



ELECTROCHEMISTRY



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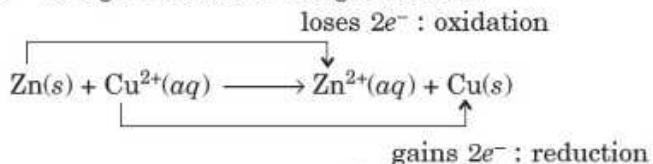


Electrical energy plays an important role in many chemical reactions. **The branch of science which deals with the production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations** is called **electrochemistry**. The basis of these types of processes are redox reactions, which we have learnt in the previous class. Large number of chemical and biological reactions are **redox reactions**. These are used in burning of fuels for obtaining energy for domestic, transport or industrial purposes, digestion of food in animals; photosynthesis to capture energy from the sun, many industrial processes for extracting metals from their ores and manufacture of important chemicals, operation of dry and wet batteries, fuel cells etc.

REDOX REACTIONS

As we have learnt in previous class, **oxidation is a process which involves loss of electrons and reduction is a process which involves gain of electrons**. The reactions which involve both oxidation and reduction are called **redox reactions**. In these reactions, electrons are transferred from one reactant to another. **The substance which can lose one or more electrons (i.e., get oxidised)** is called **reducing agent or reductant** while **the substance which can gain one or more electrons (i.e., get reduced)** is called **oxidising agent or oxidant**. Thus, in a redox reaction, one substance acts as a reducing agent and itself gets oxidised while another substance acts as an oxidising agent and itself gets reduced.

A simple example of a redox reaction is the reaction between zinc and copper (II) salt occurring in a battery. In this reaction, zinc loses electrons and gets oxidised whereas Cu^{2+} ions gain electrons and get reduced.



In this case, zinc acts as a reducing agent or reductant while Cu^{2+} ions act as oxidising agent or oxidant. Some other examples of redox reactions are :



These redox reactions are very important reactions and play significant role in chemistry.

METALLIC AND ELECTROLYTIC CONDUCTANCE

Learning Plus

Electronically conducting polymers

Mac Diarmid, Hegger and Shirakawa in 1977 discovered that when polyacetylene (a polymer of acetylene) was exposed to traces of iodine or bromine vapours, the thin polymer film behaved like a metal exhibiting metallic lustre and conductivity. It was discovered that by purposely adding selected impurities to polyacetylene, its electrical conductivity could be made to range widely behaving as an insulator like glass or to a conductor like a metal. After this discovery, several organic polymers have been made such as polyaniline, polypyrrole and polythiophene. These organic polymers mainly composed of elements like carbon, hydrogen and occasionally nitrogen, oxygen or sulphur. These are much lighter than normal metals and can be used for making light weight batteries. In addition, they have the mechanical properties of polymers such as flexibility so that these can be used to make electronic devices such as transistors which can bend like a sheet of plastic. For the discovery of conducting polymers, **Mac Diarmid, Hegger and Shirakawa were awarded Nobel Prize in Chemistry for the year 2000.**

All substances do not conduct electrical current. *The substances which allow the passage of electric current* are called **conductors**. The best conductors are metals such as copper, silver, tin, etc. On the other hand, *the substances which do not allow the passage of electric current through them* are called **non-conductors** or **insulators**. Some common examples of insulators are rubber, glass, ceramics, wood, wax, etc.

Types of conductors.

The conductors are broadly classified into two types :

1. Metallic conductors or Electronic conductors

These are *metallic substances which allow the electricity to pass through them without undergoing any chemical change*. Metals and their alloys have very large conductivity and are called **conductors**. For example, copper, silver, etc. The flow of electric current through metallic conductors is due to the **flow of electrons** in the metal atoms. Electrical conductance through metals is called **metallic conductance or electronic conductance**. The electronic conductance depends on

- (i) the nature and structure of the metal
- (ii) the number of valence electrons per atom
- (iii) the density of metal and
- (iv) temperature (it decreases with increase of temperature, discussed later).

As the electrons enter at one end and go out at the other end, the composition of the metallic conductor remains unchanged.

Certain non-metals like carbon black, graphite and some organic polymers are also electronically conducting. Hence, they are collectively called as **electronic conductors**.

2. Electrolytes or Electrolytic conductors

These are *substances which allow the electricity to pass through them in their molten states or in the form of their aqueous solutions and undergo chemical decomposition*. For example, acids, bases and salts are electrolytes. The flow of electric current through an electrolytic solution is called **electrolytic conduction**. In this type of conduction, charge is **carried by ions**. Therefore, it is also called **ionic conductance**. Thus, the conduction will not occur unless the ions of the electrolyte are free to move. Therefore, these substances do not conduct electricity in the solid state but conduct electricity in the molten state or in their aqueous solutions due to the movement of ions.

Non-electrolytes. *The substances, which do not conduct electricity either in their molten state or through their aqueous solutions* are called **non-electrolytes**. For example, sugar, glucose, ethyl alcohol, urea, etc.

Differences between Metallic and Electrolytic Conduction

Metallic conduction	Electrolytic conduction
<ol style="list-style-type: none"> 1. Metallic conduction is carried by the movement of electrons. 2. It involves no change in the chemical properties of the conductor. 3. It does not involve the transfer of any matter. 4. Metallic conduction decreases with increase in temperature. 	<p>Electrolytic conduction is carried by the movement of ions.</p> <p>It involves the decomposition of the electrolyte as a result of the chemical reaction.</p> <p>It involves the transfer of matter as ions.</p> <p>Electrolytic conduction increases with increase in temperature.</p>

Classification of Electrolytes

All electrolytes do not ionise to the same extent in solution. On this basis, electrolytes are broadly divided into two types : strong electrolytes and weak electrolytes.

(i) **Strong electrolytes.** *The electrolytes which are almost completely dissociated into ions in solution* are called **strong electrolytes**. For example, NaCl, KCl, HCl, NaOH, NH₄NO₃, etc.

(ii) **Weak electrolytes.** *The electrolytes which do not ionise completely in solution* are called **weak electrolytes**. For example, CH₃COOH, H₂CO₃, H₃BO₃, HCN, HgCl₂, ZnCl₂, NH₄OH, etc. Thus, in case of weak electrolytes, an equilibrium is established between the unionised electrolyte and the ions formed in solution. The extent of ionisation of a weak electrolyte is expressed in terms of **degree of ionisation** or **degree of dissociation**. It is defined as

the fraction of total number of molecules of the electrolyte which ionise in the solution.

It is generally denoted by alpha (α).

For strong electrolytes, α is almost equal to 1 and for weak electrolytes, it is always less than 1.

Factors Affecting Electrical Conductivity of Electrolytic Solutions

The conductivity of electrolytic (or ionic) solution depends upon the following factors :

(i) **Nature of electrolyte.** The conductance of an electrolyte depends upon the number of ions present in the solution. Therefore, the greater the number of ions in the solution, the greater is the conductance. The strong electrolytes dissociate almost completely into ions in solutions and therefore, their solutions have high conductance. On the other hand, weak electrolytes, dissociate to only small extents and give lesser number of ions. Therefore, the solutions of weak electrolytes have low conductance.

(ii) **Nature of the solvent and its viscosity.** Electrolytes ionize more in polar solvents. Therefore, greater the polarity of the solvent, larger is the ionization and hence greater is the conductance. Similarly, greater is the viscosity of a solvent, lesser is its conductance.

(iii) **Size of the ions produced and their solvation.** If the ions are strongly solvated, their effective size will increase and hence their conductance will decrease.

(iv) **Concentration of the electrolytic solution.** Higher the concentration of the solution, less is the conductance. This is because, in a weak electrolyte, the ionization is less whereas in a strong electrolyte, the interionic attractions are large at higher concentrations. In general, *the conductance of an electrolyte increases with decrease in concentration or increase in dilution*. With dilution, in case of weak electrolytes, ionization increases and hence conductance increases. In case of strong electrolytes, the interionic attractions decrease with dilution and therefore, conductance increases.

(v) **Temperature.** The conductivity of an electrolyte depends upon the temperature. **With increase in temperature, the conductivity of an electrolyte increases due to decrease in interactions between ions.**

ELECTROLYTIC CONDUCTION

When a voltage is applied to the electrodes dipped into an electrolytic solution, ions of the electrolyte move and, therefore, electric current flows through the electrolytic solution. *The power of the electrolytes to conduct electric current is termed conductance or conductivity.* Like metallic conductors, electrolytic solutions also obey Ohm's law.

Some substances like silicon, silicon doped silicon, gallium arsenide have conductivity between conductors and insulators. These are called **semiconductors** and are important electronic materials. There are certain materials which have zero resistivity or infinite conductivity known as **superconductors**. Earlier only metals and their alloys at very low temperature of the range 0 to 15 K were known to behave super conductors. But nowadays a number of ceramic materials and mixed oxides are also known to exhibit superconductivity at temperatures as high as 150 K.

REMEMBER

- Metallic conductance decreases with increase in temperature.
- Electrolytic conductance increases with increase in temperature.
- For strong electrolytes, degree of dissociation, α is almost equal to 1 and
- For weak electrolytes, degree of dissociation, α is always less than 1.

The **SI base unit of resistance** can be obtained as:

$$\begin{aligned}\Omega &= \frac{V}{A} \\ &= \frac{\text{Work per unit charge}}{A} \\ &= \frac{\text{Work}}{\text{Charge}} \times \frac{1}{A} \\ &= \frac{\text{Force} \times \text{Length}}{A \times s} \cdot \frac{1}{A} \\ &= \frac{m \times a \times l}{A^2 s} \\ &= \frac{kg \times ms^{-2} \times m}{A^2 s} \\ &= \frac{kg \ m^2}{s^3 A^2}\end{aligned}$$

IUPAC recommends the use of term **resistivity** over specific resistance. In the present book, we shall use the term resistivity.

It may be noted that the symbol G or C may be used for conductance. However, symbol G is preferred because symbol C is used for concentration or Coulomb.

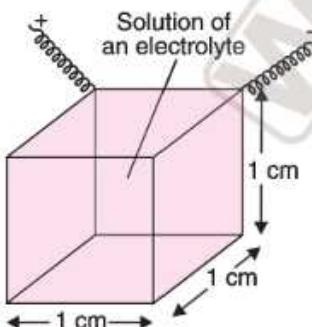


Fig. 1. Illustration of conductivity.

1. Ohm's law

This law states that *the current flowing through a conductor is directly proportional to the potential difference across it, i.e.,*

$$I \propto V$$

where I is the current strength (in amperes) and V is the potential difference applied across the conductor (in volts)

$$\text{or } I = \frac{V}{R} \quad \text{or} \quad V = IR \quad \dots(1)$$

where R is the constant of proportionality and is known as resistance of the conductor. It is expressed in *ohms* and is represented as Ω . The above equation is known as Ohm's law. Ohm's law may also be stated as *the strength of current flowing through a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the resistance of the conductor.*

Let us explain some **basic terms** commonly used.

1. Resistance. *It measures the obstruction to the flow of current.* The resistance of any conductor is directly proportional to the length (l) and inversely proportional to the area of cross-section (a) so that

$$R \propto \frac{l}{a} \quad \text{or} \quad R = \rho \frac{l}{a}$$

where ρ (Greek, rho) is the constant of proportionality and is called **specific resistance or resistivity**. The resistance depends upon the nature of the material.

Units. The unit of resistance is **ohm** (Ω). In terms of SI, base unit is equal to $(kgm^2)/(s^3A^2)$.

2. Resistivity or specific resistance. We know that resistance R is

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

Now, if $l = 1 \text{ cm}$, $a = 1 \text{ cm}^2$, then $R = \rho$

Thus, **resistivity** is defined as *the resistance of a conductor of 1 cm length and having area of cross-section equal to 1 cm².*

In other words, **resistivity or specific resistance** is *the resistance between opposite faces of one centimetre cube of the conductor.* In terms of SI units, resistivity of a substance may be defined as its resistance when it is 1m long and its area of cross section is 1 m² i.e., *resistance of one metre cube of the conductor.*

It can be seen that

$$1 \Omega \text{ m} = 100 \Omega \text{ cm} \quad \text{or} \quad 1 \Omega \text{ cm} = 0.01 \Omega \text{ m}$$

Units. The units of resistivity are

$$\rho = R \cdot \frac{a}{l} = \text{ohm} \frac{\text{cm}^2}{\text{cm}} = \text{ohm cm}$$

Its SI units are ohm metre ($\Omega \text{ m}$). But quite often ohm centimeter ($\Omega \text{ cm}$) is also used.

$$1 \text{ ohm m} = 100 \text{ ohm cm}$$

3. Conductance. *It is a measure of the ease with which the current flows through a conductor. It is expressed as 'G'. It is reciprocal of the resistance, i.e.,*

$$G = \frac{1}{R}$$

Units. The units of conductance are **reciprocal ohm (ohm⁻¹) or mho**. Ohm is also abbreviated as Ω so that ohm^{-1} may be written as Ω^{-1} .

According to **S.I. system**, the units of electrical conductance are **siemens**, S (i.e., $1 \text{ S} = 1 \Omega^{-1}$).

4. Conductivity. The inverse of resistivity is called **conductivity** (or specific conductance). It is represented by the symbol, κ (Greek kappa). It may be defined as *the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section.* In other words, **conductivity** is the *conductance of one centimetre cube of a solution of an electrolyte* (Fig. 1). Thus,

$$\kappa = \frac{1}{\rho}$$

Units. The units of conductivity are

$$\kappa = \frac{1}{\text{ohm.cm}} = \text{ohm}^{-1} \text{ cm}^{-1} \text{ or } \Omega^{-1} \text{ cm}^{-1}$$

In SI units, l is expressed in m, area of cross-section in m^2 so that the units of conductivity are S m^{-1} .

$$1 \text{ S m}^{-1} = 10^{-2} \text{ S cm}^{-1}$$

The conductivity of some substances are given in Table 1.

Table 1. Conductivities of some substances at 298 K

Material (Sm^{-1})	Conductivity	Material (Sm^{-1})	Conductivity
Conductors			
Sodium	2.1×10^3	Pure water	3.5×10^{-5}
Copper	5.9×10^3	0.1 M HCl	3.91
Silver	6.2×10^3	0.1 M NaCl	0.20
Iron	1.0×10^3	0.01 M NaCl	0.12
Gold	4.5×10^3	0.01 M KCl	0.14
Graphite	12.0	0.1 M CH_3COOH	0.047
		0.01 M CH_3COOH	0.016
Insulators			
Glass	1.0×10^{-16}	Si	1.5×10^{-3}
Teflon	1.0×10^{-18}	Ge	2.0
		CuO	1×10^{-7}
Semiconductors			

It can be seen from Table 1 that the magnitude of conductivity varies a great deal and depends upon the nature of the material.

5. Molar Conductivity or Molar Conductance

Molar conductivity is defined as *the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution*.

It is denoted by Λ_m (lambda). Molar conductance is related to specific conductance (κ) as :

$$\Lambda_m = \frac{\kappa}{C}$$

where C is the molar concentration. If C is in the units of molarity i.e. moles per litre (mol L^{-1}), then Λ_m may be expressed as :

$$\Lambda_m = \frac{\kappa \times 1000}{C} \quad \dots(2)$$

where C is molarity (M).

Relation between Conductivity and Molar Conductivity

The above relation can be easily obtained from the definitions of the terms. Suppose 1 cm^3 of a solution of an electrolyte is placed between two large electrodes of 1 sq. cm area of cross-section lying 1 cm apart. The measured conductance of the solution will be its conductivity (by definition because it gives conductance of 1 cm^3 cube of solution). Further, suppose that this solution contains one gram mole of the electrolyte, then the measured conductance of the solution will be equal to the molar conductance (Λ). Thus, for this solution containing 1 gm mole of electrolyte placed between two parallel electrodes of 1 sq. cm area of cross-section and one cm apart,

$$\begin{aligned} \text{Conductance} &= \text{Conductivity} (\kappa) \\ &= \text{Molar conductivity} (\Lambda) \end{aligned}$$

Now suppose that solution is diluted to 100 cc . There are now 100 cm^3 cubes of the solution. The conductance of each one cm^3 cube will be conductivity

The IUPAC has recommended the use of term **conductivity** over specific conductance.

REMEMBER

The **symbols** used in the present unit

- Resistance = R
 - Resistivity or specific resistance = ρ
 - Conductance = G
 - Cell constant = G^* (or $\frac{l}{a}$)
 - Conductivity or specific conductance = κ
 - Molar conductance = Λ_m ,
- $$\Lambda_m = \frac{\kappa \times 1000}{M}$$
- Equivalent conductance = Λ_e ,
- $$\Lambda_e = \frac{\kappa \times 1000}{C_{eq}}$$

so that the conductance of the solution will be 100 times of its conductivity. But even now the solution contains 1 gram mole of the electrolyte therefore, the measured conductance will be the molar conductivity. Thus,

$$\text{Molar conductivity, } \Lambda_m = 100 \times \text{Conductivity}$$

In other words,

$$\Lambda_m = \kappa \times V$$

where V is the volume of the solution in cm^3 containing one gram mole of the electrolyte.

If C is the concentration of the solution in mole per litre i.e., molarity, then M mole of electrolyte is present in 1000 cm^3 .

1 mole of electrolyte is present in

$$= \frac{1000}{M} \text{ cm}^3 \text{ of solution}$$

Thus, $\Lambda_m = \kappa \times \text{Volume in cm}^3$ containing 1 mole of electrolyte.

$$\text{or } \Lambda_m = \frac{\kappa \times 1000}{M}$$

Units of Molar Conductance

The units of molar conductance can be derived from the formula,

$$\Lambda_m = \frac{\kappa \times 1000}{C}$$

The units of κ are S cm^{-1} and units of Λ are

$$\begin{aligned} \Lambda_m &= S \text{ cm}^{-1} \times \frac{\text{cm}^3 \text{ L}^{-1}}{\text{mol L}^{-1}} \\ \text{or } &= \mathbf{S \text{ cm}^2 \text{ mol}^{-1}} \end{aligned}$$

According to **SI system**, if κ is express in Sm^{-1} and the concentration, C in mol m^{-3} then units of Λ_m are in $\text{S m}^2 \text{ mol}^{-1}$. This is because :

$$1 \text{ mol m}^{-3} = 1000 \left(\frac{\text{L}}{\text{m}^3} \right) \times \text{molarity} \left(\frac{\text{mol}}{\text{L}} \right)$$

$$\begin{aligned} \text{Now, } \Lambda_m &= \frac{\kappa}{c} = \frac{\kappa (\text{S m}^{-1})}{(1000 \text{ L m}^{-3}) \times \text{Molarity (mol L}^{-1}\text{)}} \\ &= \mathbf{S \text{ m}^2 \text{ mol}^{-1}} \end{aligned}$$

Thus, the units of molar conductivity are $\text{S m}^2 \text{ mol}^{-1}$ (SI) and $\text{S cm}^2 \text{ mol}^{-1}$. Both types of units are used in literature and are related to each other as:

$$1 \text{ S m}^2 \text{ mol}^{-1} = 10^4 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{or } 1 \text{ S cm}^2 \text{ mol}^{-1} = 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

NOTE

It may be noted that in non SI units, when κ is in S cm^{-1} and molarity is in mol L^{-1} , then

$$\Lambda_m = \frac{\kappa \times 1000}{C}$$

and Λ_m has the units $\text{S cm}^2 \text{ mol}^{-1}$. But in SI units, when κ is in S m^{-1} and molarity is in mol m^{-3} , then

$$\Lambda_m = \frac{\kappa}{C}$$

and Λ_m has the units $\text{S m}^2 \text{ mol}^{-1}$.

REMEMBER

- There is no multiplication with 1000 in SI units.

Electrolytic conductance is also expressed frequently as **equivalent conductance**. However, the recent trend is to express electrolytic conductance in terms of molar conductance.

6. Equivalent Conductivity

It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

It is expressed as Λ_e and is related to specific conductance as

$$\Lambda_e = \frac{\kappa \times 1000}{C_{\text{eq}}}$$

where C is the concentration in gram equivalent per litre (or normality). This term has earlier been quite frequently used. Now it is replaced by molar conductivity. The units of equivalent conductivity are $\text{ohm}^{-1}\text{cm}^2$ (g equiv^{-1}) as obtained from the formula :

$$\begin{aligned}\Lambda &= \frac{\kappa \times 1000}{C_{eq}} \\ &= \frac{(S \text{ cm}^{-1}) \times \text{cm}^3 \text{ L}^{-1}}{\text{g equiv L}^{-1}} = S \text{ cm}^2 (\text{g equiv}^{-1})\end{aligned}$$

In terms of SI units, the units of equivalent conductivity are $\text{S m}^2 \text{ equiv}^{-1}$ and Λ is expressed as :

$$\Lambda = \frac{\kappa}{C_{eq}}$$

where κ is in S m^{-1} and C_{eq} is in g equiv m^{-3} . It may be noted that like molar conductivity there is no multiplication with 1000 in SI units.

Experimental Measurement of Conductance and Conductivity of Ionic Solutions

1. Measurement of conductance

The conductance of a solution is reciprocal of the resistance, therefore, the experimental determination of the conductance of a solution involves the measurement of its resistance. The resistance can be measured by the principle of wheatstone bridge method as shown in Fig. 2.

It consists of four arms containing the resistance R_1 , R_2 , R_3 and R_4 . R_1 is the variable resistance and R_2 is the unknown resistance. When the current flows through the circuit, the variable resistance is so adjusted to get no current position. This is indicated by no deflection in the galvanometer and is called null point. At null point,

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$

Knowing the values of R_1 , R_3 and R_4 , unknown resistance R_2 can be calculated as :

$$R_2 = \frac{R_1 \times R_4}{R_3}$$

However, for measuring the resistance of an ionic solution, we face two main difficulties.

(i) For electrolytic solution, **direct current (dc) cannot be used because it causes electrolysis of the solution**. As a result the concentration of the electrolyte near the electrodes changes and this results in the change in the resistance of the solution. These effects are called **polarisation effects**. To overcome this problem, alternating current (ac) in the audio frequency range 550 to 5000 cycles per second is provided by using a suitable electronic circuit commercially available. However, when alternating current is used, ordinary galvanometer fails to detect null point. Since the frequency of alternating current is within the range of human ear, the galvanometer may be replaced by a set of headphones. Now, several other visual sensing devices are being used in the place of headphones.

(ii) A solution of unknown resistance cannot be connected to the bridge like a metallic wire or other solid conductor. This problem is solved by using a specially designed vessel called **conductivity cell** for taking the ionic solution. A variety of designs of conductivity cells are available. Two simple conductivity cells are shown in Fig. 3. The electrodes of the cell are made up of platinum, coated with a thin layer of finely divided platinum called platinum black. This is done by the electrolysis of a solution of chloroplatinic acid. The coating of electrodes with platinum black reduces polarization effects.

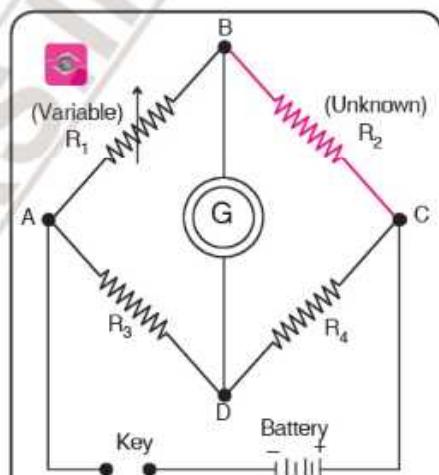


Fig. 2. Principle of wheatstone bridge.

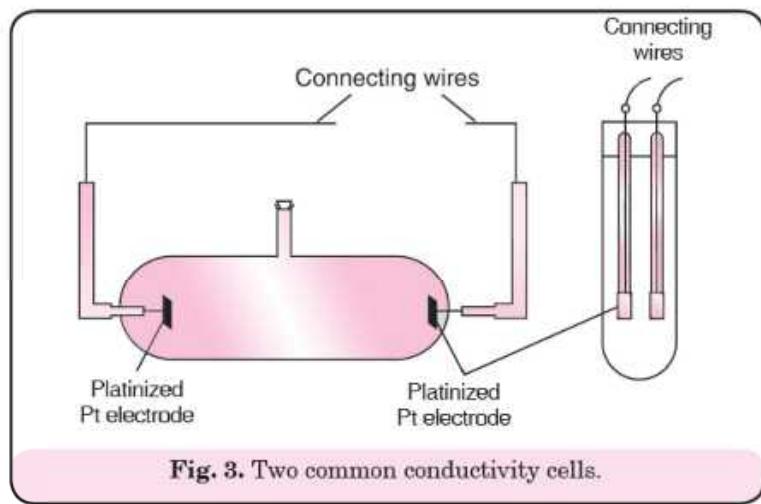


Fig. 3. Two common conductivity cells.

The complete assembly for the measurement of resistance of the electrolytic solution is shown in Fig. 4. The bridge is connected to a suitable source of alternating current. An alternating current at a frequency 550 – 5000 cycles per second is passed. The solution whose resistance is to be measured (say X) is placed in the conductivity cell and is attached to the wheatstone bridge between points B and C. The cell is placed in a thermostat to keep the temperature constant. A variable standard resistance box is attached between points A and B. A suitable value of resistance R is taken out from the standard resistance box. The null point is detected by moving the sliding contact (i.e., Jockey J) on the wire AC so that *minimum sound* is obtained in the earphone. This corresponds to null point and let this point be D. At this balance point

$$\frac{\text{Resistance R}}{\text{Resistance X}} = \frac{\text{Resistance of wire AD}}{\text{Resistance of wire CD}}$$

Now, resistance of a conductor is proportional to its length, so that,

$$\frac{\text{Resistance R}}{\text{Resistance X}} = \frac{\text{Length AD}}{\text{Length CD}}$$

$$\therefore \text{Resistance X} = \text{Resistance R (plugged out)} \times \frac{\text{Length CD}}{\text{Length AD}}$$

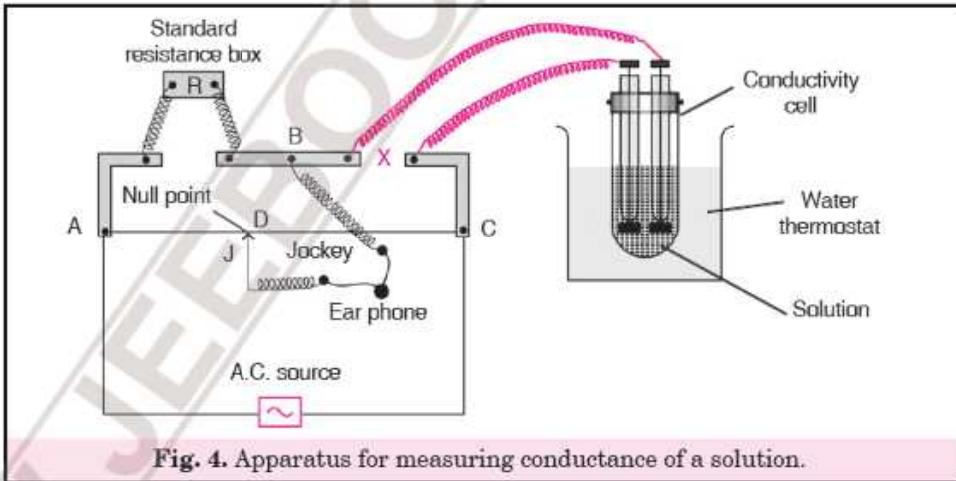


Fig. 4. Apparatus for measuring conductance of a solution.

Thus, by measuring the lengths AD and CD and knowing the resistance R at the balance point D, the resistance X of electrolytic solution can be calculated.

The reciprocal of the resistance gives the value of conductance of the solution. These days, inexpensive conductivity meters are available which can directly read resistance or conductance of the solution in the conductivity cell.

2. Calculation of conductivity

We have seen that conductivity (κ) is reciprocal of resistivity (ρ), i.e.

$$\kappa = \frac{1}{\rho} \quad \text{and} \quad \rho = R \frac{a}{l}$$

$$\therefore \kappa = \frac{1}{R} \left(\frac{l}{a} \right) \quad \text{or} \quad \kappa = G \left(\frac{l}{a} \right)$$

where G is the conductance of the cell, l is the distance of separation of two electrodes having cross-section area $a \text{ cm}^2$. The quantity $\left(\frac{l}{a} \right)$ is called **cell constant** (G^*) and is expressed in cm^{-1} . Knowing the value of cell constant and conductance of the solution, the specific conductance can be calculated as :

$$\kappa = G \times \text{Cell constant}$$

$$\text{i.e.,} \quad \text{Conductivity} = \text{Conductance} \times \text{Cell constant}$$

REMEMBER

- For electrolytic solutions, direct current (DC) cannot be used because it causes electrolysis of the solution.
- Alternating current in the audio frequency range of 550-5500 cycles per second is used.

- Conductivity water.** For accurate results of conductivity measurements, the solutions are prepared in a very purified water whose conductance is very very small. Such water is called **conductivity water**.
- Alternatively, to calculate conductance of the electrolyte, the conductance of water used for preparing the solution may be determined and then subtracted from the conductance of the solution.

3. Determination of cell constant

The cell constant is generally not calculated from the values of l and a because these are difficult to measure for a given cell. However, it is usually determined accurately by measuring the conductance of a standard solution whose conductivity is known. For this purpose, a standard solution of KCl is used whose conductivity is known at different concentrations and temperatures. The conductivities of different KCl solutions at 298 K are given in Table 2.

Table 2. Conductivity and molar conductivity of KCl solutions at 298.15 K

Molarity (mol L ⁻¹)	Concentration (mol m ⁻³)	Conductivity S cm ⁻¹	Conductivity S m ⁻¹	Molar conductivity S cm ² mol ⁻¹	Molar conductivity S m ² mol ⁻¹
1.000	1000	0.1113	11.13	111.3	111.3 × 10 ⁻⁴
0.100	100.0	0.0129	1.29	129.0	129.0 × 10 ⁻⁴
0.010	10.00	0.00141	0.141	141.0	141.0 × 10 ⁻⁴

For example, for 0.1 M KCl solution at 298 K, conductivity is 0.0129 S cm⁻¹.

Suppose the conductance of this solution in the given cell is measured, to be 'X'. Then,

$$\text{Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}} = \frac{0.0129}{X}$$

Once the cell constant is known, the conductivity of any solution can be easily calculated from the measured resistance or conductance of the electrolytic solution.

$$\kappa = G^*/R \text{ or } = G^* \times G.$$

From this, molar conductivity or equivalent conductivity may be calculated.

Units of common terms used in conductance are summed up below :

Property	Units	SI units
Resistance	ohm	ohm
Conductance	ohm ⁻¹	S
Cell constant	cm ⁻¹	m ⁻¹
Conductivity	ohm ⁻¹ cm ⁻¹	S m ⁻¹
Molar conductivity	ohm ⁻¹ cm ² mol ⁻¹	S m ² mol ⁻¹
Equivalent conductivity	ohm ⁻¹ cm ² (g equiv ⁻¹)	S m ⁻¹ (equiv L ⁻¹) ⁻¹

Solving Numerical Problems

FORMULAE AND UNITS

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

R is resistance in ohms

a = Area of cross section in cm²

l = Length between two electrodes in cm

ρ = Resistivity in ohm cm

$$\kappa = \frac{1}{\rho} = G \times \frac{l}{a}$$

κ = Conductivity in ohm⁻¹ cm⁻¹ (SI units : S m⁻¹)

G = Conductance in ohm⁻¹ (SI unit = S)

$\frac{l}{a}$ is called cell constant in cm⁻¹ (SI units : m⁻¹)

$$\Lambda_m = \frac{1000 \times \kappa}{M}$$

Λ_m = Molar conductivity in ohm⁻¹ cm² mol⁻¹ [SI units : S m⁻¹ (mol L⁻¹)⁻¹]

$$\Lambda_{\text{equiv.}} = \frac{1000 \times \kappa}{C}$$

$\Lambda_{\text{equiv.}}$ = Equivalent conductivity in ohm⁻¹ cm² equiv⁻¹

SOLVED EXAMPLES

Example 1.

The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω . What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm $^{-1}$?

(A.I.S.B. 2008; D.S.B. 2007, 2008, 2012)

Solution :

$$\text{Conductivity, } \kappa = 0.146 \times 10^{-3} \text{ S cm}^{-1}$$

$$\text{Resistance, } R = 1500 \text{ ohm}$$

$$\text{Cell constant} = \frac{\text{Conductivity, } (\kappa)}{\text{Conductance (G)}}$$

$$= \text{Conductivity } (\kappa) \times \text{Resistance (R)}$$

$$\therefore \text{Cell constant} = 0.146 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1} \times 1500 \text{ ohm}$$

$$= 0.219 \text{ cm}^{-1}$$

Example 2.

The conductivity of 0.20 M KCl solution at 298 K is 0.025 S cm $^{-1}$. Calculate its molar conductivity.

N.C.E.R.T. (D.S.B. 2008, 2013, H.P.S.B. 2015, Hr.S.B. 2018)

Solution: Molar conductivity

$$\Lambda_m = \frac{\kappa \times 1000}{C}$$

$$\kappa = 0.025 \text{ S cm}^{-1}, C = 0.20 \text{ M}$$

$$\therefore \Lambda_m = \frac{0.025 \times 1000}{0.20}$$

$$= 125.0 \text{ S cm}^2 \text{ mol}^{-1}$$

Example 3.

0.05 M NaOH solution offered a resistance of 31.6 ohm in a conductivity cell at 298 K. If the area of the plates of the conductivity cell is 3.8 cm 2 and distance between them is 1.4 cm, calculate the molar conductivity of the sodium hydroxide solution.

Solution : Cell constant, $G^* = \frac{l}{a}$

$$l = 1.4 \text{ cm and } a = 3.8 \text{ cm}^2$$

$$\therefore G^* = \frac{l}{a} = \frac{1.4 \text{ cm}}{3.8 \text{ cm}^2} = 0.368 \text{ cm}^{-1}$$

$$\text{Resistance of solution} = 31.6 \text{ ohm}$$

$$\text{Concentration, } C = 0.05 \text{ M}$$

$$\therefore \text{Conductivity,}$$

$$\kappa = G^*/R$$

$$= \left(\frac{1}{31.6} \right) \text{ ohm}^{-1} \times (0.368 \text{ cm}^{-1})$$

$$= 0.0116 \text{ S cm}^{-1}$$

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{C} = \frac{0.0116 \times 1000}{0.05}$$

$$= 232 \text{ S cm}^2 \text{ mol}^{-1}$$

Example 4.

Calculate the equivalent conductivity of 1 M H₂SO₄ solution whose conductivity is 26×10^{-2} ohm $^{-1}$ cm $^{-1}$.

Solution : Conductivity = 26×10^{-2} ohm $^{-1}$ cm $^{-1}$

Concentration = 1 M H₂SO₄ = 98 g/litre

Equivalent weight of H₂SO₄ = 49

$$\text{Gram equivalents per litre} = \frac{98}{49} = 2$$

$$\text{Equivalent conductivity} = \frac{\kappa \times 1000}{C} = \frac{26 \times 10^{-2} \times 1000}{2}$$

$$= 130 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

Example 5.

Resistance of a conductivity cell filled with 0.1 M KCl solution is 100 Ω . If the resistance of the same cell when filled with 0.02 M KCl solution is 520 Ω , calculate the conductivity and molar conductivity of 0.02 M KCl solution. (The conductivity of 0.1 M KCl solution is 1.29 S m $^{-1}$) N.C.E.R.T. (A.I.S.B. 2006, D.S.B. 2014)

Solution :

Step I. Let us first calculate the cell constant.

Cell constant, $G^* = \text{Conductivity } (\kappa) \times \text{Resistance (R)}$

Resistance of 0.1 M KCl solution = 100 Ω

Conductivity of 0.1 M KCl solution = 1.29 S m $^{-1}$

$$\therefore \text{Cell constant} = 1.29 (\text{S m}^{-1}) \times 100 \Omega$$

$$= 129 \text{ m}^{-1}$$

or

$$= 1.29 \text{ cm}^{-1}$$

Step II. Calculation of conductivity of 0.02 M KCl solution.

$$\text{Resistance of solution} = 520 \Omega$$

$$\text{Cell constant } (G^*) = 1.29 \text{ cm}^{-1}$$

$$\text{Conductivity, } \kappa = \frac{\text{Cell constant}}{\text{Resistance}}$$

$$= \frac{1.29 \text{ cm}^{-1}}{520 \Omega}$$

$$= 0.248 \times 10^{-2} \text{ S cm}^{-1}$$

Step III. Calculation of molar conductivity.

$$\Lambda_m = \frac{1000 \times \kappa}{C}$$

$$C = 0.02 \text{ M}, \kappa = 0.248 \times 10^{-2} \text{ S cm}^{-1}$$

$$\therefore \Lambda_m = \frac{1000 \times 0.248 \times 10^{-2}}{0.02}$$

$$= 124 \text{ S cm}^2 \text{ mol}^{-1}$$

Example 6.

A conductivity cell when filled with 0.01 M KCl has a resistance of 745 Ω at 25°C. When the same cell was filled with an aqueous solution of 0.005 M CaCl₂ solution the resistance was 874 Ω . Calculate

(i) Conductivity of solution

(ii) Molar conductivity of solution.

[Conductivity of 0.01 M KCl = 0.141 S m $^{-1}$]

Solution : Calculation of cell constant.

Resistance of KCl solution (R) = 745 S^{-1}

Conductivity of KCl solution (κ) = 0.141 S m^{-1}

$$\text{Conductivity } (\kappa) = \frac{1}{R} \times \text{Cell constant}$$

$$\begin{aligned}\text{or Cell constant} &= R \times \kappa \\ &= (745 \text{ S}^{-1}) \times 0.141 \text{ S m}^{-1} \\ &= 105 \text{ m}^{-1} \text{ or } 1.05 \text{ cm}^{-1}\end{aligned}$$

Calculation of conductivity and molar conductivity for CaCl_2 solution

(i) Conductivity

$$\begin{aligned}\text{Conductivity, } \kappa &= \frac{\text{Cell constant}}{R} \\ &= \frac{1.05 \text{ cm}^{-1}}{874 \text{ S}^{-1}} \\ &= 1.201 \times 10^{-3} \text{ S cm}^{-1}.\end{aligned}$$

(ii) Molar conductivity

$$\begin{aligned}\text{Conc. of solution, } C &= 0.005 \text{ M} \\ &= 0.005 \text{ mol L}^{-1}\end{aligned}$$

$$\begin{aligned}\Lambda_m &= \frac{\kappa \times 1000}{C} \\ \therefore \Lambda_m &= \frac{1.201 \times 10^{-3} \times 1000}{0.005} = 240.2 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

□ **Example 7.**

A potential difference of 20 V applied to the ends of a column of 0.1 M AgNO_3 solution, 4 cm in diameter and 12 cm in length gave a current of 0.20 amperes . Calculate

(i) conductivity and

(ii) molar conductance of the solution.

Solution : According to Ohm's law,

Resistance of solution,

$$\begin{aligned}R &= \frac{V}{I} \\ &= \frac{20}{0.20} = 100 \Omega\end{aligned}$$

$$\text{Radius of column} = \frac{4}{2} \text{ cm} = 2 \text{ cm}$$

Area of cross-section of the column,

$$\begin{aligned}a &= \pi r^2 = \frac{22}{7} \times (2)^2 \text{ cm}^2 \\ &= 12.57 \text{ cm}^2\end{aligned}$$

Length of column (distance between electrodes), $l = 12 \text{ cm}$

$$\begin{aligned}(ii) \text{ Conductivity, } \kappa &= G \times \frac{l}{a} \\ &= \frac{1}{100} \times \frac{12}{12.57} \\ &= 9.55 \times 10^{-3} \text{ S cm}^{-1}.\end{aligned}$$

(iii) Molar conductivity,

$$\begin{aligned}\Lambda_m &= \frac{\kappa \times 1000}{C} \\ &= \frac{9.55 \times 10^{-3} \times 1000}{0.1} \\ &= 95.5 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

□ **Example 8.**

The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is $5.55 \times 10^3 \text{ ohm}$. Calculate its

(i) resistivity

(ii) conductivity, and

(iii) molar conductivity.

N.C.E.R.T. (A.I.S.B. 2012, Pb. S.B. 2013)

Solution : Cell constant, $G^* = \frac{l}{a}$

$l = 50 \text{ cm}$, diameter = 1 cm ∴ radius = 0.5 cm

$$\begin{aligned}\text{Area of cross-section, } a &= \pi r^2 \\ &= 3.14 \times (0.5)^2 = 0.785 \text{ cm}^2\end{aligned}$$

$$\therefore G^* = \frac{50}{0.785} = 63.094 \text{ cm}^{-1}$$

$$(i) \text{ Resistivity, } \rho = \frac{R}{G^*}$$

$$R = 5.55 \times 10^3 \Omega$$

$$\therefore \rho = \frac{5.55 \times 10^3 \Omega}{63.694 \text{ cm}^{-1}} = 87.135 \Omega \text{ cm}.$$

$$(ii) \text{ Conductivity, } \kappa = \frac{1}{\rho}$$

$$= \frac{1}{87.135} = 1.148 \times 10^{-2} \text{ S cm}^{-1}.$$

$$(iii) \text{ Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{C}$$

$$C = 0.05 \text{ M}$$

$$\therefore \Lambda_m = \frac{1.148 \times 10^{-2} \times 1000}{0.05} = 229.6 \text{ S cm}^2 \text{ mol}^{-1}.$$

Practice Problems

1. The resistance of 0.05 M NaOH solution is 31.6Ω and its cell constant is 0.357 cm^{-1} . Calculate its conductivity and molar conductivity. (Hr.S.B. 2018)
2. The resistance of 0.01 M AgNO_3 solution dipped in a conductivity cell at 25°C was 1412 ohms . If the molar conductivity of this solution is $132.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, what is the cell constant of the conductivity cell?

3. Calculate the resistance of 0.01 N solution of an electrolyte whose equivalent conductivity is $420 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ (The cell constant of the cell is 0.88 cm^{-1}).
4. The resistance of 0.5 N solution of an electrolyte in a conductivity cell was found to be 25 ohm. Calculate the equivalent conductivity of the solution if the electrodes in the cell are 1.6 cm apart and have an area of 3.2 cm^2 . (Pb. S.B. 2009, 2013, 2016)
5. When a certain conductance cell was filled with 0.20 mol dm^{-3} aqueous KCl solution, its conductivity was $2.78 \times 10^{-3} \text{ S cm}^{-1}$ and had a resistance 82.5 ohm at 300 K. Calculate the cell constant of the cell.
6. The conductivity of a solution containing 1.0 g of anhydrous BaCl_2 in 200 cm^3 of the solution has been found to 0.0058 S cm^{-1} . Calculate the molar conductivity and equivalent conductivity of the solution.
7. The resistance of a 0.5 M solution of an electrolyte was found to be 30Ω enclosed between two platinum electrodes. Calculate the molar conductivity of the solution if the electrodes in the cell are 1.5 cm apart and having an area of cross section 2.0 cm^2 . (Pb.S.B. 2009, 2013, 2016)
8. A conductivity cell when filled with 0.02 M KCl (conductivity = $0.002768 \Omega^{-1} \text{ cm}^{-1}$) has a resistance of 457.3Ω . What will be the equivalent conductivity of 0.05 N CaCl_2 solution if the same cell filled with this solution has a resistance of 202Ω ?
9. When a certain conductance cell was filled with 0.1 mol L^{-1} KCl, it has a resistance of 85Ω at 25°C . When the same cell was filled with an aqueous solution of 0.052 mol L^{-1} of an electrolyte solution, the resistance was 96Ω . Calculate the molar conductivity of the electrolyte at this concentration. (Conductivity of 0.1 mol L^{-1} KCl solution is $1.29 \times 10^{-2} \text{ S cm}^{-1}$) (D.B.S. 2004 C)
10. The resistance of a conductivity cell with 0.1 M KCl solution is found to be 200Ω at 298 K. When the same cell was filled with 0.02 M NaCl solution, the resistance at the same temperature is found to be 1100Ω . Calculate :
- the cell constant of the cell in m^{-1} .
 - the molar conductivity of 0.02 M NaCl solution in $\text{S m}^2 \text{ mol}^{-1}$.
- Given : Conductivity of 0.1 M KCl solution at $298 \text{ K} = 1.29 \text{ S m}^{-1}$.
11. The molar conductance of 0.05 M solution of MgCl_2 is $194.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at 25°C . A cell with electrodes having 1.50 cm^2 surface area and 0.50 cm apart is filled with 0.05 M solution of MgCl_2 . How much current will flow when the potential difference between the electrodes is 5.0V?
12. Specific conductivity of N/35 KCl at 298 K is $0.002768 \text{ ohm}^{-1} \text{ cm}^{-1}$ and it has resistance of 520 ohm. A N/25 solution of a salt kept in the same cell was found to have a resistance of 300 ohm at 298 K. Calculate equivalent conductance of the solution.

Answers to Practice Problems

- $226 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
- 1.87 cm^{-1} .
- 209.5 ohm.
- $40 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$
- 0.229 cm^{-1} .
- $\Lambda_m = 241.67 \text{ S cm}^2 \text{ mol}^{-1}$,
 $\Lambda = 120.83 \text{ S cm}^2 \text{ equiv}^{-1}$.
- $50 \text{ ohm}^{-1} \text{ mol}^{-1}$.
- $125.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$.
- $219.65 \text{ S cm}^2 \text{ mol}^{-1}$.
- (i) 258 m^{-1} ,
(ii) $1.175 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$.
- 0.146 A
- $119.5 \text{ S cm}^2 \text{ equiv}^{-1}$.

Hints & Solutions on page 74

VARIATION OF CONDUCTIVITY AND MOLAR CONDUCTIVITY WITH CONCENTRATION

We have learnt that *electrolytic conductance decreases with increase in concentration or increases with increase in dilution*. This is because conductance of ions is due to the presence of ions in the solution. The greater the number of ions, the greater is the conductance. As with dilution, more ions are produced in solution so conductance also increases on dilution. Both specific conductance or conductivity and molar conductivity change with concentration of the electrolyte. However, conductivity of an electrolyte decreases with the decrease in concentration both for weak and strong electrolytes, whereas molar conductivity increases with decrease in concentration. Alternatively **upon dilution, specific conductance or conductivity decreases while molar conductivity increases**. This can be easily explained, as :

Conductivity is the conductance of one centimeter cube of the solution. Upon diluting the solution, the concentration of ions per centimeter cube decreases and therefore, the conductivity decreases.

On the other hand, the increase in molar conductivity on dilution is due to the fact that it is the product of conductivity (κ) and the volume (V) of the solution containing one mole of the electrolyte.

$$\Lambda = \kappa \times V$$

On dilution, conductivity decreases but volume containing one mole of an electrolyte increases. It has been found that the increase in volume on dilution is much more than the decrease in conductivity. As a result **molar conductivity increases with dilution**.

The molar conductivity of a few electrolytes in water at different concentrations are given in Table 3.

Table 3. Molar conductivity ($\text{S cm}^2 \text{ mol}^{-1}$) of a few electrolytes in water at 298 K

C	HCl	KCl	KNO_3	CH_3COOH	NH_4OH
0.1	391.3	129.0	120.4	5.2	3.6
0.05	399.1	133.4	126.3	—	—
0.01	412.0	141.3	132.8	16.3	11.3
0.005	415.8	143.5	131.5	—	—
0.001	421.4	146.9	141.8	49.2	34.0
0.0005	422.7	147.8	142.8	67.7	46.9
0 (infinite dilution)	426.2	149.9	146.0	390.7	271.0

Inspection of Table 3 reveals that the molar conductance of strong (HCl, KCl, KNO_3) as well as weak electrolytes (CH_3COOH , NH_4OH) increase with decrease in concentration or increase in dilution. The variation is however different for strong and weak electrolytes.

Like molar conductivity, equivalent conductivity also increases with dilution because of increase in volume containing one gram equivalent of the electrolyte.

Variation of Molar Conductivity with Concentration for Strong and Weak Electrolytes

(i) Variation of Molar Conductivity with Concentration for Strong Electrolytes

In case of strong electrolytes, molar conductivity increases slowly with dilution and there is a tendency for molar conductivity to approach a certain limiting value when the concentration approaches zero *i.e.*, when the dilution is infinite. *The molar conductivity when the concentration approaches zero (infinite dilution)* is called **molar conductivity at infinite dilution**. It is denoted by Λ_m° or Λ_m^∞ . Thus,

$$\Lambda_m = \Lambda_m^\circ \quad \text{when } C \rightarrow 0 \text{ (at infinite dilution)}$$

It has been observed that the variation of molar conductivity with concentration may be given by the expression

$$\Lambda_m = \Lambda_m^\circ - AC^{1/2}$$

where A is a constant and Λ_m° is called molar conductivity at infinite dilution. This equation is called **Debye Huckel Onsager equation** and is found to hold good at low concentrations.

The variation of molar conductivity with concentration can be studied by plotting the values of Λ_m against square root of concentration ($C^{1/2}$). The plots of variation of molar conductivity with $C^{1/2}$ for KCl and HCl are given in Fig. 5.(a). It has been noticed that the variation of Λ_m with concentration, $C^{1/2}$ is small (between 4 to 10% only) so that the plots can be extrapolated to zero concentration. The intercept gives the limiting value of molar conductivity when the concentration approaches zero, called **molar conductivity at infinite dilution**, Λ_m° . The slope of the line is equal to $-A$. The value of constant A for a given solvent and temperature depends on the type of electrolyte *i.e.*, the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl is known as 1:1 electrolyte, CaCl_2 as

REMEMBER

With dilution or decrease in concentration

- conductivity (or specific conductance) decreases
- molar conductivity increases.

NaCl is known as 1:1 electrolyte, CaCl_2 as 1:2 electrolyte, MgSO_4 as 2:2 electrolyte and AlCl_3 as 1:3 electrolyte, etc. depending upon the charges on the cation and anion.

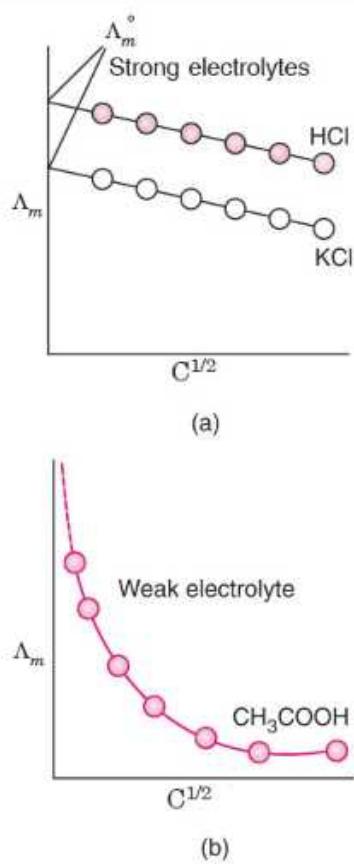


Fig. 5. Variation of molar conductance (Λ_m) with square root of concentration $C^{1/2}$ for (a) strong electrolytes and (b) weak electrolytes.

2–1 and MgSO₄ as 2–2 electrolytes. All electrolytes of a particular type have the same value for A.

(ii) Variation of Molar Conductivity with Concentration for Weak Electrolytes

The weak electrolytes dissociate to a much lesser extent as compared to strong electrolytes. Therefore, the molar conductivity is low as compared to that of strong electrolytes.

However, the variation of Λ_m with $C^{1/2}$ is very large and so much so that we cannot obtain molar conductance at infinite dilution (Λ_m°) by extrapolation of the Λ_m versus $C^{1/2}$ plots. The behaviour of weak electrolytes such as CH₃COOH is shown in Fig. 5 (b).

It may be noted that the Λ_m° value for weak electrolytes can be obtained by an indirect method based upon Kohlrausch law (discussed later).

Explanation for the Variation of Molar Conductivity with Concentration

The variation of molar conductance with concentration can be explained on the basis of conducting ability of ions for weak and strong electrolytes.

(i) **Conductance behaviour of weak electrolytes.** The variation of Λ_m with dilution can be explained on the basis of number of ions in solution. The number of ions furnished by an electrolyte in solution depends upon the degree of dissociation with dilution. With the increase in dilution, the degree of dissociation increases and as a result molar conductance increases. The limiting value of molar conductance (Λ_m°) corresponds to degree of dissociation equal to 1, i.e. the whole of the electrolyte dissociates.

Thus, the **degree of dissociation** can be calculated at any concentration as:

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} \quad \dots(3)$$

where α is the degree of dissociation, Λ_m^c is the molar conductance at concentration C and Λ_m° is the molar conductance at infinite dilution.

(ii) **Conductance behaviour of strong electrolytes.** For strong electrolytes, there is no increase in the number of ions with dilution because strong electrolytes are completely ionised in solution at all concentrations (by definition). However, in concentrated solutions of strong electrolytes there are **strong forces of attraction between the ions of opposite charges called interionic forces**. Due to these interionic forces, the conducting ability of the ions is less in concentrated solutions. With dilution, the ions become far apart from one another and interionic forces decrease. As a result, molar conductivity increases with dilution. When the concentration of the solution becomes very very low, the interionic attractions become negligible and the molar conductance approaches the limiting value called molar conductance at infinite dilution. This value is characteristic of each electrolyte.

SOLVED EXAMPLES

Example 9.

The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below :

Concentration (M)	$10^2 \times \kappa$ (S m ⁻¹)
0.001	1.237
0.010	11.85
0.020	23.15
0.050	55.53
0.100	106.74

Calculate Λ for all concentrations and draw a plot between Λ and $C^{1/2}$. Find the value of Λ_m° .

N.C.E.R.T. (Pb.S.B. 2010)

Solution: Λ_m at different concentrations may be calculated as :

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

At 0.001 M, $\kappa = 1.237 \times 10^{-2}$ S m⁻¹ = 1.237×10^{-4} S cm⁻¹

$$\therefore \Lambda_m = \frac{1.237 \times 10^{-4} \times 1000}{0.001} = 123.7 \text{ S cm}^2 \text{ mol}^{-1}$$

At 0.010 M, $\kappa = 11.85 \times 10^{-2} \text{ S m}^{-1} = 11.85 \times 10^{-4} \text{ S cm}^{-1}$

$$\therefore \Lambda_m = \frac{11.85 \times 10^{-4} \times 1000}{0.010} = 118.5 \text{ S cm}^2 \text{ mol}^{-1}$$

At 0.020 M, $\kappa = 23.15 \times 10^{-2} \text{ S m}^{-1} = 23.15 \times 10^{-4} \text{ S cm}^{-1}$

$$\therefore \Lambda_m = \frac{23.15 \times 10^{-4} \times 1000}{0.020} = 115.75 \text{ S cm}^2 \text{ mol}^{-1}$$

At 0.050 M, $\kappa = 55.53 \times 10^{-2} \text{ S m}^{-1} = 55.53 \times 10^{-4} \text{ S cm}^{-1}$

$$\therefore \Lambda_m = \frac{55.53 \times 10^{-2} \times 1000}{0.050} = 111.06 \text{ S cm}^2 \text{ mol}^{-1}$$

At 0.100 M, $\kappa = 106.74 \times 10^{-2} \text{ S m}^{-1} = 106.74 \times 10^{-4} \text{ S cm}^{-1}$

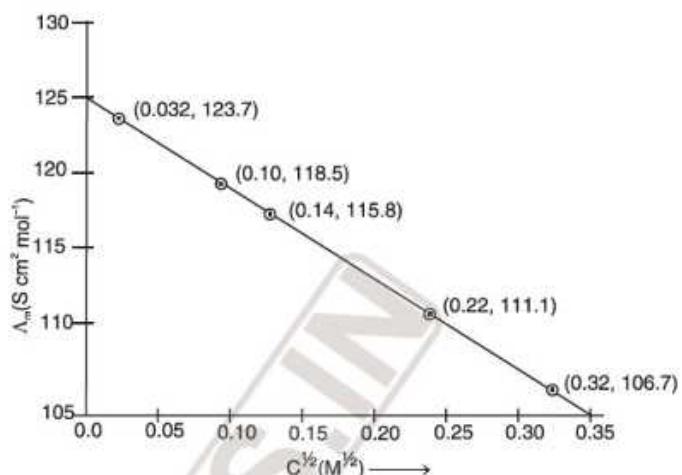
$$\therefore \Lambda_m = \frac{106.74 \times 10^{-4} \times 1000}{0.1} = 106.74 \text{ S cm}^2 \text{ mol}^{-1}$$

The values of Λ_m and $C^{1/2}$ at different concentrations are:

$\Lambda (\text{S cm}^2 \text{ mol}^{-1})$ 123.7 118.5 115.75 111.06 106.74

$C^{1/2} (\text{M}^{1/2})$ 0.0316 0.10 0.141 0.224 0.316

Plot of Λ_m and $C^{1/2}$ is given below :



The extrapolation of the straight line to zero concentration (intercept) gives the value of $\Lambda_m = 124.5 \text{ S cm}^2 \text{ mol}^{-1}$.

Practice Problems

13. The molar conductance of KCl solutions at different concentrations at 298 K are given below :

$C(\text{mol L}^{-1})$ 0.000198 0.000309 0.000521 0.000989

$\Lambda(\text{S cm}^2 \text{ mol}^{-1})$ 148.61 148.29 147.81 147.09

Show that a plot of Λ_m and $C^{1/2}$ is a straight line. Determine the values of Λ_m and A for KCl.

N.C.E.R.T. (Pb. S.B. 2010)

Answers to Practice Problems

13. $\Lambda_m = 150.0 \text{ S cm}^2 \text{ mol}^{-1}$ and
 $A(\text{slope}) = 87.46 \text{ S cm}^2 \text{ mol}^{-1}/(\text{mol L}^{-1})^{1/2}$.

Hints & Solutions on page 74

KOHLRAUSCH'S LAW

Kohlrausch obtained very interesting pattern between the values of Λ° for different strong electrolytes. It was observed that the difference of Λ° of different pairs of electrolytes having a common cation or a common anion was almost same. For example, the difference between the molar conductance of K^+ and Na^+ is $23.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ irrespective of the anion.

$$\Lambda^\circ(\text{KCl}) = 149.9 \quad \Lambda^\circ(\text{KNO}_3) = 145.0$$

$$\Lambda^\circ(\text{NaCl}) = 126.5 \quad \Lambda^\circ(\text{NaNO}_3) = 121.6$$

$$\text{Difference} = \frac{23.4}{23.4}$$

$$\Lambda^\circ(\text{KBr}) = 151.9$$

$$\Lambda^\circ(\text{NaBr}) = 128.5 \quad \therefore \Lambda^\circ(\text{K}^+) - \Lambda^\circ(\text{Na}^+) = 23.4 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\frac{23.4}{23.4}$$

Similarly, the difference between the molar conductivities of chloride and nitrate ions is $4.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ irrespective of the cation :

$$\Lambda^\circ(\text{KCl}) = 149.9 \quad \Lambda^\circ(\text{NaCl}) = 126.5$$

$$\Lambda^\circ(\text{KNO}_3) = 145.0 \quad \Lambda^\circ(\text{NaNO}_3) = 121.6$$

$$\text{Difference} = \frac{4.9}{4.9}$$

$$\Lambda^\circ(\text{LiCl}) = 115.0$$

$$\Lambda^\circ(\text{LiNO}_3) = \frac{110.1}{4.9} \quad \therefore \Lambda^\circ(\text{Cl}^-) - \Lambda^\circ(\text{NO}_3^-) = 4.9 \text{ S cm}^2 \text{ mol}^{-1}$$

Thus, it may be concluded that each ion makes definite contribution to the molar conductivity at infinite dilution irrespective of the other ions. The

individual contribution of an ion towards the total molar conductivity of the electrolyte is called **molar ionic conductivity**. This led him to postulate a law known as **Kohlrausch's law of independent migration of ions**. This law states that,

the limiting molar conductivity of an electrolyte can be expressed as the sum of the limiting ionic molar conductivities of the cation and the anion.

For example, if $\lambda^\circ(\text{K}^+)$ and $\lambda^\circ(\text{Cl}^-)$ are limiting ionic molar conductivities of potassium and chloride ions respectively, then the limiting molar conductivity for potassium chloride is given by the equation:

$$\Lambda^\circ(\text{KCl}) = \lambda^\circ(\text{K}^+) + \lambda^\circ(\text{Cl}^-)$$

In general, if an electrolyte on dissociation gives v_+ cations and v_- anions, then its limiting molar conductivity is given as :

$$\Lambda^\circ = v_+ \lambda_+^\circ + v_- \lambda_-^\circ$$

where λ_+° and λ_-° are the limiting ionic molar conductivities of the cation and the anion respectively. For example,

For NaCl

$$\Lambda^\circ(\text{NaCl}) = \lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-)$$

For KNO₃

$$\Lambda^\circ(\text{KNO}_3) = \lambda^\circ(\text{K}^+) + \lambda^\circ(\text{NO}_3^-)$$

For MgCl₂

$$\Lambda^\circ(\text{MgCl}_2) = \lambda^\circ(\text{Mg}^{2+}) + 2\lambda^\circ(\text{Cl}^-)$$

For Al₂(SO₄)₃

$$\Lambda^\circ[\text{Al}_2(\text{SO}_4)_3] = 2\lambda^\circ(\text{Al}^{3+}) + 3\lambda^\circ(\text{SO}_4^{2-})$$

The values of molar conductivities of some cations and anions are given in Table 4.

Table 4. Limiting molar conductivity for some ions in water at 298 K.

Ion	λ° (S cm ² mol ⁻¹)	Ion	λ° (S cm ² mol ⁻¹)
H ⁺	349.6	Cl ⁻	76.3
Na ⁺	50.1	Br ⁻	78.1
K ⁺	73.5	I ⁻	76.8
Mg ²⁺	106.0	OH ⁻	199.1
Ca ²⁺	119.0	NO ₃ ⁻	71.5
Ba ²⁺	127.2	SO ₄ ²⁻	160.0
Sr ²⁺	118.9	CH ₃ COO ⁻	40.9

Applications of Kohlrausch's Law

Some of the important applications of Kohlrausch's law are :

1. Calculation of Molar Conductance at Infinite Dilution for Weak Electrolytes

We have learnt that it is not possible to determine the value of limiting molar conductivity at infinite dilution for weak electrolytes by extrapolation of Λ versus \sqrt{C} graph. However, this can be calculated easily by using Kohlrausch's law.

