILITIES AND TRANSFERENCE NUMBERS

In any measurement of conductance of an electrolytic solution we get the amount of current carried by all the ions present in the solution. However, fraction of the total current carried by each type of ions is not necessarily the same. It has been found that in dilute solutions of magnesium sulfate the fraction of current carried by magnesium ion is about 0.38 (38%) of the total current, whereas the sulfate ions carry the remaining 62%. The difference in the amount of current carried by the cation and anion can also be inferred by the limiting molar conductivities of ions about which you have learnt in the previous unit. You would recall that in an aqueous solution of acetic acid at infinite dilution the molar conductivities of hydrogen ions and acetate ions are $349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $40.9 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. Since at infinite dilution, the ions are free from interionic interactions, the difference in these values can

be attributed to their different speeds or velocities. However, at ordinary concentrations though the ions do not move independent of other ions, yet they have different speeds and carry different amount of current. The speed of different ions is identified in terms of their ionic mobilities. Let us understand what is ionic mobility of an ion?

6.2.1 Ionic Mobility

In a solution of an electrolyte the ions move randomly. However, in an any act of measurement of conductivity of the solution an electric field is applied across the electrodes. The ions then move under the influence of the applied electrical field. The applied field provides a direction to the ions and accelerates them. This causes a net migration of ions in the solution towards oppositely charged electrodes; cations towards cathode and anions towards anode. In addition, as mentioned above, at moderate concentrations the ions are not free from interionic interactions. Therefore, the ions experience a frictional retardation from other ions. Thus, the ions experience two types of forces viz., electrical field and frictional retardation and these two forces act in opposite directions. When the acceleration due to the applied electric field becomes equal to the frictional retardation force the ions drift towards the opposite electrodes with a net speed called **drift speed** or **drift velocity** denoted by s . The drift speed is proportional to the electrical field, E and we can write

$$s = uE \quad \dots(6.1)$$

where, the proportionality constant, u is called **ionic mobility**. If the electrodes are at a distance of 1m apart and a potential of 1V is applied across them i.e., the potential gradient is 1 Vm^{-1} then we can write

$$s = u \quad \dots(6.2)$$

Thus, we can define ionic mobility to be the velocity with which an ion in a solution would move under a potential gradient of 1 Vm^{-1} . The SI unit for ionic mobility can be obtained as follows

$$u = \frac{s}{E} = \frac{\text{ms}^{-1}}{\text{Vm}^{-1}} = \text{m}^2 \text{ V}^{-1} \text{ s}^{-1} \quad \dots(6.3)$$

The ionic mobilities of some common ions are given in Table 6.1.

Table 6.1: Ionic Mobilities of Some Ions in Water at 298 K

Cation	$u / (10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})$	Anions	$u / (10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1})$
H^+	36.23	OH^-	20.64
Li^+	4.01	F^-	5.74
Na^+	5.19	Cl^-	7.92
K^+	7.62	Br^-	8.09
Mg^{2+}	5.50	NO_3^-	7.41
Ca^{2+}	6.17	SO_4^{2-}	8.29

The significance of ionic mobilities is that these provide a link between measurable and theoretical quantities. The theoretical quantity, ionic mobility (u) is related to measurable quantity, molar conductivity (λ) of the ions as follows:

$$\lambda = z u F \quad \dots(6.4)$$

Where, F is the Faraday's constant, ($F = N_A e = 96485 \text{ C}$). For the solution of an electrolyte at infinite dilution (when interionic interactions do not exist), we know that

$$\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0 \quad \dots(6.5)$$

Substituting for molar conductivities of ions from Eq. (6.4) we get,

$$\Lambda_m^0 = (z_+ u_+ \nu_+ + z_- u_- \nu_-) F \quad \dots(6.6)$$

Having learnt about ionic mobility and its significance, let us learn about the factors affecting ionic mobilities

Factors affecting ionic mobilities

The ionic mobility of an ion depends on several factors, some of the important factors are as under:

- **Charge on the ion:** an ion with a higher charge has higher ionic mobility as it would experience a greater force due to electric field ($F = zeE$), where z is the charge on the ion, e is the elementary charge and E is the electric field strength.
- **Radius of ion:** smaller the ion higher the ionic mobility as a smaller ion due to smaller surface area experiences lesser friction and can move easily through the solvent.
- **Viscosity of the medium:** higher the viscosity, lower the ionic mobility because the ion will experience a greater frictional force

We can make two important observations from the data given in Table 6.1. First, that the ionic mobilities of hydrogen and hydroxide ions are exceptionally high; more than that can be attributed to the small size. Secondly, the trend in case of alkali metal ions and halide ions are contrary to that expected from variation in their sizes. Let us learn about the explanation for the observations. First, we take up high ionic mobilities of hydrogen and hydroxide ions.

The exceptionally high ionic mobilities of hydrogen and hydroxide ions was explained initially by suggesting that in case of these ions in water there are two mechanisms by which the conduction takes place. The first one is same as discussed above for any other ion. The second mechanism called **Grotthus conduction mechanism** and is specific to hydrogen and hydroxide ions. According to this mechanism the proton binds to a neighbouring water molecule and momentarily converts it to a hydronium ion. This in turn transfers its proton to another molecule in neighborhood which does the same to another molecule and this process continues. As a result, a proton in any region of the solution is effectively transported very quickly to another part. This mechanism is also known as **proton hopping mechanism**. A schematic representation of such a mechanism for movement of proton and hydroxide ions is given in Fig. 6.1. It is important to note here that the actual mechanism is still under investigation.

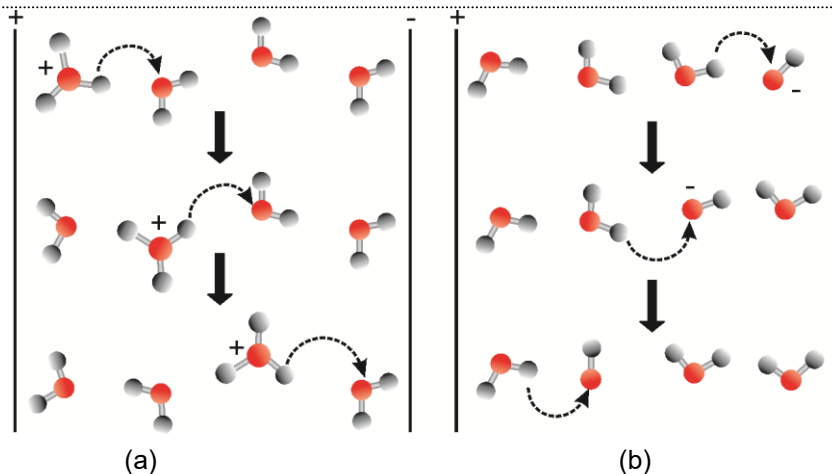


Fig. 6.1: Schematic representation of Grotthius conduction mechanism for (a) H^+ and (b) OH^- ions.

Now, we take up the second observation. That is, the trend in the ionic mobilities of alkali metal ions and halide ions. The observed trend is opposite to the expected trend because these ions get hydrated and their effective size increases. The extent of hydration depends on the charge density [charge / (radius)²] of the ions. The charge on all alkali metal ions is same (1 unit positive charge) but since Li^+ ion is the smallest it is heavily hydrated. This makes the hydrated ion large, and hence it moves only slowly. In comparison though the Na^+ and K^+ ions are larger in size; the extent of their hydration is lesser and hence their effective size is smaller than that of hydrated lithium ion. The sizes of some alkali metal ions in unhydrated and hydrated state and their ionic mobilities are given below.

Ion	Ionic radius of unhydrated ion / pm	Approximate radius of hydrated ion / pm	Ionic mobility / ($10^{-8}\text{m}^2\text{s}^{-1}\text{V}^{-1}$)
Li^+	76	340	4.01
Na^+	102	276	5.19
K^+	138	232	7.62

6.2.2 Transference Numbers

As discussed above, the current is transported through a solution by migration of positive as well as negative ions and the ionic mobility or speed of ions are different. The question comes up is that out of the total current carried in the solution what is the contribution of different ions? Are these same or different? How do we determine it? For this we define a new parameter called **transference number** (also called transport number). It is defined as the fraction of current carried by a given type of ion.

In order to derive an expression for transference number, we consider two electrodes that are separated by a distance d and contain a solution of an electrolyte between them. Let the solution have n_+ positive ions having a charge of z_+ units each and have n_- negative ions having a charge of z_- units each. When we apply a unit potential difference across the electrodes these ions move towards the oppositely charged electrodes. Let us assume that the cations have a mobility of u_+ whereas the anions have a mobility equal to u_- . A

schematic set up to establish a relationship between ionic mobility and transference number is given in Fig. 6.2.

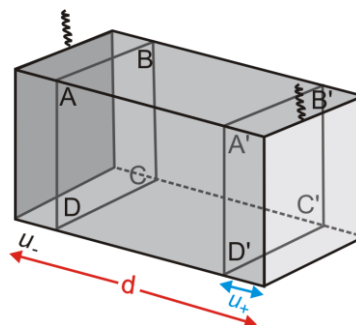


Fig. 6.2: A schematic set up to establish a relationship between ionic mobility and transference number.

Now, let us try to calculate the current transferred by the cations and anions in one second. We find that all the cations present in the volume of solution enclosed between the negative electrode (cathode) and the plane A'B'C'D' in the figure (this plane is at a distance of u_+ from the negative electrode) would move to the electrode. The current carried by the cations can be calculated as follows:

$$\text{Total number of positive ions present in the solution: } n_+ \quad \dots(6.7)$$

$$\text{Volume of the solution} = \text{area } ABCD \times d \quad \dots(6.8)$$

$$\text{Number of positive ions per unit volume} = \frac{n_+}{\text{area } ABCD \times d} \quad \dots(6.9)$$

$$\text{Volume of the solution from which all the positive ions will reach the negative electrode} = \text{area } ABCD \times u_+ \quad \dots(6.10)$$

The number of positive ions reaching electrode in one sec =

$$= \frac{n_+}{\text{area } ABCD \times d} \times \text{area } ABCD \times u_+ = \frac{n_+ u_+}{d} \quad \dots(6.11)$$

$$\text{Quantity of electricity associated with each positive ion} = z_+ e \quad \dots(6.12)$$

$$\rightarrow \text{the current carried by positive ions in one sec} = I_+ = \frac{n_+ u_+ z_+ e}{d} \quad \dots(6.13)$$

Similarly, in one second all the negative ions between the positive electrode (anode) and the plane ABCD would reach the electrode. As above, we can show that

$$\rightarrow \text{the current carried by negative ions in one sec} = I_- = \frac{n_- u_- z_- e}{d} \quad \dots(6.14)$$

Total current conducted by the ions in one second =

$$I = I_+ + I_- = \frac{n_+ u_+ z_+ e + n_- u_- z_- e}{d} \quad \dots(6.15)$$

$$\text{As the overall solution has to be neutral, } n_+ z_+ e = n_- z_- e \quad \dots(6.16)$$

Substituting in Eq. (6.15), we get total current conducted in one sec =

$$I = \frac{n_+ z_+ e (u_+ + u_-)}{d} \quad \dots(6.17)$$

The fraction of current carried by cations =

$$t_+ = \frac{I_+}{I} = \frac{n_+ z_+ e(u_+)}{d} \times \frac{d}{n_+ z_+ e(u_+ + u_-)} = \frac{u_+}{u_+ + u_-} \quad \dots(6.18)$$

Similarly, the fraction of current carried by anions =

$$t_- = \frac{I_-}{I} = \frac{n_- z_- e(u_-)}{d} \times \frac{d}{n_- z_- e(u_+ + u_-)} = \frac{u_-}{u_+ + u_-} \quad \dots(6.19)$$

Thus, $t_+ = \frac{u_+}{u_+ + u_-}$ and $t_- = \frac{u_-}{u_+ + u_-}$...(6.20)

There are two important corollaries of the expressions for transport numbers.

$$\frac{t_+}{t_-} = \frac{u_+}{u_+ + u_-} \times \frac{u_+ + u_-}{u_-} = \frac{u_+}{u_-} \quad \dots(6.21)$$

i.e., the ratio of transport numbers of two ions in an electrolyte is same as the ratio of their ionic mobilities

$$t_+ + t_- = \frac{u_+}{u_+ + u_-} + \frac{u_-}{u_+ + u_-} = \frac{u_+ + u_-}{u_+ + u_-} = 1 \quad \dots(6.22)$$

i.e., the sum of transport number of the cation and the anion is equal to one.

You may note that in this derivation we have assumed that the potential difference between the two electrodes is 1V therefore the expressions for the transport numbers are in terms of ionic mobilities which are the ionic velocities per unit potential. If we use the potential difference other than 1V, then the expressions would have velocities in place of ionic mobilities; i.e.,

$$t_+ = \frac{v_+}{v_+ + v_-} \quad \text{and} \quad t_- = \frac{v_-}{v_+ + v_-} \quad \dots(6.23)$$

You would recall that in the beginning of Section 6.2 we mentioned that in a measurement of electrical conductivity we get the total current carried by the cations and the anions. To evaluate the contribution of individual ions we defined the concept of ionic mobility and related it to the molar ionic conductivity through Eq. (6.6). However, we cannot measure the ionic mobilities directly. Therefore, we have defined a new parameter viz., transport number that represents the fraction of total current carried by a given ion in solution. The transference numbers are related to the ionic mobilities by Eq. (6.20). The transference numbers can be measured experimentally and provide a way of getting the individual ionic mobilities. Let us learn about their experimental determination. However, before that solve the following simple questions to gauge your understanding.

SAQ 1

Define ionic mobility and give its SI unit.

SAQ 2

What are transference numbers? How are these related to ionic mobilities?

6.3 DETERMINATION OF TRANSFERENCE NUMBERS

As stated above, an experimental determination of transference numbers of ions in an electrolyte are important to evaluate the contribution of individual ions to the overall electrical conductivity of the solution of an electrolyte. Three methods are generally employed for the experimental determination of transference numbers. These are

- Hittorf's method
- Moving boundary method
- Emf measurement method

We would take up the first two methods here. The Hittorf's method is based on the measurement of change in concentration in the vicinity of the electrodes whereas in the moving boundary method we study the rate of movement of the boundary between two solutions under the influence of current. Let us learn about these methods one by one.

6.3.1 Hittorf's Method

As mentioned above, in Hittorf's method we measure the changes in the concentration of electrolyte in the vicinity of electrode in an electrolytic cell. We need to first understand why the concentration around the electrodes changes and how is it related to the transport numbers. For this we consider an electrolytic cell which has an equivalent number of positive and negative ions, as shown schematically in Fig. 6.3 (A).

The arguments that follow will be valid for any kind of electrolyte but for simplicity we are considering a simple uni-univalent electrolyte. This cell is arbitrarily divided by the imaginary planes into three compartments, which can be called cathodic, central, and anodic compartments. Before we apply potential and the electrolysis begins, the condition of the cell is represented by the upper part of Fig. 6.3 (A) in which each compartment has five equivalents each of positive and negative ions.

In the first case we assume that only the cations can move under the influence of an applied potential, and further, two equivalents of these ions move from the anodic compartment to the cathode. The anions on the other hand are practically immobile. The situation can be represented by lower part of Fig. 6.3 (A), where we find that there are two equivalents of unpaired ions each around the two electrodes. The anions get discharged on the anode by giving their electrons and these electrons travel through the external circuit to the cathode where they are taken up by the cations to get discharged. It is interesting to note that though only the positive ions were able to move (i.e., carry current), equivalent amounts of the cation and anions are discharged at the respective electrodes. This is in accordance with Faraday's law which you would have learnt in your school chemistry.

Let us now consider second case where we assume that the cations as well as the anions can move and move with same velocity (mobility). The initial and final situation in this case will be represented by Fig. 6.3 (B). Here we have assumed that two equivalents of cations have moved from anodic

compartment to the cathode and two equivalents of anions have moved from the cathodic compartment to the anode. As a consequence, there are four equivalents of unpaired ions each at the two electrodes and as in the first case these would get discharged at the respective electrodes. Once again, we find that the amounts of the cation and anions discharged at the electrodes are equal.

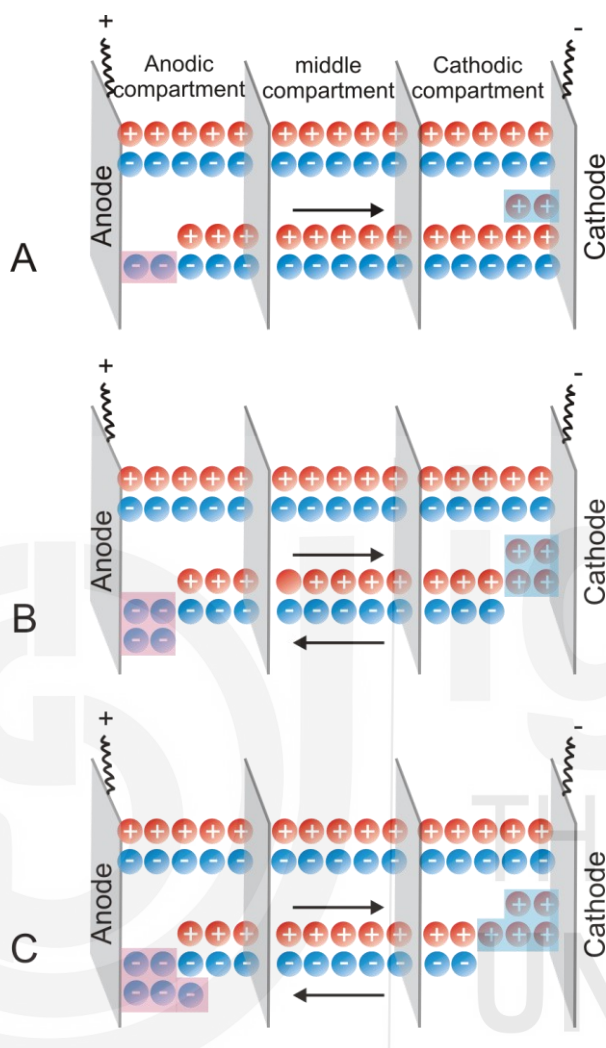


Fig. 6.3: A schematic illustration of depletion around anode and cathode.

In the third case represented by Fig. 6.3 (C) we have assumed that the cations and anions move at different velocities. The cation to anion velocity is in the ratio of 2:3. In other words, when in certain time two equivalents of cations have moved from anodic compartment to cathode, three equivalents of anions have moved from cathodic compartment to anode. Thus, there are five equivalents of unpaired ions each at the two electrodes and get discharged there.

So, what do we find in these illustrative cases? First, we find that the current is carried by those ions which move and secondly the amount of current carried by a given kind of ion is proportional to its speed. We can also say that the fraction of current carried by a given type of ion i.e., its transference number is proportional to its speed. In all these arguments we have made an important assumption that the discharged ions do not react with the material of the electrodes. If we look at Fig. 6.3 again, we can make one more observation that the loss of concentration of electrolyte around any electrode is

This statement is called as **Hittorf's rule** and forms the basis of determination of transference numbers by Hittorf's method.

proportional to the speed of the ion moving away from it. We can, therefore, write

$$\frac{\text{Moles of electrolyte lost from the anodic compartment}}{\text{Moles of electrolyte lost from the cathodic compartment}} = \frac{t_+}{t_-} \quad \dots(6.24)$$

This is valid only for a 1:1 electrolyte. Now, the total moles of electrolyte lost will be sum of the electrolyte lost from the anodic and cathodic compartments. These can also be obtained from the total amount of current passed through the cell. We can write,

$$t_+ = \frac{\text{Moles of electrolyte lost from the anodic compartment}}{\text{Total number of moles of electrolyte lost}} \quad \dots(6.25)$$

$$t_- = \frac{\text{Moles of electrolyte lost from the cathodic compartment}}{\text{Total number of moles of electrolyte lost}} \quad \dots(6.26)$$

Let's learn about the experimental method of determination of transference numbers by Hittorf's method.

Experimental determination of transference numbers by Hittorf's method

The Hittorf's apparatus for the determination of transference numbers consists of two vertical glass tubes joined through a U-tube with stopcocks at the tops of the two limbs of the U-tube. The two vertical glass tubes represent the anodic and cathodic compartments whereas the U-tube represents the middle compartment. Each of these tubes is provided with stopcocks at the bottom. The stopcocks in the two limbs of the U-tube are used to connect / disconnect the solutions in the cathodic and anodic compartments with the middle compartment.

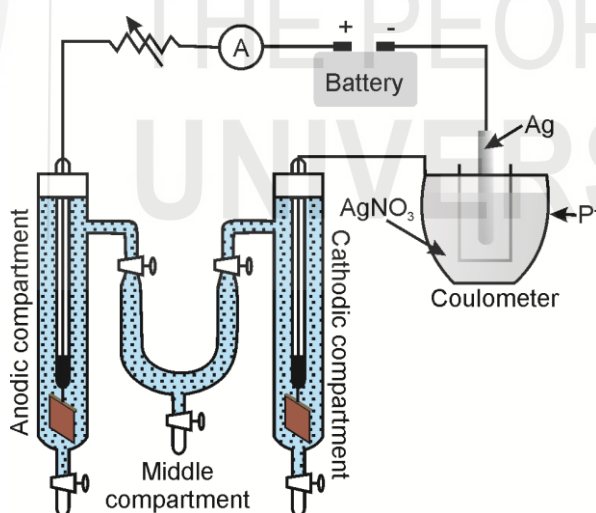


Fig. 6.4: Hittorf's experimental set up for the determination of transport numbers.

The three-tube apparatus (also called Hittorf cell or transport cell) is connected in series with a silver coulometer through a variable resistance, a milli ammeter and battery as shown in Fig. 6.4. The milliammeter allows to adjust the current to any desired value. The anodic and cathodic tubes are provided with an electrode each. (these could be platinum electrodes or metal electrodes depending on the system). The cell is filled with the electrolyte for which the transport numbers are to be determined. The current is turned on, and the solution is allowed to undergo electrolysis for sufficient amount of time such that there is appreciable change in the concentrations in the anodic and

cathodic compartments. Thereafter, the solution is drained from each electrode compartments and analysed. The total quantity of electricity passed (or total amount of electrolyte discharged) is obtained from the increase in weight of the cathode in the coulometer attached in series. The analysis of the solution from the central compartment provides the initial concentration of the electrolyte (as it is not expected to change). However, if the initial concentration is known, the analysis of solution from the central compartment may be skipped. The changes in the amount of electrolyte in the electrode compartments are then used to determine the transference numbers as discussed above. Let us understand it with the help of an example.

Example 6.1: A solution containing 19.23 g of silver nitrate in 50 cm³ of solution was taken in a Hittorf cell using platinum electrodes for the determination of transport numbers. After the experiment 50 cm³ of anodic compartment solution contained 18.47 g of silver nitrate. If 0.982 g of metallic silver was deposited on the cathode, calculate the transport number of the ions.

Solution: We know that the transport number of the cation is defined as

$$t_+ = \frac{\text{Moles of electrolyte lost from the anodic compartment}}{\text{Total number of moles of electrolyte lost}}$$

First, we would calculate the total number moles of electrolytes lost. You have learnt above that it is equal to the total amount of electricity passed. This can be calculated from the amount of silver deposited on the cathode.

$$\text{The amount of silver deposited on cathode} = \frac{0.982 \text{ g}}{107.88 \text{ g mol}^{-1}} = 0.00912 \text{ mol}$$

$$\begin{aligned} \text{Decrease in the amount of AgNO}_3 \text{ in the anode compartment} = \\ (19.23 - 18.47) = 0.76 \text{ g} \end{aligned}$$

$$\text{In terms of number of moles} = \frac{0.76 \text{ g}}{169.87 \text{ g mol}^{-1}} = 0.00447 \text{ mol}$$

$$\text{Substituting in the expression for } t_+ : t_{\text{Ag}^+} = \frac{0.00447 \text{ mol}}{0.00912 \text{ mol}} = 0.49$$

$$\text{We know that } t_+ + t_- = 1 \quad \text{So } t_{\text{NO}_3^-} = 1 - 0.49 = 0.51$$

This was quite a simple and straightforward problem because platinum electrodes are used, and it is not affected in the anode compartment. However, if we use silver electrodes then the calculation becomes a little more involved. Let us take one more example.

Example 6.2: In the determination of transport number a solution of silver nitrate containing 0.00739 g of silver nitrate per gram of water was taken in the Hittorf cell using silver electrodes. After a certain amount of current was passed for enough time, 0.0624 g of silver was deposited on the cathode. An analysis of the solution from anode compartment showed that the solution contained 18.5 g of water and 189 mg of silver nitrate. Calculate the transport number of the silver and nitrate ions.

Solution: We know that the transport number of the cation is defined as

$$t_+ = \frac{\text{Moles of electrolyte lost from the anodic compartment}}{\text{Total number of moles of electrolyte lost}}$$

Once again, first we would calculate the total number moles of electrolytes lost. This can be calculated from the amount of silver deposited on cathode.

$$\text{The amount of silver deposited on cathode} = \frac{0.0624 \text{ g}}{107.88 \text{ g mol}^{-1}} = 0.000578 \text{ mol}$$

Since in this case we are using silver electrodes, so an equivalent amount of silver will dissolve from the silver anode i.e., 0.000578 moles. Thus, the concentration of silver nitrate would increase by 0.000578 moles in the anode compartment.

We are given the final amount of silver nitrate in the anode compartment as 189 mg of silver nitrate and 18.5 g of water i.e.,

$$\text{Final number of moles of silver nitrate} = \frac{0.189 \text{ g}}{169.87 \text{ g mol}^{-1}} = 0.00111 \text{ mol}$$

Initial number of moles of silver nitrate in the anode compartment can be obtained by calculating silver nitrate in 18.5 g of water

$$\frac{18.5 \text{ g water} \times 0.00739 \text{ g AgNO}_3 \text{ per g water}}{169.87 \text{ g mol}^{-1}} = 0.0008 \text{ mol}$$

The number of moles of silver nitrate transferred from anode compartment =

$$= \text{Initial no. of moles} + \text{Moles formed by dissolution of electrode} - \text{final no. of moles}$$

$$= 0.0008 + 0.000578 - 0.00110 = 0.000278 \text{ mol}$$

Substituting in the expression for transport number, we get

$$t_{\text{Ag}^+} = \frac{0.000278 \text{ mol}}{0.000578 \text{ mol}} = 0.48$$

We know that

$$t_+ + t_- = 1$$

$$\text{So } t_{\text{NO}_3^-} = 1 - 0.48 = 0.52$$

Having learnt about the Hittorf's method let us now take up moving boundary method. However, before that answer the following questions to assess your understanding.

SAQ 3

List different experimental methods for the determination of transference numbers.

SAQ 4

A 0.2000 molal solution of copper sulphate was taken in a Hittorf cell having copper electrodes. After passing suitable current for sufficient time the cathode solution from the cell was analysed. It was found to weigh 36.4340 g and contained 0.44125 g of copper. On the other hand, the cathode in the coulometer showed a deposition of 0.0405 g of silver. Calculate the transference numbers of the copper and sulphate ions.

6.3.2 Moving Boundary Method

As the name suggests, in the moving boundary method the motion of ions under the influence of an applied potential is observed in terms of a moving boundary. It is relatively simple and accurate method and used extensively. In one of the variants of this method we use two electrolytes, one whose transference numbers are to be determined (called principal electrolyte) and the other electrolyte that acts as **indicator electrolyte**.

The indicator electrolyte must meet the following criteria

- If we wish to measure the cation of the electrolyte, then the indicator electrolyte must have an anion common with it. For example, if we wish to determine the transference number of the cation of the electrolyte MA then the indicator electrolyte would be M'A. For anion, it would be MA'.
- The speed of the M'^{+} ion shall be less than that of M^{+} and that of A'^{-} shall be less than that of the A^{-} ion.

In a typical determination, the solutions of these electrolytes are taken in the moving boundary apparatus. It is a glass tube having uniform diameter mounted vertically with two electrodes at the ends. Similar to the Hittorf's method, these electrodes are connected in series with a silver coulometer through a variable resistance, a milli ammeter and battery as shown in Fig. 6.5 (a). The solutions are so arranged that the boundary between them is quite sharp. The boundary between the solutions is generally located due to the difference in their refractive indices or the colour. Further, to avoid mixing of solutions and loss of the boundary, the solutions are placed in the order of decreasing density.

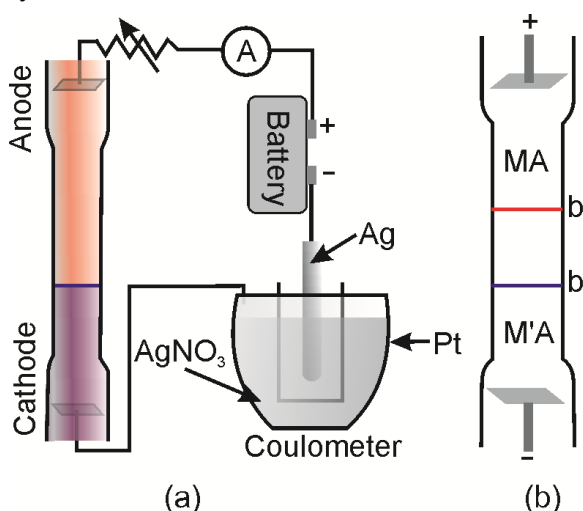


Fig. 6.5: Schematic experimental set up for the determination of transport numbers by moving boundary method.

Now, once the suitable indicator electrolyte is identified the two solutions are loaded as shown schematically in the Fig. 6.5 (b), a distinct boundary is formed at b . On applying potential, the M^+ and M'^{+} ions move towards cathode and the boundary between them also moves.

After sufficient time the boundary reaches b' . As the mobility of M'^{+} ions is lesser than the M^+ ions these are sometimes called **following ions**.

The distance bb' would depend on the speeds of the ions being determined (M^+). As there is a uniform potential through the solution MA , distance bb' will be proportional to the ionic mobility u_+ of the M^+ ion and can be used to determine the transference number. Let us understand it with the experimental determination of the transference number of hydrogen ions.

Experimental determination of transference numbers by moving boundary method

In the determination of transference number of hydrogen ions in HCl we use cadmium chloride as the indicator electrolyte having a common anion. The cell is filled first with cadmium chloride and HCl is added on top of it and a sharp boundary is obtained. A platinum wire is inserted at the top of the cell to act as the cathode and a stick of cadmium metal is used as the anode at the bottom of the cell. A silver coulometer is connected with the cell in series through a variable resistance, a milli ammeter and battery as shown in Fig. 6.6.

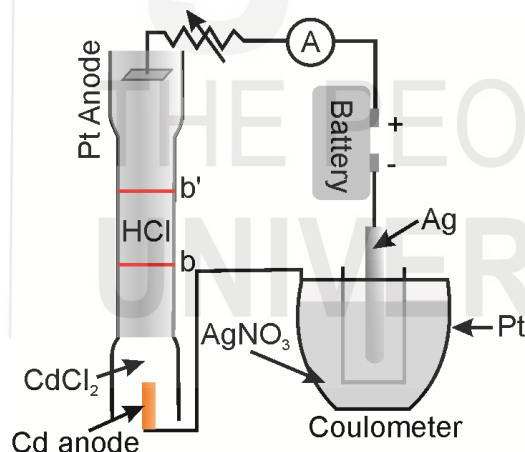


Fig. 6.6: Schematic diagram showing experimental set up for the determination of transference numbers of HCl by moving boundary method.

On applying potential, the hydrogen ions move towards the cathode at the top of the cell and get discharged as hydrogen gas. As hydrogen ions move toward the cathode their place is taken by cadmium ions, and the boundary between two electrolytic solutions also moves upward. After suitable amount of current is passed for sufficient amount of time the distance moved by the boundary is used along with the cross-section area of the cell to obtain the volume swept out by the moving boundary. This along with the total quantity of electricity passed (as measured from coulometer) is then used to calculate the transference number of hydrogen ion.

If the distance between b and b' , is l cm and a cm² is the cross-sectional area of the tube, then the volume displaced by the moving boundary is la cm³. If the

concentration of HCl is $c \text{ mol dm}^{-3}$, the number of moles of HCl contained in this volume would be $10^{-3} / ac$. If Q Coulombs of charge is passed through the cell, then the charge carried by hydrogen ions would be t_+Q . Further, as the charge carried by $10^{-3} / ac$ moles of H^+ ions will be $10^{-3} / acF$, we can write

$$t_+Q = 10^{-3} / a \times c \times F \quad \dots(6.27)$$

Rearranging we get,

$$t_+ = \frac{10^{-3} / a \times c \times F}{Q} \quad \dots(6.28)$$

Let us take an example to see the application of this expression.

Example 6.3: In the determination of transference numbers of HCl by moving boundary method a 0.10 M solution of HCl was taken in a cell having uniform area of cross section of 1.25 cm^2 . At the end of experiment the boundary moved by 7.5 cm and 0.12 g of silver was deposited on the cathode of silver coulometer. Calculate the transference numbers of ions of HCl.

Solution: We know that for determination of transference number by moving boundary method,

$$t_+ = \frac{10^{-3} / a \times c \times F}{Q}$$

We have been given the values as:

$$l = 7.5 \text{ cm} \quad a = 1.25 \text{ cm}^2 \quad \text{and} \quad c = 0.1 \text{ mol dm}^{-3}$$

Let us first find the quantity of charge (Q) passed from the coulometer data.

We know that 1 F of charge would have deposited 107.88 g of silver. In other words

$$107.88 \text{ g Ag} \equiv 96485 \text{ C}$$

$$\Rightarrow 0.12 \text{ g Ag} \equiv \frac{96485 \text{ C} \times 0.12 \text{ g}}{107.88 \text{ g}} = 107.32 \text{ C}$$

Substituting the data in the expression for t_+ , we get

$$t_+ = \frac{10^{-3} \times 7.5 \text{ cm} \times 1.25 \text{ cm}^2 \times 0.1 \text{ mol dm}^{-3} \times 96485 \text{ C mol}^{-1}}{107.32 \text{ C}} = 0.84$$

Once we know the transference number of hydrogen ions, we can calculate the same for chloride ions as

$$\Rightarrow t_- = 1 - 0.84 = 0.16$$

The data on measurements of the transference number over a range of concentration of electrolyte in dilute solutions shows that the plot between the transference number versus square root of concentration is linear. The plot can be extrapolated to $c = 0$ to obtain the value of the transference number at infinite dilution.

Having learnt about transference numbers and their experimental determination let us take up different applications of conductivity measurements. However, before that solve the following simple questions to assess your understanding.

SAQ 5

What is an indicator electrolyte? What is its role in moving boundary method?

SAQ 6

In the determination of transference number of Li^+ ion by moving boundary method a 0.10 M solution of LiCl was taken in a cell having uniform area of cross section of 1.17 cm^2 . At the end of experiment the boundary moved by 2.1 cm and 0.083 g of silver was deposited on the cathode of silver coulometer. Calculate the transference numbers Li^+ ion.

6.4 APPLICATIONS OF CONDUCTIVITY MEASUREMENTS

Conductivity measurement finds application in several analytical determinations. In Unit 5 you have learnt about Kohlrausch's law of independent migration of ions according to which at infinite dilution, where all electrolytes (strong or weak) are completely ionised and the interionic effects do not exist, each ion migrates independently of its co-ion. There are a number of important applications of conductivity measurement based on Kohlrausch's law of independent migration of ions. Some of these are

- Determination of ionisation constant for a weak acid
- Determination of solubility and solubility product of sparingly soluble salts
- Determination of ionic product of water
- Determination of hydrolysis constant of a salt

Let's learn about these applications of conductivity measurements one by one

6.4.1 Determination of Ionisation Constant of a Weak Acid

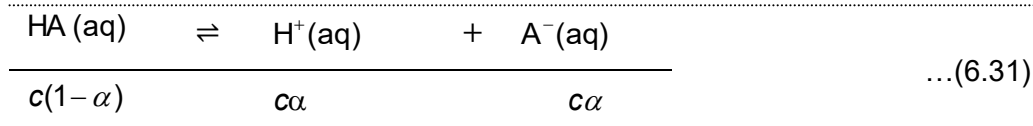
As discussed in Unit 5, the molar conductivity of a weak electrolyte (e.g., a weak acid) at a given concentration is low due to its partial ionisation. The molar conductivity increases with dilution due to further ionisation and at infinite dilution it becomes maximum where the ionisation is complete (100%). We can therefore say that the ratio of molar conductivity of a weak electrolyte at a given concentration to that at infinite dilution would be a measure of degree of ionisation of the weak electrolyte. In other words, we can say that

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} \quad \dots(6.29)$$

The ionisation of a weak acid HA can be represented as



If the degree of ionisation of the acid having concentration as $c \text{ mol dm}^{-3}$ is α then the equilibrium concentrations of different species would be



You would recall from Unit 8 of BCHCT-133 course that the ionisation constant of a weak acid (a weak electrolyte) is given as

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \quad \dots(6.32)$$

Where, c is the concentration and α is the degree of ionisation of the weak acid. Substituting the expression for α in ionisation constant expression and simplifying we get

$$K_a = \frac{c \left(\frac{\Lambda_m^c}{\Lambda_m^0} \right)^2}{\left(1 - \frac{\Lambda_m^c}{\Lambda_m^0} \right)} = \frac{c(\Lambda_m^c)^2}{(\Lambda_m^0)^2 \left(\frac{\Lambda_m^0 - \Lambda_m^c}{\Lambda_m^0} \right)} = \frac{c(\Lambda_m^c)^2}{(\Lambda_m^0)(\Lambda_m^0 - \Lambda_m^c)} \quad \dots(6.33)$$

Let us take an example to see its application.

Example 6.4: The molar conductivity of a 0.1 M aqueous solution of acetic acid is found to be 5.3 S cm² mol⁻¹. If the molar conductivity at infinite dilution for acetic acid is 390.5 S cm² mol⁻¹, calculate the ionisation constant of acetic acid.

Solution: We are given the following data:

$$c = 0.1 \text{ M}, \Lambda_m^c = 5.3 \text{ S cm}^2 \text{ mol}^{-1} \text{ and } \Lambda_m^0 = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

We know from Eq. (6.33) that ionisation constant is given as

$$K_a = \frac{c(\Lambda_m^c)^2}{(\Lambda_m^0)(\Lambda_m^0 - \Lambda_m^c)}$$

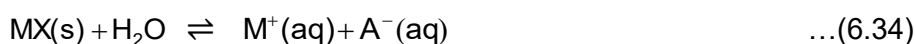
Substituting the values in the above expression we get

$$K_a = \frac{0.1 (5.3 \text{ S cm}^2 \text{ mol}^{-1})^2}{(390.5 \text{ S cm}^2 \text{ mol}^{-1})(390.5 - 5.3) \text{ S cm}^2 \text{ mol}^{-1}}$$

$$K_a = 1.87 \times 10^{-5}$$

6.4.2 Determination of Solubility and Solubility Product of Sparingly Soluble Salts

You would recall from Unit 9 of the BCHCT-133 course that when a sparingly soluble salt MX is added to water an extremely small fraction of it dissolves and generates ions by dissociation. These ions may combine back to give solid salt. Over a period of time an equilibrium is established between the ions obtained from the dissociation of dissolved salt and the solid salt i.e., we get a saturated solution of the salt along with the undissolved solid salt. Such equilibrium for a salt of MX type in aqueous solution can be represented as



As the salt happens to be sparingly soluble, i.e., having extremely low solubility and all the dissolved salt is ionised we can say that the solution can

be taken to be at infinite dilution. In other words, the measured molar conductivity will be same as the molar conductivity at infinite dilution. We know that

$$\text{Molar conductivity} = \frac{1000\text{cm}^3\text{dm}^{-3}\kappa}{c} \text{Scm}^2\text{mol}^{-1} \quad \dots(6.35)$$

If, s is the molar solubility of the sparingly soluble salt i.e., $c = s$, we can write

$$\text{Molar conductivity} = \Lambda_m = \frac{1000\text{cm}^3\text{dm}^{-3}\kappa}{s} \text{Scm}^2\text{mol}^{-1} \quad \dots(6.36)$$

Equating the measured molar conductivity with molar conductivity at infinite dilution, we get

$$= \Lambda_m^0 = \frac{1000\text{cm}^3\text{dm}^{-3}\kappa}{s} \text{Scm}^2\text{mol}^{-1} \quad \dots(6.37)$$

Rearranging, the expression for solubility becomes

$$s = \frac{1000\text{cm}^3\text{dm}^{-3}\kappa(\text{Scm}^{-1})}{\Lambda_m^0(\text{Scm}^2\text{mol}^{-1})} = \frac{1000\kappa}{\Lambda_m^0} \quad \dots(6.38)$$

The molar conductivity at infinite dilution can be obtained by using the molar conductivities of the respective ions at infinite dilution by the following expression.

$$\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0 \quad \dots(6.39)$$

For the salt, MX we can write

$$\Lambda_m^0(\text{MX}) = \lambda_m^0(\text{M}^+) + \lambda_m^0(\text{X}^-) \quad \dots(6.40)$$

The solubility product of the sparingly soluble salt (MX) can be written as

$$K_{\text{SP}} = [\text{M}^+][\text{X}^-] = s^2 \quad \dots(6.41)$$

Substituting the value of solubility in the solubility product expression, the solubility product for the salt MX can be obtained as

$$\text{Solubility product} = K_{\text{SP}} = \left(\frac{1000\kappa}{\Lambda_m^0} \right)^2 (\text{mol}^2 \text{dm}^{-6}) \quad \dots(6.42)$$

We have taken a 1:1 salt as an example; similar expressions can be obtained for other types of salts.

Note: It is important to note here that since the solubility of sparingly soluble salt is extremely low, its solution will have very low value of conductivity. In such a case we cannot ignore the conductivity of water used for preparing the solution. Therefore, the value of conductivity to be used in the expression for solubility and solubility product must be corrected for water. That is,

$$\kappa(\text{salt}) = \kappa(\text{solution}) - \kappa(\text{water}) \quad \dots(6.43)$$

Let us understand it with the help of an example.

Example 6.5: The conductivity of a saturated solution of AgCl in water (having conductivity = $1.06 \times 10^{-6} \text{ S cm}^{-1}$) at a temperature of 291 K was found to be $= 2.47 \times 10^{-6} \text{ S cm}^{-1}$. The molar conductivities of AgNO₃, NaCl and NaNO₃ at infinite dilution are given as 133.5,

126.3 and 121.6 S cm² mol⁻¹ respectively. Calculate the solubility and solubility product of AgCl.

Solution: According to Eq. (6.38) the solubility in mol dm⁻³, conductivity and molar conductivity at infinite dilution are related as

$$s = \frac{1000 \text{ cm}^3 \text{ dm}^{-3} \times \kappa (\text{S cm}^{-1})}{\Lambda_m^0 (\text{S cm}^2 \text{ mol}^{-1})}$$

Let us first calculate the conductivity of the salt. As per Eq. (6.43) the conductivity is given as

$$\kappa(\text{salt}) = \kappa(\text{solution}) - \kappa(\text{water})$$

Substituting the values, we get

$$\kappa(\text{AgCl}) = (2.47 \times 10^{-6} \text{ S cm}^{-1}) - (1.06 \times 10^{-6} \text{ S cm}^{-1}) = 1.41 \times 10^{-6} \text{ S cm}^{-1}$$

Now, the molar conductivity at infinite dilution can be obtained by using Kohlrausch's law of independent migration of ions as follows:

$$\Lambda_m^0(\text{AgCl}) = \Lambda_m^0(\text{AgNO}_3) + \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NaNO}_3)$$

Substituting the values

$$\Lambda_m^0(\text{AgCl}) = (133.5 + 126.3 - 121.6) \text{ S cm}^2 \text{ mol}^{-1} = 138.2 \text{ S cm}^2 \text{ mol}^{-1}$$

Substituting the values of conductivity and molar conductivity at infinite dilution in Eq. (6.38) we get

$$s = \frac{1000 \text{ cm}^3 \text{ dm}^{-3} \times \kappa (\text{S cm}^{-1})}{\Lambda_m^0 (\text{S cm}^2 \text{ mol}^{-1})} = \frac{1000 \times 1.41 \times 10^{-6} \text{ S cm}^{-1}}{138.2 \text{ S cm}^2 \text{ mol}^{-1}} = 1.02 \times 10^{-5} \text{ mol dm}^{-3}$$

Now for AgCl the expression for solubility product can be written as

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = s^2$$

Substituting the value of solubility, we get

$$K_{sp} = (1.02 \times 10^{-5} \text{ mol dm}^{-3})^2 = 1.04 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

SAQ 7

The molar conductivity of 0.01 M solution of acetic acid at 298 K was found to be = 6.80 S cm²mol⁻¹. If the molar conductivities of hydrogen and acetate ions at infinite dilutions are = 349.8 and 40.9 S cm²mol⁻¹, respectively. What percentage of acetic acid is ionised at this temperature and concentration?

SAQ 8

Derive an expression for the solubility product of the salt MX₂ from conductivity measurement; assuming the solubility to be s mol dm⁻³.

6.4.3 Determination of Ionic Product of Water

You have learnt in the Unit-7 of BCHCT-133 course that water is amphoteric in nature i.e., it can act as a weak acid as well as a weak base. In a sample of water, a small number of water molecules donate a proton (thus acting as an

acid), which is accepted by equal number of other water molecules (acting as base) as shown below



As a consequence, a small concentration of H_3O^+ ions and OH^- ions are formed in a sample of water and this process is called autoprotolysis (or autoionisation) of water. The product of the molar concentrations of H_3O^+ and OH^- ions in pure water sample at a given temperature is called the ionic-product constant of water and is denoted as K_w

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \dots(6.45)$$

We know that

$$\Lambda = \frac{\kappa}{c}$$

If we express κ in the units of S m^{-1} and c in mol m^{-3} , then, $\kappa = c\Lambda$

The value of K_w can be experimentally determined from the measurement of electrical conductivity of highly purified samples of distilled water. From Eq. (6.44) we can see that the concentrations of hydrogen and hydroxide ions are equal. So, we can write,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = (K_w)^{1/2} \quad \dots(6.46)$$

On the other hand, the conductivity of pure water is related to the concentration of ions by the following equation.

$$\kappa(\text{H}_2\text{O}) = \kappa(\text{H}^+) + \kappa(\text{OH}^-) \Rightarrow \kappa(\text{H}_2\text{O}) = [\text{H}_3\text{O}^+]\lambda_{\text{H}} + [\text{OH}^-]\lambda_{\text{OH}^-} \quad \dots(6.47)$$

Substituting for the concentration of hydronium and hydroxide ions we can write,

$$\kappa(\text{H}_2\text{O}) = (K_w)^{1/2} (\lambda_{\text{H}^+} + \lambda_{\text{OH}^-}) \quad \dots(6.48)$$

Since the degree of ionisation of water is exceedingly small, the concentration of the ions is also exceedingly small. Therefore, the conductivity of the ions can be taken to be at infinite dilution. We can then write,

$$\kappa(\text{H}_2\text{O}) = (K_w)^{1/2} (\lambda_{\text{H}^+}^0 + \lambda_{\text{OH}^-}^0) \quad \dots(6.49)$$

The value of $\kappa(\text{H}_2\text{O})$ has been found to be $5.5 \times 10^{-6} (\text{S m}^{-1})$ by Kohlrausch and Heydweiller. Substituting this value in the above equation along with the molar ionic conductivities of hydrogen and hydroxide ions we get

$$5.5 \times 10^{-6} (\text{S m}^{-1}) = (K_w)^{1/2} (349.81 \times 10^{-4} + 198.3 \times 10^{-4}) \text{S m}^2 \text{mol}^{-1} \quad \dots(6.50)$$

Rearranging we get,

$$(K_w)^{1/2} = \frac{5.5 \times 10^{-6} (\text{S m}^{-1})}{(548.1 \times 10^{-4}) \text{S m}^2 \text{mol}^{-1}} \quad \dots(6.51)$$

Taking squares, we get

$$(K_w) = \left[\frac{5.5 \times 10^{-6} (\text{S m}^{-1})}{(548.1 \times 10^{-4}) \text{S m}^2 \text{mol}^{-1}} \right]^2 = 1.007 \times 10^{-8} \text{mol}^2 \text{m}^{-6} \quad \dots(6.52)$$

$$(K_w) = 1.007 \times 10^{-8} \text{mol}^2 \text{m}^{-6} = 1.007 \times 10^{-14} \text{mol}^2 \text{dm}^{-6} \quad \dots(6.53)$$

Thus, we find that the value of ionic product of water at 298 K is found to be $1.007 \times 10^{-14} \text{mol}^2 \text{dm}^{-6}$ on the basis of conductance measurements.

$$\begin{aligned} 1 \text{ mol m}^{-3} &= \frac{1 \text{ mol}}{\text{m}^3} \\ &= \frac{1 \text{ mol}}{(10 \text{ dm})^3} \\ &= \frac{1 \text{ mol}}{1000 \text{ dm}^3} \\ &= 10^{-3} \text{ mol dm}^{-3} \\ (1 \text{ mol m}^{-3})^2 &= (10^{-3} \text{ mol dm}^{-3})^2 \\ &= 10^{-6} \text{ mol}^2 \text{dm}^{-6} \end{aligned}$$

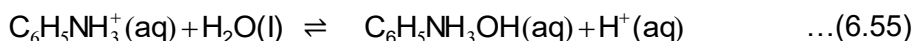
However, generally $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ is used as the value of ionic product of water at 298 K.

6.4.4 Determination of Hydrolysis Constant of a Salt

You have learnt in Unit 9 of BCHCT-133 course that the reaction of anions or/and cations produced by the salts with water is called **salt hydrolysis**. On hydrolysis, the anions of weak acids produce the conjugate acid and hydroxide ion whereas the cations of weak bases give the conjugate base and hydronium ion. For example, let us take the hydrolysis of the salt anilinium hydrochloride—a salt of weak base and strong acid. The salt would ionise as



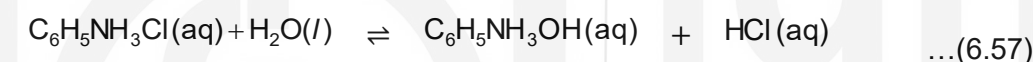
The anilinium ion so produced would react with water and get hydrolysed as



The overall reaction of anilinium hydrochloride with water can be given as



If we start with 1 mol dm^{-3} of the salt and assume that the degree of hydrolysis of the salt at this concentration is α , then at equilibrium the concentration of different species would be



$(1 - \alpha)$	α	α
----------------	----------	----------

If we further assume that the base $\text{C}_6\text{H}_5\text{NH}_3\text{OH}$ obtained by hydrolysis is very weak and does not ionise appreciably. Therefore, it will not contribute to the conductivity of the solution. Thus, the conductivity (Λ) of the solution would be due to $(1 - \alpha)$ moles of the salt that is ionised but not hydrolysed, and α moles of the strong acid (HCl). We can write,

$$\Lambda = (1 - \alpha)\Lambda_{\text{salt}} + \alpha\Lambda_{\text{HCl}}^0 \quad \dots(6.58)$$

Where, Λ_{HCl}^0 is the molar conductivity of hydrochloric acid at infinite dilution. As it is a strong acid, it is assumed to be completely ionised. The molar conductivity (Λ) of the solution can be experimentally measured. On the other hand, Λ_{salt} , the molar conductivity of anilinium hydrochloride when it is ionised but not hydrolysed can be obtained by measuring the conductivity of the salt in presence of excess of aniline. This would completely suppress the hydrolysis of the salt. Once these values are known, these can be substituted in the expression and the value of degree of hydrolysis can be obtained as follows.

$$\Lambda_{\text{solution}} = (1 - \alpha)\Lambda_{\text{salt}} + \alpha\Lambda_{\text{HCl}}^0 \quad \dots(6.59)$$

By rearranging, we get

$$\Lambda_{\text{solution}} - \Lambda_{\text{salt}} = \alpha(\Lambda_{\text{HCl}}^0 - \Lambda_{\text{salt}}) \quad \dots(6.60)$$

This gives,

$$\alpha = \frac{\Lambda_{\text{solution}} - \Lambda_{\text{salt}}}{(\Lambda_{\text{HCl}}^0 - \Lambda_{\text{salt}})} \quad \dots(6.61)$$

Now, for the equilibrium reaction given in Eq. (6.57) we can write the expression for hydrolysis constant as

$$K_h = \frac{\alpha^2}{(1-\alpha)} \quad \dots(6.62)$$

Substituting the value of α we can calculate hydrolysis constant. Let's understand it with the help of an example.

Example 6.6: The molar conductivity of a 0.011 M solution of aniline hydrochloride was observed to be $120 \text{ S cm}^2 \text{ mol}^{-1}$. The solution on saturating with excess of aniline reduced the molar conductivity to $104 \text{ S cm}^2 \text{ mol}^{-1}$. If the molar conductivity of HCl at infinite dilution is $410 \text{ S cm}^2 \text{ mol}^{-1}$, calculate the degree of hydrolysis and the hydrolysis constant for aniline hydrochloride.

Solution: We are given

$$\Lambda_{\text{solution}} = 120 \text{ S cm}^2 \text{ mol}^{-1}; \quad \Lambda_{\text{salt}} = 104 \text{ S cm}^2 \text{ mol}^{-1}; \quad \text{and} \quad \Lambda_{\text{HCl}}^0 = 410 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{From Eq. (6.61) we know that } \alpha = \frac{(\Lambda_{\text{solution}} - \Lambda_{\text{salt}})}{(\Lambda_{\text{HCl}}^0 - \Lambda_{\text{salt}})}$$

Substituting the values, we get

$$\alpha = \frac{(120 - 104) \text{ S cm}^2 \text{ mol}^{-1}}{(410 - 104) \text{ S cm}^2 \text{ mol}^{-1}} = 0.052$$

$$\text{From Eq. (6.62) we have, } K_h = \frac{\alpha^2}{(1-\alpha)}$$

Since the degree of hydrolysis is exceedingly small, we can ignore it in the denominator and also the concentration in this problem is different from 1 so we can write

$$K_h = c\alpha^2$$

Substituting the value of α , and c we get

$$K_h = 0.011 \times (0.052)^2 = 2.97 \times 10^{-5}$$

Thus, the degree of hydrolysis and hydrolysis constants would be 0.052 and 2.97×10^{-5} respectively.

In addition, the conductance measurements can also be used for the determination of equivalence point in a number of titrimetric determinations. Let us learn about the principle of different titrimetric determinations using conductance measurements.

6.5 CONDUCTOMETRIC TITRATIONS

As discussed in Unit 5, the electrical conductance of a solution is a measure of its current carrying capacity of the ions present in the solution. It is determined by the type and concentration of ions present in the solution. In the conductometric titrations we measure the conductance of analyte solution as a function of the volume of titrant added and use it for the determination of equivalence point of the titration. This method of the determination of equivalence point becomes relevant when either the solutions are of very low

concentration or the analyte sample has a dark colour that does not permit the use of common visual indicators.

In a typical conductometric titration the ionic species to be determined are converted to non-ionic forms by a suitable reaction. For this purpose, a measured volume of the solution to be titrated is taken in a beaker and a conductivity cell is dipped into it. The titrant is added from a burette into the solution and the conductance readings corresponding to the various additions of the titrant are measured and plotted against the volume of the titrant. This is then used to determine the equivalence point. Conductometric determination of the equivalence point is commonly employed for acid-base and precipitation titrations. Let us learn about these.

Acid-base titrations

In a typical determination of an acid, the hydrogen ions, mainly responsible for the conductance, can be neutralised by reacting with a base in an acid-base titration. Let us understand the changes in the conductance of the solution of a strong acid say hydrochloric acid with a strong base like sodium hydroxide. To begin with, in an aqueous solution of hydrochloric acid, the conductance will be due to the hydrogen ions and chloride ions obtained by the ionisation of the acid.



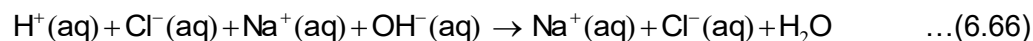
As you know, the hydrogen ions have extremely high conductivity (due to small size and Grotthus mechanism) whereas the chloride ions are bulkier and relatively slow moving. Therefore, to begin with, the solution containing hydrochloric acid would have high conductance. When we add a solution of sodium hydroxide, it would provide slow moving sodium ions and hydroxide ions with high mobility as follows.



The hydroxide ions provided by NaOH would neutralise the hydrogen ions and produce practically unionised water molecules as per the following reaction.



The overall reaction can be given as



If we see the ions in the reaction carefully, we find that effectively the hydrogen ions having high conductivity are replaced by relatively slow-moving sodium ions. As a consequence, the conductance of the solution would decrease. Adding more and more amount of NaOH solution would neutralise more and more of hydrogen ions and the conductance would continue to decrease. This trend would continue till all the hydrogen ions are neutralised i.e., the equivalence point is reached.

Adding a drop of NaOH solution at this stage would provide additional sodium ions and hydroxide ions. Therefore, the conductance of the solution would start to increase; and the trend would continue with addition of more and more of NaOH solution. If we plot a graph between the conductance of the solution versus the volume of NaOH solution, we will get the titration curve as given in Fig. 6.7 (a).

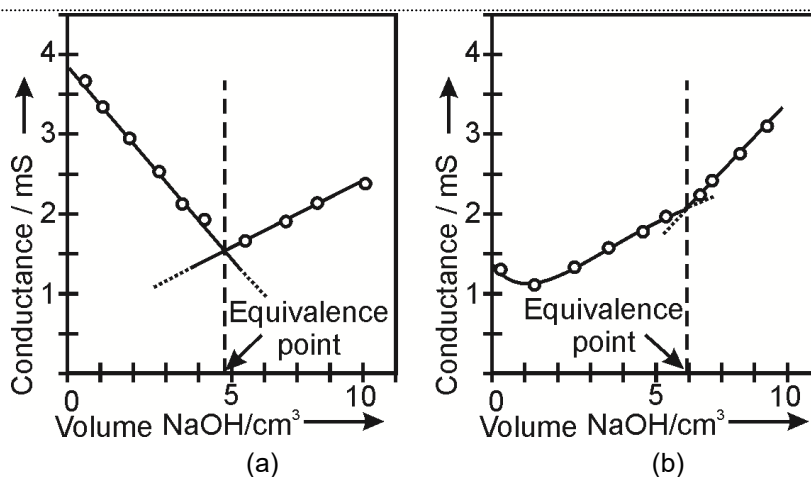
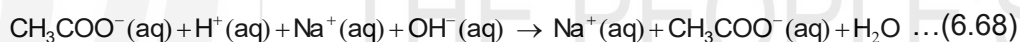


Fig. 6.7: Schematic graphs showing the expected conductometric titration curves for a) HCl versus sodium hydroxide and b) acetic acid versus sodium hydroxide titration.

Let us consider another example, viz. conductometric titration between acetic acid (a weak acid) and NaOH (a strong base). To begin with, in an aqueous solution of acetic acid, the conductance will be due to the hydrogen ions and acetate ions obtained from the ionisation of the acid as given below.



As the acid is weak there will be a small fraction of acetic acid in the ionised form accordingly the solution will have a low concentration of hydrogen ions and acetate ions. Therefore, the overall conductance will be low. On adding a drop of sodium hydroxide, the few hydrogen ions present will combine with the hydroxide ions provided by the base as shown below.



Effectively, what happens is that the fast-moving hydrogen ions are replaced by slower sodium ions and the conductance decreases a bit. The acetate ions will suppress the ionisation of acetic acid by common ion effect. Once all the free hydrogen ions are neutralised, further addition of sodium hydroxide reacts with the unionised acetic acid molecules. The reaction can be represented as follows.



As a result of the reaction, the number of ions in the solution would increase and the conductance would also increase.

With the addition of more and more of sodium hydroxide this process will continue, and the conductance of the solution will continue to increase gradually. This process will continue till the equivalence point where all the undissociated acetic acid would have reacted with the base. The solution at this stage will contain sodium and acetate ions in concentration equal to the initial concentration of the acetic acid.

As in case of titration of HCl, any further addition of sodium hydroxide will provide additional sodium and hydroxide ions. This would cause a further increase in the conductance of the solution. However, as the hydroxide ions have quite a high mobility, the increase in the conductance now will be much

faster. This change in the rate of increase of the conductance marks the equivalence point of the titration. A typical conductometric titration curve expected for the titration of acetic acid and sodium hydroxide is given in Fig. 6.7(b).

As you have learnt earlier that in the measurement of conductance, we measure the conductance of all the ions present in the column of solution contained within the electrodes of the conductivity cell. During the titration, the measured conductance changes due to the change in the concentration of the ions in the region due to the reaction taking place. In addition to the reaction, the dilution of the solution during the titration also affects the conductance. It is, therefore, advantageous to use a titrant solution in a relatively higher concentration. Generally, in conductometric titrations the titrant is taken about ten times stronger than the titrand to minimise the dilution effect.

Precipitation titrations

As a typical case of conductometric precipitation titrations, we take the example of titration of BaCl_2 with sulphuric acid. A schematic titration curve for the titration of barium chloride with sulphuric acid is given in Fig.6.8.

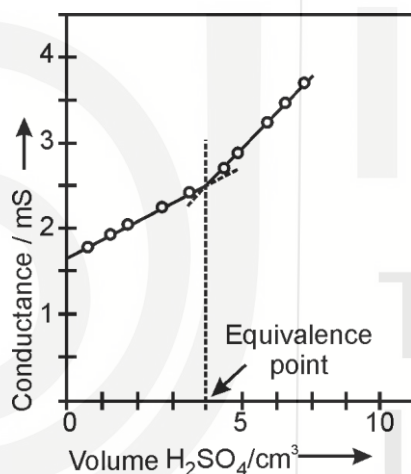
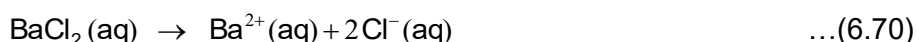
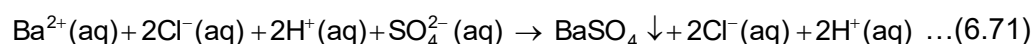


Fig. 6.8: A schematic graph showing the expected conductometric titration curve for barium chloride versus sulphuric acid titration.