Let us calculate the limiting molar conductivity for CH₃COOH. According to Kohlrausch's law,

$$\Lambda^\circ(\text{CH}_3\text{COOH}) = \lambda^\circ(\text{CH}_3\text{COO}^-) + \lambda^\circ(\text{H}^+) \quad \dots(i)$$

This equation can be obtained by the knowledge of molar conductivity at infinite dilution for some strong electrolytes. For example, consider the strong electrolytes HCl, NaCl and CH₃COONa. From Kohlrausch's law,

$$\Lambda^\circ(\text{CH}_3\text{COONa}) = \lambda^\circ(\text{CH}_3\text{COO}^-) + \lambda^\circ(\text{Na}^+) \quad \dots(ii)$$

$$\Lambda^\circ(\text{HCl}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{Cl}^-) \quad \dots(iii)$$

$$\Lambda^\circ(\text{NaCl}) = \lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-) \quad \dots(iv)$$

It is clear that

$$\begin{aligned} \lambda^\circ(\text{CH}_3\text{COO}^-) + \lambda^\circ(\text{H}^+) &= [\lambda^\circ(\text{CH}_3\text{COO}^-) + \lambda^\circ(\text{Na}^+)] + [\lambda^\circ(\text{H}^+) + \lambda^\circ(\text{Cl}^-)] \\ &\quad - [\lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-)] \end{aligned}$$

$$\text{or } \Lambda^\circ(\text{CH}_3\text{COOH}) = \Lambda^\circ(\text{CH}_3\text{COONa}) + \Lambda^\circ(\text{HCl}) - \Lambda^\circ(\text{NaCl})$$

Similarly, we have

$$\Lambda^\circ(\text{NH}_4\text{OH}) = \Lambda^\circ(\text{NH}_4\text{Cl}) + \Lambda^\circ(\text{NaOH}) - \Lambda^\circ(\text{NaCl})$$

2. Calculation of Degree of Dissociation of Weak Electrolytes

Molar conductance of a weak electrolyte depends upon its degree of dissociation. Higher the degree of dissociation, larger is the molar conductance. With increase in dilution, the conductance increases and at infinite dilution, the electrolyte is completely dissociated so that degree of dissociation becomes one i.e.,

$$\Lambda = \Lambda^\circ \text{ (at } C \rightarrow 0\text{). Thus, if}$$

$$\Lambda^c = \text{molar conductance of solution at any concentration}$$

$$\Lambda^\circ = \text{molar conductance at infinite dilution.}$$

Then, degree of dissociation at any concentration is:

$$\alpha = \frac{\Lambda^c}{\Lambda^\circ}$$

Thus, measuring the molar conductance at any concentration (Λ^c) helps to calculate degree of dissociation (α) if Λ° is known.

3. Calculation of Dissociation Constant of Weak Electrolytes

In previous class, we have learnt that the dissociation constant (K) of weak electrolytes can be given as

$$K = \frac{C\alpha^2}{1-\alpha}$$

where C is the concentration and α is the degree of dissociation. Substituting value of α (calculated from molar conductance) in the above relation the dissociation constant (K) for weak electrolytes can be calculated.

$$K = \frac{C \left(\frac{\Lambda}{\Lambda^\circ} \right)^2}{\left(1 - \frac{\Lambda}{\Lambda^\circ} \right)} = \frac{C \Lambda^2}{\Lambda^\circ (\Lambda^\circ - \Lambda)}$$

4. Calculation of solubility of sparingly soluble salts

The sparingly soluble salts such as AgCl , PbSO_4 , BaSO_4 etc. dissolve to a very little extent in water. Since these dissolve only to a small extent, their solutions are considered as infinite dilute. Moreover, as their solutions are saturated, their concentration may be taken equal to their solubility. Therefore, by measuring the specific conductivity (κ) and knowing molar conductivity (Λ_m°) of such a solution, the solubility can be calculated as :

$$\Lambda_m^\circ = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{\kappa \times 1000}{\text{Solubility}}$$

$$\therefore \text{Solubility} = \frac{\kappa \times 1000}{\Lambda_m^\circ}$$

Λ_m° can be calculated by applying Kohlrausch law. For example, for AgCl

$$\Lambda_m^\circ(\text{AgCl}) = \lambda^\circ(\text{Ag}^+) + \lambda^\circ(\text{Cl}^-)$$

SOLVED EXAMPLES

Example 10

The molar conductivities at infinite dilution for sodium acetate, hydrochloric acid and sodium chloride are 91.0, 425.9 and $126.4 \text{ S cm}^2 \text{ mol}^{-1}$ respectively at 298 K. Calculate the molar conductivity of acetic acid at infinite dilution.

N.C.E.R.T. (D.S.B. 2010, Uttarakhand S.B. 2014, H.P.S.B. 2015, Meghalaya S.B. 2016, Assam S.B. 2015, 2017, Mizoram S.B. 2017, Nagaland S.B. 2017, Kerala S.B. 2017)

WATCH OUT !

Ionic mobility or absolute velocity

The actual velocity of an ion depends upon the potential gradient. If the potential gradient is 1 V cm^{-1} , the velocity of the ion is called its **absolute velocity** or **ionic mobility**. It is defined as *the speed of the ion in cm/sec under a potential gradient of 1 volt per cm*. (Potential gradient is applied EMF/distance between the electrodes).

It can be shown that

Ionic mobility (μ_\pm)

$$= \frac{\text{Ionic conductance}}{96500}$$

e.g., ionic conductance of Li^+ is $38.6 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$. Its ionic mobility is :

$$\mu(\text{Li}^+) = \frac{38.6 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}}{96500 \text{ C eq}^{-1}}$$

$$= 4.0 \times 10^{-4} \Omega^{-1} \text{ cm}^2 \text{ C}^{-1}$$

$$\text{or } = 4.0 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$$

$$(C = As; C\Omega = As \Omega \text{ but } A\Omega = V \\ \therefore C^{-1} \Omega^{-1} = V^{-1} s^{-1})$$

Learning Plus

Transport Number

The fraction of the total current carried by an ion is called its transport number.

Transport number of a cation,

$$t_+ = \frac{\text{Current carried by cation}}{\text{Total Current}}$$

Transport number of anion

$$t_- = \frac{\text{Current carried by anion}}{\text{Total Current}}$$

If, there is only one cation and one anion, then

$$t_+ + t_- = 1$$

Solution : Molar conductivity at infinite dilution for acetic acid can be calculated as :

$$\begin{aligned} \Lambda^\circ(\text{CH}_3\text{COOH}) &= \lambda^\circ_{\text{H}^+} + \lambda^\circ_{\text{CH}_3\text{COO}^-} \\ &= \lambda^\circ_{\text{CH}_3\text{COO}^-} + \lambda^\circ_{\text{Na}^+} + \lambda^\circ_{\text{H}^+} + \lambda^\circ_{\text{Cl}^-} - \lambda^\circ_{\text{Na}^+} - \lambda^\circ_{\text{Cl}^-} \end{aligned}$$

$$\Lambda^\circ(\text{CH}_3\text{COOH}) = \Lambda^\circ(\text{CH}_3\text{COONa}) + \Lambda^\circ(\text{HCl}) - \Lambda^\circ(\text{NaCl})$$

$$\Lambda^\circ(\text{CH}_3\text{COONa}) = 91.0 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ(\text{HCl}) = 425.9 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\begin{aligned}\Lambda^\circ(\text{NaCl}) &= 126.4 \text{ S cm}^2 \text{ mol}^{-1} \\ \therefore \Lambda^\circ(\text{CH}_3\text{COOH}) &= 91.0 + 425.9 - 126.4 \\ &= \mathbf{390.5 \text{ S cm}^2 \text{ mol}^{-1}}.\end{aligned}$$

Example 11.

The molar conductivities at infinite dilution for NaI , CH_3COONa and $(\text{CH}_3\text{COO})_2\text{Mg}$ are 12.69, 9.10 and $18.78 \text{ mSm}^2 \text{ mol}^{-1}$ respectively at 25°C . What is the molar conductivity of MgI_2 at infinite dilution?

Solution : Molar conductivity at infinite dilution for MgI_2 may be calculated as :

$$\begin{aligned}\Lambda^\circ(\text{MgI}_2) &= \Lambda^\circ[(\text{CH}_3\text{COO})_2\text{Mg}] + 2\Lambda^\circ(\text{NaI}) \\ &\quad - 2\Lambda^\circ(\text{CH}_3\text{COONa}) \\ \Lambda^\circ[(\text{CH}_3\text{COO})_2\text{Mg}] &= 18.78 \text{ m Sm}^2 \text{ mol}^{-1} \\ \Lambda^\circ(\text{NaI}) &= 12.69 \text{ m Sm}^2 \text{ mol}^{-1} \\ \Lambda^\circ(\text{CH}_3\text{COONa}) &= 9.10 \text{ m Sm}^2 \text{ mol}^{-1} \\ \therefore \Lambda^\circ(\text{MgI}_2) &= 18.78 + 2(12.69) - 2(9.10) \\ &= \mathbf{25.96 \text{ m Sm}^2 \text{ mol}^{-1}}.\end{aligned}$$

Example 12.

The molar conductances of ammonium hydroxide at concentrations 0.1 M and 0.001 M are 3.6 and $34.0 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. Calculate the degree of dissociation of NH_4OH at these concentrations. Molar conductance at infinite dilution for NH_4OH is $271.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Solution : Degree of dissociation is given as $\alpha = \frac{\Lambda^c}{\Lambda^\circ}$ where

Λ^c is the molar conductance at concentration C and Λ° is the molar conductance at infinite dilution.

$$(i) \text{ At } C = 0.1 \text{ M}, \Lambda^c = 3.6,$$

$$\Lambda^\circ = 271.1$$

$$\therefore \alpha = \frac{3.6}{271.1} = 0.013$$

i.e. 1.3% dissociated.

$$(ii) \text{ At } C = 0.001 \text{ M}, \Lambda^c = 34.0, \Lambda^\circ = 271.1$$

$$\therefore \alpha = \frac{34.0}{271.1} = 0.125$$

i.e., 12.5% dissociated.

Example 13.

Calculate the molar conductivity of a solution of MgCl_2 at infinite dilution given that the molar ionic conductivities of $\lambda^\circ(\text{Mg}^{2+}) = 106.1 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^\circ(\text{Cl}^-) = 76.3 \text{ S cm}^2 \text{ mol}^{-1}$.

$$\begin{aligned}\text{Solution : } \Lambda^\circ(\text{MgCl}_2) &= \lambda^\circ(\text{Mg}^{2+}) + 2\lambda^\circ(\text{Cl}^-) \\ \lambda^\circ(\text{Mg}^{2+}) &= 106.1 \text{ S cm}^2 \text{ mol}^{-1}, \\ \lambda^\circ(\text{Cl}^-) &= 76.3 \text{ S cm}^2 \text{ mol}^{-1}. \\ \therefore \Lambda^\circ(\text{MgCl}_2) &= 106.1 + 2(76.3) \\ &= \mathbf{258.7 \text{ S cm}^2 \text{ mol}^{-1}}.\end{aligned}$$

Example 14.

The molar conductivity at infinite dilution of $\text{Al}_2(\text{SO}_4)_3$ is $858 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the molar ionic conductivity of Al^{3+} ion given that $\lambda^\circ(\text{SO}_4^{2-}) = 160 \text{ S cm}^2 \text{ mol}^{-1}$.

(Mizoram S.B. 2014, 2018)

Solution : According to Kohlrausch's law,

$$\Lambda^\circ[\text{Al}_2(\text{SO}_4)_3] = 2\lambda^\circ(\text{Al}^{3+}) + 3\lambda^\circ(\text{SO}_4^{2-})$$

$$\Lambda^\circ[\text{Al}_2(\text{SO}_4)_3] = 858 \text{ S cm}^2 \text{ mol}^{-1},$$

$$\lambda^\circ(\text{SO}_4^{2-}) = 160 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore 858 = 2\lambda^\circ(\text{Al}^{3+}) + 3 \times 160$$

$$\text{or } 2\lambda^\circ(\text{Al}^{3+}) = 858 - 480$$

$$= 378$$

$$\therefore \lambda^\circ(\text{Al}^{3+}) = \frac{378}{2} = \mathbf{189 \text{ S cm}^2 \text{ mol}^{-1}}.$$

Example 15.

The molar conductivity at infinite dilution for HCl , KCl and CH_2ClCOOK are 4.26×10^{-2} , 1.50×10^{-2} and $1.13 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$ respectively. Calculate the molar conductivity at infinite dilution for monochloro acetic acid ($\text{CH}_2\text{Cl}(COOH)$).

Solution : Molar conductivity at infinite dilution for monochloro acetic acid (CH_2ClCOOH) may be calculated as:

$$\Lambda^\circ(\text{CH}_2\text{ClCOOH}) = \Lambda^\circ(\text{CH}_2\text{Cl COOK}) + \Lambda^\circ(\text{HCl}) - \Lambda^\circ(\text{KCl})$$

$$\Lambda^\circ(\text{CH}_2\text{ClCOOK}) = 1.13 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ(\text{HCl}) = 4.26 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ(\text{KCl}) = 1.50 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$$

$$\therefore \Lambda^\circ(\text{CH}_2\text{ClCOOH}) = 1.13 \times 10^{-2} + 4.26 \times 10^{-2} - 1.50 \times 10^{-2} \\ = \mathbf{3.89 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}}.$$

Example 16.

The conductivity of a 0.01 M solution of acetic acid at 298 K is $1.65 \times 10^{-4} \text{ S cm}^{-1}$. Calculate

(i) molar conductivity of the solution

(ii) degree of dissociation of CH_3COOH

(iii) dissociation constant for acetic acid.

Given that

$$\lambda^\circ(\text{H}^+) = 349.1 \text{ and}$$

$$\lambda^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}.$$

Solution : (i) Calculation of molar conductivity of solution.

$$\Lambda = \frac{\kappa \times 1000}{C}$$

$$\kappa = 1.65 \times 10^{-4} \text{ S cm}^{-1}, C = 0.01 \text{ M}$$

$$\therefore \Lambda = \frac{1.65 \times 10^{-4} \times 1000}{0.01} = \mathbf{16.5 \text{ S cm}^2 \text{ mol}^{-1}}.$$

(ii) Calculation of degree of dissociation of acetic acid.

$$\alpha = \frac{\Lambda^c}{\Lambda^\circ}$$

$$\begin{aligned}\Lambda^\circ(\text{CH}_3\text{COOH}) &= \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{CH}_3\text{COO}^-) \\ &= 349.1 + 40.9 = 390 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\therefore \alpha = \frac{16.5}{390} = \mathbf{0.0423}.$$

(iii) Calculation of dissociation constant, K

Acetic acid dissociates as :



Initial conc.	c	0	0
Equilibrium conc.	$c(1 - \alpha)$	$c\alpha$	$c\alpha$

Dissociation constant, $K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{\text{CH}_3\text{COOH}}$

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

or $K = \frac{c\alpha^2}{1-\alpha}$

Substituting the values,

$$K = \frac{0.01 \times (0.0423)^2}{1 - 0.0423}$$

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

Example 17.

Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and if Λ° for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$. What is its dissociation constant? (A.I.S.B. 2004; D.S.B. 2004; 2008)

Solution : Molar conductivity,

$$\Lambda = \frac{\kappa \times 1000}{M}$$

$$\kappa = 7.896 \times 10^{-5} \text{ S cm}^{-1}, M = 0.00241 \text{ M}$$

$$\therefore \Lambda = \frac{7.896 \times 10^{-5} \times 1000}{0.00241}$$

$$= 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

Now, $\alpha = \frac{\Lambda^c}{\Lambda^\circ} = \frac{32.76}{390.5} = 0.0839$

$$K = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.00241 \times (0.0839)^2}{(1-0.0839)}$$

$$= 1.85 \times 10^{-5}$$

Example 18.

The specific conductance of a saturated solution of AgCl at 298 K is found to be $1.386 \times 10^{-6} \text{ S cm}^{-1}$. Calculate its solubility ($\kappa^\circ_{\text{Ag}^+} = 62.0 \text{ S cm}^2 \text{ mol}^{-1}$ and $\kappa^\circ_{\text{Cl}^-} = 76.3 \text{ S cm}^2 \text{ mol}^{-1}$).

Solution : $\Lambda_m^\circ(\text{AgCl}) = \kappa^\circ(\text{Ag}^+) + \kappa^\circ(\text{Cl}^-)$

$$= 62.0 + 76.3$$

$$= 138.3 \text{ S cm}^2 \text{ mol}^{-1}$$

Practice Problems

14. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m°) is $39.05 \text{ S cm}^2 \text{ mol}^{-1}$. Given $\kappa^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\kappa^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$. (D.S.B. 2017)
15. Calculate the molar conductivity at infinite dilution of AgCl from the following data : $\Lambda^\circ(\text{AgNO}_3) = 13.34 \text{ m S m}^2 \text{ mol}^{-1}$, $\Lambda^\circ(\text{KCl}) = 14.99 \text{ m S m}^2 \text{ mol}^{-1}$ and $\Lambda^\circ(\text{KNO}_3) = 14.49 \text{ m S m}^2 \text{ mol}^{-1}$
16. The Λ° values of KNO_3 and LiNO_3 are 145.0 and $110.1 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. The κ° value for K^+ ion is $73.5 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate $\kappa^\circ(\text{Li}^+)$. (Pb.S.B. 2011)
17. The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is $3.905 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation (α).

$$\kappa = 1.386 \times 10^{-6} \text{ S cm}^{-1}$$

$$\Lambda_m^\circ = \frac{\kappa \times 1000}{M} = \frac{\kappa \times 1000}{\text{Solubility}}$$

$$\therefore \text{Solubility} = \frac{\kappa \times 1000}{\Lambda_m^\circ}$$

$$= \frac{1.386 \times 10^{-6} \times 1000}{138.3}$$

$$= 1.0 \times 10^{-5} \text{ mol L}^{-1}$$

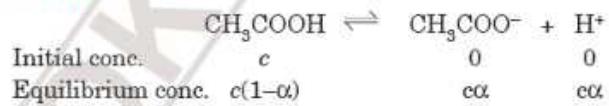
$$1.0 \times 10^{-5} \times 143.5 \text{ g L}^{-1}$$

$$= 1.435 \times 10^{-3} \text{ g L}^{-1}$$

Example 19.

The molar conductance of acetic acid at infinite dilution is $390.7 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the molar conductance of 0.01 M acetic acid solution, given that the dissociation constant of acetic acid is 1.8×10^{-5} .

Solution : Acetic acid dissociates as :



$$\text{Dissociation constant, } K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

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

Assuming $1-\alpha \approx 1$, we get $K_a = c\alpha^2$

$$\text{or } \alpha = \left(\frac{K_a}{c} \right)^{\frac{1}{2}}$$

$$\text{Now } \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{\Lambda_m}{390.7}$$

Substituting the values, we get

$$\frac{\Lambda_m}{390.7} = \left(\frac{1.8 \times 10^{-5}}{0.01} \right)^{\frac{1}{2}} = 4.243 \times 10^{-2}$$

$$\therefore \Lambda_m = 4.243 \times 10^{-2} \times 390.7$$

$$= 16.58 \text{ S cm}^2 \text{ mol}^{-1}$$

Answers to Practice Problems

14. 10%.
15. $13.84 \text{ m S m}^2 \text{ mol}^{-1}$.
16. $38.6 \text{ S cm}^2 \text{ mol}^{-1}$.

Hints & Solutions on page 74

Given $\Lambda^\circ(\text{H}^+) = 349.65 \text{ S cm}^2 \text{ mol}^{-1}$ and $\Lambda^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$.
(A.I.S.B. 2016)

18. The molar conductivity at infinite dilution for NH_4Cl , NaOH and NaCl are 129.8, 217.4 and $108 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. If the molar conductivity of 0.01 M solution of NH_4OH is $9.33 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate
 (i) what is the percentage dissociation of NH_4OH at this dilution ?
 (ii) dissociation constant of NH_4OH . (A.I.S.B. 2005 C)
19. The conductivity of 0.1 M solution of AgNO_3 is $9.47 \times 10^{-3} \text{ S cm}^{-1}$ at 291 K. The ionic conductivities of Ag^+ and NO_3^- at the same temperature are 55.7 and $50.8 \text{ S cm}^2 \text{ equiv}^{-1}$ respectively. Calculate the degree of dissociation of AgNO_3 in 0.1 M solution.
20. The molar conductivity of 0.025 M HCOOH (*aq*) solution was measured as $4.61 \text{ m S m}^2 \text{ mol}^{-1}$. Calculate pK_a value for formic acid ($\Lambda^\circ(\text{H}^+) = 34.96$, $\Lambda^\circ(\text{HCOO}^-) = 5.46 \text{ m S m}^2 \text{ mol}^{-1}$). **N.C.E.R.T.**
21. Calculate Λ° for CaCl_2 and MgSO_4 from the following data :
 Λ° values are $\text{Ca}^{2+} = 119.0$, $\text{Cl}^- = 76.3$, $\text{Mg}^{2+} = 106.0$, $\text{SO}_4^{2-} = 160.0$ all in $\text{S cm}^2 \text{ mol}^{-1}$. **N.C.E.R.T.**
22. The conductivity of $0.001028 \text{ mol L}^{-1}$ acetic acid is $4.95 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its dissociation constant if $\Lambda^\circ(\text{CH}_3\text{COOH})$ is 390.5 $\text{S cm}^2 \text{ mol}^{-1}$. **N.C.E.R.T.**
23. The molar conductances of NaOH , NaCl and BaCl_2 at infinite dilution are 2.481×10^{-2} , 1.265×10^{-2} and $2.800 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$ respectively. Calculate Λ_m° for $\text{Ba}(\text{OH})_2$.
24. The conductivity of a saturated solution of BaSO_4 at 295 K, is found to be $3.758 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ and that of water used is $1.36 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. Molar ionic conductances at infinite dilution of Ba^{2+} and SO_4^{2-} ions are 110 and 136.6 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. Calculate the solubility of BaSO_4 at 295 K (Atomic masses: Ba = 137, S = 32, O = 16).

Hints & Solutions on page 74

Competition Plus

Conductometric titrations can also be used for titrations of acids and bases and precipitation reactions. For detail, refer **Competition File** (Page 98).

Learning Plus

Ionic product of water can also be calculated by knowing the specific conductivity of water as illustrated below.

► At 298 K, specific conductivity of water, κ is $5.54 \times 10^{-8} \text{ S cm}^{-1}$ and limiting molar ionic conductances of H^+ and OH^- are 349.6 and 199.1 $\text{S cm}^2 \text{ mol}^{-1}$ respectively. Calculate ionic product of water at 298K.

□ $\Lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$
 $\Lambda^\circ(\text{OH}^-) = 199.1 \text{ S cm}^2 \text{ mol}^{-1}$
 $\Lambda^\circ(\text{H}_2\text{O}) = \Lambda^\circ(\text{H}^+) + \Lambda^\circ(\text{OH}^-)$
 $= 349.6 + 199.1$
 $= 548.7 \text{ S cm}^2 \text{ mol}^{-1}$

Now, $\Lambda_m^\circ = \frac{\kappa \times 1000}{\text{Molarity}}$

or $\text{Molarity} = \frac{\kappa \times 1000}{\Lambda_m^\circ}$
 $= \frac{5.54 \times 10^{-8} \times 1000}{548.7}$
 $= 1.01 \times 10^{-7} \text{ mol L}^{-1}$

Now, $\text{Molarity} = [\text{H}^+] \text{ or } [\text{OH}^-] = 1.01 \times 10^{-7}$

\therefore Ionic product of water, $K_w = [\text{H}^+] [\text{OH}^-]$
 $= (1.01 \times 10^{-7}) (1.01 \times 10^{-7})$
 $= 1.02 \times 10^{-14}$

Advanced Level

PROBLEMS

Accelerate Your Potential
(for JEE Advance)

Problem 1. The conductivity of a saturated solution of AgBr at 25°C is $8.5 \times 10^{-7} \text{ S cm}^{-1}$. If the limiting molar ionic conductances of Ag^+ and Br^- ions are 62 and $78 \text{ S cm}^2 \text{ mol}^{-1}$, then calculate the solubility product of AgBr.

$$\begin{aligned}\Lambda_m^\circ(\text{AgBr}) &= \lambda_m^\circ(\text{Ag}^+) + \lambda_m^\circ(\text{Br}^-) \\ &= 62 + 78 = 140.0 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Now for saturated solution,

$$\Lambda_m^\circ(\text{AgBr}) = \frac{\kappa \times 1000}{s}$$

where s is the solubility

$$140.0 = \frac{8.5 \times 10^{-7} \times 1000}{s}$$

$$\text{or } s = \frac{8.5 \times 10^{-7} \times 1000}{140.0} = 6.07 \times 10^{-6} \text{ mol L}^{-1}$$



$$\begin{aligned}K_{sp} &= [\text{Ag}^+] [\text{Br}^-] \\ &= (6.07 \times 10^{-6}) \times (6.07 \times 10^{-6}) \\ &= 36.8 \times 10^{-12} \text{ mol}^2 \text{ L}^{-2}\end{aligned}$$

Problem 2. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized platinum electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm^2 . The conductance of the solution was found to be $5 \times 10^{-7} \text{ S}$. The pH of the solution is 4. Calculate the limiting molar conductivity (Λ_m°) of this solution. (JEE Advance 2017)

$$\begin{aligned}\text{Solution} \quad \text{Cell constant } \left(\frac{l}{a} \right) &= \frac{120 \text{ cm}}{1 \text{ cm}^2} = 120 \text{ cm}^{-1} \\ \kappa &= C \times \text{Cell constant} \\ &= (5 \times 10^{-7} \text{ S}) \times (120 \text{ cm}^{-1}) \\ &= 6 \times 10^{-5} \text{ S cm}^{-1} \\ \Lambda_m &= \frac{\kappa \times 1000}{M} \\ &= \frac{6 \times 10^{-5} \times 1000}{0.0015} \\ &= 40 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Now, pH} &= -\log [\text{H}^+] = 4 \\ \therefore [\text{H}^+] &= 10^{-4}\end{aligned}$$

For dissociation of a weak monobasic acid,

$$[\text{H}^+] = c \times \alpha$$

where α = degree of dissociation

$$10^{-4} = 0.0015 \times \alpha$$

$$\text{or } \alpha = \frac{10^{-4}}{0.0015} = \frac{1}{15}$$

$$\text{Also } \alpha = \frac{\Lambda_m^\circ}{\Lambda_m^\circ}$$

$$\frac{1}{15} = \frac{40}{\Lambda_m^\circ}$$

$$\therefore \Lambda_m^\circ = 40 \times 15$$

$$= 6 \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$$

Problem 3. The limiting molar conductances of sodium chloride, potassium chloride and potassium bromide are 126.45, 149.86 and $151.92 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. Calculate limiting molar ionic conductance of Na^+ given that limiting molar ionic conductance of Br^- ion is $76.34 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Solution This can be calculated with the help of Kohlrausch's law because limiting molar ionic conductances are additive:

$$\begin{aligned}\Lambda_m^\circ(\text{KBr}) &= \lambda_m^\circ(\text{K}^+) + \lambda_m^\circ(\text{Br}^-) \\ \Lambda_m^\circ(\text{KBr}) &= 151.92 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}, \\ \lambda_m^\circ(\text{Br}^-) &= 76.34 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \\ \therefore \lambda_m^\circ(\text{K}^+) &= \Lambda_m^\circ(\text{KBr}) - \lambda_m^\circ(\text{Br}^-) \\ &= 151.92 - 76.34 \\ &= 75.58 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Now } \Lambda_m^\circ(\text{KCl}) &= \lambda_m^\circ(\text{K}^+) + \lambda_m^\circ(\text{Cl}^-) \\ \Lambda_m^\circ(\text{KCl}) &= 149.86 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}, \\ \lambda_m^\circ(\text{K}^+) &= 75.58 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \\ \therefore \lambda_m^\circ(\text{Cl}^-) &= \Lambda_m^\circ(\text{KCl}) - \lambda_m^\circ(\text{K}^+) \\ &= 149.86 - 75.58 \\ &= 74.28 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Now } \Lambda_m^\circ(\text{NaCl}) &= \lambda_m^\circ(\text{Na}^+) + \lambda_m^\circ(\text{Cl}^-) \\ \Lambda_m^\circ(\text{NaCl}) &= 126.45 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}, \\ \lambda_m^\circ(\text{Cl}^-) &= 74.28 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \\ \therefore \lambda_m^\circ(\text{Na}^+) &= \Lambda_m^\circ(\text{NaCl}) - \lambda_m^\circ(\text{Cl}^-) \\ &= 126.45 - 74.28 \\ &= 52.17 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

add on

Conceptual Questions

Q. 1. What is the relationship between equivalent conductance and molar conductance? Illustrate by taking the example of $\text{Al}_2(\text{SO}_4)_3$.

Ans. Molar conductivity Λ_m and equivalent conductivity Λ_e are :

$$\Lambda_m = \frac{1000\kappa}{M} \quad \Lambda_e = \frac{1000\kappa}{C}$$

$$\frac{\Lambda_m}{\Lambda_e} = \frac{C}{M}$$

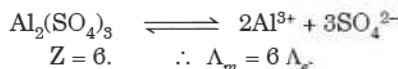
Now,

Normality = $Z \times \text{Molarity}$

where Z is the number of unit positive charge or negative charge per molecule of the electrolyte.

$$\therefore \frac{\Lambda_m}{\Lambda_e} = Z$$

For $\text{Al}_2(\text{SO}_4)_3$, which ionises as :



Q. 2. Which will have greater molar conductivity?

- (i) Solution containing 1 mol of KCl in 200 cc or 1 mol of KCl in 500 cc.
- (ii) Solution containing 1 mol of LiCl in 500 cc or 1 mol of KCl in 500 cc.

Ans. (i) 1 mol of KCl in 500 cc (ii) 1 mol of KCl in 500 cc.

Q. 3. Why is it not possible to determine Λ_m° for weak electrolytes by extrapolation ?

Ans. Because Λ_m° for weak electrolytes does not increase linearly with dilution as for strong electrolytes.

Q. 4. What are the units of cell constant ?

Ans. cm^{-1} or m^{-1} .

Q. 5. Why is alternating current used in place of direct current in measuring the electrolytic conduction ?

Ans. Direct current results in the electrolysis of the electrolytic solution. As a result, concentration of the electrolyte near the electrodes changes and these results change in the resistance of the solution.

Q. 6. Which of 0.1 M HCl and 0.1 M NaCl do you expect to have greater Λ_m° and why ?

Ans. 0.1 M HCl will have greater Λ_m° value because H^+ ions are smaller than Na^+ ions and hence have greater ionic mobility.

Q. 7. Which of the following pairs, will have greater conduction ?

- (i) 0.1 M acetic acid solution or 1 M acetic acid solution.
- (ii) 0.1 M NaCl solution at 25°C and 0.1 M NaCl solution at 50°C.
- (iii) Copper wire at 25°C and copper wire at 50°C.

Ans. (i) 0.1 M acetic acid because with dilution dissociation increases and therefore, conductivity increases.

(ii) 0.1 M NaCl solution at 50°C because with increase in temperature, ionic mobilities of strong electrolytes increase.

(iii) Copper wire at 25°C because with increase in temperature metallic conduction decreases due to vibration of kernels.

Q. 8. A solution is placed in two different cells having cell constant 0.1 and 0.5 cm^{-1} respectively. Which of the two will have greater value of specific conductance ?

Ans. Both will have same value of specific conductance.

Q. 9. Define conductivity and give its units.

(H.P.S.B. 2005)

Ans. Conductivity is the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section.

Units : $\Omega^{-1} \text{ cm}^{-1}$.

Q. 10. Write an expression for molar conductivity of $\text{Al}_2(\text{SO}_4)_3$ at infinite dilution in terms of their ionic molar conductivities.

$$\Lambda_m^{\circ} = 2\Lambda_{\text{Al}^{3+}}^{\circ} + 3\Lambda_{\text{SO}_4^{2-}}^{\circ}$$

Q. 11. What is the effect of temperature on the electrical conductance of

- (i) metallic conductor (ii) electrolytic conductor ?

Ans. With increase in temperature, the electrical conductance of metallic conductor decreases whereas that of electrolytic conductor increases.

Q. 12. Express the relation between conductivity and molar conductivity of a solution.

(A.I.S.B. 2008, D.S.B. 2008, 2011)

Ans. Molar conductivity (Λ_m°) is related to conductivity (κ) as :

$$\Lambda_m^{\circ} = \frac{\kappa \times 1000}{M} \quad \text{where } M \text{ is the molarity of the solution.}$$

Q. 13. Calculate the limiting molar conductivity of CaSO_4 if limiting molar conductivities of calcium and sulphate ions are 119.0 and 106.0 $\text{S cm}^2 \text{ mol}^{-1}$ respectively. (CBSE Sample Paper 2012)

$$\begin{aligned} \Lambda_m^{\circ} (\text{CaSO}_4) &= \Lambda_m^{\circ} (\text{Ca}^{2+}) + \Lambda_m^{\circ} (\text{SO}_4^{2-}) \\ &= 119.0 + 106.0 \\ &= 225.0 \text{ S cm}^2 \text{ mol}^{-1}. \end{aligned}$$

Q. 14. A 0.01 M solution of MgCl_2 is diluted by adding water. What will happen to its conductivity and molar conductivity?

Ans. With dilution, conductivity will decrease while molar conductivity will increase.

Q. 15. Arrange the following solutions in the decreasing order of specific conductance.

- (i) 0.01M NaCl (ii) 0.05M NaCl (iii) 0.1M NaCl (iv) 0.5M NaCl

(Kolkata S.B 2016)

Ans. (iv) 0.5M NaCl > (iii) 0.1M NaCl > (ii) 0.05M NaCl > (i) 0.01M NaCl

ELECTROCHEMICAL CHANGES : ELECTROCHEMICAL CELLS AND ELECTROLYTIC CELLS

The chemical changes which involve the flow of electric current are called *electrochemical changes*. These are broadly of two types :

1. Electrochemical cells or Galvanic cells

These constitute the electrochemical reactions in which chemical energy is converted to electrical energy. In these cells, spontaneous redox reaction is used to generate an electric current.

The devices in which chemical energy of a spontaneous redox reaction is converted into electrical energy are called electrochemical cells or galvanic cells.

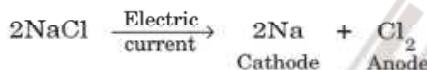
These cells are very important because of their many practical applications. An early example of a galvanic cell is a Daniell cell which was invented by the British chemist John Daniell in 1836. Daniell cell was constructed on the basis of the following spontaneous redox reaction :



2. Electrolytic cells or Electrolysis

These constitute the electrochemical reactions in which electrical energy is converted into chemical energy.

The phenomenon of chemical changes taking place by the passage of electrical energy from an external source is called electrolysis. The devices or cells used to carry out electrolysis are called electrolytic cells. For example, when electric current is passed through molten sodium chloride, sodium is produced at cathode and chlorine is liberated at anode.



The electrolysis is used to extract many metals such as Na, K, Ca, Sr, Mg, Al, etc. and manufacture of chemicals such as NaOH, Cl₂, F₂, etc. H. Davy isolated the element potassium by passing electric current through molten KOH.

ELECTROCHEMICAL CELL OR GALVANIC CELL

The devices in which electrical energy is produced from chemical reactions are called electrochemical cells or galvanic cells or voltaic cells. In these cells, oxidation and reduction reactions occur in separate containers called *half cells* and the redox reaction is spontaneous. Electrical energy is produced during such reactions. Let us explain the working of an electrochemical cell, known as **Daniell cell** with the help of a redox reaction:



The arrangement consists of two beakers, one of which contains 1.0 M solution of zinc sulphate and the other 1.0 M solution of copper sulphate. A zinc rod is dipped into ZnSO₄ solution while a copper rod is dipped into CuSO₄ solution. *These metallic rods are known as electrodes.* The metallic rods in the beaker are connected to the ammeter by means of an insulated wire through a key. Ammeter is used to know the passage of current which moves in opposite direction to the flow of electrons. The solutions in the two beakers are connected by an inverted U-tube containing saturated solution of some electrolyte such as KCl, KNO₃ or NH₄NO₃ which does not undergo a chemical change during the process. The saturated solution is generally taken in agar-agar jelly or gelatin.

The two openings of the U-tube are plugged with some porous material such as glass wool or cotton. The U-tube which connects the two glass beakers is called a **salt-bridge**. Its function will be discussed later. The arrangement is shown in Fig. 6.

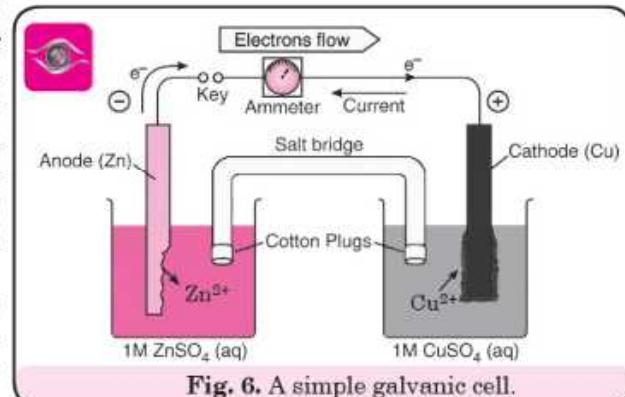
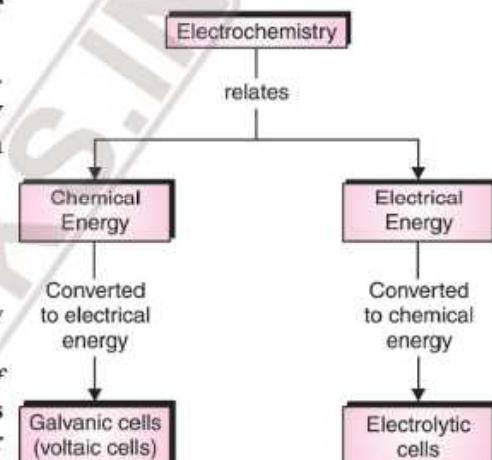


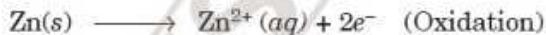
Fig. 6. A simple galvanic cell.

When the circuit is completed by inserting the key in the circuit, it is observed that electric current flows through external circuit as indicated by the ammeter. The following observations are made :

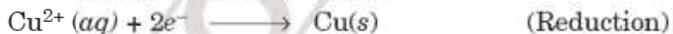
- (i) Zinc rod gradually loses its weight.
- (ii) The concentration of $Zn^{2+}(aq)$ in the $ZnSO_4(aq)$ solution increases.
- (iii) Copper gets deposited on the electrode.
- (iv) The concentration of $Cu^{2+}(aq)$ in the $CuSO_4(aq)$ solution decreases.
- (v) There is a flow of electrons in the external circuit from zinc rod to copper rod. Therefore, the current flows from copper to zinc. *It may be noted that as a convention, the flow of electric current is taken opposite to the flow of electrons.*

These observations can be explained as follows :

During the reaction, zinc is oxidised to Zn^{2+} ions which go into the solution. Therefore,



the zinc rod gradually loses its weight. The electrons released at the zinc electrode move towards the other electrode through outer circuit. Here, these are accepted by Cu^{2+} ions of $CuSO_4$ solution which are reduced to copper. The metal gets deposited on the copper electrode.



The zinc electrode where electrons are released or oxidation occurs is called **anode** while the copper electrode where electrons are accepted or reduction occurs is called **cathode**. As the electrons move from zinc rod to the copper rod, the zinc rod is regarded as *negative terminal* while copper rod is regarded as *positive terminal*. There is flow of electrons from negative terminal (anode) to positive terminal (cathode).

The two containers involving oxidation and reduction half reactions are called **half cells**. The zinc rod dipping into a $ZnSO_4$ solution is **oxidation half cell** and the copper electrode dipping into a $CuSO_4$ solution is **reduction half cell**.

Salt Bridge and its functions. A salt bridge has a vital role to play in an electrochemical cell. It is usually an inverted U-tube filled with concentrated solution of *inert electrolyte*. The essential requirements of electrolyte are :

- (i) The mobility of the anion and cation of the electrolyte should be almost same.
- (ii) The ions of the electrolyte are not involved in electrochemical change.
- (iii) The ions do not react chemically with the species of the cell. Generally, salts like KCl , KNO_3 , NH_4NO_3 , etc. are used. The saturated solutions of these electrolytes are prepared in agar agar jelly or gelatin. The jelly keeps the electrolyte in semi-solid phase and thus prevents mixing.

The **important functions** of the salt bridge are :

(i) **Salt bridge completes the electrical circuit.** The salt bridge connects the two solutions of the half cells and their electrodes are connected by means of a wire. Therefore, the salt bridge completes the circuit.

(ii) **Salt bridge maintains electrical neutrality of two half cell solutions.** To understand the function of the salt bridge, let us consider the cell without a salt bridge. The electrons released by the oxidation of Zn to Zn^{2+} ions will be accepted by the Cu^{2+} ions of $CuSO_4$ in the other half cell and the latter will be reduced to copper. The positively charged Zn^{2+} ions pass into the solution. After sometimes, this results into accumulation of extra positive charge in the solution around the anode. Similarly, due to reduction of some Cu^{2+} ions to Cu , the solution around cathode will acquire extra negative charge due to excess of SO_4^{2-} ions. The accumulation of positive charge around zinc rod will prevent the further flow of electrons from the zinc rod. Similarly, the accumulation of negative charge around copper electrode will prevent the flow of electrons to the copper

REMEMBER

- In an electrochemical cell
- Oxidation occurs at anode (-ve terminal)
- Reduction occurs at cathode (+ve terminal)
- Electrons flow from anode to cathode.

In salt bridge, the electrolytes such as KCl , KNO_3 or NH_4NO_3 are generally preferred because their ions have almost equal mobility.

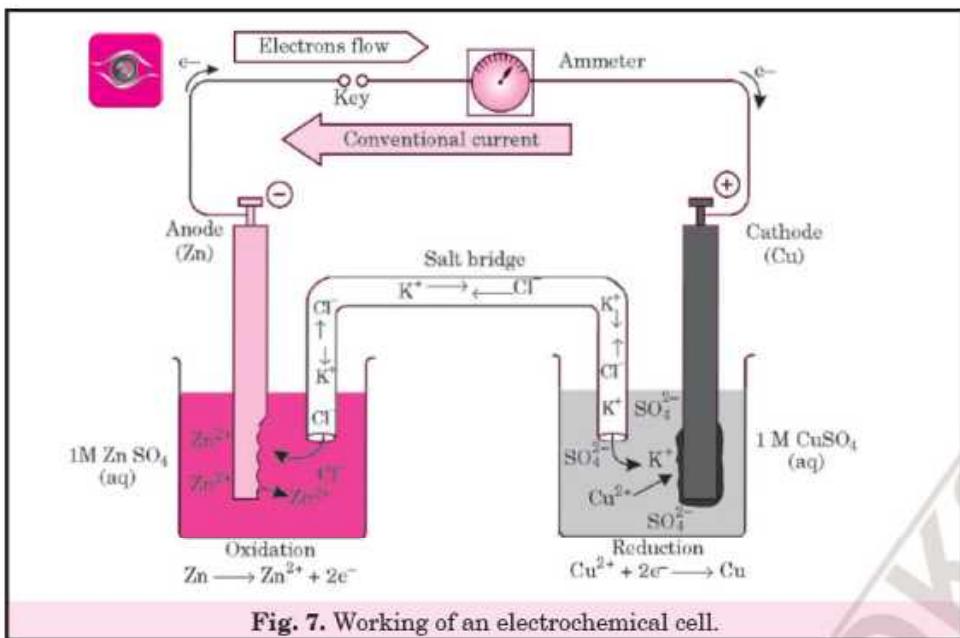


Fig. 7. Working of an electrochemical cell.

ions. Thus, the flow of electrons will occur only momentarily and the cell will stop working.

However, the accumulation of charges in the two half cells is prevented by using salt bridge, which provides a passage for the flow of the charge in the internal circuit. When the concentration of Zn^{2+} ions around anode increases, sufficient number of Cl^- ions migrate from the salt bridge to the anode half cell. Similarly, to neutralise the excess negative charge due to the additional SO_4^{2-} ions in cathode half cell, sufficient number of K^+ ions migrate from the salt bridge to this half cell. Thus, *the salt bridge provides cations and anions to replace the ions lost or produced in the two half cells*.

The working of the electrochemical cell and the functions of salt bridge are represented in Fig. 7.

Functioning of the cell when external opposing potential is applied

Consider a Daniell cell in which the zinc electrode is dipped in ZnSO_4 (aq) and copper electrode is dipped in CuSO_4 (aq). The cell reaction occurring is



The electrical potential (called emf) of the cell is 1.10 V when concentration of Zn^{2+} and Cu^{2+} ions is 1 M (1 mol dm^{-3})*.

Let us consider an arrangement in which an external opposite potential is applied as shown in Fig. 8(a). When the external opposite potential is increased slowly, we observe that the reaction continues to take place till the opposing voltage reaches the value of 1.1 V.

As long as the external opposite is less than 1.10V, the electron continue to flow from Zn rod to Cu rod and hence current flows from Cu to Zn. Zinc dissolves in anode and copper deposits at cathode.

When the opposing voltage reaches the value 1.10 V, the cell reaction stops altogether and no current flows through the cell as shown in [Fig. 8(b)] ahead. There is no chemical reaction.

Further increase in the external potential now again starts the reaction but in the opposite direction shown in [Fig. 8(c)] ahead. The cell now starts functioning as an electrolytic cell. In this case electrical energy is used to carry out non-spontaneous chemical reaction. The electrons flow from Cu to Zn rod and current flows from Zn to Cu. As a result of electrolysis, zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

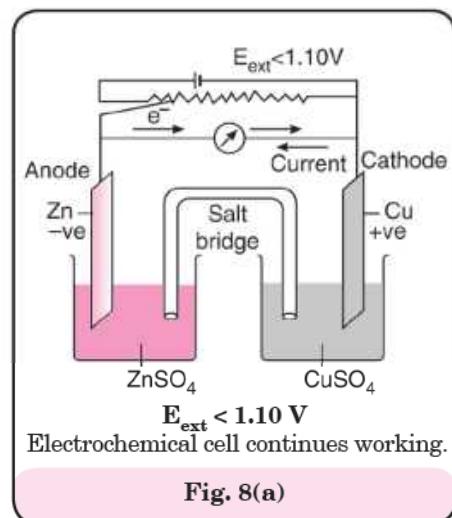


Fig. 8(a)

* Strictly speaking, 'activity' should be used instead of concentration. It is directly proportional to concentration. However, in dilute solutions, it is equal to concentration. You will learn about it in higher classes.

Thus, it may be **concluded** that for a Daniell cell having emf 1.10 V,

(a) When $E_{ext} < 1.1 \text{ V}$ (Fig. 8 a)

(i) Electrons flow from Zn rod to Cu rod

(ii) Current flows from Cu to Zn

(iii) Zn dissolves at anode and Cu deposits at cathode

(b) When $E_{ext} = 1.1 \text{ V}$ (Fig. 8 b)

(i) No flow of electrons.

(ii) No flow of current.

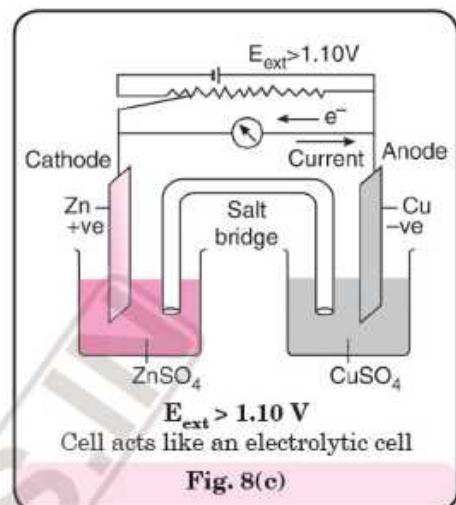
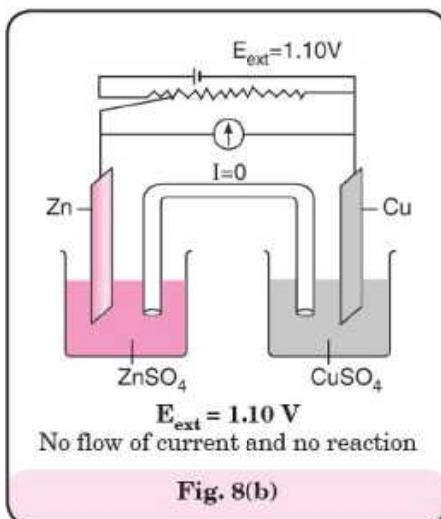
(iii) No chemical reaction.

(c) When $E_{ext} > 1.10 \text{ V}$ (Fig. 8 c)

(i) Electrons flow from Cu to Zn.

(ii) Current flows from Zn to Cu

(iii) Zn is deposited at Zn electrode and Cu dissolves at Cu electrode.



REPRESENTATION OF AN ELECTROCHEMICAL CELL

An electrochemical cell or galvanic cell consists of two electrodes : anode and cathode. The electrolyte solution containing these electrodes are called *half cells*. When these two half cells are combined, a cell is formed. The following **conventions** are used in representing an electrochemical cell :

1. A galvanic cell is represented by writing the anode (where oxidation occurs) on the left hand side and cathode (where reduction occurs) on the right hand side.

2. The anode of the cell is represented by writing metal or solid phase first and then the electrolyte (or cation of the electrolyte) while the cathode is represented by writing the electrolyte first (or cation) and then metal and solid phase.

The metal and the cation are separated either by a semicolon (;) or by a vertical line. For further information, the concentration of the electrolyte is also mentioned within bracket after the cation, i.e.,

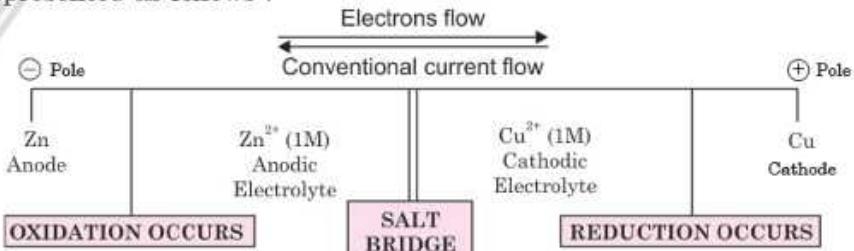
$\text{Zn} ; \text{Zn}^{2+} \text{ or } \text{Zn} | \text{Zn}^{2+} \text{ or } \text{Zn} | \text{Zn}^{2+} (1\text{M})$ (Anode)

$\text{Cu}^{2+} ; \text{Cu} \text{ or } \text{Cu}^{2+} | \text{Cu} \text{ or } \text{Cu}^{2+} (1\text{M}) | \text{Cu}$ (Cathode)

3. The salt bridge which separates the two half cells is indicated by two vertical lines. For example,

$\text{Zn} | \text{Zn}^{2+} (1\text{M}) || \text{Cu}^{2+} (1\text{M}) | \text{Cu}$

The complete formulation of a cell which is also known as **cell notation** is represented as follows :

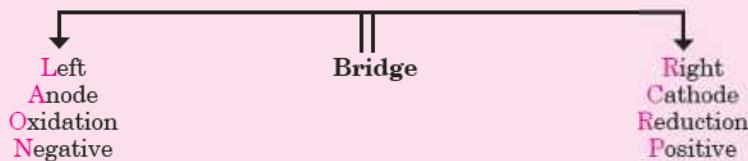


Sometimes negative and positive signs are also put on the electrodes to show the release and loss of electrons taking place on them. Anode is a negative pole while cathode acts as positive pole. The electrons flow from the negative pole (anode) to the positive pole (cathode) in the external circuit. On the other hand, conventionally, the current is said to flow in the opposite direction.

Memory Aid

Sometimes we get confused in the nomenclature of electrodes. As a **memory aid** keep in mind the **alphabetical order** of the first letter e.g., A(anode) comes before O(cathode). The cell may be written by arranging each of the pair left-right,

anode-cathode, oxidation-reduction, negative and positive in the alphabetical order as :



- where reduction occurs
- where electrons are consumed
- towards cations migrate
- has +ve sign

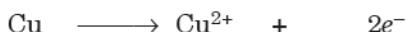
CATHODE

Representation of Some Common Cells by Cell Notation

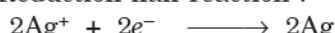
Some common cells may be represented as given below :

(i) **Cu-AgNO₃ cell.** The reactions occurring in the cell are :

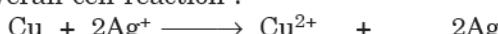
Oxidation half reaction :



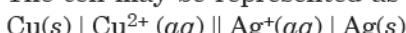
Reduction half reaction :



Overall cell reaction :

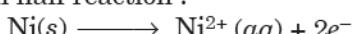


The cell may be represented as :

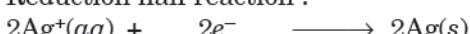


(ii) **Ni-AgNO₃ cell**

Oxidation half reaction :



Reduction half reaction :



Overall cell reaction :

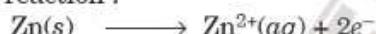


The cell may be represented as :

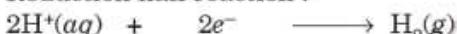


(iii) **Zn-HCl reaction**

Oxidation half reaction :



Reduction half reaction :



Overall cell reaction :



Cell may be represented as :



ELECTRODE POTENTIAL AND E.M.F. OF A GALVANIC CELL

Electrode Potential

The flow of electric current in an electrochemical cell indicates that a potential difference exists between two electrodes. To understand the potential difference between two electrodes or electrode potentials let us consider the redox reactions occurring at these electrodes.

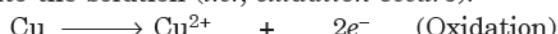
When an electrode say copper, is immersed in a solution of its ions, then either of the following three possibilities can take place :

(a) The metal ions (Cu^{2+}) may collide with the electrode and do not undergo any change.

(b) Cu^{2+} ions may collide with the electrode, gain electrons and get converted into metal atoms (i.e., the ions are reduced).

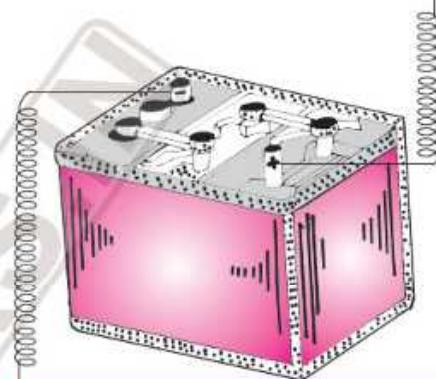


(c) Cu atoms on the electrode may lose electrons to the electrode and become Cu^{2+} ions and go into the solution (i.e., oxidation occurs).



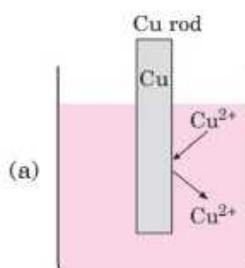
These possibilities are shown in Fig. 9.

Now, if the metal has relatively high tendency to get oxidised, its atoms will lose electrons readily and form Cu^{2+} ions, which go into the solution. The

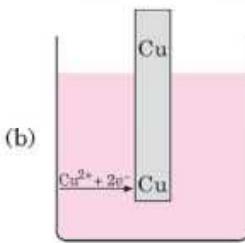


ANODE

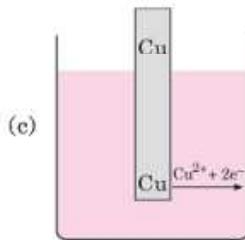
- where oxidation occurs
- where electrons are produced
- towards anions move
- has -ve sign



Metal ions collide but do not undergo any change.



Metal ions gain electrons and get converted to metal i.e., **reduction** occurs, (electrons are lost by metal rod and it **acquires +ve charge**).



Metal atoms on electrode lose electrons to form metal ions i.e., **oxidation occurs**. Electrons lost by metal accumulates on metal rod. (**Metal rod acquires -ve charge**).

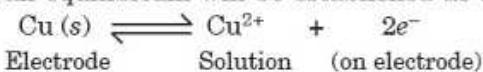
Fig. 9. Electrode equilibrium.

NOTE

It may be remembered that for calculating e.m.f. of the cell,

- The electrode potentials are always taken as **reduction potentials** (as a convention) for both the electrodes.
- The cell is always written as anode on the left (where oxidation occurs) and cathode on the right (where reduction occurs).
- Reduction potential =
– Oxidation potential

electrons lost on the electrode would be accumulated on the metal electrode and the electrode acquires a slight negative charge with respect to the solution. Some of the Cu^{2+} ions from the solution will take up electrons and become Cu atoms. After some time, an equilibrium will be established as :



When such an equilibrium is attained, it results in separation of charges (negative on the electrode with respect to the solution).

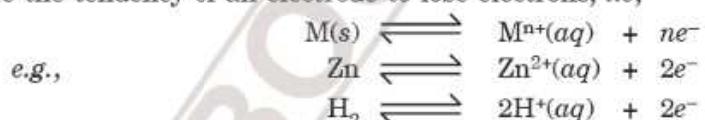
Similarly, if the metal ions have relatively greater tendency to get reduced, they will take electrons from the electrode. As a result, a net positive charge will be developed on the electrode with respect to the solution. This will also result into separation of charges (positive on the electrode with respect to the solution).

Due to separation of charges between the electrode and the solution, an electrical potential is set up between metal electrode and its solution.

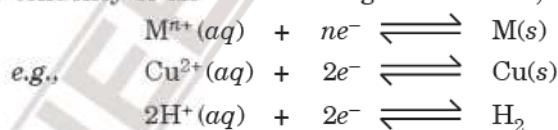
The electrical potential difference set up between the metal and its ions in the solution is known as **electrode potential**.

Thus, the electrode potential is a measure of the tendency of an electrode to gain or lose electrons when it is in contact with solution of its own ions. The electrode potential may be of two types:

(i) **Oxidation potential.** *The tendency of an electrode to lose electrons or to get oxidised* is called its **oxidation potential**. Thus, oxidation potentials give the tendency of an electrode to lose electrons, i.e.,



(ii) **Reduction potential.** *The tendency of an electrode to gain electrons or to get reduced* is called its **reduction potential**. Therefore, it measures the tendency of an electrode to gain electrons, i.e.,



It is evident that *the oxidation potential is the reverse of reduction potential*. For example, if reduction potential of Zn is – 0.76 volts, its oxidation potential is +0.76 volts.

According to the latest convention, the half cell reactions are always written as reduction half reactions and their potentials are represented as reduction potentials. These are called electrode potentials.

The electrode potential depends upon :

- (i) the nature of the metal and its ions,
- (ii) concentration of the ions in the solution, and
- (iii) temperature.

E.M.F. or Cell Potential of a Cell

Electrochemical cell consists of two half cells. The electrodes in these half cells have different reduction potentials. Therefore, they have different tendency to lose or gain electrons. The electrode having higher reduction potential will have higher tendency to gain electrons whereas the electrode having lower reduction potential will have lesser tendency to gain electrons, rather it loses electrons. As a result of this potential difference, there is a flow of electrons from the electrode with a lower reduction potential (higher tendency to lose electrons) to the electrode with higher reduction potential. **The difference between the electrode potentials of the two electrodes constituting an electrochemical cell** is known as **electromotive force or cell potential of a cell**. This acts as a driving force for the cell reaction. The potential difference is expressed in **volts**.

Therefore, the cell potential or e.m.f. arises from the difference in the tendencies of the two ions to get reduced. It is equal to the reduction potential for the substance that actually undergoes reduction minus the reduction potential of the substance that undergoes oxidation.

As already studied, the reduction occurs at cathode and oxidation occurs at anode. Therefore,

$$\text{e.m.f.} = \text{Reduction potential of cathode} - \text{Reduction potential of anode}$$

$$\text{or } E_{\text{cell}} = E(\text{cathode}) - E(\text{anode})$$

In the representation of an electrochemical cell as a convention, cathode is written on right hand side and anode on the left hand side. Therefore, e.m.f. of a cell may also be written as :

$$E_{\text{cell}} = E(\text{Right}) - E(\text{Left})$$

Thus, **e.m.f.** of a cell may be defined as

the potential difference between two electrodes of the cell when either no or negligible current is allowed to flow in the circuit.

The e.m.f. of the cell is measured with the help of a potentiometer. It depends upon the nature of the electrodes, temperature and the concentrations of the solutions in the two half cells. For example, the e.m.f. of a Daniell cell in which the concentrations of aqueous solutions of CuSO_4 and ZnSO_4 in the two half cells is 1 M at 298 K is 1.10 volts.

Difference between E.M.F. and Potential Difference

The differences between e.m.f. and potential difference may be given as follows :

E.M.F.	Potential difference
1. It is the potential difference between the two electrodes when no current is flowing in the circuit i.e., in an open circuit.	It is the difference of the electrode potentials of the two electrodes when the cell is sending current through the circuit.
2. It is maximum voltage obtainable from the cell.	It is less than the maximum voltage obtainable from the cell (i.e., e.m.f. of the cell).
3. The work calculated from e.m.f. is the maximum work obtainable from the cell.	The work calculated from potential difference is less than the maximum work obtainable from cell.
4. It is responsible for the flow of steady current in the cell.	It is not responsible for the flow of steady current in the cell.

STANDARD ELECTRODE POTENTIAL

Since a half cell in an electrochemical cell can work only in combination with the other half cell and does not work independently, it is not possible to determine the absolute electrode potential of an electrode. We can, therefore, find only the relative electrode potential.

This difficulty can be solved by selecting one of the electrodes as a reference electrode and arbitrarily fixing the potential of this electrode as zero. For this purpose, reversible hydrogen electrode has been universally accepted as a reference electrode. It is called *standard hydrogen electrode* (S.H.E.) or *normal hydrogen electrode* (N.H.E.).

Standard hydrogen electrode. It consists of platinum wire sealed in a glass tube and has a platinum foil attached to it (Fig. 10). The foil is coated with finely divided platinum and acts as platinum electrode. It is dipped into an acid solution containing H^+ ions in 1 M concentration (1 M HCl). Pure hydrogen gas

Competition Plus

There are different types of electrodes such as metal-metal ion electrodes, metal-metal insoluble salt electrodes, gas electrodes, amalgam electrodes, oxidation-reduction electrodes. For detail, refer **Competition File** (Page 98).