Let us understand the changes in the conductance of the solution of barium chloride during its titration with sulphuric acid. In a solution containing barium chloride, initially the conductance of the solution is due to the barium and chloride ions obtained from the dissociation of BaCl_2 . Barium chloride being a strong electrolyte is completely dissociated; dissociation of one mole of barium chloride generates one mole of barium ions and two moles of chloride ions as per the following equation.



Addition of sulphuric acid provides hydrogen ions and sulphate ions. The sulphate ions precipitate out the barium ions as per the following equation.



The net result of the reaction is that each barium ion present in the solution is replaced by two hydrogen ions. As the conductivity of two hydrogen ions is much more than that of a single barium ion; the conductance of the solution

increases. This trend continues with further addition of the titrant sulphuric acid. Once all the barium ions are precipitated i.e., at the equivalence point, further addition of the titrant provides additional ions in the form of sulphate and hydrogen ions. This leads to a sharper increase in the solution conductance. This switchover from a slower increase in conductance to a sharper increase in the conductance marks the equivalence point. Let us sum up what we have discussed in this unit. However, before that answer the following simple question to assess your learning of conductometric titration.

SAQ 9

Draw a schematic conductometric titration curve for the neutralisation of oxalic acid by NaOH.

6.6 SUMMARY

In this unit we continued our discussion on electrolytic conduction and took up two main aspects viz., the migration of ions and the application of conductance measurements. We started the unit by discussing about migration of ions in an electrolytic solution under the influence of applied potential. In this context we introduced the concepts of ionic mobility and transference numbers. The ionic mobility has been defined as the velocity with which an ion moves in a solution under a potential gradient of 1 V m^{-1} whereas transference numbers refer to the fraction of total current carried by a given type of ion in solution. We established relationship between the two. This was followed by a discussion on the principle and experimental determination of transference numbers. Herein, we have explained in detail the principles of Hittorf's method and moving boundary method and described the procedure for the determination of transference numbers by these methods. We used examples to clarify these methods.

In the context of applications of conductivity measurement, we took up a number of applications, like determination of ionisation constant of a weak acid, determination of solubility and solubility product of sparingly soluble salts, determination of ionic product of water and determination of hydrolysis constant of a salt. In addition to explaining the principle of these applications we showed their importance with the help of examples. In the end we took up another important application of conductivity measurement, viz., conductometric titrations and discussed their significance.

6.7 TERMINAL QUESTIONS

1. List and explain different factors affecting ionic mobility.
2. Explain exceptionally high ionic mobilities of hydrogen ions.
3. The molar ionic conductivities of Li^+ ions and Na^+ ions at 298 K are $3.87 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$ and $5.01 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$ respectively. Calculate their ionic mobilities.
4. In the determination of transport number, a solution of silver nitrate having 1.19 mg of silver nitrate per gram of water was taken in the Hittorf cell using silver electrodes. After a certain amount of current was passed for enough time, 20.37 mg of silver was deposited on the cathode. An

analysis of the solution from anode compartment showed that the solution contained 18 g of water and 38.8 mg of silver nitrate. Calculate the transport number of the silver and nitrate ions.

5. The molar conductivity of 0.001028 M acetic acid solution at 298 K is observed to be $48.15 \text{ S cm}^{-2} \text{ mol}^{-1}$. If the same at infinite dilution is found to be $390.6 \text{ S cm}^{-2} \text{ mol}^{-1}$ calculate the degree of ionisation of acetic acid at this concentration.
6. The conductivity of a saturated solution of AgCl at 298 K was found to be $3.41 \times 10^{-6} \text{ S cm}^{-1}$. The water used for dissolving AgCl had a conductivity of $1.6 \times 10^{-6} \text{ S cm}^{-1}$. If the molar conductivity at infinite dilution for AgCl at 298 K is given as $138.2 \text{ S cm}^{-2} \text{ mol}^{-1}$ calculate the solubility and solubility product of AgCl at 298 K.
7. Draw and explain the conductometric titration curve for the titration between formic acid and NaOH.

6.8 ANSWERS

Self-Assessment Questions

1. The ionic mobility may be defined as the velocity with which an ion in a solution would move under a potential gradient of 1 V m^{-1} . It is denoted as u and its SI unit is $\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$.
2. The transference number is defined as the fraction of total current carried by a given type of ion in solution. The transference numbers of cation and anion are denoted as t_+ and t_- respectively. The transference numbers and ionic mobilities are related as under

$$t_+ = \frac{u_-}{u_+ + u_-} \quad \text{and} \quad t_- = \frac{u_+}{u_+ + u_-}$$

where, u_+ and u_- respectively are the ionic mobilities of the cation and the anion.

3. In this case copper sulphate is electrolysed using copper electrodes so copper ions proportional to the total current passed in the solution (as determined from the coulometer) would deposit on the cathode thereby decreasing their concentration by same amount. However, copper ions proportional to their transport number would move away from anode compartment and move into the cathode compartment and increase their concentration.

Let us first calculate the total amount of current passed:

The amount of silver deposited in the coulometer = 0.0405 g

We know that $107.88 \text{ g Ag} \equiv 1 \text{ Faraday}$

$$\rightarrow 0.0405 \text{ g Ag} = \frac{1 \times 0.0405}{107.88} = 3.75 \times 10^{-4} F$$

As copper ion has a charge of 2 units, $3.75 \times 10^{-4} F$ of current would deposit

$$= \frac{3.75 \times 10^{-4}}{2} = 1.877 \times 10^{-4} \text{ moles of Cu}^{2+} \text{ ion}$$

i.e., 1.87×10^{-4} mol of copper sulphate will be lost from the cathodic compartment.

It is given that the cathodic compartment after electrolysis has 0.44125 g of Cu^{2+} ions; this is equivalent to

$$= \frac{0.44125 \times 159.6}{63.5} = 1.1090 \text{ g of CuSO}_4$$

Mass of water in cathodic compartment = $36.4340 - 1.1090 = 35.3250$ g

Initially, the solution was 0.2 molal i.e., 0.2×159.6 g of CuSO_4 per kg of water

The mass of CuSO_4 initially in 35.3250 g of water was

$$= \frac{0.2 \times 159.6}{1000} \times 35.3250 = 1.1276 \text{ g}$$

Loss in the mass of $\text{CuSO}_4 = 1.1276 - 1.1090 \text{ g} = 0.0186 \text{ g}$

$$= \frac{0.0186 \text{ g}}{159.6 \text{ g mol}^{-1}} = 0.0001165 \text{ mol}$$

The expected loss of copper sulphate in the cathodic compartment due to passage of current was 1.877×10^{-4} mol. However, the observed loss is just 1.165×10^{-4} mol.

→ $(1.877 - 1.165) \times 10^{-4} \text{ mol} = 7.12 \times 10^{-5} \text{ mol}$ of Cu^{2+} ions have migrated into the cathodic compartment or have carried the current.

We know that transference number of cation is

$$t_+ = \frac{\text{Moles of electrolyte lost from the anodic compartment}}{\text{Total number of moles of electrolyte lost}}$$

Substituting the values,

$$t_+ = \frac{0.712 \times 10^{-4}}{1.877 \times 10^{-4}} = 0.379$$

$$t_- = 1 - t_+ = 1.0 - 0.379 = 0.621$$

Thus, the transport numbers of copper and sulphate ions have been found to be 0.379 and 0.621 respectively

4. The methods generally employed for the experimental determination of transference numbers are
 - Hittorf's method
 - Moving boundary method
 - Emf measurement method
5. In moving boundary method for the determination of transference number of the ions of an electrolyte (called principal electrolyte) the additional electrolyte that is used to create a boundary is called indicator electrolyte. An indicator electrolyte must have anion or cation common with the

electrolyte being determined and the other ion should not move faster than the ion whose transport number is to be determined.

6. We know that for determination of transference number by moving boundary method,

$$t_+ = \frac{10^{-3} \times l \times a \times c \times F}{Q}$$

We have been given the values as:

$$l = 2.1 \text{ cm} \quad a = 1.17 \text{ cm}^2 \quad \text{and} \quad c = 0.10 \text{ mol dm}^{-3}$$

Let us first find the value of Q (amount of charge passed) from the coulometer data. We know that 1 F of charge would have deposited 107.88 g of silver. In other words

$$107.88 \text{ g Ag} = 96485 \text{ C} \Rightarrow 1 \text{ g Ag} = \frac{96485}{107.88} \text{ C}$$

$$0.083 \text{ g Ag} = \frac{96485 \times 0.083}{107.88} = 74.23 \text{ C}$$

Substituting the data in the expression, we get

$$t_+ = \frac{10^{-3} \times 2.1 \text{ cm} \times 1.17 \text{ cm}^2 \times 0.10 \text{ mol dm}^{-3} \times 96485 \text{ C mol}^{-1}}{74.23 \text{ C}} = 0.319 = 0.32$$

$$t_- = 1 - 0.32 = 0.68$$

7. We are given:

$$c = 0.01 \text{ M}, \quad \Lambda_m^c = 16.8 \text{ S cm}^2 \text{ mol}^{-1}$$

First, we calculate the molar conductivity of acetic acid at infinite dilution by using Kohlrausch's law. According to the law, the molar conductivity for acetic acid can be calculated as given below

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = \lambda_m^0(\text{H}^+) + \lambda_m^0(\text{CH}_3\text{COO}^-) = (349.8 + 40.9) \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{\text{CH}_3\text{COOH}}^0 = 390.7 \text{ S cm}^2 \text{ mol}^{-1}$$

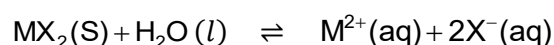
Further, we know that the percent ionisation of a weak electrolyte is given as

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} \times 100\%$$

Substituting the values, we get

$$\alpha = \frac{16.8 \text{ S cm}^2 \text{ mol}^{-1}}{390.7 \text{ S cm}^2 \text{ mol}^{-1}} \times 100\% = 4.30\%$$

8. If we dissolve a sparingly soluble salt of MX_2 type in water the solubility equilibrium can be represented as



The corresponding expression for K_{sp} would be : $K_{sp} = [M^{2+}][X^-]^2$

As the salt has extremely low solubility, we can assume that all the dissolved salt is ionised and the measured molar conductivity will be same as the molar conductivity at infinite dilution. We can therefore write

$$\text{Molar conductivity} = \Lambda_m = \frac{1000\kappa}{s} = \text{Scm}^2 \text{mol}^{-1} = \Lambda_m^0$$

Where, s is the molar solubility of the sparingly soluble salt,

Rearranging and simplifying,

$$s = \frac{1000\text{cm}^3 \text{dm}^{-3} \times \kappa (\text{Scm}^{-1})}{\Lambda_m^0 (\text{Scm}^2 \text{mol}^{-1})}$$

The molar conductivity at infinite dilution can be obtained by using the molar conductivities of the respective ions at infinite dilution by the following expression.

$$\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$$

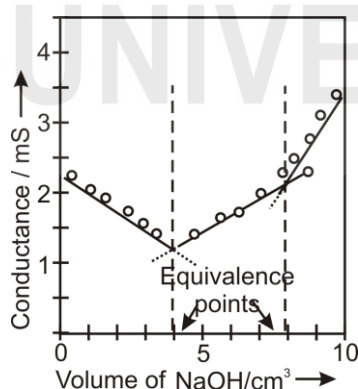
For the salt, MX_2 we can write,

$$\Lambda_m^0(\text{MX}_2) = \lambda_m^0(\text{M}^+) + 2\lambda_m^0(\text{X}^-)$$

Substituting the value of solubility in the solubility product expression, we get

$$K_{sp} = s(2s)^2 = 4s^3 = 4 \left(\frac{1000\kappa}{\Lambda_m^0} \right)^3 (\text{mol}^3 \text{dm}^{-9})$$

9. A schematic conductometric titration curve for the titration between oxalic acid and NaOH is given below



There will be two equivalence points corresponding to the stepwise neutralisation of diprotic oxalic acid.

Terminal Questions

- The ionic mobility of an ion depends on the following factors:
 - Charge on the ion
 - Size of the ion
 - Viscosity of the medium

An ion with a higher charge has higher ionic mobility because it would experience a greater force due to electric field under which it is moving. The force experienced is given as ($F = zeE$) where z is the charge on the ion, e is the elementary charge and E is the electric field strength. Secondly, a smaller ion has higher ionic mobility because it experiences lesser friction with solvent molecules and other ions due to smaller surface area. Thirdly, the ions slow down in a medium of higher viscosity due to greater retardation force due to friction.

- The exceptionally high ionic mobilities of hydrogen ions can be explained in terms of Grotthuss conduction mechanism. According to this mechanism the proton in solution binds to a neighbouring water molecule and momentarily converts it to a hydronium ion. This in turn transfers its proton to another water molecule in neighbourhood which does the same to another molecule and this process continues. As a result, a proton in any region of the solution is effectively transported quickly to another part. This mechanism is also known as proton hopping mechanism.

- We know that the ionic conductivity λ is related to ionic mobility (u) as follows

$$\lambda = zuF$$

Where, z is the charge on the ion and F is the Faraday's constant.

The ionic mobilities can be calculated by rearranging the expression as,

$$u = \frac{\lambda}{zF}$$

Substituting the values.

$$\text{For Li}^+ \text{ ion: } u = \frac{3.87 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}}{1 \times 96485 \text{ Cmol}^{-1}} = 4.011 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$$

$$\text{For Na}^+ \text{ ion: } u = \frac{5.01 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}}{1 \times 96485 \text{ Cmol}^{-1}} = 5.193 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$$

- We know that the transport number of the cation is defined as

$$t_+ = \frac{\text{Moles of electrolyte lost from the anodic compartment}}{\text{Total number of moles of electrolyte lost}}$$

First, we calculate the total number of moles of electrolytes lost by using the amount of silver deposited on cathode.

The amount of silver deposited on cathode

$$= \frac{0.2037 \text{ g}}{107.88 \text{ g mol}^{-1}} = 0.000189 \text{ mol}$$

Since in this case we are using silver electrodes, so 0.000189 moles of silver will dissolve from the silver anode.

We are given the final amount of silver nitrate in the anode compartment as 38.8 mg of silver nitrate and 18 g of water i.e.,

$$\text{Final number of moles of silver nitrate} = \frac{0.0388\text{g}}{169.87\text{g mol}^{-1}} = 0.000228\text{mol}$$

Initial number of moles of silver nitrate in the anode compartment can be obtained by calculating silver nitrate in 18 g of water

$$= \frac{18\text{g water} \times 0.0119\text{g AgNO}_3 \text{ per g water}}{169.87\text{g mol}^{-1}} = 0.000126\text{ mol}$$

The number of moles of silver nitrate transferred from anode compartment

= Initial no. of moles + Moles formed by dissolution of electrode – final no. of moles

$$= 0.000126 + 0.000189 - 0.000228 = 0.000087$$

Substituting in the expression for transport number, we get

$$t_{\text{Ag}^+} = \frac{0.000087\text{mol}}{0.000189\text{mol}} = 0.46$$

We know that $t_+ + t_- = 1$ so $t_{\text{NO}_3^-} = 1 - 0.46 = 0.54$

5. We know that the degree of ionisation (α) of the weak electrolyte is given as

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0}$$

Where, Λ_m^c and Λ_m^0 are the molar conductivities of the weak electrolyte at a given concentration and at infinite dilution, respectively.

Substituting the values, we get

$$\alpha = \frac{48.15\text{S cm}^2\text{ mol}^{-1}}{390.6\text{S cm}^2\text{ mol}^{-1}} = 0.123$$

6. We know that the solubility, conductivity, and molar conductivity at infinite dilution are related as

$$s = \frac{1000\text{cm}^3\text{ dm}^{-3} \times \kappa(\text{S cm}^{-1})}{\Lambda_m^0(\text{S cm}^2\text{ mol}^{-1})}$$

Let us first calculate the conductivity of the salt only by correcting given conductivity of solution for water as follows

$$\kappa(\text{salt}) = \kappa(\text{solution}) - \kappa(\text{water})$$

Substituting the values, we get

$$\kappa(\text{AgCl}) = (3.41 \times 10^{-6}) - (1.60 \times 10^{-6}) = 1.81 \times 10^{-6}\text{ S cm}^{-1}$$

The molar conductivity for AgCl at infinite dilution is given as

$$= 138.2\text{S cm}^2\text{ mol}^{-1}$$

Substituting the values of conductivity and molar conductivity at infinite dilution in the expression for solubility (Eq. (6.38)) we get

$$s = \frac{1000 \text{ cm}^3 \text{ dm}^{-3} \times \kappa (\text{S cm}^{-1})}{\Lambda_m^0 (\text{S cm}^2 \text{ mol}^{-1})}$$

$$s = \frac{1000 \text{ cm}^3 \text{ dm}^{-3} \times 1.81 \times 10^{-6} \text{ S cm}^{-1}}{138.2 \text{ S cm}^2 \text{ mol}^{-1}} = 1.31 \times 10^{-5} \text{ mol dm}^{-3}$$

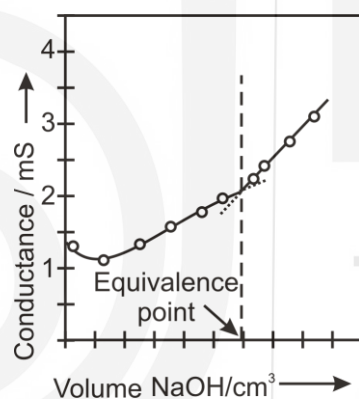
Now for AgCl the expression for solubility product can be written as

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = s^2$$

Substituting the value of solubility, we get

$$K_{sp} = (1.31 \times 10^{-5})^2 = 1.72 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

7. Formic acid is a weak acid and its titration with a strong base like NaOH will be similar to the one described for acetic acid in the text. A schematic diagram for the conductometric titration between formic acid and NaOH is given below.



Initially, the solution of formic acid would have a few hydrogen and formate ions due to the poor ionisation of formic acid; the overall conductivity is low. Initial addition of sodium hydroxide neutralises the fast moving hydrogen ions and the conductivity decreases slightly. Further addition of NaOH neutralises unionised formic acid and the conductivity increases due to the formation of salt, sodium formate. Once all the formic acid is neutralised i.e., at the equivalence point further addition of NaOH increases conductivity sharply due to addition of sodium ions and hydroxide ions (having high conductivity). The change in the slope vindicates equivalence point.

Electrochemistry-I |

Structure

7.1	Introduction	Experimental Measurement of EMF of Cell
	Expected Learning Outcomes	
7.2	Electrochemical Cells	7.6 Thermodynamics of Reversible Cell
	Galvanic Cells	Cell EMF and Spontaneity
	Electrolytic cells	Cell EMF and Equilibrium Constant
7.3	Reversible and Irreversible Cells	7.7 Nernst Equation
		Applications of Nernst equation
7.4	Representing Electrochemical Cells	7.8 Types of Electrodes
	Cell Diagram and Cell Reaction	7.9 Summary
7.5	EMF of a Cell	7.10 Terminal Questions
	Standard Reduction Potential	7.11 Answers

7.1 INTRODUCTION

In the previous two units you have learnt about different aspects of conduction in electrolytic solutions. You would recall from Unit 5 that while discussing about the mechanism of electrolytic conduction, we mentioned that when the ions carrying current through the bulk of the electrolytic solution reach the electrode, they undergo chemical reactions there. These reactions are characteristic and depend on the nature of the electrolyte and the electrode. In this and the next unit you would learn about electrochemical cells where we would discuss the processes occurring at the electrodes in the cells and their consequences.

In this unit dealing with first part of our discussion on electrochemistry we would begin by introducing the domain of electrochemistry and discussing electrochemical cells. Since most of the practical applications of electrochemistry require electrochemical cells working reversibly so we would clarify the meaning of reversible cells. This will be followed by discussion on galvanic cells, their representation and writing cell reactions. Then we would take up the concept of emf of a cell and its measurement. In this context we would introduce the concepts of electrode potential; and standard electrode potential.

We would then take up thermodynamic aspect of reversible cells. Herein, we would take up the relationship between cell emf and thermodynamic parameters like, Gibbs energy, equilibrium constant etc. We would also take up Nernst equation and its applications before describing different types of electrodes. In the next unit we would focus our discussion on the principles of concentration cells, electrolytic cells, and applications of emf measurements.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define electrochemistry and state its importance;
- ❖ differentiate between galvanic and electrolytic cells;
- ❖ differentiate between reversible and irreversible cells;
- ❖ describe a galvanic cell and explain its principle in terms of electrode reactions;
- ❖ represent given galvanic cell in terms of cell diagram and write cell reactions for it;
- ❖ explain the meaning and outline the significance of standard electrode potential;
- ❖ define emf of a cell and calculate the same using standard electrode potentials of the redox couples involved;
- ❖ describe the method for experimental measurement of cell emf;
- ❖ derive a relationship between cell emf and the Gibbs energy and predict the spontaneity of cell reaction of a given galvanic cell;
- ❖ calculate the equilibrium constant of a redox reaction by using cell emf;
- ❖ write Nernst equations for half-cell reactions and cell reactions;
- ❖ outline the significance of Nernst equation and predict the spontaneity of the cell reaction of a non-standard galvanic cell using the same;
- ❖ explain the principle of determination of pH of an aqueous solution using emf measurement;
- ❖ list and describe different types of electrodes; and
- ❖ write the half-cell reactions and representations of different electrodes.

7.2 ELECTROCHEMICAL CELLS

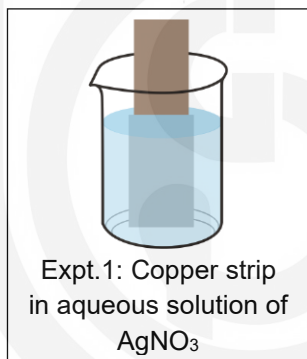
As you are aware, electrochemistry is the branch of physical chemistry that deals with the relationship between electricity, and chemical change in the system. There are two possibilities where such a relationship exists; in one of these, the spontaneous chemical reactions produce electricity and in the other, we use electricity to bring about non-spontaneous chemical reactions. In

simple words, we can say that *electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to make non-spontaneous reactions possible.*

Further, you are also familiar with redox reactions-the chemical reactions that involve transfer of electrons between two reactants participating in it. A cell in which the progress of such an oxidation-reduction reaction is associated with electric current is called an *electrochemical cell*. These are of two types. The electrochemical cell in which the progress of a spontaneous chemical reaction causes an electric current to flow is called a *galvanic cell*. On the other hand, the electrochemical cell in which a current is passed by an external voltage, to make an otherwise non-spontaneous chemical reaction to proceed is called an *electrolytic cell*. An electrochemical cell typically consists of a solution of an electrolyte and two electrodes at which oxidation and reduction processes occur, respectively. The electrolyte usually is a solution of an acid, base or a salt or a pure liquid. Here, in this unit we are going to take up the study of galvanic cells. Let's understand what are galvanic cells.

7.2.1 Galvanic Cells

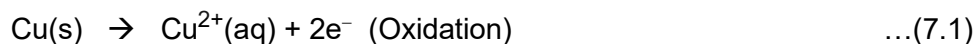
In order to learn about galvanic cells, let us take up some simple experiments. In the first experiment we take an aqueous solution of silver nitrate in a beaker and dip a strip of copper in it. We would observe the following:



- The part of copper strip dipped into the solution becomes thinner (some copper metal is lost);
- The colour of otherwise colourless solution becomes bluish;
- A silvery layer is formed on the dipped copper strip
- The solution temperature increases slightly

These observations can be explained in terms of the following changes

- The copper atoms in the copper plate get oxidised to cupric ions releasing two electrons, as per the following equation



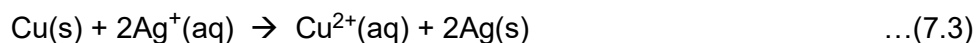
The blue colour of the solution is due to the formation of these cupric ions.

- The silver ions get reduced to silver metal by accepting the electrons released by copper as per the following equation



The metallic silver so obtained is deposited on the copper plate.

The overall reaction can be given as the following redox reaction



In simpler words, we can say that copper metal has a greater tendency to get oxidised and displaces silver ions from the solution and there is a transfer of electrons from copper atom to silver ions. Let's take the second experiment to be a familiar one; dipping a zinc rod in an aqueous solution (blue coloured) of Copper (II) sulphate. In this case, we observe the following

- The part of zinc rod dipped into the solution becomes thinner (some zinc metal is lost);
- The colour of blue solution fades and eventually becomes colourless;
- Reddish-brown solid (elemental copper) deposits on the surface of zinc rod
- The solution temperature increases slightly

These observations can be explained in terms of the following changes

- The zinc atoms in the zinc rod get oxidised to zinc ions by releasing two electrons, as per the following equation



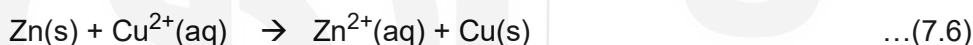
This accounts for the thinning of zinc rod

- The copper ions in the solution get reduced to copper metal by accepting the electrons released by zinc atoms as per the following equation



This results in the formation of reddish-brown solid on the surface of zinc rod

The overall reaction can be given as the following redox reaction

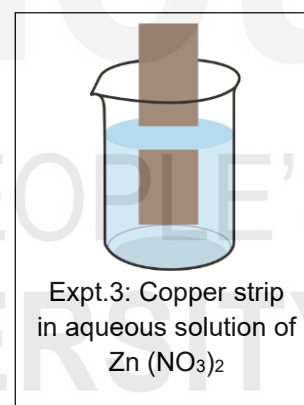
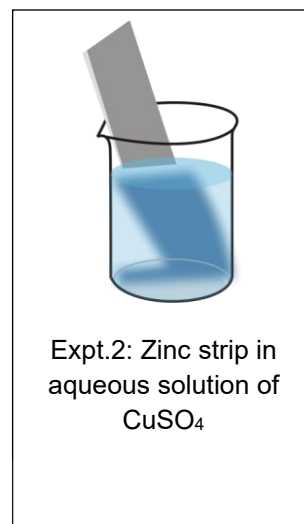


In simpler words, we can say that zinc metal has a greater tendency to get oxidised and displaces copper ions from the solution and there is a transfer of electrons from zinc atom to copper ions. In the third experiment we dip a strip of copper in an aqueous solution of Zinc (II) nitrate. In this case, we do not observe any reaction.



What do we conclude from these experiments? We conclude that the experiment 1 and 2 involve spontaneous reactions as represented by the Eqs.(7.3) and (7.6) whereas, the reaction between copper metal and zinc ions (experiment 3) is not spontaneous. You know from your earlier studies on chemical energetics that a spontaneous reaction is accompanied by a decrease in Gibbs energy. This Gibbs energy change leads to a change in the temperature of the solution in experiment 1 and 2.

Now, the question comes up is 'can we use the Gibbs energy change in spontaneous reactions for doing some work?' and if yes, 'how do we do so?' The answer is yes and we can do so by *not* allowing a direct transfer of electrons between the reactants. Practically speaking, this can be achieved by separating the process of release of electrons and their consumption i.e., separating zinc metal from the copper sulphate solution in experiment 2. Such a set up is called a **Galvanic** or a **voltaic cell**. Let us learn about the construction and working of Galvanic cells by taking the example of Daniell Cell in which the redox reaction given by Eq.(7.6) takes place.



Daniell Cell

In order to separate the process of release of electrons and their consumption, in Daniell cell we take two different electrodes. In one of the electrodes we take an aqueous solution of zinc sulphate in a beaker and dip a zinc strip or rod in it. For the second electrode we take a copper rod or strip and dip it in an aqueous solution of copper sulphate taken in a beaker. Let us see what happens in these electrodes. We begin with zinc electrode.

In case of zinc electrode, the strip of zinc is dipped in a dilute solution of zinc sulphate. As zinc sulphate is a strong electrolyte, it is fully dissociated, and initially the solution contains equal number of positive (Zn^{2+}) and negative (SO_4^{2-}) ions and the solution as such is neutral. Similarly, the metal strip can be visualised as an array of positively charged kernels in the sea of electron and the overall metal is also electroneutral.

Galvanic cells are named after an Italian anatomist Luigi Galvani, who demonstrated that passage of electricity caused frog muscles to contract and two different metals in contact with the muscle tissue produce an electric current.

Now, since zinc is an electropositive element, some of the zinc atoms from the electrode's surface lose electrons to the electrode and enter the solution as Zn^{2+} ions, i.e., the zinc atoms get oxidized. As a consequence, the charge balance in the metal is disturbed and the metal has a small excess of negative charge. On the other hand, due to the release of zinc ions from metal to the solution there is a small excess of positive charge in the solution. In time, some zinc ions may get attracted back to the negative metal and get deposited on it by taking electrons from there, i.e., the zinc ions get reduced. At a certain stage, the following redox equilibrium is established between the zinc strip and the zinc ions.



Eventually, a potential develops between the negatively charged electrode and the excess positive charge in the solution near the electrode. A system containing a metal strip or rod dipped in a solution of its ions is called **half-cell** (or **electrode**) and the potential developed is called **half-cell potential** (or **electrode potential**). A similar process occurs in case where a copper strip is dipped in a solution of copper sulphate.



Now, if we connect these two electrodes by a metal wire the electron would flow from zinc electrode to copper electrode. We can say so on the basis of experiment 2 and 3 described above. You would recall that in experiment 2 zinc could displace copper ions from solution but in experiment 3 it's reverse was not true. This implies that the potential of zinc to get oxidized is more than that of copper. Alternatively, we can visualise that the voltage, or potential difference, between the zinc rod and the zinc ions around it is more than that between the copper rod and copper ions. This difference of voltages (or potential differences) is the driving force for the transfer of electrons. It is like the flow of water from a higher level to a lower level.

Further, this flow of electrons from zinc to copper would cause deposition of copper on the copper electrode due to reduction of copper ions from the solution. These conclusions are supported by the experimental observation that in Daniell cell the mass of zinc electrode decreases whereas that of copper electrode increases.

The voltaic cell involving zinc and copper electrodes is called a Daniell cell after the English chemist John Daniell, who developed it in 1836.

The reactions at the two electrodes would be:



The overall reaction occurring in the cell can be obtained by adding Eq. (7.4) and Eq. (7.5) to give



Thus, the chemical change in the cell is basically an electron-transfer reaction. As a result of the flow of electrons from zinc to copper electrode and the accompanied reactions there will be an excess of positive charge around zinc (due to excess Zn^{2+} ions) and excess of negative charge around copper electrode (due to excess SO_4^{2-} ions) as Cu^{2+} ions here get reduced. Therefore, the process would stop very soon. For this process to continue we need to connect the electrolytes in two half cells i.e., complete the electrical circuit between the two solutions. In other words, the charge carried by the electrons in the external circuit must be followed by a transport of ions between the two half cells. That is, we must provide a way for ions to move from one half cell to the other.

This is achieved by using a **salt bridge** to link the two electrolytic solutions. The salt bridge is basically an inverted U-shaped tube containing a saturated solution of an inert electrolyte like KCl, KNO_3 or NaNO_3 etc., whose ions are neither involved in the net chemical change nor do these interact with the electrodes. This solution is mixed with a gelatinous material, such as agar-agar, so that it does not flow into the electrode compartments. Other way to do so is to place a sintered disc on each end of the tube.

Once the two solutions are connected through the salt bridge, the excess positive charge around the zinc electrode is neutralised by the transfer of negative ions from the salt bridge and to a small extent by migration of zinc ions to the salt bridge. Similarly, the excess negative charge around the copper electrode is neutralized mainly by the transfer of positive ions from the salt bridge and to a small extent by migration of sulphate ions to the salt bridge. Due to the neutralisation of the charges around the electrodes, the oxidation of zinc from the zinc electrode and reduction of copper ions on the copper electrode resumes. The process of transfer of electrons from zinc to copper electrode in the external circuit and transfer of ions across the electrolytes resumes. A schematic diagram of Daniell cell constructed by using salt bridge to connect the two electrolytes is given in Fig. (7.1)

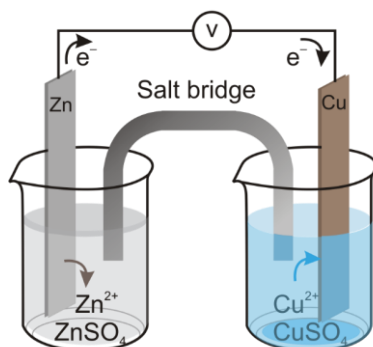


Fig. 7.1: A schematic diagram of Daniell cell.

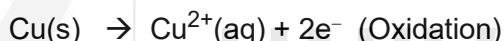
The function of salt bridge can be given as under:

- It completes the cell circuit by connecting the electrolyte solutions of two half cells.
- It helps in maintaining the electrical neutrality of the solutions in the two half cells.
- It does not allow the transfer or diffusion of the electrolyte solution from one half cell to the other.
- It prevents the liquid-liquid junction potential i.e., the potential difference that would develop between two electrolyte solutions if the two are allowed to be in contact with each other. (you would learn about liquid junction potential in the next unit.)

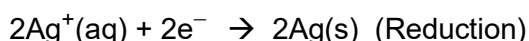
The half-cell in which the oxidation reaction takes place is called the **anode**, and the half-cell involving the reduction reaction is called the **cathode**. The two half-cells put together constitute a **voltaic cell**. Now, if we attach some electrical device such as a lightbulb to the wire, connecting two electrodes we can operate the device (the bulb glows). In other words, by separating the half-reactions, we can extract work from the spontaneous electrochemical reaction. Having learnt about the working of a galvanic cell using the example of Daniell cell let's learn about writing the cell reaction for a galvanic cell.

Example 7.1: Write down the cell reaction for the galvanic cell on the basis of the observation that a strip of copper metal when placed in an aqueous solution of silver nitrate, displaces silver ions from the solution. However, its reverse is not true.

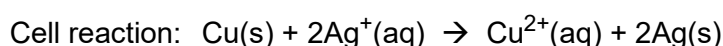
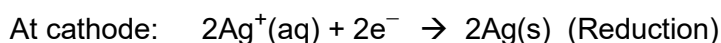
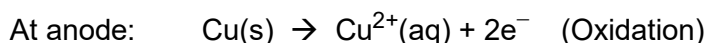
Solution: The given observation means that copper is more electropositive than silver; i.e., it has a greater tendency to get oxidised; i.e., the following reaction takes place at the anode



We know that an oxidation reaction must be accompanied by a reduction reaction; i.e., in the given system the silver ions get reduced to silver atoms. Since each copper atom loses two electrons to form copper ion and each silver ion requires just one electron to produce silver atom; therefore, for every copper ion formed two silver atoms are deposited on the cathode as per the following reaction



Now, if we combine, copper and silver electrodes, they will form a galvanic cell in which copper electrode would act as an anode whereas silver electrode will act as a cathode. Further, there will be a transfer of electrons from copper electrode to silver electrode when the current is drawn from the cell. The overall cell reaction can be obtained by adding the reactions occurring at anode (oxidation) and cathode (reduction) as follows:



It is important to note that while combining the half-cell equations to produce the overall cell equation, we must ensure that the number of electrons involved in reduction reaction are equal to the number involved in oxidation reaction.

On the basis of the above example, we can outline the procedure for writing the cell reaction for a galvanic cell.

Step 1: Write the half-cell reaction taking place at the anode i.e., the oxidation reaction

Step 2: Write the half-cell reaction taking place at the cathode i.e., the reduction reaction

Step 3: Combine the above two half-cell reactions ensuring that the number of electrons released at the anode is equal to the number of electrons used at the cathode.

Having learnt about Galvanic or Voltaic cells in which we use the spontaneous redox reactions to get useful electrical work let us learn about the cells in which we use external potential to cause a non-spontaneous reaction.

7.2.2 Electrolytic Cells

As stated above, the electrochemical cells in which non-spontaneous reactions are made to occur by causing a flow of electricity (electric current) through the cell by using an outside source, such as a battery or a generator are called electrolytic cells. In an electrolytic cell two electrodes are dipped into a solution of an electrolyte taken in a container. These electrodes are then connected to an external source of electricity. As a consequence, the ions in the electrolyte move towards the oppositely charged electrode and undergo chemical reactions on the electrodes. The movement of ions is an electric current. The whole process is called **electrolysis**. A schematic diagram of an electrolytic cell is given in Fig. (7.2).

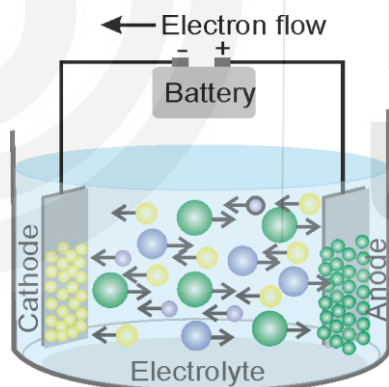


Fig. 7.2: A schematic diagram of an electrolytic cell.

As in case of galvanic cells, the flow of current through the electrolyte is due to the movement of ions to oppositely charged electrodes whereas in the external circuit it is due to flow of electrons. We would discuss about electrolytic cells in details in the next unit. For now, let us learn about the reversible and irreversible cells. However, before that answer the following simple question to assess your understanding of electrochemical cells.

SAQ 1

What are galvanic cells? It is observed that a strip of aluminum kept in a solution of silver nitrate displaces silver ions from solution. Formulate the cell-equation for a galvanic cell prepared by using aluminum and silver electrodes.

7.3 REVERSIBLE AND IRREVERSIBLE CELLS

As stated above, in galvanic cells the Gibbs energy change of the spontaneous redox reaction causes the development of potential difference across the electrodes and this can be used to get useful work. We can relate other thermodynamic parameters with the potential difference and obtain their values from electrochemical measurements. However, for this to be possible the electrochemical cell must be reversible.

A reversible cell may be defined as the one in which the reactions are always in state of equilibrium and only infinitesimally small currents are drawn from it. A reversible cell must satisfy the following conditions.

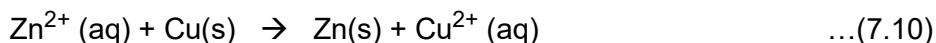
- i) If we connect an external source of emf to the cell such that the driving force (applied voltage) and the opposing force (the cell potential difference) are equal *no* reaction should occur in the cell
- ii) If the applied voltage is infinitesimally smaller than the cell voltage, then the cell reaction would occur to an infinitesimally small extent and infinitesimally small current would flow from the cell to external source.
- iii) If the applied voltage is infinitesimally greater than the cell voltage, then the cell reaction would occur to an infinitesimally extent in the reverse direction and infinitesimally small current would flow from the external source to the cell

A cell not satisfying the above requirements is called an **irreversible cell**. Let us take an example each of reversible and irreversible cells.

Daniell cell discussed above is an example of a reversible cell. If we connect an external source having slightly lower voltage than the cell, then the following reaction would occur in the cell and a small amount of current would flow from the cell to the external source.

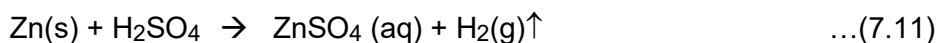


However, if the connected external source has slightly greater voltage than the cell, then the reaction occurring in the cell would get reversed and a small amount of current would flow from the external source to the cell.



On the other hand, if the applied external voltage is exactly equal to the cell voltage, there will be no reaction in the cell.

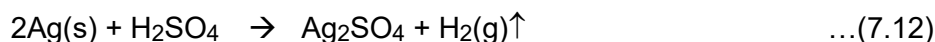
Let us now consider a cell containing zinc and silver electrodes dipped in a solution of sulphuric acid taken in a container. On connecting the two electrodes by a wire it is observed that zinc dissolves with the evolution of hydrogen gas and zinc sulphate is formed in the solution. The change can be represented as the following reaction:



On the other hand, if we connect the cell with an external source having potential slightly greater than of the cell, we find that silver dissolves and

In a typical galvanic cell, the half-cells consist of a metallic electrode dipped into corresponding salt solution. The metallic electrodes are connected externally by a metallic wire and electrolytes of the two half-cells are connected internally through a salt bridge

hydrogen is evolved at the zinc electrode. The change can be represented as the following reaction:



Thus, we find that in this case, the condition of reversibility i.e., on applying an external voltage greater than the cell voltage, the reaction should reverse is not being followed. Therefore, it is an example of irreversible cell. In such a case, we cannot relate the cell emf with thermodynamic properties.

7.4 REPRESENTING GALVANIC CELLS

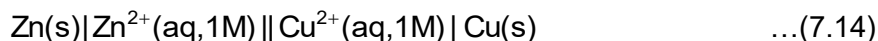
In our discussion above, we used the example of Daniell cell to describe the formation and the functioning of a galvanic cell. In principle, we can create any number of galvanic cells by using combinations of two different metal electrodes. However, in order to learn about or describe different galvanic cells we do not need to draw sketches like the one given in Fig. (7.1); we use a symbolic representation for these. Such a representation is called a **cell diagram** or **cell notation**. There are certain rules (conventions) that need to be followed while writing the cell diagram for a given galvanic cell. Let us learn about these rules by using the example of Daniell cell as follows:

- i) The anode, the electrode at which oxidation occurs, is placed at the left side of the diagram and the cathode, the electrode at which reduction occurs, is placed at the right side of the diagram i.e.,



Here, a single vertical line indicates the boundary separating species in different phases in a given electrode (half-cell). The double vertical line indicates the salt bridge. [Sometimes, a single broken (dashed) vertical line is used to represent a porous boundary, or some other means of preventing the electrolytes from mixing while allowing ion to flow.]

- ii) The concentrations or activities of aqueous solutions are written in parentheses after the symbol of the ions in the cell notation



- iii) Sometimes, the electrolyte used in the salt bridge is also indicated. In such a case the cell diagram for Daniell cell becomes,



It is important to note that the spectator ions, (the counter ions of the electrolytes) that are present in the system but do not participate in the cell reaction, are not shown in the cell diagram.

7.4.1 Cell Diagram and Cell Reaction

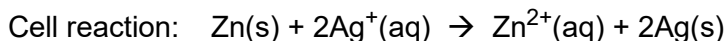
The representation of a galvanic cell in terms of cell diagram is quite convenient way of expressing the cell. It is but natural that the cell diagram and the reaction taking place in the cell are related. In principle, we should be able to write the cell notation from the cell reaction and also, we should be

In case of cells with transference; involving the development of liquid junction potential a broken vertical line is used in place of two vertical lines to indicate the porous boundary.

You may note here that left and right here refer to the way the electrode is represented in the cell diagram. It has nothing to do with the physical location of the two electrodes in the actual galvanic cell.

able to work out the cell reaction from the cell notation. Let us first learn how to write cell diagram from the cell reaction. You know that a cell reaction is basically a redox reaction; and is a combination of two half-cell reactions. In the process of writing cell diagram from cell reaction the first step is to identify and write the two half-cell reactions. Once that is done then the process becomes quite straight forward. Let us take an example to understand it.

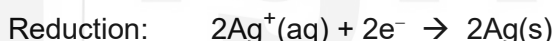
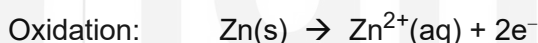
Example 7.2: Write the cell diagram for a galvanic cell in which the following reaction takes place.



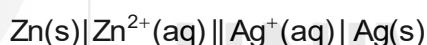
Assume that potassium nitrate is used as electrolyte in the salt bridge and the concentrations of zinc ions and silver ions are c_1 and c_2 respectively.

Solution: As stated above, the first step in the process of writing cell diagram from cell reaction is to separate the two half-cell reactions. This basically means that we need to identify the species undergoing oxidation and reduction, respectively.

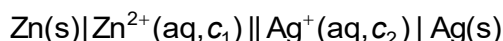
Here, we see that the metallic zinc is getting oxidised and the silver ions are getting reduced to silver metal. So, we can write the oxidation and reduction half-cell reactions as



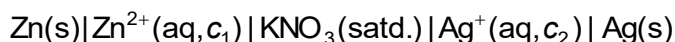
We place the anode at the left side and the cathode, at the right side of the diagram by separating different phases of the two half-cells by a single vertical line and by representing the salt bridge by a double vertical line as follows.



Note that the physical states of different species are indicated in the parenthesis. As the concentrations of the ions are given, we include them as



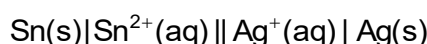
Further, as the electrolyte used in the salt bridge is also given, we include that also in the cell notation as follows



This is the required cell diagram for the given galvanic cell

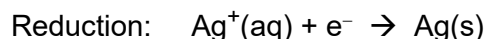
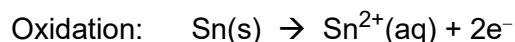
Having learnt to write cell diagram from the cell reaction let us now learn to write cell reaction on the basis of the cell diagram. We will again take an example to do so.

Example 7.3: Write the balanced cell reaction for the galvanic cell represented by the following cell diagram.

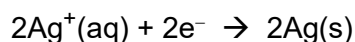


Solution: As we know that the balanced cell reaction for a galvanic cell can be obtained by adding the oxidation and reduction reactions in such a way that total number of electrons lost and gained are equal.

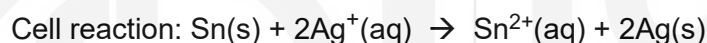
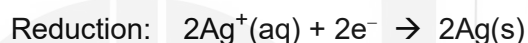
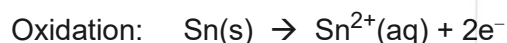
Further, we know that in a cell diagram the electrode on which the oxidation occurs is given on the left and the electrode at which reduction takes place is given on the right. Therefore, in this case tin is undergoing oxidation whereas silver ions are getting reduced. The corresponding equations can be written as



We find that tin atom gives two electrons while getting oxidised and a silver ion needs just one electron to be reduced. So, to balance the electrons we multiply the reduction equation by 2 to get,



We can get the cell reaction by adding the oxidation and reduction equations as follows



Having learnt about galvanic cells, their working and representation let us now learn about the emf of the cell. However, before that solve the following simple question to assess your understanding.

SAQ 2

What is a cell diagram? Write the cell diagram for a galvanic cell in which the following reaction takes place.



7.5 EMF OF A CELL

As discussed above, in galvanic cells there is a transfer of electrons from the negative electrode (anode) to the positive electrode (cathode). This transfer of electrons causes a current to flow from the electrode at higher potential to the one at lower potential. This difference between the electrode potentials of the electrodes when no current is drawn through the cell is known as the **cell electromotive force** (emf) and is expressed in volts. In terms of the cell notation in which the anode is written on the left and the cathode on the right we can write, the standard cell emf as

$$E_{\text{cell}}^0 = E_R^0 - E_L^0 \quad \dots(7.16)$$

Where, E_R^0 and E_L^0 are the standard electrode potentials of the cathode and the anode, respectively. In order to understand and determine emf of a cell we

need to first understand the meaning and significance of electrode potential also conventionally expressed as reduction potential

7.5.1 Standard Electrode Potential

Let us recall from above, that when a metal (e.g., Zn or Cu) is placed in an aqueous solution of its salt, some kind of charge separation develops between the metal and nearby solution. The equilibrium processes can be represented by the equations like,

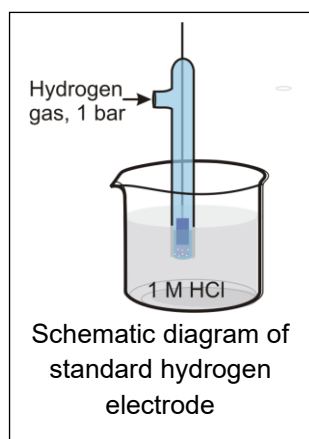


The charge separation leads to development of a potential difference and this is called **electrode potential** or **half-cell potential**. When all the species involved in a half-cell are at unit concentration (in case a gas appears in the electrode reaction, then it is to be at a pressure of 10^5 Pa), then the electrode potential is known as **standard electrode potential**.

Determination of Standard Reduction Potentials

The potential of an individual electrode or half-cell cannot be measured. If we try to measure the half-cell potential using a voltmeter, we will place one of the test leads on the metal and the other in the adjoining solution. The moment we place the metallic test lead in the solution a new half-cell comes into the existence. As a consequence, the measured potential will not be that of the half-cell being measured. However, we can measure the difference between the two half-cell potentials that gives the emf of the cell. This can be measured with the help of a potentiometer.

For Daniell cell, the cell emf is found to be 1.11 V. This is the difference between the potential of the zinc half-cell (anode) and copper half-cell (cathode). The question comes is that how do we find out the potential of individual half cells? As stated above, we cannot directly measure the potential of a half-cell, so we need to combine the half cell with some electrode (or half-cell) for which the potential is zero. In other words, we need to have a reference, like we take the temperature at the freezing point of water to be zero-degree Celsius.



The standard hydrogen electrode (SHE) is taken to be such a reference whose potential is arbitrarily taken to be equal to zero volt at all temperatures. The SHE consists of a platinum electrode (coated with platinum black) is partially dipped in a 1M HCl solution and pure hydrogen gas is bubbled through it. The pressure of hydrogen gas is maintained at 10^5 Pa. Now, to measure the electrode potential of the given half-cell, it is combined with the SHE to form a galvanic cell. It's emf is then measured with the help of a potentiometer. The value so obtained gives the potential of the given half-cell. In the hydrogen electrode either the protons are reduced, or hydrogen molecules are oxidized at the Pt surface according to the following equation:



As a matter of convention, the standard hydrogen electrode is always taken as the electrode on the left of the cell diagram (anode) and the electrode under

consideration on the right (cathode). In other words, there is oxidation at the hydrogen electrode and reduction at the half-cell being measured. The cell diagram for the combination of SHE and zinc electrode would then be,



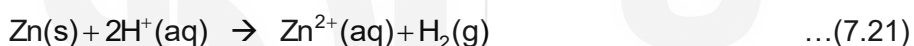
For such a combination of zinc electrode, and SHE the half-cell reactions can be written as



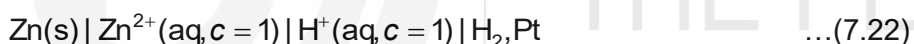
Adding the two equations we get the overall cell reaction as



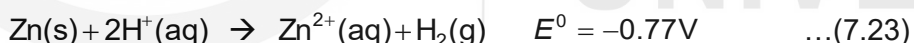
The measured potential of the cell containing zinc electrode and hydrogen electrode is found to be 0.77 V. However, it is observed that the zinc electrode starts to dissolve to give Zn^{2+} and the concentration of H^+ ions in the hydrogen electrode decreases (You may recall from your earlier studies that if we place a piece of zinc metal in an acid, it displaces hydrogen ions and H_2 gas is evolved). This suggests that the zinc electrode is acting as anode whereas hydrogen electrode acts as cathode. In other words, we can say that the reaction as given in Eq. (7.20) is not spontaneous. The spontaneous cell reaction is as follows



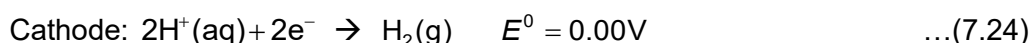
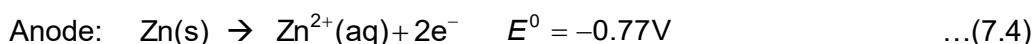
And the cell diagram for this galvanic cell can be given as follows:



As we have reversed the reaction, the sign of the potential would also be reversed, i.e.,



It is important to note here that though we have reversed the sign, the absolute value of the potential difference as measured would still be 0.77. The half-cell reactions would be



As mentioned before, the standard cell emf is always taken as

$$E_{\text{cell}}^0 = E_R^0 - E_L^0 \quad \dots(7.16)$$

Substituting the values, we get

$$E_{\text{cell}}^0 = 0.00 - (-0.77) = 0.77\text{V} \quad \dots(7.25)$$

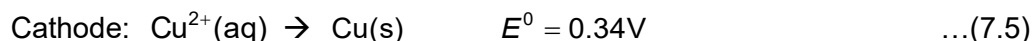
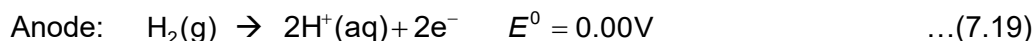
Now, if we take a combination of copper electrode (under standard conditions) with SHE and measure the cell potential we get a value of 0.34 V. Here, Cu^{2+} ions would get reduced to copper metal (i.e., copper electrode would act as

The measured potential of the cell between a redox couple (under standard conditions; solutes at 1 M concentration, gases at 101.3 kPa) and standard hydrogen electrode is called the standard reduction potential or standard electrode potential.

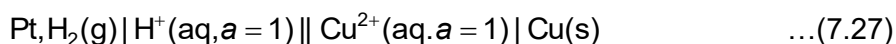
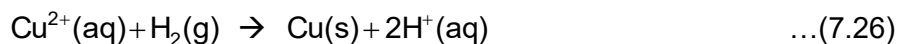
A half-cell that takes electrons from the standard hydrogen cell is assigned a positive value of E^0 , and one that donates electrons to the hydrogen electrode, a negative value.

You may note here that the half-reactions are written to show the oxidation and reductions taking place at the anode and cathode, respectively. The overall cell reaction is obtained as the sum of the two half-reactions. However, the cell potential is the difference between the reduction potentials of the two redox couples.

cathode) whereas hydrogen gas would get oxidised to hydrogen ions (i.e., hydrogen electrode would act as anode) i.e., the following half-cell reactions would occur.



The overall cell reaction and the cell notation would be as follows



The corresponding standard cell emf would be

$$E_{\text{cell}}^0 = E_{\text{R}}^0 - E_{\text{L}}^0 \quad \dots(7.16)$$

Substituting the values, we get

$$E_{\text{cell}}^0 = 0.34 - (0.00) = 0.34\text{V} \quad \dots(7.28)$$

Different electrodes or redox couples are arranged in terms of decreasing value of their standard electrode potentials as given in Table 7.1. This arrangement is referred to as **electrochemical series**. A negative value of the electrode potential means that the redox couple is a stronger reducing agent than the H^+/H_2 couple whereas a positive value conveys that the redox couple is a weaker reducing agent than the H^+/H_2 couple. In other words, the redox couples below hydrogen in the series would reduce hydrogen ions to hydrogen gas i.e., they will displace hydrogen ions from acid solutions. On the other hand, the redox couples higher than hydrogen in the series will not be able to displace hydrogen ions from an acid solution.

You may note that the electrodes or the half-cell reactions are arranged in order of their decreasing E^0 values and can be used to predict the relative strengths of various oxidants and reductants. In general, we can say that a species on the left side of a half reaction (i.e., the oxidised form) will spontaneously oxidise any species on the right side of another half-reaction that lies above it in the table. Similarly, any species on the right side of a half-reaction (i.e., the reduced form) will spontaneously reduce any species on the left side of another half-reaction that lies below it in the table.

In the event of an electrochemical cell constructed by the combination of any two electrodes; the electrode with a higher value of electrode potential, E^0 would act as cathode and the one with a lower value would act as anode. If we make a galvanic cell by combining zinc electrode and copper electrode (i.e., make Daniell cell); there would be oxidation at the zinc electrode (anode, lower E^0) and reduction at the copper electrode (cathode, higher E^0). The cell would be represented as



The standard cell emf for the cell can be obtained by using Eq. (7.16).

$$E_{\text{cell}}^0 = 0.34 - (-0.77) = 1.11\text{V} \quad \dots(7.29)$$

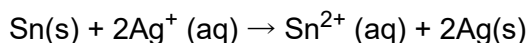
Table 7.1: Standard electrode potentials (E^0) for some redox half-cell reactions at 298 K

Reduction half-reactions		E^0 , Volts
Oxidising agent	Reducing agent	
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$		+2.65
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$		+2.01
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$		+1.44
$O_2 + H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$		+1.23
$Br_2(g) + 2e^- \rightleftharpoons 2Br^-(aq)$		+1.07
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$		+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$		+0.77
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$		+0.34
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$		+0.15
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$		0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$		-0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$		-0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$		-0.25
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$		-0.40
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$		-0.42
$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$		-0.424
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$		-0.77
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$		-1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$		-2.38
$Be^{2+}(aq) + 2e^- \rightleftharpoons Be(s)$		-1.99
$K^+(aq) + e^- \rightleftharpoons K(s)$		-2.92
$Li^+(aq) + e^- \rightleftharpoons Li(s)$		-3.04

Having learnt about the meaning and significance of cell emf, let us now learn how do we actually measure the cell emf. However, before that answer the following simple question to assess your understanding.

SAQ 3

The cell reaction for a galvanic cell is given below



- Write the half-cell reactions at the anode and the cathode
- Calculate the value of cell emf under standard conditions

7.5.2 Experimental Measurement of EMF

The emf of a cell is usually measured with a potentiometer. The ends of a uniform wire (XY) of high resistance is connected to a cell (C) of large emf. Then we connect one electrode of the test cell, T (whose emf has to be measured) to one end (X) of the wire and the second electrode is connected to a sliding contact through a galvanometer to detect the flow of current as shown in the Fig. (7.3).

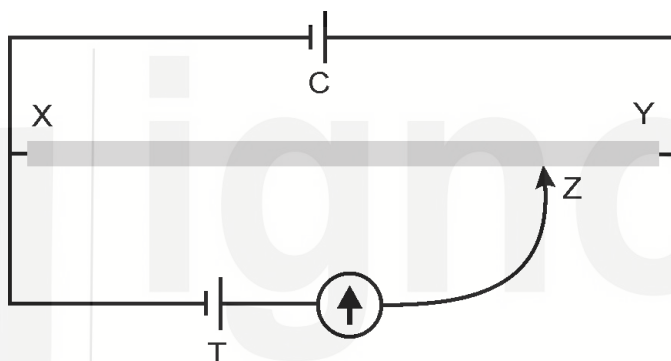


Fig. 7.3: A schematic diagram of potentiometer setup for measuring cell emf.

In the event of measurement of emf of the cell T, the sliding contact connected to the second terminal of the galvanometer is moved along the wire XY till we reach a point, Z where the galvanometer shows zero current flow. At this stage, the potential from cell C across the segment XZ is exactly balanced by the emf of cell T.

Then we take another cell A, of accurately known emf E_A and replace cell T with cell A and once again the point (now Z') where the galvanometer shows zero current flow is located. Under these conditions we can write,

$$\frac{E_T}{E_A} = \frac{XZ}{XZ'} \quad \dots(7.30)$$

Using the values of XZ and XZ' along with the known emf of the cell, A we can determine the emf of the given cell T.

7.6 THERMODYNAMICS OF REVERSIBLE CELLS

The measured values of the emf of reversible cells can provide us useful thermodynamic parameters of the cell reaction occurring in them. This linkage between the cell emf and thermodynamic parameters like, Gibbs energy change (and hence spontaneity) and equilibrium constant are very significant from the point of view of applications of emf measurements. Let us explore these linkages.

7.6.1 Cell EMF and Spontaneity

You have learnt that in galvanic cells the Gibbs energy of the spontaneous redox reaction is extracted as work. This work is electrical in nature and is due to the movement of ions. Conventional current moves from a point of higher potential to a point of lower potential. Electrons move in opposite direction. This work done due to the moving charges depends on the difference in the electrode potentials (E_{cell}), the number (n) of moles of electrons being transferred, and the charge per mole of the electrons (F). We can write,

$$w_{\text{elec}} = -nFE_{\text{cell}} \quad \dots(7.31)$$

The negative sign in this relation indicates that the work is done by the system. Now since this work is equal to the change in Gibbs energy of reaction i.e., we can write,

$$w_{\text{elec}} = \Delta_r G = -nFE_{\text{cell}} \quad \dots(7.32)$$

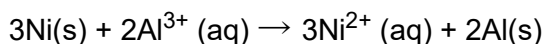
Thus, $\Delta_r G = -nFE_{\text{cell}} \quad \dots(7.33)$

It is an important relation that connects the Gibbs energy change with the cell emf. Since, n , and F (Faraday's constant), both are positive, we can conclude (from Eq. (7.33)) that a galvanic cell for which E_{cell} is positive, the cell reaction would be spontaneous (as $\Delta_r G$ will be negative). For the cell under standard conditions we can write,

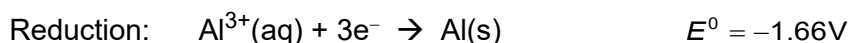
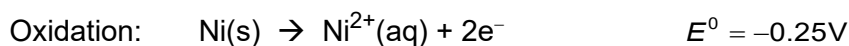
$$\Delta_r G^0 = -nFE_{\text{cell}}^0 \quad \dots(7.34)$$

We can therefore say that if the value of E_{cell}^0 for a cell is positive, then the reaction written as discussed above will occur spontaneously. On the other hand, if the value of E_{cell}^0 is negative, it means that the reaction for the cell (as constructed) is not spontaneous, and under standard conditions it will not occur as written. It would be spontaneous in the opposite direction. However, the reaction as written can be made to occur with a sufficient input of electrical energy, i.e., we make it happen electrolytically. Let us take an example to see how we can use electrochemical series to predict whether a given redox reaction would be spontaneous or not.

Example 7.4: Predict, using data from Table 7.1, whether the following redox reaction would be spontaneous or not under standard conditions.



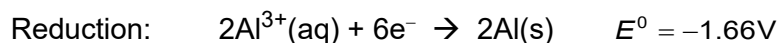
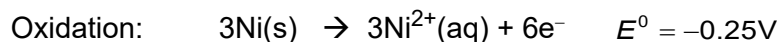
Solution: The first step is to identify the species getting oxidised and reduced respectively and to write two half reactions. We find here that nickel is getting oxidised whereas aluminum ions are getting reduced. The corresponding half-cell reactions would be



The reduction potentials for Ni / Ni²⁺ and Al / Al³⁺ redox couples, as given in Table 7.1, are –0.25 and –1.66 respectively

You may note that we have suitably multiplied the oxidation and reduction reactions to balance the electrons, the corresponding reduction potentials are not multiplied.