REMEMBER

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= [\text{Reduction potential of reduction half reaction}] \\ &\quad - [\text{Reduction potential of oxidation half reaction}] \\ &= E_{\text{R.H.S. electrode}} - E_{\text{L.H.S. electrode}} \end{aligned}$$

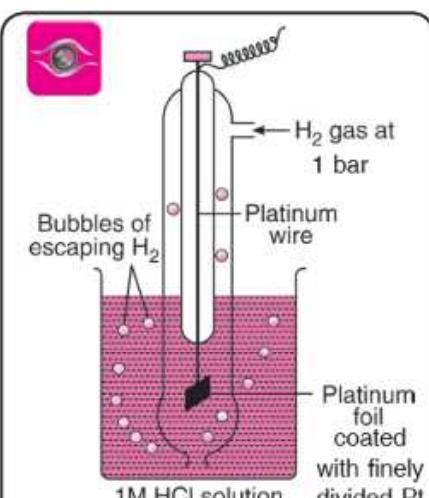


Fig. 10. Standard hydrogen electrode.

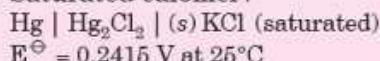
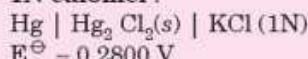
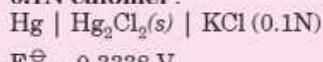
NOTE**Reference Electrodes**

It may be noted that it is not always convenient to use standard hydrogen electrode as reference electrode because of experimental difficulties in its preparation and use. Some of these are :

- It is difficult to maintain unit concentration of H^+ ions.
- The hydrogen electrode gets poisoned even in the presence of traces of impurities.
- It is difficult to maintain 1 atm pressure of H_2 gas uniformly for a long time.

Therefore, some other **secondary reference electrodes** are used.

The most commonly used reference electrode is **calomel electrode**. Its reduction potential depends upon the concentration of KCl solution used as given below :

(a) **Saturated calomel** :(b) **1N calomel** :(c) **0.1N calomel** :

at 1 bar (atmosphere) pressure is constantly bubbled into solution at constant temperature of 298 K. The surface of the foil acts as a site for the reaction.

The following reactions occur in this half cell depending upon whether it acts as anode or as cathode.

If S.H.E. acts as anode



If S.H.E. acts as cathode



This standard hydrogen electrode is also regarded as reversible electrode



The electrode potential of an electrode can be determined by connecting this half cell with a *standard hydrogen electrode*. The electrode potential of the standard hydrogen electrode is taken as zero. The *electrode potential of a metal electrode as determined with respect to a standard or normal hydrogen electrode* is called **standard electrode potential (E^\ominus or E°)**. Standard electrode potentials are always associated with the reduction reactions occurring at the electrodes.

Measurement of the Standard Electrode Potential (E^\ominus)

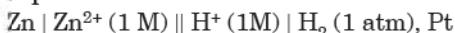
To measure the standard electrode potential of a metal electrode, 1.0 M solution of the electrolyte is taken in a beaker and a metal electrode is dipped in it. This constitutes the metal-metal ion electrode, $M/M^{n+}(aq)$. This half cell is connected to S.H.E. through a salt bridge. The electrodes are connected to a voltmeter. From the measured e.m.f. of the cell, the standard electrode potential of the half cell is calculated. This method is illustrated as follows :

1. Measurement of Electrode Potential of $Zn^{2+} | Zn$ Electrode

An electrode consisting of zinc rod immersed in 1 M solution of $ZnSO_4$ is combined with S.H.E. as shown in Fig. 11.

To obtain the cell reaction, we have to know what is oxidised and what is reduced to know the cathode and anode in the cell. We can determine this by measuring the charges of the electrodes because we know that in a galvanic cell, cathode is the +ve electrode and anode is the -ve electrode. When we connect the two electrodes with a voltmeter, the proper measurements (e.m.f. of the cell) are obtained only if the +ve terminal of the voltmeter is connected to the +ve electrode and -ve terminal of the voltmeter is connected to the -ve electrode. If the connections are not correct, no reading will be obtained in the voltmeter. Thus, if the voltmeter gives the proper reading, it indicates that the electrode connected to +ve terminal of the voltmeter is +ve (acts as cathode) and the electrode connected to -ve terminal of the voltmeter is -ve (acts as anode). The electrons flow from anode to cathode.

In this case, the electrons flow from zinc electrode to hydrogen electrode and therefore, the zinc electrode acts as anode and S.H.E. acts as a cathode. The cell may be represented as :



The cell potential has been measured to be 0.76 V.

Now, e.m.f. of cell,

$$\begin{aligned} E^\ominus_{cell} &= E^\ominus_R - E^\ominus_L \\ &= E^\ominus(H^+ | H_2) - E^\ominus(Zn^{2+} | Zn) \\ 0.76 &= 0 - E^\ominus(Zn^{2+} | Zn) \end{aligned}$$

$$\therefore E^\ominus(Zn^{2+} | Zn) = -0.76 \text{ V}$$

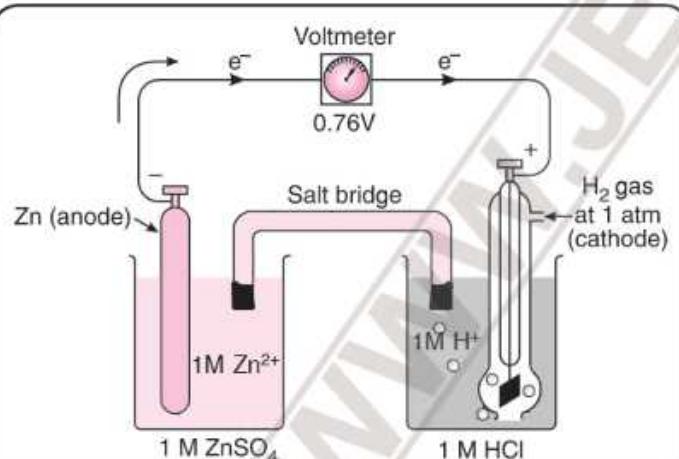


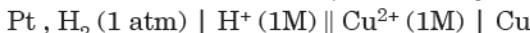
Fig. 11. Measurement of a standard electrode potential (reduction potential) of zinc by combining with S.H.E.

Thus, by combining with S.H.E. reduction potential value of Zn has been found to be -0.76 V.

2. Measurement of Electrode Potential of Cu^{2+} | Cu Electrode

To measure electrode potential of copper-copper ions, a cell consisting of copper electrode immersed in 1M CuSO_4 solution and S.H.E. is set up as shown in Fig. 12.

In this case, the hydrogen has greater tendency to lose electrons in comparison to copper. Therefore, oxidation occurs at hydrogen electrode and reduction occurs at copper electrode. Consequently, the hydrogen electrode acts as anode and copper electrode acts as cathode. Thus, the cell may be represented as



The cell potential has been measured to be 0.34 V.

$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{R}} - E^\ominus_{\text{L}} \\ &= E^\ominus(\text{Cu}^{2+} \mid \text{Cu}) - E^\ominus(\text{H}^+ \mid \text{H}_2) \\ 0.34 &= E^\ominus(\text{Cu}^{2+} \mid \text{Cu}) - 0 \end{aligned}$$

$$\text{or } E^\ominus(\text{Cu}^{2+} \mid \text{Cu}) = 0.34 \text{ V}$$

Thus, the standard electrode potential of copper is + 0.34 V.

Similarly, the standard reduction potentials of other metals can be calculated.

Thus, the electrode at which **reduction** occurs with respect to S.H.E. has **+ve reduction potential** while the electrode at which oxidation occurs with respect to S.H.E. has **-ve reduction potential**.

SOLVED EXAMPLES

Example 20

Calculate the standard reduction electrode potential of the $\text{Ni}^{2+} \mid \text{Ni}$ electrode when the cell potential for the cell $\text{Ni} \mid \text{Ni}^{2+}(1\text{M}) \parallel \text{Cu}^{2+}(1\text{M}) \mid \text{Cu}$ is 0.59 V ($E^\ominus(\text{Cu}^{2+} \mid \text{Cu}) = 0.34$ V).

Solution : The cell is



The e.m.f. of the cell

$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{R}} - E^\ominus_{\text{L}} \\ &= E^\ominus(\text{Cu}^{2+} \mid \text{Cu}) - E^\ominus(\text{Ni}^{2+} \mid \text{Ni}) \end{aligned}$$

Here,

$$E^\ominus_{\text{cell}} = 0.59 \text{ V}, E^\ominus(\text{Cu}^{2+} \mid \text{Cu}) = 0.34 \text{ V}$$

∴

$$0.59 = 0.34 - E^\ominus(\text{Ni}^{2+} \mid \text{Ni})$$

$$\text{or } E^\ominus(\text{Ni}^{2+} \mid \text{Ni}) = 0.34 - 0.59 = -0.25 \text{ V.}$$

ELECTROCHEMICAL SERIES

The standard reduction potentials or standard electrode potentials of a large number of electrodes have been measured using standard hydrogen electrode as the reference electrode. These various electrodes can be arranged in increasing or decreasing order of their reduction potentials.

The arrangement of elements in order of increasing electrode potential values is called **electrochemical series**.

The electrochemical series, also called *activity series*, of some typical electrodes is being given in Table 5.

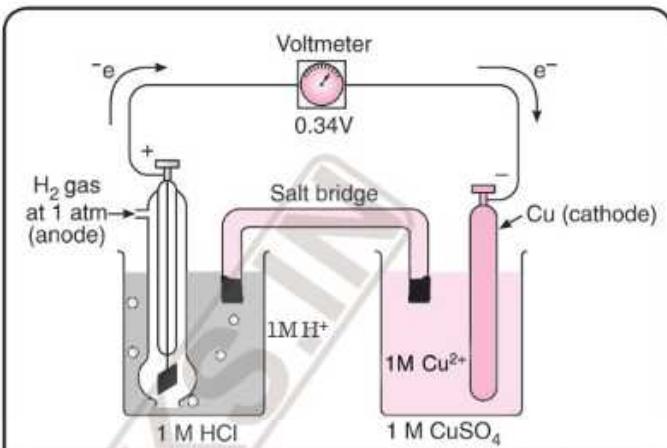


Fig. 12. Measurement of standard electrode potential of copper.

REMEMBER

- A negative E^\ominus means that the redox couple is a stronger reducing agent than H^+H_2 couple.
- A positive E^\ominus value means that the redox couple is a weaker reducing agent than H^+H_2 couple.

Table 5. Standard reduction electrode potentials at 298 K.

Electrode	Electrode reaction (Oxidized form + ne ⁻ → Reduced form)	E [⊖] (V)
F ₂ F ⁻		
Co ³⁺ Co ²⁺	Strongest oxidizing agent	2.87
H ₂ O ₂ H ₂ O	F ₂ (g) + 2e ⁻ → 2F ⁻ (aq)	1.81
MnO ₂ , H ⁺ Mn ²⁺	Co ³⁺ + e ⁻ → Co ²⁺	1.78
Au ³⁺ Au	H ₂ O ₂ + 2H ⁺ + 2e ⁻ → 2H ₂ O	1.61
MnO ₄ ⁻ Mn ²⁺	MnO ₂ (s) + 4H ⁺ + 2e ⁻ → Mn ²⁺ + 2H ₂ O	1.50
Cl ₂ Cl ⁻	Au ³⁺ + 3e ⁻ → Au (s)	1.49
Cr ₂ O ₇ ²⁻ , H ⁺ Cr ³⁺	MnO ₄ ⁻ + 8H ⁺ + 5e ⁻ → Mn ²⁺ + 4H ₂ O	1.36
O ₂ , H ⁺ H ₂ O	Cl ₂ (g) + 2e ⁻ → 2Cl ⁻	1.33
Br ₂ Br ⁻	Cr ₂ O ₇ ²⁻ + 4H ⁺ + 6e ⁻ → 2Cr ³⁺ + 7H ₂ O	1.23
NO ₃ ⁻ , H ⁺ NO	O ₂ + 4H ⁺ + 4e ⁻ → 2H ₂ O	1.09
Hg ²⁺ Hg ₂ ²⁺	Br ₂ (l) + 2e ⁻ → 2Br ⁻	0.97
ClO ⁻ Cl ⁻	NO ₃ ⁻ + 4H ⁺ + 3e ⁻ → NO (g) + 2H ₂ O	0.92
Hg ²⁺ Hg	2Hg ²⁺ + 2e ⁻ → Hg ₂ ²⁺	0.89
Ag ⁺ Ag	ClO ⁻ + H ₂ O + 2e ⁻ → Cl ⁻ + 2OH ⁻	0.85
Hg ₂ ²⁺ Hg	Hg ²⁺ + 2e ⁻ → Hg	0.80
Fe ³⁺ Fe ²⁺	Ag ⁺ + e ⁻ → Ag	0.79
MnO ₄ ⁻ MnO ₄ ²⁻	Hg ₂ ²⁺ + e ⁻ → 2Hg	0.78
I ₂ I ⁻	Fe ³⁺ + e ⁻ → Fe ²⁺	0.56
Cu ⁺ Cu	MnO ₄ ⁻ + e ⁻ → MnO ₄ ²⁻	0.54
Cu ²⁺ Cu	I ₂ + 2e ⁻ → 2I ⁻	0.52
AgCl Ag	Cu ⁺ + e ⁻ → Cu	0.34
Cu ²⁺ Cu	Cu ²⁺ + 2e ⁻ → Cu	0.22
AgBr Ag	AgCl + e ⁻ → Ag + Cl ⁻	0.15
H ⁺ H ₂	Ag ⁺ + e ⁻ → Ag ⁺	0.10
	2H ⁺ + 2e ⁻ → H ₂	0.00
Fe ³⁺ Fe		
Pb ²⁺ Pb	Fe ³⁺ + 3e ⁻ → Fe	-0.04
Sn ²⁺ Sn	Pb ²⁺ + 2e ⁻ → Pb	-0.13
Ni ²⁺ Ni	Sn ²⁺ + 2e ⁻ → Sn	-0.16
Co ²⁺ Co	Ni ²⁺ + 2e ⁻ → Ni	-0.25
Cd ²⁺ Cd	Co ²⁺ + 2e ⁻ → Co	-0.28
Fe ²⁺ Fe	Cd ²⁺ + 2e ⁻ → Cd	-0.40
Cr ³⁺ Cr	Fe ²⁺ + 2e ⁻ → Fe	-0.44
Zn ²⁺ Zn	Cr ³⁺ + 3e ⁻ → Cr	-0.74
Mn ²⁺ Mn	Zn ²⁺ + 2e ⁻ → Zn	-0.76
Al ³⁺ Al	Mn ²⁺ + 2e ⁻ → Mn	-1.18
Mg ²⁺ Mg	Al ³⁺ + 3e ⁻ → Al	-1.66
Ce ³⁺ Ce	Mg ²⁺ + 2e ⁻ → Mg	-2.36
Na ⁺ Na	Ce ³⁺ + 3e ⁻ → Ce	-2.48
Ca ²⁺ Ca	Na ⁺ + e ⁻ → Na	-2.71
Ba ²⁺ Ba	Ca ²⁺ + 2e ⁻ → Ca	-2.87
Cs ⁺ Cs	Ba ²⁺ + 2e ⁻ → Ba	-2.91
K ⁺ K	Cs ⁺ + e ⁻ → Cs	-2.92
Li ⁺ Li	K ⁺ + e ⁻ → K	-2.93
	Li ⁺ + e ⁻ → Li	-3.05

STRENGTH OF OXIDIZING AGENT ↑

INCREASING

Weakest oxidizing agent

STRENGTH OF REDUCING AGENT ↓

INCREASING

Strongest reducing agent

Applications of the Electrochemical Series

The main applications of the electrochemical series are given below :

1. Relative strengths of oxidising and reducing agents. With the help of electrochemical series, we can predict the relative oxidising or reducing strengths of substances. In the electrochemical series, the substances are arranged in the decreasing order of electrode potential i.e. decreasing tendency for reduction to occur or power as oxidising agent. Therefore,

- the elements at the top of the table have **maximum tendency to get reduced** and consequently, they will act as **good oxidising agents**. On the other hand,

- the substances at the bottom of the table have lower electrode potential values, therefore they have **least tendency to get reduced**. Consequently, they may be oxidised and act as **good reducing agents**.

- Table 4 shows that standard electrode potential of fluorine is the highest in the table indicating that the fluorine gas (F_2) has maximum tendency to get reduced to fluoride ions (F^-) and therefore, fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent. On the other hand, lithium has the lowest electrode potential in the table indicating that lithium has the maximum tendency to get oxidised and hence lithium metal is the most powerful reducing agent or lithium ion is the weakest oxidising agent in aqueous solution.

2. Calculation of the E.M.F. of the cell. The E.M.F. of the cell which is the difference between the reduction potential of the cathode and anode is determined by the following steps :

Step I.

Write the two half cell reactions in such a way that the reaction taking place at the left hand electrode is written as an oxidation reaction and that taking place at the right hand electrode is written as reduction.

Step II.

Multiply one of the equations if necessary by suitable number to equate the number of electrons in the two equations. *However, it may be noted that electrode potential values, E^\ominus are not multiplied.*

Step III.

The e.m.f. of the cell (E^\ominus_{cell}) is equal to the difference between the standard electrode potential of the cathode and the standard electrode potential of the anode. Thus,

$$E^\ominus_{cell} = E^\ominus(\text{cathode}) - E^\ominus(\text{anode})$$

The electrode potentials of both the electrodes are taken to be reduction potentials.

Step IV.

If the e.m.f. of the cell is +ve, the reaction is feasible in the given direction. But if e.m.f. of the cell is -ve, the cell reaction is not feasible in the given direction. The reaction must be occurring in the reverse direction. Thus, to get positive value for the e.m.f. of the cell, the electrodes are reversed.

REMEMBER

- The substances which have lower electrode potentials are stronger reducing agents while those which have higher electrode potentials are stronger oxidising agents.

SOLVED EXAMPLES

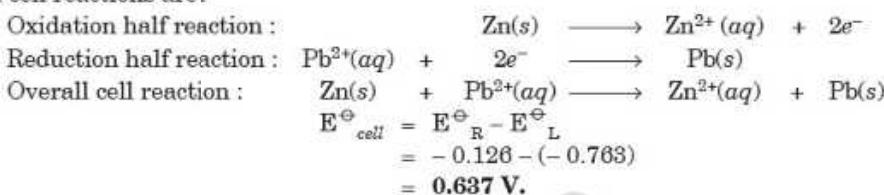
Example 21.

Write the halfcell reaction and the overall cell reaction for the electrochemical cell :



Calculate the standard e.m.f. for the cell if standard electrode potentials (reduction) for $\text{Pb}^{2+} \mid \text{Pb}$ and $\text{Zn}^{2+} \mid \text{Zn}$ electrodes are -0.126 V and -0.763 V respectively.

Solution: Zn electrode acts as anode while Pb electrode acts as cathode and, therefore, oxidation occurs at zinc electrode and reduction occurs at lead electrode. The half cell reactions are:



WATCH OUT !

- For cell reaction to be spontaneous, EMF must be positive.
- Reduction will occur at the electrode having higher reduction potential.
- Oxidation will occur at the electrode having lower reduction potential (or higher oxidation potential)
- EMF of cell
 $= E^\ominus(\text{cathode}) - E^\ominus(\text{anode})$
 $= E^\ominus(\text{R.H.S.}) - E^\ominus(\text{L.H.S.})$

REMEMBER

- In general, metals having negative E^\ominus values can evolve hydrogen from an acid on reacting with dilute acids while those with positive E^\ominus values cannot do so.
- Metals like Na, K, Zn, Mg, Ni, Al etc. which can liberate H_2 from an acid are called **active metals**. Metals like Cu, Hg, Ag etc. which do not liberate H_2 from an acid are called **inactive metals**.

3. Predicting feasibility of the reaction. The electrochemical series helps in finding out whether a given redox reaction is feasible or not in the given direction from the E^\ominus values of the two electrodes. *In general, a redox reaction is feasible only if the species which has higher reduction potential is reduced i.e., accepts the electrons and the species which has lower electrode potential is oxidised i.e., loses the electrons. Otherwise, a redox reaction is not feasible. In other words, the species to release electrons must have lower electrode potential as compared to the species which is to accept electrons.*

The electrochemical series (Table 4) gives the increasing order of electrode potential (reduction) of different electrodes on moving down the table. This means that the species to accept the electrons (getting reduced) must be lower in the electrochemical series as compared to the other which is to lose electrons (getting oxidised).

Let us illustrate this by predicting the feasibility of the reaction :



From the electrochemical series (Table 5), E^\ominus value of Cu = +0.34 V and the E^\ominus value of Ag = +0.80 V. Since the electrode potential of Ag is more than that of Cu, this means that silver has greater tendency to get reduced in comparison to copper. Thus, the reaction



occurs more readily than the reaction



Similarly, since reduction potential of Cu is less than that of Ag, this means that Cu will be readily oxidised in comparison to Ag. Thus, the reaction



occurs more readily than the reaction



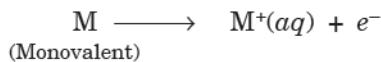
Therefore, silver will be reduced and copper will be oxidised and the above reaction is not feasible. Rather the reverse reaction,



Similarly, we can predict that iron will reduce Cu^{2+} to Cu, zinc will reduce Pb^{2+} to Pb, zinc will also reduce Cu^{2+} to Cu, etc. and the following redox reactions can occur :



4. To predict whether a metal can liberate hydrogen from acid or not. The electrochemical series can also be used to predict whether a metal can liberate hydrogen from the acid or not. Metals like zinc, magnesium and nickel can liberate hydrogen from the acids like HCl , H_2SO_4 , etc. while metals like copper and silver cannot do so. In general, *only those metals can liberate hydrogen from the acid which have negative values of reduction potentials i.e., $-E^\ominus$ values*. Obviously, hydrogen will have greater tendency to get reduced (accept electrons) and the metal can lose electrons (get oxidised) and hydrogen gas is liberated. These metals are also called **active metals**.





Metals like copper and silver have $+E^\ominus$ values i.e., electron accepting tendencies. Their atoms are not in a position to lose electrons to H^+ ions of the acid. Therefore, hydrogen gas is not liberated.

This can also be stated as if the standard electrode potential of an electrode is greater than zero (i.e., +ve), then its reduced form is more stable as compared to hydrogen gas. On the other hand, if the standard electrode potential is negative, then hydrogen gas is more stable than the reduced form of the species.

SOLVED EXAMPLES

Example 22.

Iodine (I_2) and bromine (Br_2) are added to a solution containing iodide (I^-) and bromide (Br^-) ions. What reaction would occur if the concentration of each species is 1M? The electrode potentials for the reactions are :

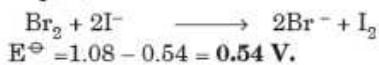
- (i) $\text{I}_2 + 2e^- \longrightarrow 2\text{I}^-, E^\ominus = +0.54 \text{ V}$
(ii) $\text{Br}_2 + 2e^- \longrightarrow 2\text{Br}^-, E^\ominus = +1.08 \text{ V}$

Solution : Since the reduction potential of Br_2 is more than that of I_2 , it means that bromine can readily be reduced and it will oxidise I^- to I_2 . Therefore, the following reaction will occur:



Since for the feasibility of the reaction, the E.M.F. should be +ve, therefore, to get +ve value for the overall cell reaction, subtract the equation representing lower value of E^\ominus from the equation representing the higher value of E^\ominus . Thus, subtract

Eq. (i) from Eq. (ii).



Example 23.

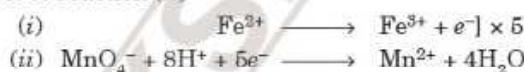
What will be the spontaneous reaction when the following half reactions are combined?

- (i) $\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}, E^\ominus = +0.77 \text{ V}$
(ii) $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}, E^\ominus = +1.49 \text{ V}$

What is the value of E^\ominus_{cell} ?

Solution : The reduction potential of (ii) half reaction is more than that of (i) half reaction. It means that reduction will occur in (ii) half cell and oxidation will occur in (i) half cell. Therefore, (i) half cell reaction will proceed to the left, and

(ii) half reaction will proceed to the right. We therefore, reverse the first reaction and after multiplying by appropriate coefficients add it to reaction (ii)

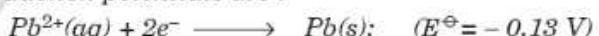


The above reaction will be spontaneous.

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}} \\ = 1.49 - 0.77 = +0.72 \text{ V.}$$

Example 24.

In a simple electrochemical cell, which is in the standard state, the half cell reactions with their appropriate reduction potentials are :



- (a) What is the cell reaction for the cell?
(b) Calculate the e.m.f. of the cell.

Solution : The reaction potentials of the two half cell reactions are :



The reduction potential of $\text{Ag}^+ | \text{Ag}$ electrode is more than that of $\text{Pb}^{2+} | \text{Pb}$. Therefore, reduction will occur at silver electrode and oxidation will occur at lead electrode and the cell reaction will be



The cell may be represented as :

$\text{Pb} | \text{Pb}^{2+} \parallel \text{Ag}^+ | \text{Ag}$ and

$$\therefore E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}} \\ = 0.80 - (-0.13) = 0.93 \text{ V.}$$

Practice Problems

25. An iron wire is immersed in a solution containing ZnSO_4 and NiSO_4 . When the concentration of each salt is 1M, predict giving reasons which of the following reactions is likely to proceed ?
(i) Iron reduces Zn^{2+} ions (ii) Iron reduces Ni^{2+} ions
Given $E^\ominus(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$, $E^\ominus(\text{Fe}^{2+}/\text{Fe}) = -0.44 \text{ V}$ and $E^\ominus(\text{Ni}^{2+}/\text{Ni}) = -0.25 \text{ V}$.
26. Can a solution of 1 M CuSO_4 be stored in a vessel made of nickel metal ? Given $E^\ominus(\text{Ni}^{2+} | \text{Ni}) = -0.25 \text{ V}$ and $E^\ominus(\text{Cu}^{2+} | \text{Cu}) = 0.34 \text{ V}$.

27. What is the standard e.m.f. of the cell containing $\text{Sn}^{2+}|\text{Sn}$ and $\text{Br}_2|\text{Br}^-$ electrodes ?
 $(E^\ominus(\text{Sn}^{2+}|\text{Sn}) = -0.14 \text{ V}, E^\ominus(\text{Br}_2|\text{Br}^-) = 1.08 \text{ V})$
28. Calculate the standard reduction potential of $\text{Ag}^+|\text{Ag}$ electrode when the cell potential for the cell, $\text{Cu}(s)|\text{Cu}^{2+}(1\text{M}) \parallel \text{Ag}^+(1\text{M})|\text{Ag}$ is 0.46 V. Given that $\text{Cu}^{2+}|\text{Cu} = 0.34 \text{ V}$
29. Calculate the standard reduction potentials of galvanic cells in which reactions are as follows :
(i) $2\text{Cr}(s) + 3\text{Cd}^{2+} \longrightarrow 2\text{Cr}^{3+} + 3\text{Cd}(s)$
(ii) $\text{Fe}^{2+}(aq) + \text{Ag}^+(aq) \longrightarrow \text{Fe}^{3+}(aq) + \text{Ag}(s)$
Given that $E^\ominus(\text{Cr}^{3+}/\text{Cr}) = -0.74 \text{ V}, E^\ominus(\text{Cd}^{2+}/\text{Cd}) = -0.40 \text{ V}, E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77 \text{ V}, E^\ominus(\text{Ag}^+/\text{Ag}) = 0.80 \text{ V}$
30. Can chlorine gas be stored in a copper cylinder ? Given $E^\ominus(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$ and $E^\ominus(\text{Cl}_2/\text{Cl}^-) = 1.36 \text{ V}$.
31. Why does blue colour of copper sulphate get discharged when zinc rod is dipped in it ?
Given $E^\ominus(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}, E^\ominus(\text{Zn}^{2+}|\text{Zn}) = -0.76 \text{ V}$.
32. A copper wire is dipped in silver nitrate solution in beaker A and a silver wire is dipped in a solution of copper sulphate kept in beaker B. If the standard electrode potential for
 $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$ is +0.34 and for $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$ is 0.80 V
Predict in which beaker the ions present will get reduced ?

Hints & Solutions on page 74

Answers to Practice Problems

25. Iron reduces Ni^{2+} ions.
26. No.
27. 1.22 V.
28. 0.80 V.
29. (i) 0.34V, (ii) 0.03V.
30. No.
32. In beaker A, Ag^+ will be reduced.

DEPENDENCE OF ELECTRODE AND CELL POTENTIALS ON CONCENTRATION : NERNST EQUATION

The standard electrode potentials given in Table 4 are measured in their standard states when the concentration of the electrolyte solutions are fixed as 1M and temperature is 298 K. However, in actual practice electrochemical cells do not have always fixed concentration of the electrolyte solutions. The electrode potentials depend on the concentration of the electrolyte solutions. Nernst gave a relationship between electrode potentials and the concentration of electrolyte solutions known as **Nernst equation**. For a general electrode reaction,



the Nernst equation is

$$E(M^{n+}|M) = E^\circ(M^{n+}|M) - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}(aq)]}$$

$$\text{or } E(M^{n+}|M) = E^\ominus(M^{n+}|M) - \frac{2.303RT}{nF} \log \frac{[M(s)]}{[M^{n+}(aq)]}$$

$$(\because \ln x = 2.303 \log x)$$

where $E(M^{n+}|M)$ = Electrode potential.

$E^\ominus(M^{n+}|M)$ = Standard electrode potential [for a 1 M solution of metal ions, $M^{n+}(aq)$].

R = Gas constant, T = Temperature, F = Faraday of electricity

n = Number of electrons gained during the electrode reaction.

$[M^{n+}(aq)]$ = Molar concentration of ions, $[M]$ = Molar concentration of metal

Substituting the values of R ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), T (298 K) and F (96500 coulombs), the Nernst equation at 25°C becomes

$$E(M^{n+}|M) = E^\ominus(M^{n+}|M) - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[M(s)]}{[M^{n+}(aq)]}$$

$$\text{or } E(M^{n+}|M) = E^\ominus(M^{n+}|M) - \frac{0.059}{n} \log \frac{1}{[M^{n+}(aq)]}$$

It may be noted that concentration of the solid phase, $[M(s)]$ is taken to be unity.

The above equation may also be written as :

$$E(M^{n+} | M) = E^\ominus(M^{n+} | M) - \frac{0.059}{n} \log \frac{1}{[M^{n+}(aq)]}$$

For simplicity, we may write this equation as :

$$E = E^\ominus - \frac{0.059}{n} \log \frac{1}{[M^{n+}(aq)]} \quad \text{at } 25^\circ\text{C.}$$

SOLVED EXAMPLES

Example 25.

Zinc rod is dipped in 0.1M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential given that $E^\ominus(Zn^{2+} | Zn) = -0.76$ V. (H.P.S.B. 2009)

Solution : The electrode reaction is :



According to Nernst equation, at 298 K

$$E(Zn^{2+} | Zn) = E^\ominus(Zn^{2+} | Zn) - \frac{0.059}{n} \log \frac{[Zn]}{[Zn^{2+}(aq)]}$$

$$E^\ominus(Zn^{2+} | Zn) = -0.76 \text{ V}, [Zn] = 1, \\ [Zn^{2+}(aq)] = 0.1 \times 95/100 = 0.095 \text{ M}$$

$$\therefore E(Zn^{2+} | Zn) = -0.76 - \frac{0.059}{2} \log \frac{1}{0.095} \\ = -0.76 - 0.03 = -0.79 \text{ V.}$$

Example 26.

If E° for copper electrode is + 0.34 V, how will you calculate e.m.f. value when the solution in contact with it is 0.1 M in copper ions? How does e.m.f. for copper electrode change when concentration of Cu^{2+} ion in the solution is decreased? (A.I.S.B. 2000)

Solution : EMF of the cell can be calculated by using Nernst equation as

$$Cu^{2+} + 2e^- \longrightarrow Cu \\ E = E^\ominus - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}$$

When $[Cu^{2+}] = 0.1 \text{ M}$

$$E = 0.34 - \frac{0.059}{2} \log \frac{1}{(0.1)} \\ = 0.34 - \frac{0.059}{2} \times 1 = 0.34 - 0.0295 \\ = 0.31 \text{ V.}$$

Example 27.

Calculate the reduction potential of the following electrode at 298 K:

$Pt, Cl_2(2.5 \text{ atm}) | HCl (0.01M); E^\ominus Cl_2 | 2 Cl^- = 1.36 \text{ V.}$

Solution : The electrode reaction is :



$$E(Cl_2 | 2Cl^-) = E^\ominus(Cl_2 | 2Cl^-) - \frac{0.059}{2} \log \frac{[Cl^-]^2}{p(Cl_2)}$$

$p(Cl_2) = 2.5 \text{ atm}, [Cl^-] = 0.01 \text{ M}$ (same as the concentration of HCl)

$$E^\ominus(Cl_2 | 2Cl^-) = 1.36 \text{ V}$$

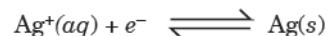
$$\therefore E(Cl_2 | 2Cl^-) = 1.36 - \frac{(0.059)}{2} \log \frac{(0.01)^2}{(2.5)} \\ = 1.36 + 0.0295 \times 4.398 \\ = 1.36 + 0.13 = 1.49 \text{ V.}$$

Example 28.

(a) Calculate the electrode potential of a silver electrode dipped in a 0.1M solution of silver nitrate at 298 K assuming $AgNO_3$ to be completely dissociated. The standard electrode potential of $Ag^+ | Ag$ is 0.80 V at 298 K.

(b) At what concentration of silver ions will this electrode have a potential of 0 volt?

Solution : (a) The reduction electrode reaction is :



$$E(Ag^+ | Ag) = E^\ominus(Ag^+ | Ag) - \frac{(0.059)}{2} \log \frac{[Ag]}{[Ag^+]}$$

$$[Ag^+] = 0.1 \text{ M}, [Ag] = 1, E^\ominus(Ag^+ | Ag) = 0.80 \text{ V}$$

$$\therefore E(Ag^+ | Ag) = 0.80 - \frac{(0.059)}{2} \log \frac{1}{(0.1)} \\ = 0.80 - 0.059 = 0.741 \text{ V.}$$

(b) For the reduction electrode reaction of silver,

$$E(Ag^+ | Ag) = E^\ominus(Ag^+ | Ag) - \frac{(0.059)}{2} \log \frac{[Ag]}{[Ag^+]}$$

$$E(Ag^+ | Ag) = 0, E^\ominus(Ag^+ | Ag) = 0.80,$$

$$[Ag^+] = ?, [Ag] = 1$$

$$0 = 0.80 - 0.059 \log \frac{[Ag]}{[Ag^+]}$$

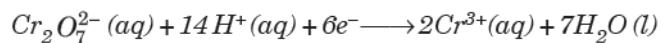
$$\therefore 0.059 \log [Ag^+] = -0.80$$

$$\text{or } \log [Ag^+] = \frac{-0.80}{0.059} = -13.559$$

$$\therefore [Ag^+] = 2.76 \times 10^{-14} \text{ M.}$$

Example 29.

Calculate the potential for half-cell containing 0.10 M $K_2Cr_2O_7(aq)$, 0.20 M $Cr^{3+}(aq)$ and $1.0 \times 10^{-4} \text{ M } H^+(aq)$. The half-cell reaction is :



and the standard electrode potential is given as

$$E^\circ = 1.33 \text{ V.}$$

(A.I.S.B. 2011)

$$\text{Solution : } E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^{+}]^{14}}$$

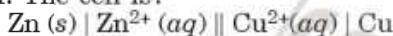
$$E_{\text{cell}}^\circ = 1.33 \text{ V}, [\text{Cr}^{3+}] = 0.20 \text{ M}$$

$$[\text{Cr}_2\text{O}_7^{2-}] = 0.1 \text{ M}, [\text{H}^{+}] = 1.0 \times 10^{-4} \text{ M}, n = 6$$

$$\begin{aligned} E_{\text{cell}} &= 1.33 - \frac{0.0591}{6} \log \frac{(0.20)^2}{(0.10)(10^{-4})^{14}} \\ &= 1.33 - \frac{0.0591}{6} \log 0.4 \times 10^{56} \\ &= 1.33 - \frac{0.0591}{6} \times 55.60 \\ &= 1.33 - 0.55 = 0.78 \text{ V.} \end{aligned}$$

Applications of Nernst Equation

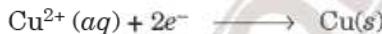
1. Calculation of cell potential using Nernst equation. Let us illustrate this by considering a Daniell cell in which the concentration of the solution may not be 1M. The cell is:



The e.m.f. of the cell is :

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{(\text{Cu}^{2+} | \text{Cu})} - E_{(\text{Zn}^{2+} | \text{Zn})} \quad \dots(i) \end{aligned}$$

The electrode reactions are :



The electrochemical cell reaction is



The electrode potential for the two electrodes can be calculated by using Nernst equation as :

Electrode potential for copper electrode,

$$E_{(\text{Cu}^{2+} | \text{Cu})} = E_{(\text{Cu}^{2+} | \text{Cu})}^\circ - \frac{2.303 \text{ RT}}{nF} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}(aq)]}$$

Similarly, electrode potential for zinc electrode,

$$E_{(\text{Zn}^{2+} | \text{Zn})} = E_{(\text{Zn}^{2+} | \text{Zn})}^\circ - \frac{2.303 \text{ RT}}{nF} \log \frac{[\text{Zn}]}{[\text{Zn}^{2+}(aq)]}$$

Substituting these values in Eq. (i)

$$\begin{aligned} E_{\text{cell}} &= \left\{ E_{(\text{Cu}^{2+} | \text{Cu})}^\circ - \frac{2.303 \text{ RT}}{2F} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}(aq)]} \right\} \\ &\quad - \left[E_{(\text{Zn}^{2+} | \text{Zn})}^\circ - \frac{2.303 \text{ RT}}{2F} \log \frac{[\text{Zn}]}{[\text{Zn}^{2+}(aq)]} \right] \end{aligned}$$

$$\text{or } E_{\text{cell}} = E_{(\text{Cu}^{2+} | \text{Cu})}^\circ - E_{(\text{Zn}^{2+} | \text{Zn})}^\circ - \frac{2.303 \text{ RT}}{nF} \log \frac{[\text{Cu}][\text{Zn}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)][\text{Zn}]}$$

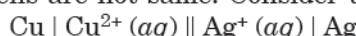
Now $E_{(\text{Cu}^{2+} | \text{Cu})}^\circ - E_{(\text{Zn}^{2+} | \text{Zn})}^\circ = E_{\text{cell}}^\circ$ and the concentration of solids is taken as unity so that $[\text{Zn}] = 1$, $[\text{Cu}] = 1$.

$$\therefore E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303 \text{ RT}}{2F} \log \frac{[\text{Zn}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]}$$

$$\text{or } E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]} \text{ at } 298 \text{ K}$$

$$\left(\because \frac{2.303 \text{ RT}}{F} = 0.059 \text{ at } 298 \text{ K} \right)$$

In the Daniell cell, the valencies of zinc and copper are the same i.e., $n = 2$. Let us consider an example, in which the valencies of the two metals used in the two half cells are not same. Consider the cell.



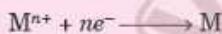
Important Note

It must be remembered that while writing the Nernst equation for the overall cell reaction, the log term is the same as the expression for the equilibrium constant for the reaction. However, some books use the expression in the reverse form as the expression for the equilibrium constant but, sign after E° is changed. The two relations are same.

$$E = E^\circ - \frac{2.303 \text{ RT}}{nF} \log \frac{[\text{C}]^r [\text{D}]^t}{[\text{A}]^s [\text{B}]^p}$$

$$E = E^\circ + \frac{2.303 \text{ RT}}{nF} \log \frac{[\text{A}]^s [\text{B}]^p}{[\text{C}]^r [\text{D}]^t}$$

Similarly, for the electrode reaction:



The Nernst equation is

$$\text{or } E = E^\circ - \frac{2.303 \text{ RT}}{nF} \log \frac{1}{[\text{M}^{n+}]}$$

$$E = E^\circ + \frac{2.303 \text{ RT}}{nF} \log [\text{M}^{n+}]$$

But in the present text, we shall use the **first form**, which is same as equilibrium expression.

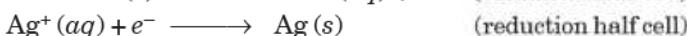
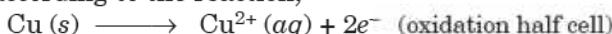
The cell reaction is :



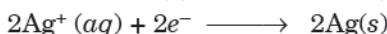
The EMF of the cell,

$$E_{cell} = E(\text{cathode}) - E(\text{anode}) \quad \dots(i)$$

During the reaction, two electrons are released by one copper atom but one electron is accepted by Ag^+ according to the reaction,



To balance the loss and gain of electrons, the reduction half cell is multiplied by 2 so that the net reactions are :



The electrode potentials of two electrodes may be written according to Nernst equation as

Electrode potential for copper electrode,

$$E_{(\text{Cu}^{2+}|\text{Cu})} = E^\ominus_{(\text{Cu}^{2+}|\text{Cu})} - \frac{2.303 RT}{nF} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}(aq)]}$$

Electrode potential for silver electrode,

$$E_{(\text{Ag}^+|\text{Ag})} = E^\ominus_{(\text{Ag}^+|\text{Ag})} - \frac{2.303 RT}{2F} \log \frac{[\text{Ag}]^2}{[\text{Ag}^+(aq)]^2}$$

It must be remembered that $E^\ominus(\text{Ag}^+|\text{Ag})$ remains unchanged.

Substituting the values in Eq. (i)

$$E_{cell} = E^\ominus_{(\text{Ag}^+|\text{Ag})} - \frac{2.303 RT}{2F} \log \frac{[\text{Ag}]^2}{[\text{Ag}^+(aq)]^2}$$

$$- \left\{ E_{(\text{Cu}^{2+}|\text{Cu})} - \frac{2.303 RT}{2F} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}(aq)]} \right\}$$

$$\text{or } E_{cell} = [E^\ominus_{(\text{Ag}^+|\text{Ag})} - E^\ominus_{(\text{Cu}^{2+}|\text{Cu})}] - \frac{2.303 RT}{2F} \log \frac{[\text{Ag}]^2 [\text{Cu}^{2+}(aq)]}{[\text{Ag}^+(aq)]^2 [\text{Cu}]}$$

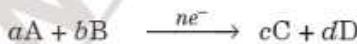
Now $E^\ominus_{(\text{Ag}^+|\text{Ag})} - E^\ominus_{(\text{Cu}^{2+}|\text{Cu})} = E^\ominus_{cell}$ and $[\text{Cu}] = 1$, $[\text{Ag}] = 1$

$$E_{cell} = E^\ominus_{cell} - \frac{2.303 RT}{2F} \log \frac{[\text{Cu}^{2+}(aq)]}{[\text{Ag}^+(aq)]^2}$$

At 298 K, the relation becomes

$$E_{cell} = E^\ominus_{cell} - \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}(aq)]}{[\text{Ag}^+(aq)]^2}$$

In general, for an electrochemical cell reaction :



The Nernst equation may be written as :

$$E_{cell} = E^\ominus_{cell} - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E^\ominus_{cell} - \frac{2.303 RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At 298 K, the equation becomes

$$E_{cell} = E^\ominus_{cell} - \frac{0.059}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The value of a , b , c , d and n are obtained from the balanced cell reactions.

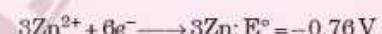
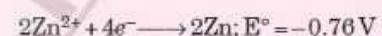
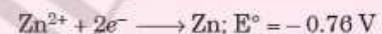
R U Curious...



□ Will E^\ominus value change when the coefficients in chemical equation change?

➤ E^\ominus values do not depend on the coefficients in the chemical equation i.e. when you double or triple the coefficients, E^\ominus values do not change.

For example :



In a half reaction, if the coefficients change, the number of electrons, n will change to cancel the effect of the change in the coefficient.

Important Note

□ **Liquid Junction Potential.** In a concentration cell when the two electrolytic solutions are directly in contact, ions move across the junction with different speeds. As a result, a potential difference is set up at the liquid junction and it is called liquid junction potential (LJP). The e.m.f. of the cell will depend upon the speeds of the ions. Such cells are also called **concentration cells with transference**. The e.m.f. of the cell will be equal to $E_{cell} + E_j$ where E_{cell} is the potential of the cell that would be observed in the absence of junction potential and E_j is the junction potential. It can be calculated as :

$$E_j = E - E_{cell}$$

This type of junction generally applied in galvanic cells is the salt bridge which contains salts like KCl , in which the mobility of the ions is almost equal. Hence E_j is taken as zero.

Competition Plus

The solubility product of sparingly soluble salts can be determined from e.m.f. data. For detail, refer Competition File (Page 98).

Concentration cells

A cell in which both the electrodes are of the same type but the solutions of electrolyte in which they dip have different concentrations is called **concentration cell**. For example, consider a copper ion concentration cell in which copper electrodes are dipped in two different concentrations C_1 and C_2 .



In this case, the standard potential of the two electrodes will cancel and the cell potential is given as:

$$E_{\text{cell}} = \frac{RT}{2F} \ln \frac{C_2}{C_1}$$

$$\text{or } E_{\text{cell}} = \frac{0.059}{n} \log \frac{C_2}{C_1} \text{ at } 25^\circ\text{C}$$

Obviously for EMF to be positive

$$C_2 > C_1$$

so that the reaction proceeds in the direction indicated. In such a cell, **oxidation** occurs at the electrode with **lower concentration**. Hence, it acts as **anode** (-ve pole). The **reduction** occurs at the electrode with **higher concentration** and therefore, it acts as **cathode** (+ve pole)

This type of cell is shown in Fig. 13.

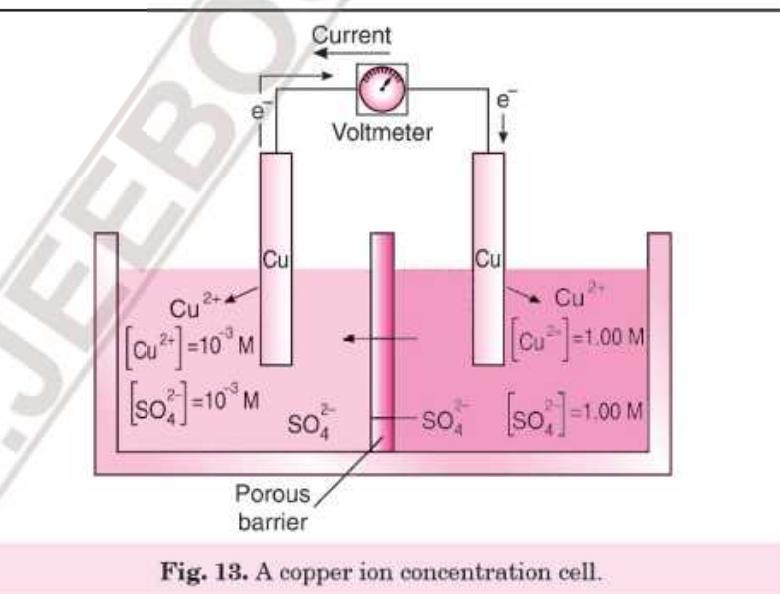


Fig. 13. A copper ion concentration cell.

For example, consider the following concentration cell:

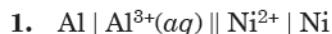


The e.m.f. of the cell will be

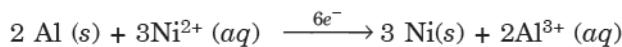
$$E = \frac{0.059}{n} \log \frac{C_2}{C_1}$$

$$E = \frac{0.059}{2} \log \frac{0.10}{0.01} = 0.0295 \text{ V}$$

Some Examples of Nernst Equation for Cells

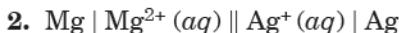


The cell reaction is :



Here $n = 6$. The Nernst equation is :

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{6} \log \frac{[\text{Al}^{3+}(aq)]^2}{[\text{Ni}^{2+}(aq)]^3} \text{ at } 298 \text{ K}$$

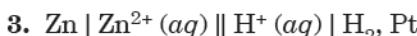


The cell reaction is :



Here $n = 2$. The Nernst equation is :

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{[\text{Mg}^{2+}(aq)]}{[\text{Ag}^{+}(aq)]^2} \text{ at } 298 \text{ K}$$



The cell reaction is :



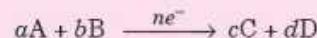
Here $n = 2$. The Nernst equation is :

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}(aq)]}{[\text{H}^{+}(aq)]^2} \text{ at } 298 \text{ K.}$$

Solving Numerical Problems

FORMULAE AND UNITS

For the cell reaction :



Nernst equation is

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{nF} \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

$$\text{or} \quad E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{n} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

at 298 K.

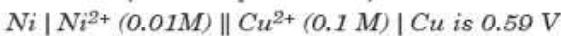
For pure solids, pure liquids and gases at 1 atm pressure, molar concentration is taken as 1.

► While applying Nernst equation, electrode potential is always taken as reduction potential.

SOLVED EXAMPLES

Example 30.

Calculate the standard electrode potential of $\text{Ni}^{2+} | \text{Ni}$ electrode if the cell potential of the cell :



Given : $E_{\text{cell}}^{\ominus} = 0.34 \text{ V.}$

(Mizoram S.B. 2013, Nagaland S.B. 2015)



The cell reaction for the cell is :



$$E = E_{\text{cell}}^{\ominus} - \frac{0.059}{n} \log \frac{[\text{Ni}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]}$$

$$0.59 = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{0.01}{0.1} \quad (\text{Here } n = 2)$$

$$0.59 = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{1}{10}$$

$$0.59 = E_{\text{cell}}^{\ominus} + 0.0295$$

$$\therefore E_{\text{cell}}^{\ominus} = 0.59 - 0.0295 = 0.5605$$

Now, $E_{\text{cell}}^{\ominus} = E_{(\text{Cu}^{2+} | \text{Cu})}^{\ominus} - E_{(\text{Ni}^{2+} | \text{Ni})}^{\ominus}$
 $0.5605 = 0.34 - E_{(\text{Ni}^{2+} | \text{Ni})}^{\ominus}$

$$\therefore E_{(\text{Ni}^{2+} | \text{Ni})}^{\ominus} = 0.34 - 0.5605 = -0.2205 \text{ V.}$$

Example 31.

Write the Nernst equation and calculate the e.m.f. of the following cell at 298 K :

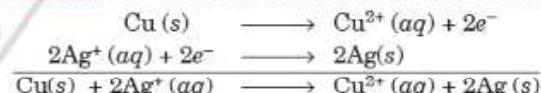


Given : $E_{(\text{Cu}^{2+} | \text{Cu})}^{\ominus} = +0.34 \text{ V}$ and

$$E_{(\text{Ag}^{+} | \text{Ag})}^{\ominus} = +0.80 \text{ V}$$

(A.I.S.B. 2004, Pb. S.B. 2010, 2013, 2015,
Mizoram S.B. 2015, Hr. S.B. 2017)

Solution : The electrode reactions and cell reaction are :



Nernst equation is :

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^2}$$

$$E_{\text{cell}}^{\ominus} = E_{(\text{Ag}^{+} | \text{Ag})}^{\ominus} - E_{(\text{Cu}^{2+} | \text{Cu})}^{\ominus}$$

$$= 0.80 - 0.34 = 0.46 \text{ V}$$

$$E_{\text{cell}} = 0.46 - \frac{0.059}{2} \log \frac{(0.130)}{(1.0 \times 10^{-4})^2}$$

$$= 0.46 - \frac{0.059}{2} \log 1.30 \times 10^7 = 0.46 - 0.21 = 0.25 \text{ V.}$$

WATCH OUT !

While balancing oxidation and reduction reaction, we multiply by certain number to cancel the electrons in the overall reaction. But it must be remembered that electrode potential is not to be multiplied.

Example 32.

Write Nernst equation and calculate e.m.f. of the following cells at 298 K :



$$\text{Given : } E_{(\text{Mg}^{2+} | \text{Mg})}^{\ominus} = -2.37 \text{ V}, E_{(\text{Cu}^{2+} | \text{Cu})}^{\ominus} = 0.34 \text{ V}$$

(Pb.S.B. 2010, 2014, Uttarakhand S.B. 2014,
Hr. S.B. 2013, 2017, Karnataka S.B. 2018)



$$\text{Given: } E^\ominus_{(Fe^{2+}|Fe)} = -0.44\text{V}$$

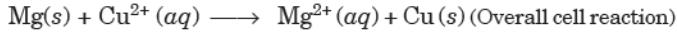
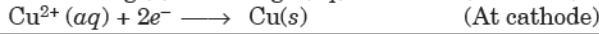
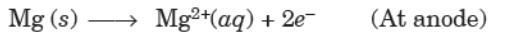
(D.S.B. 2013, Hr.S.B. 2013, Pb.S.B. 2013, 2015)



$$\text{Given: } E^\ominus_{(Sn^{2+}|Sn)} = -0.14\text{V}$$

(Hr.S.B. 2013, Pb.S.B. 2015, A.I.S.B. 2018)

Solution : (i) The electrode reactions and cell reactions are:



Since the reaction involves 2 moles of electrons and therefore, $n = 2$ and the Nernst equation for the cell at 298 K is :

$$\text{or } E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{0.059}{2} \log \frac{[Mg^{2+}(aq)]}{[Cu^{2+}(aq)]} \quad \dots(i)$$

$$E^\ominus_{\text{cell}} = E^\ominus(Cu^{2+} | Cu) - E^\ominus(Mg^{2+} | Mg)$$

$$E^\ominus(Cu^{2+} | Cu) = 0.34\text{ V}, E^\ominus(Mg^{2+} | Mg) = -0.237\text{ V}$$

$$\therefore E^\ominus_{\text{cell}} = 0.34 - (-0.237) = 0.577\text{ V}$$

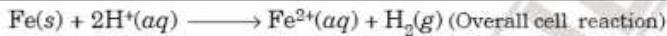
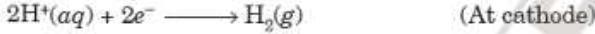
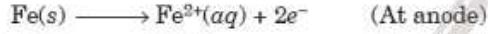
Substituting the values in Eq. (i)

$$E_{\text{cell}} = 0.577 - \frac{0.059}{2} \log \frac{0.001}{0.0001}$$

$$E_{\text{cell}} = 0.577 - 0.0295 = 0.5475\text{ V.}$$



The electrode reactions and overall cell reactions are:



Since the reaction involves 2 moles of electrons, therefore, $n = 2$ and the Nernst equation at 298 K is :

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{0.059}{2} \log \frac{[Fe^{2+}]}{[H^+]^2}$$

$$E^\ominus_{\text{cell}} = E^\ominus(H^+ | H_2) - E^\ominus(Fe^{2+} | Fe)$$

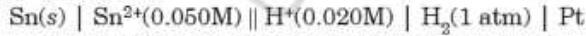
$$E^\ominus(H^+ | H_2) = 0.0\text{ V}, E^\ominus(Fe^{2+} | Fe) = -0.44\text{ V}$$

$$E^\ominus_{\text{cell}} = 0.0 - (-0.44) = 0.44\text{ V}$$

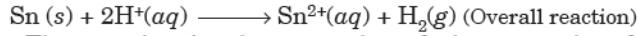
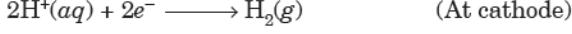
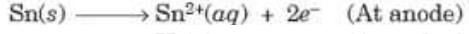
$$E_{\text{cell}} = 0.44 - \frac{0.059}{2} \log \frac{0.001}{(1)^2}$$

$$= 0.44 + 0.0295 = 0.4695\text{ V.}$$

(iii) The cell is :



The electrode reactions and cell reactions are :



The reaction involves 2 moles of electrons, therefore, $n = 2$ and the Nernst equation is :

$$E = E^\ominus - \frac{0.059}{2} \log \frac{[Sn^{2+}]}{[H^+]^2}$$

$$E^\ominus_{\text{cell}} = E^\ominus(H^+ | H_2) - E^\ominus(Sn^{2+} | Sn)$$

$$E^\ominus(H^+ | H_2) = 0.0\text{ V}, E^\ominus(Sn^{2+} | Sn) = -0.14\text{ V}$$

$$E^\ominus_{\text{cell}} = 0.00 - (-0.14) = 0.14\text{ V}$$

$$[H^+] = 0.020\text{ M}, [Sn^{2+}] = 0.050\text{ M}$$

$$\therefore E = 0.14 - \frac{0.059}{2} \log \frac{(0.050)}{(0.020)^2}$$

$$= 0.14 - 0.0295 = 0.1105\text{ V.}$$

Example 33.

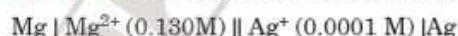
Represent the cell in which the following reaction takes place :



Calculate its E if E^\ominus is 3.17 V

N.C.E.R.T. (Pb.S.B. 2011, H.P.S.B. 2015, Assam S.B. 2018)

Solution : The cell may be represented as



The cell reaction for the cell is



The Nernst equation for the cell is

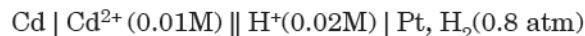
$$E = E^\ominus - \frac{0.059}{2} \log \frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$= 3.17 - \frac{0.059}{2} \log \frac{(0.130)}{(0.0001)^2}$$

$$= 3.17 - 0.21 = 2.96\text{ V.}$$

Example 34.

Calculate the e.m.f. of the following cell:



Given : $E^\ominus(Cd^{2+} | Cd) = -0.40\text{ V}$

Solution : The cell reaction is :



According to Nernst equation,

$$E = E^\ominus - \frac{0.059}{2} \log \frac{[Cd^{2+}] \times p(H_2)}{[H^+]^2}$$

$$E = E^\ominus(H^+ | \frac{1}{2} H_2) - E^\ominus(Cd^{2+} | Cd)$$

$$= 0 - (-0.40) = 0.40\text{ V}$$

$$E = 0.40 - \frac{0.059}{2} \log \frac{(0.01) \times 0.8}{(0.02)^2}$$

$$= 0.40 - \frac{0.059}{2} \times 1.3010$$

$$= 0.40 - 0.04$$

$$= 0.36\text{ V}$$

Example 35.

Calculate E^\ominus_{cell} for the following reaction at 298K:



(Given : $E_{\text{cell}} = 0.261\text{V}$)

(A.I.S.B. 2016)

Solution : $2\text{Cr}(s) + 3\text{Fe}^{2+}(aq) \rightleftharpoons 2\text{Cr}^{3+}(aq) + 3\text{Fe}(s)$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}(aq)]^2}{[\text{Fe}^{2+}(aq)]^3}$$

$$E_{\text{cell}} = 0.261 \text{ V}$$

$$0.261 = E^{\circ}_{\text{cell}} - \frac{0.059}{6} \log \frac{(0.01)^2}{(0.01)^3}$$

$$E^{\circ}_{\text{cell}} = 0.261 + \frac{0.059}{6} \log \frac{(0.01)^2}{(0.01)^3}$$

$$= 0.261 + \frac{0.059}{6} \log 10^2$$

$$= 0.261 + \frac{0.059}{6} \times (2)$$

$$= 0.261 + 0.0197$$

$$= 0.2807 \text{ V.}$$

2. Calculation of Concentration of a Solution of Half Cell

When in a galvanic cell, all the concentrations except one are known, then the unknown concentration can be calculated by measuring the cell potential and using Nernst equation. This can be illustrated by the following example:

Example 36.

The EMF of the cell, $\text{Zn} | \text{Zn}^{2+}(0.1\text{M}) || \text{Cd}^{2+}(M_1) | \text{Cd}$ has been found to be 0.3305 V at 298 K. Calculate the value of M_1 [$E^{\circ}_{(\text{Zn}^{2+} | \text{Zn})} = -0.76\text{V}$, $E^{\circ}_{(\text{Cd}^{2+} | \text{Cd})} = -0.40\text{V}$].

Solution : The cell is :



The cell reaction is :



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]} \text{ at } 298 \text{ K}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{(\text{Cd}^{2+} | \text{Cd})} - E^{\circ}_{(\text{Zn}^{2+} | \text{Zn})} \\ = -0.40 - (-0.76) = 0.36 \text{ V}$$

$$E = 0.3305 \text{ V}, [\text{Zn}^{2+}(aq)] = 0.1 \text{ M}$$

$$\therefore 0.3305 = 0.36 - \frac{0.059}{2} \log \frac{0.1}{M_1}$$

$$-0.0295 = 0.0295 \log 10 M_1$$

$$\text{or } 0.0295 \log 10 M_1 = -0.0295$$

$$0.0295 + 0.0295 \log M_1 = -0.0295$$

$$0.0295 \log M_1 = -0.0295 - 0.0295 \\ = -0.059$$

$$\log M_1 = -\frac{0.059}{0.0295} = -2$$

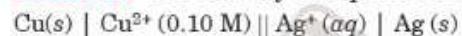
$$\therefore M_1 = 0.01 \text{ M.}$$

Example 37.

A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell. (Given $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ V}$, $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$)

(D.S.B. 2010)

Solution : The cell may be represented as :



The cell reaction is



$$E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}, E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ V}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Ag}^{+}/\text{Ag}} - E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} \\ = 0.80 - 0.34 = 0.46 \text{ V}$$

$$[\text{Cu}^{2+}] = 0.10 \text{ M}, [\text{Ag}^{+}] = ?$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^2}$$

$$0.422 = 0.46 - \frac{0.059}{2} \log \frac{0.10}{[\text{Ag}^{+}]^2}$$

$$\frac{0.059}{2} \log \frac{0.10}{[\text{Ag}^{+}]^2} = 0.46 - 0.422$$

$$\frac{0.059}{2} \log \frac{0.10}{[\text{Ag}^{+}]^2} = 0.038$$

$$\log \frac{0.10}{[\text{Ag}^{+}]^2} = \frac{2 \times 0.038}{0.059} = 1.2881$$

$$\frac{0.1}{[\text{Ag}^{+}]^2} = 19.42$$

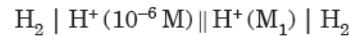
$$[\text{Ag}^{+}]^2 = \frac{0.1}{19.42} = 5.15 \times 10^{-3}$$

$$[\text{Ag}^{+}] = 0.0717 \text{ M}$$

Example 38.

A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The e.m.f. of the cell is 0.118 V at 25°C. Calculate the concentration of hydrogen ions at the positive electrode.

Solution : The cell may be written as :



Applying Nernst equation,

$$E = E^{\circ} - \frac{0.059}{1} \log \frac{[\text{H}^+]_{\text{anode}}}{[\text{H}^+]_{\text{cathode}}}$$

$$0.118 = 0 - \frac{0.059}{1} \log \frac{(10^{-6})}{M_1}$$

$$\log \frac{10^{-6}}{M_1} = -\frac{0.118}{0.059} = -2$$

$$\frac{10^{-6}}{M_1} = 10^{-2}$$

$$\therefore M_1 = 10^{-4} \text{ M}$$

Practice Problems

33. Calculate E^\ominus emf of the following cell at 298 K:
 $Mg(s) | Mg^{2+}(0.1M) || Cu^{2+}(0.01M) | Cu(s)$. Given $E^\circ_{cell} = +2.71\text{ V}$, $F = 96500\text{ C mol}^{-1}$.
(D.S.B. 2014)
34. One half cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. Its other half cell consists of a zinc electrode dipping in 1.0 M solution of $Zn(NO_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver nitrate solution used.
 $[E^\ominus]_{Zn^{2+}|Zn} = -0.76\text{ V}$, $E^\ominus_{Ag^+|Ag} = +0.80\text{ V}$
(D.S.B. 2009)
35. Calculate the potential of the following cell reaction at 298 K:
 $Sn^{4+}(1.50\text{ M}) + Zn(s) \longrightarrow Sn^{2+}(0.5\text{ M}) + Zn^{2+}(2.0\text{ M})$
The standard potential of the cell is 0.89 V. Will the potential of the cell will increase or decrease if the concentration of Sn^{2+} is increased in the cell?
36. Consider a cell composed of the following half cells:
(i) $Mg(s) | Mg^{2+}(aq)$ and (ii) $Ag(s) | Ag^+(aq)$
The e.m.f. of the cell is 2.96 V at $[Mg^{2+}] = 0.130\text{ M}$ and $[Ag^+] = 1.0 \times 10^{-4}\text{ M}$. Calculate the standard e.m.f. of the cell ($R = 8.3\text{ JK}^{-1}\text{ mol}^{-1}$, $F = 96500\text{ C}$).
37. Calculate the e.m.f. of the cell at 25°C
 $Zn | Zn^{2+}(0.01\text{ M}) || Fe^{2+}(0.005\text{ M}) | Fe$
 $E^\ominus(Zn^{2+} | Zn) = -0.763\text{ V}$ and $E^\ominus(Fe^{2+} | Fe) = -0.44\text{ V}$
(Pb.S.B. 2005, 2010, 2011)
38. Calculate the e.m.f. of the following cell at 298 K,
 $Fe | Fe^{2+}(0.1\text{ M}) || Ag^+(0.1\text{ M}) | Ag$
Given: $E^\ominus(Fe^{2+} | Fe) = -0.44\text{ V}$
and $E^\ominus(Ag^+ | Ag) = 0.80\text{ V}$
($R = 8.31\text{ JK}^{-1}\text{ mol}^{-1}$, $F = 96500\text{ C mol}^{-1}$)
(Pb. S.B. 2005, 2011, Mizoram S.B. 2014)
39. Calculate e.m.f. of the following cell at 298K
 $2Cr(s) + 3Fe^{2+}(0.1\text{ M}) \longrightarrow 2Cr^{3+}(0.01\text{ M}) + 3Fe(s)$
Given: $E^\circ(Cr^{3+} | Cr) = -0.74\text{ V}$, $E^\circ(Fe^{2+} | Fe) = -0.44\text{ V}$
(D.S.B. 2016)
40. (i) Calculate the electrode potential at a copper electrode dipped in a 0.1 M solution of copper sulphate at 298 K, assuming $CuSO_4$ to be completely ionised. The standard electrode potential of $Cu^{2+} | Cu$ is 0.34 V at 298 K.
(ii) At what concentration of copper ions will this electrode have a potential of zero volt?

Answers to Practice Problems

33. 2.6805 V.
34. 0.044 M.
35. 0.895 V.
36. 3.17 V.
37. 0.314 V.
38. 1.2105 V.
39. 0.31 V.
40. (i) 0.3105 V (ii) 2.98×10^{-12} .

Hints & Solutions on page 74

Advanced Level

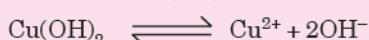
PROBLEMS

Accelerate Your Potential
(for JEE Advance)

Problem 4. The standard reduction potential for $Cu^{2+} | Cu$ is + 0.34V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1.0×10^{-19} .

Solution For pH = 14, $[H^+] = 10^{-14}$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-14}} = 1\text{ M}$$



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

$$1.0 \times 10^{-19} = [Cu^{2+}](1)^2$$

$$\therefore [Cu^{2+}] = 1.0 \times 10^{-19}$$

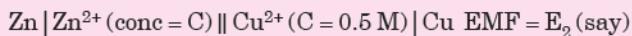
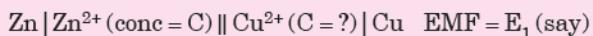
For the cell reaction,

$$\begin{aligned} Cu^{2+} + 2e^- &\longrightarrow Cu \\ E &= E^\circ - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]} \\ &= 0.34 - \frac{0.059}{2} \log \frac{1}{1.0 \times 10^{-19}} \\ &= 0.34 - \frac{0.059}{2} \times 19 = -0.22\text{ V} \end{aligned}$$

Problem 5. Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The e.m.f. of one cell is 0.03V higher than the other. The concentration of $CuSO_4$

in the cell with higher e.m.f. value is 0.5 M. Find out the concentration of CuSO_4 in the other cell. ($2.303 \text{ RT/F} = 0.06$)

Solution The two cells may be represented as :



$$E_2 - E_1 = 0.03 \text{ V}$$

The cell reaction is



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 \text{ RT}}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= E^{\circ}_{\text{cell}} - \frac{0.06}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\therefore E_1 = E^{\circ}_{\text{cell}} - \frac{0.06}{2} \log \frac{C}{[\text{Cu}^{2+}]}$$

$$E_2 = E^{\circ}_{\text{cell}} - \frac{0.06}{2} \log \frac{C}{0.5}$$

$$\therefore E_2 - E_1 = \frac{0.06}{2} \left\{ \log \left(\frac{C}{\text{Cu}^{2+}} \right) - \log \left(\frac{C}{0.5} \right) \right\}$$

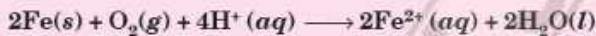
$$0.03 = 0.03 \log \frac{0.5}{[\text{Cu}^{2+}]}$$

$$\text{or } \log \frac{0.5}{[\text{Cu}^{2+}]} = 1$$

$$\text{or } \frac{0.5}{[\text{Cu}^{2+}]} = 10$$

$$\therefore [\text{Cu}^{2+}] = \frac{0.5}{10} = 0.05 \text{ M.}$$

Problem 6. Consider the following cell:



$E^{\circ}_{\text{cell}} = 1.67 \text{ V}$. When $[\text{Fe}^{2+}] = 1 \times 10^{-3} \text{ M}$, $p(\text{O}_2) = 0.1 \text{ atm}$, e.m.f. of the cell is 1.57 V. Calculate the pH of the solution.

Solution pH can be calculated from the concentration of H^+ ions in the solution.

For the cell reaction,

$$E = E^{\circ} - \frac{0.059}{4} \log \frac{[\text{Fe}^{2+}]^2}{p(\text{O}_2) \times [\text{H}^+]^4}$$

$$1.57 = 1.67 - \frac{0.059}{4} \log \frac{(10^{-3})^2}{(0.1) \times [\text{H}^+]^4}$$

$$-0.10 = -\frac{0.059}{4} \log \frac{10^{-5}}{[\text{H}^+]^4}$$

$$\frac{0.10 \times 4}{0.059} = \log \frac{(10^{-5})}{[\text{H}^+]^4}$$

$$6.78 = -5 \log 10 - 4 \log [\text{H}^+]$$

$$\text{or } -4 \log [\text{H}^+] = 6.78 + 5 = 11.78$$

$$\text{or } -\log [\text{H}^+] = \frac{11.78}{4} = 2.95$$

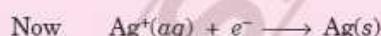
$$\text{or } \text{pH} = 2.95 \quad (-\log [\text{H}^+] = \text{pH})$$

Problem 7. The K_{sp} for AgCl at 298 K is 1.0×10^{-10} . Calculate the electrode potential for $\text{Ag}^+ | \text{Ag}$ electrode immersed in 1.0 M KCl solution. Given : $E^{\circ}_{\text{Ag}^+ | \text{Ag}} = 0.80 \text{ V}$.

Solution $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-], \quad [\text{Cl}^-] = 1.0 \text{ M}$$

$$\text{or } [\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1.0 \times 10^{-10}}{1.0} = 1 \times 10^{-10} \text{ M}$$



According to Nernst equation,

$$E = E^{\circ} - \frac{0.059}{1} \log \frac{1}{[\text{Ag}^+]}$$

$$= 0.80 - \frac{0.059}{1} \log \frac{1}{10^{-10}}$$

$$= 0.80 - 0.059 \times 10 = 0.80 - 0.59 = 0.21 \text{ V}$$

Problem 8. For the electrochemical cell

$\text{Mg}(s) | \text{Mg}^{2+}(aq, 1 \text{ M}) \parallel \text{Cu}^{2+}(aq, 1 \text{ M}) | \text{Cu}(s)$ the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to $x \text{ M}$, the cell potential changes to 2.67 V at 300 K. What is the value of x ?

(Given, $\frac{F}{R} = 11500 \text{ KV}^{-1}$, where F is the Faraday constant and R is the gas constant, $\ln(10) = 2.30$)

(JEE Advance 2018)

Solution The cell reaction.



$$E^{\circ} = 2.70 \text{ V}$$

$$E = E^{\circ} + \frac{0.059}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$2.67 = 2.70 - \frac{2.303 \text{ RT}}{nF} \log x$$

$$2.67 - 2.70 = -\frac{2.303 \times 300}{2} \times \left(\frac{R}{F} \right) \log x$$

$$-0.03 = -\frac{2.303 \times 300}{2 \times 11500} \log x$$

$$\log x = \frac{0.03 \times 2 \times 11500}{2.303 \times 300} = 1$$

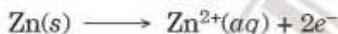
$$\text{or } x = 10.0$$

EQUILIBRIUM CONSTANT FROM NERNST EQUATION

The e.m.f. of the cell may be used to calculate the equilibrium constant for the cell reaction. At equilibrium, the electrode potentials of the two electrodes become equal so that e.m.f. of the cell is zero. Consider the following redox reaction :

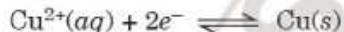


(i) The reaction taking place in the oxidation half cell is



As the reaction progresses the concentration of Zn^{2+} ions in the solution increases and consequently its reduction potential increases.

(ii) The reaction taking place in the reduction half cell is



As the reaction progresses, there is a decrease in the concentration of Cu^{2+} ions and consequently the reduction potential of copper electrode decreases with passage of time.

Thus, the reduction potential of anode (oxidation half cell) increases whereas reduction potential of the cathode (reduction half cell) decreases with the progress of the reaction. The change in reduction potentials of the two electrodes with progress of the reaction are graphically shown in Fig. 14. Ultimately a stage is reached when the reduction potentials of the two electrodes become equal and have the same value. The e.m.f. of the cell becomes zero and the reaction stops. Under these conditions, the electrochemical cell is said to **have attained equilibrium value**.

Let us assume that the concentrations of $\text{Zn}^{2+}(aq)$ and $\text{Cu}^{2+}(aq)$ are equilibrium concentrations and the equilibrium constant, K_c is:

$$K_c = \frac{[\text{Zn}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]} \quad \because [\text{Zn}(s)] = 1 \text{ and } [\text{Cu}(s)] = 1$$

The Nernst equation for the above reaction is :

$$E_{\text{cell}}^\ominus = E_{\text{cell}}^\ominus - \frac{2.303 RT}{2F} \log \frac{[\text{Zn}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]}$$

At equilibrium,

$E_{\text{cell}}^\ominus = 0$ so that the above equation becomes

$$\text{or} \quad E_{\text{cell}}^\ominus = \frac{2.303 RT}{2F} \log \frac{[\text{Zn}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]}$$

$$\text{or} \quad E_{\text{cell}}^\ominus = \frac{2.303 RT}{2F} \log K_c$$

$$\text{where} \quad K_c = \frac{[\text{Zn}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]} \quad \text{At 298 K,}$$

$$E_{\text{cell}}^\ominus = \frac{0.059}{n} \log K_c \quad \text{at 298 K}$$

$$\text{or} \quad \log K_c = \frac{n E_{\text{cell}}^\ominus}{0.059} \quad \text{at 298 K}$$

In general,

$$E_{\text{cell}}^\ominus = \frac{2.303 RT}{nF} \log K_c$$

Significance of K_c . The value of K_c gives the extent of the cell reaction. If the value of K_c is large, the reaction proceeds to larger extent.

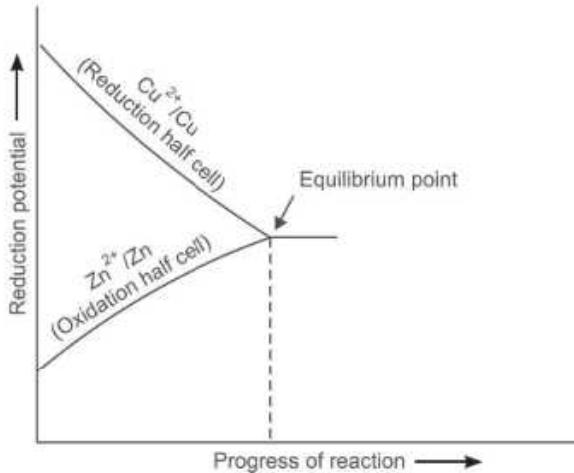


Fig. 14. Change in reduction potential of the electrodes with the progress of the reaction.

Important Note

It may be noted that the expression for equilibrium involves E_{cell}^\ominus and not E_{cell} because E_{cell} at equilibrium is zero.

SOLVED EXAMPLES

Example 39.

Calculate the equilibrium constant for the reaction at 298 K



Given that $E^\ominus_{(Ag^+|Ag)} = 0.80\text{ V}$ and $E^\ominus_{(Cu^{2+}|Cu)} = 0.34\text{ V}$.

N.C.E.R.T. (Kolkata S.B. 2016)

Solution : E^\ominus_{cell} is related to equilibrium constant K_c at 298 K as :

$$E^\ominus_{cell} = \frac{0.059}{n} \log K_c \quad \text{or} \quad \log K_c = \frac{nE^\ominus_{cell}}{0.059}$$

$$\begin{aligned} E^\ominus_{cell} &= E^\ominus_{(Ag^+|Ag)} - E^\ominus_{(Cu^{2+}|Cu)} \\ &= 0.80 - 0.34 = 0.46\text{ V} \end{aligned}$$

$$\text{or} \quad \log K_c = \frac{2 \times 0.46}{0.059} = 15.59$$

$$\therefore K_c = 3.92 \times 10^{15}.$$

Example 40.

Calculate the value of equilibrium constant for the following cell reaction :



Given that $E^\ominus_{cell} = 0.16\text{ V}$. Comment on the reaction.

Solution : E^\ominus_{cell} is related to equilibrium constant, K_c as :

$$E^\ominus_{cell} = \frac{0.059}{n} \log K_c \quad \text{or} \quad \log K_c = \frac{nE^\ominus_{cell}}{0.059}$$

In this reaction, four electrons are transferred so that $n = 4$

$$\log K_c = \frac{4 \times 0.16\text{ V}}{0.059\text{ V}} = 10.847$$

$$K_c = 7.03 \times 10^{10}.$$

The value of equilibrium constant shows that the equilibrium position lies far to the right and therefore, large amount of products are formed.

Practice Problems

41. Calculate the equilibrium constant for the reaction,



if $E^\ominus_{cell} = 0.235\text{ V}$.

42. Calculate K_c for the reaction :



at 298 K if E^\ominus_{cell} is 0.320 V .

43. Calculate at $25^\circ C$, the equilibrium constant for the reaction:



Given that $E^\ominus_{(Fe^{3+}|Fe^{2+})} = 0.771\text{ V}$, $E^\ominus_{(Sn^{4+}|Sn^{2+})} = 0.150\text{ V}$.

44. For a cell reaction :



the equilibrium constant is 1×10^4 . Calculate E^\ominus_{cell} .

45. Calculate the equilibrium constant for the reaction :



If $E^\ominus_{(Cd^{2+}|Cd)} = -0.403\text{ V}$ and

$E^\ominus_{(Zn^{2+}|Zn)} = -0.763\text{ V}$

(CBSE Sample Paper 2007)

Answers to Practice Problems

41. 9.25×10^7 .

42. 7.04×10^{10} .

43. 1.0×10^{21} .

44. 0.118 V .

45. 1.596×10^{12} .

Hints & Solutions on page 74

ELECTROCHEMICAL CELL AND GIBBS ENERGY OF THE REACTION

In electrochemical cells, the chemical energy is converted into electrical energy. The cell potential is related to Gibbs energy change. In an electrochemical cell, the system does work by transferring electrical energy through an electric circuit. Electrical work done in one second is equal to the electrical potential multiplied by the total charge passed. We know that $\Delta_r G$ for a reaction is a measure of the maximum useful work that can be obtained from a chemical reaction. We may write

$$\Delta_r G = \text{maximum work}$$

For a reaction, occurring in an electrochemical cell whose electrodes differ in a potential by E_{cell} , the work done when amount of charge nF is pushed along by the potential of the cell is given by $nF E_{cell}$ so that

$$\text{Maximum work} = nF E_{cell}$$

Relationship between Cell Potential, Gibbs Energy and Equilibrium Constant

The relation between cell potential (E_{cell}^\ominus), Gibbs energy change (ΔG^\ominus) and equilibrium constant can be easily understood as:

$$\Delta G^\ominus = -nF E_{cell}^\ominus$$

$$\text{But } E_{cell}^\ominus = \frac{2.303}{nF} RT \log K_c$$

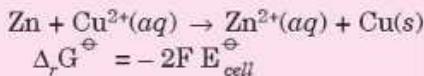
$$\therefore \Delta G^\ominus = -nF \times \frac{2.303}{nF} RT \log K_c \\ = -2.303 RT \log K_c$$

$$\text{or } = -RT \ln K_c \\ (2.303 \log X = \ln X)$$

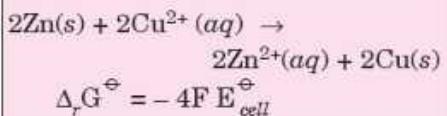
So, if we know the standard free energy change or e.m.f. of the cell, equilibrium constant can be calculated.

Important Note

It may be noted that E^\ominus is an intensive property but $\Delta_r G^\ominus$ is an extensive property and the value depends upon n . For example, for the reaction :



But when we write the reaction as:



where F is the Faraday constant (the charge on one mole of electrons) and n is the number of moles of electrons transferred in them. When voltaic cell operates, work is done on the surroundings, as electrical energy flows through the external circuit. Such work by convention is taken as negative.

Thus,

$$\Delta_r G^\ominus = w_{max} = -nF E_{cell}^\ominus$$

In order to compare cell voltage, we use standard cell potential, E_{cell}^\ominus . Therefore,

$$\Delta_r G^\ominus = -nF E_{cell}^\ominus$$

where $\Delta_r G^\ominus$ is the standard Gibbs energy for the reaction.

If the activity of all the reacting species is unity, then $E = E^\ominus$ and we have

$$\Delta_r G^\ominus = -nF E^\ominus$$

Thus, from the measurement of E^\ominus we can calculate an important thermodynamic property. From the temperature dependence of E^\ominus we can also calculate $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$.

From the standard Gibbs energy, we can also calculate equilibrium constant by the equation :

$$\Delta_r G^\ominus = -RT \ln K$$

Significance. The above equation helps us to predict the feasibility of the cell reaction. For a cell reaction to be spontaneous, $\Delta_r G$ must be negative. This means that E must be positive for a spontaneous cell reaction.

Summary of relationship among E_{cell}° , ΔG° and K and spontaneity of a redox reaction

E_{cell}°	ΔG°	K	Redox reaction
Positive	-ve	> 1	favours formation of products
0	0	= 1	reactants and products are equally favoured
Negative	+ve	< 1	favours formation of reactants

SOLVED EXAMPLES

Example 41.

Calculate $\Delta_r G^\circ$ for the reaction:



Given $E_{cell}^\circ = 2.71 \text{ V}$, $1 F = 96500 \text{ C mol}^{-1}$ (A.I.S.B. 2014)

Solution. $\Delta_r G^\circ = -nF E_{cell}^\circ$

$$E_{cell}^\circ = 2.71 \text{ V}, 1 \text{ F} = 96500 \text{ C mol}^{-1}, n = 2$$

$$\Delta_r G^\circ = -2 \times 96500 \text{ C mol}^{-1} \times 2.71 \text{ V} \\ = -523030 \text{ J mol}^{-1} \quad (1 \text{ CV} = 1 \text{ J})$$

$$\text{or } = -523.030 \text{ kJ mol}^{-1}$$

Example 42.

Calculate the maximum work that can be obtained from the Daniell cell :



Given that $E_{(Zn^{2+}/Zn)}^\ominus = -0.76 \text{ V}$ and

$E_{(Cu^{2+}/Cu)}^\ominus = 0.34 \text{ V}$. (Mizoram S.B. 2013, 2018)

Solution : The maximum work that can be obtained from a cell is equal to free energy change for the cell reaction.



$$E_{cell}^\ominus = E^\ominus(\text{cathode}) - E^\ominus(\text{anode}) \\ = E^\ominus(\text{Cu}^{2+}/\text{Cu}) - E^\ominus(\text{Zn}^{2+}/\text{Zn}) \\ = 0.34 - (-0.76) = 1.10 \text{ V}$$

$$\text{Now, } \Delta G^\ominus = -nF E_{cell}^\ominus$$

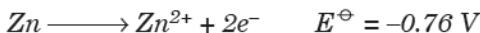
$$E_{cell}^\ominus = 1.10 \text{ V}, n = 2, F = 96500 \text{ C}$$

$$\therefore \Delta G^\ominus = -(2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (1.10 \text{ V}) \\ = -212,300 \text{ CV} \quad (1 \text{ J} = 1 \text{ C} \times \text{V}) \\ = -212,300 \text{ J} \quad \text{or} \quad -212.3 \text{ kJ.}$$

Thus, 212.3 kJ is the maximum work that can be obtained by the operation of this type of cell.

Example 43.

The zinc / silver oxide cell is used in hearing aids and electric watches.



(a) Which is oxidised and which is reduced?

(b) Find E^\ominus of the cell and ΔG^\ominus in joules.

(CBSE Sample Paper 2011)

Solution : (a) Zn is oxidised and Ag_2O is reduced.

$$(b) \quad E_{\text{cell}}^\ominus = E_{(\text{cathode})}^\ominus - E_{(\text{anode})}^\ominus$$

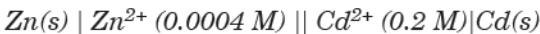
$$\begin{aligned} E_{\text{cell}}^\ominus &= E_{(\text{Ag}_2\text{O} | \text{Ag})}^\ominus - E_{(\text{Zn}^{2+} | \text{Zn})}^\ominus \\ &= 0.344 - (-0.76) = 1.104 \text{ V} \end{aligned}$$

$$\text{Now, } n = 2 \text{ mol, } F = 96500 \text{ C mol}^{-1}, E_{\text{cell}}^\ominus = 1.104 \text{ V}$$

$$\begin{aligned} \therefore \Delta G^\ominus &= -nF E_{\text{cell}}^\ominus \\ &= -(2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (1.104 \text{ V}) \\ &= -213072 \text{ CV} \quad (1 \text{ CV} = 1 \text{ J}) \\ &= -213072 \text{ J} \quad \text{or} = -2.13 \times 10^2 \text{ kJ.} \end{aligned}$$

Example 44.

Calculate the cell emf and ΔG for the cell reaction at 25°C for the cell :



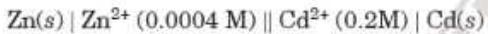
E^\ominus values at 25°C : $\text{Zn}^{2+} | \text{Zn} = -0.763 \text{ V}$;

$\text{Cd}^{2+} | \text{Cd} = -0.403 \text{ V}$

$F = 96500 \text{ C, } R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

(D.S.B. 2000, Hr. S.B. 2005, Pb.S.B. 2013)

Solution : Cell is



$$\begin{aligned} E_{\text{cell}}^\ominus &= E_{(\text{Cd}^{2+} | \text{Cd})}^\ominus - E_{(\text{Zn}^{2+} | \text{Zn})}^\ominus \\ &= -0.403 - (-0.763) = 0.36 \text{ V} \end{aligned}$$

According to Nernst equation,

$$\begin{aligned} E &= E^\ominus - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]} \\ [\text{Zn}^{2+}] &= 0.0004 \text{ M, } [\text{Cd}^{2+}] = 0.2 \text{ M} \\ E &= 0.36 - \frac{0.059}{2} \log \frac{0.0004}{0.2} \\ &= 0.36 - \frac{0.059}{2} \log 2 \times 10^{-3} \\ &= 0.36 - \frac{0.059}{2} \times (-2.6990) \\ &= 0.36 + 0.08 = 0.44 \text{ V} \end{aligned}$$

Cell emf = 0.44 V

Now $\Delta G = -nFE$

$n = 2 \text{ mol, } F = 96500 \text{ C, } E = 0.44 \text{ V}$

$\Delta G = -2 \times 96500 \times 0.44 \text{ CV}$

= -84020 CV = -84.020 kJ.

Example 45.

The ΔG^\ominus for the Daniell cell has been found to be -212.3 kJ at 25°C . Calculate the equilibrium constant for the cell reaction.

Solution : $\Delta G^\ominus = -RT \ln K_c$

Here $\Delta G^\ominus = -212.3 \text{ kJ} = -212300 \text{ J, } T = 298 \text{ K,}$

$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

$$-212300 \text{ J} = -(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \ln K_c$$

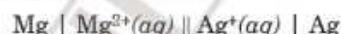
$$\text{or} \quad \ln K_c = \frac{212300}{8.314 \times 298} = 85.69$$

$$\text{or} \quad K_c = 1.64 \times 10^{37}.$$

Example 46.

For the cell, $\text{Mg} | \text{Mg}^{2+} (\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}$, calculate the equilibrium constant at 25°C and also the maximum work that can be obtained by operating the cell. $E^\ominus_{(\text{Mg}^{2+} | \text{Mg})} = -2.37 \text{ V}$ and $E^\ominus_{(\text{Ag}^+ | \text{Ag})} = +0.80 \text{ V}$.

Solution : The cell is :



The cell reaction is :



Calculation of E_{cell}^\ominus

$$\begin{aligned} E_{\text{cell}}^\ominus &= E_{(\text{cathode})}^\ominus - E_{(\text{anode})}^\ominus \\ &= E^\ominus_{(\text{Ag}^+ | \text{Ag})} - E^\ominus_{(\text{Mg}^{2+} | \text{Mg})} \\ &= 0.80 - (-2.37) = 3.17 \text{ V.} \end{aligned}$$

Calculation of equilibrium constant

$$\log K_c = \frac{nE_{\text{cell}}^\ominus}{0.059} \text{ at } 298 \text{ K}$$

$$n = 2, E_{\text{cell}}^\ominus = 3.17 \text{ V}$$

$$\log K_c = \frac{2 \times 3017}{0.059} = 107.457$$

$$K_c = 2.56 \times 10^{107}$$

Calculation of maximum work that can be obtained from the cell. The maximum work obtained is equal to ΔG^\ominus so that

$$\Delta G^\ominus = -nF E_{\text{cell}}^\ominus$$

$$n = 2, F = 96500 \text{ C, } E_{\text{cell}}^\ominus = 3.17 \text{ V}$$

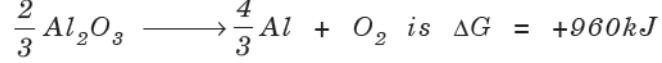
$$\begin{aligned} \therefore \Delta G^\ominus &= -2 \times (96500 \text{ C}) \times (3.17 \text{ V}) \\ &= -611800 \text{ CV} = -611810 \text{ J} \end{aligned}$$

$$(1 \text{ CV} = 1 \text{ J})$$

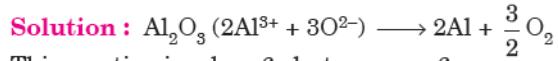
\therefore Maximum work obtained = 611.8 kJ.

Example 47.

Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C . The free energy change for the decomposition reaction :



($F = 96500 \text{ C mol}^{-1}$) (D.S.B. 2002)



This reaction involves 6 electrons, $n = 6$

$$\therefore \frac{2}{3} \text{Al}_2\text{O}_3 \longrightarrow \frac{4}{3} \text{Al} + \text{O}_2 ; n = \frac{6 \times 2}{3} = 4e^-$$

$$\Delta G = -nFE$$

$$\Delta G = 960 \times 10^3 \text{ J, } n = 4, F = 96500 \text{ C mol}^{-1}$$

$$\therefore 960 \times 10^3 = -4 \times 96500 \times E$$

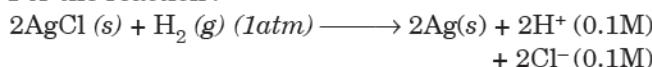
$$\text{or } E = -\frac{960 \times 10^3}{4 \times 96500} = -2.487 \text{ V}$$

\therefore Minimum potential difference needed to reduce

$$\text{Al}_2\text{O}_3 = 2.487 \text{ V.}$$

Example 48.

For the reaction :



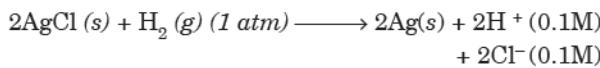
$$\Delta G^\circ = -43600 \text{ J at } 25^\circ\text{C}$$

Calculate the *e.m.f.* of the cell. (A.I.S.B 2018)

Solution : $\Delta G^\circ = -nFE_{\text{cell}}^\circ$

$$-43600 = -2 \times 96500 \times E_{\text{cell}}^\circ$$

$$E_{\text{cell}}^\circ = \frac{43600}{2 \times 96500} = 0.226 \text{ V}$$



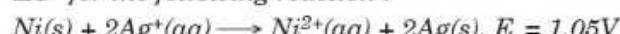
$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{[\text{H}^+]^2 [\text{Cl}^-]^2}{[\text{H}_2(\text{g})]}$$

$$= 0.226 - 0.0295 \log \frac{(0.1)^2 \times (0.1)^2}{1}$$

$$= 0.226 - 0.0295 \times \log 10^{-4}$$

Example 49.

Determine the values of equilibrium constant (K_c) and ΔG° for the following reaction :



($1F = 96500 \text{ C mol}^{-1}$) (D.S.B. 2011)

Solution : $\Delta G^\circ = -nFE_{\text{cell}}^\circ$

$$n = 2, E_{\text{cell}}^\circ = 1.05 \text{ V}, F = 96500 \text{ C mol}^{-1}$$

$$\therefore \Delta G^\circ = -(2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (1.05 \text{ V})$$

$$= -202650 \text{ CV}$$

$$= -202.650 \text{ kJ} \quad (\text{CV} = \text{J})$$

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

$$\ln K_c = -\frac{\Delta G^\circ}{RT} = -\frac{-202.650 \times 10^3}{8.314 \times 298} = 81.79$$

$$K_c = 3.32 \times 10^{35}.$$

Practice Problems

46. Calculate ΔG^\ominus and the equilibrium constant for the cell reaction,



Given that $E^\ominus_{(\text{Cl}_2, \text{Cl}^-)} = 1.36 \text{ V}$, $E^\ominus_{(\text{I}_2, \text{I}^-)} = 0.536 \text{ V}$.

47. The cell in which the following reaction occurs :



has $E_{\text{cell}}^\ominus = 0.236 \text{ V}$ at 298 K . Calculate the standard Gibbs energy of the cell reaction. (Given : $1 \text{ F} = 96500 \text{ C/mol}$) (A.I.S.B. 2017)

48. Calculate ΔG^\ominus and E_{cell}° for the cell



Given that $E^\ominus_{(\text{Al}^{3+} | \text{Al})} = -1.66 \text{ V}$ and $E^\ominus_{(\text{Fe}^{2+} | \text{Fe})} = -0.44 \text{ V}$.

49. Calculate the standard cell potential of the galvanic cell in which the following reaction takes place :



Also calculate the $\Delta_r G^\ominus$ value of the reaction.

[Given $E^\ominus_{(\text{Cr}^{3+} | \text{Cr})} = -0.74 \text{ V}$, $E^\ominus_{(\text{Cd}^{2+} | \text{Cd})} = -0.40 \text{ V}$ and $F = 96500 \text{ C mol}^{-1}$]

(A.I.S.B. 2007)

50. Write the Nernst equation and calculate the value of ΔG^\ominus for the galvanic cell :



Given $E^\ominus_{\text{Cu}^{2+} | \text{Cu}} = 0.34 \text{ V}$, $E^\ominus_{\text{Ag}^+ | \text{Ag}} = 0.80 \text{ V}$

(Hr. S.B. 2005)

Answers to Practice Problems

46. -150.0 kJ , 7.35×10^{27} .

47. $-45.548 \text{ kJ mol}^{-1}$.

48. 1.209 V , -706.38 kJ .

49. 0.34 V , $-196.86 \text{ kJ mol}^{-1}$.

50. -48.250 kJ .

Hints & Solutions on page 74

Advanced Level

PROBLEMS

Accelerate Your Potential
(for JEE Advance)

Problem 9. For the cell reaction :


$$E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.140, E^\circ_{\text{Pb}^{2+}/\text{Pb}} = -0.126 \text{ V}$$

Calculate the ratio of concentration of Pb^{2+} to Sn^{2+} ion at which the cell reaction be reversed.

Solution For the cell,

$$\begin{aligned} E^\circ &= E^\circ_{\text{Pb}^{2+}/\text{Pb}} - E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.126 - (-0.140) \\ &= 0.014 \text{ V} \end{aligned}$$

Applying Nernst equation

$$\begin{aligned} E &= E^\circ - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} \\ &= 0.014 + \frac{0.059}{2} \log \frac{[\text{Pb}^{2+}]}{[\text{Sn}^{2+}]} \end{aligned}$$

At equilibrium, $E = 0$

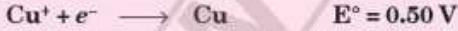
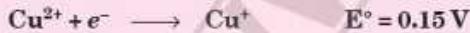
$$\therefore 0.014 + \frac{0.059}{2} \log \frac{[\text{Pb}^{2+}]}{[\text{Sn}^{2+}]} = 0$$

$$\text{or } \log \frac{[\text{Pb}^{2+}]}{[\text{Sn}^{2+}]} = -\frac{0.014 \times 2}{0.059} = -0.474$$

$$\therefore \frac{[\text{Pb}^{2+}]}{[\text{Sn}^{2+}]} = \text{antilog}(-0.474) = 0.336$$

Thus, the cell reaction will occur till $\frac{[\text{Pb}^{2+}]}{[\text{Sn}^{2+}]}$ is more than 0.336 V.

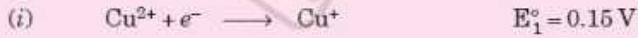
When $\frac{[\text{Pb}^{2+}]}{[\text{Sn}^{2+}]}$ becomes less than 0.336 V, E_{cell} will become negative and the reaction will be reversed.

Problem 10. The reduction potential for the two half cell reactions are:


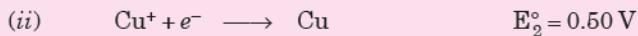
Calculate reduction potential for the following reaction:



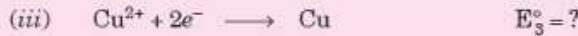
Solution This can be solved in terms of their free energy changes.



$$\Delta G^\circ_1 = -1 \times F \times 0.15 = -0.15 \text{ F}$$



$$\Delta G^\circ_2 = -1 \times F \times 0.50 = -0.50 \text{ F}$$



$$\Delta G^\circ_3 = -2 \times F \times E^\circ_3 = -2E^\circ_3 \text{ F}$$

$$\text{Now } \Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2$$

$$-2E^\circ_3 \text{ F} = -0.15 \text{ F} - 0.50 \text{ F} = -0.65 \text{ F}$$

$$\therefore E^\circ_3 = \frac{0.65 \text{ F}}{2 \text{ F}} = 0.325 \text{ V}$$

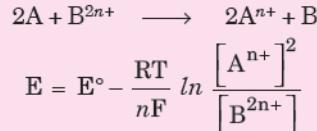
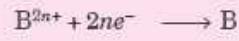
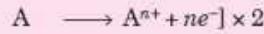
Problem 11. Consider an electrochemical cell :

$A(s) | A^{n+}(aq, 2M) \parallel B^{2n+}(aq, 1M) | B(s)$. The value of ΔH° for the cell reaction is twice that of ΔG° at 300 K. Calculate ΔS° (in $\text{JK}^{-1} \text{ mol}^{-1}$) of the cell per mole of B formed at 300 K if the e.m.f. of the cell is zero.

(Given: $\ln(2) = 0.7$, R (universal gas constant) = $8.3 \text{ JK}^{-1} \text{ mol}^{-1}$, H, S and G are enthalpy, entropy and Gibbs energy, respectively).

(JEE Advance 2018)

Solution



$$E = E^\circ - \frac{RT}{nF} \ln(2)^2$$

$$\text{or } 0 = E^\circ - \frac{RT}{2nF} \ln 4$$

$$E^\circ = \frac{RT}{2nF} \ln 4$$

$$\Delta G^\circ = -2nFE^\circ = \frac{-2nF RT}{2nF} \ln 4$$

$$= -RT \ln 4$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 2\Delta G^\circ - T\Delta S^\circ$$

$$T\Delta S^\circ = \Delta G^\circ$$

$$\Delta S^\circ = \frac{\Delta G^\circ}{T} = -\frac{RT}{T} \ln 4 = -R \ln 4 = -R \times 2 \ln 2$$

$$\therefore \Delta S^\circ = -8.3 \times 2 \times 0.7$$

$$= -11.62 \text{ JK}^{-1} \text{ mol}^{-1}$$

ELECTROLYTIC CELLS AND ELECTROLYSIS

Electrolysis is a *process of decomposition of an electrolyte by the passage of electricity through its aqueous solution or molten (fused) state of electric current.*

The cells used to carry out electrolysis are electrolytic cells.

Process of electrolysis

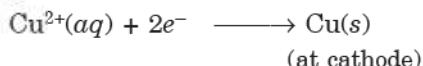
The process of electrolysis is carried out by taking the solution of an electrolyte in a suitable vessel. The vessel is called **electrolytic tank** (Fig. 15.) It is made up of either glass or of a material which is a bad conductor of electricity. Two metallic rods or plates are suspended in the electrolytic solution. These are connected to the terminal of a battery with the help of metallic wires. These metallic rods or plates allow the passage of current and are called **electrodes**. The electrode connected to the positive terminal of the battery is called **anode** while the electrode connected to the negative terminal of the battery is called **cathode**.

When an electrolyte is dissolved in water, it splits up into negative and positive ions. The positively charged ions are called **cations** and negatively charged ions are called **anions**. On passing electric current through the solution, the ions are attracted by the oppositely charged electrodes. As a result, cations move towards cathode while anions move towards anode. This movement of ions in solution is known as **electrolytic or ionic conduction** and constitutes flow of current through the solution.

The anions on reaching the anode give up their electrons (which flow out of the solution). On the other hand, cations take up the electrons from the cathode. Therefore, cations and anions get discharged at the respective electrodes and are converted to neutral particles. This is known as **primary change**. The primary products may be collected as such or they undergo further changes to form molecules or compounds. These are called secondary products and the change is known as **secondary change**.

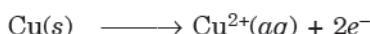
The process of electrolysis was explained by the theory of ionisation. According to ionic theory, the electrolytes are present as ions in solution and the function of electricity is only to direct these ions to their respective electrodes. The electrolytes can be electrolysed only in the dissolved or molten state.

One of the simplest electrolytic cell consists of two copper rods dipping in an aqueous solution of copper sulphate. When electric current (DC voltage) is applied to the two electrodes, then Cu^{2+} ions discharge at the cathode (negatively charged electrode) and the following reaction takes place :



Copper metal is deposited at the cathode.

At the anode, copper is converted to Cu^{2+} ions by the reaction :



Thus, copper is dissolved at the anode. In terms of oxidation and reduction, we can say that copper is oxidised at anode while it is reduced at cathode. This is the basis of an important industrial process in which impure copper is converted into copper of high purity. Many other metals such as Na, Mg, Al, etc are also produced on a large scale by electrochemical reduction of their respective cations where no suitable chemical reducing agents are available for the reduction. This is one of the important method in metallurgy.

For example, sodium and magnesium metals are produced by the electrolysis of their fused chlorides and aluminium is produced by the electrolysis of aluminium oxide in the presence of cryolite (Na_3AlF_6).

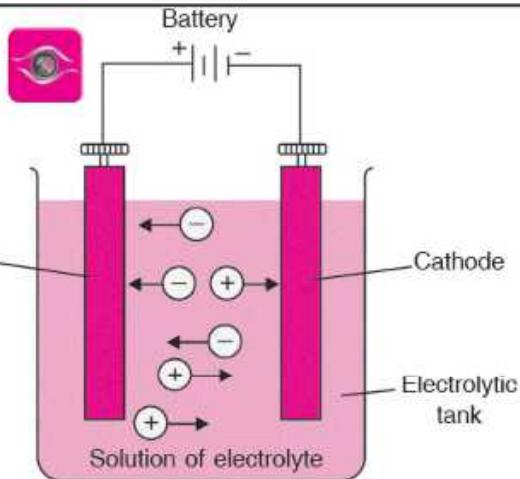


Fig. 15. Process of electrolysis.

Quantitative Aspects of Electrolysis

Michael Faraday performed a large number of experiments during 1833–34 on electrolysis and summarized the results of his experiments in the form of two laws known as Faraday's laws of electrolysis.

Faraday's laws of electrolysis

1. Faraday's first law of electrolysis. It states that

the amount of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte (solution or melt).

The amount of any substance obtained gives the amount of chemical reaction which occurs at any electrode during electrolysis.

Thus, if w gram of the substance is deposited on passing Q coulombs of electricity, then

$$w \propto Q \quad \text{or} \quad w = ZQ$$

where Z is a constant of proportionality and is called *electrochemical equivalent*.

If a current of I amperes is passed for t seconds, then

$$Q = I \times t$$

so that

$$w = Z \times Q = Z \times I \times t$$

Now, if

$$Q = 1 \text{ coulomb}$$

or

$I = 1 \text{ ampere}$ and $t = 1 \text{ second}$, then

$$w = Z \times 1 \times 1 \quad \text{or} \quad w = Z$$

Hence *electrochemical equivalent* of a substance may be defined

as the mass of the substance deposited when a current of one ampere is passed for one second, i.e., a quantity of electricity equal to one coulomb is passed.

Faraday's second law of electrolysis. It states that

when same quantity of electricity is passed through different electrolytic solutions connected in series, the weights of the substances produced at the electrodes are directly proportional to their chemical equivalent weights.

For example, when same current is passed through two electrolytic solutions, containing copper sulphate (CuSO_4) and silver nitrate (AgNO_3) connected in series, the weights of copper and silver deposited are :

$$\frac{\text{Weight of Cu deposited}}{\text{Weight of Ag deposited}} = \frac{\text{Eq. wt. of Cu}}{\text{Eq. wt. of Ag}}$$

However, in modern terms, the term *equivalent weight* is not used.

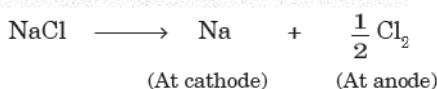
The Faraday's laws of electrolysis may be stated in terms of moles of electrons exchanged during an electrochemical change.

According to **Faraday's law**, the amount of chemical change occurred i.e., the moles of substances deposited or liberated is proportional to the number of moles of electrons exchanged during the oxidation-reduction reactions that occur.

Therefore, by knowing the amount of electricity passed, we can easily calculate the number of moles of products formed from the appropriate electrode reaction. From the moles of the products formed, we can calculate the masses of the products or their volumes if they are gases.

Therefore, the amount of electricity needed or amount of products formed can be calculated from the equation for the appropriate electrode reaction.

For example, during the passage of electric current through molten NaCl , sodium gets deposited at cathode and chlorine is liberated at anode.



During electrolysis, sodium ions move towards cathode, accept electrons and get deposited as :



It is clear that the passage of one electron produces one sodium atom. *The passage of 1 mol of electrons produce 1 mol of sodium (or 23 g).*

The **chemical equivalent weight** is atomic mass divided by the number of electrons required to reduce the cation.

Important Note

During Faraday's times, there were no devices available to supply constant current. Therefore, the quantity of electricity passed was measured by using an apparatus called **coulometer**. Generally, copper and silver coulometers were used and the quantity of electricity passed was calculated from the amount of copper or silver deposited or consumed in the coulometer. From the weight, the quantity of electricity passed through the coulometer could be calculated using Faraday's laws of electrolysis. Nowadays coulometers are not used and we have devices which supply constant current and quantity of electricity can be calculated from the formula:

$$Q = I \times t$$

where I is the current in ampere and t is the time in second during which current was passed. The quantity of electricity, Q will be in coulombs.

NOTE

It may be noted that earlier, the term equivalent weight was used. This can be easily correlated to mole ratio. For example, for the above experiment, we can say

$$\frac{\text{Weight of silver}}{\text{Weight of copper}}$$

$$= \frac{\text{Equivalent weight of silver}}{\text{Equivalent weight of copper}}$$

$$\text{and } \frac{\text{Weight of silver}}{\text{Weight of gold}}$$

$$= \frac{\text{Equivalent weight of silver}}{\text{Equivalent weight of copper}}$$

Now, equivalent weight of metal

$$= \frac{\text{Molecular Mass}}{\text{Charge on its ions}}$$

Thus, when 96500 C of electricity (corresponding to 1 mol of electrons) is passed then amounts of silver, copper and gold deposited will be equal to their equivalent weights i.e.,

For 1 mol of electrons or 96500 C of electricity passed.

Silver deposited

$$= 1 \text{ gm equivalent of Ag} = 107.87 \text{ g}$$

or $\equiv 1 \text{ mol}$

Copper deposited

$$= 1 \text{ gm equivalent of Cu} = 31.77 \text{ g}$$

$$= \frac{1 \text{ mol}}{2}$$

Gold deposited = 1 gm equivalent of

$$\text{Au} = 65.66 \text{ g} \equiv \frac{1 \text{ mol}}{3}$$

Similarly, at anode, chloride ions give up electrons and produce Cl atoms as:



It is clear that 2 mol of electrons produce 1 mol of Cl_2 or 1 mol of electrons produce 1/2 mol of Cl_2 (35.5 g).

We know that charge on an electron = $1.602 \times 10^{-19} \text{ C}$

Now 1 mole of electrons = 6.022×10^{23} electrons

$$\therefore \text{Charge on 1 mole of electrons} = 6.022 \times 10^{23} \times 1.602 \times 10^{-19} \text{ C}$$

$$= 96485 \text{ C mol}^{-1}$$

The charge on one mole of electrons is called 1 Faraday, F, in honour of Michael Faraday. Thus,

$$1 \text{F} = 96485 \text{ C} \text{ or approximately } 96500 \text{ C.}$$

Thus, charge on n mol of electrons will be equal to

$$Q = nF$$

Now, the production of 1 mol of sodium or 23.0 g by reduction of sodium ions require 1 mol of electrons. Therefore, amount of charge required,

$$Q = nF = 1 \times 96500 \text{ C} = 96500 \text{ C}$$

Similarly, 1 mol of Cl_2 is obtained by 2 mol of electrons or $2 \times 96500 \text{ C}$ of charge during electrolysis of NaCl. Similarly, in the reaction :

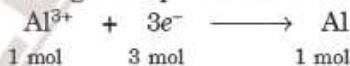


One mole of electrons is required for the reduction of 1 mol of silver ions. Therefore, the quantity of electricity required for reduction of 1 mol of Ag^+ ions is 96500 C or 1 Faraday.

Now, 1 mole of copper will be produced by 2 mol of electrons or $2 \times 96500 \text{ C}$ of charge :



Thus, from the knowledge of moles of electrons required during the electrode reaction, the amount of substance deposited or evolved can be calculated. For example, aluminium gets deposited as :



Thus, 1 mol of Al will be deposited by 3 mol of electrons or 3 Faraday (or $3 \times 96500 \text{ C}$) of electricity.

Similarly, when the same quantity of electricity is passed through different electrolyte solutions, connected in series, the weights of different substances produced at the electrodes can be calculated from the mole ratios of their electrode reactions.

For example, consider an experiment in which same amount of current is passed simultaneously through three aqueous electrolytic solutions connected in series containing aqueous solutions of silver nitrate, copper sulphate and gold chloride as shown in Fig. 16.

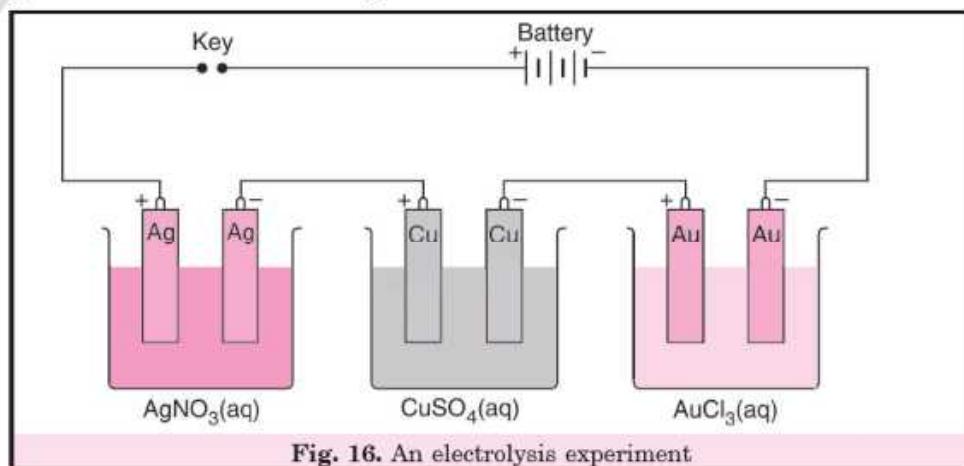


Fig. 16. An electrolysis experiment

When enough current is passed through the cells to deposit 1 mol of silver (107.87 g), it is observed that amount of copper and gold deposited are also in the ratio of their molecular masses. Using the mole ratio of reduction half cell reaction shows that liberation of 1 mol of Ag has required the passage of 1 mol of electrons (or 96500 C of electricity). Simultaneously with the deposition of 1 mol of silver, it is found that 1/2 mol of copper and 1/3 mol of gold have been produced in their respective cells. The formation of these products is explained on the basis of the stoichiometry of the half cell reactions and the passage of 1 mol of electrons through the solutions.



1 mol of Cu is deposited by 2 mol electrons

$$\therefore 1 \text{ mol of electrons deposit} = \frac{1}{2} \text{ mol Cu}$$

Similarly,



∴ 1 mol of Au is deposited by 3 mol electrons

$$\therefore 1 \text{ mol of electrons deposit} = \frac{1}{3} \text{ mol of Au.}$$

Thus, we conclude from these observations :

1 mol of electrons will deposit 1 mol of Ag, $\frac{1}{2}$ mol of Cu and $\frac{1}{3}$ mol of Au.

of Au.

In general, amount of element deposited (in mol)

$$= \frac{\text{No. of moles of electrons}}{\text{No. of charges on ion of the element}}$$

For example, during electrolysis of $\text{CrCl}_3(aq)$, 1 mol of electrons (96500 C of electricity) will deposit:



$$\text{Amount of chromium deposited} = \frac{1}{3} \text{ mol}$$

Similarly, 2 mol of electrons (2×96500 C of electricity) will deposit:

$$\text{Amount of Cr deposited} = \frac{2}{3} \text{ mol.}$$

PRODUCTS OF ELECTROLYSIS

We have seen that during electrolysis, the reactions occurring at the electrodes are oxidation and reduction reactions. Therefore, the products of electrolysis can be predicted on the basis of electrode potentials of different reactions. The products of electrolysis depend on the nature of material being electrolysed and the types of electrodes being used. If the electrode is inert such as gold or platinum, it does not take part in the chemical reaction and acts only as a source or sink for electrons. On the other hand, if the electrode is reactive, it takes part in the electrode reaction. Thus, the products of electrolysis may be different for inert and reactive electrodes.

The products of electrolysis mainly depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials. It may be noted that some electrochemical processes, though feasible, are so slow kinetically that at lower voltages, these do not seem to occur. The slowness of electrode reaction creates electrical resistance at the electrode surface. Therefore, for the occurrence of such reactions (e.g., processes involving liberation of gases) some extra potential or voltage is required than the theoretical value of their standard electrode potential. **This extra voltage required** is called **over voltage**.

Let us discuss some examples :

1. Electrolysis of molten sodium chloride. The molten sodium chloride has Na^+ and Cl^- ions,



During electrolysis, it has been observed that sodium metal is deposited at the cathode while chlorine gas is liberated at the anode. When electric current is passed through molten sodium chloride, the chloride ions are attracted towards anode. These ions give up one electron each to the anode and become chlorine atoms. The chlorine atoms are unstable and combine in pairs to form chlorine molecules.

On the other hand, Na^+ ions move towards the cathode, take up one electron each and become neutral atoms. As a result, sodium metal is obtained at the cathode.

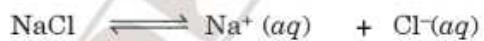
The reactions may be expressed as :



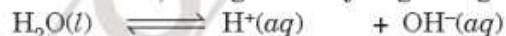
Thus, the **overall reaction** is :



2. Electrolysis of aqueous sodium chloride. In water, sodium chloride ionises as :

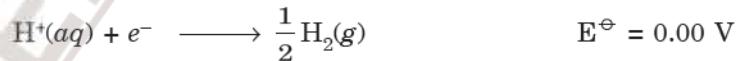


Water also dissociates into ions, though to very slight degree as :

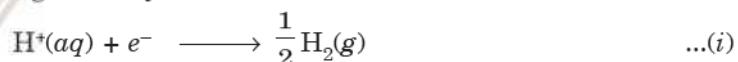


Thus, the aqueous solution of sodium chloride contains Na^+ , H^+ , OH^- and Cl^- ions. When electric current is passed through the solution, Cl_2 gas is evolved at the anode and hydrogen is evolved at the cathode. The resulting solution contains Na^+ and OH^- ions.

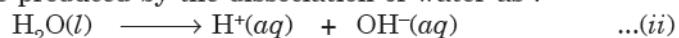
At cathode, there is a competition for reduction between the following reactions:



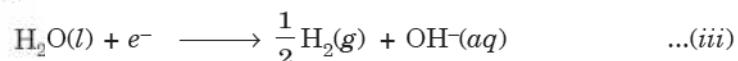
The reaction with higher value of E^\ominus is preferred and therefore, the reaction at the cathode during electrolysis is :



But $\text{H}^+(aq)$ ions are produced by the dissociation of water as :



Therefore, the net reaction at the cathode may be written as the sum of reactions (i) and (ii)



On the other hand, at the anode, the following reactions are possible :



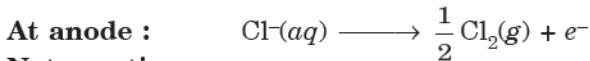
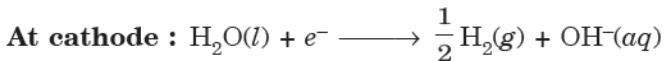
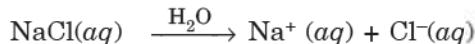
The standard reduction potential of water is slightly less and therefore, it has slightly more chances of getting oxidised. However, in concentrated solution of NaCl , oxidation of chloride ions is preferred than water at anode and therefore, Cl_2 gas is liberated. The unexpected result is due to the fact that sometimes higher voltage is required for electrolysis due to *over voltage*.*

*It has been found experimentally that the actual voltage required for the electrolysis is larger than that calculated from standard electrode potentials. This extra voltage is required because the rate of transfer of electrons at the interface of electrode and solution for both the half reactions is slow. The slowness of the electrode reactions create an electrical resistance at the electrode surface. Therefore, some extra voltage is required to overcome the resistance. This extra voltage required is called **over voltage**. The over voltage for the formation of oxygen is much larger than that required for the formation of Cl_2 . Therefore, the half reaction at anode is oxidation of Cl^- to Cl_2 gas.

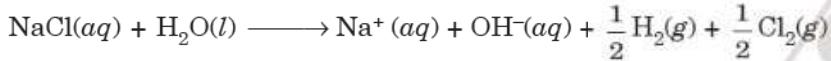
The reaction occurring at anode is :



Thus, the net reactions during the electrolysis of aqueous sodium chloride solution may be summarized as :



Net reaction :



Thus, during the electrolysis of aqueous sodium chloride, H_2 gas is liberated at the cathode and Cl_2 gas is liberated at the anode and the solution contains sodium hydroxide.

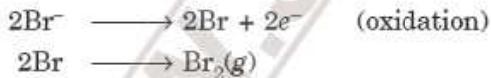
3. Electrolysis of molten lead bromide using platinum electrodes

In the molten state, PbBr_2 exists as

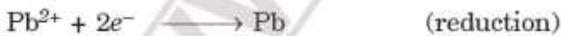


The electrolysis may be carried out by taking solid lead bromide in a silica crucible. Two electrodes of graphite are used (Fig. 17). When a D.C. voltage source is applied, no current is observed. However, when the crucible is heated so that lead bromide melts the current is found to pass. During electrolysis, metallic lead is produced at the cathode while bromine gas is liberated at the anode. When electric current is passed through the molten lead bromide Pb^{2+} ions move towards the cathode while Br^- ions move towards the anode. The following reactions occur at the electrodes :

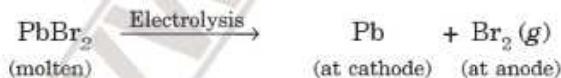
At anode :



At cathode :



Thus, the **overall reaction** is



4. Electrolysis of water. Pure water is a poor conductor of electricity. However, water containing a few drops of acid or alkali becomes good conductor. The electrolysis of water may be carried out by taking some water in an electrolytic cell as shown in Fig. 18. Introduce two graphite electrodes into it. Connect these electrodes through an ammeter to a battery. It is observed that ammeter does not show any deflection. This shows that **water is a bad conductor** of electricity. However, when a few drops of dil. H_2SO_4 are added to water, the ammeter shows deflection and electrolysis starts.

Water is only weakly ionized but in the presence of an acid, its degree of ionization increases. Upon passing the electric current, it dissociates as :

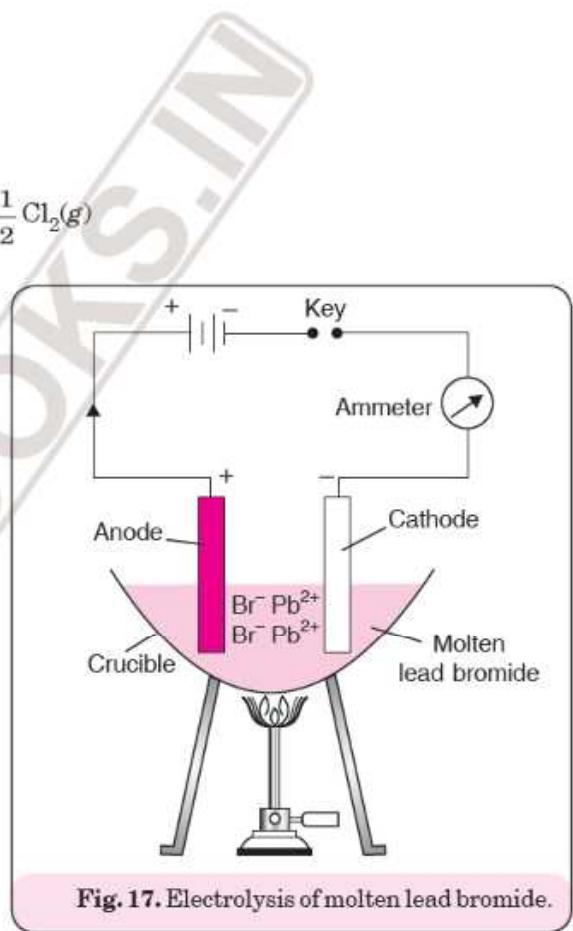
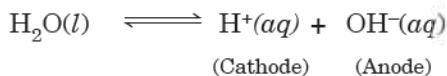


Fig. 17. Electrolysis of molten lead bromide.

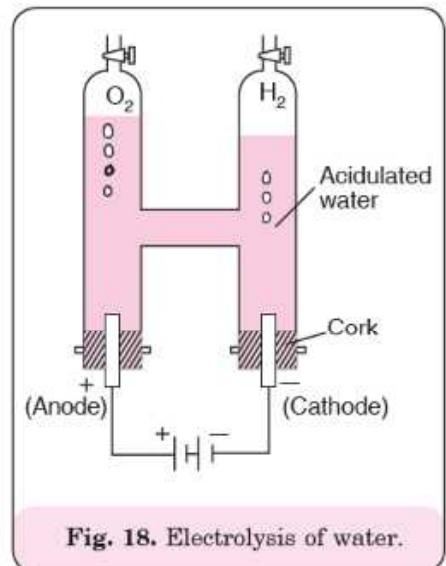
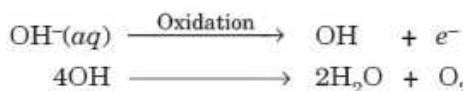


Fig. 18. Electrolysis of water.

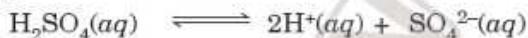
At cathode :



At anode :



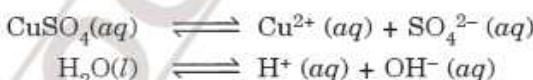
It may be noted that in case we add a few drops of dilute H_2SO_4 to water before carrying electrolysis, the SO_4^{2-} ions will also be formed at the anode along with OH^- ions.



In this case, both OH^- and SO_4^{2-} ions move towards anode. However, SO_4^{2-} ions will not be released since their discharge potential is more as compared to OH^- ions.

The gases oxygen and hydrogen are collected at the anode and cathode respectively. On measuring the volumes, the volume of hydrogen collected is found to be twice the volume of oxygen. This shows that the two elements H and O are present in water in the ratio of 2 : 1 and thus, the formula of the compound is H_2O .