We find that nickel atom gives two electrons while getting oxidised and an aluminum ion needs three electrons to be reduced. So, to balance the electrons we multiply the oxidation reaction by 3 and the reduction reaction by 2 to get,



We know that

$$E_{\text{cell}}^0 = E_{\text{R}}^0 - E_{\text{L}}^0$$

Substituting the values, we get

$$E_{\text{cell}}^0 = -1.66 - (-0.25) = -1.41\text{V}$$

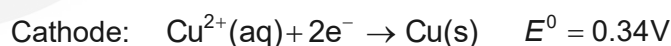
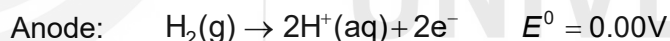
As the cell emf is found to be negative it means that the reaction as written will not be spontaneous.

As we have seen above that the Gibbs energy change for a reaction and the E_{cell}^0 for a galvanic cell are related so we can calculate the Gibbs energy change for a redox reaction by measuring the standard cell emf of the galvanic cell based on the reaction. Let us learn it with the help of an example,

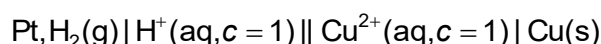
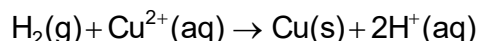
Example 7.5: Calculate the Gibbs energy change for the reaction taking place in the galvanic cell formed by combining copper electrode with hydrogen electrode.

Solution: We start with writing the cell notation for the given galvanic cell.

The half-cell reactions, as discussed before, can be written as



The overall cell reaction and the cell notation would be



The corresponding standard cell emf would be

$$E_{\text{cell}}^0 = E_{\text{R}}^0 - E_{\text{L}}^0$$

Substituting the values, we get

$$E_{\text{cell}}^0 = 0.34 - (0.00) = 0.34\text{V}$$

As per Eq. (7.34) the standard Gibbs energy change is given as

$$\Delta_r G^0 = -nFE_{\text{cell}}^0$$

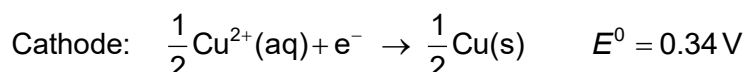
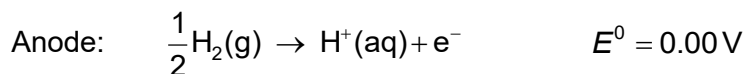
The value of $n=2$ here, as two electrons are getting transferred from copper to hydrogen ions in the cell reaction.

Substituting the values, we get

$$\Delta_r G^0 = -2 \times 96485 \text{ C mol}^{-1} \times 0.34 \text{ V}$$

$$\Delta_r G^0 = -65.61 \text{ kJ mol}^{-1}$$

You may note here that for the given cell we could write the half-cell reactions as follows also

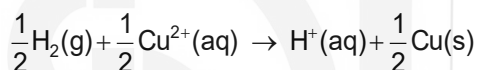


In such a case the value of $n=1$ and the calculated value of Gibbs energy change would be

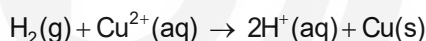
$$\Delta_r G^0 = -1 \times 96485 \text{ C mol}^{-1} \times 0.34 \text{ V}$$

$$\Delta_r G^0 = -328 \text{ kJ mol}^{-1}$$

This value of Gibbs energy change would be for one mole of the following cell reaction.



Whereas the value ($= -65.6 \text{ kJ mol}^{-1}$) we calculated above was for one mole of the following reaction



You may take a note of the fact that the Gibbs energy we get from the measurement of the cell emf would depend on the number of electrons participating in the reaction. This in turn, would depend on the way we write the electrode reactions.

7.6.2 Cell EMF and Equilibrium Constant

We have just related the cell emf with the Gibbs energy of the redox reaction occurring in a galvanic cell in terms of the following equation,

$$\Delta_r G^0 = -nFE_{\text{cell}}^0 \quad \dots(7.34)$$

You would recall from your earlier studies on chemical energetics that the Gibbs energy change and the equilibrium constant of a reaction are related as

$$\Delta_r G^0 = -RT \ln K \quad \dots(7.35)$$

We can use these two expressions to relate the cell emf and the equilibrium constant as follows

$$-RT \ln K = -nFE_{\text{cell}}^0 \quad \dots(7.36)$$

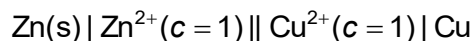
Rearranging, we get

$$\ln K = \frac{nF}{RT} E_{cell}^0 \quad \text{or} \quad E_{cell}^0 = \frac{RT}{nF} \ln K \quad \dots(7.37)$$

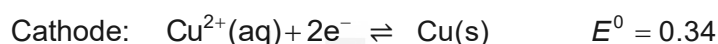
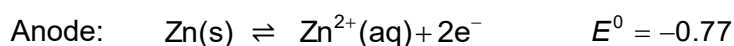
This is an important relation that facilitates the determination of equilibrium constant of a redox reaction by measuring the emf of the corresponding galvanic cell. Let us take an example to understand this application of emf measurement.

Example 7.6: Calculate the equilibrium constant for the cell reaction for Daniell cell working under standard conditions.

Solution: The Daniell cell under standard conditions can be represented as



The corresponding half-cell reactions are



The standard cell emf for the cell can be obtained by using Eq. (7.16).

$$E_{cell}^0 = 0.34 - (0.77) = 1.11\text{V}$$

We know from Eq. (7.33) that

$$\ln K = \frac{nF}{RT} E_{cell}^0$$

Substituting the values,

$$\ln K = \frac{2 \times 96485 \text{C mol}^{-1}}{8.314 \text{J K}^{-1} \text{mol}^{-1} \times 298.15 \text{K}} \times 1.11\text{V}$$

Solving, we get

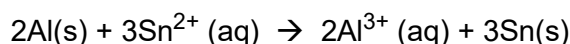
$$K = 10^{37.52} = 3.3 \times 10^{37}$$

Thus, the equilibrium constant for the reaction occurring in Daniell cell under standard conditions would be, 3.3×10^{37}

You have learnt that the value of standard cell emf for a voltaic cell can provide useful thermodynamic data like, the Gibbs energy change and equilibrium constant. However, what if the cell is not operating under standard conditions? We need to use Nernst equation under these conditions. Let us learn about the Nernst equation-an important equation in electrochemistry. However, before that solve the following simple questions to gauge your understanding.

SAQ 4

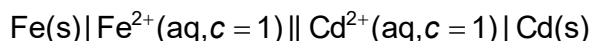
The cell reaction for a galvanic cell is given below



- Write the half-cell reactions at the anode and the cathode
 - Predict whether the given cell reaction be spontaneous; use data from Table 7.1.
-

SAQ 5

Calculate the equilibrium constant for the reaction occurring in the following voltaic cell. (Use data from Table 7.1).



7.7 NERNST EQUATION AND ITS APPLICATIONS

The discussion above has been on the standard electrode potential i.e., the standard reduction potential of a redox couple when all the species are at standard conditions (1 M concentrations / 1 bar pressure). However, in real systems, the conditions may not be standard, therefore, the electrode potential/ cell emf would be different. In such cases the actual potential of the redox couple would depend on the standard electrode potential and the actual concentrations of the species involved. The relationship between the actual electrode potential and standard electrode potential for a given redox couple was formulated by Walther Nernst. It is expressed in terms of an equation called **Nernst equation** which can be derived on the basis of the relationship between the Gibbs energy change and the cell emf as given in Eq. (7.33) and Eq. (7.34). We can rewrite the equations as

$$\Delta_r G = -nFE_{\text{cell}} \quad \dots(7.33)$$

$$\Delta_r G^0 = -nFE_{\text{cell}}^0 \quad \dots(7.34)$$

Further, you would recall from the course BCHCT-133 that the Gibbs energy change under standard and non-standard conditions are related as

$$\Delta_r G = \Delta_r G^0 + RT \ln Q \quad \dots(7.38)$$

Where, Q is the reaction quotient; R is gas constant and T is the absolute temperature. Substituting expressions for Gibbs energy changes we get,

$$-nFE_{\text{cell}}^0 = -nFE_{\text{cell}} + RT \ln Q \quad \dots(7.39)$$

Dividing the expression by $-nF$ on both sides we get

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q \quad \dots(7.40)$$

This is the **Nernst equation**. Here, R is the gas constant, T is the absolute temperature, n is the number of electrons participating in the reaction, and F is the Faraday's constant. Substituting these values and converting natural logarithm to the one to the base 10 we get

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{n \times 96485 \text{ C mol}^{-1}} \times 2.303 \log Q \quad \dots(7.41)$$

Simplifying, we get

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log Q \quad \dots(7.42)$$

Nernst Equation for Electrode (half-cell) Reactions

Let us consider the following electrode reaction,



The electrode potential of the electrode at any concentration measured with respect to standard hydrogen electrode will be given by the following equation

$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{0.0592}{n} \log \frac{[M]}{[M^{n+}]} \quad \dots(7.44)$$

The logarithm term is the ratio of the concentrations of the reduced and oxidised forms of the species. As the concentration (rather activities) for pure solids and liquids are taken as 1, the equation becomes,

$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{0.0592}{n} \log \frac{1}{[M^{n+}]} \quad \dots(7.45)$$

As an example, for copper electrode, the Nernst equation at 298 K would be

$$E_{Cu^{2+}/Cu} = E_{Cu^{2+}/Cu}^0 - \frac{0.0592}{2} \log \frac{1}{[Cu^{2+}(aq)]} \quad \dots(7.46)$$

7.7.1 Applications of Nernst Equation

The Nernst equation finds extensive applications in analytical chemistry and life processes. Electrochemical cells are extensively used for calculating the pH of solutions, solubility product, equilibrium constant and other thermodynamic properties. In all these applications of electrochemical cells the Nernst equation has a role to play. We will take up following simple common applications

- Determination of equilibrium constant
- Determination of cell emf under non-standard conditions
- Predicting spontaneity of a cell reactions under non-standard conditions
- Determination of pH value of a solution
- Determination of K_{sp} of a sparingly soluble salt

Let us take up these applications with the help of examples.

Determination of equilibrium constant

Once again, you may recall from your earlier study about chemical equilibrium that at equilibrium, $Q = K$ and $\Delta_r G = 0$ which means that $E_{cell} = 0$.

Substituting in Eq. (7.40), we get

$$0 = E_{cell}^0 - \frac{RT}{nF} \ln K \rightarrow \ln K = \frac{nF}{RT} E_{cell}^0 \quad \dots(7.47)$$

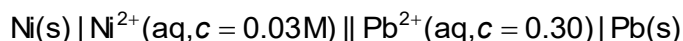
Which is the same expression we got before, Eq. (7.37). In other words, we can determine the equilibrium constant from cell emf measurement. In example 7.6 you have seen how this equation can be used to determine the equilibrium constant of a redox reaction.

Determination of cell emf under non-standard conditions

If a galvanic cell is working under standard conditions, then its emf can be easily obtained by using the standard electrode potentials of the redox couples involved. The Nernst equation allows to do the same when the cell is working under non-standard conditions say the concentrations (activities) of the ions are different from unity.

Let us understand it with the help of an example.

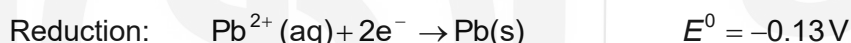
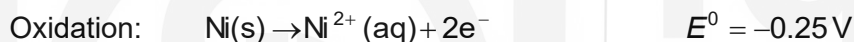
Example 7.7: Calculate the emf of the galvanic cell given by the following cell diagram. (Given: $E_{\text{Ni}^{2+}/\text{Ni}}^0 = -0.25$ and $E_{\text{Pb}^{2+}/\text{Pb}}^0 = -0.13$)



Solution: We know that according to the Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log Q$$

Therefore, to calculate the value of E_{cell} we need to know E_{cell}^0 and Q . To calculate the value of E_{cell}^0 we would proceed as in Example 7.4. We note here that nickel is getting oxidised whereas lead ions are getting reduced. The corresponding half-cell reactions would be



The cell reaction would be



We know that

$$E_{\text{cell}}^0 = E_{\text{Right}}^0 - E_{\text{Left}}^0$$

Substituting the values, we get

$$E_{\text{cell}}^0 = -0.13 - (-0.25) = 0.12 \text{ V}$$

You would recall from your earlier study on chemical equilibrium that the reaction quotient, Q for a reaction has the same expression as that of equilibrium constant but the concentrations are not at equilibrium. So for the cell reaction given above, we can write

$$Q = \frac{[\text{Ni}^{2+}]}{[\text{Pb}^{2+}]}$$

Note here that in this expression we have not included the concentrations of solid lead and nickel as these are taken as 1. Substituting the standard cell emf, value of Q and the number of electrons (n) in the Nernst equation we get

$$E_{\text{cell}} = 0.12 - \frac{0.0592}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Pb}^{2+}]}$$

Substituting the given concentrations of ions, we get

$$E_{cell} = 0.12 - \frac{0.0592}{2} \log \frac{0.03}{0.30}$$

Simplifying, we get

$$E_{cell} = 0.1496 \text{ V}$$

As the cell emf is found to be positive it means that the reaction as written will be spontaneous under given conditions.

Predicting spontaneity of a cell reactions under non-standard conditions

You have learnt above that the cell emf is directly related to the Gibbs energy change and the expressions for the cells under standard and non-standard conditions are as given below

$$\Delta_r G^0 = -nFE_{cell}^0 \quad \dots(7.33)$$

$$\Delta_r G = -nFE_{cell} \quad \dots(7.34)$$

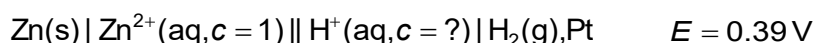
You have learnt about the determination of E_{cell} for a voltaic cell under nonstandard conditions in example 7.7. Once its value is known it can be used to get the Gibbs energy change for the reaction. The algebraic sign of either the cell emf or of Gibbs energy change can be used to predict the spontaneity of a cell reaction under non-standard conditions.

Determination of pH value of a solution

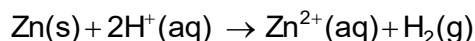
You know that the pH value is a measure of the concentration of hydrogen ions in an aqueous solution. In other words, if we can measure the concentration of hydrogen ions in a solution, we can in principle determine its pH value. Now the question is can we use the emf measurement to find the pH of a solution? The answer is yes. We can do so by making the given solution a hydrogen electrode by dipping a platinum electrode in it and bubbling hydrogen gas around it at a pressure of 1 bar. This hydrogen electrode can be combined with another electrode to form a galvanic cell. As the concentration of hydrogen ions in the given solution is different from standard conditions, the cell so formed will be under non-standard conditions. The measured emf of such a cell can then be used to determine the concentration of hydrogen ions and hence the pH of the solution. Let us understand it with the help of an example.

Example 7.8: The aqueous solution of an acid is provided with a platinum electrode around which hydrogen gas is bubbled at a pressure of 1 bar. The hydrogen electrode so obtained is combined with a standard zinc electrode to construct a galvanic cell. If the emf of the cell at 298 K is found to be 0.39 V, find the pH of the solution. (Given: $E_{Zn^{2+}/Zn}^0 = -0.77 \text{ V}$)

Solution: The cell can be represented as



The corresponding cell reaction would be



The standard cell emf would be

$$E_{\text{cell}}^0 = 0.00 - (-0.77) = +0.77 \text{ V}$$

The Nernst equation for the cell can be written on the basis of cell reaction as

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log \frac{[\text{Zn}^{2+}] p_{\text{H}_2}}{[\text{Zn}][\text{H}^+]^2}$$

As the concentration of pure solids is taken as 1 and $p_{\text{H}_2} = 1$ bar we can write,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

Since we have standard zinc electrode, $[\text{Zn}^{2+}] = 1\text{M}$, substituting the values,

$$0.39 = 0.77 - \frac{0.0592}{2} \log \frac{[1]}{[\text{H}^+]^2}$$

Rearranging we write,

$$-0.38 = -\frac{0.0592}{2} \log \frac{[1]}{[\text{H}^+]^2} = \frac{0.0592}{2} \log [\text{H}^+]^2$$

$$-0.38 = 0.0592 \log [\text{H}^+] \Rightarrow 0.38 = -0.0592 \log [\text{H}^+]$$

$$\Rightarrow 0.38 = 0.0592 \text{ pH} \Rightarrow \text{pH} = \frac{0.38}{0.0592} = 6.42$$

Thus, the pH of given solution is calculated to be 6.42

Determination of K_{sp} of a sparingly soluble salt

You have learnt about the solubility and solubility product of sparingly soluble salts in BCHCT-133 course. You would recall that these salts have extremely low solubility. The dissolved part of the sparingly soluble salt in its solution can be considered to be fully dissociated. The product of the molar concentrations of the constituent ions in solution, each raised to the power of its stoichiometric coefficient in the solubility equilibrium is called solubility product. The emf measurement can be used to determine the solubility product of a sparingly soluble salt. The principle of such a determination is similar to that of the determination of pH of an aqueous solution explained above. Let's understand it with the help of an example.

Example 7.9: A silver-silver ion electrode formed by dipping a silver rod in a saturated solution of AgCl showed a potential of 0.50 V when combined with a standard hydrogen electrode. Calculate the solubility product of AgCl. (Given: $E_{\text{Ag}^+/\text{Ag}}^0 = 0.80 \text{ V}$)

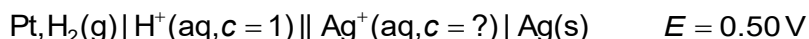
Solution: We know that for AgCl, $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$

Also, we know that the concentration of silver ions and chloride ions will be equal. If the solubility of the salt is 's', then the concentrations of silver and chloride ions would be $s \text{ mol dm}^{-3}$ each.

We can write

$$K_{sp} = s^2 \text{ mol}^2 \text{ dm}^{-6}$$

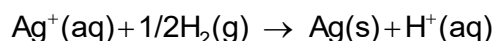
Thus, if we know the concentration of silver ions in the solution, we can find the solubility product. The concentration of the silver ions can be obtained from the emf of given cell. The cell can be represented as



The standard cell emf would be

$$E_{cell}^0 = 0.80 \text{ V} - (0.00 \text{ V}) = +0.80 \text{ V}$$

The cell reaction would be



We can write the Nernst equation as

$$E_{cell} = E_{cell}^0 - \frac{0.0592}{n} \log \frac{[\text{Ag}][\text{H}^+]}{[\text{Ag}^+]p_{\text{H}_2}^{1/2}}$$

As the concentration of pure solids is taken as 1, and for standard hydrogen electrode the concentration of hydrogen ions is 1M and the pressure of hydrogen gas is $p_{\text{H}_2} = 1 \text{ bar}$ we can write,

$$E_{cell} = E_{cell}^0 - \frac{0.0592}{n} \log \frac{1}{[\text{Ag}^+]}$$

Substituting the values,

$$0.50 = 0.80 - \frac{0.0592}{n} \log \frac{1}{[\text{Ag}^+]}$$

Simplifying, we get

$$\log[\text{Ag}^+] = \frac{-0.30}{0.0592} - 5.07 \Rightarrow [\text{Ag}^+] = 8.5 \times 10^{-6} \text{ mol dm}^{-3}$$

Substituting in the solubility product expression, we get

$$\Rightarrow K_{sp} = (8.5 \times 10^{-6})^2 = 7.225 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$$

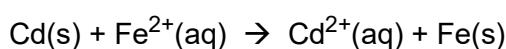
Thus, the solubility product of silver chloride is calculated to be

$$= 7.225 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$$

Having learnt about the Nernst equation and its applications, let's now take up different types of electrodes used in electrochemical cells. However, before that solve the following simple questions to assess your understanding.

SAQ 6

Will the following reaction as written, be spontaneous if the concentrations of Fe^{2+} and Cd^{2+} ions are 1.00 M and 0.20 M respectively? (Use Table 7.1)



SAQ 7

The emf of a voltaic cell containing copper and silver electrodes is found to be 0.40 V. If the concentration of silver ions is 0.70 M, calculate the concentration of copper ions. (Use Table 7.1)

7.8 TYPES OF ELECTRODES

A large number of different types of electrodes are employed in the electrochemical cells. These are classified as

- Gas electrodes
- Metal-metal ion electrodes
- Metal-sparingly soluble salt electrode
- Redox electrodes
- Amalgam electrodes
- Membrane electrodes

Let's learn about these types of electrodes with their representative examples.

Gas electrodes: These consist of a gas bubbled around an inert metal rod / strip like platinized platinum dipped in a solution containing ions to which the gas is reversible. Over a period of time, the gas gets adsorbed on the inert metal and an equilibrium is established between the gas and its own ions in the solution. Standard hydrogen electrode, about which you have learnt above is an important example of this class. The reduction half-cell reaction for hydrogen electrode and its representation is given as



The potential of the gas electrode depends on the pressure of the gas, and the concentration of the ions in solution. For hydrogen gas electrode, the Nernst equation can be written as

$$E = E^0 - \frac{0.0592}{1} \log \frac{p_{\text{H}_2}^{1/2}}{c_{\text{H}^+}} \quad \dots(7.50)$$

Since for standard hydrogen electrode, E^0 is taken as zero, we can write

$$E = -\frac{0.0592}{1} \log \frac{p_{\text{H}_2}^{1/2}}{c_{\text{H}^+}} \Rightarrow E = 0.0592 \log \frac{c_{\text{H}^+}}{p_{\text{H}_2}^{1/2}} \quad \dots(7.51)$$

Other commonly used gas electrodes, their representation and half-cell reactions are given below.

Gas electrode	Half-cell reaction	Representation
Oxygen electrode	$\frac{1}{2} \text{O}_2(\text{g}) + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{OH}^-(\text{aq})$	$\text{Pt}, \text{O}_2(\text{g}) 1\text{bar} \text{OH}^-(\text{aq}, c = 1) $
Chlorine electrode	$\frac{1}{2} \text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq})$	$\text{Pt}, \text{O}_2(\text{g}) 1\text{bar} \text{Cl}^-(\text{aq}, c = 1) $

Metal-metal ion electrode

It is the one of the most commonly used categories of electrodes. A metal-metal ion electrode typically consists of a metal strip /rod in contact with a solution of its own ions to which the electrode is reversible. The half-cell reaction for such an electrode can be given as



A standard metal-metal ion electrode is represented as



The potential of metal-metal ion electrode depends on the concentration of the metal ions in the solution and the temperature. The Nernst equation for the electrode can be given as

$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{0.0592}{n} \log \frac{1}{[M^{n+}]} \quad \dots(7.53)$$

Zn | Zn²⁺; Cu | Cu²⁺; Pb | Pb²⁺ and Ag | Ag⁺; are common examples of metal-metal ion electrodes.

Amalgam electrode

In case of certain metals it is not possible to use pure metal as it can react with water, e.g., potassium. In such cases, an amalgam of the metal is used and the electrodes are called **amalgam electrodes**. Electrical contact is made by a platinum wire dipped into the amalgam pool. For example, the potassium amalgam electrode can be represented as



The potential of amalgam electrodes depend on the concentration (activity) of the metal in the amalgam. The potential of amalgam electrode can be given as

$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{0.0592}{n} \log \frac{[M(Hg)]}{[M^{n+}]} \quad \dots(7.55)$$

The amalgam electrodes have an added advantage as these attain equilibrium relatively easily as compared to pure metal electrodes.

Metal –sparingly soluble salt electrode: such an electrode consists of a metal in contact with one of its sparingly soluble salts and a salt solution containing negative ion common with the salt. The electrode reaction involves a reversible reaction between the metal and the negative ion to form sparingly soluble salt accompanied by the liberation of electrons. Calomel electrode and silver-silver chloride electrodes are common examples of this type of electrodes.

The calomel electrode consists of mercury (Hg) in contact with its insoluble salt, mercurous chloride (Hg₂Cl₂) and a solution of KCl. The electrode is represented as



The calomel electrode is reversible to chloride ions and its potential depends on the concentration of chloride ions. However, if we take a saturated solution of KCl then it's half-cell potential becomes constant (0.2682 V) and the electrode is called **Saturated Calomel Electrode** (SCE). As a consequence, it is commonly used as a reference electrode. The SCE is represented as



When used as a cathode in a galvanic cell, the mercurous chloride is reduced to mercury as per the following equation

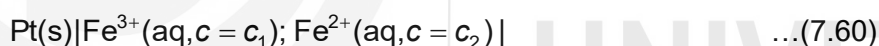


As it is inconvenient to use standard hydrogen electrode, the saturated calomel electrode is commonly employed as a reference electrode in electrochemical work. Once it has been calibrated against the SHE, it can be used to determine the standard electrode potentials of many other electrodes

Redox electrodes

This type of electrodes consists of an inert metal like platinum in contact with an aqueous solution of the ions of an element in different oxidation state. The metal electrode does not react with the species in solution, it merely acts as a carrier of electrons. A system in which a platinum electrode is dipped in an aqueous solution containing ferrous and ferric ions is one of the most commonly used redox electrode.

The half-cell reaction, and electrode representation for it can be given as



The potential of such an electrode depends on the ratio of the concentrations of the metal ions in the two different oxidation states. For the Ferric/ferrous ion electrode, we can write

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - \frac{0.0592}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \quad \dots(7.61)$$

Membrane electrodes

In this type of electrode two solutions having different concentrations of the same salt are separated by a membrane that is selectively permeable to one of the ions of the salt. This ion would tend to diffuse through the membrane whereas the other ion will not be able to do so. As a consequence, a potential develops across the membrane. A glass electrode used for the measurement of pH of aqueous solutions is one of the most common examples of this class. You would learn in detail about glass electrode in the next unit when we would take up pH determination as an application of emf measurements.

Let us now sum up what we have discussed in this unit. However, before that solve the following simple question to assess your understanding.

SAQ 8

A redox electrode contains aqueous solution of Sn^{4+} and Sn^{2+} ions in which a platinum rod is dipped.

- Write the electrode reaction
- Give the half-cell representation
- Using data from Table 7.1 calculate the potential of the electrode if the concentrations of stannous and stannic ions are 0.50M and 0.25 M respectively.

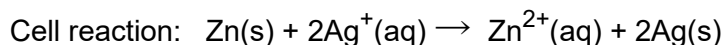
7.9 SUMMARY

In this first unit on electrochemistry, we started by introducing the domain of electrochemistry as the one that deals with the study of production of electricity from energy released during spontaneous chemical reactions and also the use of electrical energy to make non-spontaneous reactions possible. Thereafter, we took up electrochemical cells wherein we talked about Galvanic and electrolytic cells. Since our main focus in this unit was on galvanic cells we explained different aspects of galvanic cells by taking Daniell cell as a representative example. This was followed by differentiating between reversible and irreversible cells.

The next topic we took up was the representation of galvanic cells wherein we talked about writing cell-notation or cell diagram for a given galvanic cell, and its relationship with the cell reaction. This was followed by the concept of emf of the cell and its measurement. In this context we introduced the concepts of electrode potential; standard electrode potential and cell emf etc. Thereafter, we explained the relationship between cell emf and thermodynamic parameters like, Gibbs energy, equilibrium constant etc. We also discussed about the Nernst equation and its applications. Towards the end of the unit we described different types of electrodes used and also explained the reactions taking place in them along with their advantages.

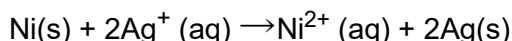
7.10 TERMINAL QUESTIONS

- Write the cell diagram for a galvanic cell in which the following reaction takes place.



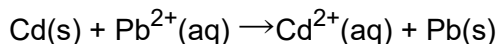
Assume that potassium nitrate is used as electrolyte in the salt bridge and the concentrations of zinc ions and silver ions are c_1 and c_2 , respectively.

- Calculate the emf of a Daniell cell in which the concentration of zinc ions in zinc electrode and copper ions in copper electrode are 0.050 and 0.025 M respectively.
- The cell reaction for a galvanic cell is given below



- Write the half-cell reactions at the anode and the cathode

- b) Calculate the value of standard cell emf
 - c) Predict whether the cell reaction given above is spontaneous or not
4. The standard electrode potential of zinc electrode is -0.77V . Calculate the potential of zinc electrode containing 2M aqueous solution at 300K
5. The cell reaction for a galvanic cell is given below



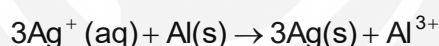
- a) Write the half-cell reactions at the anode and the cathode
- b) Calculate the value of cell emf under standard conditions
- c) Calculate the cell emf if the concentrations of cadmium and zinc ions are 0.02 M and 0.2 M respectively.

7.11 ANSWERS

Self Assessment Questions

1. Galvanic cells are the electrochemical cells in which the Gibbs energy change of the redox reaction is utilised to perform electrical work.

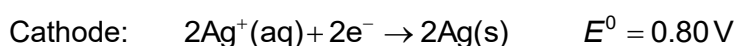
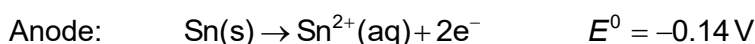
As the silver ions are getting displaced this means that these ions are getting reduced. Further, since the reduction must be accompanied by oxidation, the aluminium metal would get oxidised to give aluminum ions. Therefore, if a galvanic cell is formed by using aluminum and silver electrodes, the aluminium electrode would act as anode whereas silver electrode would act as cathode. The cell reaction can be given as



2. A cell-diagram is a shorthand notation (a symbolic representation) of an electrochemical cell. The cell-diagram of the galvanic cell in which the given reaction takes place will be



3. In the given reaction tin is getting oxidised and silver ions are getting reduced. The half-cell reactions at the anode and cathode would be



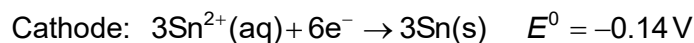
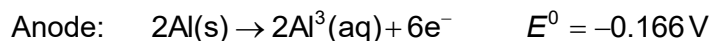
(You may note here that we have multiplied the cathodic equation by 2 to balance electrons but we have not multiplied the half-cell potential)

We know that $E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$

Substituting the values from Table 7.1, we get

$$E_{\text{cell}}^0 = 0.80 - (-0.14) = 0.94\text{ V}$$

4. In the given reaction aluminum is getting oxidised and tin ions are getting reduced. The half-cell reactions at the anode and cathode would be



(You may note here that we have multiplied the cathodic reaction by 3 and the anodic reaction by 2 to balance electrons but we have not multiplied the half-cell potential)

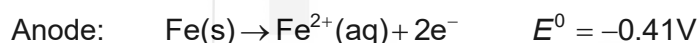
$$\text{We know that } E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

Substituting the values from Table 7.1, we get

$$E_{\text{cell}}^0 = -0.14 - (-0.166) = 0.026\text{ V}$$

Since the standard cell emf is found to be positive, the cell reaction is spontaneous.

5. The half-cell reactions for the given voltaic cell can be given as



The standard cell emf for the cell can be obtained by using the following equation

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

Substituting the values, we get

$$E_{\text{cell}}^0 = -0.40 - (-0.41) = 0.01\text{ V}$$

We know that,

$$\ln K = \frac{nF}{RT} E_{\text{cell}}^0$$

Substituting the values,

$$\ln K = \frac{2 \times 96485\text{ C mol}^{-1}}{8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 298.15\text{ K}} \times 0.01\text{ V}$$

$$\text{Solving, we get } K = 10^{0.338} = 2.17$$

Thus, the equilibrium constant for the reaction occurring in the given voltaic cell under standard conditions would be, $K = 2.17$

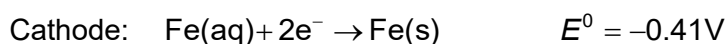
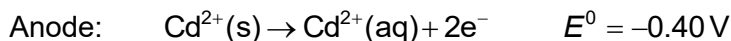
6. As the given voltaic cell is not under standard conditions, we would need to use Nernst equation to calculate cell emf.

We know that according to Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log Q$$

First, we calculate E_{cell}^0

For the given cell, the half-cell reactions can be written as



The value of E_{cell}^0 would be

$$E_{\text{cell}}^0 = 0.40 - (-0.41) = 0.01 \text{ V}$$

For the given cell reaction, the reaction quotient, Q would be

$$Q = \frac{[\text{Cd}^{2+}]}{[\text{Fe}^{2+}]} = \frac{0.2}{1.0} = 0.2$$

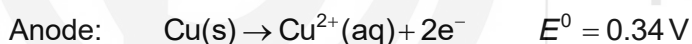
Substituting the standard cell emf, value of Q and the number of electrons (n) in the Nernst equation we get

$$E_{\text{cell}} = 0.01 - \frac{0.0592}{2} \log 0.2$$

Simplifying, we get $E_{\text{cell}}^0 = 0.03$

As the cell emf is found to be positive it means that the reaction as written will be spontaneous under given conditions.

7. From Table 7.1 we observe that the standard electrode potential of silver electrode (0.80 V) is more positive than that of copper electrode (0.34 V). This implies that there will be reduction at the silver electrode (cathode) and oxidation at copper electrode (anode). We can write the half-cell reactions as



The value of E_{cell}^0 would be

$$E_{\text{cell}}^0 = 0.80 - (0.34) = 0.46 \text{ V}$$

As the cell is not under standard conditions, we use Nernst equation, i.e.,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log Q$$

Substituting the given value of cell emf along with the computed standard cell emf, we get

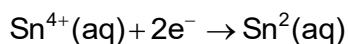
$$0.40 = 0.46 - \frac{0.0592}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

Substituting the concentration of silver ions and simplifying we get

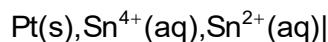
$$\Rightarrow 2.027 = \log \frac{[\text{Cu}^{2+}]}{0.0049}$$

Solving, we get $[\text{Cu}^{2+}] = 0.52 \text{ M}$

8. The electrode reaction can be written as



The corresponding half-cell can be represented as



From Table 7.1 we can see that the standard electrode potential is +0.15 V

The half-cell potential under given conditions can be obtained by using Nernst equation,

$$E = E^0 - \frac{0.0592}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}$$

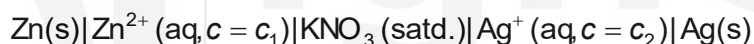
Substituting the values

$$E = 0.15 - \frac{0.0592}{2} \log \frac{0.50}{0.25}$$

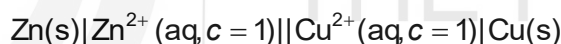
Simplifying, we get, $E = 0.141 \text{ V}$

Terminal Questions

1. The cell diagram for the given galvanic cell would be



2. The cell diagram for the Daniell cell under standard conditions can be written as



The standard cell emf, E_{cell}^0 can be obtained as

$$E_{\text{cell}}^0 = 0.34 - (-0.77) = 1.11 \text{ V}$$

The cell potential of the Daniell cell under given conditions can be obtained by using Nernst equation

$$E = 1.11 - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

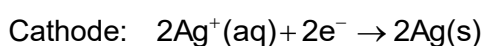
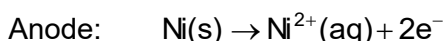
Substituting the given concentrations, we get

$$E = 1.11 - \frac{0.0592}{2} \log \frac{[0.050]}{[0.025]}$$

Solving, we get $E = 1.101 \text{ V}$

3. For the given galvanic cell

- a) The half-cell reactions can be written as



- b) The standard cell emf can be obtained as

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$

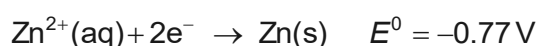
Substituting the values from Table 7.1, we get

$$E_{cell}^0 = 0.80 - (-0.25) = 1.05 \text{ V}$$

- c) As the value of the cell potential is positive, the reaction as written is spontaneous.
4. We know that the potential of an electrode under non-standard conditions can be obtained by using Nernst equation, viz.,

$$E = E^0 - \frac{RT}{nF} \ln Q$$

For zinc electrode, the half-cell reaction is



Substituting in the Nernst equation, we write

$$E = -0.77 - \frac{8.31 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{2 \times 96485 \text{ C mol}^{-1}} 2.303 \log \frac{1}{[\text{Zn}^{2+}]}$$

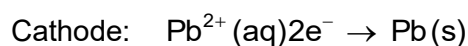
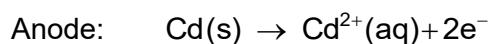
$$E = -0.77 - 0.02977 \log \frac{1}{[\text{Zn}^{2+}]}$$

Substituting the value of concentration of zinc ions, we get

$$E = -0.77 - 0.02977 \log \frac{1}{2} = -0.761 \text{ V}$$

5. For the given galvanic cell

- a) The half-cell reactions can be written as



- b) The standard cell emf can be obtained as

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$

Substituting the values from Table 7.1, we get

$$E_{cell}^0 = -0.13 - (-0.40) = 0.27 \text{ V}$$

- c) As the cell is not under standard conditions, we use Nernst equation to obtain cell emf. i.e.,

$$E_{cell} = E_{cell}^0 - \frac{0.0592}{n} \log Q$$

For the given cell, the equation becomes

$$E_{cell} = E_{cell}^0 - \frac{0.0592}{2} \log \frac{[Cd^{2+}]}{[Pb^{2+}]}$$

Substituting the values, we get

$$E_{cell} = 0.27 - \frac{0.0592}{2} \log \frac{0.02}{0.20} = 0.30 \text{ V}$$



UNIT 8

Electrochemistry-II |

Structure

8.1	Introduction	8.4	Electrolytic Cells
	Expected Learning Outcomes		Electrolysis in Different Systems
8.2	Concentration Cells		Faraday's Laws of Electrolysis
	Concentration Cells without Transference	8.5	Applications of Electrolysis
	Concentration Cells with Transference	8.6	Summary
8.3	Applications of EMF Measurements	8.7	Terminal Questions
	Determination of pH of aqueous solutions	8.8	Answers
	Potentiometric Titrations		

8.1 INTRODUCTION

In the previous unit you have learnt about galvanic cells in terms of their formation, principle of working, cell reactions and cell emf etc. You have also learnt about the thermodynamic applications of emf measurements besides different types of electrodes. In this unit, to begin with we would continue with galvanic cells and take up concentration cells, a type of galvanic cells that are obtained by combining two electrodes (or half cells) that differ only in concentration of electrolytes or the electrode material. We would take up their classification and discuss different types of concentration cells in terms of the electrode reactions, cell reactions and mechanism of their action. In this context we would also bring in the concept of liquid junction potential and its significance.

Thereafter, we would take up two important experimental applications of emf measurements. Herein, we would take up measurement of pH of aqueous solutions and potentiometric titrations. This would be followed by discussion on the other type of electrochemical cells, viz., faradaic, or electrolytic cells. We would differentiate between the voltaic and electrolytic cells and discuss about the phenomenon of electrolysis. In this context you would study the electrolysis of different types of systems that include molten salts and aqueous

solutions. Thereafter, we would take up the quantitative aspect of electrolysis and discuss about the Faraday's laws of electrolysis and their significance.

In the next unit we would take up the study of carboxylic acids.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define and classify concentration cells giving examples of different types;
- ❖ write the cell reactions and Nernst equations for different types of concentration cells;
- ❖ differentiate between electrode concentration cells and electrolyte concentration cells giving examples;
- ❖ differentiate between concentration cells with and without transference giving examples;
- ❖ define liquid junction potential and describe its development;
- ❖ derive expressions for the emf of concentration cells with and without transference;
- ❖ explain different methods of pH determination using emf measurement;
- ❖ describe the construction of glass electrode and explain the principle of its working;
- ❖ define potentiometric titration and draw a schematic graph of a redox potentiometric titration;
- ❖ discuss the differences between voltaic and electrolytic cells;
- ❖ define electrolysis and explain the electrolysis of molten salts and aqueous solutions; and
- ❖ state Faraday's laws of electrolysis and give their significance.

In principle, if two identical electrodes are immersed in the same solution, the cell potential will be zero. However, if either the electrodes have different composition or they are immersed in solutions of different concentrations, a cell potential will develop

8.2 CONCENTRATION CELLS

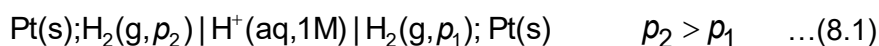
You would recall from the previous unit that the galvanic cells we considered had two different electrodes having different half-cell reactions. Such cells are commonly referred to as **chemical cells** as these produce electrical energy from chemical changes. In another type of galvanic cells, we use two identical electrodes having the same half-cell reactions; however, these differ in terms of concentration of electrolytes or the composition of electrode material. Such galvanic cells are called **concentration cells**. In such cells, there is no overall chemical reaction; the change in emf is due to the change in the concentration of the electrolyte or the electrodes. The concentration cells can be divided into two groups depending on whether they differ in the electrode material or the concentration of the electrolyte. The two types are:

- Electrode concentration cells
- Electrolyte concentration cells

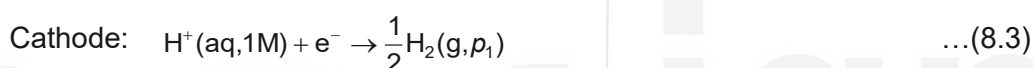
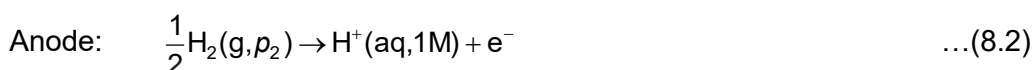
Let us learn about these in somewhat details.

8.2.1 Electrode Concentration Cells

As the name suggests, in such concentration cells the composition of electrode material is different. For example, if we take two hydrogen electrodes in which the hydrogen gas at different pressures is bubbled around the platinum electrode and dip them in an aqueous solution containing 1 M hydrogen ions. This will form a electrode concentration cell and can be represented by the following cell-diagram



You may note here that the electrode in which the pressure of hydrogen gas is more, would form the anode (i.e., oxidation would take place at this electrode). The two half-cell reactions would be



The overall cell-reaction (obtained by adding Eq. 8.2 and Eq. 8.3) would be



The Eq. (8.4) implies that the cell reaction involves a transfer of hydrogen gas from higher pressure to lower pressure. The cell emf can be expressed in terms of the following Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{F} 2.303 \log \frac{p_1}{p_2} \quad \dots(8.5)$$

It is important to note that the standard cell emf, E_{cell}^0 of any concentration cell would be zero. This is so because the electrodes are identical, and their standard electrode potentials would be equal, and their difference would be zero.

$$E_{\text{cell}}^0 = E_{\text{H}^+/\text{H}_2}^0 - E_{\text{H}^+/\text{H}_2}^0 = 0 \quad \dots(8.6)$$

So, we can write,

$$E_{\text{cell}} = -\frac{RT}{F} 2.303 \log \frac{p_1}{p_2} = 2.303 \frac{RT}{F} \log \frac{p_2}{p_1} \quad \dots(8.7)$$

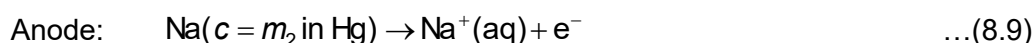
Since p_2 is greater than p_1 , the value of E_{cell} will be positive and the net cell reaction would be spontaneous and proceed till the two pressures become equal. This is why it was stated that the hydrogen electrode with greater pressure of hydrogen would form anode. If we had taken the electrode with lower pressure as anode, then the cell reaction would not have been spontaneous. *You may note here that the E_{cell} in this case depends only on the pressure of hydrogen gas in the two electrodes and is independent of the concentration (or activity) of hydrogen ions.*

Two **amalgam electrodes** having different electrode compositions (activities) in contact with the solution of an electrolyte having the ion of the metal in the amalgam can also combine to form concentration cells. For examples, two sodium amalgam electrodes having varying concentrations (molalities) of sodium metal are dipped in a solution of sodium chloride to form an electrode concentration cell.

The cell diagram and the cell reaction for the electrode concentration cell so obtained can be given as



Here again, the electrode with higher concentration of sodium metal in the amalgam would form the anode.



The overall cell-reaction would be



Again, the cell reaction involves a transfer of sodium from the amalgam having higher concentration of sodium to the one having lower concentration. The cell emf can be expressed in terms of the following Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{F} 2.303 \log \frac{m_1}{m_2} \dots (8.12)$$

As E_{cell}^0 will be zero, we can write that

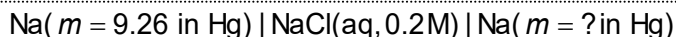
$$E_{\text{cell}} = -\frac{RT}{F} 2.303 \log \frac{m_1}{m_2} = 2.303 \frac{RT}{F} \log \frac{m_2}{m_1} \dots (8.13)$$

Since $m_2 > m_1$, the E_{cell} will be positive, and the net cell reaction would be spontaneous and proceed till the concentrations of sodium in the two electrodes become equal. You may also note that the E_{cell} depends only on the concentration of sodium in the amalgam electrodes and is independent of the concentration of sodium ions. Let us take an example to learn about the use of electrode concentration cell.

Example 8.1: The label of a sample of sodium amalgam having small amount of sodium was lost. In order to determine its composition, it was combined with another sample of sodium amalgam in which the concentration of sodium was 9.26 *m*. The two electrodes were dipped into a sample of 0.2 M sodium ions and the cell emf was found to be 0.03V at 298 K. Determine the composition of the sample of sodium amalgam with lost label.

Solution: As the given sample of sodium amalgam is supposed to have a small amount of sodium, this would act as cathode in the electrode concentration cell formed with another sample of sodium amalgam having a concentration of 9.26 *m*. The cell can be represented as

You may note here that in case of amalgam concentration cells we have used molality as the unit for concentration. This is only for convenience. We could use molarity also as used in other cases.



The cell emf would be

$$E_{\text{cell}} = 2.303 \log \frac{RT}{F} \log \frac{9.26}{m}$$

Substituting the values at 298 K, we get

$$0.03 = 0.0592 \log \frac{9.26}{m}$$

Simplifying, we get $\log \frac{9.26}{m} = \frac{0.03}{0.0592} = 0.507$

Taking antilog and solving

$$\frac{9.26}{m} = 3.214 \Rightarrow m = \frac{9.26}{3.214} = 2.88 m$$

Thus, the concentration of sodium metal in the sample of sodium amalgam with lost label would be 2.88 *m*.

Let us take the second type of concentration cells, viz., electrolyte concentration cells. However, before that answer the following simple question to assess your understanding.

SAQ 1

Write the electrode reactions, cell reaction, and calculate the E_{cell} of the following electrode concentration cell at 298 K.



8.2.2 Electrolyte Concentration Cells

In this type of concentration cells, the composition of electrode material of both electrodes is same, but these are dipped in the electrolyte solutions of different concentrations. For example, if we take two copper electrodes ($\text{Cu} \mid \text{Cu}^{2+}$) in which the concentrations of copper ions are different (say c_1 and c_2 respectively; $c_2 > c_1$) and combine them to form a galvanic cell, these will give an electrolyte concentration cell as shown in Fig. (8.1).

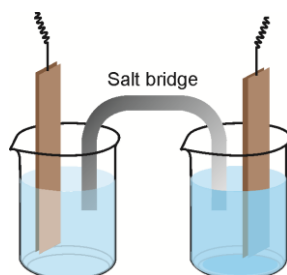
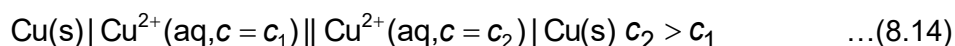
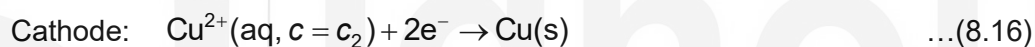


Fig. 8.1: The arrangement of two copper half-cells in a electrolyte concentration cell.

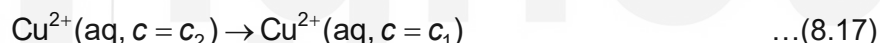
Let us ask a question; in which direction will the electrons flow in this cell? Or which half cell would act as the anode and which one would be the cathode. To answer this question we use the fact that the system would have a natural tendency to equalise the concentration of copper ions in the two half-cells. This is possible if the concentration of copper ions increases in the half-cell with lower concentration and decreases in the one with higher concentration. We know that the concentration of metal ion in metal-metal ion electrode can increase by the oxidation of metal. Similarly, the concentration of metal ions can decrease by their reduction. Thus, we can say that the electrode with higher metal ion concentration would act as the cathode where metal ions would get reduced and the one with lower concentration of metal ion would act as anode where metal ions would be formed. On the basis of these arguments, we can represent the cell by the following cell-diagram



By adding two half-cell reaction, the half-cell reactions would be



The overall cell-reaction would be



This reaction represents the transport of cupric ion from a region of higher concentration to that of lower concentration. The cell emf would be given in terms of the following Nernst equation

$$E_{\text{cell}} = -\frac{RT}{F} 2.303 \log \frac{c_1}{c_2} = 2.303 \frac{RT}{F} \log \frac{c_2}{c_1} \quad \dots(8.18)$$

You may note that in the concentration cells the net reaction involves only changes in composition of species and there is no net oxidation or reduction.

As c_2 is greater than c_1 , the cell emf would be positive and the cell reaction would be spontaneous.

You might have noticed that in the three different concentration cells considered above, we have stated that the cell reaction corresponds to the transfer / transport from the region of higher concentration (activity) to the region of lower concentration (activity). Now the question is how does it happen? What is the mechanism? Let us understand it with the example of the electrolyte concentration cell given above.

You may see here that in the cell we have used a salt bridge (two vertical lines in the cell diagram to separate the two half cells and allow for the completion of the circuit. You would recall from the previous unit that when we use a salt bridge containing high concentration of an inert electrolyte like KCl or KNO_3 , the ion transport across the electrolytic solutions is in terms of the ions of the electrolyte taken in the salt bridge. Actually, there is no direct transfer of ions from a region of higher concentration to that of the lower concentration. What happens is that when the circuit is completed, copper atoms from the anode get oxidised to copper ions and the concentration of copper ions in the anodic

half-cell increases. At the same time, an equivalent amount of copper ions from the cathodic half-cell get reduced and deposited on the cathode. Effectively, whatever amount of cupric ions disappear at the cathode, an equal amount of cupric ions appear at the anode. The changes are similar to that would happen if an actual transfer of these ions had taken place from cathodic half-cell to anodic half-cell.

With the passage of time the concentration of anodic half-cell electrolyte keeps on increasing and that of the cathodic half-cell electrolyte keeps on decreasing. This is accompanied by a decrease in the emf of the cell. Once the concentrations of copper ions in the two half-cells become equal the emf of the cell would become zero and the further reaction stops.

The electrolyte concentration cells are further divided into two types depending on whether they involve transference of electrolyte or not. The two types are

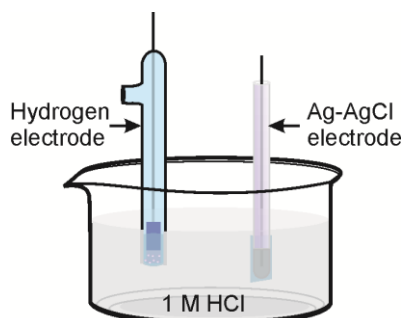
- A. Concentration cells without transference
- B. Concentration cells with transference

Let us learn about these concentration cells

A. Concentration cells without transference

A galvanic cell using $\text{Zn}|\text{Zn}^{2+}$ and $\text{Cu}|\text{Cu}^{2+}$ electrodes, can be constructed in two different ways. In one of the ways, the two electrolytic solutions are separated by a porous membrane which allows the ions to migrate through but does not allow the mixing of electrolyte solution. Such a cell is called it **cell with transference**. On the other hand, the second method involves using a salt bridge to provide connectivity between the solutions of two electrolytes and this gives a **cell without transference**. There are chemical cells; let us take up an example to see how we can construct a concentration cell without transference.

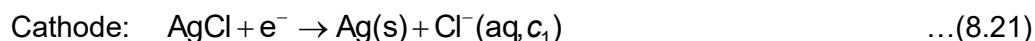
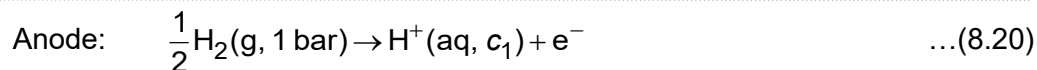
Let us take the following cell consisting of hydrogen electrode and silver-silver chloride electrode in hydrochloric acid having concentration c_1 . As the two electrodes dip directly into a solution of HCl; it is a *cell without transference*.



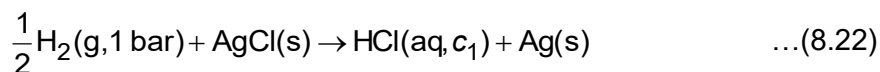
In this cell, the hydrogen electrode is reversible to the hydrogen ions whereas, Ag-AgCl electrode is reversible to chloride ions.

Fig. 8.2: A schematic diagram showing cell without transference.

On the left-hand electrode, hydrogen gas gets oxidised to form hydrogen ions, whereas at the right-hand electrode, chloride ions pass into solution and silver metal is deposited. The half-cell reactions can be written as



The overall cell reaction can be written as



The cell emf is given by the following Nernst equation,

$$E_{\text{cell}} = E_{\text{Cl}^-|\text{AgCl}|\text{Ag}(\text{s})}^0 - \frac{RT}{F} \ln c_1 \quad \dots(8.23)$$

If we take two such cells having the concentration of HCl to be c_1 and c_2 respectively and combine them opposite to each other as shown in Fig. 8.3 we get a concentration cell. If the emf of the two cells are E_1 and E_2 respectively, then the emf of the concentration cell would be $E_1 - E_2$.

The concentration cell can be represented as

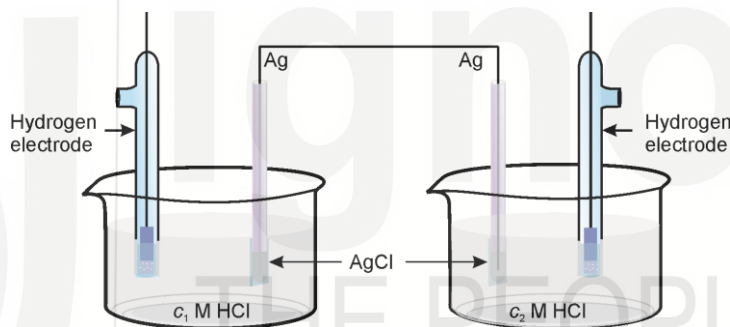
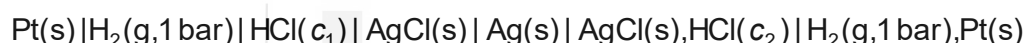
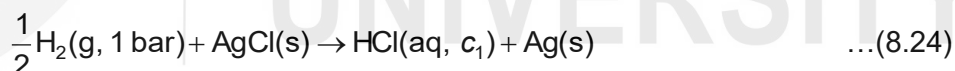
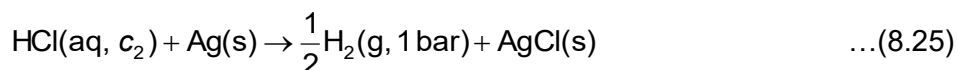


Fig. 8.3: A schematic diagram showing concentration cell without transference.

We can write the cell reaction for the cell at the left as



For the cell on the right the cell reaction would be its opposite, i.e.,



Combining the two cell reactions we get the overall reaction for the concentration cell as



Thus, the net effective change in this concentration cell is the transfer of HCl from a region of higher concentration (c_2) to the region of lower concentration (c_1).

The emf of the concentration cell without transference described above can be obtained as

$$\text{Cell on the left: } E_1 = E_{\text{Cl}^-|\text{AgCl}|\text{Ag}(\text{s})}^0 - \frac{2RT}{F} \ln c_1 \quad \dots(8.27)$$

Cell on the right: $E_2 = E_{\text{Cl}^-|\text{AgCl}|\text{Ag(s)}}^0 - \frac{2RT}{F} \ln c_2$... (8.28)

As stated above, the emf for the concentration cell would be

$$E_{\text{cell}} = E_1 - E_2 \quad \dots (8.29)$$

$$E_{\text{cell}} = E_{\text{Cl}^-|\text{AgCl}|\text{Ag(s)}}^0 - \frac{2RT}{F} \ln c_1 - E_{\text{Cl}^-|\text{AgCl}|\text{Ag(s)}}^0 + \frac{2RT}{F} \ln c_2 \quad \dots (8.30)$$

$$E_{\text{cell}} = -\frac{2RT}{F} \ln \frac{c_1}{c_2} = \frac{2RT}{F} \ln \frac{c_2}{c_1} \quad \dots (8.31)$$

You may note here that there is an indirect transfer of HCl from the region of higher (right cell) to the region of lower (left cell) concentration. With time, the concentration of HCl in the left cell increases as per Eq. (8.24) whereas that in the right cell decreases as per Eq. (8.25).

Further, we see that in this concentration cell, the electrolyte is hydrochloric acid, and one electrode (hydrogen electrode) is reversible with respect to hydrogen ions while the other electrode (Ag-AgCl) is reversible with respect to chloride ions. From this example, we can say that whenever two simple cells whose electrodes are reversible with respect to an ion each of the electrolyte are combined in opposition, a concentration cell without transference is obtained.

The concentration terms in Eq. 8.27 to Eq. 8.31 in fact, are the mean ionic activities (a_1 and a_2) of HCl in the two cells. The factor 2 in the expression appears due to conversion of product of ionic activities of hydrogen ions and chloride ions to mean ionic activity of HCl. Its derivation is beyond the scope of this course.

B. Concentration cells with transference

If we take two identical cells differing only in the concentration of the electrolyte and combine them to form a concentration cell in a way that we allow the electrolytes to be in direct contact with each other, then the cell obtained would be called *concentration cell with transference*. In such a case there will be formation of a liquid junction and consequently development of liquid junction potential. Let us take an example to learn about such a system and see how this system is different from the one without transference.

The electrodes should be reversible to one of the ions of the electrolyte.

Let us take two hydrogen electrodes in which the pressure of hydrogen gas around the platinum electrode is 1 bar each but the concentration of HCl in the solutions is c_1 and c_2 ($c_2 > c_1$) respectively.

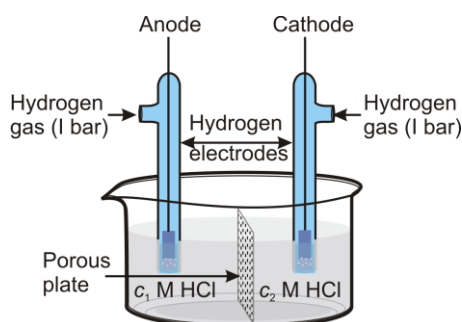


Fig. 8.4: A schematic diagram showing concentration cell with transference.

Further, we combine the two in such a fashion that the two solutions of HCl are separated by a porous plate. This allows transfer of ions across the membrane, but the direct mixing of solution is not allowed. A schematic diagram showing concentration cell with transference is given in Fig. (8.4).

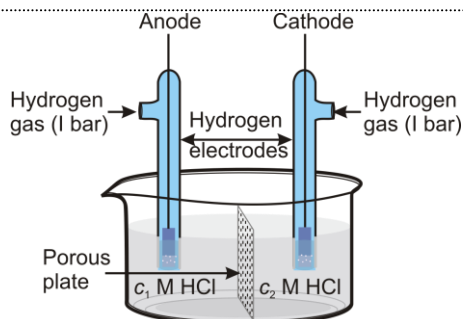
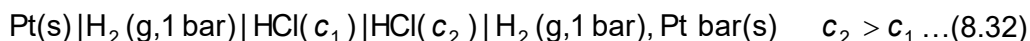
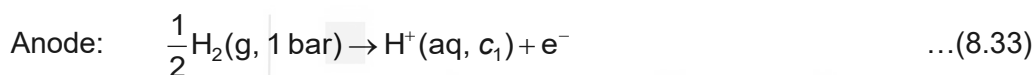


Fig. 8.4: A schematic diagram showing concentration cell with transference.

Such a cell can be represented as



You may note here that the two hydrogen electrodes are separated by a single vertical line indicating a porous membrane (you know that a salt bridge is indicated by two vertical lines). The half cell reactions can be given as



The overall cell reaction would be



Let us try to visualise the changes taking place in the cell when one Faraday of current passes through the cell.

In case of concentration cell without transference one of the electrodes was reversible to the cation whereas the other electrode was reversible to the anion. However, in case of concentration cell with transference the electrodes are reversible to one of the ions of the electrolyte.

1. Half a mole of hydrogen gas would get oxidised to give one mole of hydrogen ions at the anode
2. One mole of hydrogen ions would get reduced on the cathode and liberate half a mole of hydrogen gas
3. t_{H^+} moles of hydrogen ions will migrate across the boundary from left to right (t_{H^+} is the transport number of hydrogen ions)
4. $t_{\text{Cl}^-} = (1 - t_{\text{H}^+})$ moles of chloride ions will move in the opposite direction, i.e., from right to the left t_{Cl^-} is the transport number of hydrogen ions)

These processes can be summarised as in Fig. (8.5) given below:

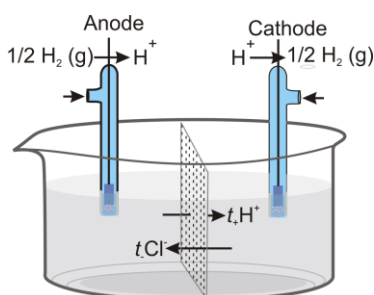
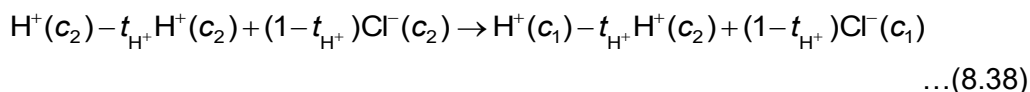


Fig. 8.5: A representation of electrode reactions and the migration of ions in a concentration cell with transference.