5. Electrolysis of aqueous copper sulphate solution. Copper sulphate and water ionise as

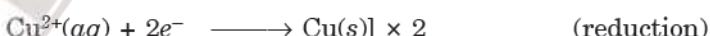


During electrolysis, copper is deposited at the cathode while oxygen is liberated at the anode. The following reactions occur at the electrodes :

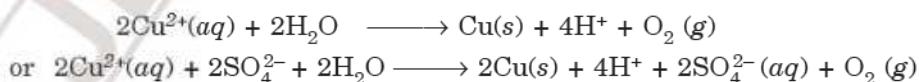
At anode :



At cathode :

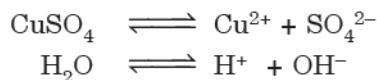


The overall reaction is :



It may be noted here that in the above examples, the electrodes used are those which are not attacked by the ions (for example, platinum). However, if the electrodes are attacked by the ions, then the reactions taking place during electrolysis are different. For example, let us consider the *electrolysis of aqueous solution of CuSO_4 using copper electrodes*.

6. Electrolysis of CuSO_4 using copper electrodes. In the electrolysis, copper sulphate and water ionise as :



At cathode : Cu^{2+} ions are deposited at the cathode.

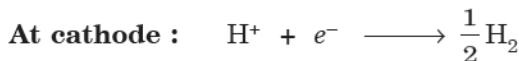


At anode : Unlike electrolysis of CuSO_4 using Pt electrodes, no ions are liberated. On the other hand, anode itself undergoes loss of electrons to form Cu^{2+} ions which go into the solution.



So, the net result of electrolysis is that copper is deposited at the cathode from the solution and an equivalent amount of copper from the anode dissolves into solution as Cu^{2+} ions.

7. Electrolysis of sulphuric acid. During the electrolysis of sulphuric acid, hydrogen is liberated at cathode :



The following two reactions occur at anode :

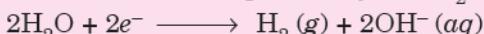


For dilute solution, reaction (i) is preferred and O₂ liberates at anode. But at higher concentration of sulphuric acid, reaction (ii) is preferred and solution of peroxodisulphuric acid (H₂S₂O₈) is obtained.

Thus, when more than one substances are present in an electrolytic cell during electrolysis, we can make the following generalisations :

1. The ion which has higher reduction potential will be reduced first at the cathode. For example,

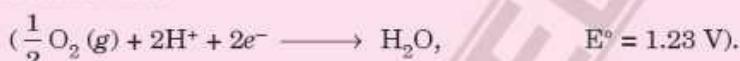
(i) The ions such as Na⁺ (E° = - 2.71 V), Ca²⁺ (E° = - 2.87 V), K⁺ (E° = - 2.93 V), Mg²⁺ (E° = - 2.37 V), Al³⁺ (E° = - 1.66 V) etc. cannot be reduced in aqueous solution as their reduction potentials are less than water (E° = - 0.83 V). Water will be reduced preferably and H₂ will be liberated as:



(ii) The ions such as Cu²⁺ (E° = 0.34 V), Ag⁺ (E° = 0.80 V) have larger reduction potential than water and, therefore, are easily reduced and get deposited at the cathode as Cu and Ag respectively.

2. The ion which has lower reduction potential will be oxidised first at the anode. For example,

(i) Br⁻ (E° = 1.08 V) and I⁻ (E° = 0.77 V) are preferably oxidised to Br₂ and I₂ respectively in aqueous solution because they have lower reduction potentials than water



(ii) F⁻ ion (E° = + 2.87 V) is not oxidised to F₂ in aqueous solution because it has higher reduction potential. In this case, water will be oxidised.

SOLVED EXAMPLES

Example 50.

A solution of CuSO₄ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode ?

N.C.E.R.T. (Pb. S.B. 2012, Meghalaya S.B. 2017)

Solution : Current strength (I) = 1.5 A

$$\text{Time (t)} = 10 \text{ min} = 10 \times 60 = 600 \text{ s}$$

$$\begin{aligned} \text{Quantity of electricity passed} &= I \times t \\ &= (1.5 \text{ A}) \times (600 \text{ s}) \\ &= 900 \text{ C} \quad (\text{A s} = \text{C}) \end{aligned}$$

Copper is deposited as :



$$\begin{aligned} 2 \text{ mol of electrons or } 2 \times 96500 \text{ C of current deposit copper} \\ &= 63.56 \text{ g} \end{aligned}$$

900 C of current will deposit copper

$$\begin{aligned} &= \frac{63.56}{2 \times 96500} \times 900 \\ &= 0.296 \text{ g.} \end{aligned}$$

Example 51.

- (a) How many moles of electrons are required to
(i) reduce 1 mol of MnO₄⁻ to Mn²⁺

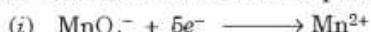
(ii) produce 10.0 g of Al from molten Al₂O₃ ?

(b) How many moles of electrons are given by

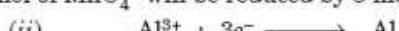
$$(i) 8960 \text{ C} \quad (ii) a \text{ current of } 1.5 \text{ A for } 30 \text{ s}?$$

(c) How many minutes it would take to reduce 0.20 mol of Cu²⁺ to Cu using a current of 10 A.

Solution : (a) Moles of electrons required :



1 mol of MnO₄⁻ will be reduced by 5 mol of electrons



3 mol of electrons are required to produce 1 mol or 27 g of Al

$$\therefore 10 \text{ g of Al will be produced by} = \frac{3}{27} \times 10$$

$$= 1.11 \text{ mol electrons.}$$

$$(b) \quad (i) 96500 \text{ C of electricity} \equiv 1 \text{ mol of electrons}$$

$$8960 \text{ C of electricity} = \frac{1}{96500} \times 8960$$

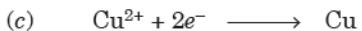
$$= 0.0928 \text{ mol electrons.}$$

(ii) Quantity of electricity,

$$Q = I \times t = 1.5 \times 30 = 45 \text{ C}$$

Now, 96500 C of electricity = 1 mol of electrons

$$\therefore 45 \text{ C of electricity} = \frac{1}{96500} \times 45 \\ = 4.66 \times 10^{-4} \text{ mol electrons.}$$



2 mol of electrons are required to reduce 1 mol of Cu^{2+}

$$\therefore 0.20 \text{ mol of } \text{Cu}^{2+} \text{ will be reduced by } \frac{2}{1} \times 0.20 \\ = 0.40 \text{ mol of electrons}$$

Now, 1 mol of electrons \equiv 96500 C
0.4 mol of electrons $= 96500 \times 0.04 = 38600 \text{ C}$

$$Q = I \times t$$

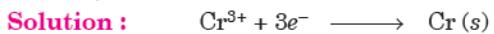
$$38600 = 10 \text{ A} \times t (\text{s})$$

or $t = \frac{38600}{10} = 3860 \text{ s}$

or $= 64.3 \text{ min.}$

Example 52.

Calculate how long it will take to deposit 1.0 g of chromium when a current of 1.25 A flows through a solution of chromium (III) sulphate. (Molar mass of Cr = 52).



3 mol or $3 \times 96500 \text{ C}$ of electricity are needed to deposit 1 mol or 52 g of Cr.

$$52 \text{ g of Cr require current} = 3 \times 96500 \text{ C}$$

$$1 \text{ g of Cr will require current} = \frac{3 \times 96500}{52} \text{ C} \\ = 5567.3 \text{ C}$$

Now, number of coulombs = Current (Ampere) $\times t$ (seconds)

$$\therefore \text{Time (s) required} = \frac{\text{No. of coulombs}}{\text{Current (Ampere)}} \\ = \frac{5567.3 \text{ C}}{1.25 \text{ A}} \\ = 4453.8 \text{ s}$$

or $= 1.24 \text{ hr.}$

Example 53.

How many coulombs are required to deposit 40.5 g of aluminium when the electrode reaction is :



1 mol of Al requires 3 mol of electrons or $3 \times 96500 \text{ C}$

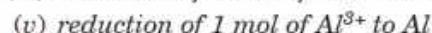
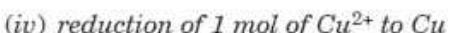
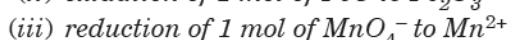
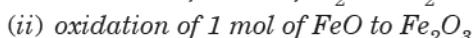
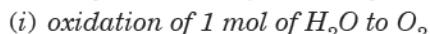
$$1 \text{ mol of Al} = 27 \text{ g}$$

$$27 \text{ g of Al require} = 3 \times 96500 \text{ C}$$

$$40.5 \text{ g of Al require} = \frac{3 \times 96500 \text{ C} \times 40.5}{27} \\ = 434,250 \text{ C.}$$

Example 54.

How many coulombs of electricity are required for



Solution : (i) **Oxidation of H_2O to O_2**



Oxidation of 2 mol of H_2O require $= 4 \times 96500 \text{ C}$

Oxidation of 1 mol of H_2O requires $= 2 \times 96500 \text{ C}$

$$= 1.93 \times 10^5 \text{ C.}$$

(ii) **Oxidation of 1 mol of FeO to Fe_2O_3**



Oxidation of 1 mol of Fe^{2+} require $= 1 \times 96500 \text{ C}$
 $= 96500 \text{ C.}$

(iii) **Reduction of 1 mol of MnO_4^- to Mn^{2+}**



Reduction of 1 mol of MnO_4^- requires $= 5 \times 96500 \text{ C}$
 $= 4.825 \times 10^5 \text{ C.}$

(iv) **Reduction of Cu^{2+} to Cu**



Reduction of 1 mol of Cu^{2+} requires $= 2 \times 96500 \text{ C}$
 $= 1.93 \times 10^5 \text{ C.}$

(v) **Reduction of 1 mol of Al^{3+} to Al**



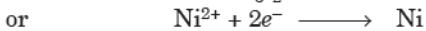
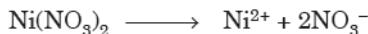
Reduction of 1 mol of Al^{3+} requires $= 3 \times 96500 \text{ C}$
 $= 2.895 \times 10^5 \text{ C.}$

Example 55.

A solution of $\text{Ni}(\text{NO}_3)_2$ was electrolysed between platinum electrodes using a current of 5 amp for 30 min. What is the mass of Ni deposited at the cathode ?

(Pb. S.B. 2012, Meghalaya S.B. 2013)

Solution : The electrolysis of $\text{Ni}(\text{NO}_3)_2$ may be represented as :



Quantity of electricity passed

$$= \text{Current in amperes (I)} \times \text{Time in seconds (t)} \\ = 5.0 \times 30 \times 60 = 9000 \text{ C} (t = 30 \times 60 \text{ sec})$$

2 mol of electrons or $2 \times 96500 \text{ C}$ of current produce 1 mol or 58.5 g of Ni so that $2 \times 96500 \text{ C}$ of electricity deposit

$$\text{Ni} = 58.5 \text{ g}$$

$$9000 \text{ C of electricity deposit Ni} = \frac{58.5 \times 9000}{2 \times 96500} = 2.73 \text{ g.}$$

Example 56.

How many hours does it take to reduce 3 mol of Fe^{3+} to Fe^{2+} with 2.0 A current? ($F = 96500 \text{ C}$)

Solution : Reduction of Fe^{3+} to Fe^{2+}



Reduction of 1 mol of Fe^{3+} requires $= 96500 \text{ C}$

$$\text{Reduction of 3 mol of } \text{Fe}^{3+} \text{ require} = 3 \times 96500 \text{ C} \\ = 2.895 \times 10^5 \text{ C}$$

Now, Quantity of electricity = Current \times Time
 $2.895 \times 10^5 = 2 \times \text{Time}$

$$\therefore \text{Time} = \frac{2.895 \times 10^5}{2} = 1.4475 \times 10^5 \text{ s}$$

$$= \frac{1.4475 \times 10^5}{60 \times 60} = 40.21 \text{ hours.}$$

Example 57.

Three electrolytic cells A, B and C containing electrolytes of zinc sulphate, silver nitrate and copper sulphate respectively were connected in series. A steady current of 1.50 amp was passed through them until 1.45 g of silver were deposited at the cathode of cell B.

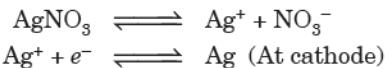
(i) How long did the current flow?

(ii) What weight of copper and zinc get deposited?

(D.S.B. 2008, Assam S.B. 2013, 2017)

Meghalaya S.B. 2014, 2016)

Solution : Cell B contains AgNO_3 and reaction may be represented as :



According to the equation,

1 mol or 108 g of silver is deposited by 96500 C

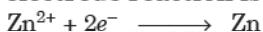
$$\begin{aligned}1.45 \text{ g silver is deposited by} &= \frac{96500 \times 1.45}{108} \\ &= 1295.6 \text{ C.}\end{aligned}$$

Now,

$$\begin{aligned}Q &= I \times t \\ 1295.6 &= 1.5 \times t \\ t &= \frac{1295.6}{1.5} = 863 \text{ s.}\end{aligned}$$

The weights of copper and zinc can be calculated by using Faraday's second law of electrolysis.

In cell A, the electrode reaction is



2 mol of electrons or 2×96500 C of current produce 1 mol or 65.3 g of Zn so that

2×96500 C of electricity deposit Zn = 65.3 g

$$\begin{aligned}1295.6 \text{ C of electricity deposit Zn} &= \frac{65.3}{2 \times 96500} \times 1295.6 \\ &= 0.438 \text{ g.}\end{aligned}$$

In cell C, the electrode reaction is

2 mol of electrons or 2×96500 C of current produce

1 mol or 63.5 g of Cu so that

2×96500 C of current deposit Cu = 63.5 g

$$\begin{aligned}1295.6 \text{ C of current deposit Cu} &= \frac{63.5 \times 1295.6}{2 \times 96500} \\ &= 0.426 \text{ g.}\end{aligned}$$

Example 58.

In the electrolysis of acidulated water, it is desired to obtain hydrogen at the rate of 1cc per second at STP conditions. What should be the current passed?

Solution :



1 mol of H_2 or 22400 cc of H_2 at STP requires = 2×96500 C

$$\therefore 1 \text{cc of } \text{H}_2 \text{ at N.T.P. requires} = \frac{2 \times 96500}{22400} = 8.616 \text{ C}$$

Now,

$$Q = I \times t$$

$$\begin{aligned}I &= \frac{Q}{t} = \frac{8.616}{1 \text{ s}} \\ &= 8.616 \text{ ampere.}\end{aligned}$$

Example 59.

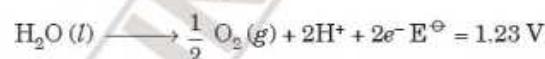
Predict the products of electrolysis of an aqueous solution of CuBr_2 .

Solution : The probable reactions at cathode are :

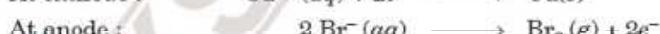
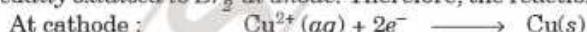
- (i) $\text{Cu}^{2+}(aq) + 2e^- \longrightarrow \text{Cu}(s), E^\ominus = 0.34 \text{ V}$
- (ii) $2\text{H}_2\text{O}(l) + 2e^- \longrightarrow \text{H}_2(g) + 2\text{OH}^-(aq), E^\ominus = -0.83 \text{ V}$

Since the reduction potential of Cu^{2+} ions is higher than that of water, copper will be reduced preferably at cathode.

The probable reactions at anode are :



Since the reduction potential of Br^- is less than water, it will be readily oxidised to Br_2 at anode. Therefore, the reactions are:



Example 60.

Two electrolytic cells containing silver nitrate solution and dilute sulphuric acid solution were connected in series. A steady current of 2.5 amp was passed through them till 1.078 g of silver was deposited.

[$\text{Ag} = 107.8 \text{ g mol}^{-1}, 1F = 96500 \text{ C}]$

(i) How much electricity was consumed?

(ii) What was the weight of oxygen gas liberated?

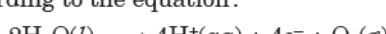
(C.B.S.E. Sample Paper 2011)

Solution : (i) In first cell, silver is deposited at cathode as $\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s)$

107.8 g of Ag require electricity = 96500 C

1.078 g of Ag require electricity = 965 C

(ii) O_2 gas liberated at anode of first cell and second cell according to the equation:



4×96500 C electricity = 1 mol of O_2 at each cell

= 32 g of O_2 at each cell

$965 \text{ C of electricity} = \frac{32}{4 \times 96500} \times 965 = 0.08 \text{ g O}_2$ at each cell

Total amount of O_2 at anode of both cells = $2 \times 0.08 = 0.16 \text{ g.}$

Example 61.

How many moles of mercury will be produced by electrolysing $1.0 \text{ M Hg(NO}_3)_2$ solution with a current of 2.00 A for 3 hours?

[$\text{Hg}(\text{NO}_3)_2 = 200.6 \text{ g mol}^{-1}$]

(A.I.S.B. 2011)

Solution : $\text{Hg}^{2+} + 2e^- \longrightarrow \text{Hg}$

Quantity of electricity passed = $I \times t$ (sec.)

= $2.0 \text{ A} \times 3.0 \times 60 \times 60$

= 21600 C

2×96500 C of electricity produce mercury = 1 mol

21600 C of electricity will produce mercury

$$\begin{aligned}&= \frac{1}{2 \times 96500} \times 21600 \\ &= 0.112 \text{ mol.}\end{aligned}$$

Practice Problems

51. Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of AgNO_3 for 15 minutes.
(Given : Molar mass of Ag = 108 g mol⁻¹, 1F = 96500 C mol⁻¹) (D.S.B. 2017)
52. When a current of 0.75 A is passed through a CuSO_4 solution for 25 min, 0.369 g of copper is deposited. Calculate the atomic mass of copper.
53. How many grams of chlorine can be produced by the electrolysis of molten NaCl with a current of 1.00 A for 15 minutes?
54. How many coulombs of electricity are required for the following processes :
 (i) oxidation of 1 mol of FeO to Fe_2O_3
 (ii) oxidation of 1 mol of H_2O_2 to O_2
 (iii) reduction of 1 mol of F_2 to 2F^- ?
55. The same quantity of electrical charge that deposited 0.583 g of silver was passed through a solution of gold salt and 0.355 g of gold was formed. What is the oxidation state of gold in this salt ?
56. How many hours does it require to reduce 3 mol of Fe^{3+} to Fe^{2+} by passing 2.00 A current ?
57. What current in amperes is required to produce 50.0 ml of O_2 gas measured at STP by electrolysis of water for a period of 3 hrs ?
58. How much electricity in terms of Faradays is required to produce ?
 (i) 10.0 g of Ca from molten CaCl_2
 (ii) 81 g of Al from molten Al_2O_3
59. Silver is electrodeposited on a metallic vessel of surface area 800 cm² by passing a current of 0.2 ampere for 3 hours. Calculate the thickness of silver deposited, given its density is 10.47 g/cc. (At. wt. of Ag = 107.92).
60. How much electricity in terms of Faraday is required to produce 40 g of Al from molten Al_2O_3 ? (Atomic mass of Al = 27) (Hr. S.B. 2011)

Answers to Practice Problems

51. 2.014 g.
 52. 63.3 u.
 53. 0.331 g.
 54. (i) 96500 C
 (ii) 193000 C
 (iii) 193000 C.
 55. +3
 56. 40.21 hr.
 57. 0.0798 A.
 58. (i) 0.5 F (ii) 9.0 F
 59. 2.89×10^{-4} cm.
 60. 4.44 F.

Hints & Solutions on page 74

Advanced Level

PROBLEMS

Accelerate Your Potential

Problem 12. Silver is electrodeposited on a metallic vessel of total surface area 900 cm² by passing a current of 0.5 ampere for two hours. Calculate the thickness of silver deposited (given density of silver = 10.5 g cm⁻³, atomic mass of silver = 108 amu, F = 96500 C mol⁻¹). (A.I.S.B. 2006)

Solution Silver is deposited as



$$\text{Quantity of electricity passed, } Q = I \times t$$

$$I = 0.5 \text{ amp., } t = 2 \times 60 \times 60 \text{ s}$$

$$\therefore Q = 0.5 \times 2 \times 60 \times 60 = 3600 \text{ C}$$

$$96500 \text{ C of electricity deposited} = 108 \text{ g Ag}$$

$$\begin{aligned} 3600 \text{ C of electricity deposited Ag} &= \frac{108}{96500} \times 3600 \\ &= 4.029 \text{ g} \end{aligned}$$

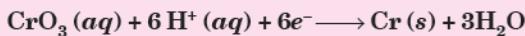
Let the thickness of silver deposited = x cm

$$\begin{aligned} \text{Weight} &= \text{Volume} \times \text{Density} \\ &= \text{Area} \times \text{Thickness} \times \text{Density} \end{aligned}$$

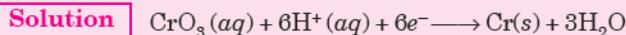
$$4.029 = 900 \times x \times 10.59$$

$$\text{or } x = \frac{4.029}{900 \times 10.59} = 4.23 \times 10^{-4} \text{ cm.}$$

Problem 13. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following reaction :



Calculate (i) how many grams of chromium will be plated out by 24,000 coulombs and (ii) how long will it take to plate out 1.5 g of chromium using 12.5 amp current ? (Atomic mass of Cr = 52).



Since 6 mole of electrons are required to deposit 1 mol of Cr,

$$(i) 6 \times 96500 \text{ C of electricity deposit Cr} = 52 \text{ g}$$

24,000 C of electricity will deposit Cr

$$= \frac{52}{96500 \times 6} \times 24,000 = 2.1554 \text{ g}$$

$$(ii) \text{ Amount of electricity needed to plate out 1 mol Cr} \\ (52 \text{ g}) = 96500 \times 6 \text{ C}$$

Amount of electricity required to deposit 1.5 g of Cr

$$= \frac{96500 \times 6}{52} \times 1.5 = 16071.9 \text{ C}$$

Time for which electricity is to be passed,

$$Q = I \times t$$

$$16071.9 = 12.5 \times t$$

$$t = \frac{16071.9}{12.5} = 1330.15$$

$$s = 22.27 \text{ min.}$$

Problem 14. An aqueous solution of an unknown salt of palladium is electrolysed by a current of 3.0 A passing for 1 hr. During electrolysis, 2.977 g of palladium ions are reduced at the cathode. What is the charge on the palladium ions in solutions?

Solution Quantity of electricity passed,

$$Q = I \times t$$

$$= 3.0 \times 1.0 \times 60 \times 60 = 10800 \text{ C}$$

Now, palladium ions are reduced at cathode as



n mol of electrons or $n \times 96500$ C produce 106.4 g of palladium.

$96500 n$ C of current reduce palladium ions = 106.4 g

10800 C of current reduce palladium ions

$$= \frac{106.4 \text{ g}}{96500 n} \times 10800$$

But amount of palladium ions reduced = 2.977 g

$$\therefore \frac{106.4}{96500 n} \times 10800 = 2.977$$

$$\text{or } n = \frac{106.4 \times 10800}{96500 \times 2.977} = 4.0$$

\therefore Palladium ions are Pd^{4+} or charge on palladium is +4.

Problem 15. A current of 1.5 A is passed through 500 mL of 0.25 M solution of zinc sulphate for 1 hr with a current efficiency of 90%. Calculate the final molarity of Zn^{2+} assuming volume to be constant.

Solution Quantity of electricity passed, $Q = I \times t$

$$I = 1.5 \times \frac{90}{100}, t = 1 \times 60 \times 60 = 3600 \text{ s}$$

$$Q = 1.5 \times \frac{90}{100} \times 3600 \\ = 4860 \text{ C}$$

$$\text{Faraday of electricity passed} = \frac{4860}{96500} = 0.050 \text{ F}$$

Now $\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$

2F of electricity convert 1 mol of Zn^{2+} to Zn.

$$0.05 \text{ F of electricity will convert } \text{Zn}^{2+} \text{ to Zn} = \frac{1}{2} \times 0.05 \\ = 0.025 \text{ mol}$$

$$\text{Initial moles of } \text{Zn}^{2+} \text{ in 500 mL solution} = \frac{0.25}{1000} \times 500 \\ = 0.125 \text{ mol}$$

$$\text{Moles of } \text{Zn}^{2+} \text{ ions left in the solution} = 0.125 - 0.025 \\ = 0.10 \text{ mol}$$

$$\therefore \text{Final molarity of } \text{Zn}^{2+} \text{ solution} = \frac{0.1}{500} \times 1000 \\ = 0.2 \text{ M}$$

Electrochemical cell

Cathode is +ve (Reduction)
Anode is -ve (Oxidation)

Electrolytic cell

Cathode is -ve (Reduction)
Anode is +ve (Oxidation)

REMEMBER

	Electro chemical cell	Electrolytic cell
Cathode		
Sign	+ve	-ve
Function	electron accepting (reduction)	cation attracting or cation reduced
Anode		
Sign	-ve	+ve
Function	electron supplying (oxidation)	anion attracting or anion oxidised

DIFFERENCES BETWEEN GALVANIC CELL AND ELECTROLYTIC CELL

The main points of differences are summed up below :

Electrochemical cell	Electrolytic cell
<ol style="list-style-type: none"> It is a device which converts chemical energy into electrical energy. In this case, the redox reaction is spontaneous and is responsible for the production of electrical energy. The two half cells are set up in different containers and are connected through salt bridge or porous partition. In electrochemical cell, anode is negative and cathode is positive electrode. Oxidation occurs at negative electrode and reduction occurs at positive electrode. The electrons move from anode to cathode in external circuit. 	<p>It is a device which converts electrical energy into chemical energy.</p> <p>The redox reaction is non-spontaneous and electrical energy is supplied to make the reaction to occur (<i>i.e.</i>, chemical change to take place).</p> <p>Both the electrodes are placed in the solution or molten electrolyte in the same container.</p> <p>In electrolytic cell, anode is positive and cathode is negative electrode.</p> <p>Oxidation occurs at positive electrode and reduction occurs at negative electrode.</p> <p>The electrons are supplied by the external battery and enter through cathode and come out through anode.</p>

SOME COMMERCIAL CELLS : BATTERIES

One of the main uses of galvanic cells is the generation of portable electrical energy. These cells are also popularly known as batteries. The term battery is generally used for two or more galvanic cells connected in series. Thus, a **battery** is an arrangement of electrochemical cells that can be used as a source of direct electric current at a constant voltage. The basis of an electrochemical cell is an oxidation-reduction reaction. However, for practical purposes there are some limitations to the use of redox reactions.

A useful battery should also fulfil the following requirements :

- (i) It should be light and compact so that it can be easily transported.
- (ii) It should have reasonably long life both when it is being used and when it is not used.
- (iii) The voltage of the battery should not vary appreciably during its use.

Types of commercial cells. There are mainly two types of commercial cells :

- (i) Primary batteries or cells
- (ii) Secondary batteries or cells.

(i) **Primary batteries or cells.** In these cells, the electrode reactions cannot be reversed by an external electric energy source. In these cells, reactions occur only once and after use they become dead. Therefore, they are **not chargeable**. Some common examples are dry cell, mercury cell.

(ii) **Secondary batteries or cells.** In the secondary cells, the reactions can be reversed by an external electric energy source. Therefore, these cells can be **recharged** by passing electric current and used again and again. These are also called **storage cells**. Examples of secondary cells are : lead storage battery and nickel-cadmium storage cell.

Let us discuss some examples :

A. Primary Cells

1. Dry cells. The most familiar commercial cells are dry cells. These are used in torches, toys, flash lights, calculators, tape recorders and many other devices. These are based on Leclanche cell invented by G. Leclanche in 1868. A dry cell is shown in Fig. 19. It consists of a zinc cylinder. This is filled with a moist paste of NH_4Cl and little of ZnCl_2 . The zinc cylinder acts as an anode. The cathode is a graphite (carbon) rod. The carbon rod is surrounded by a black paste of manganese dioxide (MnO_2) and carbon powder. The zinc case has an outer insulation of cardboard case. During use, the zinc case gets consumed and in the end, it will develop holes which are responsible for leakages. The leak proof cells or dry cells have an iron or steel sheet covering the zinc.

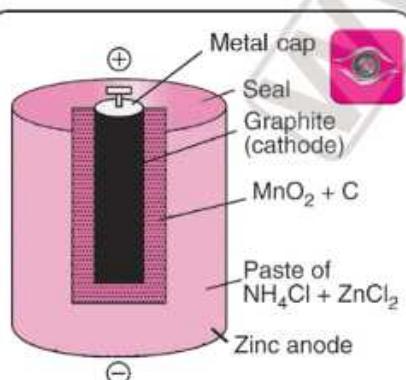
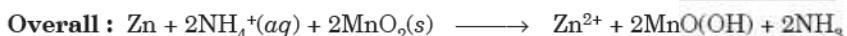
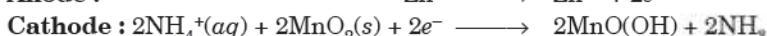


Fig. 19. A dry cell.

When the cell is working, zinc loses electrons and Zn^{2+} ions dissolve in the electrolyte. The electrons pass around the external circuit and are taken up at cathode. This causes discharge of NH_4^+ ions from the electrolyte. The reactions taking place at the electrodes are :



In the cathode reaction, manganese is reduced from +4 oxidation state to +3 oxidation state. Ammonia formed is not liberated as a gas but it combines with some of the Zn^{2+} ions and Cl^- ions produced from the anode to form complex ion having the formula $[Zn(NH_3)_2Cl_2]$. This also prevents the seal of the cell to crack because of developed pressure.

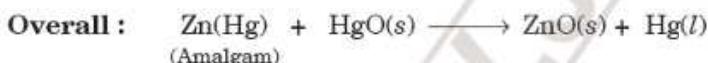
It gives voltage of approximately 1.2 to 1.5 V. There are many varieties of dry cells such as silver cell or lithium cell.

This dry cell does not have an indefinite life because of acidic conditions due to the presence of NH_4Cl . Due to the action of H^+ ions from NH_4^+ , the zinc container (anode) corrodes even when not in use.



To avoid this difficulty, a modified form of dry cell called **alkaline dry cell** has been prepared. In alkaline dry cell the electrolyte $NaOH$ or KOH is used in place of NH_4Cl .

2. Mercury cell. A new type of cell which has found use in small electrical circuits such as hearing aids, watches and cameras is the mercury cell. It consists of a zinc-mercury amalgam as anode and a paste of mercury (II) oxide and carbon as the cathode. The electrolyte is a paste of KOH and ZnO . A lining of porous paper keeps the electrolyte separated from the zinc anode. A commercially used mercury cell is shown in Fig. 20. The reactions occurring in the cell are as follows :



In this case, the overall cell reaction does not involve any ion in solution whose concentration can change. Therefore, it has the advantage that its potential remains almost constant throughout its life. This is its special feature. By contrast, the potential of the ordinary dry cell decreases slowly but continuously as it is used. The voltage of mercury cell is approximately **1.35 V**.

B. Secondary Cells

Ordinary cells are not rechargeable. However, there are some cells which can be recharged. These are called accumulators or storage cells. These can be recharged and used again and again as a source of electric current. The most popular example is lead storage cell which is used in automobiles such as cars, buses, trucks, etc.

1. Lead Storage Cell

This is the most commonly used battery in automobiles. Each battery consists of a number of voltaic cells connected in series. Three to six such cells are generally combined to get 6 to 12 volt battery. In each cell, the anode is a grid of lead packed with finely divided spongy lead and the cathode is a grid of lead packed with PbO_2 . The electrolyte is aqueous solution of sulphuric acid (38% by mass) having a density 1.30 g mL^{-1} sulphuric acid (Fig. 21). When the lead plates are kept for sometimes, a deposit of lead sulphate is formed on them.

At the anode, lead is oxidised to Pb^{2+} ions and insoluble $PbSO_4$ is formed. At the cathode, PbO_2 is reduced to Pb^{2+} ions and $PbSO_4$ is formed.

REMEMBER

- Primary cells in which electrode reactions cannot be reversed by external electric energy source.
⇒ not chargeable.
- Secondary cells in which electrode reactions can be reversed by external electric energy source.
⇒ chargeable
are called batteries.

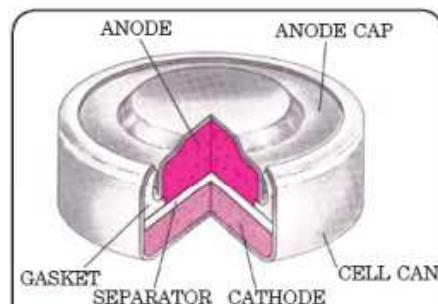


Fig. 20. A commercially used mercury cell.

R U Curious...

- When a car is running its battery gets charged itself.
- When an engine of an automobile (car) is running, electrical energy is produced in the alternator which keeps on charging the battery.

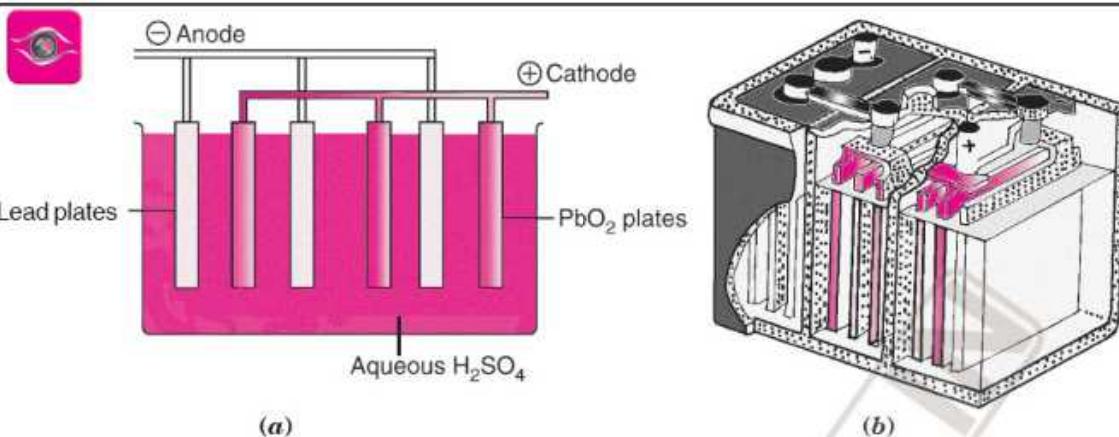
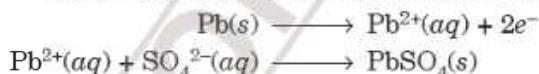


Fig. 21. (a) Lead storage battery; (b) Lead storage battery (commercial design).

The following reactions take place in the lead storage cell :

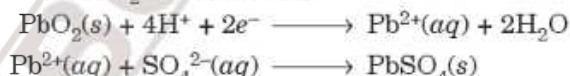
At anode. Lead loses two electrons and is oxidised to Pb²⁺ ions



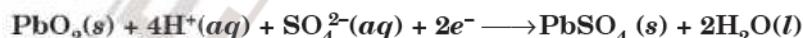
The overall anode reaction may be written as :



At cathode. The PbO₂ is reduced as :



The overall cathode reaction is :

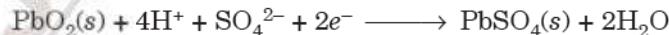


Thus, the complete electrode reactions and overall cell reaction are :

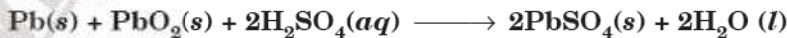
Anode :



Cathode :



Overall :



The cell may be represented as :



The potential of the cell depends on the concentration (density) of H₂SO₄. It is clear from the above reactions that during the working of the cell, PbSO₄ is formed at each electrode and sulphuric acid is used up. As a result, the concentration of H₂SO₄ decreases and the density of the solution also decreases. When the density of H₂SO₄ falls below 1.2 g mL⁻¹, the battery needs recharging.

Recharging the Battery

The cell can be recharged by passing electric current of a suitable voltage in the opposite direction. The cell works like an electrolytic cell and the electrode reactions get reversed. All the cell reactions that occur during discharge are reversed where H₂SO₄ is generated and its concentration is increased. During charging process, the functions of anode and cathode are reversed. Now PbO₂ electrode is anode (+ve) and Pb is cathode (-ve).

At anode. It is the reverse reaction at cathode during discharge.



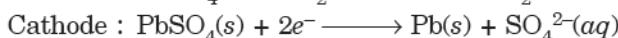
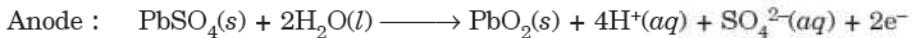
At cathode. It is reverse of oxidation at anode during discharge.



Lithium Batteries

- These days a large number of batteries are known in which lithium metal is used as an anode and are known as **lithium batteries** and have different cathode and electrolyte. Lithium is a light metal and has low electrode potential and good conductivity. Therefore, lithium is a good material for batteries which provide high potential. These may be primary or secondary.
- Lithium ion batteries are rechargeable and are now becoming very popular for use in lap tops, computers, cell phones, MP-3 players, etc. These provide high voltage in the range 3.6–3.7 V. These cannot be discharged by themselves easily and therefore, can be used for longer periods. These consist of cathode made of lithium cobalt oxide (LiCoO₂) and anode made of graphite. The electrolyte used is lithium salt (commonly LiPF₆) dissolved in some organic solvent (ethylene carbonate or dimethyl carbonate).

The net cell reaction is



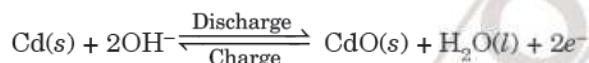
Such an operation is possible because the PbSO_4 formed during discharge is a solid and sticks to the electrodes. Therefore, it can either take or give up electrons during electrolysis. Thus, **the overall reaction is exactly opposite the normal cell reaction**. The reaction shows that H_2SO_4 is regenerated and its density increases. Hence, cell potential increases and the cell is recharged.

It may be noted that storage battery acts as voltaic cell as well as electrolytic cell. For example, when it is used to start the engine of the automobile, it acts as a voltaic cell and produces electric energy. During recharging, it acts as an electrolytic cell.

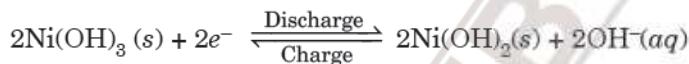
2. Nickel Cadmium Storage Cell

This is also a rechargeable cell. It has longer life than the lead storage cell but more expensive than lead storage battery. However, it has some advantages because it is smaller and lighter. It can be used in portable and cordless appliances. It consists of a cadmium anode and a metal grid containing NiO_2 acting as a cathode as shown in Fig. 22. The electrolyte in this cell is KOH. The reactions taking place during discharge and charge are :

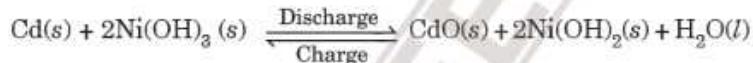
Anode :



Cathode :



Overall :



In these reactions, there is no formation of gaseous products. The reaction products generally remain sticking to the electrodes and can be reconverted by recharging the cell. The charging process is similar to lead storage battery.

It produces a potential of about 1.4 V. It has longer life than lead storage cell.

Some **main characteristics** of common cells are :

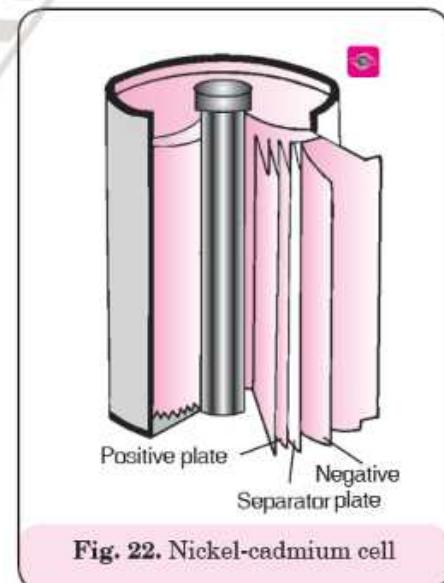
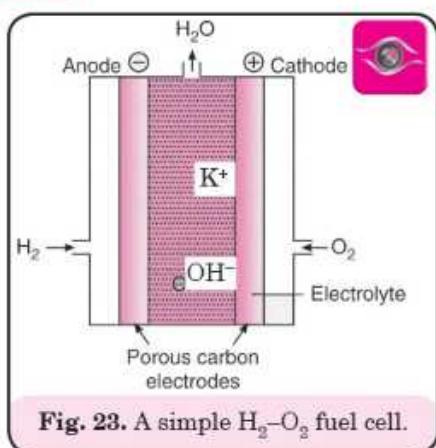


Fig. 22. Nickel-cadmium cell

Cell	Cathode/Anode	Electrolyte	Cell reaction
Dry cell	Graphite/Zinc	$\text{MnO}_2 + \text{C}$ (touching cathode) $\text{NH}_4\text{Cl} + \text{ZnCl}_2$ (touching anode)	Anode : $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$ Cathode : $\text{MnO}_2(s) + \text{NH}_4^+(aq) + e^- \longrightarrow \text{MnO(OH)} + \text{NH}_3 \times 2$ $\text{Zn} + 2\text{MnO}_2(s) + 2\text{NH}_4^+(aq) \longrightarrow \text{Zn}^{2+} + 2\text{MnO(OH)} + 2\text{NH}_3$
Mercury cell	Hg(II) oxide/Zinc	Paste of KOH and ZnO	Anode : $\text{Zn}(\text{Hg}) + 2\text{OH}^- \longrightarrow \text{ZnO}(s) + \text{H}_2\text{O} + 2e^-$ Cathode : $\text{HgO}(s) + \text{H}_2\text{O} + 2e^- \longrightarrow \text{Hg(l)} + 2\text{OH}^-$ $\text{Zn}(\text{Hg}) + \text{HgO}(s) \longrightarrow \text{ZnO}(s) + \text{Hg(l)}$
Lead storage cell	Lead packed with PbO_2 / Lead	38% H_2SO_4 solution	Anode : $\text{Pb}(s) + \text{SO}_4^{2-}(aq) \longrightarrow \text{PbSO}_4(s) + 2e^-$ Cathode : $\text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^- \longrightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}$ $\text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4(aq) \longrightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}$
Nickel-Cadmium storage cell	NiO_2 / Cd	KOH solution	Anode : $\text{Cd}(s) + 2\text{OH}^- \longrightarrow \text{CdO}(s) + \text{H}_2\text{O}(l) + 2e^-$ Cathode : $2\text{Ni(OH)}_3(s) + 2e^- \longrightarrow 2\text{Ni(OH)}_2(s) + 2\text{OH}^-(aq)$ $\text{Cd}(s) + 2\text{Ni(OH)}_3(s) \longrightarrow \text{CdO}(s) + 2\text{Ni(OH)}_2(s) + \text{H}_2\text{O}(l)$

FUEL CELLS

Fuel cells are galvanic cells in which the energy of combustion of fuels like hydrogen, methane, methanol, etc is directly converted into electrical energy.



Learning Plus

Fuel cells are undergoing intensive developments. Fuel cells based on the combustion of hydrocarbons such as CH_4 , C_2H_6 , C_3H_8 , etc. in the presence of catalysts have been designed. Many varieties of fuel cells are possible and in some the electrolyte is a solid polymer membrane or a ceramic. Depending upon the different types of electrolytes used, the fuel cells are classified as

- alkali fuel cells* [electrolyte is KOH(aq)]
- phosphoric acid fuel cells* [electrolyte is $\text{H}_3\text{PO}_4\text{(aq)}$]
- Molten carbonate fuel cells [electrolyte is $\text{K}_2\text{CO}_3(l)$ / $\text{Li}_2\text{CO}_3(l)$].

In this, methane is used as a fuel. Recently, a zinc-air fuel cell (ZAFC) is developed in USA as a source of power in automobiles in which zinc metal is used in place of hydrogen gas.

Efficiency of a Fuel Cell

The theoretical efficiency of a fuel cell can be calculated from enthalpy of combustion (ΔH) and useful work done (ΔG) i.e., electricity produced. The thermodynamic efficiency (η) of a fuel cell is

$$\text{Efficiency } (\eta) = \frac{\Delta G}{\Delta H} \times 100$$

For example, ΔH for $\text{H}_2\text{-O}_2$ fuel cell has been found to be $-285.5 \text{ kJ mol}^{-1}$ and theoretical voltage of the cell has been found to be 1.23 V .

$$\begin{aligned}\Delta G(\text{fuel cell}) &= -nFE_{\text{cell}}^{\circ} \\ &= (-2) \times (96500 \text{ C mol}^{-1}) \\ &\quad \times (1.23 \text{ V}) \\ &= -237390 \text{ J mol}^{-1} \\ &= -237.39 \text{ kJ mol}^{-1} \\ \therefore \eta &= \frac{-237.39 \text{ kJ mol}^{-1}}{-285.5 \text{ kJ mol}^{-1}} \times 100 = 83\%\end{aligned}$$

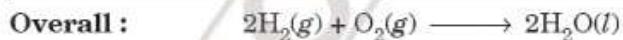
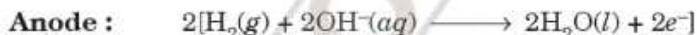
The actual efficiency of the cell is 60–70%

In these cells, the reactants are continuously supplied to the electrodes and the products are continuously removed from the electrolyte compartment. Therefore, these fuel cells differ from the ordinary galvanic cells in that the reactants are not placed in the cell but are continuously supplied to the electrodes from the reservoir. The common example is hydrogen-oxygen fuel cell as described below:

Hydrogen-Oxygen Fuel Cell

In $\text{H}_2\text{-O}_2$ fuel cell, hydrogen gas is used as fuel and oxygen gas acts as the oxidising agent. The energy of combustion of H_2 is converted into electrical energy.

The cell consists of porous carbon electrodes immersed in concentrated aqueous sodium hydroxide or potassium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. Hydrogen and oxygen are bubbled through porous electrodes into the NaOH or KOH solution (Fig. 23). Hydrogen (the fuel) is fed into the anode compartment where it is oxidised. The oxygen is fed into cathode compartment where it is reduced. The diffusion rates of the gases into the cell are carefully regulated to get maximum efficiency. The net reaction is the same as burning of hydrogen and oxygen to form water.



The theoretical voltage of an ideal $\text{H}_2\text{-O}_2$ fuel cell at standard conditions of 1 atm pressure and 298 K temperature is 1.23 V . However, the typical operating voltage is about $0.6 - 0.7 \text{ V}$ for high performance fuel cells. This cell runs continuously as long as the reactants are fed. These fuel cells are more efficient than conventionally used methods of generating electricity on a large scale by burning hydrogen, carbon, fuels because these fuel cells convert the energy of the fuel directly into electricity.

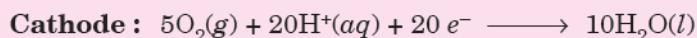
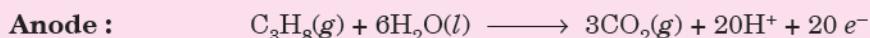
This cell has been used for providing electric power in the Apollo space programme. Fuel cells offer great promises for energy conversion in future. The important advantages of fuel cells over ordinary batteries are:

(i) **High efficiency.** The fuel cells convert the energy of a fuel directly into electricity and therefore, they are more efficient than the conventional methods of generating electricity on a large scale by burning hydrogen, carbon fuels. Though we expect 100% efficiency in fuel cells, so far 60 – 70% efficiency has been attained. The conventional methods of production of electrical energy involve combustion of a fuel to liberate heat which is then used to produce electricity. The efficiency of these methods is only about 40%.

(ii) **Continuous source of energy.** There is no electrode material to be replaced as in ordinary battery. The fuel can be fed continuously to produce power. For this reason, $\text{H}_2\text{-O}_2$ fuel cells have been used in space crafts.

(iii) **Pollution free working.** There are no objectionable by-products and, therefore, they do not cause pollution problems.

Another common fuel cell is propane-oxygen cell. The half cell reactions are:



Since fuel cells are efficient and free from pollution, attempts are being made to get better commercially practical fuel cells.

CORROSION

When metals are exposed to atmospheric conditions, they react with air or water in the environment to form undesirable compounds (usually oxides). This process is called **corrosion**. Almost all metals *except the least active metals such as gold, platinum and palladium are attacked by environment i.e., undergo corrosion*. For example, silver tarnishes, copper develops a green coating, lead or stainless steel lose their lustre due to corrosion. Corrosion causes enormous damage to buildings, bridges, ships and many other articles made of iron. Thus,

corrosion is a process of deterioration of a metal as a result of its reaction with air or water (environment) surrounding it.

In case of iron, corrosion is called **rusting**. Chemically, rust is hydrated form of ferric oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. Rusting of iron is generally caused by moisture, carbon dioxide and oxygen present in air. It has been observed that rusting takes place only when iron is in contact with moist air. *Iron does not rust in dry air and in vacuum.*

Factors which affect corrosion. The main factors which affect corrosion are :

- (i) **Position of metals in e.m.f. series.** The reactivity of metal depends upon its position in the electrochemical series. More the reactivity of metal, the more will be the possibility of the metal getting corroded.
- (ii) **Presence of impurities in metals.** The impurities help in setting up voltaic cells, which increase the speed of corrosion.
- (iii) **Presence of electrolytes.** Presence of electrolytes in water also increases the rate of corrosion. For example, corrosion of iron in sea water takes place to larger extent than in distilled water.
- (iv) **Presence of CO_2 in water.** Presence of CO_2 in natural water increases rusting of iron. Water containing CO_2 acts as an electrolyte and increases the flow of electrons from one place to another.
- (v) **Presence of protective coatings.** When the iron surface is coated with layers of metals more active than iron, then the rate of corrosion is retarded. For example, coating of zinc on iron prevents rusting.

Mechanism of Rusting of Iron

Electrochemical theory of rusting. The phenomenon of corrosion can be explained with the help of electrochemical theory which involves oxidation and reduction reactions. According to electrochemical theory of corrosion, it is believed that non-uniform surface of metal or impurities present in iron behave like small electric cells (called corrosion couples) in the presence of water containing dissolved oxygen or carbon dioxide. A film of moisture with dissolved CO_2 constitutes electrolytic solution covering the metal surface at various places.

The schematic representation of mechanism of rusting of iron is shown in Fig. 24.

In the small electrolytic cells, pure iron acts as anode while cathodes are impure portions. The overall rusting involves the following steps :

At a particular spot of an object made up of iron, oxidation takes place and the spot behaves as an anode.



Thus, the metal atoms in the lattice pass into the solution as ferrous (Fe^{2+}) ions, leaving electrons on the metal itself.

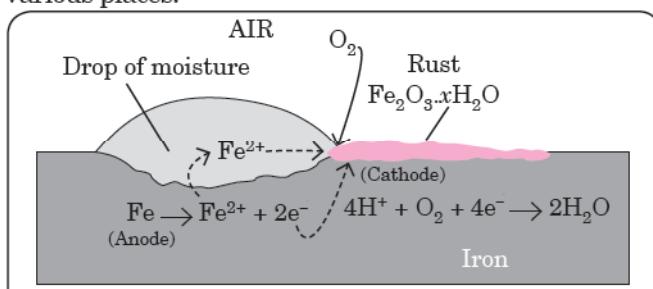
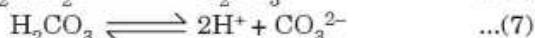
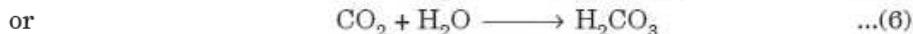


Fig. 24. Schematic representation of mechanism of rusting of iron.

These electrons go to another spot on the metal and reduce atmospheric oxygen to water in the presence of H^+ ions.

The H^+ ions are obtained either from water or from acidic substances (e.g., CO_2) in water:

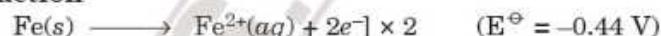


This spot behaves as cathode and the reaction is



The **overall redox reaction** may be written by multiplying reaction at anode Eq. (4) by 2 and adding reaction at cathode Eq. (8) to equalise number of electrons lost and gained i.e.,

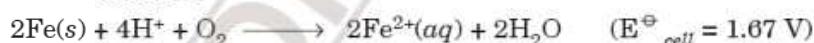
Oxidation half reaction



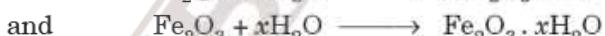
Reduction half reaction



Overall cell reaction



The ferrous ions are oxidised further by dissolved oxygen or atmospheric oxygen from air to form ferric oxide with further production of H^+ ions. The ferric oxide then undergoes hydration and the hydrated form of iron(III) oxide is known as rust:



Rust

It may be noted that *salt water accelerates corrosion. This is mainly due to the fact that salt water increases the electrical conduction of electrolyte solution formed on the metal surface. Therefore, rusting becomes more serious problem where salt water is present.*

Prevention of Corrosion

The prevention of corrosion is very important and essential. It not only saves money but also helps in preventing serious accidents such as a bridge collapse or a failure of a key component due to corrosion. This can be prevented or retarded by the methods given below :

1. Barrier protection. This is one of the simplest methods to prevent rusting of iron. In this method, a barrier is placed between iron and atmospheric air. The barrier protection can be achieved by any of the following methods :

(i) the surface is coated with paint or some chemicals (e.g., bisphenol).

(ii) the surface is protected by applying a thin film of oil or grease.

(iii) the metal is electroplated with metals like tin, nickel, zinc, chromium, aluminium, etc.

For example, many vehicles such as cycles, motors, cars made from iron sheets are protected from rusting by paints. Many iron articles are electroplated with coating of other metals. The electroplating is carried not only for achieving brightness but also to protect from corrosion.

2. Sacrificial protection. In this method, iron is protected from rusting by covering it with a layer of a metal more active than iron. This prevents loss of electrons from iron. The active metal loses electrons in preference to iron and goes into ionic state. Therefore, the covering metal is consumed with time, but as long as it is present on the surface of iron, the latter is not rusted. This type of process in which rusting of iron is protected is called **sacrificial protection**.

Zinc is commonly used for covering iron surfaces. The process of covering iron with zinc is called **galvanization**. The galvanized iron materials maintain their lustre due to the coating of invisible layer of basic zinc carbonate, ZnCO_3 , $\text{Zn}(\text{OH})_2$ on the zinc film. If some scratches occur on the protective zinc film on coated iron, even then iron will not be rusted. This is due to the fact that because of scratches, both zinc and iron get exposed to oxidation but zinc undergoes oxidation in preference to iron. This is so because the reduction potential of zinc is less than the reduction potential of iron.

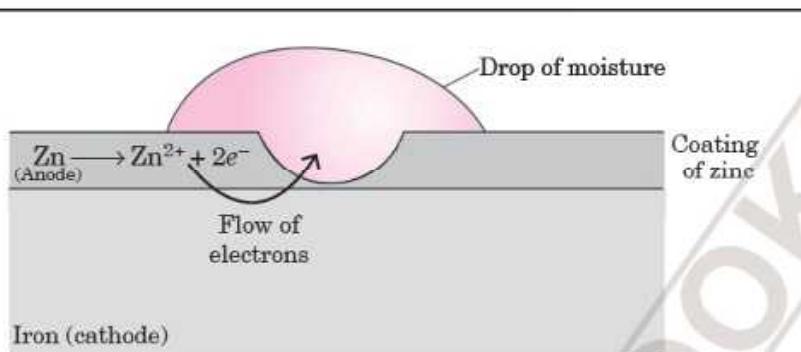
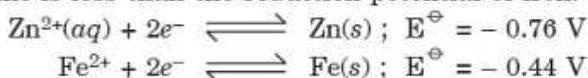
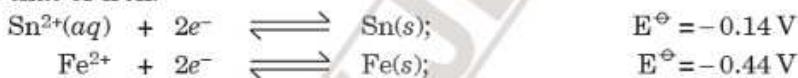


Fig. 25. Protection of rusting of iron with a film of zinc. Rusting will not occur even when iron surface is exposed.

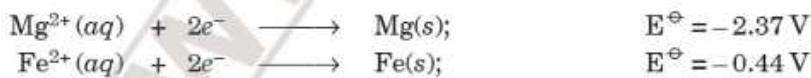
Therefore, zinc undergoes oxidation in preference to iron.

However, it may be noted that in the case of tin plating, i.e., tin coating on iron, the film will be effective as long as it is intact. When scratches occur at the coating surface both the metals are exposed to oxygen and iron is preferably oxidised and is rusted. This is due to the fact the reduction potential of tin is more than that of iron.



Thus, iron will be oxidised in preference to tin.

3. Electrical protection. This method is used for protecting iron articles which are in contact with water such as underground water pipes. The article of iron is connected with more active metals like magnesium or zinc (Fig. 26). The active metal has lower reduction potential than iron and will lose electrons in preference to iron. For example, magnesium has lower reduction potential than iron :



Therefore, magnesium will be oxidised in preference to iron and therefore, it will protect iron from being rusted.

4. Using anti-rust solutions. To retard the corrosion of iron, certain anti-rust solutions are used. For example, solutions of alkaline phosphates and alkaline chromates are generally used as anti-rust solutions. Due to the alkaline nature of these solutions, the H^+ ions are removed from the solutions and rusting is prevented. For example, iron articles are dipped in boiling alkaline sodium phosphate solutions, when a protective insoluble sticking film of iron phosphate is formed.

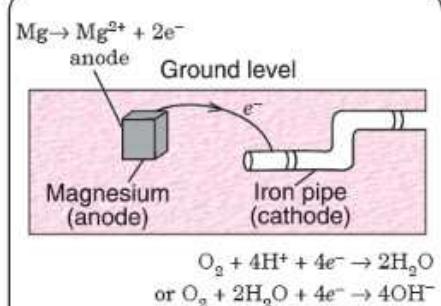


Fig. 26. Protection of rusting of underground iron pipes by electrical protection method.

add on**Conceptual Questions**

2

Q. 1. How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours?

(Given : 1F = 96,500 C mol⁻¹)

Ans.

$$\begin{aligned} Q &= I \times t \\ &= 0.5 \times 2 \times 60 \times 60 \\ &= 3600 \text{ C} \end{aligned}$$

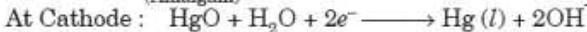
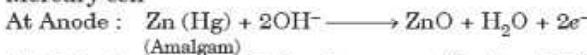
Now, 96500 C = 6.022 × 10²³ electrons

$$\begin{aligned} 3600 \text{ C} &= \frac{6.022 \times 10^{23} \times 3600}{96500} \\ &= 2.25 \times 10^{22} \text{ electrons} \end{aligned}$$

(A.I.S.B. 2017)

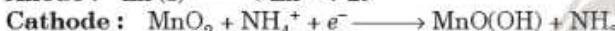
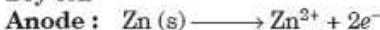
Q. 2. Write the name of the cell which is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell.

Ans. Mercury cell



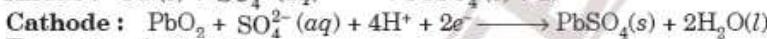
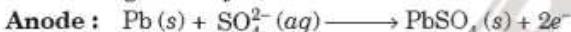
Q. 3. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell.

Ans. Dry cell



Q. 4. Write the name of the cell which is generally used in inverters. Write the reactions taking place at the anode and the cathode of this cell.

Ans. Lead storage battery



Q. 5. From the given cells:

Lead storage cell, Mercury cell, Fuel cell and Dry cell

Answer the following:

(i) Which cell is used in hearing aids?

(ii) Which cell was used in Apollo Space Programme?

(iii) Which cell is used in automobiles and inverters?

(iv) Which cell does not have long life?

(D.S.B. 2016)

Ans. (i) Mercury cell

(ii) Fuel cell

(iii) Lead storage cell

(iv) Dry cell

Q. 6. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell?

(A.I.S.B. 2016)

Ans. If E°_{cell} (external) is greater than E°_{cell}, the cell starts acting as an electrolytic cell. In this case, electrical energy is used to carry out non-spontaneous chemical reaction.

Q. 7. Using the E° values of A and B, predict which one is better for coating the surface of iron [E°(Fe²⁺/Fe = -0.44V) to prevent corrosion and why?

Given : E° ((A²⁺ | A) = -2.37 V and E° (B²⁺ | B) = -0.14 V

(A.I.S.B. 2016)

Ans. 'A' will prevent iron from rusting. So, we can coat the iron surface with metal A because it has more negative value.

Q. 8. Given that the standard electrode potentials (E°) of metals are :

K⁺ | K = -2.93V, Ag⁺ | Ag = 0.80V, Cu²⁺ | Cu = 0.34V, Mg²⁺ | Mg = -2.37V, Cr³⁺ | Cr = -0.74V and

Fe²⁺ | Fe = -0.44V.

(A.I.S.B. 2010)

Arrange the metals in the increasing order of their reducing power.

Ans. Ag⁺ | Ag < Cu²⁺ | Cu < Fe²⁺ | Fe < Cr³⁺ | Cr < Mg²⁺ | Mg < K⁺ | K.

Q. 9. What is change in free energy for (a) galvanic cell and (b) electrolytic cell ?

Ans. (a) For a galvanic cell, free energy decreases i.e., ΔG < 0

(b) For electrolytic cell, free energy increases i.e., ΔG > 0.

Q. 10. Is it safe to stir 1 M AgNO₃ solution with a copper spoon ? Given E° Ag⁺ | Ag = 0.80 V, E°_{Cu2+ | Cu} = 0.34 V. Explain.

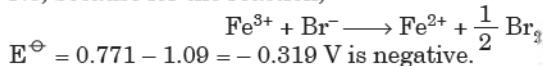
(Pb.S.B. 2004)

Ans. No, copper spoon will dissolve as Cu²⁺ ions because copper has more tendency to get oxidised than silver.

Q. 11. Can Fe³⁺ oxidise Br⁻ to Br₂ under standard conditions ?

E°_{Fe3+ | Fe2+} = 0.771 V, E°_{Br2 | Br-} = 1.09 V.

Ans. No, because for the reaction,



Q. 12. Two metals A and B have reduction potential values - 0.76 V and + 0.34 V respectively. Which of these will liberate H₂ from dil H₂SO₄?

Ans. Metal having higher oxidation potential (or lower reduction potential) will liberate H₂ from H₂SO₄. Thus, A will liberate H₂ from H₂SO₄.

Q. 13. Can tin coating on iron act as sacrificial anode in protecting iron against corrosion?

Ans. No, because tin is less readily oxidised in comparison to iron ($E^\ominus_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$, $E^\ominus_{\text{Sn}^{2+}/\text{Sn}} = -0.14 \text{ V}$). Tin protects iron only as a cover.

Q. 14. What is role of ZnCl₂ in a dry cell?

Ans. ZnCl₂ combines with NH₃ produced to form the complex [Zn(NH₃)₂Cl₂], otherwise the pressure developed due to NH₃ would crack the seal of the cell.

Q. 15. When the silver electrode having reduction potential 0.80 V is attached to NHE, will it act as anode or cathode?

Ans. It will act as cathode.

Q. 16. Name the cell which were used in Apollo space programme.

Ans. Hydrogen-oxygen fuel cell.

Q. 17. How does concentration of sulphuric acid change in lead storage battery when current is drawn from it?

Ans. Concentration of sulphuric acid decreases.

Q. 18. What is the effect of carbon dioxide in water on corrosion?

Ans. The presence of carbon dioxide in water increases rusting of iron. Water containing CO₂ acts as an electrolyte and increases the flow of electrons from one place to another.

Q. 19. Why is it not possible to measure the voltage of an isolated half reaction?

Ans. It is not possible to measure the voltage of an isolated half reaction because neither the oxidation nor the reduction can occur by itself. Therefore, we can only calculate the relative electrode potential by connecting it to some standard electrode.

Q. 20. Why does a dry cell become dead after a long time, even if it has not been used?

Ans. A dry cell becomes dead after a long time because the acidic NH₄Cl corrodes the zinc container.

Q. 21. Why does the cell potential of mercury cell remains constant throughout its life? (A.I.S.B. 2015)

Ans. This is because the overall cell reaction does not involve any ion in the solution whose concentration changes during its life time.

Q. 22. Why is the equilibrium constant K related to only E°_{cell} and not E_{cell}?

(D.S.B. 2003)

Ans. This is because at equilibrium, E_{cell} = 0.

Q. 23. How can you increase the reduction potential of an electrode?

Ans. By increasing the concentration of the ions.

Q. 24. The E° values of MnO₄⁻, Ce⁴⁺ and Cl₂ are 1.507, 1.61 and 1.358 V respectively. Arrange these in order of increasing strength as oxidising agent.

Ans. Cl₂ < MnO₄⁻ < Ce⁴⁺.

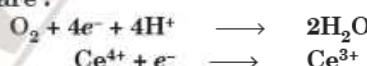
Q. 25. E° values for Fe³⁺ | Fe²⁺ and Ag⁺ | Ag are respectively 0.771 V and 0.800 V. Is the reaction:



Ans. E° for the reaction is 0.771 - 0.800 = -0.029 V.

Therefore, the reaction is not spontaneous.

Q. 26. The electrode potentials are :



E° = 1.228 V

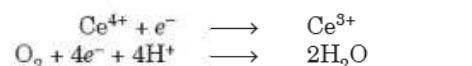
E° = 1.60 V

Will Ce⁴⁺ oxidize H₂O to O₂ in acidic solution?

Ans. Ce⁴⁺ can oxidize water as : 4Ce⁴⁺ + 2H₂O → O₂ + 4Ce³⁺ + 4H⁺

...(i)

Let us calculate its E°.



E° = 1.60 V

...(ii)

Reversing eqn. (iii)



E° = -1.228 V

...(iii)

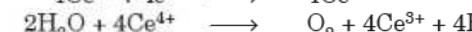
Multiply eqn. (ii) by 4



E° = 1.60 V

...(iv)

Adding eqn. (iv) and (v)



E° = 0.372 V

...(v)

Since E° is positive, reaction is spontaneous and so Ce⁴⁺ will oxidize H₂O to O₂.

Q. 27. What is the chemical formula of rust?

(H.P.S.B. 2005)

Ans. The chemical formula of rust is Fe₂O₃.x H₂O.

Q. 28. Can we store copper sulphate in an iron vessel or not? Explain.

(H.P.S.B. 2005)

Ans. The reduction potentials of Cu²⁺ | Cu and Fe²⁺ | Fe are + 0.34 V and - 0.44 V respectively. This means Cu²⁺ will be reduced to Cu and iron will be oxidised to Fe²⁺. In other words, the vessel will dissolve. Therefore, it is not possible to store CuSO₄ in an iron vessel.

Q. 29. Is e.m.f. extensive or intensive property?

Ans. Intensive property.

Q. 30. What is the use of platinum foil in the hydrogen electrode?

Ans. It is used for inflow and outflow of electrons.



Solution File

Hints & Solutions for Practice Problems

□ 1. Conductivity (κ) = $\frac{\text{Cell constant}}{\text{Resistance}}$
 $= \frac{0.357 \text{ cm}^{-1}}{31.6 \text{ ohm}}$
 $= 0.0113 \text{ ohm}^{-1} \text{ cm}^{-1}$

Molar conductivity = $\frac{\kappa \times 1000}{M}$
 $= \frac{0.0113 \times 1000}{0.05}$
 $= 226 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

□ 2. $\Lambda_m = \frac{\kappa \times 1000}{M}$
 $132.6 = \frac{\kappa \times 1000}{0.01}$
or $\kappa = \frac{132.6 \times 0.01}{1000} = 1.326 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$

Now $\kappa = \frac{\text{Cell constant}}{R}$
or cell constant = $\kappa \times R$
 $= (1.326 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}) \times (1412 \text{ ohm})$
 $= 1.87 \text{ cm}^{-1}$

□ 3. $\Lambda = \frac{\kappa \times 1000}{C}$ or $\kappa = \frac{\Lambda \times C}{1000}$
 $\kappa = \frac{420 \times 0.01}{1000} = 4.2 \times 10^{-3} \text{ S cm}^{-1}$
Conductance = $\frac{\kappa}{\text{Cell constant}} = \frac{4.2 \times 10^{-3}}{0.88}$
 $= 4.77 \times 10^{-3} \text{ ohm}^{-1}$

Resistance = $\frac{1}{4.77 \times 10^{-3}} = 209.5 \text{ ohm}$

□ 4. Cell constant = $\frac{l}{a} = \frac{1.6}{3.2} = 0.5 \text{ cm}^{-1}$
 $\kappa = \frac{1}{25} \times 0.5 = 2.0 \times 10^{-2} \text{ S cm}^{-1}$
 $\Lambda = \frac{2.0 \times 10^{-2} \times 1000}{0.5} = 40 \text{ S cm}^2 \text{ equiv}^{-1}$

□ 5. Cell constant (G^*) = $\frac{\kappa}{C} = \frac{2.78 \times 10^{-3}}{1/82.5}$
 $= 0.229 \text{ cm}^{-1}$

□ 6. Molarity of solution = $\frac{1/208 \times 1000}{200} = 0.0240 \text{ M}$
 $\Lambda_m = \frac{0.0058 \times 1000}{0.0240} = 241.67 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
Normality of solution = $\frac{1/104 \times 1000}{200} = 0.0480 \text{ N}$
 $\Lambda = \frac{0.0058 \times 1000}{0.0480} = 120.83 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$

□ 7. $\kappa = G \times \frac{l}{a}$
 $= \frac{1}{30} \times \frac{1.5}{2.0} = 0.025 \text{ S cm}^{-1}$
 $\Lambda_m = \frac{\kappa \times 1000}{M}$
 $= \frac{0.025 \times 1000}{0.5} = 50 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

□ 8. Cell constant = $\frac{\text{conductivity}}{\text{conductance}} = \frac{0.002768}{1/457.3}$
 $= 1.266 \text{ cm}^{-1}$

For CaCl_2 solution,
 $\kappa = \frac{1}{202} \times 1.266 = 0.00627 \text{ ohm}^{-1} \text{ cm}^{-1}$
 $\Lambda = \frac{\kappa \times 1000}{C} = \frac{0.00627 \times 1000}{0.05}$
 $= 125.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$

□ 9. $\kappa = G \times G^*$ or $G^* = \frac{\kappa}{G}$
where G is conductance and G^* is cell constant

$$G^* = \frac{1.29 \times 10^{-2} \text{ S cm}^{-1}}{1/85} = 1.0965 \text{ cm}^{-1}$$

κ for 0.052 mol L^{-1} solution,
 $\kappa = G \times G^*$

$$= \frac{1}{96} \times 1.0965 = 1.142 \times 10^{-2} \text{ S cm}^{-1}$$

$$\Lambda = \frac{\kappa \times 1000}{M}$$

$$= \frac{1.142 \times 10^{-2} \times 1000}{0.052}$$

$$= 219.6 \text{ S cm}^2 \text{ mol}^{-1}$$

□ 10. Cell constant = $1.29 \times 200 = 258 \text{ m}^{-1}$ or = 2.58 cm^{-1}

$$\kappa = 2.58 \times \frac{1}{1100} = 2.345 \times 10^{-2} \text{ S cm}^{-1}$$

$$\Lambda = \frac{2.345 \times 10^{-2} \times 1000}{0.02} = 117.25 \text{ S cm}^2 \text{ mol}^{-1}$$

or $= 1.175 \times 10^{-2} \text{ Sm}^2 \text{ mol}^{-1}$.

□ 11. $\Lambda_m = \frac{\kappa \times 1000}{M}$

$$194.5 = \text{_____}$$

or $\kappa = \frac{194.5 \times 0.05}{1000}$
 $= 0.725 \times 10^{-3} \text{ S cm}^2 \text{ mol}^{-1}$

Now,
 $R = \frac{1}{\kappa} \times \frac{l}{a}$
 $= \frac{1}{9.725 \times 10^{-3}} \times \frac{0.5}{1.50} = 34.27 \text{ ohm}$
 $V = IR$ or $I = \frac{V}{R} = \frac{5.0}{34.27} = 0.146 \text{ A}$

Solution File

□ 12. Cell constant = $\kappa \times R$

$$= 0.002768 \times 520 = 1.43936 \text{ cm}^{-1}$$

specific conductivity for salt solution,

κ = Cell constant \times conductance

$$= 1.43936 \times \frac{1}{300}$$

$$= 0.00478 \text{ ohm}^{-1} \text{ cm}^{-1}$$

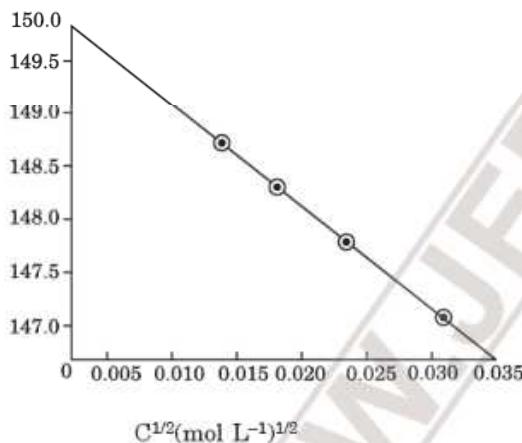
$$\Lambda = \frac{0.00478 \times 1000}{1/25}$$

$$= 119.5 \text{ S cm}^2 \text{ equiv}^{-1}.$$

□ 13. Taking the square root of concentrations, we get,

C (mol L ⁻¹)	C ^{1/2} (mol L ⁻¹) ^{1/2}	Λ_m (S cm ² mol ⁻¹)
0.000198	0.01407	148.61
0.000309	0.01758	148.29
0.000521	0.02283	147.81
0.000989	0.03145	147.09

Plot of Λ_m and C^{1/2} is given below :



The extrapolation of the straight line to zero concentration (intercept) gives the value of $\Lambda_m^\circ = 150.0 \text{ S cm}^2 \text{ mol}^{-1}$.

A = - slope = $87.46 \text{ S cm}^2 \text{ mol}^{-1} / (\text{mol L}^{-1})^{1/2}$

□ 14. $\Lambda^\circ(\text{CH}_3\text{COOH}) = \lambda^\circ(\text{CH}_3\text{COO}^-) + \lambda^\circ(\text{H}^+)$

$$= 40.9 + 349.6$$

$$= 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda = 39.05 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_c}{\Lambda^\circ} = \frac{39.05}{390.5} \\ = 0.10 \text{ or } 10\%$$

□ 15. $\Lambda^\circ(\text{AgCl}) = \Lambda^\circ(\text{AgNO}_3) + \Lambda^\circ(\text{KCl}) - \Lambda^\circ(\text{KNO}_3)$

$$= 13.84 \text{ m S m}^2 \text{ mol}^{-1}$$

□ 16. $\lambda_m^\circ(\text{NO}_3^-) = \Lambda^\circ(\text{KNO}_3) - \lambda^\circ(\text{K}^+)$

$$= 145.0 - 73.5 = 71.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda^\circ(\text{Li}^+) = \Lambda^\circ(\text{LiNO}_3) - \lambda^\circ(\text{NO}_3^-)$$

$$= 110.1 - 71.5 = 38.6 \text{ S cm}^2 \text{ mol}^{-1}$$

□ 17.

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{3.905 \times 10^{-5} \times 1000}{0.001}$$

$$= 39.05 \text{ S cm}^2 \text{ mol}^{-1}$$



$$\Lambda_m = \lambda^\circ_{\text{CH}_3\text{COO}^-} + \lambda^\circ_{\text{H}^+}$$

$$= 40.9 + 349.6 = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

Degree of dissociation,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{39.05}{390.5} = 0.1$$

□ 18.

$$(i) \quad \Lambda^\circ(\text{NH}_4\text{OH}) = \Lambda^\circ(\text{NH}_4\text{Cl}) + \Lambda^\circ(\text{NaOH}) - \Lambda^\circ(\text{NaCl}) \\ = 239.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$(ii) \quad \alpha = \frac{9.33}{239.2} = 0.039 \text{ or } 3.90\%$$

$$\kappa = \frac{\alpha^2}{1-\alpha} = \frac{0.01 \times (0.039)^2}{1-0.039} = 1.58 \times 10^{-5}$$

□ 19.

$$\Lambda = \frac{\kappa \times 1000}{C} = \frac{9.47 \times 10^{-3} \times 1000}{0.1} \\ = 94.7 \text{ S cm}^2 \text{ equiv}^{-1}$$

$$\Lambda^\circ = \lambda^\circ(\text{Ag}^+) + \lambda^\circ(\text{NO}_3^-) = 106.5 \text{ S cm}^2 \text{ equiv}^{-1}$$

$$\alpha = \frac{94.7}{106.5} = 0.89 \text{ or } 89\%$$

□ 20.

$$\Lambda^\circ(\text{HCOOH}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{HCOO}^-) \\ = 40.42 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{4.61}{40.42} = 0.114$$

$$K_a = \frac{\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{(1-0.114)} = 3.30 \times 10^{-4}$$

$$pK_a = -\log K_a = -\log (3.30 \times 10^{-4}) \\ = 3.4815$$

□ 21.

$$\Lambda^\circ(\text{CaCl}_2) = \lambda^\circ(\text{Ca}^{2+}) + 2\lambda^\circ(\text{Cl}^-) \\ = 271.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ(\text{MgSO}_4) = \lambda^\circ(\text{Mg}^{2+}) + \lambda^\circ(\text{SO}_4^{2-}) \\ = 266 \text{ S cm}^2 \text{ mol}^{-1}$$

□ 22.

$$\Lambda = \frac{4.95 \times 10^{-5} \times 1000}{1.028 \times 10^{-3}} = 48.15 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{48.15}{390.5} = 0.1233$$

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

$$= \frac{1.028 \times 10^{-3} \times (0.1233)^2}{1-0.123} = 1.78 \times 10^{-5}$$

□ 23.

$$\Lambda^\circ[\text{Ba}(\text{OH})_2] = \Lambda^\circ[\text{BaCl}_2] + 2\Lambda^\circ[\text{NaOH}] - 2\Lambda^\circ[\text{NaCl}]$$

$$= 2.800 \times 10^{-2} + 2(2.481 \times 10^{-2}) - 2(1.265 \times 10^{-2})$$

$$= 5.232 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$$

Solution File

24. $\kappa(\text{BaSO}_4) = \kappa(\text{solution}) - \kappa(\text{water})$
 $= 3.758 \times 10^{-6} - 1.36 \times 10^{-6}$
 $= 2.398 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$
 $\Lambda_m^\circ = 110 + 136.6 = 246.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

Molar mass = $137 + 32 + 4 \times 16 = 233$
Solubility = $\frac{\kappa \times 1000}{\Lambda_m}$
 $= \frac{2.398 \times 10^{-6} \times 1000}{246.6}$

$= 9.724 \times 10^{-6} \text{ mol L}^{-1}$

or $= 9.724 \times 10^{-6} \times 233 = 2.266 \times 10^{-3} \text{ g L}^{-1}$

25. Reduction potential of $\text{Ni}^{2+}|\text{Ni}$ is more than that of $\text{Fe}^{2+}|\text{Fe}$. Therefore, nickel will be reduced by iron.

26. No, nickel will gradually pass into solution and copper will be precipitated.

27. $\text{Sn}|\text{Sn}^{2+}||\text{Br}_2|\text{Br}^-$
 $E^\ominus = 1.08 - (-0.14) = 1.22 \text{ V}$

28. $E^\ominus_{\text{Cell}} = E^\ominus_{(\text{Ag}^+|\text{Ag})} - E^\ominus_{(\text{Cu}^{2+}|\text{Cu})}$
 $0.46 = E^\ominus_{(\text{Ag}^+|\text{Ag})} - 0.34$
 $\therefore E^\ominus_{(\text{Ag}^+|\text{Ag})} = 0.80 \text{ V}$

29. (i) $\text{Cr}|\text{Cr}^{3+}||\text{Cd}^{2+}|\text{Cd}$
 $E^\ominus = E^\ominus_{(\text{Cathode})} - E^\ominus_{(\text{Anode})}$
 $= 0.40 - (-0.74) = 0.34 \text{ V}$

(ii) $\text{Fe}^{2+}|\text{Fe}^{3+}||\text{Ag}^+|\text{Ag}$
 $E^\ominus = E^\ominus_{(\text{Cathode})} - E^\ominus_{(\text{Anode})}$
 $= 0.80 - 0.77 = 0.03 \text{ V}$

30. No, because reduction potential of $\text{Cu}^{2+}|\text{Cu}$ is less than that of Cl_2 .

31. Copper ions get reduced to copper.

32. In beaker A, Ag^+ will be reduced to Ag because reduction potential of $\text{Ag}^+|\text{Ag}$ is more than that of copper.



33. Cell reaction: $\text{Mg}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Cu}(s)$

$$\begin{aligned} E &= E^\ominus - \frac{0.059}{2} \log \frac{[\text{Mg}^{2+}(aq)]}{[\text{Cu}^{2+}(aq)]} \\ &= 2.71 - \frac{0.059}{2} \log \frac{0.1}{0.01} \\ &= 2.71 - 0.0295 \times 1 = 2.6805 \text{ V} \end{aligned}$$

34. $\text{Zn}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}(s)$

$$\begin{aligned} E^\ominus &= E^\ominus_{(\text{Ag}^+|\text{Ag})} - E^\ominus_{(\text{Zn}^{2+}|\text{Zn})} \\ &= 0.80 - (-0.76) = 1.56 \text{ V} \\ E &= E^\ominus - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \\ 1.48 &= 1.56 - \frac{0.059}{2} \log \frac{1.0}{[\text{Ag}^+]^2} \\ 1.48 - 1.56 &= -\frac{0.059}{2} \log \frac{1.0}{[\text{Ag}^+]^2} \end{aligned}$$

$$\begin{aligned} -0.08 &= -\frac{0.059}{2} \log \frac{1.0}{[\text{Ag}^+]^2} \\ \log \frac{1.0}{[\text{Ag}^+]^2} &= \frac{2 \times 0.08}{0.059} = 2.712 \\ \frac{1.0}{[\text{Ag}^+]^2} &= 515.2 \\ [\text{Ag}^+]^2 &= \frac{1.0}{515.2} = 1.941 \times 10^{-3} \\ [\text{Ag}^+] &= 0.044 \text{ M} \end{aligned}$$

35. For the cell reaction
 $\text{Sn}^{4+} + \text{Zn}(s) \longrightarrow \text{Sn}^{2+} + \text{Zn}^{2+}$

The Nernst equation is

$$\begin{aligned} E &= E^\ominus - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}][\text{Zn}^{2+}]}{[\text{Sn}^{4+}]} \\ &= 0.89 - \frac{0.059}{2} \log \frac{(0.5) \times (2.0)}{(1.50)} \\ &= 0.89 - \frac{0.059}{2} \log 0.667 \\ &= 0.89 - (-0.005) = 0.895 \text{ V.} \end{aligned}$$

36. $\text{Mg}(s) | \text{Mg}^{2+}(0.130 \text{ M}) || \text{Ag}^+(1.0 \times 10^{-4} \text{ M}) | \text{Ag}(s)$
The cell reaction is :



According to Nernst equation,

$$\begin{aligned} E &= E^\ominus - \frac{0.059}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2} \\ 2.96 &= E^\ominus - \frac{0.059}{2} \log \frac{(0.130)}{(1.0 \times 10^{-4})^2} \\ 2.96 &= E^\ominus - \frac{0.059}{2} \log (0.130 \times 10^8) \\ 2.96 &= E^\ominus - \frac{0.059}{2} \times 7.114 \\ 2.96 &= E^\ominus - 0.2099 \\ E^\ominus &= 2.96 + 0.2099 = 3.1699 \text{ V} = 3.17 \text{ V.} \end{aligned}$$

37. $E = E^\ominus_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]}$

$$\begin{aligned} E^\ominus_{\text{cell}} &= -0.44 - (-0.763) = 0.323 \text{ V} \\ E &= 0.323 - \frac{0.059}{2} \log \frac{0.01}{0.005} \\ &= 0.314 \text{ V} \end{aligned}$$

38. $E = E^\ominus_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{Ag}^+]^2}$

$$\begin{aligned} E^\ominus_{\text{cell}} &= 0.80 - (-0.44) = 1.24 \text{ V} \\ E &= 1.24 - \frac{0.059}{2} \log \frac{(0.1)}{(0.1)^2} \\ &= 1.2105 \text{ V} \end{aligned}$$

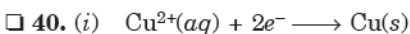
39. $2\text{Cr}(s) + 3\text{Fe}^{2+}(aq) \longrightarrow 2\text{Cr}^{3+}(aq) + 3\text{Fe}(s)$

$$E = E^\ominus_{\text{cell}} - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

Solution File

$$E^\ominus_{\text{cell}} = -0.44 - (-0.74) = 0.30 \text{ V}$$

$$E_{\text{cell}} = 0.30 - \frac{0.059}{6} \log \frac{(0.01)^2}{(0.1)^3} = 0.31 \text{ V}$$



$$\begin{aligned} E &= E^\ominus - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]} \\ &= 0.34 - \frac{0.059}{2} \log \frac{1}{0.1} \\ &= 0.3105 \text{ V} \end{aligned}$$

(ii) For $E = 0$

$$0 = 0.34 - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

$$\log \frac{1}{[\text{Cu}^{2+}]} = \frac{0.34}{0.0295} = 11.5254$$

$$[\text{Cu}^{2+}] = 2.98 \times 10^{-12}.$$

□ 41. $E^\ominus_{\text{cell}} = \frac{0.059}{n} \log K_c$

$$\begin{aligned} \text{or } \log K_c &= \frac{E^\ominus_{\text{cell}}}{0.059} \\ &= \frac{2 \times 0.235}{0.059} \\ K_c &= 9.25 \times 10^7 \end{aligned}$$

□ 42. $\log K_c = \frac{2 \times 0.320}{0.059} = 10.847$

$$K_c = 7.04 \times 10^{10}$$

□ 43. $E^\ominus_{\text{cell}} = E^\ominus_{(\text{Fe}^{3+}|\text{Fe}^{2+})} - E^\ominus_{(\text{Sn}^{4+}|\text{Sn}^{2+})} = 0.771 - 0.150 = 0.621 \text{ V}$

$$\log K_c = \frac{2 \times 0.621}{0.059} = 21.05$$

$$K_c = 1.0 \times 10^{21}$$

□ 44. $E^\ominus_{\text{cell}} = \frac{0.059}{2} \log K_c = \frac{0.059}{2} \times \log 1 \times 10^4 = 0.118 \text{ V.}$

□ 45. $E^\ominus_{\text{cell}} = E^\ominus_{(\text{Cd}^{2+}|\text{Cd})} - E^\ominus_{(\text{Zn}^{2+}|\text{Zn})} = 0.403 - (-0.763) = 0.360$

$$\begin{aligned} \log K_c &= \frac{2E^\ominus_{\text{cell}}}{0.059} \\ &= \frac{2 \times 0.36}{0.059} = 12.203 \end{aligned}$$

$$K_c = 1.596 \times 10^{12}$$

□ 46. $E^\ominus_{\text{cell}} = E^\ominus_{(\text{Cl}_2, \text{Cr})} - E^\ominus_{(\text{I}_2, \text{I})} = 0.824 \text{ V}$

$$\begin{aligned} \Delta G^\ominus &= -nFE^\ominus_{\text{cell}} = -2 \times (96500 \text{ C mol}^{-1}) \times (0.824 \text{ V}) \\ &= -159 \times 10^3 \text{ J} \end{aligned}$$

$$\log K_c = \frac{\Delta G^\ominus}{2.303RT}$$

$$= \frac{-159 \times 10^3}{2.303 \times 8.314 \times 298} = -27.8661$$

$$K_c = 7.35 \times 10^{27}$$

$$\Delta_r G^\ominus = -nFE^\ominus_{\text{cell}}$$

$$\Delta_r G^\ominus = (2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.236 \text{ V}) = -45.548 \text{ kJ mol}^{-1}$$

□ 47.

□ 48.

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{0.059}{6} \log \frac{[\text{Al}^{3+}]}{[\text{Fe}^{2+}]}$$

$$E^\ominus_{\text{cell}} = -0.44 - (-1.66) = 1.22 \text{ V}$$

$$\begin{aligned} E &= 1.22 - \frac{0.059}{6} \log \frac{(1 \times 10^{-2})^2}{(2 \times 10^{-2})^3} \\ &= 1.209 \text{ V} \end{aligned}$$

□ 49.

$$\Delta G^\ominus = -(6 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (1.22 \text{ V}) = -706.38 \text{ kJ}$$

$$E^\ominus_{\text{cell}} = E^\ominus_{(\text{Cd}^{2+}|\text{Cd})} - E^\ominus_{(\text{Cr}^{3+}|\text{Cr})} = -0.40 - (-0.74) = +0.34 \text{ V}$$

$$\begin{aligned} \Delta G^\ominus &= -nFE^\ominus \\ &= -6 \times (96500 \text{ C mol}^{-1}) \times (0.34 \text{ V}) \\ &= -196.86 \text{ kJ mol}^{-1}. \end{aligned}$$

□ 50.

$$E^\ominus_{\text{cell}} = 0.80 - 0.34 = 0.46 \text{ V}$$

$$\begin{aligned} E &= E^\ominus - \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \\ &= 0.46 - \frac{0.059}{2} \log \frac{(0.130)}{(1.0 \times 10^{-4})^2} \\ &= 0.25 \text{ V} \end{aligned}$$

$$\Delta G = -2 \times 96500 \times 0.25$$

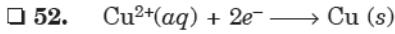
$$= -48.250 \text{ kJ}$$

□ 51. $I = 2A, t = 15 \text{ min} = 15 \times 60 = 900 \text{ s}$

$$Q = I \times t = 2 \times 900 = 1800 \text{ C}$$

96500 C of electricity deposit Ag = 108 g

$$\begin{aligned} 1800 \text{ C of electricity will deposit Ag} &= \frac{108 \times 1800}{96500} \\ &= 2.014 \text{ g} \end{aligned}$$



$$\text{Quantity of electricity passed} = I \times t$$

$$\begin{aligned} &= 0.75 \times 25 \times 60 \\ &= 1125 \text{ C} \end{aligned}$$

1125 C of electricity produces copper = 0.369 g

2 × 96500 C of electricity produce copper

$$= \frac{0.369}{1125} \times 2 \times 96500 = 63.3 \text{ u}$$

Atomic mass of Cu = 63.3 u.

□ 53. Quantity of electricity = $1.0 \times 15 \times 60 = 900 \text{ C}$

$$2 \times 96500 \text{ C of electricity produced Cl}_2 = 71 \text{ g}$$

900 C of electricity will produce

$$\begin{aligned} \text{Cl}_2 &= \frac{71}{2 \times 96500} \times 900 \\ &= 0.331 \text{ g} \end{aligned}$$

Solution File

54. (i) $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^- \therefore 96500 \text{ C}$
(ii) $2\text{H}_2\text{O}_2 \longrightarrow 4\text{H}^+ + \text{O}_2 + 4e^- \therefore 2 \times 96500 \text{ C}$
(for 1 mole of H_2O_2)
(iii) $\text{F}_2 + 2e^- \longrightarrow 2\text{F}^- \therefore 2 \times 96500 \text{ C}$
55. 0.583 g of Ag is deposited by charge = $\frac{96500}{108} \times 0.583$
= 520.9 C

Now, 197 g of Au is deposited by electric current
= $n \times 96500 \text{ C}$

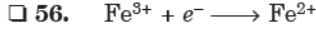
(n is the oxidation state of gold)

0.355 g of Au will be deposited by current

$$= \frac{n \times 96500}{197} \times 0.355$$

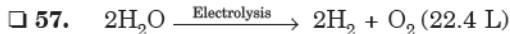
$$\frac{n \times 96500}{197} \times 0.355 = 520.9$$

$$n = 2.99 \text{ or } = +3$$



3.0 mol of Fe^{3+} will require = $3 \times 96500 \text{ C}$

Now, $t = \frac{Q}{I} = \frac{3 \times 96500}{2.0}$
= 144750 s or 40.21 hr.



22.4 L of O_2 is produced by electricity = $4 \times 96500 \text{ C}$
 $50.0 \times 10^{-3} \text{ L of } \text{O}_2$ is produced by electricity

$$= \frac{4 \times 96500}{22.4} \times 50.0 \times 10^{-3}$$

= 861.6 C

Now, $Q = I \times t$

$$861.6 = I \times 3 \times 60 \times 60$$

$$\therefore I = 0.0798 \text{ A}$$

58. (i) 40 g of Ca is produced by 2F

$$\therefore 10 \text{ g of Ca will be produced by } \frac{2}{40} \times 10 = 0.5 \text{ F}$$

(ii) 27 g of Al is produced by 3F

$$81 \text{ g of Al will be produced by } \frac{3}{27} \times 81 = 9 \text{ F.}$$



Quantity of electricity passed = $I \times t$

$$\therefore Q = 0.20 \times 3 \times 60 \times 60 \text{ C} = 2160 \text{ C}$$

96500 C of electricity deposit = 107.92 g Ag

$$2160 \text{ C of electricity deposit} = \frac{107.92}{96500} \times 2160 = 2.42 \text{ g}$$

Let the thickness of silver deposited = x cm

Weight = volume × density
= area × thickness × density

(∴ Volume = area × thickness)

$$2.42 = 800 \times x \times 10.47$$

$$x = 0.000289 \text{ or } 2.89 \times 10^{-4} \text{ cm.}$$



1 mol of Al requires 3 mol of electrons or 3F

27 g of Al require = 3F

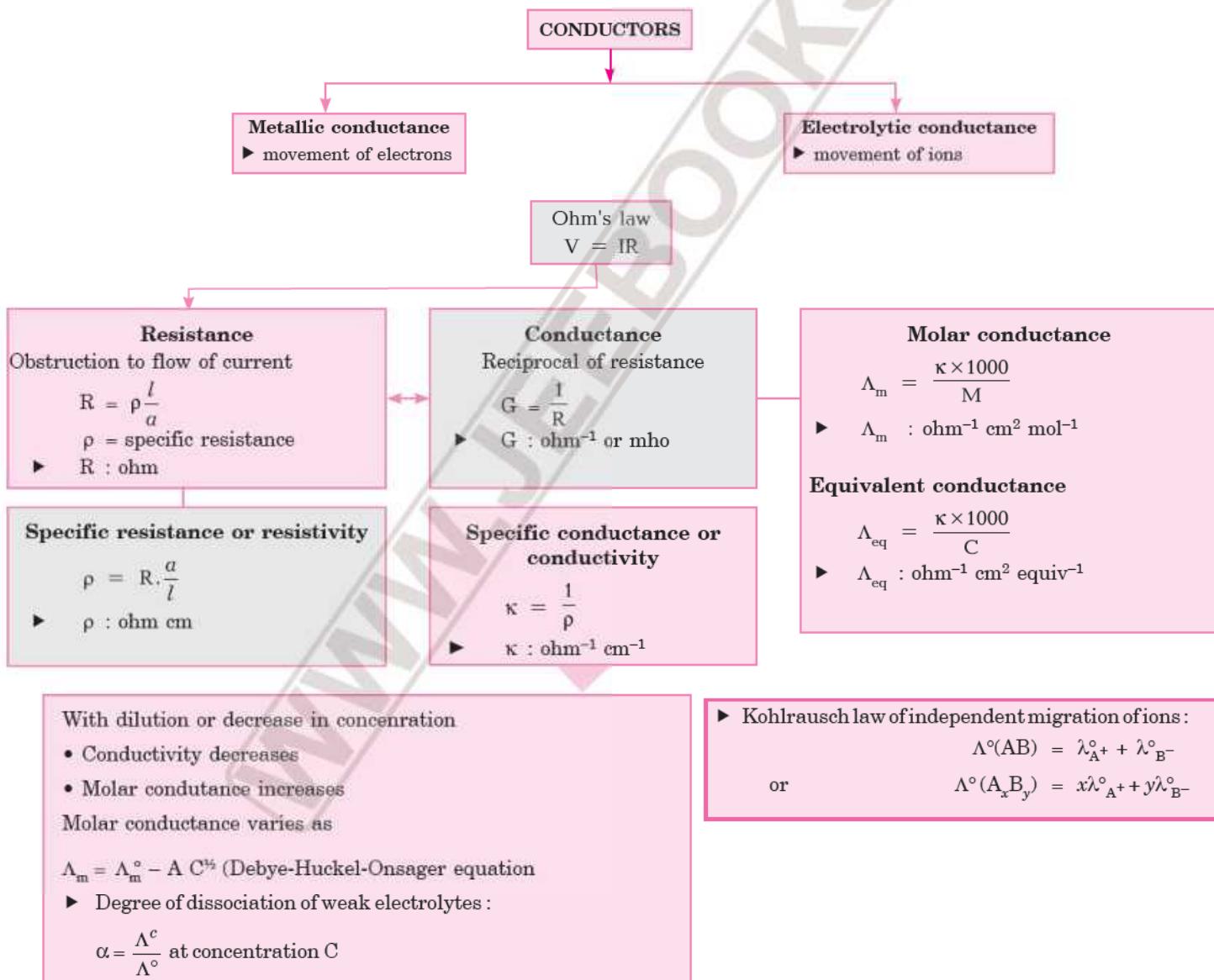
$$40 \text{ g of Al require} = \frac{3}{27} \times 40 = 4.44 \text{ F.}$$

Key Terms & Laws

- **Metallic conductors** are the substances which allow the passage of electric current through them without undergoing any chemical change.
- **Electrolytes** are the substances which allow the passage of electric current through them in their molten states or in the form of their aqueous solutions and undergo chemical decomposition.
- **Specific resistance or resistivity**. The resistance of a conductor 1 cm in length and having 1 cm^2 area of cross-section.
- **Specific conductance or conductivity**. It is the conductance of a solution of 1 cm length and having 1 square centimetre as the area of cross-section. Or it is the conductance between the opposite faces of 1 centimetre cube of a conductor.
- **Molar conductance**. It is the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.
- **Electrochemical cell**. It is the device in which electrical energy is produced from chemical reactions.
- **Electrode potential**. It is a measure of tendency of an electrode in a half cell to lose or gain electrons.
- **Electromotive force or cell potential**. It is the difference between the electrode potentials of two electrodes constituting an electrochemical cell.
- **Electrochemical series**. The arrangement of elements in the order of increasing reduction potential values is called electrochemical series.

- **Electrolysis.** It is the process of decomposition of an electrolyte by the passage of electricity through its aqueous solution or molten state.
- **Electrolytic cell.** The device which converts electrical energy into chemical energy.
- **Corrosion.** It is a redox reaction which occurs at the surfaces of metals when exposed to atmospheric conditions and form undesirable products (usually oxides).
- **Kohlrausch law.** It states that at infinite dilution when the dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of other ions with which it is associated.
- **Faraday's first law of electrolysis.** It states that the amount of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolytic solution.
- **Faraday's second law of electrolysis.** It states that when same quantity of electricity is passed through different electrolytic solutions connected in series, the weights of the substances produced at the electrodes are directly proportional to their chemical equivalent weights.

QUICK CHAPTER ROUND UP



Electrochemical Cells

⇒ convert chemical energy into electrical energy
Cathode is +ve (reduction), Anode is -ve (oxidation)

$$\text{E.M.F of cell} = E^\circ \text{ (cathode)} - E^\circ \text{ (anode)} = E^\circ \text{ (R.H.S.)} - E^\circ \text{ (L.H.S.)}$$

- For an electrode reaction, Nernst equation is :



$$E = E^\circ - \frac{RT}{nF} \ln \left[\frac{1}{M^{n+}} \right]$$

- For a cell reaction



Nernst equation is

$$E = E^\circ - \frac{0.059}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- $E_{\text{cell}}^\circ = \frac{2.303 RT}{nF} \log K \text{ or } = \frac{0.059}{n} \log K \text{ at } 25^\circ\text{C}$

- $\Delta G^\circ = -RT \ln K \text{ or } = -2.303 RT \log K$

Faraday's laws of Electrolysis

- First law : $w = Z \times Q$ or $w = Z I t$
- Second law : amount of substance deposited \propto moles of electrons exchanged during oxidation-reduction reaction

Cells or Batteries

Primary cells

- electrode reactions cannot be reversed
- not chargeable

Dry cell :	Anode	Cathode	Electrolyte
	Zinc	Graphite	$MnO_2 + C$
Mercury cell :	Zinc	Graphite	$NH_4Cl + ZnCl_2$

Secondary cells (batteries)

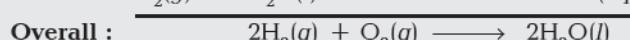
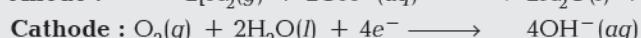
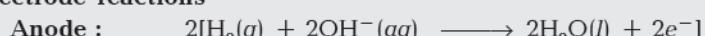
- electrode reactions can be reversed
- chargeable

Lead storage cell

Anode : Lead
Cathode : PbO_2
Electrolyte : Aqueous H_2SO_4

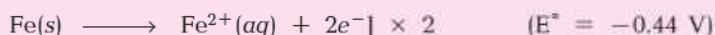
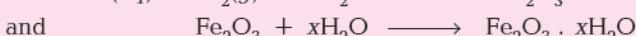
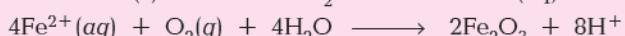
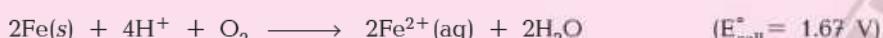
Fuel cell : $H_2 - O_2$ Fuel cell ► Energy of combustion → Electrical energy
Porous carbon electrodes immersed in NaOH or KOH solution (Electrolyte).

Electrode reactions



CORROSION :

Process of deterioration of a metal as a result of its reaction with air or water (environment) surrounding it
 \Rightarrow corrosion of iron \rightarrow **Rusting** ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$)

Redox reactions during rusting**Oxidation half reaction:****Reduction half reaction****Overall cell reaction**

Rust

The process of covering iron with zinc to protect it from rusting is **galvanization**.



NCERT FILE

Solved

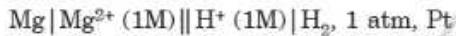


NCERT

In-text Questions

Q.1. How would you determine the standard electrode potential of the system $\text{Mg}^{2+}|\text{Mg}$?

Ans. The standard electrode potential of $\text{Mg}^{2+}|\text{Mg}$ system can be measured by connecting the Mg electrode immersed in 1M Mg^{2+} solution with S.H.E. This may be represented as:



From the measured potential $E^\ominus_{(\text{Mg}^{2+}|\text{Mg})}$ can be calculated

$$E^\ominus_{\text{cell}} = E^\ominus_{(\text{H}^+|\text{H}_2)} - E^\ominus_{(\text{Mg}^{2+}|\text{Mg})}$$

$$\therefore E^\ominus_{(\text{Mg}^{2+}|\text{Mg})} = 0 - E^\ominus_{\text{cell}}$$

This is similar to the method discussed for $\text{Zn}^{2+}|\text{Zn}$ system. (Refer Page 30, Fig 11).

Q.2. Can you store copper sulphate solution in a zinc pot ?

Ans. No, because zinc is more reactive than copper and it will displace copper from copper sulphate solution as :



As a result, zinc will gradually pass into the solution and copper will be precipitated.

Q.3. Consult the table of standard electrode potentials and suggest three substances which can oxidize ferrous ions under suitable conditions.

Ans. The electrode potential of $\text{Fe}^{3+}|\text{Fe}^{2+}$ is 0.78 V. The substances having electrode potential more than 0.78 V will be reduced and hence act as oxidising agent. For example,

- (i) acidified KMnO_4 (ii) acidified $\text{Cr}_2\text{O}_7^{2-}$ (iii) acidified H_2O_2 .

Q.4. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Ans.

$$\text{pH} = 10$$

$$[\text{H}^+] = 10^{-10}$$

$$E = E^\ominus - \frac{0.059}{1} \log \frac{1}{[\text{H}^+]}$$

$$E = 0 - \frac{0.059}{1} \log \frac{1}{10^{-10}}$$

$$E = 0 - 0.059 \times 10$$

$$= -0.59 \text{ V.}$$

Q.5. Calculate the e.m.f of the cell in which the following reaction takes place :



Given that $E^\ominus_{\text{cell}} = 1.05 \text{ V}$

Ans.

$$E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 1.05 - \frac{0.059}{2} \log \frac{0.160}{(0.002)^2}$$

$$= 1.05 - \frac{0.059}{2} \times 4.602$$

$$= 1.05 - 0.14 = 0.91 \text{ V.}$$

Q.6. The cell in which the following reaction occurs :



has $E^\ominus_{\text{cell}} = 0.236 \text{ V}$ at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Ans.

$$\begin{aligned}E_{\text{cell}}^{\circ} &= 0.236 \text{ V} \\ \Delta G^{\ominus} &= -nFE^{\ominus} \\ n = 2, F &= 96500 \text{ C} \\ \Delta G^{\ominus} &= 2 \times (96500 \text{ C}) \times (0.236 \text{ V}) \\ &= -45548 \text{ J or } = -45.55 \text{ kJ} \\ \Delta G^{\ominus} &= -2.303 RT \log K_c\end{aligned}$$

or

$$\begin{aligned}\log K_c &= - \frac{\Delta G^{\ominus}}{2.303 RT} \\ &= \frac{-45.55}{2.303 \times 8.314 \times 10^{-3} \times 298} \\ &= 7.983\end{aligned}$$

$$K_c = \text{antilog}(7.983) = 9.62 \times 10^7$$

Q.7. Why does the conductivity of a solution decrease with dilution?

Ans. Conductivity of an electrolyte solution decreases with dilution because the number of ions per unit volume furnished by an electrolyte decreases with dilution.

Q.8. Suggest a way to determine Λ_m° value of water.

$$\Lambda_m^{\circ}(\text{H}_2\text{O}) = \Lambda_m^{\circ}(\text{H}^+) + \Lambda_m^{\circ}(\text{OH}^-)$$

We determine $\Lambda_m^{\circ}(\text{HCl})$, $\Lambda_m^{\circ}(\text{NaOH})$, and $\Lambda_m^{\circ}(\text{NaCl})$. Then

$$\begin{aligned}\Lambda_m^{\circ}(\text{H}_2\text{O}) &= \Lambda_m^{\circ}(\text{HCl}) + \Lambda_m^{\circ}(\text{NaOH}) - \Lambda_m^{\circ}(\text{NaCl}) \\ &= \Lambda_m^{\circ}(\text{H}^+) + \Lambda_m^{\circ}(\text{Cl}^-) + \Lambda_m^{\circ}(\text{Na}^+) \\ &\quad + \Lambda_m^{\circ}(\text{OH}^-) - \Lambda_m^{\circ}(\text{Na}^+) - \Lambda_m^{\circ}(\text{Cl}^-) \\ &= \Lambda_m^{\circ}(\text{H}^+) + \Lambda_m^{\circ}(\text{OH}^-)\end{aligned}$$

Q.9. The molar conductivity of 0.025 mol L⁻¹ methanoic acid is 46.1 S cm² mol⁻¹. Calculate its degree of dissociation and dissociation constant. Given $\Lambda^{\circ}(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\Lambda^{\circ}(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$.

$$\begin{aligned}\Lambda^{\circ}(\text{HCOOH}) &= \Lambda^{\circ}(\text{H}^+) + \Lambda^{\circ}(\text{HCOO}^-) \\ &= 349.6 + 54.6 \\ &= 404.2 \text{ S cm}^2 \text{ mol}^{-1} \\ \alpha &= \frac{\Lambda_c^m}{\Lambda_0^m} = \frac{46.1}{404.2} = 0.114 \\ K_c &= \frac{c\alpha^2}{1-\alpha} \\ &= \frac{0.025 \times (0.114)^2}{1-0.114} \\ &= 3.67 \times 10^{-4}\end{aligned}$$

Q.10. If a current of 0.5 ampere flows through a metallic wire for 2 hour, then how many electrons would flow through the wire?

$$\begin{aligned}\text{Coulombs of electrons} &= \text{Current} \times \text{time} \\ &= 0.5 \text{ A} \times 2 \times 60 \times 60 \text{ s} = 3600 \text{ C}\end{aligned}$$

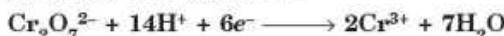
Now, the current of 1F (96500 C) is equivalent to 1 mole i.e., 6.022×10^{23} electrons.

$$\begin{aligned}\therefore 3600 \text{ C of current is equivalent to flow of electrons} \\ &= \frac{6.022 \times 10^{23}}{96500} \times 3600 = 2.246 \times 10^{22} \text{ electrons.}\end{aligned}$$

Q.11. Suggest a list of metals that are extracted electrolytically.

Ans. Sodium, potassium, calcium, magnesium, aluminium, etc.

Q.12. Consider the reaction :



What is the quantity of electricity in coulombs needed to reduce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$?

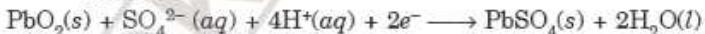
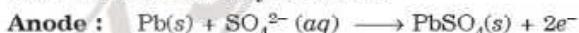
Ans. 6 mol of electrons are required to reduce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$

Now 1 mol of electrons = 96500 C

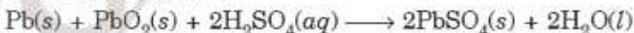
$$6 \text{ mol of electrons} = 96500 \times 6 = 5.79 \times 10^5 \text{ C}$$

Q.13. Write the chemistry of recharging of the lead storage battery, highlighting all the materials that are involved during discharging.

Ans. A lead storage battery consists of anode of lead, cathode of a grid of lead packed with lead dioxide (PbO_2) and 38% H_2SO_4 solution as electrolyte. The following reactions occur when the battery is in use :



Overall reaction :



On charging the battery, the reverse reaction takes place i.e., PbSO_4 deposited on the electrodes is converted back into lead and PbO_2 and H_2SO_4 in regenerated.

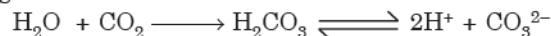
Q.14. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Ans. (i) Methane (ii) Ethane

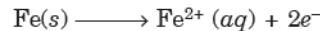
Recently zinc metal has been used in place of hydrogen gas in USA to develop a source of power for automobiles.

Q.15. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

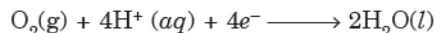
Ans. Water layer present on the surface of iron (particularly during rainy season) dissolves acidic oxides present in air such as CO_2 , SO_2 , etc to form acids which dissociate to give H^+ ions :



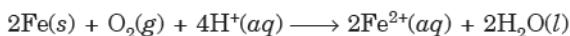
In the presence of H^+ ions, iron starts losing electrons at a particular spot of iron object to form ferrous ions. Therefore, oxidation takes place and that spot behaves as anode.



The electrons released at anodic spot move through the metal to reach another spot where H^+ ions and the dissolved oxygen take up these electrons and reduction takes place. Hence this spot behaves as cathode



The overall reaction is :



Thus, an electrochemical cell sets up on the surface. Ferrous ions are further oxidised by atmospheric oxygen to ferric ions which combine with water molecules to form hydrated ferric oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, which is rust.



Q.1. Arrange the following metals in the order in which they displace each other from the solution of their salts

Al, Cu, Fe, Mg and Zn.

Ans. Mg, Al, Zn, Fe, Cu.

Q.2. Given the standard electrode potentials,

$$\text{K}^+/\text{K} = -2.93 \text{ V}, \text{Ag}^+/\text{Ag} = 0.80 \text{ V}$$

$$\text{Hg}^{2+}/\text{Hg} = 0.79 \text{ V}$$

$$\text{Mg}^{2+}/\text{Mg} = -2.37 \text{ V}, \text{Cr}^{3+}/\text{Cr} = -0.74 \text{ V}$$

Arrange these metals in their increasing order of reducing power.

Ans. Ag⁺/Ag, Hg²⁺/Hg, Cr³⁺/Cr, Mg²⁺/Mg, K⁺/K

Q.3. Depict the galvanic cell in which the reaction



takes place. Further show :

- (i) Which of the electrode is negatively charged ?
- (ii) The carriers of the current in the cell.
- (iii) Individual reaction at each electrode.

(D.S.B. 2008; A.I.S.B. 2008)

Ans. The cell may be depicted similar to Fig. 6 (Page 23). The cell may be represented as :



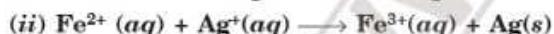
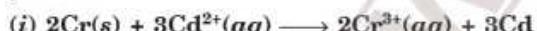
(i) Zinc electrode (anode)

(ii) Current will flow from silver to zinc in the external circuit.

(iii) At anode : $\text{Zn}(s) \longrightarrow \text{Zn}^{2+} + 2e^-$

At cathode : $\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s)$

Q.4. Calculate the standard cell potentials of galvanic cells in which of the following reactions take place :



Calculate the $\Delta_r G^\ominus$ and equilibrium constant of the reactions.

Ans. (i)

$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{(\text{cathode})} - E^\ominus_{(\text{anode})} \\ &= -0.40 - (-0.74) = +0.34 \text{ V} \end{aligned}$$

$$\begin{aligned} \Delta_r G^\ominus &= -nFE^\ominus_{\text{cell}} \\ &= -6 \times 96500 \times 0.34 \\ &= -196860 \text{ CV mol}^{-1} \\ &= -196860 \text{ J mol}^{-1} \\ &= -196.86 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \log K_c &= \frac{nE^\ominus_{\text{cell}}}{0.059} \\ &= \frac{6 \times 0.34}{0.059} = 34.576 \end{aligned}$$

$$K_c = 3.76 \times 10^{34}$$

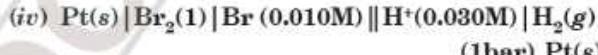
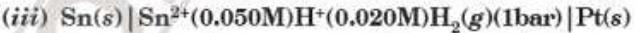
$$(ii) E^\ominus_{\text{cell}} = E^\ominus_{(\text{cathode})} - E^\ominus_{(\text{anode})}$$

$$\therefore = 0.80 - 0.77 = +0.03 \text{ V}$$

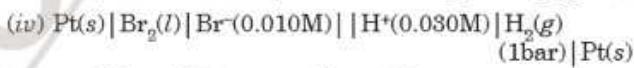
$$\begin{aligned} \Delta_r G^\ominus &= -nFE^\ominus_{\text{cell}} \\ &= -1 \times 96500 \times 0.03 \\ &= -2896500 \text{ CV mol}^{-1} \\ &= -289600 \text{ J mol}^{-1} \\ &= -289.6 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \log K_c &= \frac{nE^\ominus_{\text{cell}}}{0.059} \\ &= \frac{1 \times 0.03}{0.059} = 0.508 \\ K_c &= 3.22 \end{aligned}$$

Q.5. Write the Nernst equation and calculate emf of the following cells at 298K :



Ans. Parts (i), (ii) and (iii) Refer Solved Example 32 (page 41)



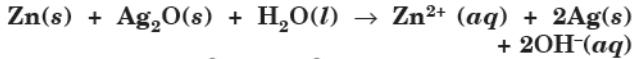
$$E = E^\ominus - \frac{0.059}{2} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2}$$

$$E^\ominus = 0 - 1.08 = -1.08$$

$$\begin{aligned} E &= -1.08 - \frac{0.059}{2} \log \frac{1}{(0.01)^2 (0.030)^2} \\ &= -1.08 - \frac{0.059}{2} \log (1.11 \times 10^7) \\ &= -1.08 - \frac{0.059}{2} \times 7.0457 \\ &= -1.08 - 0.208 \\ &= -1.288 \text{ V} \end{aligned}$$

The given reaction is not feasible. Thus, oxidation will occur at the hydrogen electrode and reduction on the Br₂ electrode and E[⊖] cell = 1.288 V.

Q.6. In the button cells widely used in watches and other devices the following reaction takes place :



Determine $\Delta_r G^\ominus$ and E[⊖] for the reaction.

(Meghalaya S.B. 2015)

Ans. Refer Solved Example 43.(page 48)

Q.7. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Ans. Refer Text page 4, 5 and 12.

Q.8. The conductivity of 0.20 M solution of KCl at 298K is 0.0248 S cm⁻¹. Calculate its molar conductivity.

Ans. Refer Solved Example 2. (page 10)

Q.9. The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is $1500\ \Omega$. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is $0.146 \times 10^{-3}\ \text{S cm}^{-1}$?

$$\text{Ans. Cell constant, } G^* = \frac{\text{Conductivity}}{\text{Conductance}}$$

$$\text{Conductance} = \frac{1}{1500}\ \text{S}$$

$$\therefore \text{Cell constant} = \frac{0.146 \times 10^{-3}\ \text{S cm}^{-1}}{1/1500} \\ = 0.219\ \text{cm}^{-1}$$

Q.10. The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below :

Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa/\text{S m}^{-1}$	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m^c for all concentrations and draw a plot between Λ_m^c and $C^{1/2}$. Find the value of Λ_m° .

Ans. Refer Solved Example 9. (page 14)

Q.11. Conductivity of 0.00241M acetic acid is $7.896 \times 10^{-5}\ \text{S cm}^{-1}$. Calculate its molar conductivity and if Λ_m° for acetic acid is $390.5\ \text{S cm}^2\ \text{mol}^{-1}$, what is its dissociation constant ?

$$\text{Ans. } \Lambda_m^c = \frac{\kappa \times 1000}{M}$$

$$= \frac{7.896 \times 10^{-5}\ \text{S cm}^{-1} \times 1000\ \text{cm}^3\ \text{L}^{-1}}{0.00241\ \text{mol L}^{-1}}$$

$$= 32.76\ \text{S cm}^2\ \text{mol}^{-1}$$

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

$$= \frac{32.76}{390.5} = 8.39 \times 10^{-2}$$

$$K_a = \frac{\alpha^2}{1 - \alpha} = \frac{0.00241 \times (8.39 \times 10^{-2})^2}{(1 - 8.39 \times 10^{-2})}$$

$$= 1.86 \times 10^{-5}$$

Q.12. How much charge is required for the following reduction of

- (i) 1 mol of Al^{3+} to Al.
- (ii) 1 mol of Cu^{2+} to Cu
- (iii) 1 mol of MnO_4^- to Mn^{2+} ?

Ans. Refer Solved Example 54. (page 60)

Q.13. How much electricity in terms of Faraday is required to produce

- (i) 20.0 g of Ca from molten CaCl_2
- (ii) 40.0 g of Al from molten Al_2O_3 ?

Ans. (i) $\text{Ca}^{2+} + 2e^- \longrightarrow \text{Ca}$

1 mol of Ca i.e., 40 g require electricity = $2F$

$$20\ \text{g of Ca will require electricity} = \frac{2 \times 20}{40}\ F$$

$$= 1\ F$$

(ii) $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$

1 mol of Al = 27 g

$\therefore 27\ \text{g of Al require electricity} = 3F$

$$40\ \text{g of Al will require electricity} = \frac{3}{27} \times 40F$$

$$= 4.4F$$

Q.14. How much electricity is required in coulomb for the oxidation of

- (i) 1 mol of H_2O to O_2
- (ii) 1 mol of FeO to Fe_2O_3 ?

Ans. Refer Solved Example 54. (page 60)

Q.15. A solution of $\text{Ni}(\text{NO}_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode ?

Ans. Refer Solved Example 54. (page 60)

Q.16. Three electrolytic cells A, B, C containing solution of ZnSO_4 , AgNO_3 and CuSO_4 , respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and of zinc were deposited ?

Ans. Refer Solved Example 57. (page 61)

Q.17. Predict if the reaction between the following is feasible :

- (i) $\text{Fe}^{3+}(\text{aq})$ and $\text{I}^-(\text{aq})$
- (ii) $\text{Ag}^+(\text{aq})$ and $\text{Cu}(\text{s})$
- (iii) $\text{Fe}^{3+}(\text{aq})$ and $\text{Br}^-(\text{aq})$
- (iv) $\text{Ag}(\text{s})$ and $\text{Fe}^{3+}(\text{aq})$
- (v) $\text{Br}_2(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$

Given standard electrode potentials :

$$E^\ominus_{1/2} \text{I}_2/\text{I}^- = 0.54\ \text{V}, E^\ominus_{1/2} \text{Cu}^{2+}/\text{Cu} = 0.34\ \text{V},$$

$$E^\ominus_{1/2} \text{Br}_2/\text{Br}^- = 1.09\ \text{V}, E^\ominus_{1/2} \text{Ag}^+/\text{Ag} = 0.80\ \text{V} \text{ and}$$

$$E^\ominus_{1/2} \text{Fe}^{3+}/\text{Fe}^{2+} = 0.77\ \text{V}$$

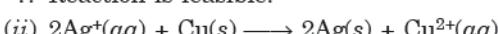
Ans. (i) A reaction is feasible if EMF of the cell is positive.



Cell is : $\text{Pt}|\text{I}_2|\text{I}^-(\text{aq})||\text{Fe}^{3+}(\text{aq})|\text{Fe}^{2+}(\text{aq})|\text{Pt}$

$$E^\ominus_{\text{cell}} = E^\ominus(\text{Fe}^{3+}|\text{Fe}^{2+}) - E^\ominus(1/2\text{I}_2|\text{I}^-) \\ = 0.77 - 0.54 = 0.23\ \text{V}$$

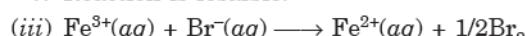
\therefore Reaction is feasible.



$\text{Cu}|\text{Cu}^{2+}(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag}$

$$E^\ominus_{\text{cell}} = E^\ominus(\text{Ag}^+|\text{Ag}) - E^\ominus(\text{Cu}^{2+}|\text{Cu}) \\ = 0.80 - 0.34 \\ = 0.46\ \text{V}$$

\therefore Reaction is feasible.



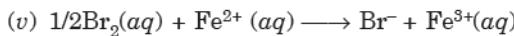
$$E^\ominus_{\text{cell}} = E^\ominus(\text{Fe}^{3+}|\text{Fe}^{2+}) - E^\ominus(\text{Br}_2|\text{Br}^-) \\ = 0.77 - 1.09 \\ = -0.32\ \text{V}$$

\therefore Reaction is not feasible.



$$E^\ominus_{\text{cell}} = E^\ominus(\text{Fe}^{3+}|\text{Fe}^{2+}) - E^\ominus(\text{Ag}^+|\text{Ag}) \\ = 0.77 - 0.80 \\ = -0.03\ \text{V}$$

\therefore Reaction is not feasible.



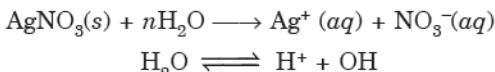
$$E^\ominus_{\text{cell}} = E^\ominus(\text{Br}_2|\text{Br}^-) - E^\ominus(\text{Fe}^{3+}|\text{Fe}^{2+}) \\ = 1.09 - 0.77 \\ = 0.32\ \text{V}$$

\therefore Reaction is feasible.

Q.18. Predict the products of electrolysis in each of the following :

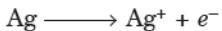
- An aqueous solution of AgNO_3 with silver electrode.
- An aqueous solution of AgNO_3 with platinum electrodes.
- A dilute solution of H_2SO_4 with platinum electrodes.
- An aqueous solution of CuCl_2 with platinum electrodes.

Ans. (i) Electrolysis of aqueous solution of AgNO_3 using silver electrodes :



At cathode : Ag^+ ions have lower discharge potential than H^+ ions. Hence Ag^+ ions will be deposited as silver (in preference to H^+ ions).

At anode : Since silver electrode is attacked by NO_3^- ions, Ag anode will dissolve to form Ag^+ ions in the solution.



- Electrolysis of aqueous solution of AgNO_3 using platinum electrodes

At cathode : Same as above.

At anode : Since silver is not attacked, out of



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Note:

Objective Questions from Exemplar Problems are given in Competition File, page 114.

Short Answer Type Questions

- Can absolute electrode potential of an electrode be measured?

Ans. No, absolute electrode potential of an electrode cannot be measured.

- Can E_{cell}^\ominus or $\Delta_r G^\ominus$ for a cell reaction ever be equal to zero?

Ans. No, $\Delta G^\circ = nFE^\circ$, if E° is zero, cell reaction will not occur.

- Under what condition is $E_{\text{cell}} = 0$ or $\Delta_r G = 0$?

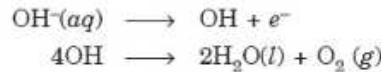
Ans. When the cell reaction reaches equilibrium, $E_{\text{cell}} = 0$, so that ΔG is also zero.

- What does the negative sign in the expression $E_{\text{Zn}^{2+}/\text{Zn}}^\ominus = -0.76 \text{ V}$ mean?

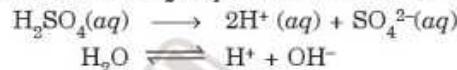
Ans. It means that zinc is more reactive than hydrogen. When zinc electrode is connected to SHE, zinc will get oxidised and H^+ will get reduced.