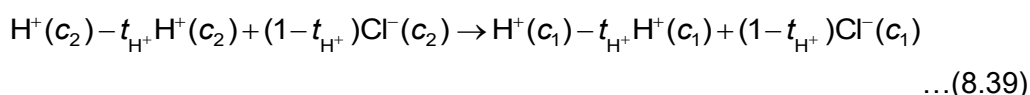
Therefore, to calculate the emf of the cell we need to consider the following changes along with the overall electrode reactions, Eq.(8.35)



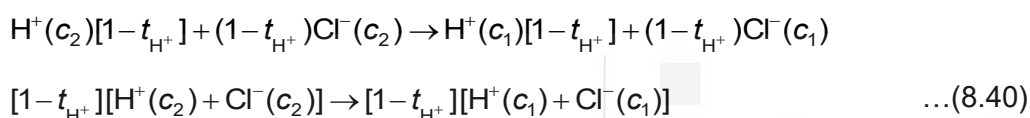
The total cell reaction can be obtained by combining Eq.(8.35), Eq. (8.36), and Eq. (8.37) as follows:



Rearranging,



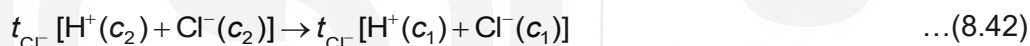
Simplifying



Now, we know that,

$$[1-t_{H^+}] = t_{Cl^-} \quad \dots(8.41)$$

Substituting, we get,



This simplified expression of the overall changes in the cell suggests that when one Faraday of current passed through the cell, t_{Cl^-} moles of HCl are transferred from the region of higher concentration to that of lower concentration. The expression for cell emf can be written as

$$E_{cell} = -\frac{2RT}{F} \ln \frac{(c_1)^{t_{Cl^-}}}{(c_2)^{t_{Cl^-}}} = t_{Cl^-} \times \frac{2RT}{F} \ln \frac{(c_2)}{(c_1)} \quad \dots(8.44)$$

You may note here that the electrodes are reversible to the cation and the expression for E_{cell} has t_{Cl^-} . It can be shown that if in the concentration cell with transference the electrode is reversible to the anion then the expression for E_{cell} would have the transport number of the cation.

In addition to the electrode reactions as given above and the consequent migration of the ions across the membrane, there will be additional transfer of ions across the membrane due to the difference in the concentration of the two electrolytes. The ions will move from the region of higher concentration to the region of lower concentration. As the hydrogen ions move faster than the chloride ions, they would travel more distance as compared to chloride ions. As a result of the difference in the speeds of the two ions there is an unequal distribution of the cations and the anions across the boundary. That is, there will be opposite charge accumulation across the boundary; positive charge

As in the case of cell without transference, the concentration terms here are the mean ionic activities (a_1 and a_2) of HCl in the two cells

towards the left compartment and negative charge towards the right compartment. Due to this charge distribution, an additional potential is developed at the junction of the two liquids. This is called **liquid junction potential**.

A schematic illustration of the development of liquid junction potential is given in Fig. (8.6).

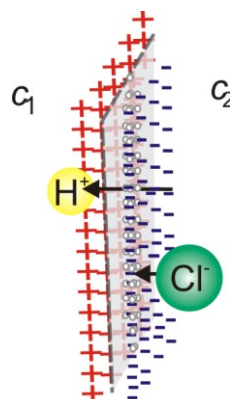


Fig 8.6: Schematic illustration of the development of liquid junction potential.

The overall emf of the cell would depend on the electrode reactions and migration of ions discussed above as well as liquid junction potential.

Determination of transport numbers using concentration cells

One important application of concentration cells is the determination of transport numbers. For this we take concentration cells having the same electrolyte and measure their emf under the conditions of with and without transference. Eq. (8.44) and Eq. (8.31) give the expressions for the emf of concentration cells with and without transference respectively, i.e.,

$$(E_{cell})_{wt} = t_{Cl^-} \frac{2RT}{F} \ln \frac{(c_2)}{(c_1)} \quad \dots(8.44)$$

$$(E_{cell})_{wt} = \frac{2RT}{F} \ln \frac{c_2}{c_1} \quad \dots(8.31)$$

Dividing Eq. (8.44) by Eq. (8.31) we get,

$$t_{Cl^-} = \frac{(E_{cell})_{wt}}{(E_{cell})_{wt}} \quad \dots(8.45)$$

Thus, the ratio of the cell emf under conditions of with transference and without transference gives the transport number. Having learnt about concentration cells; its different types and their principle, let's now take up some important applications of emf measurements. However, before that answer the following simple questions to assess your understanding of concentration cells.

SAQ 2

Two potassium amalgam electrodes having molalities of potassium as 0.015 and 0.0225 respectively are dipped in a solution of 0.01 M potassium chloride to form an electrode concentration cell. Write the cell diagram and the cell reaction for the concentration cell.

SAQ 3

Outline the requirements for the construction of concentration cells with and without transference.

8.3 APPLICATIONS OF EMF MEASUREMENTS

You would recall that in the previous unit we had discussed about a number of applications of emf measurement of simple galvanic cells e.g., the prediction of spontaneity and the determination of equilibrium constant for cell reactions in galvanic cells working under standard conditions. Further, in the context of applications of Nernst equation we took a number of applications of emf measurements of the galvanic cells working under non-standard conditions. Here, we are going to take up two important applications of emf measurements that find extensive use in analytical chemistry. We begin with the determination of pH of an aqueous solution.

8.3.1 pH Determination of Aqueous Solutions

You have learnt in the Unit 7 of BCHCT-133 course and Experiment 6 of the BCHCL-134 course about the concept of pH as a scale to quantitatively express the concentration or 'potential' of H^+ ions in the aqueous solutions especially of dilute solutions ($< 0.01 \text{ M}$). It is defined as the negative logarithm (to the base 10) of the molar concentration of hydrogen ions in solution. That is,

$$\text{pH} = -\log_{10}[\text{H}^+] \quad \text{or} \quad -\log_{10}[\text{H}_3\text{O}^+] \quad \dots(8.46)$$

Thus, to know the pH of a given solution we need to measure the concentration of hydrogen ions in it. There are a number of ways in which we can use emf measurement to find the concentration of hydrogen ions in an aqueous solution. The commonly used methods are:

- Using voltaic cell involving hydrogen electrode
- Using redox electrode: quinhydrone electrode
- Using membrane electrode: glass electrode

Let's learn about these one by one

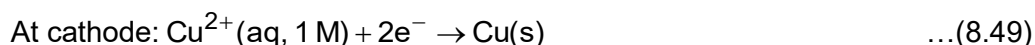
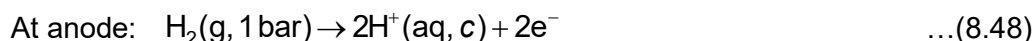
a) Using voltaic cell involving hydrogen electrode

In the previous unit, you have learnt about the standard hydrogen electrode in which hydrogen gas is bubbled at a pressure of 1 bar around the platinum electrode partially dipped in an aqueous solution of 1M HCl. Its electrode potential is defined to be zero at all temperatures. However, if the concentration of HCl is different from 1 M then the electrode potential would be different and would depend on the concentration of hydrogen ions. In other words, the measured electrode potential of the hydrogen electrode can provide the concentration of hydrogen ions. However, as you know that we cannot measure the electrode potential of a single electrode, so we need to combine it with some other standard electrode and construct a galvanic cell. The measured emf of the cell so obtained can then be related to the concentration of hydrogen ions and hence to the pH of the solution.

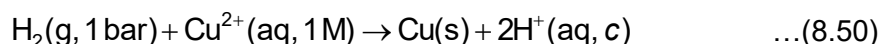
Let us take $\text{Cu} | \text{Cu}^{2+}$ electrode in which copper electrode is dipped in an aqueous solution of 1M copper ions, and combine it with the hydrogen electrode obtained by partially dipping a platinum electrode in the solution whose pH is to be measured and passing hydrogen gas at 1 bar pressure around it. The voltaic cell so obtained is represented as



The half-cell reactions would be



The overall cell reaction would be



The standard cell emf, E_{cell}^0 would be

$$E_{\text{cell}} = E_{\text{R}}^0 - E_{\text{L}}^0$$

Substituting the values, we get

$$E_{\text{cell}} = 0.34 - 0.00 = 0.34 \text{ V}$$

The emf of the constructed cell is given by the following Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{2F} \ln \frac{[\text{H}^+]^2}{[\text{Cu}^{2+}]p_{\text{H}_2}} \quad \dots(8.51)$$

Substituting the values at 298 K, we get

$$E_{\text{cell}} = 0.34 - \frac{0.0592}{2} \log[\text{H}^+]^2 \quad \dots(8.52)$$

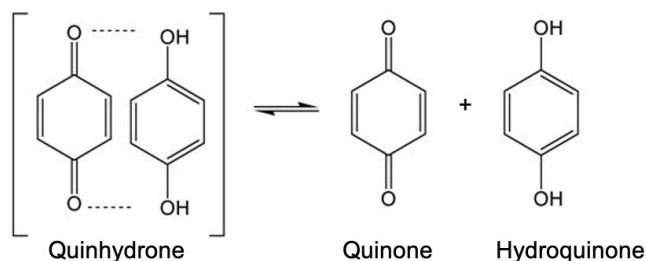
Simplifying,

$$E_{\text{cell}} = 0.34 - 0.0592 \log[\text{H}^+] \Rightarrow E_{\text{cell}} = 0.34 + 0.0592 \text{pH} \quad \dots(8.53)$$

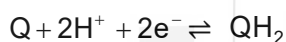
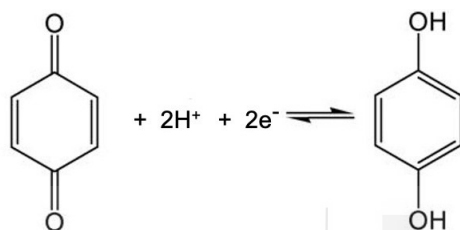
Thus, by measuring the emf of the cell we can get the value of pH of the solution. The method is quite simple and straight forward, however, using a hydrogen electrode is not very practical as firstly it is quite cumbersome to set up and secondly, the platinum electrode may lose its ability over time due to its poisoning. A better method involves using quinhydrone electrode-a redox electrode.

b) Using quinhydrone electrode (redox electrode)

You have learnt in the previous unit that a redox electrode consists of an inert electrode dipped in a solution containing a mixture of the oxidised and the reduced forms of a substance. The substance could be ionic or molecular species. We use the compound, quinhydrone (represented as Q.QH₂) for measuring the pH of a solution. It is sparingly soluble in water and produces equal concentrations of the oxidised species, quinone (Q), and the reduced species, hydroquinone (QH₂).



A shiny platinum electrode dipped in the test solution saturated with quinhydrone forms the quinhydrone electrode and is reversible to protons. The electrode reaction involves transfer of electrons between the quinone and hydroquinone and can be represented as:



The potential of the electrode is given by the following expression

$$E_{Q/QH_2} = E_{Q/QH_2}^0 - \frac{RT}{2F} \ln \frac{[QH_2]}{[Q][H^+]^2} \quad \dots(8.54)$$

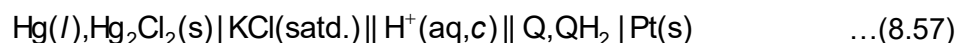
At 298 K, the standard potential of the quinhydrone electrode is found to be 0.6994 V. Further, since the amounts of the oxidised and reduced forms are equal, the expression simplifies to

$$E_{Q/QH_2} = 0.6994 - \frac{RT}{2F} \ln \frac{1}{[H^+]^2} \quad \dots(8.55)$$

Substituting the values at 298 K and simplifying, we get

$$E_{Q/QH_2} = 0.6994 + \frac{0.0592}{2} \log[H^+]^2 = (0.6994 - 0.0592\text{pH})V \quad \dots(8.56)$$

Thus, we see that the potential of the electrode depends on the pH of the solution. Now, since we cannot measure the potential of a single electrode we combine it with a standard electrode (typically saturated calomel electrode) and construct a galvanic cell and measure the emf of the cell. The cell so obtained is represented as



The cell emf will be given as

$$E_{\text{cell}} = E_R - E_L$$

The electrode potential of saturated calomel electrode at 298 K is 0.2682 V.

Substituting the values, we get

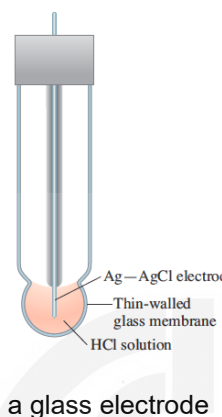
$$E_{\text{cell}} = (0.6994 - 0.0592 \text{ pH}) V - 0.2682 V = (0.4312 - 0.0592\text{pH})V$$

Rearranging, we get

$$\text{pH} = \frac{(0.4312 - E_{\text{cell}})}{0.0592} \quad \dots(8.58)$$

Thus, the measurement of the emf of the cell obtained by combining quinhydrone electrode formed from the test solution and the saturated calomel electrode provides the pH of the test solution.

The quinhydrone electrode has an advantage over the hydrogen electrode as it is quite easy to set up. However, it has a disadvantage that it gives accurate results only if the pH of the solution is less than 8. In more alkaline solutions errors arise due to the aerial oxidation of hydroquinone and the ionization of the hydroquinone that acts as an acid. Let us take up a yet another method of pH determination using emf measurements.

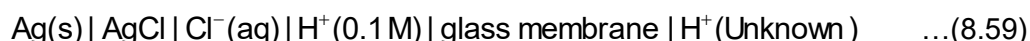


A calomel electrode can also be used in place of Ag - AgCl electrode

c) Using glass electrode (membrane electrode)

In the previous unit you have learnt that a membrane electrode consists of a membrane that separates two solutions of different concentrations of the same electrolyte and is selectively permeable to one of the ions of the salt. This ion diffuses through the membrane whereas the other ion will not be able to do so. As a consequence, a potential develops across the membrane. The potential of such an electrode depends on the concentrations of the solutions of the electrolyte.

One such electrode, a glass electrode is used for the measurement of pH of aqueous solutions. It consists of a glass tube having a thin glass membrane bulb (that is permeable to H^+ ions) at one end. The bulb is filled with a solution of a constant pH (e.g., 0.1 M HCl) and a reversible electrode like Ag-AgCl electrode (silver wire coated with silver chloride) is dipped in it. When this glass electrode is dipped in an aqueous solution whose pH is to be determined, a potential is developed across the glass membrane. This potential depends on the difference in the concentrations of hydrogen ions across the glass membrane. The glass electrode having Ag-AgCl electrode can be represented as



and the potential of the glass electrode is given by the following Nernst equation

$$E = E_{\text{glass}}^0 - \frac{RT}{nF} \ln[\text{H}^+] \quad \dots(8.60)$$

Substituting the values of R , T , F and n ; the equation at 298 K becomes

$$E_{\text{glass}} = E_{\text{glass}}^0 - 0.0592 \text{ pH} \quad \dots(8.61)$$

Generally, an electrode like saturated calomel electrode (SCE) is combined with the glass electrode that acts as a reference. The combination is called combination glass electrode and is represented as



The emf of this combination is given as

$$E_{\text{cell}} = E_{\text{SCE}} - E_{\text{glass}} \quad \dots(8.63)$$

Substituting for E_{glass} from Eq. 8.61

$$E_{\text{cell}} = E_{\text{SCE}} - (E_{\text{glass}}^0 - 0.0592\text{pH}) \quad \dots(8.64)$$

The potential of saturated calomel electrode is = 0.2682 V

Substituting the value, we get,

$$E_{\text{cell}} = 0.2682 \text{ V} - (E_{\text{glass}}^0 - 0.0592\text{pH}) \quad \dots(8.65)$$

On simplification we get,

$$\text{pH} = \frac{E_{\text{cell}} - 0.2682 + E_{\text{glass}}^0}{0.0592} \quad \dots(8.66)$$

Thus, we find that there is a direct relationship between the pH and E_{Cell} .

However, we need to find the value of E_{glass}^0 . As this value depends on the membrane; this is obtained by calibration with a buffer solution of known pH.

You may look into experiment 6 of BCHCL-134 course for the method of calibration for determination of E_{glass}^0 for glass electrode.

Having learnt about pH determination using emf measurements let us take up another important application of emf measurement, i.e., potentiometric titrations.

8.3.2 Potentiometric Titrations

You are familiar with volumetric determinations wherein a known volume of the given sample whose concentration is to be determined is made to react with a suitable reagent of known concentration with which it reacts stoichiometrically.

The volume of the reagent required for the stoichiometric reaction is determined and then used to find the concentration of the sample in question. The completion of the reaction between the sample and reagent is determined by a suitable indicator that changes its colour at the end point, indicative of the completion of the reaction. However, sometimes it may not be possible to perform such a titration because of unavailability of a suitable indicator or sometimes the sample may be deeply coloured that may mask the colour change of the indicator. In such cases an alternative process of titration is followed with the help of an instrument that can monitor the change in some physical property of the system. The potential of an electrode set up using the solution is one such physical property and potentiometer is the instrument. The titrations based on potential measurement are called **potentiometric titrations**. We would take up two types of potentiometric titrations. We begin with potentiometric titration between an acid and a base.

Acid-base potentiometric titration

You are familiar with acid-base titrations and are aware of the fact that in the course of an acid base titration the pH of the solution changes. For example,

in the titration of a sample of hydrochloric acid with NaOH, to begin the solution pH will be low (in the acidic range). When we titrate it with NaOH the added base would neutralise some of the hydrogen ions and as a consequence the concentration of hydrogen ions decreases and the pH increases. (You know that the pH of a solution is inversely related to the concentration of hydrogen ions.). This way the progress of titration can be followed by measuring the pH of the solution.

You have learnt above that the pH of a solution can be measured with the help of a glass electrode or a quinhydrone electrode whose potential is directly related to the pH of the solution being measured. Thus, we can say that a pH titration is essentially a potentiometric titration. The pH meter used for the measurement of pH in fact measures the emf of the cell formed using the test solution and converts it to the pH that is displayed on the instrument panel. It will be worthwhile that you have a relook at Experiment 7 of BCHCL-134 course.

The plot of change in emf of the cell formed from the test solution as a function of the volume of titrant gives a potentiometric titration curve. A schematic diagram showing the potentiometric titration curve of a strong acid and a strong base is given in Fig. (8.7).

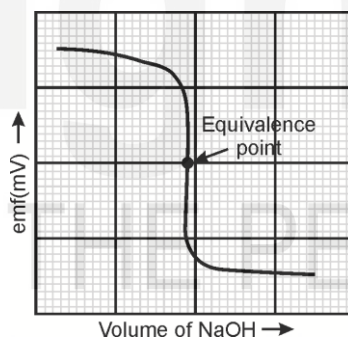


Fig. 8.7: Schematic potentiometric titration curve for a strong acid strong base titration.

The equivalence point is determined from the sharp change in the emf of the solution at the equivalence point. It is located by plotting derivative plots about which you would learn in BCHCL-136 course.

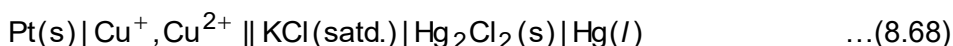
Redox potentiometric titration

As you know, a large number of analytical determinations involve estimation of strengths of oxidising or reducing agents. These are typically carried out by titrating the sample with a suitable reagent and involve oxidation-reduction or redox reactions. These titrations use redox indicators for the purpose of determining the end point. We can use emf measurement to follow such titrations and to determine the equivalence point. In such determinations we construct a galvanic cell using the redox electrode formed from the test solution and a reference electrode. You would recall from the previous unit that a redox electrode consists of an inert metal like platinum in contact with an aqueous solution of the ions of an element in different oxidation states. The inert metal does not react with the species in solution, it merely acts as a carrier of electrons. Let us understand the principle of redox potentiometric titration with the help of an example.

Let us take the following redox titration between cuprous ions and ferric ions.



In order to perform this titrations potentiometrically i.e., by emf measurement, we create the following galvanic cell



You may note that before we start the titration the cell mentioned above does not exist as the test solution contains only Cu^+ ions. However, when we add even a drop of the titrant (Fe^{3+} ions), the cell will come into existence because the added ferric ions would oxidise some cuprous ions and we would have the redox couple, $\text{Cu}^{2+} | \text{Cu}^+$. The potential of the redox electrode will be governed by the following nernst equation

$$E_{\text{Cu}^{2+} | \text{Cu}^+} = E_{\text{Cu}^{2+} | \text{Cu}^+}^0 - 0.0592 \log \frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]} \quad \dots(8.69)$$

As we add more and more of ferric ions the $\frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]}$ ratio would keep on

changing and the electrode potential and therefore the cell emf will also on keep changing.

When, all the cuprous ions are oxidised i.e., at the equivalence point once again there will not be any redox couple (we will have Cu^{2+} and Fe^{2+} ions) and the potential will be the average of the standard potentials of the $\text{Cu}^{2+} | \text{Cu}^+$ and $\text{Fe}^{3+} | \text{Fe}^{2+}$ redox couples. After the equivalence point, on addition of more ferric ions the reaction vessel will have $\text{Fe}^{3+} | \text{Fe}^{2+}$ redox couple and its electrode potential will be governed by in following expression

$$E_{\text{Fe}^{3+} | \text{Fe}^{2+}} = E_{\text{Fe}^{3+} | \text{Fe}^{2+}}^0 - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \quad \dots(8.70)$$

Addition of more and more of ferric ion solution would change the ratio leading to the change in electrode potential and hence the cell emf. A schematic diagram showing the change in the cell emf with the volume of the titrant is given in Fig. (8.8). Such a curve is called a **redox potentiometric titration curve**.

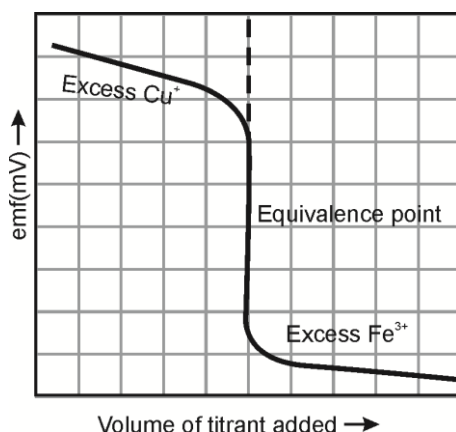


Fig. 8.8: A schematic diagram showing the redox potentiometric titration curve for titration between Cu^+ and Fe^{3+} ions.

The equivalence point of the titration can be obtained by drawing a differential curve. You would learn about these in the course BCHCL-136. Having learnt about the applications of emf measurements let's now take up electrolytic cells. However, before that, answer the following simple question to assess your understanding.

SAQ 4

pH titration is a potentiometric titration. Justify.

8.4 ELECTROLYTIC CELLS

In this and the previous unit on electrochemistry we have so far discussed about galvanic cells in which we use the Gibbs energy of a spontaneous reaction to get useful electrical work. Now, we would consider the other type of electrochemical cells in which a current is passed through the cell by an applied external voltage, to make an otherwise non-spontaneous chemical reaction to proceed. We mentioned in the previous unit that in an electrolytic cell we dip two electrodes into a solution of an electrolyte and connect them to an outside source of electricity. As a consequence, the ions in the electrolyte move towards the oppositely charged electrode and undergo chemical reactions at the electrodes; the process is called **electrolysis**. On the basis of detailed studies on different types of electrolytic reactions Michael Faraday the British chemist and physicist discovered two simple and fundamental rules that govern the decomposition of electrolyte solutions and melts by the passage of electric current. These are called Faraday's laws of electrolysis. We would take up these laws; however, before that let's first learn about electrolytic cell with the help of an example and compare it with the galvanic cells.

You would recall from the previous unit that in Daniell cell the following reaction takes place spontaneously

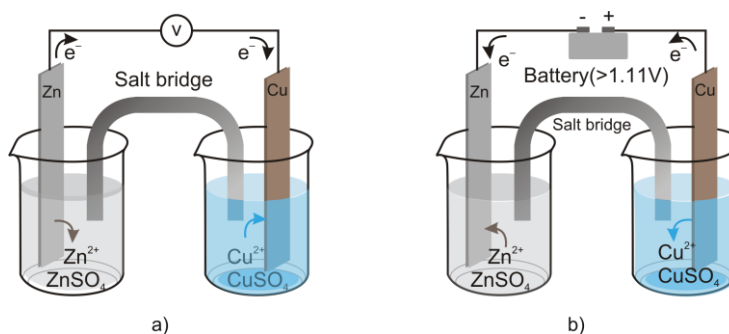
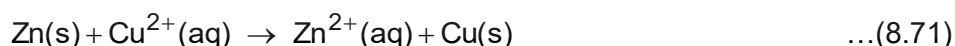
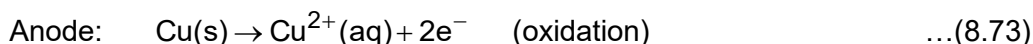
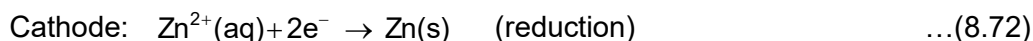


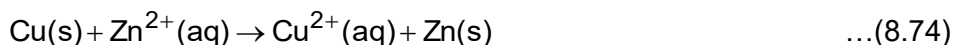
Fig. 8.9: A schematic diagram showing a) galvanic and b) electrolytic cell.

At anode, zinc is oxidised to zinc ions whereas the copper ions get reduced to copper at the cathode, Fig. (8.9(a)). The electrons flow from zinc to copper electrode in the external circuit whereas within the cell the sulphate ions carry current from copper to zinc electrode. The zinc electrode is negative whereas the copper electrode is positive and the cell emf is 1.1V.

Now when we apply a voltage greater than 1.1V by using an external battery such that the electrons are forced into the zinc electrode (acts as cathode now) and removed from the copper electrode (acts as anode now); Fig.(8.9 (b)). As a consequence, the zinc ions will get reduced and the copper metal would get oxidised to copper ions as per the following reactions.



The overall reaction would be



This reaction is opposite to the spontaneous reaction given in Eq. (8.71) i.e., it is a non-spontaneous reaction. Thus, we see that by applying a voltage greater than 1.1V, an otherwise non-spontaneous reaction is made to occur. It is important to note a few points of differentiation between voltaic and electrolytic cells here. First, in electrolytic cells the signs of anode and cathode become opposite to that in the voltaic cell; anode is positive now whereas cathode becomes negative. Secondly, and very importantly, we still have oxidation at anode and reduction at cathode. Thirdly, the cell emf becomes negative. These are summarized in the Table given below.

Cell Type	EMF	Electrode	Process	Sign
Voltaic / galvanic	Positive	Anode	Oxidation	Negative
		Cathode	Reduction	Positive
Electrolytic /Faradaic	Negative	Anode	Oxidation	Positive
		Cathode	Reduction	Negative

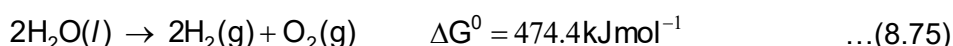
Having understood the difference between voltaic and electrolytic cell, let us now take up electrolysis of different systems in terms of the electrode reactions and products of electrolysis. It is important to note that the basic principles involved in galvanic and electrolytic cells are similar.

8.4.1 Electrolysis in Different Systems

The term electrolysis can be broken into two parts viz., *electro* and *lysis*. You know that lysis refers to cutting or breaking, so electrolysis can be seen as the process of splitting of a substance by the input of electrical energy. This is one of extensively used process in the preparation of a number of industrial chemicals and other industrial processes. We would take up the applications of electrolysis a little later; for now, let us understand about the products of electrolysis of some systems and the reasons thereof. We begin with the electrolysis of water to give hydrogen and oxygen gases.

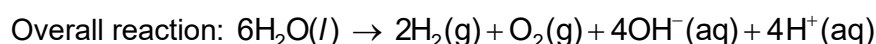
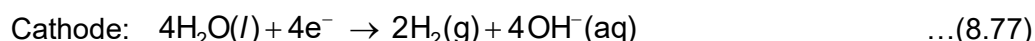
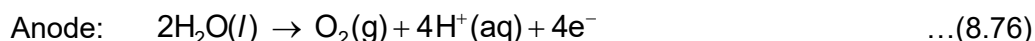
Electrolysis of Water

We know that water is a stable compound and it does not decompose on its own to form hydrogen and oxygen gas. This is due to very high standard Gibbs energy change for the following reaction.



In electrolysis we force a current through a cell to produce a chemical change for which the cell potential is negative; in other words, electrical work is used to make an otherwise nonspontaneous chemical reaction possible.

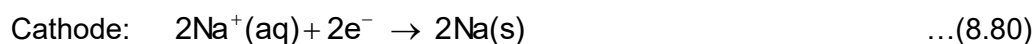
That is, the reaction is highly non-spontaneous. If we dip two non-reactive platinum electrodes in water taken in a beaker and connect them to a 6V battery to form an electrolytic cell we find that no reaction is observed. It is so because pure water contains only about $1 \times 10^{-7}\text{M}$ each of hydrogen and hydroxide ions from autoionisation. Therefore, only a negligible amount of current can flow. However, if we add a few drops of dilute sulphuric acid (or a small amount of a soluble salt) to water, we immediately observe formation of hydrogen and oxygen gases at the cathode and anode respectively. The electrode reactions are given as



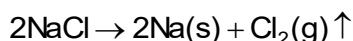
You may note that here sulphuric acid does not participate in the electrode reactions, it just provides ions for the flow of current.

Electrolysis of Molten Sodium Chloride

The electrolysis of sodium chloride is used to produce industrially important chemicals. Its electrolysis is carried out in the molten state as well as in aqueous solutions. The products of electrolysis are different in the two cases. The electrolysis of molten NaCl is an important industrial process used commercially to obtain sodium metal from sodium chloride. Two electrodes dipped into molten sodium chloride are connected to a battery. As the melting point of NaCl is extremely high ($\sim 800^\circ\text{C}$), it is mixed with CaCl_2 to decrease the melting point. On passing current, globules of sodium metal are observed at the electrode connected to the negative pole of the battery, and the evolution of chlorine gas is observed at the positive electrode. The electrode reactions are given as



The overall reaction is



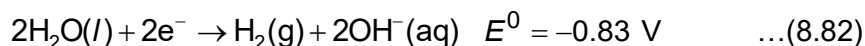
Electrolysis of aqueous solution of Sodium Chloride (Brine)

If we electrolyse aqueous solution of sodium chloride (brine) we get hydrogen gas, chlorine gas and sodium hydroxide as the products. The question comes up is that why the products are different from that obtained from molten salt.

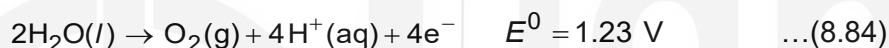
The reason for this is that in the electrolysis of a molten salt, only the ions from the salt are available to undergo reactions at the electrodes. However, in case of the electrolysis of an aqueous solution of an electrolyte, we have water as a part of the system and when we pass current through the system, we also need to consider the possibility of water undergoing reaction at one or both the electrodes. In case of electrolysis of solution of NaCl, there are two species

Of the possible electrode reactions at the cathode, the one with less negative (more positive) electrode potential will occur. Similarly, of the possible electrode reactions at the anode, the one with more negative (less positive) electrode potential will occur.