- Aqueous copper sulphate solution and aqueous silver nitrate solution are electrolysed by 1 Ampere current for 10 minutes in separate electrolytic

OH^- and NO_3^- ions, OH^- ions have lower discharge potential and hence OH^- ions will be discharged in preference to NO_3^- . The OH^- will decompose to give O_2 .



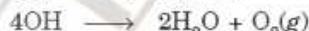
- Electrolysis of H_2SO_4 with Pt electrodes



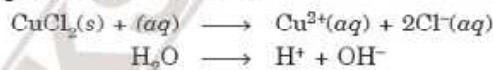
At cathode : $\text{H}^+ + e^- \longrightarrow \text{H}$



At anode : $\text{OH}^- \longrightarrow \text{OH} + e^-$



- Electrolysis of aqueous solution of CuCl_2 with platinum electrodes



At cathode : Cu^{2+} will be reduced in preference to H^+ ions



At anode : Cl^- ions will be oxidized in preference to OH^- ions



Thus, copper will be deposited on the cathode and Cl_2 will be liberated at anode.

Exemplar Problems

Subjective Questions

cells. Will the mass of copper and silver deposited on the cathode be same or different? Explain your answer.

Ans. Mass of copper and silver deposited on cathode will be different. It depends upon equivalent mass.

- Depict the galvanic cell in which the cell reaction is $\text{Cu} + 2\text{Ag}^+ \longrightarrow 2\text{Ag} + \text{Cu}^{2+}$

Ans. $\text{Cu} | \text{Cu}^{2+}(\text{aq}, 1\text{M}) \parallel \text{Ag}^+(\text{aq}, 1\text{M}) | \text{Ag}$.

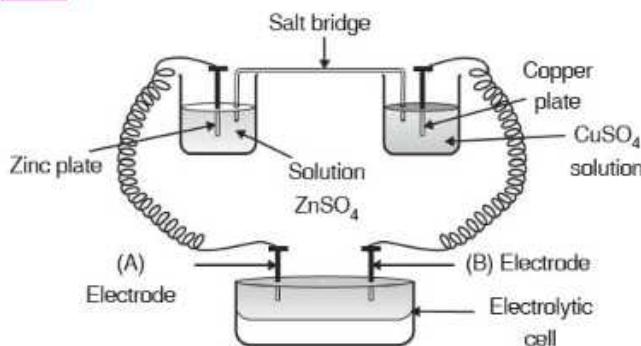
- Value of standard electrode potential for the oxidation of Cl^- ions is more positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is Cl^- oxidised at anode instead of water?

Ans. Under the conditions of electrolysis of aqueous sodium chloride, oxidation of water at anode requires over potential and therefore, Cl^- is oxidised instead of water.

- What is electrode potential?

Ans. The electrical potential difference set up between the metal and its solution is called electrode potential.

- Consider the following diagram in which an electrochemical cell is coupled to an electrolytic cell. What will be the polarity of electrodes 'A' and 'B' in the electrolytic cell?



Ans. 'A' will have -ve polarity and 'B' will have +ve polarity.

- 10. Why is alternating current used for measuring resistance of an electrolytic solution?**

Ans. The alternating current is used to prevent electrolysis so that the concentration of ion in the solution remains constant.

- 11. A galvanic cell has electrical potential of 1.1V. If an opposing potential of 1.1V is applied to this cell, what will happen to the cell reaction and current flowing through the cell?**

Ans. When the opposing potential becomes equal to electrical potential, the cell reaction stops and no current flows through the cell. Thus, there is no chemical reaction.

- 12. How will the pH of brine (aq. NaCl solution) be affected when it is electrolysed?**

Ans. Since NaOH is formed during electrolysis, pH of the brine solution will increase.

- 13. Unlike dry cell, the mercury cell has a constant cell potential throughout its life. Why?**

Ans. Because ions are not involved in the overall cell reaction of mercury cells.

- 14. Solutions of two electrolytes 'A' and 'B' are diluted. The Λ_m of 'B' increases 1.5 times while that of A increases 25 times. Which of the two is a strong electrolyte? Justify your answer.**

(C.B.S.E. Sample Paper 2017-18)

Ans. Electrolyte B is strong because on dilution Λ_m increases only small.

- 15. When acidulated water (dil. H_2SO_4 solution) is electrolysed, will the pH of the solution be affected? Justify your answer.**

Ans. pH of the solution remains same because $[H^+]$ remains constant.



- 16. In an aqueous solution how does specific conductivity of electrolytes change with addition of water?**

Ans. On the addition of water, number of ions per unit volume decreases and therefore conductivity decreases.

- 17. Which reference electrode is used to measure the electrode potential of other electrodes?**

Ans. The standard hydrogen electrode is used as a reference electrode whose electrode potential is taken to be zero. The electrode potential of other electrodes is measured with respect to it.

- 18. Consider a cell given below**



Write the reactions that occur at anode and cathode.

Ans. Anode : $Cu \longrightarrow Cu^{2+} + 2e^-$

Cathode : $Cl_2 + 2e^- \longrightarrow 2Cl^-$

Cu is anode because it is getting oxidised.

Cl_2 is cathode because it is getting reduced.

- 19. Write the Nernst equation for the cell reaction in the Daniel cell. How will the E_{Cell} be affected when concentration of Zn^{2+} ions is increased?**

Ans. The cell reaction for Daniel cell is :



$$E_{\text{Cell}} = E^\ominus_{\text{cell}} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

E_{Cell} decreases when concentration of Zn^{2+} ions $[Zn^{2+}]$ increases.

- 20. What advantage do the fuel cells have over primary and secondary batteries?**

Ans. Primary batteries contain a limited amount of reactants and are discharged when the reactants have been consumed. Secondary batteries can be recharged but take a long time to recharge. Fuel cell runs continuously as long as the reactants are supplied to it and products are removed continuously.

- 21. Write the cell reaction of a lead storage battery when it is discharged. How does the density of the electrolyte change when the battery is discharged?**



Density of electrolyte decreases because water is formed and sulphuric acid is consumed as the product during discharge of the battery.

- 22. Why on dilution the Λ_m of CH_3COOH increases drastically, while that of CH_3COONa increases gradually?**

Ans. In the case of CH_3COOH , which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation.



In the case of strong electrolyte such as CH_3COONa , the number of ions remains the same but the interionic attraction decreases.

**QUICK****MEMORY TEST****A. Say True or False**

1. An electrochemical cell works only if emf is negative.
2. In an electrolytic cell reduction occurs at cathode.
3. Electrolytic conductance generally decreases with rise in temperature.
4. Greater reduction potential represents greater reducing power of the substance.
5. In Zn-Cu cell, copper acts as a cathode while in Cu-Ag cell, copper acts as anode.
6. Metallic conductance decreases with increase in temperature.
7. Both E_{cell}° and ΔG° for the cell reaction are intensive properties.
8. Reduction potential and oxidation potential for a half cell reaction are numerically equal but of opposite sign.
9. Out of HCl and NaCl, Δ_m° of HCl is higher.
10. CuSO₄ solution can be stirred with a silver spoon but AgNO₃ solution cannot be stirred with a copper spoon.

B. Complete the missing links

1. In an electrochemical cell, oxidation occurs at and reduction occurs at
2. ΔG° is related to e.m.f. (E°) of the cell as
3. The units of cell constant are
4. In a Leclanche cell, MnO₂ acts as
5. Protection of iron by coating with zinc is called
6. For the spontaneous electrochemical cell reaction, E° should be

7. The electrolyte used in H₂ – O₂ fuel cell is
8. In Leclanche dry cell, the cathode is
9. In electrolytic cell, reduction occurs at
10. In lead storage cell, the cathode consists of
11. The chemical formula of rust is
12. The units of molar conductance are
13. The equilibrium constant (K_c) and e.m.f. of the cell (E°) are related as

C. Choose the correct alternative

1. In an electrochemical cell, reduction will occur at the electrode having *lower/higher* oxidation potential.
2. E_{cell}° is *intensive/extensive* property.
3. Electrolytic conductance *increases/decreases* with decrease in temperature.
4. In a Daniell cell, when $E_{\text{ext}} > 1.10$ V, then current flows from *Zn to Cu/Cu to Zn*.
5. E_{cell}° is *directly/inversely* proportional to ΔG° .
6. By passing 96500 C of electricity through aqueous Al₂O₃, the amount of Al produced is *27g/9g*.
7. In the electrolysis of molten PbBr₂, *Br₂/Pb* is produced at anode.
8. In Leclanche cell, zinc cylinder acts as a *anode/cathode*.
9. Secondary cells are *chargeable/not chargeable*.
10. In mercury cell, zinc acts as *anode/cathode*.
11. Presence of CO₂ in natural water *increases/decreases* rusting of iron.
12. Presence of electrolytes in water *increases/decreases* corrosion of iron.

Answers**QUICK****MEMORY TEST****A. Say True or False**

1. **False.** For spontaneous electrochemical cell reaction emf should be positive.
2. **True**
3. **False.** Electrolytic conductance increases with rise in temperature.
4. **False.** Greater reduction potential represents greater oxidising power of the substance.
5. **True** **6. True**
7. **False.** E_{cell}° is intensive but ΔG° is extensive.
8. **True** **9. True** **10. True**

B. Complete the missing links

1. anode, cathode 2. $\Delta G^{\circ} = - nFE^{\circ}$ 3. cm^{-1} or m^{-1}

4. depolarizer **5. galvanization**
6. +ve **7. conc. KOH solution**
8. carbon (graphite) rod
9. Cathode **10. lead packed with PbO₂**
11. Fe₂O₃.xH₂O **12. ohm⁻¹ cm² mol⁻¹**
13. $\log K_c = \frac{nE^{\circ}}{0.059}$ at 298 K.

C. Choose the correct alternative

- | | | |
|----------------------|--------------------------|---------------------|
| 1. lower | 2. intensive | 3. decreases |
| 4. Zn to Cu | 5. directly | |
| 6. 9 g | 7. Br₂ | |
| 8. anode | 9. chargeable | 10. anode |
| 11. increases | 12. increases | |

HOTS**Higher Order Thinking Skills & Advanced Level****QUESTIONS WITH ANSWERS**

Q.1. What are the signs of ΔG , K and E°_{cell} for a spontaneous cell reaction?

Ans. $\Delta G = -\text{ve}$, $K = +\text{ve}$, $E^\circ_{\text{cell}} = +\text{ve}$

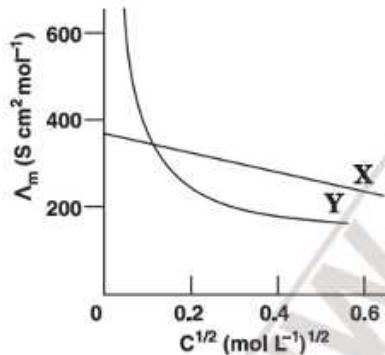
Q.2. Why is a salt bridge or a porous plate not needed in a lead storage battery?

Ans. The half cells in a cell must be separated only if the oxidizing and reducing agent can migrate to the other half cell. In lead storage cell, the oxidizing agent, PbO_2 and the reducing agent, Pb as well as their oxidation and reduction product PbSO_4 are solids. Therefore, there is no need to separate half cells.

Q.3. Blocks of magnesium are often strapped to the steel hulls of ocean going ships. Why?

Ans. Magnesium prevents the oxidation of steel by transferring the excess of electrons to the steel. Thus, rusting of steel is protected and it is called cathodic protection.

Q.4. The following curve is obtained when molar conductivity, Λ_m is plotted against the square root of concentration, $C^{1/2}$ along y and x-axis respectively for the two electrolytes X and Y.



(i) What can you say about the nature of these two electrolytes?

(ii) How do you account for the increase in Λ_m for the electrolytes X and Y with dilution?

(iii) How can you determine Λ_m^∞ for these electrolytes?

Ans. (i) Electrolyte X is a strong electrolyte and Y is a weak electrolyte.

(ii) Molar conductivity, Λ_m of X (strong electrolyte) increases slowly with dilution. This is because interionic forces of attraction decrease on dilution, although the number of ions remain the same. As a result ions move more freely and hence Λ_m increases with dilution.

On the other hand, for Y (weak electrolyte) Λ_m increases sharply with dilution. This is because, degree of dissociation increases on dilution resulting in greater number of ions on dilution. Hence Λ_m increases.

(iii) For X, Λ_m^∞ can be obtained by extrapolation to zero concentration.

For Y, Λ_m^∞ can be calculated by using Kohlrausch law.

Q.5. Consider the following half cell reactions:

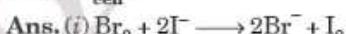


If I_2 and Br_2 are added to solution containing 1 M concentration of I^- and Br^- respectively.

(i) Write an equation for the overall cell reaction and E° of the cell.

(ii) Write the cell in which the reaction takes place, using Pt as the inert electrolyte for each electrode.

(iii) How will the increase in the concentration of Br^- affect E_{cell}° ?



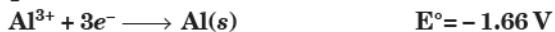
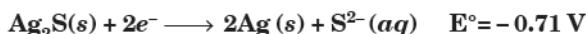
$$E^\ominus = E^\ominus \left(\frac{1}{2} \text{Br}_2 | \text{Br}^- \right) - E^\ominus \left(\frac{1}{2} \text{I}_2 | \text{I}^- \right)$$

$$= 1.09 - 0.54 = 0.55 \text{ V.}$$



(iii) The value of E^\ominus will be reduced.

Q.6. Tarnished silver contains Ag_2S . Can this tarnish be removed by placing tarnished silver article in an aluminium pan containing an inert electrolyte solution such as NaCl ? The standard electrode potentials for the half cell reactions are :



Ans. Tarnish due to silver sulphide can be removed if the following cell reaction occurs :



E.M.F. of the cell will be

$$E^\ominus = E^\ominus (\text{Ag}_2\text{S} | 2\text{Ag}, \text{S}^{2-}) - E^\ominus (\text{Al}^{3+} | \text{Al}) \\ = -0.71 - (-1.66) = +0.95 \text{ V}$$

Since E°_{cell} is positive, the reaction will occur and tarnish will be removed.

Q.7. If charge on the electron is $1.60 \times 10^{-19} \text{ C}$ and 96500 C deposit 107.9 g of silver from its solution, calculate the value of Avogadro's number. (At. mass of Ag = 107.9 u)

Ans. 1 mol = 107.9 g

1 mol of Ag is deposited by 96500 C

If charge of electron is $1.60 \times 10^{-19} \text{ C}$

$$\text{No. of electrons in 1 mol of silver} = \frac{96500 \text{ C}}{1.60 \times 10^{-19} \text{ C}}$$

$$= 6.03 \times 10^{23} e^-$$

$$\text{Avogadro number} = 6.03 \times 10^{23}.$$

Q.8. On the basis of the following data :



explain why Co³⁺ salts are unstable in water ?

Ans. The potential (Co³⁺ | Co) is large and sufficient to oxidize water. Therefore, Co(III) in aqueous solution has a tendency to change to Co(II). Hence Co(III) is unstable in aqueous solution.

Q.9. Show that for two half reactions having potentials E₁ and E₂ which are combined to give a third half reaction having potential E₃ is

$$E_3 = \frac{n_1 E_1 + n_2 E_2}{n_3}$$

Ans. Let ΔG₁, ΔG₂ and ΔG₃ are the free energy changes for the half cell reactions having potentials E₁, E₂ and E₃ respectively, then

$$\Delta G_3 = \Delta G_1 + \Delta G_2$$

Since ΔG = -nFE

$$\text{or } -n_3 FE_3 = -n_1 FE_1 - n_2 FE_2$$

Dividing both sides by -n₃F

$$E_3 = \frac{n_1 E_1 + n_2 E_2}{n_3}$$

Q.10. Calculate the reduction potential of a half cell consisting of a platinum electrode immersed in 2.0 M Fe²⁺ and 0.02 M Fe³⁺ solution (E° Fe³⁺ | Fe²⁺ = 0.771 V).

Ans. The electrode reaction is



$$E = E^\circ - \frac{0.059}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$E^\circ = 0.771 \text{ V},$$

$$[\text{Fe}^{3+}] = 0.02 \text{ M},$$

$$[\text{Fe}^{2+}] = 2.0 \text{ M}$$

$$\therefore E = 0.771 - \frac{0.059}{1} \log \frac{(2.0)}{(0.02)}$$

$$= 0.771 - 0.059 \log 100$$

$$= 0.771 - 0.118 = 0.653 \text{ V}$$

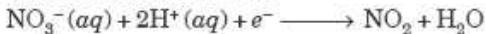
Q.11. The standard reduction potential for the half cell:



(i) Calculate the reduction potential at 8 M H⁺.

(ii) What will be the reduction potential of the half cell in a neutral solution ? Assume all other species to be at unit concentration.

Ans. (i) The half cell reaction :



According to Nernst equation,

$$E = E^\circ - \frac{0.059}{1} \log \frac{[\text{NO}_2][\text{H}_2\text{O}]}{[\text{NO}_3^-][\text{H}^+]^2}$$

$$E = 0.78 - 0.059 \log \frac{1}{(8)^2}$$

$$= 0.78 - 0.1062 = 0.8862 \text{ V}$$

(ii) In neutral solution, [H⁺] = 10⁻⁷ M

$$\therefore E = 0.78 - \frac{0.059}{1} \log \frac{1}{(10^{-7})^2}$$

$$= 0.78 - 0.059 \times 14 = 0.78 - 0.826 \\ = -0.046 \text{ V}$$

Q. 12. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in + 1 oxidation state for a period of 8.0 hours at a current of 8.46 amperes ? What is the area of the tray if the thickness of the silver plating is 0.0025 cm ? Density of silver is 10.5 g/cm³.

Ans. Quantity of electricity passed

$$= 8.46 \times 8 \times 60 \times 60 \text{ C}$$

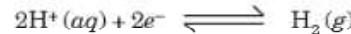
$$\text{Amount of silver deposited} = \frac{107.8}{96500} \times 8.46 \times 8 \times 60 \times 60 \\ = 272.18 \text{ g}$$

$$\text{Volume of silver} = \frac{272.18}{10.5} = 25.92 \text{ cc}$$

$$\text{Area of tray} = \frac{25.92}{0.00254} = 1.02 \times 10^4 \text{ cm}^2$$

Q. 13. What pressure of H₂ would be required to make the e.m.f. of the hydrogen electrode zero in pure water at 25°C ?

Ans. The cell reaction is :



According to Nernst equation,

$$E = E^\circ - \frac{0.059}{2} \log \frac{p(\text{H}_2)}{[\text{H}^+]^2}$$

Since

$$E = 0, [\text{H}^+] = 10^{-7} \text{ M (pure water)}$$

$$0 = 0 - \frac{0.059}{2} \log \frac{p(\text{H}_2)}{(10^{-7})^2}$$

$$0 = -\frac{0.059}{2} \log p(\text{H}_2) + \frac{0.059}{2} \log 10^{-14}$$

$$\therefore \log p(\text{H}_2) = \log 10^{-14}$$

$$\therefore p(\text{H}_2) = 10^{-14} \text{ atm.}$$

Q. 14. Conductivity of a saturated solution of Co₂[Fe(CN)₆] is 2.06 × 10⁻⁶ ohm⁻¹ cm⁻¹ and that of water used is 4.0 × 10⁻⁷ ohm⁻¹ cm⁻¹. Calculate the solubility and solubility product of Co₂[Fe(CN)₆] in water at 25°C. [Ionic molar conductivities: Co²⁺ = 86.0, [Fe(CN)₆]⁴⁻ = 444.0 ohm⁻¹ cm² mol⁻¹]

Ans. Since conductivity is additive property,

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

$$= 2.06 \times 10^{-6} - 4.0 \times 10^{-7}$$

$$= 16.6 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\Lambda_m(\text{complex salt}) = 2 \times \lambda_m(\text{Co}^{2+}) + \lambda_m([\text{Fe}(\text{CN})_6]^{4-}) \\ = 2 \times 86 + 444.0 = 616 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

where M is the solubility of saturated solution

$$616 = \frac{16.6 \times 10^{-7} \times 1000}{M}$$

or $M = \frac{16.6 \times 10^{-7} \times 1000}{616} = 2.69 \times 10^{-6} \text{ mol L}^{-1}$



If s is the solubility

$$\begin{aligned} [\text{Co}^{2+}] &= 2s, \quad [\text{Fe}(\text{CN})_6]^{4-} = s \\ K_{sp} &= (2s)^2(s) = 4s^3 \\ &= 4 \times (2.69 \times 10^{-6})^3 = 7.79 \times 10^{-17} \text{ mol}^3 \text{ L}^{-3} \end{aligned}$$



Revision Exercises

Very Short Answer Questions carrying 1 mark

- Write Nernst equation for the following cell reaction :
 $2\text{Al}(s) + 3\text{Fe}^{2+}(aq) \longrightarrow 2\text{Al}^{3+}(aq) + 3\text{Fe}(s)$
- State Kohlrausch law of electrical conductance of an electrolyte at infinite dilution.
- Write the overall cell reaction for lead storage battery.
- How is cell potential related to the free energy change ? State meaning of each term used.
- Can we store CuSO_4 solution in an iron vessel ?
- What is salt bridge? *(Nagaland S.B. 2018)*
- How is $\Delta_p G$ related to e.m.f. of the cell ?
- How does the concentration of sulphuric acid change in lead storage battery when current is drawn from it ?
- How many coulombs are required for the reduction of 1 mol of Al^{3+} to Al ?
- Define molar conductivity. *(Nagaland S.B. 2016)*
- Why a dry cell becomes dead after a long time even if it has not been used? *(Hr. S.B. 2002)*
- What is the basis of obtaining electrical energy in fuel cells ? *(D.S.B. 1998)*
- Give an example of a fuel cell. *(D.S.B. 2002)*
- What are the units of molar conductivity ? *(H.P.S.B. 2009)*
- Write the product obtained at anode on electrolysis of concentrated sulphuric acid using platinum electrodes.
- Express the relation between conductivity and molar conductivity of a solution held in a cell. *(D.S.B. 2011)*
- Express the relation among the conductivity of a solution in the cell, the cell constant and the resistance of the solution in the cell. *(D.S.B. 2011)*
- Which cell was used in Apollo Space programme ? What was the product used for ? *(Pb.S.B. 2012)*
- What is the amount of electricity required to deposit one mole of aluminium from a solution of AlCl_3 ? *(Pb.S.B. 2012)*
- How can you increase the reduction potential of an electrode ? *(Pb.S.B. 2012)*
- What is the amount of electricity required to deposit one mole of zinc from the solution of ZnSO_4 ? *(Pb.S.B. 2012)*
- What is the reference electrode in determining the standard electrode potential ? *(Pb.S.B. 2012)*
- What is the effect of decreasing concentration on the molar conductivity of weak electrolyte ? *(Pb.S.B. 2012)*
- The products of electrolysis of aqueous NaCl at the respective electrodes are:

Cathode : H_2

Anode : Cl_2 and not O_2 . Explain.

(C.B.S.E. Sample Paper 2017-18)

- Can we keep CuSO_4 solution in a zinc container? (Given that $E^\circ_{(\text{Cu}^{2+}/\text{Cu})} = +0.34\text{V}$, $E^\circ_{(\text{Zn}^{2+}/\text{Zn})} = -0.76\text{V}$) *(Meghalaya S.B. 2014)*
- Name one substance other than hydrogen that can be used for constructing fuel cell. *(Assam S.B. 2016)*

CBSE QUESTIONS

- Write Nernst equation for a single electrode potential. *(A.I.S.B. 2003)*
- How does electrical resistivity of metallic conductors vary with temperature? *(A.I.S.B. 2006)*
- What is molar conductivity? *(A.I.S.B. 2010)*

MCQs. from State Boards' Examinations

- For redox reaction to proceed in a cell, the e.m.f. must be

(a) positive	(b) negative
(c) fixed	(d) zero

(H.P.S.B. 2013)
- The units of conductivity are

(a) $\text{ohm}^{-1} \text{cm}^{-1}$	(b) $\text{ohm}^{-1} \text{cm}^2$
(c) ohm^{-1}	(d) $\text{ohm}^{-2} \text{cm}^2 \text{ equiv}^{-1}$

(H.P.S.B. 2013)
- The metal used for galvanization of iron is

(a) zinc	(b) magnesium
(c) copper	(d) aluminium

(H.P. S.B. 2013, 2014)
- Which of the following statements is false?

(a) Oxidation and reduction half-reactions occur at electrodes in electrochemical cells.
(b) All voltaic (galvanic) cells involve the use of electricity to initiate non-spontaneous chemical reactions.
(c) Reduction occurs at the cathode.
(d) Oxidation occurs at the anode. <i>(H.P. S.B., 2013, 2014)</i>
- The tendency of the electrodes made up of Cu, Zn and Ag to release electrons when dipped in their respective salt solutions decreases in the order:

(a) $\text{Zn} > \text{Ag} > \text{Cu}$	(b) $\text{Cu} > \text{Zn} > \text{Ag}$
(c) $\text{Zn} > \text{Cu} > \text{Ag}$	(d) $\text{Ag} > \text{Cu} > \text{Zn}$

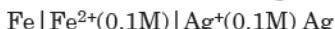
(H.P. S.B. 2015)
- The units of cell constant are:

(a) $\text{ohm}^{-1} \text{cm}^{-1}$	(b) cm
(c) $\text{ohm}^{-1} \text{cm}$	(d) cm^{-1}

(H.P. S.B. 2015, 2016, Hr. S.B. 2015, 2018)

36. In a galvanic cell, which one of the following statement is not correct?
 (a) Anode is negatively charged
 (b) Cathode is positively charged
 (c) Reduction takes place at the anode
 (d) Reduction takes place at the cathode (H.P. S.B. 2017)
37. Conductance of an electrolytic solution depends on
 (a) nature of electrolyte
 (b) power of AC source
 (c) distance between two electrodes
 (d) none of the above. (Hr. S.B. 2017)
38. For the given cell :
 $Mg | Mg^{2+} || Cu^{2+} | Cu$
 (a) Mg acts as cathode (b) Cu acts as cathode
 (c) Mg is oxidising agent (d) None of these (Hr. S.B. 2017)
39. The units of molar conductivity are :
 (a) $\text{ohm}^{-1} \text{m}^2 \text{mol}^{-1}$ (b) $\text{ohm} \text{m}^2 \text{mol}^{-1}$
 (c) $\text{ohm}^{-1} \text{m}^2 \text{mol}$ (d) $\text{ohm}^{-2} \text{m}^2 \text{mol}^{-1}$ (Hr. S.B. 2018)
40. The electrode potential of SHE is fixed as
 (a) 0.34 V (b) -0.44 V
 (c) 0 V (d) -0.76 V (H.P. S.B. 2018)
41. Number of Faradays (F) required to reduce 1 mole of MnO_4^- into Mn^{2+} are
 (a) 5F (b) 2F
 (c) 1F (d) 7F (Hr. S.B. 2018)
- Short Answer Questions carrying 2 or 3 marks**
1. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with temperature.
2. How will you distinguish between :
 (i) Metallic conduction and electrolytic conductance ?
 (ii) Strong and weak electrolytes ?
3. How is molar conductivity related to concentration of an electrolyte ? How will you explain weak and a strong electrolyte based on their conductivity values ?
4. What are the factors which affect the conductivity of an electrolyte solution ? Illustrate with examples.
5. (a) Explain normal or standard hydrogen electrode.
 (b) How much amount of substance is deposited by passing one Faraday of electricity? (Pb.S.B. 2018)
6. (a) Explain lead-storage cell.
 (b) Define primary cell.
 Or
 (a) Explain electrochemical theory of rusting of iron.
 (b) Define fuel cell. (H.P.S.B. 2018)
7. Why do we get different products at cathode during the electrolysis of molten $NaCl$ and aqueous sodium chloride ?
8. (a) Explain Ni–Cd storage cell.
 (b) Define secondary cells.
 Or
 (a) Define Faraday's first law.
 (b) Differentiate between primary and secondary cells. (H.P.S.B. 2018)
9. Can we use aluminium or copper for cathode protection of iron ? Explain giving reasons.
10. Define Kohlrausch's law. How does it help in (i) calculation of Λ° for a weak electrolyte and (ii) degree of dissociation of a weak electrolyte ? (Jammu S.Z. 2018)
11. (a) Discuss second law of Faraday of electrolysis. (Hr.S.B. 2018)
 (b) What is corrosion ? Give two methods to prevent it. (Hr.S.B. 2018)
 (c) Explain Kohlrausch law with a suitable example. (Hr.S.B. 2018)
12. (a) What is a Galvanic cell ? Give the function of salt bridge.
 (b) Can a zinc spoon be used to stir a solution of copper sulphate ? Support your answer with reason.
 $E^\ominus_{(Zn^{2+} | Zn)} = -0.76V, E^\ominus_{(Cu^{2+} | Cu)} = +0.34V$
 Or
 What are weak electrolytes ? Give the product formed in the electrolysis of molten $PbBr_2$. (Hr. S.B. 2010)
13. (a) Why does an alkaline medium inhibit the rusting of iron ?
 (b) Why does a dry cell become dead after a long time even if it has not been used ?
 (c) Why is zinc better than tin in protecting iron from corrosion ? (CBSE Sample Paper 2011)
14. What are fuel cells ? Discuss H_2-O_2 fuel cell. List two advantages of fuel cells. (H.P. S.B. 2012, 2015)
15. (a) State the law which helps to determine the limiting molar conductivity of weak electrolyte.
 (b) Calculate limiting molar conductivity of $CaSO_4$, limiting molar conductivities of calcium and sulphate ions are 119.0 and 106.0 $S \text{cm}^2 \text{mol}^{-1}$ respectively. (C.B.S.E. Sample Paper 2012)
16. (a) (i) Give two points of differences between emf and potential difference.
 (ii) Calculate the standard electrode potential of $Ni^{2+} | Ni$ electrode if the cell potential of the cell :
 $Ni(s) | Ni^{2+}(0.01 M) || Cu^{2+}(0.1 M) | Cu(s)$ is 0.59V.
 Given that $E^\ominus_{(Cu^{2+} | Cu)} = +0.34 V$
 Or
 (b) (i) Write two points of differences between galvanic cell and electrolytic cell.
 (ii) Calculate the maximum work that can be obtained from Daniel cell.
 $Zn | Zn^{2+}(\text{aq}) || Cu^{2+}(\text{aq}) || Cu$
 Given : $E^\ominus_{(Zn^{2+} | Zn)} = -0.76 V$ and $E^\ominus_{(Cu^{2+} | Cu)} = 0.34 V$ (Mizoram S.B. 2013)
17. (a) State Faraday's laws of electrolysis.
 (b) How much copper will be deposited at cathode of an electrolytic cell containing Cu^{2+} ions by the passage of 2 ampere current for 60 minutes? (Jharkhand S.B. 2013, 2016)
18. Define molar conductivity of an electrolytic solution. How does molar conductivity vary with concentration for a weak electrolyte ? (Assam S.B. 2015)
19. (a) (i) What are the functions of salt bridge in a galvanic cell?
 (ii) The molar conductivity at infinite dilution of $Al_2(SO_4)_3$ is 858 $S \text{cm}^2 \text{mol}^{-1}$. Calculate the molar ionic conductivity of Al^{3+} ion given that $\lambda^\circ(SO_4^{2-}) = 160 S \text{cm}^2 \text{mol}^{-1}$.
 Or
 (i) Write two differences between primary cells and secondary cells.

(ii) Calculate the emf of the following cell at 298 K:



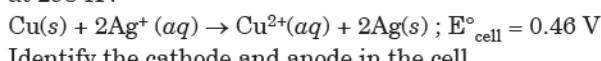
Given: $E^\circ(\text{Fe}^{2+} \mid \text{Fe}) = -0.44 \text{ V}$ and

$$E^\circ(\text{Ag}^+ \mid \text{Ag}) = 0.80 \text{ V}$$

$$(R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}, F = 96500 \text{ C mol}^{-1})$$

(Mizoram S.B. 2014)

20. (a) Find the equilibrium constant of the following reaction at 298 K :



Identify the cathode and anode in the cell.

(b) Three electrolytic cells containing ZnSO_4 , AgNO_3 and CuSO_4 were connected in series. A steady current of 1.5 A was allowed to pass through them till 1.45 g of Ag is deposited. How long did the current flow? What weight of Cu and Zn were deposited? (Atomic mass of Ag = 108, Cu = 63.5 and Zn = 65.3).

(c) Can we keep AgNO_3 solution in a copper container ?

$$[E^\circ_{(\text{Cu}^{2+} \mid \text{Cu})} = +0.34 \text{ V}, E^\circ_{(\text{Ag}^+ \mid \text{Ag})} = +0.80 \text{ V}]$$

(Meghalaya S.B. 2014)

21. What are primary cells ? Give the construction and working of a dry cell. (H.P. S.B. 2015)

22. What are secondary cells ? Explain the working of lead storage battery. (H.P. S.B. 2015)

23. What is a secondary battery ? Write the mechanism of recharging of lead storage battery with the help of chemical reaction.

Or

(a) Define standard electrode potential.

(b) The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:



(Uttarakhand S.B. 2015)

24. (a) Draw a neat labeled diagram of $\text{H}_2 - \text{O}_2$ fuel cell. Write the reaction which occurs at cathode of the cell (Karnataka S.B. 2018)

(b) Calculate e.m.f. of the cell for the reaction.



Given that: $E^\circ_{\text{Mg}^{2+} \mid \text{Mg}} = -2.37 \text{ V}$

$$E^\circ_{\text{Cu}^{2+} \mid \text{Cu}} = +0.34 \text{ V}$$

(c) (i) State Kohlrausch law.

(ii) What is meant by limiting molar conductance?

(Karnataka S.B. 2018)

25. (a) Explain electrochemical series.

(b) Can we store 1 M CuSO_4 in Zn vessel or not why?

or

(a) Explain the working of a fuel cell.

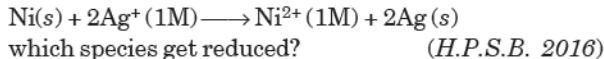
(b) Define Faraday's Second Law.

(H.P.S.B. 2018)

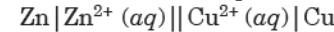
26. (a) What are primary cells?

(b) Write short note on lead storage battery.

(c) For the reaction:



27. Write the Nernst equation for the following cell:



Write the reaction occurring at each of the electrode and the net cell reaction. Also determine its cell potential when $[\text{Zn}^{2+}(aq)] = 1\text{M}$, $[\text{Cu}^{2+}(aq)] = 1\text{M}$, $E^\circ_{\text{Zn}^{2+} \mid \text{Zn}} = -0.76 \text{ V}$ and $E^\circ_{\text{Cu}^{2+} \mid \text{Cu}} = +0.34 \text{ V}$.

Or

Explain the recharging of a discharge lead storage battery with electrode reactions. (Nagaland S.B. 2016)

28. Which of the following is a secondary cell?

(i) Dry cell (ii) Leclanche cell

(iii) Mercury cell (iv) None of these

(a) What is the relationship between resistance and conductance?

(b) One of the fuel cell uses the reaction of hydrogen and oxygen to form water. Write down the cell reaction taking place in the anode and cathode of that fuel cell. (Kerala S.B. 2016)

29. Give the Nernst equation for the cell:



and also find the cell potential.

$$\text{Given : } E^\circ(\text{Ag}^+ \mid \text{Ag}) = 0.80 \text{ V}, E^\circ(\text{Ni}^{2+} \mid \text{Ni}) = -0.25 \text{ V}$$

(Meghalaya S.B. 2016)

30. (a) Define molar conductivity of an electrolytic solution. Show the variation of molar conductivity of a strong electrolyte with square root of concentration.

(b) State Kohlrausch law.

The limiting molar conductances of NaCl , HCl and CH_3COONa are 126.45, 426.16 and 91.0 $\text{S cm}^2 \text{ mol}^{-1}$ respectively at 298K. Calculate limiting molar conductance of acetic acid at 298K. (Assam S.B. 2017)

31. (a) Describe the construction and working of Normal Hydrogen Electrode.

(b) Calculate the standard EMF of a cell involving cell reaction:



$$\text{Given : } E^\circ_{\text{Zn} \mid \text{Zn}^{2+}} = 0.76 \text{ V}; E^\circ_{\text{Ag} \mid \text{Ag}^+} = -0.80 \text{ V}$$

(c) Give two differences between metallic and electrolytic conductors. (Hr. S.B. 2017)

32. What is electrochemical theory of rusting of iron and give two methods of prevention of rusting of iron?

Or

Write the Nernst equation and calculate the emf of following cell at 298 K.



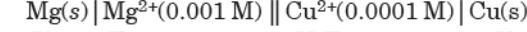
$$\text{Given : } E^\circ(\text{Cu}^{2+} \mid \text{Cu}) = +0.34 \text{ V}, E^\circ(\text{Ni}^{2+} \mid \text{Ni}) = -0.22 \text{ V}$$

(Pb. S.B. 2017)

33. Explain the variation of molar conductivity of strong and weak electrolytes with dilution.

Or

Write the Nernst equation and calculate the emf of following cell at 298 K.



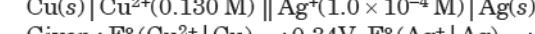
$$\text{Given : } E^\circ_{\text{Mg}^{2+} \mid \text{Mg}} = -2.37 \text{ V}, E^\circ_{\text{Cu}^{2+} \mid \text{Cu}} = 0.34 \text{ V}$$

(Pb. S.B. 2017)

34. What is corrosion ? What are the factors affecting corrosion?

Or

Write the Nernst equation and calculate the emf of following cell at 298 K.



$$\text{Given : } E^\circ(\text{Cu}^{2+} \mid \text{Cu}) = +0.34 \text{ V}, E^\circ(\text{Ag}^+ \mid \text{Ag}) = +0.80 \text{ V}$$

(Pb. S.B. 2017)

35. (a) Zinc protects iron from corrosion better than tin. Give reason.

(b) What are primary cells and secondary cells?

(Manipur S.B. 2017)

36. (a) How many Faradays of electricity is required to liberate 1 mole of copper from copper sulphate solution?
 (b) Arrange K⁺, Zn²⁺, H⁺ and Cu²⁺ ions in order of their tendency to be liberated at the cathode.

[Given : E°_(Cu²⁺ | Cu) = + 0.34 V; E°_(H⁺ | H₂) = 0.0V;

E°_(Zn²⁺ | Zn) = -0.76 V; E°_(K⁺ | K) = -2.93V]

(West Bengal S.B. 2018)

37. (a) Why can limiting molar conductivity of CH₃COOH not be determined experimentally ?
 (b) How many coulombs of charge are required to produce 20.0 g of calcium from calcium chloride ?
 (c) What is a salt bridge ? Give two functions of salt bridge. (Meghalaya S.B. 2018)

38. (a) What is electrochemical series? Write one of its application. Calculate the e.m.f. of the cell Cr | Cr³⁺ (0.1M) || Fe²⁺ (0.01M) | Fe. [E°_(Cr³⁺ | Cr) = -0.75 V and E°_(Fe²⁺ | Fe) = -0.45V, log 10 = 1].
 (b) Write the Nernst equation for the cell:



where E°_(Zn²⁺ | Zn) = -0.76V; E°_(Cu²⁺ | Cu) = + 0.34V. Write the reaction occurring at each of the electrode and its net cell reaction. Also determine its cell potential.

(Nagaland S.B. 2018)

CBSE QUESTIONS

39. Express the relation among the cell constant, the resistance of the solution in the cell and the conductivity of the solution. How is the conductivity of a solution related to its molar conductivity ? (A.I.S.B. 2010, 2012)
 40. Given that the standard electrode potentials (E°) of metals are : K⁺ | K = - 2.93 V, Ag⁺ | Ag = 0.80 V, Cu²⁺ | Cu = 0.34 V, Mg²⁺ | Mg = - 2.37 V, Cr³⁺ | Cr = - 0.74 V, Fe²⁺ | Fe = - 0.44 V. Arrange these metals in an increasing order of their reducing power.

Or

Two half-reactions of an electrochemical cell are given below : MnO₄⁻ (aq) + 8H⁺(aq) + 5e⁻ → Mn²⁺(aq) + 4H₂O(l),

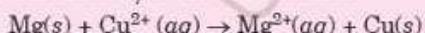
$$E^\ominus = + 1.51 \text{ V}$$



Construct the redox reaction equation from the two Half-reactions and calculate the cell potential from the standard potentials and predict if the reaction is reactant or product favoured. (A.I.S.B. 2010)

41. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? (A.I.S.B. 2014)

42. (a) Calculate Δ_rG° for the reaction



Given : E°_{cell} = +2.71 V, 1 F = 96500 C mol⁻¹

- (b) Name the type of cell which was used in Apollo space programme for providing electrical power. (A.I.S.B. 2014)

43. Define the following terms:

(i) Fuel cell

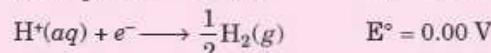
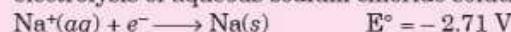
(ii) Limiting molar conductivity (Λ_m°) (A.I.S.B. 2014)

44. Define the following terms:

(i) Molar conductivity (Λ_m)

(ii) Secondary batteries (A.I.S.B. 2014)

45. (a) Following reactions occur at cathode during the electrolysis of aqueous sodium chloride solution:



On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?

- (b) Why does the cell potential of mercury cell remain constant throughout its life? (A.I.S.B. 2015)

Long Answer Questions

carrying 5 marks

1. (a) Explain Kohlrausch's law of independent migration of ions. Mention one application of the law.

- (b) With the help of a graph, explain why it is not easy to determine Λ₀ for a weak electrolyte by extrapolating the concentration vs molar conductivity curve as for strong electrolytes ?

2. (a) What type of a battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it.

- (b) In the button cell, widely used in watches, the following reaction takes place :



Determine E° and ΔG° for the reaction.

(Given : E°_(Ag⁺ | Ag) = + 0.80 V, E°_(Zn²⁺ | Zn) = - 0.76 V

Or

- (a) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.

- (b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146 × 10⁻³ S cm⁻¹? (D.S.B. 2012)

3. You are provided with the following substances: copper rod, zinc rod, salt bridge, two glass beakers, a piece of wire, 1 M CuSO₄ solution, 1 M ZnSO₄ solution.

- (a) Represent the cell made using the above materials.

- (b) (i) Write the Nernst equation for the above cell.

- (ii) Calculate the standard e.m.f. of the cell, if

E°_(Zn²⁺ | Zn) = -0.76V, E°_(Cu²⁺ | Cu) = +0.34V

(Kerala S.B. 2015)

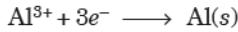
4. (a) Write two points of differences between metallic conductance and electrolytic conductance.

- (b) State Kohlrausch's law. Molar conductivity at infinite dilution for NH₄Cl, NaOH and NaCl solution at 298K are 110, 100 and 105 S cm² mol⁻¹ respectively. Calculate the molar conductivity of NH₄OH solution.

Or

- (a) What is equivalent conductivity and molar conductivity of an electrolyte in solution?
- (b) Write the Nernst equation and calculate emf of the following cell at 298K.
- $$\text{Cu(s)} \mid \text{Cu}^{2+}(0.130 \text{ M}) \parallel \text{Ag}^+(1.0 \times 10^{-4} \text{ M}) \mid \text{Ag(s)}$$
- Given : $E^\circ(\text{Cu}^{2+} \mid \text{Cu}) = +0.34 \text{ V}$, $E^\circ(\text{Ag}^+ \mid \text{Ag}) = +0.80 \text{ V}$
(Mizoram S.B. 2015)
5. (a) Define specific conductivity and molar conductivity for the solution of an electrolyte. How do they vary with dilution?
- (b) Calculate Λ_m° for NH_4OH given that the values of Λ_m° for $\text{Ba}(\text{OH})_2$, BaCl_2 and NH_4Cl are 523.28, 280.0 and 129.8 $\text{S cm}^2 \text{ mol}^{-1}$ respectively. *(Meghalaya S.B. 2015)*

6. (a) State Faraday's first and second law of electrolysis.
- (b) Calculate the number of coulombs required to deposit 40.5 g of Al when the electrode reaction is :



Or

- (a) What is electro chemical series? Write one application of electrochemical series. Calculate the standard electrode potential of $\text{Ni}^{2+} \mid \text{Ni}$ electrode, if the cell potential of the cell: $\text{Ni} \mid \text{Ni}^{2+}(0.01 \text{ M}) \parallel \text{Cu}^{2+}(0.1 \text{ M}) \mid \text{Cu}$, is 0.59V.
[Given $E^\circ(\text{Cu}^{2+} \mid \text{Cu}) = 0.34 \text{ V}$] *(Nagaland S.B. 2015)*

7. (a) What is a fuel cell? Write its one advantage over other ordinary cells.
- (b) A voltaic cell is set up at 25°C with the given half cells:
 $\text{Ag}^+(0.001 \text{ M}) \mid \text{Ag}$ and $\text{Cu}^{2+}(0.10 \text{ M}) \mid \text{Cu}$.
What would be the voltage of the cell ($E^\circ_{\text{cell}} = 0.46 \text{ V}$)?

Or

- (a) What is meant by 'molar conductivity' of a solution? Describe how for weak and strong electrolytes, molar conductivity changes with concentration of solution. How is such change explained?
- (b) The molar conductivity of 1.5 M solution of an electrolyte is found to be 138.9 $\text{S cm}^2 \text{ mol}^{-1}$. Calculate the conductivity of this solution. *(Tripura S.B. 2016)*

8. (a) Represent the galvanic cell based on the cell reaction given below:



- (b) Write the half cell reactions of the above cell.

- (c) Λ_m° for NaCl , HCl and NaAc are 126.4, 425.9 and 91.0 $\text{S cm}^2 \text{ mol}^{-1}$ respectively. Calculate Λ_m° for HAc . *(Kerala S.B. 2016)*

9. (i) Explain how salt-bridge maintains the electrical neutrality of the two half cell solutions in a galvanic cell.
- (ii) The molar conductivities at infinite dilution for CH_3COONa , HCl and NaCl are 91.0, 425.9 and 126.4 $\text{S cm}^2 \text{ mol}^{-1}$ respectively at 298 K. Calculate the molar conductivities of CH_3COOH at infinite dilution.

Or

- (i) What is the difference between strong electrolytes and weak electrolytes? Give examples.

- (ii) Calculate the equilibrium constant for the reaction at 298 K:



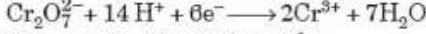
(Given : $E^\circ_{(\text{Ag}^+ \mid \text{Ag})} = 0.80 \text{ V}$, $E^\circ_{(\text{Cu}^{2+} \mid \text{Cu})} = 0.34 \text{ V}$) *(Mizoram S.B. 2017)*

10. (a) Calculate the equilibrium constant of the reaction:



(Given : $E^\circ_{\text{cell}} = 0.46 \text{ V}$)

- (b) State Faraday's first law of electrolysis. What is the quantity of electricity in coulombs needed to reduce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ ion for the following reaction ?



(Given : $1\text{F} = 96,500 \text{ C mol}^{-1}$)

- (c) Why does mercury cell give a constant voltage throughout its life?

Or

- (d) A solution of CuSO_4 is electrolyzed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode? (Given : Atomic mass of $\text{Cu} = 63 \text{ g mol}^{-1}$, $1\text{F} = 96500 \text{ C mol}^{-1}$)

- (e) The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 $\text{S cm}^2 \text{ mol}^{-1}$. Calculate the degree of dissociation. Given :

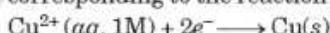
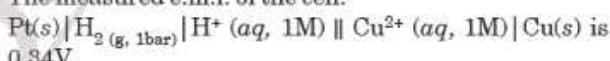
$$\lambda^\circ_{\text{H}^+} = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda^\circ_{\text{HCOO}^-} = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$$

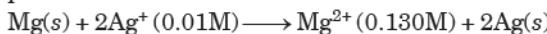
- (f) What are secondary cells? *(Meghalaya S.B. 2017)*

11. (a) What is the standard electrode potential?

- (b) The measured e.m.f. of the cell:



- (c) Represent the cell in which the following reaction takes place.



Write the Nernst equation and calculate the emf of the cell at 298 K. Given $E^\circ_{\text{cell}} = 3.17 \text{ V}$. *(Assam S.B. 2018)*

12. (a) What are primary batteries?

- (b) The cell potential of mercury cell is 1.35 V, and remain constant during its life. Given reason.

- (c) Write the equations of the reactions involved at each electrode in a $\text{H}_2 - \text{O}_2$ fuel cell. *(Kerala S.B. 2018)*



CBSE QUESTIONS



13. (a) State two advantages of $\text{H}_2 - \text{O}_2$ fuel cell over ordinary cell.

- (b) Silver is electrodeposited on a metallic vessel of total surface area 900 cm^2 by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited. (Given density of silver = 10.5 g cm^{-3} , atomic mass of silver = 108 amu, $F = 96500 \text{ C mol}^{-1}$)

Or

- (a) Give reason for the following :

- (i) Rusting of iron is quicker in saline water than in ordinary water.

- (ii) Aluminium metal cannot be produced by electrolysis of aqueous solution of aluminium salt.

- (b) Resistance of a conductivity cell filled with 0.1M KCl solution is 100 ohm. If the resistance of same cell when filled with 0.02 M KCl is 520 ohms, calculate the conductivity and molar conductivity of 0.02 M

KCl solution. Conductivity of 0.1 M KCl solution is 1.29 S m^{-1} . (A.I.S.B. 2006)

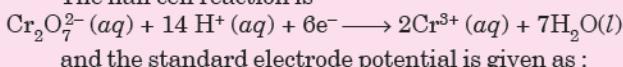
14. (a) Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery.

(b) A copper silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.

[Given : $E^\circ_{(\text{Ag}^+|\text{Ag})} = +0.80 \text{ V}$, $E^\circ_{(\text{Cu}^{2+}|\text{Cu})} = +0.34 \text{ V}$] (A.I.S.B. 2010)

15. (a) What type of battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.

(b) Calculate the potential for half cell containing 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7(aq)$, 0.20 M $\text{Cr}^{3+}(aq)$ and $1.0 \times 10^{-4} \text{ M H}^+(aq)$. The half cell reaction is



$E^\circ = 1.33 \text{ V}$. (A.I.S.B. 2011)

16. (a) How many moles of mercury will be produced by electrolysing 1.0 M $\text{Hg}(\text{NO}_3)_2$ solution with a current of 2.00 A for 3 hours? [$\text{Hg}(\text{NO}_3)_2 = 200.6 \text{ g mol}^{-1}$].

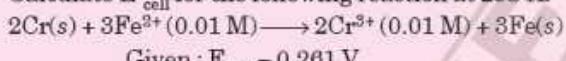
(b) A voltaic cell is set up at 25°C with the following half cells :

$\text{Al}^{3+}(0.001 \text{ M})$ and $\text{Ni}^{2+}(0.50 \text{ M})$.

Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

[Given : $E^\circ_{(\text{Ni}^{2+}|\text{Ni})} = -0.25 \text{ V}$, $E^\circ_{(\text{Al}^{3+}|\text{Al})} = -1.66 \text{ V}$] (A.I.S.B. 2011)

17. (a) Calculate E°_{cell} for the following reaction at 298 K :



(b) Using the E° values of A and B, predict which one is better for coating the surface of iron [$E^\circ(\text{Fe}^{2+}|\text{Fe}) = -0.44 \text{ V}$] to prevent corrosion and why?

Given : $E^\circ_{(\text{A}^{3+}|\text{A})} = -2.37 \text{ V}$; $E^\circ_{(\text{B}^{2+}|\text{B})} = -0.14 \text{ V}$

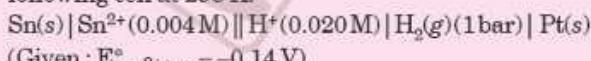
(a) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is $3.905 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation (α).

Given $\lambda^\circ(\text{H}^+) = 349.65 \text{ cm}^2 \text{ mol}^{-1}$ and

$\lambda^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$.

(b) Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell? (A.I.S.B. 2016)

18. (a) Write the cell reaction and calculate the e.m.f. of the following cell at 298 K :

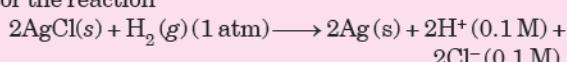


(b) Give reasons :

(i) On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.

(ii) Conductivity of CH_3COOH decreases on dilution.
Or

(a) For the reaction



$\Delta G^\circ = -43600 \text{ J at } 25^\circ\text{C}$

Calculate the e.m.f. of the cell.

$[\log 10^{-n} = -n]$

- (b) Define fuel cell and write its two advantages.

(A.I.S.B. 2018)

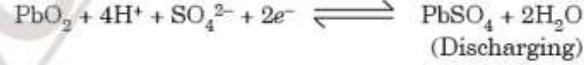
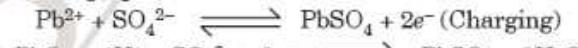
NUMERICAL PROBLEMS

1. At equimolar concentration of Fe^{2+} and Fe^{3+} , what must be the $[\text{Ag}^+]$ so that the voltage of the galvanic cell made from $\text{Ag}^+|\text{Ag}$ and $\text{Fe}^{3+}|\text{Fe}^{2+}$ electrodes equals zero? The cell reaction is



[Ans. 0.335 M]

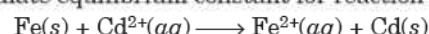
2. During the discharge of a lead storage battery, the density of sulphuric acid fell down from 1.294 to 1.139 g/ml. Sulphuric acid of density 1.294 g/ml is 39% H_2SO_4 by weight and that of density 1.139 g/ml is 20% H_2SO_4 by weight. The battery holds 3.5 L of acid and the volume remains practically constant during discharge. Calculate the number of ampere-hours for which the battery must have been used. The charging and discharging reactions are :



[Ans. 264.9 amp-hr]

3. A current of 4 amp was passed for 1.5 hours through a solution of copper sulphate when 3.2 g of copper was deposited. Calculate the current efficiency. [Ans. 45.1%]

4. Calculate equilibrium constant for reaction :



Given : $E^\circ_{(\text{Cd}^{2+}|\text{Cd})} = -0.40 \text{ V}$, $E^\circ_{(\text{Fe}^{2+}|\text{Fe})} = -0.44 \text{ V}$

(D.S.B. 2009) [Ans. 22.7]

5. A voltaic cell is set up at 25°C with the following half cells:

$\text{Al} | \text{Al}^{3+}(0.001 \text{ M})$ and $\text{Ni} | \text{Ni}^{2+}(0.50 \text{ M})$

Calculate the cell voltage



(D.S.B. 2009, A.I.S.B. 2009) [Ans. 1.463 V]

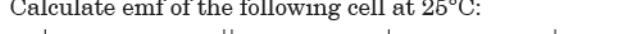
6. Calculate ΔG and E°_{cell} for the cell



Given that $E^\circ_{(\text{Al}^{3+}|\text{Al})} = -1.66 \text{ V}$ and

$E^\circ_{(\text{Fe}^{2+}|\text{Fe})} = -0.44 \text{ V}$ (Pb.S.B. 2013)

7. Calculate emf of the following cell at 25°C :

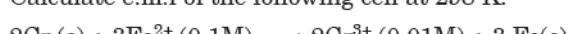


$E^\circ(\text{Fe}^{2+}|\text{Fe}) = -0.44 \text{ V}$, $E^\circ(\text{H}^+|\text{H}_2) = 0.00 \text{ V}$

(D.S.B. 2015) [Ans. 0.4105]

8. A current of 0.5 ampere is passed for 30 minutes through a voltmeter containing copper sulphate solution. Calculate the mass of copper deposited at the cathode. (At. mass of Cu = 63.0 amu) (Assam S.B. 2016)

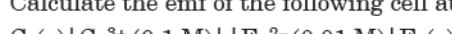
9. Calculate e.m.f of the following cell at 298 K :



Given $E^\circ(\text{Cr}^{3+}|\text{Cr}) = -0.74 \text{ V}$, $E^\circ(\text{Fe}^{2+}|\text{Fe}) = -0.44 \text{ V}$

(D.S.B. 2016)

10. Calculate the emf of the following cell at 298 K :



[Given : $E^\circ_{\text{cell}} = 0.30 \text{ V}$] (C.B.S.E. Sample Paper 2017-18)

11. The conductivity of 10^{-3} mol / L acetic acid at 25°C is 4.1×10^{-5} S cm $^{-1}$. Calculate its degree of dissociation, if Λ_m° for acetic acid at 25°C is 390.5 S cm 2 mol $^{-1}$.

(C.B.S.E. Sample Paper 2017-18)

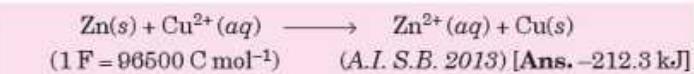
CBSE QUESTIONS

12. A copper-silver cell is set up. The copper ion concentration in it is 0.10 M. The concentration of silver ion is not known. The cell potential measured is 0.422 V. Determine the concentration of silver ion in the cell.

Given : $E^\ominus_{(\text{Ag}^+|\text{Ag})} = +0.80$ V, $E^\ominus_{(\text{Cu}^{2+}|\text{Cu})} = +0.34$ V.
(A.I.S.B.E. 2009) [Ans. 0.0718 M]

13. Calculate the emf of the following cell at 298 K:
 $\text{Fe(s)} | \text{Fe}^{2+}(0.001 \text{ M}) \parallel \text{H}^+(1 \text{ M}) | \text{H}_2(\text{g}), 1 \text{ bar}, \text{Pt(s)}$
(Given $E^\ominus_{\text{cell}} = +0.44$ V) (A.I.S.B. 2012) [Ans. 0.5285 V]

14. The standard electrode potential (E°) for Daniell cell is $+1.1$ V. Calculate ΔG° for the reaction:



15. Calculate the emf of the following cell at 25°C :
 $\text{Ag(s)} | \text{Ag}^+(10^{-3} \text{ M}) \parallel \text{Cu}^{2+}(10^{-1} \text{ M}) | \text{Cu(s)}$
Given $E^\ominus_{\text{cell}} = +0.46$ V and $\log 10^n = n$ (A.I.S.B. 2013)
[Ans. 0.3125 V]

16. The conductivity of 0.20 M solution of KCl at 298K is 0.025 S cm $^{-1}$. Calculate its molar conductivity.
(A.I.S.B. 2013, D.S.B. 2013) [Ans. 125]

17. Calculate emf of the following cell at 25°C :
 $\text{Sn} | \text{Sn}^{2+}(0.001 \text{ M}) \parallel \text{H}^+(0.01 \text{ M}) | \text{H}_2(\text{g})(1 \text{ bar}) | \text{Pt(s)}$
 $E^\circ(\text{Sn}^{2+} | \text{Sn}) = -0.14$ V, $E^\circ(\text{H}^+ | \text{H}_2) = 0.00$ V
(A.I.S.B. 2015) [Ans. 0.1105 V]

18. The cell in which the following reaction occurs:
 $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \longrightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{s})$
has E^\ominus_{cell} 0.236 V at 298 K. Calculate the standard Gibbs energy of the cell reaction. (Given : $1\text{F} = 96500 \text{ C/mol}^{-1}$)
(A.I.S.B. 2017)

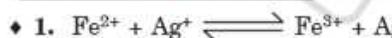
Hints & Answers

for Revision Exercises

Very Short Answer Questions

1. $E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{2.303RT}{6F} \log \frac{[\text{Al}^{3+}]^2}{[\text{Fe}^{2+}]^3}$
5. No
6. $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
8. Concentration decreases
9. $3 \times 96500 \text{ C}$
11. Because acidic NH_4Cl corrodes the zinc container.
12. Chemical energy of the fuel is converted to electrical energy.
13. H_2-O_2 cell.
14. $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
16. $\Lambda_m = \frac{\kappa \times 1000}{M}$
17. Conductivity = $\frac{\text{Cell constant}}{\text{Resistance}}$
18. Fuel cell
19. $3 \times 96500 \text{ C}$
20. Decreasing conc. of the electrolytic solution
21. $2 \times 96500 \text{ C}$
22. Hydrogen electrode
23. Molar conductivity increases
26. propane
30. (a) 31. (a) 32. (a) 33. (b) 34. (c) 35. (d)
36. (c) 37. (a) 38. (b) 39. (a) 40. (c) 41. (a)

Numerical Problems



$$E = E^\ominus - \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^+]}$$

$$E^\ominus = E^\ominus_{(\text{Ag}^+|\text{Ag})} - E^\ominus_{(\text{Fe}^{3+}|\text{Fe}^{2+})}$$

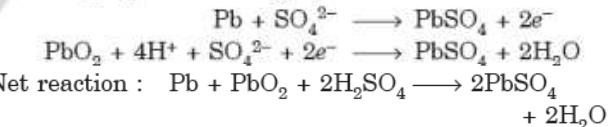
$$= 0.799 - 0.771 = 0.028 \text{ V}$$

For $E^\ominus = 0$, $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$

$$0 = 0.028 - \frac{0.059}{1} \log \frac{1}{[\text{Ag}^+]}$$

$$\therefore [\text{Ag}^+] = 0.335 \text{ M}$$

- ♦ 2. The charging and discharging reactions are :



The reaction indicates that 2 mol of e^- are transferred for the consumption of 2 mol of H_2SO_4 .