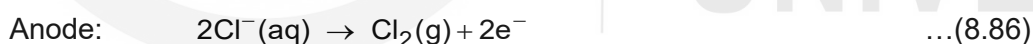
each that can get reduced or oxidised. Let us first look at the reaction at cathode, i.e., reduction. Two possible reactions are



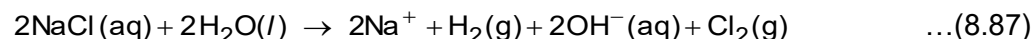
As the reduction potential for the reduction of sodium ions is highly negative; it is water that will get reduced at the cathode in preference to sodium ions. It is important to note that in cases of reactions involving formation of gaseous products in electrolysis some extra voltage is required in addition to the reduction potential of the electrode reaction. This is called **overpotential** or **overvoltage** and is of the order of about 0.4 to 0.6 V for gases like hydrogen and oxygen. The overpotential is required to overcome interactions at the electrode surface. In the present case even if we consider 0.6 V as the overpotential it would still be easier for water to get reduced as its electrode potential would still be lesser negative ($-0.83\text{V} - 0.60 \text{ V} = -1.43 \text{ V}$). On the other hand, at the anode also there are two possibilities as given below



For oxidation the electrode reaction with lesser positive potential is preferred. Here, the electrode potentials are comparable, and one may expect both the reactions to occur to some extent i.e., both the gases (Cl_2 and O_2) may form. However, due to a higher overpotential of oxygen the effective potential for the reaction 8.84 becomes ($1.23 + 0.60 = 1.83$) and it is the chlorine gas that is formed at the anode. Thus, the effective reactions at the electrodes and the overall reaction for the electrolysis of brine would be

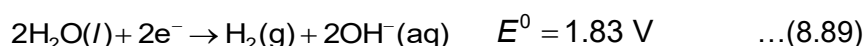


Overall reaction:

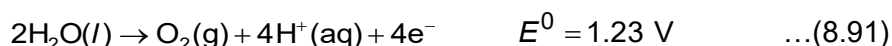
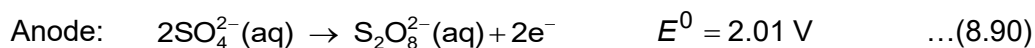


Electrolysis of Sulphuric Acid

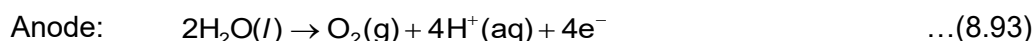
The electrolysis of sulphuric acid solution is an interesting system let us understand what happens when we electrolyse sulphuric acid solution. You know that sulphuric acid is a strong acid and practically completely ionized in its solution. Therefore, a solution of sulphuric acid will have three species i.e., hydrogen ions, sulphate ions and water that can undergo electrode reactions. Let's first look at the possible reactions at the cathode. The following two reactions are possible



As per the values of electrode potential it is the hydrogen ions that will get reduced to give hydrogen gas at the cathode. Now, let us look at possible reactions at the anode



On the basis of electrode potentials, we expect that the water will undergo oxidation in preference to the sulphate ions even if we consider the over potential for oxygen gas. Thus, the electrode reactions and overall reaction in the electrolysis of sulphuric acid can be given as



This expression is same as the expression for the electrolysis of water. You may recall from above that when we discussed about electrolysis of water, we had added a few drops of sulphuric acid to provide ionic conductivity.

So far we have discussed about the electrolysis qualitatively in terms of the products of electrolysis. From industrial perspective, it is also important to know about the amount of the products formed in an electrolytic process. The quantitative aspect of electrolysis can be understood in terms of Faraday's laws of electrolysis. Let's learn about these laws and their significance. However, before that solve the following simple questions to assess your understanding of the phenomenon of electrolysis.

SAQ 5

Give the sign and nature of process on anode in an electrolytic cell.

SAQ 6

Write the possible electrode reactions in the electrolysis of aqueous solution of potassium chloride. Using the electrode potential values given in Table 7.1, predict the reactions that would actually take place and write the overall cell reaction.

8.4.2 Faraday's Laws of Electrolysis

As stated above, Faraday formulated two laws that govern the decomposition of electrolyte solutions and melts by the passage of electric current. These laws can be stated as under:

Faraday's first law of electrolysis: It states that the amount of chemical reaction which occurs at any electrode of the electrolytic cell during

electrolysis by passage of current through the solution (or melts) proportional to the quantity of electricity passed through the electrolyte. In simple words, the amount of substance produced at each electrode is directly proportional to the quantity of charge flowing through the cell.

Faraday's second law of electrolysis: states that the amounts of different substances formed at the electrodes by the passage of a given quantity of electricity through an electrolytic cell or through different electrolytic cells connected in series are proportional to their chemical equivalent weights (masses). This law allows us to calculate the quantity of electricity that has passed through the electrolytic cell from the amounts of the substances formed at the electrodes and vice-versa. That is, if we know the amount of electricity passed, we can calculate the amounts of the substances formed or consumed at the electrodes.

We can rationalise these statements by considering the electrolysis of molten sodium chloride as discussed above. In the electrolysis of molten sodium chloride, the electrons pushed into the negative electrode (cathode) are picked up by sodium ions to form sodium metal. At the same time, an equivalent number of electrons are pulled up by the battery from the positive electrode (anode). These electrons are provided by the chloride ions that get oxidised to chlorine gas by losing electrons to the electrode. Now, if we pass more current, i.e., we push in more electrons to the cathode then more sodium and chlorine would be formed. A look at the electrode reactions reveal that there is a stoichiometric relationship.



Thus, when one mole of electrons passes through the cell, one mole of sodium metal is deposited at cathode, and one-half mole of chlorine gas is evolved at the anode. You know that an electron carries 1.602×10^{-19} coulombs of charge, therefore, the charge carried by passing 1 mole (6.022×10^{23}) of electrons will be equal to

$$1.602 \times 10^{-19} \text{ C} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 96485 \text{ C mol}^{-1} \quad \dots(8.97)$$

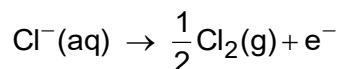
This quantity of electricity is called a Faraday of electricity and is represented as, F . In the laboratory the amount of electricity passed through the electrolytic cell is determined by measuring the amount of current and the time for which it is passed. You know that the current (I) has the units of coulombs per second (Cs^{-1}), so the product of current and time would give charge in coulombs.

$$Q(\text{C}) = I \left(\frac{\text{C}}{\text{s}} \right) \times t(\text{s}) \quad \dots(8.98)$$

The first law of electrolysis provides a method for calculating the amount of product formed at an electrode on passing a certain amount of current. This can also be used to calculate the amount of current that needs to be passed through the electrolytic cell for getting a certain amount of the product. Let us take some simple examples to understand it.

Example 8.2: Calculate the amount of chlorine gas evolved during the electrolysis of molten sodium chloride on passing a current of 0.5 A for an hour through it. (Given: $M_m(\text{Cl}_2) = 70.90 \text{ g mol}^{-1}$)

Solution: You know that in the electrolysis of molten sodium chloride, chlorine gas is evolved at the anode due to the oxidation of chloride ions as per the following reaction



This means that passage of 1 mole of electrons ($1F$) through molten sodium chloride would evolve half a mole of chlorine gas. So, first we need to calculate the amount of electricity passed.

We know that $Q = I \times t$

Substituting the values, we get

$$Q = 0.5 \text{ C s}^{-1} \times 1 \text{ h} \times 60 \text{ min h}^{-1} \times 60 \text{ s min}^{-1} = 0.5 \times 1 \times 60 \times 60 \text{ C} = 1800 \text{ C}$$

In order to calculate the number of Faradays, we divide this with Faraday's constant as

$$Q = 1800 \text{ C} = \frac{1800 \text{ C}}{96485 \text{ C F}^{-1}} = 0.0187 F$$

As per the cathode reaction $1F$ of electricity would evolve $\frac{1}{2}$ mole of chlorine; the moles of chlorine evolved by passing $0.0187 F$ of electricity would be

$$\text{Number of moles of chlorine evolved} = 0.5 \text{ mol F}^{-1} \times 0.0187 F = 0.00935 \text{ mol}$$

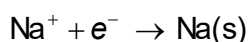
The molar mass of chlorine is 70.90 g mol^{-1} , so the mass of chlorine evolved would be

$$= 0.00935 \text{ mol} \times 70.90 \text{ g mol}^{-1} = 0.6629 \text{ g}$$

If needed, we can calculate the volume of chlorine gas evolved by using ideal gas equation $V = \frac{nRT}{p}$.

Example 8.3: Calculate the time for which a 0.6 A current be passed through a sample of molten sodium chloride to get 1 g of sodium metal. (Given: $M_m(\text{Na}) = 23 \text{ g mol}^{-1}$)

Solution: You know that in the electrolysis of molten sodium chloride sodium metal is formed at the cathode due to the reduction of sodium ions as per the following reaction



This means that passage of 1 mole of electrons ($1F$ of electricity) through molten sodium chloride would form one mole of sodium metal.

We desire to get 1 g of sodium, so we convert it to number of moles by dividing with the molar mass of sodium i.e. $= 23 \text{ g mol}^{-1}$.

$$\text{The number of moles of sodium required} = \frac{1 \text{ g}}{23 \text{ g mol}^{-1}} = 0.04348 \text{ mol}$$

As per the electrode reaction, to get 0.04348 mol of sodium we need to pass

$$Q = 0.0434 \text{ mol} \times 96485 \text{ C mol}^{-1} = 4195 \text{ C}$$

We know that $Q = I \times t$

$$4195 \text{ C} = 0.6 \text{ C s}^{-1} \times t(\text{s}) \Rightarrow t(\text{s}) = \frac{4195 \text{ C}}{0.6 \text{ C s}^{-1}} = 6991 \text{ s}$$

Thus, we need to pass 0.6 A current for 6991 s through molten sodium chloride to get 1 g of sodium metal.

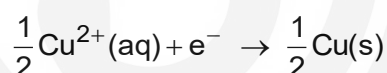
Example 8.4: Two electrolytic cells; one containing an aqueous solution of copper sulphate and the other containing an aqueous solution of silver nitrate are connected in series and a constant current of 2A is passed through them for a certain amount of time. If 16 g of silver was deposited in the electrolytic cell containing silver nitrate, calculate the time for which the current was passed, and the mass of copper deposited in the electrolytic cell containing copper sulphate. (Given molar masses of silver and copper are 107.87 and 63.55 g mol⁻¹ respectively)

Solution: We need to consider the following two reactions occurring on the cathodes of the two electrolytic cells connected in series.

Cell with AgNO₃ as electrolyte: $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$

Cell with CuSO₄ as electrolyte: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$

If we write the electrode reaction in case of copper ion as



We find that for every mole of the electrons passed through the cells the amounts (in moles) of silver and copper deposited in the respective cells are in the ratio of 1 : 1/2. We are given the mass of silver deposited that can be used to calculate the moles of silver, which in turn can be used to calculate the moles of copper.

The mass of silver deposited = 16 g

The molar mass of silver = 107.87 g mol⁻¹

$$\rightarrow \text{the number of moles of silver deposited} = \frac{16 \text{ g}}{107.87 \text{ g mol}^{-1}} = 0.1483 \text{ mol}$$

This means that 0.1483 moles of electrons have been passed, we can calculate the quantity of electricity passed by using Faraday's constant as follows

$$\text{Quantity of electricity passed} = Q = 0.1483 \text{ mol} \times 96485 \text{ C mol}^{-1} = 14309 \text{ C}$$

We know that $Q(\text{C}) = I(\text{A}) \times t(\text{s})$

$$\text{Rearranging, } t(\text{s}) = \frac{Q(\text{C})}{I(\text{A})}$$

Substituting the values, we get $t(s) = \frac{14309C}{2A} = 7154s$

Now, as stated above, amounts (in moles) of silver and copper deposited in the respective cells are in the ratio of $1:\frac{1}{2}$

Therefore, the amount of copper deposited will be $= \frac{0.1483}{2} = 0.07415\text{mol}$

In terms of mass, we get $= 0.07425\text{mol} \times 63.55\text{g mol}^{-1} = 4.7122\text{g}$

Thus, the current was passed for 7154 s and 4.7122 g of copper would be deposited on the cathode of the electrolytic cell containing CuSO_4 .

You may note that earlier constant current sources were not available and we could not get the amount of current passed by multiplying the current with time. The amount of current passed in an electrolytic cell was obtained by connecting an other electrolytic cell in series and this cell typically was made up of silver and contained silver nitrate as the electrolyte. It was called as a **coulometer** as it was used to get the current in coulombs. After the electrolysis was complete in the cell under observation, the amount of current was calculated by measuring the increase in the mass of coulometer due to silver deposited in the silver coulometer. You can now look at the above example by taking the second electrolytic cell as coulometer.

Having learnt about the quantitative aspects of electrolysis in terms of Faraday's laws and their applications we would like to take up some important applications of electrolysis. However, before that solve the following simple questions to assess your understanding of Faraday's laws of electrolysis.

SAQ 7

For how long a constant current of 5.0 A be passed through a solution of silver ions to get 25 g of silver metal? (Given: $M_m(\text{Ag}) = 107.87\text{ g mol}^{-1}$)

SAQ 8

The electrolysis of aqueous solution of KI is similar to that of aqueous sodium chloride. Calculate the volume of iodine gas evolved at the anode under normal conditions of temperature and pressure (1 atm, 273 K). Assume the gas to behave ideally.

8.5 APPLICATIONS OF ELECTROLYSIS

Electrolysis is used extensively in the area of extraction, refining and protection of elements. There are a number of elements that are produced commercially almost exclusively by this process. Some of the important ones are the metals like magnesium and aluminum and non-metals like chlorine, and fluorine. In addition, a number of inorganic compounds like, sodium hydroxide, sodium persulphate, potassium permanganate and potassium

dichromate are also prepared by electrolysis. Let us take up some general applications of electrolysis

Extraction of elements

Most of the metals in the earth's crust exist in the combined form as metal oxides. Extracting metals from these ores requires reduction of the metal ions, which is a non-spontaneous process. There are two methods based on electrolysis for the extraction of metal. In one of the methods, the ore is treated with a strong acid to get a salt. The aqueous solution of the salt is then electrolysed to obtain the metal. The other method involves the electrolysis of the ore in molten state. This process is performed in a furnace. The advantage of electrolytic extraction is that the metal is obtained in fairly pure state which can then be refined.

The chlor-alkali process is one of the most important industrial electrolytic processes based on the electrolysis of aqueous NaCl solution discussed above. This process gives two very important industrial chemicals viz., chlorine and NaOH (alkali) hence the name of the process.

Refining of metals (electrorefining)

Though electrolytic extraction of metals and non-metals provides elements in fairly pure form; they need to be further refined. Some of these refining processes also involve electrolysis. In such a process, the anode is made of the extracted metal and the electrolyte happens to be solution of metal ion. In such a process the pure metal is deposited at the cathode. For example, in the electrolytic refining of copper the block of impure copper is made the anode and acidified aqueous solution of copper sulphate is taken as the electrolyte in the electrolytic cell. The cathode where the purified metal gets deposited is made of pure copper tubes. When electric current is passed through the cell, the copper ions from the solution get reduced and deposited on the pure copper cathode. An equivalent amount of these are brought back into the solution by oxidation of copper from the impure block of the extracted metal. This process continues and the pure metal keeps depositing on the cathode and the anode keeps dissolving.

Once the process is over, a number of less reactive metals, such as gold, silver, and platinum, that are present in the impure copper are recovered as a mud that collects on the bottom of the electrolytic cell; it is called **anode mud**. On the other hand, the metals in impure copper block that are more reactive than copper remain as ions in the electrolytic bath. Other metals like silver and gold are also refined in a similar process.

Electroplating

A number of metals are protected from corrosion by plating them with other metals that are less prone to corrosion. For example, iron can be protected by a coating of zinc. Sometimes, such a coating is done for the decorative purposes also. For example, a thin coating of metallic silver is electroplated on an

underlying base of iron. The process is similar to the one described for purification of copper. In electroplating the item to be electroplated is made the

cathode in an electrolytic cell and the electrolyte contains ions of the metal to be plated. On passing electric current through the cell, the metal ions get reduced and deposited on the article made as cathode. In a similar process, steel is electrogalvanized to protect it from corrosion. The steel object to be electroplated is made the cathode and is dipped in the electrolyte containing zinc ions. Let us summarise what have we learnt in this unit.

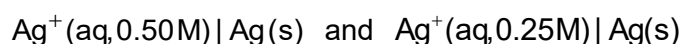
8.6 SUMMARY

In this second unit on electrochemistry, we continued with our discussion on galvanic cells and took up concentration cells. These are galvanic cells that contain two equivalent electrodes having same half-cell reactions; however, these differ in concentration of electrolytes or the composition of electrode material. In such cells there is no overall chemical reaction; the change in emf is due to the change in the concentration of the composition of the electrolyte or the electrodes. In case of electrode concentration cells, the composition of the electrodes is different whereas in case of electrolyte concentration cells it is the composition of the electrolyte in which the electrodes are dipped is different. In this context we discussed about the concept of liquid junction potential; its significance and elimination by salt bridge.

Thereafter, we took up two important experimental applications of emf measurements. The first application was the measurement of pH of aqueous solutions. In this context we discussed different methods that can be used for the determination of pH of aqueous solutions using emf measurement. The second application we discussed was the potentiometric titrations. Herein we discussed the principle of acid-base and redox of potentiometric titrations. This was followed by discussion on the other type of electrochemical cells, viz., electrolytic cells. We started this discussion by differentiating between the voltaic and electrolytic cells and then discussed about the electrolysis of different types of systems that include molten NaCl and aqueous solutions of NaCl and sulphuric acid. Towards then, we took up the quantitative aspect of electrolysis and explained the Faraday's laws of electrolysis and discussed their significance. In the end we discussed industrial application applied of electrolysis.

8.7 TERMINAL QUESTIONS

1. What are electrode concentration cells? Give any two examples.
2. An electrolyte concentration cell is formed by combining two zinc electrodes having the concentration of zinc ions as c_1 and c_2 respectively, where c_1 is greater than c_2 . Write the cell diagram, half-cell reactions and the cell reaction for it.
3. List different methods based on emf measurement that can be used for the determination of pH of aqueous solutions.
4. Consider the following two electrodes and construct a concentration cell from them.

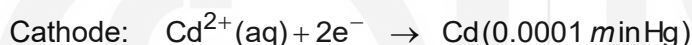
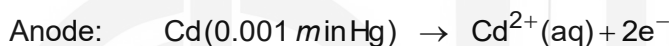


- Write the cell diagram, half-cell reactions and the cell reaction for the same and calculate the value of E_{cell}
- What is a glass electrode? Describe the construction of glass electrode.
 - Draw a schematic graph for a potentiometric titration
 - Write the possible electrode reactions in the electrolysis of aqueous solution of sodium sulphate. On the basis of electrode potential values given in Table 7.1, predict the reactions that would take place and write the overall cell reaction.
 - Calculate the constant current in amperes that will be required to pass through a sample of molten $MgCl_2$ for 24 h to get 600 kg of chlorine.
 - Give the polarity and nature of process on anode in a galvanic cell.

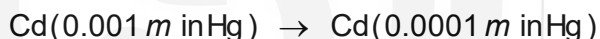
8.8 ANSWERS

Self-Assessement Questions

- For the given concentration cell, the electrode reactions would be as follows



Overall reaction would be



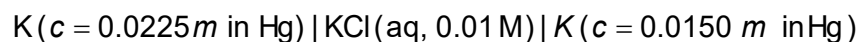
The cell emf, E_{cell} would be

$$E_{cell} = E_{cell}^0 - \frac{RT}{2F} 2.303 \log \frac{0.0001}{0.001}$$

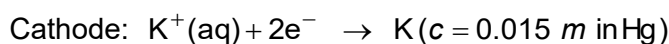
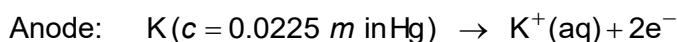
As E_{cell}^0 will be zero, so by substituting different values, we can write

$$E_{cell} = \frac{0.0592}{2} \log \frac{0.001}{0.0001} = 0.0296 \log 10 = 0.0296 \text{ V}$$

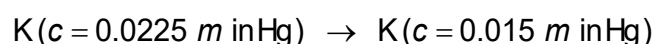
- Before we write the cell reaction, we need to remember that for an electrode concentration cell reaction to be spontaneous, the electrode with higher concentration should be the anode. Therefore, we can write the cell diagram as



The electrode reactions would be



The overall reaction would be



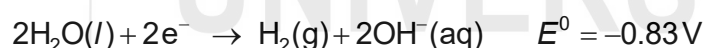
3. The following are the requirements for the construction of concentration cells

For concentration cell without transference

- The two half cells are separated by a salt bridge,
- Two half cells are combined in opposition of each other, and
- one of the electrode is reversible to the cation whereas the other electrode is reversible to the anion.

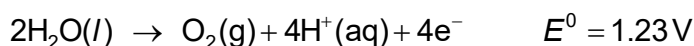
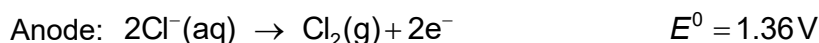
For concentration cell with transference

- The two half cells are separated by a porous plate allowing the passage of ions, but the direct mixing of solution is not allowed, and
 - The electrodes are reversible to one of the ions of the electrolyte.
4. The process of pH measurement of a solution using glass electrode actually involves the measurement of a potential developed between the hydrogen ions in the solution and the ones contained in the electrode. Therefore, if we perform an acid-base titration using a glass electrode for measuring the pH then we can say that we have performed a potentiometric titration.
5. The anode in an electrolytic cell has a positive sign and the nature of reaction at anode is oxidation.
6. In the electrolysis of aqueous solution of KCl, there are three species that can undergo electrode reactions. These are potassium ions, chloride ions and water molecules. At cathode, the following reduction reactions are possible

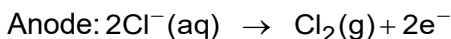
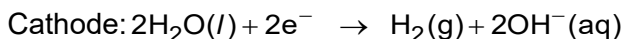


As the electrode potential for the reduction of potassium ions is highly negative; it is water that will get reduced at the cathode in preference to potassium ions. The choice will remain the same even if we consider an overpotential of about 0.4-0.6 V for formation of hydrogen.

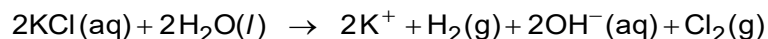
At the anode again there are two possibilities:



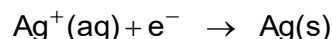
For oxidation reaction the electrode reaction with lesser positive potential is preferred. Here, the electrode potentials are comparable, and one may expect both the reactions to occur to some extent i.e., both the gases (Cl_2 and O_2) may form. However, due to a higher overpotential of oxygen, it is the chlorine gas that is formed at the anode. Thus, the effective reactions at the electrodes and the overall reaction for the electrolysis of KCl would be



Overall reaction:



7. In the electrolysis of a solution containing silver ions the following reaction will occur at cathode.



That is, the passage of 1F of electricity would deposit one mole of silver metal. We need to get 25 g of silver, so we convert it to number of moles by dividing with the molar mass of silver

$$\text{The number of moles of silver} = \frac{25\text{g}}{107.87\text{g mol}^{-1}} = 0.2318\text{mol}$$

As per the electrode reaction, to get 0.2318 mol of silver we need to pass

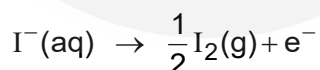
$$Q = 0.2318\text{mol} \times 96485\text{C mol}^{-1} = 22365\text{C}$$

of charge; we know that $Q = I \times t$

$$22365\text{C} = 5.0\text{C s}^{-1} \times t(\text{s}) \Rightarrow t(\text{s}) = \frac{22365\text{C}}{5.0\text{C s}^{-1}} = 4473\text{s}$$

Thus, we need to pass 5.0 A current for 74 min 55 s through the solution of silver ions to get 25 g of silver metal.

8. As the electrolysis of aqueous solution of KI is given to be similar to aqueous sodium chloride, this means that iodine gas will be liberated at the anode. The electrode reaction would be



This implies that on passage of 1 Faraday of electricity half a mole of iodine will be liberated.

We are given the current strength and time, so let us first calculate the coulombs of electricity passed.

$$\text{We know that } Q = I \times t$$

Substituting the values

$$Q = 5\text{A} \times 60\text{min} \times 60\text{s min}^{-1} = 18000\text{C}$$

$$\text{The number of Faradays} = \frac{18000\text{C}}{96485\text{C F}^{-1}} = 0.187\text{F}$$

$$\text{Number of moles of iodine liberated will be} = \frac{0.187}{2} = 9.35 \times 10^{-2}\text{mol}$$

We know that the volume of an ideal gas at NTP is given as $V = \frac{nRT}{p}$

Substituting the values, we get

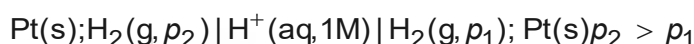
$$V = \frac{9.35 \times 10^{-2} \text{ mol} \times 0.0821 \text{ L.atm K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}{1 \text{ atm}} = 2.096 \text{ L}$$

Thus, the volume of iodine liberated will be 2.096 liters.

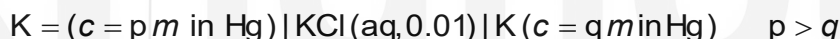
Terminal Questions

1. The concentration cells in which the composition of electrode material is different are called electrode concentration cells. The two examples are as under

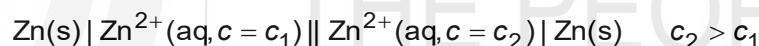
- i. An electrode concentration cell constructed by combining two hydrogen electrodes in which the pressure of the hydrogen gas is different. It can be represented as



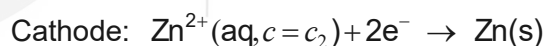
- ii. A concentration cell constructed by combining two potassium amalgam electrodes having different molalities of potassium metal in them.



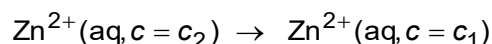
2. As we know that in an electrolyte concentration cell the electrode having lower concentration of the electrolyte forms the anode. So, we can write the cell diagram as



The half-cell reactions would be as under



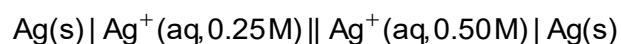
The overall cell-reaction would be



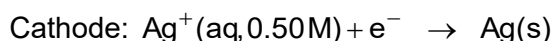
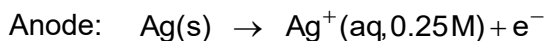
3. The following methods based on emf measurement can be used for the determination of pH of aqueous solutions.

- a) Using voltaic cell having a hydrogen electrode
- b) Using quinhydrone electrode-a redox electrode
- c) Using glass electrode- a membrane electrode

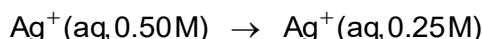
4. In an electrolyte concentration cell, the electrode with lower concentration of the electrolyte acts as an anode, therefore the electrode with silver ion concentration of 0.25 M would be the anode. The cell diagram can be given as



The electrode reactions would be as follows:



The overall reaction would be



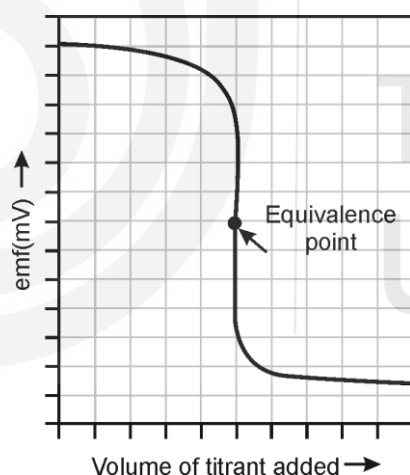
The cell emf, E_{cell} would be

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{F} 2.303 \log \frac{0.25}{0.50}$$

As E_{cell}^0 will be zero, so we can write that

$$E_{\text{cell}} = 0.0592 \log 2 = 0.018 \text{ V}$$

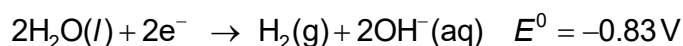
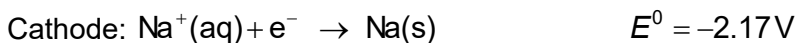
5. Glass electrode is an example of membrane electrode that is used for the measurement of pH of aqueous solutions. A glass electrode consists of a glass tube having a thin glass membrane bulb (that is permeable to H^+ ions) at one end. The bulb is filled with a solution of a constant pH (e.g., 0.1 M HCl) and a reversible electrode like Ag–AgCl electrode (silver wire coated with silver chloride) is dipped in it.
6. A schematic graph for a emf titration is given below



7. We know that sodium sulphate dissociates in water as follows

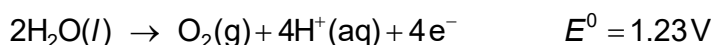
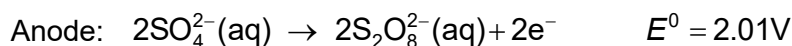


Thus, in an aqueous solution of sodium sulphate there will be three species that can undergo electrode reactions. These are sodium ions, sulphate ions and water molecules. At cathode, the following reduction reactions are possible

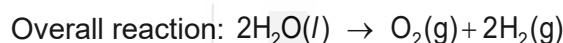
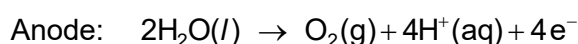
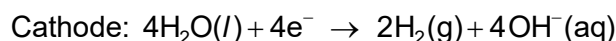


As the electrode potential for the reduction of sodium ions is highly negative; it is water that will get reduced at the cathode in preference to sodium ions. The choice will remain the same even if we consider an overpotential of about 0.4-0.6 V for formation of hydrogen.

At the anode again there are two possibilities:



On the basis of electrode potentials, we expect that the water will undergo oxidation in preference to the sulphate ions. Thus, the electrode reactions and overall reaction in the electrolysis of sulphuric acid can be given as



8. In the electrolysis of molten magnesium chloride, the following reaction will occur at anode



That is, the passage of 2F of electricity would liberate one mole of chlorine. We need to get 6 kg of chlorine; so we first convert it to number of moles by dividing with the molar mass of chlorine

$$\text{The number of moles of chlorine} = \frac{6\text{ kg} \times 1000\text{ g kg}^{-1}}{70.90\text{ g mol}^{-1}} = 84.63\text{ mol}$$

As per the electrode reaction, to get 84.63 mol of chlorine we need to pass

$$Q = 84.63\text{ mol} \times 2 \times 96485\text{ C mol}^{-1} = 1.633 \times 10^7\text{ C}$$

We know that $Q = I \times t$

Substituting the values,

$$1.633 \times 10^7\text{ C} = I(\text{A}) \times 24\text{ h} \times 60\text{ min h}^{-1} \times 60\text{ s min}^{-1}$$

Solving, we get

$$I(\text{A}) = \frac{1.633 \times 10^7\text{ C}}{86400\text{ s}} = 189\text{ A}$$

Thus, we need to pass 189 A current for 24 hours to get 6 kg of chlorine.

9. The anode in a galvanic cell is the negative electrode and the nature of reaction occurring at anode is oxidation.