$\therefore 2$ mol of H_2SO_4 required electric charge = 2×96500 C. Calculation of moles of H_2SO_4 in 3.5 L solution of density 1.294 g cm^{-3}

$$\text{Mass of H}_2\text{SO}_4 \text{ in } 1 \text{ cm}^3 = 1.294 \times \frac{39}{100} \text{ g}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ in } 3.5 \text{ L} = 1.294 \times \frac{39}{100} \times 3.5 \times 1000 \text{ g}$$

$$\text{Moles of H}_2\text{SO}_4 \text{ in } 3.5 \text{ L} = \frac{1.294 \times 39 \times 3.5 \times 1000}{100 \times 98}$$

$$= 18.02 \text{ mol}$$

Calculation of moles of H_2SO_4 in 3.5 L of density 1.139 g cm^{-3}

$$\text{Mass of H}_2\text{SO}_4 \text{ in } 1 \text{ cm}^3 = \frac{1.139 \times 20}{100}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ in } 3.5 \text{ L} = \frac{1.139 \times 20 \times 3.5 \times 1000}{100}$$

$$\text{Moles of H}_2\text{SO}_4 = \frac{1.139 \times 20 \times 3.5 \times 1000}{100 \times 98}$$

$$= 8.136 \text{ mol}$$

Moles of H_2SO_4 consumed during discharging
= $18.02 - 8.136 = 9.884$ mol

Now, 2 moles of H_2SO_4 correspond to $= 2 \times 96500 \text{ C}$
 9.884 mol of H_2SO_4 correspond to

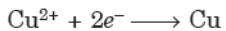
$$= \frac{2 \times 96500 \times 9.884}{2} = 953806 \text{ C}$$

1 Coulomb = 1 amp . sec.

3600 Coulomb = 1 amp . hr.

$$\therefore 953806 \text{ C} = \frac{1}{3600} \times 953806 = 264.9 \text{ amp.hr}$$

♦ 3. Quantity of electricity passed = $4 \times 1.5 \times 60$
 $= 21600 \text{ C}$



2 × 96500 C of electricity deposit Cu = 63.5 g

21600 C of electricity will deposit Cu

$$= \frac{63.5}{2 \times 96500} \times 21600 = 7.1 \text{ g}$$

Amount of copper deposited = 3.2 g

$$\text{Efficiency} = \frac{3.2}{7.1} \times 100 = 45.1\%$$

♦ 4. $E^\circ_{\text{cell}} = E^\circ(\text{Cd}^{2+}|\text{Cd}) - E^\circ(\text{Fe}^{2+}|\text{Fe})$
 $E^\circ_{\text{cell}} = -0.40 - (-0.44) = 0.04 \text{ V}$

$$\log K_c = \frac{nE^\circ_{\text{cell}}}{0.059} \text{ at } 25^\circ\text{C}$$

$$= \frac{2 \times 0.04}{0.059} = 1.356$$

$$K_c = 22.7$$

♦ 5. Al | Al³⁺(0.001M) || Ni²⁺(0.50M) | Ni



$$E = E^\ominus - \frac{0.059}{6} \log \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3}$$

$$E^\ominus = E^\ominus(\text{Ni}^{2+}|\text{Ni}) - E^\ominus(\text{Al}^{3+}|\text{Al})
= -0.25 - (-1.66) = 1.41 \text{ V}$$

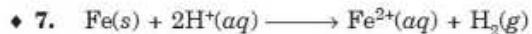
$$E = 1.41 - \frac{0.059}{6} \log \frac{(0.001)^2}{(0.50)^3}
= 1.41 - \frac{0.059}{6} \log 8 \times 10^{-6}
= 1.41 + 0.053 = 1.463 \text{ V}$$

♦ 6. 2Al³⁺ + 3Fe \longrightarrow 2Al + 3Fe²⁺

$$E^\ominus = E^\ominus(\text{Fe}^{2+}|\text{Fe}) - E^\ominus(\text{Al}^{3+}|\text{Al})
= -0.44 - (-1.66) = 1.22 \text{ V}$$

$$E = E^\ominus - \frac{0.059}{6} \log \frac{[\text{Fe}^{2+}]^3}{[\text{Al}^{3+}]^2}
= 1.22 - \frac{0.059}{6} \log \frac{(0.02)^3}{(0.01)^2}
= 1.22 - \frac{0.059}{6} \log 0.08
= 1.22 - (-0.01) = 1.23$$

$$\Delta G = -nFE
= -6 \times 96500 \times 1.23
= -712170 \text{ J mol}^{-1} = 712.17 \text{ kJ mol}^{-1}$$

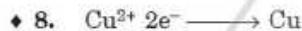


$$E^\circ_{\text{cell}} = 0.0 - (-0.44) = 0.44 \text{ V}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

$$= 0.44 - \frac{0.059}{2} \log \frac{(0.001)}{(0.01)^2}$$

$$E = 0.44 - 0.0295 = 0.4105 \text{ V}$$



$$\text{Quantity of electricity} = 0.5 \times 30 \times 60
= 900 \text{ C}$$

$$2 \times 96500 \text{ C of electricity deposit Cu} = 63.0 \text{ g}$$

$$900 \text{ C of electricity will deposit Cu} = \frac{63.0 \times 900}{2 \times 96500}$$

$$= 0.294 \text{ g}$$

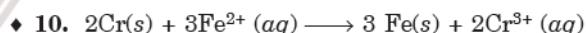
♦ 9. $E = E^\circ - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$

$$E^\circ = -0.44 - (-0.74) = 0.30 \text{ V}$$

$$E = 0.30 - \frac{0.059}{6} \log \frac{[0.01]^2}{[0.1]^3}$$

$$= 0.30 - \frac{0.059}{6} \log 0.1$$

$$= 0.30 - 0.01(-1) = 0.31 \text{ V}$$



$$E = E^\circ - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

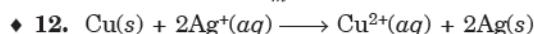
$$= 0.30 - \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.059}{6} \times 4 = 0.26 \text{ V}$$

♦ 11. $\Lambda_m = \frac{K \times 1000}{C}$

$$= \frac{4.1 \times 10^{-5} \times 1000}{10^{-3}} = 41 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{41}{390.5} = 0.105$$



The Nernst equation is

$$E = E^\ominus - \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$E^\ominus = E^\ominus(\text{Ag}^+|\text{Ag}) - E^\ominus(\text{Cu}^{2+}|\text{Cu})
= 0.80 - 0.34 = 0.46 \text{ V}$$

$$0.422 = 0.46 - \frac{0.059}{2} \log \frac{(0.1)}{[\text{Ag}^+]^2}$$

$$0.422 - 0.46 = -\frac{0.059}{2} \log \frac{(0.1)}{[\text{Ag}^+]^2}$$

$$\therefore \log \frac{0.1}{[\text{Ag}^+]^2} = \frac{0.038 \times 2}{0.059} = 1.2881$$

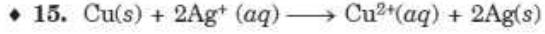
$$\text{or } \frac{0.1}{[\text{Ag}^+]^2} = 19.413$$

$$\text{or } [\text{Ag}^+]^2 = \frac{0.1}{19.413} = 5.15 \times 10^{-3}$$

$$\text{or } [\text{Ag}^+] = 0.0718 \text{ M}$$

♦ 13. Refer Solved Example 32 (ii) (page 41–42).

$$\Delta G^\circ = -nFE^\circ \\ = -2 \times 96500 \times 1.1 = -212.3 \text{ kJ}$$

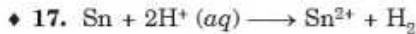


$$E = E^\circ - \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 0.46 - \frac{0.059}{2} \log \frac{(10^{-1})}{(10^{-3})^2} = 0.3125 \text{ V}$$

♦ 16.

$$\Lambda_m = \frac{\kappa \times 1000}{M} \\ = \frac{0.025 \times 1000}{0.20} = 125 \text{ S cm}^2 \text{ mol}^{-1}$$



$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2}$$

$$n = 2, [\text{Sn}^{2+}] = 0.001 \text{ M}, [\text{H}^+] = 0.01$$

$$E_{\text{cell}}^\circ = E_{\text{R}}^\circ - E_{\text{L}}^\circ \\ = 0.00 - (-0.14) = 0.14$$

$$E = 0.14 - \frac{0.059}{2} \log \frac{0.001}{(0.01)^2} \\ = 0.14 - \frac{0.059}{2} \log 10 \\ = 0.14 - 0.0295 \times 1 = 0.1105 \text{ V}$$

♦ 18. Refer Solved Example 48 (page 50).

Competition File

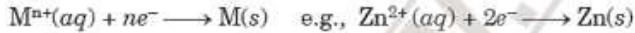
Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

□ TYPES OF ELECTRODES

Some common types of electrodes and their reduction potentials are :

A. Metal-metal ion electrodes. These electrodes consist of a pure metal (M) in contact with a solution of its cations (M^{n+}). It is represented as $M^{n+} | M(s)$ e.g., $Zn^{2+} | Zn$, $Cu^{2+} | Cu$, etc. Its electrode reaction is



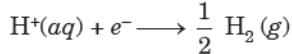
$$\text{and } E(M^{n+} | M) = E^\circ(M^{n+} | M) - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

B. Metal-metal insoluble salt electrodes. These are prepared by coating a piece of metal with an insoluble salt of the same metal dipped in a solution containing the anion of the insoluble salt. For example, silver is coated with $AgCl$ and dipped in a solution containing Cl^- ions. It is represented as : $Cl^- | AgCl | Ag$. The electrode reaction is



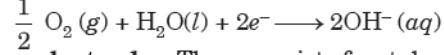
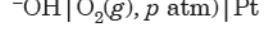
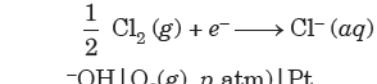
$$E(Cl^- | AgCl | Ag) = E^\circ(Cl^- | AgCl | Ag) - \frac{0.059}{1} \log [Cl^-]$$

C. Gas electrodes. These consist of an inert metal (usually Au or Pt) in contact with a gas bubbling into a solution containing corresponding anion. For example, the common hydrogen electrode in which H_2 gas is bubbled over platinized platinum electrode dipped in an acid solution. It is represented as $H^+ | (H_2, p \text{ atm}) | Pt$. The reaction is



$$E = E^\circ - \frac{0.059}{1} \log \frac{(pH_2)^{1/2}}{[H^+]}$$

Other examples are $Cl^- | Cl_2(g, p \text{ atm}) | Pt$,



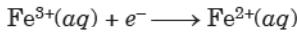
D. Amalgam electrodes. These consist of metal amalgams dipping in a solution of their ions. For example, lead amalgam dipping in a solution of Pb^{2+} ions. It is represented as $Pb(Hg) | Pb^{2+}$. The reaction is



$$E = E^\circ - \frac{0.059}{2} \log \frac{1}{[Pb^{2+}]}$$

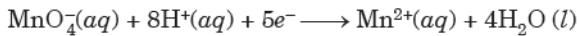
Other example is zinc amalgam electrode; $Zn(Hg) | Zn^{2+}$.

E. Oxidation-reduction electrodes. These types of electrodes are made by using an inert metal (e.g. Pt) immersed in a solution which contain two ions of the same element in different oxidation states. For example, $Fe^{3+}(aq) | Fe^{2+}(aq) | Pt$, $MnO_4^-(aq) | Mn^{2+}(aq)$, $H^+(aq) | Pt$. The reaction is



$$E(Fe^{3+} | Fe^{2+}) = E^\circ(Fe^{3+} | Fe^{2+}) - \frac{0.059}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

and

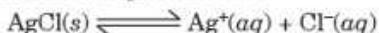


$$E = E^\circ - \frac{0.059}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]}$$

Competition File

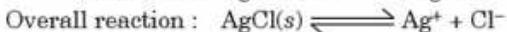
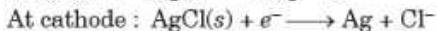
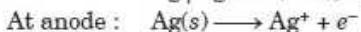
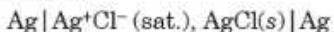
□ SOLUBILITY PRODUCT FROM EMF DATA

In a saturated solution of a sparingly soluble salt such as AgCl, equilibrium is represented as



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

Since solubility product is the equilibrium constant, it must be related to e.m.f. of the selected cell having an overall reaction as above. For example, for determining solubility product of AgCl, the cell is



$$\begin{aligned} E^\circ_{\text{cell}} &= \frac{2.303 RT}{nF} \log [\text{Ag}^+][\text{Cl}^-] \\ &= \frac{2.303 RT}{nF} \log K_{sp} \end{aligned}$$

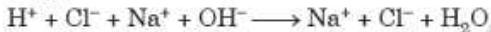
Knowing E°_{cell} , K_{sp} can be calculated.

□ CONDUCTOMETRIC TITRATIONS

The principle of conductometric titrations is that during the titration, one of the ions is replaced by the other. Since the ions differ in their ionic conductances, the conductance of the solution will vary during the course of the titration. The end point may be detected by the break in the titration curves. Let us illustrate by taking some examples :

A. Titration of a strong acid vs strong base

(e.g., HCl + NaOH).



In the beginning H^+ ions are replaced by slow moving Na^+ ions and therefore, conductance decreases (Fig. a). After the end point, Na^+ and OH^- ions increase and hence the conductance increases.

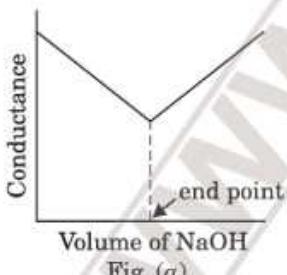


Fig. (a)

B. Titration of weak acid vs strong base

(e.g., $\text{CH}_3\text{COOH} + \text{NaOH}$)



After an initial decrease due to the titration of free H^+ ions, the conductance increases because of the net gain of CH_3COO^- and Na^+ ions (as neutralization proceeds). After neutralization,

the conductance increases sharply due to excess Na^+ and OH^- ions.

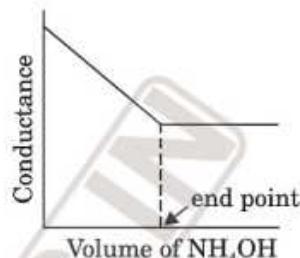


Fig. (b)

C. Titration of strong acid vs weak base

(e.g., HCl + NH_4OH)



The conductance decreases initially because of the replacement of fast moving H^+ ions by slow moving NH_4^+ ions (Fig. c). After neutralization, the further addition of NH_4OH does not make much change.

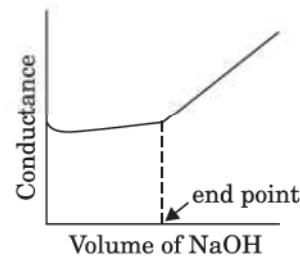
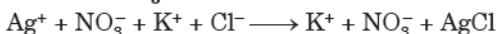


Fig. (c)

D. Titration of silver nitrate vs halide ion

(e.g., $\text{AgNO}_3 + \text{KCl}$)



Initially conductance remains almost constant because Ag^+ ions are replaced by K^+ ions and both have almost the same mobility. After the end point, it increases because of the addition of more K^+ and Cl^- ions.

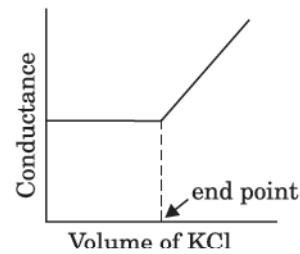


Fig. (d)

Competition File

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions

M. C. Q.

A *Topicwise* MULTIPLE CHOICE QUESTIONS with only one correct answer

Electrolytic Conductance

- A9.** The values of limiting ionic conductance of H^+ and HCOO^- ions are respectively 347 and $53 \text{ S cm}^2 \text{ mol}^{-1}$ at 298 K. If the molar conductance of 0.025 M methanoic acid at 298 K is $40 \text{ S cm}^2 \text{ mol}^{-1}$, the dissociation constant of methanoic acid at 298 K is

(a) 1×10^{-5} (b) 2×10^{-5}
 (c) 1.5×10^{-4} (d) 2.5×10^{-4}

A10. The ionization constant of a weak electrolyte is 2.5×10^{-5} and molar conductance of its 0.01 M solution is $19.6 \text{ S cm}^2 \text{ mol}^{-1}$. The molar conductance at infinite dilution ($\text{S cm}^2 \text{ mol}^{-1}$) is

(a) 402 (b) 392
 (c) 306 (d) 39.2

Electrochemical Cells

- A11.** Which of the following statements is incorrect about electrochemical cell?

 - Electrons are released at anode.
 - Chemical energy is converted into electrical energy.
 - Salt bridge maintains the electrical neutrality of the electrolytes.
 - Cell can work indefinitely.

A12. Point out the correct statement in a cell of zinc and copper:

 - Zinc acts as cathode and copper as anode.
 - Zinc acts as anode and copper as cathode.
 - The standard reduction potential of zinc is more than that of copper.
 - The flow of electrons is from copper to zinc.

A13. The standard electrode potentials for $\text{Pb}^{2+} \mid \text{Pb}$ and $\text{Zn}^{2+} \mid \text{Zn}$ are -0.126 V and -0.763 V respectively. The e.m.f. of the cell

$$\text{Zn} \mid \text{Zn}^{2+}(0.1 \text{ M}) \parallel \text{Pb}^{2+}(0.1 \text{ M}) \mid \text{Pb}$$

is :

 - 0.637 V
 - $< 0.637 \text{ V}$
 - $> 0.637 \text{ V}$
 - 0.889 V

A14. A zinc electrode is placed in 0.1 M solution of ZnSO_4 at 25°C . Assuming that the salt is dissociated to an extent of 20% at this dilution, the potential of this electrode is ($E^\circ = -0.76 \text{ V}$)

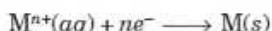
 - -0.81 V
 - -0.79 V
 - 0.81 V
 - 0.79 V

Answers

- A1.** (a) **A2.** (b) **A3.** (c) **A4.** (a) **A5.** (a) **A6.** (c) **A7.** (c) **A8.** (b) **A9.** (d) **A10.** (b)

Competition File

A15. For the electrode reaction



Nernst equation is

$$(a) E = E^\circ + \frac{RT}{nF} \log \frac{1}{[M^{n+}]}$$

$$(b) E^\circ = E^\circ + RT \ln [M^{n+}]$$

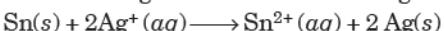
$$(c) E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

$$(d) \frac{E}{E^\circ} = \frac{RT}{nF} \ln [M^{n+}]$$

A16. E°_{cell} and ΔG° are related as :

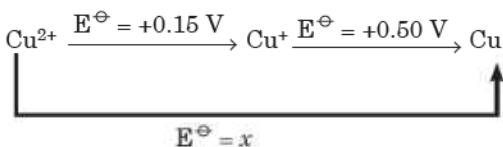
- | | |
|--|---|
| (a) $\Delta G^\circ = nFE^\circ_{cell}$ | (b) $\Delta G = -nFE^\circ_{cell}$ |
| (c) $\Delta G^\circ = -nFE^\circ_{cell}$ | (d) $\Delta G^\circ = nFE^\circ_{cell} = 0$ |

A17. Which of the following will decrease the voltage of the cell ?



- (a) increase in the size of silver rod
- (b) increase in the concentration of Sn^{2+} ions
- (c) increase in the concentration of Ag^+ ions
- (d) None of the above.

A18. In the diagram given below, the value of x is



- (a) 0.35 V
- (b) 0.65 V
- (c) 0.325 V
- (d) -0.65 V

A19. By how much will the potential of a zinc electrode change if the solution of $ZnSO_4$ in which it is immersed is diluted to 10 times at 298 K?

- (a) Decreases by 30 mV
- (b) Increases by 30 mV
- (c) Increases by 60 mV
- (d) Decreases by 60 mV

A20. The e.m.f. of the cell :



is 0.46 V. The standard reduction potential of $Ag^+ | Ag$ is 0.80 V. The standard reduction potential of $Cu^{2+} | Cu$ is

- (a) -0.34 V
- (b) 1.26 V
- (c) -1.26 V
- (d) 0.34 V

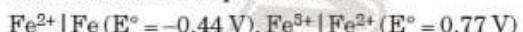
A21. Saturated solution of KNO_3 is used to make salt bridge because

- (a) velocity of K^+ is greater than that of NO_3^-
- (b) velocity of NO_3^- is greater than that of K^+
- (c) velocity of both K^+ and NO_3^- are nearly the same
- (d) KNO_3 is highly soluble in water.

A22. Aluminium displaces hydrogen from acids, but copper does not. A galvanic cell prepared by combining $Cu | Cu^{2+}$ and $Al | Al^{3+}$ has an emf of 2.0 V at 298 K. If the potential of copper electrode is + 0.34 V, that of aluminium electrode is

- | | |
|-------------|-------------|
| (a) -2.3 V | (b) +2.34 V |
| (c) -1.66 V | (d) 1.66 V |

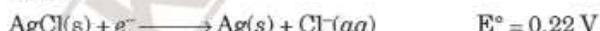
A23. Standard electrode potentials are :



Fe^{2+}, Fe^{3+} and Fe blocks are kept together, then

- | | |
|---|-------------------------|
| (a) Fe^{3+} increases | (b) Fe^{3+} decreases |
| (c) $Fe^{2+} Fe^{3+}$ remains unchanged | (d) Fe^{2+} decreased |

A24. The standard reduction potentials for two reactions are given below :



The solubility product of $AgCl$ under standard conditions of temperature (298 K) is given by

- | | |
|---------------------------|---------------------------|
| (a) 1.6×10^{-5} | (b) 1.5×10^{-8} |
| (c) 3.2×10^{-10} | (d) 1.5×10^{-10} |

A25. The e.m.f. of the following Daniell cell at 298 K is E_1 . $Zn | ZnSO_4(0.01 M) || CuSO_4(1.0) | Cu$

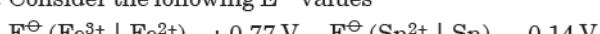
When concentration of $ZnSO_4$ is 1.0 M and that of $CuSO_4$ is 0.01 M, the e.m.f. changed to E_2 . What is the relationship between E_1 and E_2 ?

- | | |
|-----------------|------------------------|
| (a) $E_1 > E_2$ | (b) $E_1 < E_2$ |
| (c) $E_1 = E_2$ | (d) $E_2 = 0 \neq E_1$ |

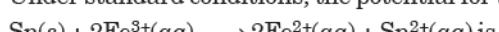
A26. $E^\circ_{Cu} = 0.34 V$ and $E^\circ_{Zn} = -0.76 V$. A Daniell cell contains 0.1 M $ZnSO_4$ solution and 0.01 M $CuSO_4$ solution at its electrodes. The EMF of the cell is

- | | |
|------------|------------|
| (a) 1.10 V | (b) 1.04 V |
| (c) 1.16 V | (d) 1.07 V |

A27. Consider the following E° values

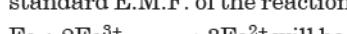


Under standard conditions, the potential for the reaction :



- | | |
|------------|------------|
| (a) 0.91 V | (b) 1.40 V |
| (c) 1.68 V | (d) 0.63 V |

A28. If $E^\circ(Fe^{2+} | Fe) = -0.441 V$ and $E^\circ(Fe^{3+} | Fe^{2+}) = 0.771 V$, the standard E.M.F. of the reaction :



- | | |
|-----------|-------------|
| (a) 1.653 | (b) 1.212 V |
| (c) 0.111 | (d) 0.330 V |

(C.B.S.E. P.M.T. 2006)

Answers

- | | | | | | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| A15. (c) | A16. (c) | A17. (b) | A18. (c) | A19. (a) | A20. (d) | A21. (c) | A22. (c) | A23. (b) | A24. (d) |
| A25. (a) | A26. (d) | A27. (a) | A28. (b) | | | | | | |

Competition File

Electrolysis

A29. Number of coulombs required to deposit 90 g of Al when the electrode reaction



- (a) 9.65×10^4 (b) 8.685×10^5
 (c) 9.65×10^5 (d) 6.955.

A30. 10800 C of electricity through the electrolyte deposited 2.977 g of metal with atomic mass 106.4 a.m.u. The valency of metal cation is :

- (a) 4 (b) 3
 (c) 2 (d) 1

A31. The charge on 1 gram mole ion of N^{3-} is

- (a) 6.00×10^5 C (b) 2.89×10^5 C
 (c) 3.98×10^5 C (d) 4.89×10^5 C

A32. A current of 3A was passed through a solution of AuCl_4^- ions using gold electrodes and it caused deposition of 1.234 g of Au (Atomic mass of Au = 197). The time for which the current was passed is

- (a) 20 min 8s (b) 30 min 12s
 (c) 10 min 4s (d) 10 min 40s

A33. An electric current is passed through silver voltameter connected to a water voltameter. The cathode of silver voltameter weighed 0.108 g more at the end of electrolysis. The volume of O_2 at STP evolved is

- (a) 5.6 cm³ (b) 550 cm³
 (c) 22.4 cm³ (d) 11.2 cm³

A34. Same amount of electric current is passed through solution of AgNO_3 and HCl. If 1.08 g of silver is obtained in the first case, the amount of hydrogen liberated at S.T.P. in the second case is :

- (a) 112 cm³ (b) 22400 cm³
 (c) 224 cm³ (d) 1.008 g

A35. 4.5 g of aluminium (at. mass = 27. a.m.u) is deposited at cathode from Al^{3+} solution by certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in solution by the same quantity of electric charge will be

- (a) 44.8 L (b) 22.4 L
 (c) 11.2 L (d) 5.6 L

A36. The quantity of electricity needed to separately electrolyse 1 M solution of ZnSO_4 , AlCl_3 and AgNO_3 completely is in the ratio of

- (a) 2 : 3 : 1 (b) 2 : 1 : 1
 (c) 2 : 1 : 3 (d) 2 : 2 : 1

Batteries and Corrosion

A37. When lead storage battery discharges

- (a) SO_2 is evolved (b) PbSO_4 is consumed
 (c) Lead is formed (d) H_2SO_4 is consumed.

A38. In a Leclanche dry cell, anode is :

- (a) Graphite rod (b) FeO and Fe(OH)_2
 (c) Zinc container (d) $\text{MnO}_2 + \text{C}$.

A39. Rust is a mixture of

- (a) FeO and Fe(OH)_3 (b) FeO and Fe(OH)_2
 (c) Fe_2O_3 and Fe(OH)_3 (d) Fe_3O_4 and Fe(OH)_3 .

A40. Which of the following will be formed when lead storage battery is charged?

- (a) Sulphuric acid is consumed
 (b) lead is consumed
 (c) sulphuric acid is formed
 (d) lead sulphate is formed.

A41. For a $\text{H}_2 - \text{O}_2$ fuel cell, the theoretical voltage has been found to be 1.23V and ΔH to be -285 kJ mol^{-1} . The efficiency of the fuel cell is

- (a) 76% (b) 83%
 (c) 89% (d) 72%

A42. Which of the following reaction occurs at cathode in $\text{H}_2 - \text{O}_2$ fuel cell ?

- (a) $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$
 (b) $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4 \text{OH}^-$
 (c) $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$
 (d) $\text{H}_2 + 2\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + 2e^-$

A43. Which of the following reaction occurs at anode during the recharging of lead storage battery ?

- (a) $\text{PbSO}_4 + 2\text{H}_2\text{O} \longrightarrow \text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^-$
 (b) $\text{Pb} + \text{SO}_4^{2-} \longrightarrow \text{PbSO}_4 + 2e^-$
 (c) $\text{PbSO}_4 + 2e^- \longrightarrow \text{Pb} + \text{SO}_4^{2-}$
 (d) $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2e^- \longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$

A44. In nickel-cadmium storage cell, the electrolyte is

- (a) moist KOH (b) dil H_2SO_4
 (c) aqueous NH_4Cl (d) $\text{Ni}(\text{OH})_3(aq)$

Answers

- A29.** (c) **A30.** (a) **A31.** (b) **A32.** (c) **A33.** (a) **A34.** (a) **A35.** (d) **A36.** (a) **A37.** (d) **A38.** (c)
A39. (c) **A40.** (c) **A41.** (b) **A42.** (b) **A43.** (a) **A44.** (a)

Competition File

B MULTIPLE CHOICE QUESTIONS from Competitive Examinations

AIPMT & Other State Boards' Medical Entrance

B1. The efficiency of a fuel cell is given by:

- (a) $\frac{\Delta G}{\Delta S}$ (b) $\frac{\Delta G}{\Delta H}$
 (c) $\frac{\Delta S}{\Delta G}$ (d) $\frac{\Delta H}{\Delta G}$ (C.B.S.E.P.M.T. 2007)

B2. Standard free energies of formation (in kJ/mol) at 298 K are -237.2 , -394.4 and -8.2 for $H_2O(l)$, $CO_2(g)$ and pentane (g), respectively. The value of E_{cell}° for the pentane-oxygen fuel cell is:

- (a) 2.0968 V (b) 1.0968 V
 (c) 0.0968 V (d) 1.968 V (C.B.S.E. P.M.T. 2008)

B3. Al_2O_3 is reduced by electrolysis at low potentials and high currents. If 4.0×10^4 amperes of current is passed through molten Al_2O_3 for 6 hours, what mass of aluminium is produced? (Assume 100% current efficiency, atomic mass of $Al = 27\text{ g/mol}$)

- (a) $8.1 \times 10^4\text{ g}$ (b) $2.4 \times 10^5\text{ g}$
 (c) $1.3 \times 10^4\text{ g}$ (d) $9.0 \times 10^3\text{ g}$ (C.B.S.E. PMT 2009)

B4. The equivalent conductance of M/32 solution of a weak monobasic acid is 8 mho cm^2 and at infinite dilution is 400 mho cm^2 . The dissociation constant of this acid is

- (a) 1.25×10^{-6} (b) 6.25×10^{-4}
 (c) 1.25×10^{-4} (d) 1.25×10^{-5} (C.B.S.E. PMT 2009)

B5. For the reduction of silver ions with copper metal the standard cell potential was found to be $+0.46\text{ V}$ at 25°C . The value of standard Gibbs energy, ΔG° will be ($F = 96500\text{ C mol}^{-1}$):

- (a) -44.5 kJ (b) -98.0 kJ
 (c) -89.0 kJ (d) -89.0 J (C.B.S.E. P.M.T. 2010)

B6. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to:

- (a) increase in both i.e. number of ions and ionic mobility of ions.
 (b) increase in number of ions
 (c) increase in ionic mobility of ions
 (d) 100% ionization of electrolyte at normal dilution.

(C.B.S.E. P.M.T. 2010)

Answers

- | | | | | | | | | | |
|-----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|
| B1. (b) | B2. (b) | B3. (a) | B4. (d) | B5. (c) | B6. (c) | B7. (c) | B8. (d) | B9. (b) | B10. (b) |
| B11. (d) | B12. (a) | B13. (c) | | | | | | | |

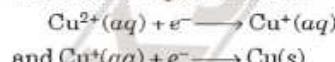
B7. Standard electrode potential of three metals X, Y and Z are -1.2 V , $+0.5\text{ V}$ and -3.0 V respectively. The reducing power of these metals will be

- (a) $Y > Z > X$ (b) $Y > X > Z$
 (c) $Z > X > Y$ (d) $X > Y > Z$ (CBSE PMT 2011)

B8. If the E_{cell}° for a given reaction has a negative value, then which of the following gives the correct relationships for the values of ΔG° and K_{eq} ?

- (a) $\Delta G^\circ > 0$; $K_{eq} > 1$ (b) $\Delta G^\circ < 0$; $K_{eq} > 1$
 (c) $\Delta G^\circ < 0$; $K_{eq} < 1$ (d) $\Delta G^\circ > 0$; $K_{eq} < 1$ (CBSE PMT 2011, NEET 2016)

B9. The electrode potentials for



are $+0.15\text{ V}$ and $+0.50\text{ V}$ respectively. The value of $E_{\text{Cu}^{2+}/\text{Cu}}$

- (a) 0.500 V (b) 0.325 V
 (c) 0.650 V (d) 0.150 V (CBSE PMT 2011)

B10. Standard electrode potential for $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple is $+0.15\text{ V}$ and that for the Cr^{3+}/Cr couple is -0.74 V . These two couples in their standard state are connected to make a cell. The cell potential will be

- (a) $+1.19\text{ V}$ (b) $+0.89\text{ V}$
 (c) $+0.18\text{ V}$ (d) $+1.83\text{ V}$ (CBSE PMT 2011)

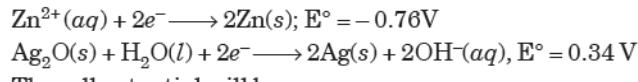
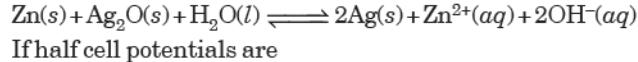
B11. Limiting molar conductivity of NH_4OH [i.e. $\Lambda_{m(\text{NH}_4\text{OH})}^\circ$] is equal to

- (a) $\Lambda_{m(\text{NH}_4\text{Cl})}^\circ + \Lambda_{m(\text{NaCl})}^\circ - \Lambda_{m(\text{NaOH})}^\circ$
 (b) $\Lambda_{m(\text{NaOH})}^\circ + \Lambda_{m(\text{NaCl})}^\circ - \Lambda_{m(\text{NH}_4\text{Cl})}^\circ$
 (c) $\Lambda_{m(\text{NH}_4\text{OH})}^\circ + \Lambda_{m(\text{NH}_4\text{Cl})}^\circ - \Lambda_{m(\text{HCl})}^\circ$
 (d) $\Lambda_{m(\text{NH}_4\text{Cl})}^\circ + \Lambda_{m(\text{NaOH})}^\circ - \Lambda_{m(\text{NaCl})}^\circ$ (A.I.P.M.T. 2012)

B12. At 25°C , molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is $9.54\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ and at infinite dilution its molar conductance is $238\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is

- (a) 4.008% (b) 40.800%
 (c) 2.080% (d) 20.800% (NEET 2013)

B13. A button cell used in watches function as following.



The cell potential will be

- (a) 0.84 V (b) 1.34 V
 (c) 1.10 V (d) 0.42 V (NEET 2013)

Competition File

- B14.** A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode would be?
- (a) 0.118 V (b) 1.18 V
 (c) 0.059 V (d) 0.59 V (NEET 2013)
- B15.** When 0.1 mol MnO_4^{2-} is oxidised, the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is
- (a) 96500 C (b) 2×96500 C
 (c) 9650 C (d) 96.50 C (AIPMT 2014)
- B16.** The weight of silver (at. wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be
- (a) 5.4 g (b) 10.8 g
 (c) 54.0 g (d) 108.0 g (AIPMT 2014)
- B17.** A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as
- (a) dynamo (b) Ni–Cd cell
 (c) fuel cell (d) electrolytic cell
 (AIPMT 2015)
- B18.** The pressure of H_2 required to make the potential of H_2 -electrode zero in pure water at 298 K is
- (a) 10^{-10} atm (b) 10^{-4} atm
 (c) 10^{-14} atm (d) 10^{-12} atm
 (NEET 2016)
- B19.** The molar conductivity of a 0.5 mol dm^{-3} solution of $AgNO_3$ with electrolytic conductivity of $5.76 \times 10^{-3} S\ cm^{-1}$ at 298 K in $S\ cm^2\ mol^{-1}$ is
- (a) 2.88 (b) 11.52
 (c) 0.086 (d) 28.8 (NEET 2016)
- B20.** During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 amperes is
- (a) 55 min. (b) 110 min.
 (c) 220 min. (d) 330 min.
 (NEET 2016)
- B21.** The number of electrons delivered at the cathode during electrolysis by a current of 1 ampere in 60 seconds is
- (a) 6×10^{23} (b) 6×10^{20}
 (c) 3.75×10^{20} (d) 7.48×10^{23}
 (NEET 2016)
- B22.** Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because
- (a) zinc is lighter than iron
 (b) zinc has lower melting point than iron
 (c) zinc has lower negative electrode potential than iron
- (d) zinc has higher negative electrode potential than iron
 (NEET 2016)
- B23.** In the electrochemical cell : $Zn | ZnSO_4(0.01\ M) || CuSO_4(1.0\ M) | Cu$, the emf of this Daniell cell is E_1 . When the concentration of $ZnSO_4$ is changed to 1.0 M and that $CuSO_4$ changed to 0.01 M, the emf changes to E_2 . From the following, which one is the relationship between E_1 and E_2 ?
 (Given, $RT/F = 0.059$)
- (a) $E_1 < E_2$ (b) $E_1 > E_2$
 (c) $E_2 = 0 \neq E_1$ (d) $E_1 = E_2$ (NEET 2017)
- B24.** Consider the change in oxidation state of bromine corresponding to different emf values as shown in the diagram below :
-
- Then the species undergoing disproportionation is:
- (a) BrO_3^- (b) BrO_4^-
 (c) Br_2 (d) $HBrO$ (NEET 2018)
- B25.** The equilibrium constant of the following redox reaction at 298 K is 1×10^8 .
- $$2Fe^{3+}(aq) + 2I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(s)$$
- If the standard reduction potential of iodine becoming iodide is +0.54 V, what is the standard reduction potential of $Fe^{3+} | Fe^{2+}$?
- (a) + 1.006 V (b) – 1.006 V
 (c) + 0.77 V (d) – 0.77 V
 (e) – 0.652 V (Kerala P.M.T. 2008)
- B26.** A solution of nickel sulphate in which nickel rod is dipped is diluted 10 times. The reduction potential of Ni at 298 K
- (a) Decreases by 60 mV (b) Decreases by 30 mV
 (c) Decreases by 30 V (d) Increases by 30 mV
 (e) Increases by 30 V (Kerala P.M.T. 2009)
- B27.** When molten magnesium oxide was electrolysed for a certain period, 150 mg of Mg was deposited on the cathode. The volume of oxygen gas in cm^3 at STP conditions liberated at the anode during the same period is (Atomic mass of Mg = 24 g mol^{-1})
- (a) 140 (b) 280
 (c) 70 (d) 120
 (e) 240 (Kerala P.M.T. 2014)

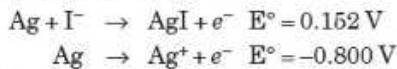
Answers

- | | | | | | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| B14. (d) | B15. (c) | B16. (d) | B17. (c) | B18. (c) | B19. (b) | B20. (b) | B21. (c) | B22. (d) | B23. (b) |
| B24. (d) | B25. (c) | B26. (b) | B27. (c) | | | | | | |

Competition File

JEE (Main) & Other State Boards' Engineering Entrance

B28. Given the data at 25°C :



(2.303 RT/F = 0.059 V)

What is the value of $\log K_{\text{sp}}$ for AgI?

- (a) +8.612 (b) -37.83
(c) -16.13 (d) -8.12 (A.I.E.E. 2006)

B29. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100Ω. The conductivity of this solution is 1.29 S m^{-1} . Resistance of the same cell when filled with 0.2 M of the same solution is 520Ω. The molar conductivity of 0.2 M solution of the electrolyte will be

- (a) $1240 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ (b) $1.24 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
(c) $12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ (d) $124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$

(A.I.E.E. 2006)

B30. The cell $\text{Zn} | \text{Zn}^{2+}(1\text{M}) || \text{Cu}^{2+}(1\text{M}) | \text{Cu}$

($E^\circ_{\text{cell}} = 1.10 \text{ V}$) was allowed to be completely discharged at

298 K. The relative concentration of Zn^{2+} to Cu^{2+} ($\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$) is :

- (a) 37.3 (b) $10^{37.3}$
(c) 9.65×10^4 (d) antilog (24.08)

(A.I.E.E. 2007)

B31. Given $E^\circ(\text{Cr}^{3+} | \text{Cr}) = -0.72 \text{ V}$ and $E^\circ(\text{Fe}^{2+} | \text{Fe}) = -0.42 \text{ V}$.

The potential for the cell



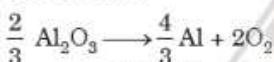
- (a) -0.26 V (b) 0.26 V
(c) 0.339 V (d) -0.339 V (A.I.E.E. 2008)

B32. Given $E^\circ_{\text{Fe}^{3+} | \text{Fe}} = -0.36 \text{ V}$, $E^\circ_{\text{Fe}^{2+} | \text{Fe}} = -0.439 \text{ V}$. The value of standard electrode potential for the change,



- (a) -0.072 V (b) 0.385 V
(c) 0.770 V (d) -0.270 V (A.I.E.E. 2009)

B33. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows:



The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least

- (a) 2.5 V (b) 5.0 V
(c) 4.5 V (d) 3.0 V (A.I.E.E. 2010)

B34. The reduction potential of hydrogen half-cell will be negative if:

- (a) $p(\text{H}_2) = 2 \text{ atm}$ and $[\text{H}^+] = 1.0 \text{ M}$

- (b) $p(\text{H}_2) = 2 \text{ atm}$ and $[\text{H}^+] = 2.0 \text{ M}$

- (c) $p(\text{H}_2) = 1 \text{ atm}$ and $[\text{H}^+] = 2.0 \text{ M}$

- (d) $p(\text{H}_2) = 1 \text{ atm}$ and $[\text{H}^+] = 1.0 \text{ M}$ (A.I.E.E. 2011)

B35. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.3 S m^{-1} . If resistance of the 0.4 M solution of the same electrolyte is 260 Ω, its molar conductivity is :

- (a) $6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ (b) $625 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$

- (c) $62.5 \text{ S m}^2 \text{ mol}^{-1}$ (d) $6250 \text{ S m}^2 \text{ mol}^{-1}$

(A.I.E.E. 2011)

B36. The standard reduction potentials for $\text{Zn}^{2+} | \text{Zn}$, $\text{Ni}^{2+} | \text{Ni}$, and $\text{Fe}^{2+} | \text{Fe}$ are -0.76, -0.23 and -0.44 V respectively. The reaction $\text{X} + \text{Y}^{2+} \longrightarrow \text{X}^{2+} + \text{Y}$ will be spontaneous when

- (a) $\text{X} = \text{Ni}$, $\text{Y} = \text{Zn}$ (b) $\text{X} = \text{Fe}$, $\text{Y} = \text{Zn}$
(c) $\text{X} = \text{Zn}$, $\text{Y} = \text{Ni}$ (d) $\text{X} = \text{Ni}$, $\text{Y} = \text{Fe}$

(A.I.E.E. 2012, Kerela P.E.T. 2016)

B37. Given

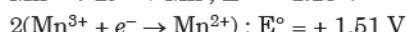
$$E^\circ_{\text{Cr}^{3+} | \text{Cr}} = -0.74 \text{ V}; \quad E^\circ_{\text{MnO}_4^- | \text{Mn}^{2+}} = 1.51 \text{ V}$$

$$E^\circ_{\text{Cr}_2\text{O}_7^{2-} | \text{Cr}^{3+}} = 1.33 \text{ V}; \quad E^\circ_{\text{Cl}_3 | \text{Cr}^{3+}} = 1.36 \text{ V}$$

Based on the data given above, strongest oxidising agent will be

- (a) MnO_4^- (b) Cl^-
(c) Cr^{3+} (d) Mn^{2+} (JEE Main 2013)

B38. Given below are the half-cell reactions:



The E° for $3\text{Mn}^{2+} \rightarrow \text{Mn} + 2\text{Mn}^{3+}$ will be

- (a) -0.33 V ; the reaction will occur
(b) -2.69 V ; the reaction will not occur
(c) -2.69 V ; the reaction will occur
(d) -0.33 V ; the reaction will not occur (JEE Main 2014)

B39. The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_c and λ_∞ , respectively. The correct relationship between λ_c and λ_∞ is given as (where, the constant B is positive)

- (a) $\lambda_c = \lambda_\infty + (B) \sqrt{C}$ (b) $\lambda_c = \lambda_\infty + (B) C$

- (c) $\lambda_c = \lambda_\infty - (B) C$ (d) $\lambda_c = \lambda_\infty - (B) \sqrt{C}$

(JEE Main 2014)

B40. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.4 S m^{-1} . The resistance of 0.5 M solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in $\text{S m}^2 \text{ mol}^{-1}$ is

- (a) 5×10^2 (b) 5×10^4

- (c) 5×10^{-3} (d) 5×10^3 (JEE Main 2014)

Answers

- B28.** (c) **B29.** (c) **B30.** (b) **B31.** (b) **B32.** (c) **B33.** (a) **B34.** (a) **B35.** (a) **B36.** (c) **B37.** (d)
B38. (b) **B39.** (d) **B40.** (b)

Competition File

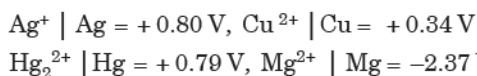
B53. Given that the standard reduction potentials for M^+/M and N^+/N electrodes at 298 K are 0.52 V and 0.25 V respectively. Which of the following is correct in respect of the following electrochemical cell?



- (a) The overall cell reaction is a spontaneous reaction.
- (b) The standard EMF of the cell is -0.27 V.
- (c) The standard EMF of the cell is 0.77 V.
- (d) The standard EMF of the cell is -0.77 V.
- (e) The standard EMF of the cell is 0.27 V.

(Kerala P.E.T. 2012)

B54. 1M solution each of $Cu(NO_3)_2$, $AgNO_3$, $Hg(NO_3)_2$ and $Mg(NO_3)_2$ is electrolysed using Pt-electrodes. The values of standard reduction electrode potentials in volts are:

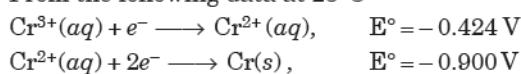


The sequence of deposition of metals on the cathode will be

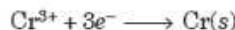
- (a) Mg, Ag, Cu
- (b) Mg, Cu, Ag
- (c) Ag, Hg, Cu
- (d) Cu, Hg, Ag

(A.M.U. Engg. 2012)

B55. From the following data at 25°C



Find E° at 25°C for the reaction:



- (a) -0.741 V
- (b) -1.324 V
- (c) -0.476 V
- (d) +0.741 V

(A.M.U. Engg. 2012)

B56. Equivalent conductivity at infinite dilution for sodium-potassium oxalate $[(COO^-)_2Na^+K^+]$ will be [given: molar conductivities of oxalate, K^+ and Na^+ ions at infinite dilution are 148.2, 50.1, 73.5 S cm² mol⁻¹, respectively]

- (a) 271.8 S cm² eq⁻¹
- (b) 67.95 S cm² eq⁻¹
- (c) 543.6 S cm² eq⁻¹
- (d) 135.9 S cm² eq⁻¹

(W.B. JEE Engg. 2013)

B57. A current strength of 9.65 amperes is passed through excess fused $AlCl_3$ for 5 hours. How many litres of chlorine will be liberated at STP? ($F = 96500 \text{ C}$)

- (a) 2.016
- (b) 1.008
- (c) 11.2
- (d) 20.16
- (e) 10.08

(Kerala P.E.T. 2013)

B58. At 25°C, the molar conductance of 0.007 M hydrofluoric acid is 150 mho cm² mol⁻¹ and its $\Lambda_m^\circ = 500 \text{ mho cm}^2 \text{ mol}^{-1}$. The value of the dissociation constant of the acid at the given concentration at 25°C is

- | | |
|----------------------------------|--|
| (a) $7 \times 10^{-4} \text{ M}$ | (b) $7 \times 10^{-5} \text{ M}$ |
| (c) $9 \times 10^{-3} \text{ M}$ | (d) $9 \times 10^{-4} \text{ M}$ (WB JEE 2014) |

B59. The change in potential of the half-cell $Cu^{2+}|Cu$, when aqueous Cu^{2+} solution is diluted 100 times at 298 K?

- (a) Increases by 120 mV
- (b) Decreases by 120 mV
- (c) Increases by 60 mV
- (d) Decreases by 60 mV
- (e) No change

B60. Conductivity of a saturated solution of a sparingly soluble salt AB at 298 K is $1.85 \times 10^{-5} \text{ S m}^{-1}$. Solubility product of the salt AB at 298 K is

$$[\text{Given } \Lambda_m^\circ (\text{AB}) = 140 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}]$$

- | | |
|---------------------------|----------------------------|
| (a) 5.7×10^{-12} | (b) 1.32×10^{-12} |
| (c) 7.5×10^{-12} | (d) 1.74×10^{-12} |

(Karnataka CET 2011)

B61. For $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

$E^\circ = 1.33 \text{ V}$. At $[Cr_2O_7^{2-}] = 4.5 \text{ millimole}$, $[Cr^{3+}] = 15 \text{ millimole}$, $E = 1.067 \text{ V}$. The pH of the solution is nearly

- | | |
|-------|-------|
| (a) 2 | (b) 3 |
| (c) 5 | (d) 4 |

B62. In H_2-O_2 fuel cell the reaction occurring at cathode is

- | |
|---|
| (a) $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH_{(aq)}^-$ |
| (b) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$ |
| (c) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ |
| (d) $H^+ + e^- \longrightarrow \frac{1}{2}H_2$ |

(Karnataka CET 2015)

B63. In the lead - acid battery during charging, the cathode reaction is

- (a) formation of PbO_2
- (b) formation of $PbSO_4$
- (c) reduction of Pb^{2+} to Pb
- (d) decomposition of Pb at the anode. (A.M.U. Engg. 2015)

B64. What pressure of H_2 would be required to make emf of the hydrogen electrode zero in pure water at 25°C?

- | | |
|---------------------------|---------------------------------|
| (a) 10^{-7} atm | (b) 10^{-14} atm |
| (c) 1 atm | (d) 0.5 atm (A.M.U. Engg. 2015) |

B65. How many Faradays are required to reduce 1 mol of Cr_2O_7 to Cr^{3+} in acid medium?

- | | |
|-------|-------|
| (a) 2 | (b) 3 |
| (c) 5 | (d) 6 |

(W.B. J.E.E. 2017)

B66. By passing electric current, $NaClO_3$ is converted into $NaClO_4$ according to the following equation:



How many moles of $NaClO_4$ will be formed when three Faradays of charge is passed through $NaClO_3$?

- | | |
|----------|---------|
| (a) 0.75 | (b) 3.0 |
| (c) 1.5 | (d) 1.0 |

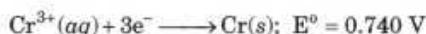
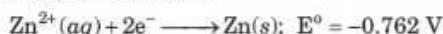
(Karnataka C.E.T. 2017)

Answers

- | | | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| B53. (b) | B54. (c) | B55. (a) | B56. (d) | B57. (d) | B58. (d) | B59. (d) | B60. (d) | B61. (a) | B62. (a) |
| B63. (c) | B64. (c) | B65. (d) | B66. (c) | | | | | | |

Competition File

- B67.** The standard reduction potential at 298 K for the following half cell reactions :

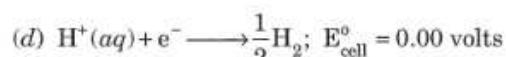
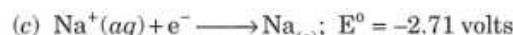
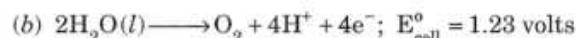
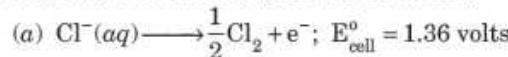


Which of the following is the strongest reducing agent?

- (a) Cr(s)
- (b) Zn(s)
- (c) H₂(g)
- (d) F₂(g)

(Karnataka C.E.T. 2017)

- B68.** In the electrolysis of aqueous sodium chloride solution, which of the half cell reaction will occur at anode?



(Karnataka C.E.T. 2017)

- B69.** Consider a fuel cell supplied with 1 mole of H₂ gas and 10 moles of O₂ gas. If fuel cell is operated at 96.5 mA current, how long will it deliver power?

(Assume 1 F = 96500 C/mol of electrons)

- (a) $1 \times 10^6 \text{ s}$
- (b) $0.5 \times 10^6 \text{ s}$
- (c) $2 \times 10^6 \text{ s}$
- (d) $4 \times 10^6 \text{ s}$
- (e) $5 \times 10^6 \text{ s}$

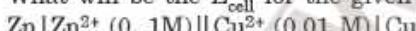
(Kerala P.E.T. 2013)

- B70.** Which of the following statements is/are true for an electrochemical cell?

- (a) Oxidation occurs at the anode only
- (b) Reduction occurs at the anode only
- (c) Oxidation occurs at both the anode and cathode
- (d) Reduction occurs at both the anode and cathode.

(J.K. C.E.T. 2018)

- B71.** What will be the E_{cell} for the given cell?



Given : $E^\circ_{\text{Zn}^{2+}|\text{Zn}} = 0.76 \text{ V}$ and $E^\circ_{\text{Cu}^{2+}|\text{Cu}} = 0.34 \text{ V}$.

Also predict whether the reaction is spontaneous or non-spontaneous.

- (a) 1.07 V and spontaneous
- (b) -1.13 V and non-spontaneous
- (c) -1.07 V and non-spontaneous
- (d) 1.13 V and spontaneous

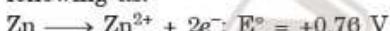
(J.K. C.E.T. 2018)

- B72.** What amount of electricity can deposit 1 mol of Al metal at cathode when passed through molten AlCl₃?

- (a) 0.3 F
- (b) 1 F
- (c) 3 F
- (d) 1/3 F

(WB J.E.E. 2018)

- B73.** Given the standard half-cell potentials (E°) of the following as:



Then, the standard e.m.f of the cell with the reaction



- (a) -0.35 V
- (b) +0.35 V
- (c) +1.17 V
- (d) -1.17 V

(WB J.E.E. 2018)

- B74.** At a particular temperature, the ratio of molar conductance to specific conductance of 0.01 M NaCl solution is

- (a) $10^5 \text{ cm}^3 \text{ mol}^{-1}$
- (b) $10^3 \text{ cm}^3 \text{ mol}^{-1}$
- (c) $10 \text{ cm}^3 \text{ mol}^{-1}$
- (d) $10^5 \text{ cm}^2 \text{ mol}^{-1}$

(Karnataka C.E.T. 2018)

- B75.** For a cell involving two electron change, $E_{\text{cell}}^\circ = 0.3 \text{ V}$ at 25°C. The equilibrium constant of the reaction is

- (a) 10^{-10}
- (b) 3×10^{-2}
- (c) 10
- (d) 10^{10}

(Karnataka C.E.T. 2018)

- B76.** The charge required for the reduction of 1 mol of MnO₄⁻ to MnO₂ is

- (a) 1 F
- (b) 3 F
- (c) 5 F
- (d) 7 F

(Karnataka C.E.T. 2018)

- B77.** Consider the electrochemical reaction between Ag(s) and Cl₂(g) electrodes in 1 litre of 0.1 M KCl aqueous solution. Solubility product of AgCl is 1.8×10^{-10} and F = 96500 C/mol. At 1 μA current, calculate the time required to start observing the AgCl precipitation in the galvanic cell.

- (a) 173 s
- (b) 346 s
- (c) $1.25 \times 10^6 \text{ s}$
- (d) $1.25 \times 10^5 \text{ s}$

(Kerala P.E.T. 2018)

- B78.** The voltage of the cell consisting of Li(s) and F₂(g) electrodes is 5.92 V at standard condition at 298 K. What is the voltage if the electrolyte consists of 2 M LiF. (ln 2 = 0.693, R = 8.314 J K⁻¹ mol⁻¹ and F = 96500 C mol⁻¹)

- (a) 5.90 V
- (b) 5.937 V
- (c) 5.88 V
- (d) 4.9 V
- (e) 4.8 V

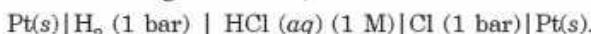
(Kerala P.E.T. 2018)

Answers

- | | | | | | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| B67. (b) | B68. (a) | B69. (c) | B70. (a) | B71. (a) | B72. (c) | B73. (b) | B74. (a) | B75. (d) | B76. (b) |
| B77. (a) | B78. (a) | | | | | | | | |

Competition File

B79. Consider the galvanic cell,



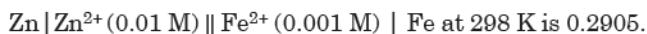
After running the cell for sometime, the concentration of the electrolyte is automatically raised to 3 M HCl. Molar conductivity of the 3 M HCl is about $240 \text{ S cm}^2 \text{ mol}^{-1}$ and limiting molar conductivity of HCl is about $420 \text{ S cm}^2 \text{ mol}^{-1}$. If K_b of water is $0.52 \text{ K kg mol}^{-1}$, calculate the boiling point of the electrolyte at the end of the experiment.

- (a) 375.6 K (b) 376.3 K
 (c) 378.1 K (d) 380.3 K
 (e) 381.6 K

(Kerala P.E.T. 2018)

JEE (Advance) for IIT Entrance

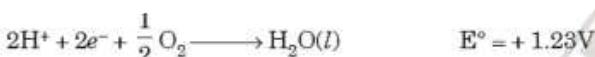
B80. The e.m.f. of the cell :



at 298 K is 0.2905. The value of equilibrium constant for the reaction is

- (a) $e^{0.32/0.0295}$ (b) $10^{0.32/0.0295}$
 (c) $100.26/0.0295$ (d) $10^{0.32/0.0591}$ (I.I.T. 2004)

B81. The rusting of iron takes place as follows :



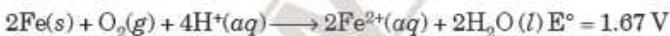
Calculate ΔG^\ominus for the net process

- (a) -322 kJ mol^{-1} (b) -161 kJ mol^{-1}
 (c) -152 kJ mol^{-1} (d) -76 kJ mol^{-1} (I.I.T. 2005)

B82. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milliamperes current. The time required to liberate 0.01 mol of H_2 gas at the cathode is ($1 \text{ Faraday} = 96500 \text{ C mol}^{-1}$)

- (a) $9.65 \times 10^4 \text{ sec}$ (b) $19.3 \times 10^4 \text{ sec}$
 (c) $28.95 \times 10^4 \text{ sec}$ (d) $38.6 \times 10^4 \text{ sec}$ (I.I.T. 2008)

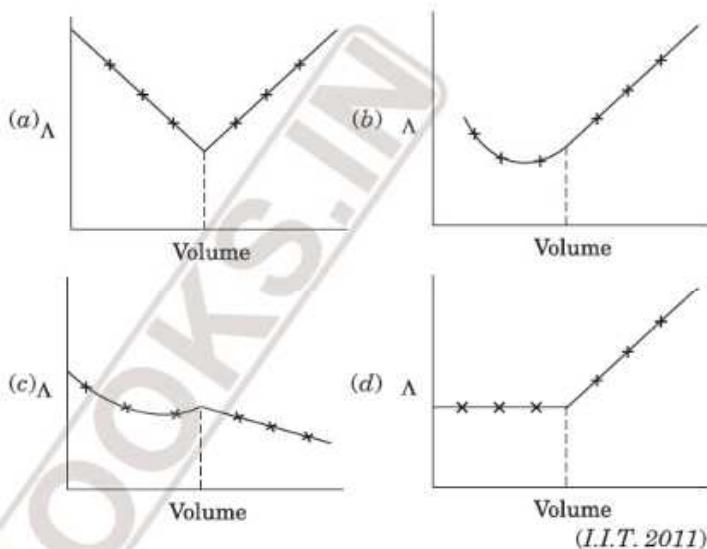
B83. Consider the following cell reaction



At $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$, $p(\text{O}_2) = 0.1 \text{ atm}$ and $\text{pH} = 3$, the cell potential at 25°C is

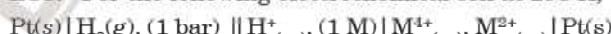
- (a) 1.47 V (b) 1.77 V
 (c) 1.87 V (d) 1.57 V (I.I.T. 2011)

B84. $\text{AgNO}_3(aq)$ was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) versus the volume of AgNO_3 is



(I.I.T. 2011)

B85. For the following electrochemical cell at 298 K,

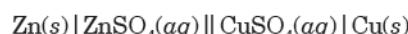


$E_{\text{cell}} = 0.092 \text{ V}$ when $\frac{[\text{M}^{2+}_{(aq)}]}{[\text{M}^{4+}_{(aq)}]} = 10^x$. Given : $E^\circ_{\text{M}^{4+}/\text{M}^{2+}} = 0.151 \text{ V}$;

$$2.303 \frac{RT}{F} = 0.059 \text{ V}$$
. The value of x is

- (a) -2 (b) -1
 (c) 1 (d) 2 (JEE Advance 2016)

B86. For the following cell,



when the concentrations of Zn^{2+} is 10 times the concentration of Cu^{2+} , the expression for ΔG (in J mol^{-1}) is [F is Faraday constant; R is gas constant; T is temperature; $E^\circ_{\text{cell}} = 1.1 \text{ V}$]

- (a) $2.303 RT - 2.2 F$ (b) $-2.2 F$
 (c) $2.303 RT + 1.1 F$ (d) $1.1 F$ (J.E.E. Advance 2017)

Answers

- B79.** (a) **B80.** (b) **B81.** (a) **B82.** (b) **B83.** (d) **B84.** (d) **B85.** (d) **B86.** (a)

C
MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. Which of the following relations are not correct?

- (a) $\Lambda_m = \frac{\kappa \times 1000}{M}$ (b) $\kappa = C \times \frac{a}{l}$
 (c) $R = p \frac{l}{a}$ (d) $\frac{l}{a} (\text{cell constant}) = \kappa \times \frac{1}{R}$

C2. Which of the following statements are not true?

- (a) Molar conductivity of weak electrolytes is low as compared to that of strong electrolytes.
 (b) Molar conductance of an electrolyte increases with increase in concentration of electrolyte.
 (c) Conductivity of an electrolyte increases with decrease in temperature.
 (d) Conductivity of an electrolyte increases with increase in concentration of electrolyte.

C3. In which of the following pairs, the first can reduce the second?

- (a) $Zn^{2+} | Zn, Ni^{2+} | Ni$ (b) $Sn^{2+} | Sn, Mg^{2+} | Mg$
 (c) $Cu^{2+} | Cu, Ag^{2+} | Ag$ (d) $Fe^{2+} | Fe, Al^{3+} | Al$

C4. For the cell, $Tl | Tl^+(0.001\text{ M}) || Cu^{2+}(0.1\text{ M}) | Cu$, E_{cell} at 25°C is 0.826 V. The EMF can be increased

- (a) by increasing $[Tl^+]$ (b) by decreasing $[Tl^+]$
 (c) by increasing $[Cu^{2+}]$ (d) by decreasing $[Cu^{2+}]$

C5. Which of the following increases with dilution?

- (a) Conductance (b) Specific conductance
 (c) Molar conductance (d) None of these

C6. Which of the following statements are correct regarding dry cell?

- (a) Zinc container acts as anode.
 (b) Zinc container is in touch with a paste of MnO_2 and carbon.

(c) Dry cell can easily be charged.

(d) Graphite rod acts as cathode

C7. Given E° values (in V) as :

$Zn^{2+} | Zn = -0.76$, $Ni^{2+} | Ni = 0.25$, $Ag^+ | Ag = 0.80$ and $Cu^{2+} | Cu = 0.34$. Which of the following reactions under standard conditions will take place in the specific direction?

- (a) $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$
 (b) $Zn(s) + Ni^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Ni(s)$
 (c) $Cu(s) + Ni^{2+}(aq) \longrightarrow Cu^{2+}(aq) + Ni(s)$
 (d) $Cu(s) + 2H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2(g)$

C8. Which of the following reactions are not correct?

- (a) $E_{\text{cell}} = \log \frac{2.303 RT}{nF} \log K_c$
 (b) $\Delta G^\circ = nFE^\circ$
 (c) $\Delta G^\circ = RT \ln K_c$
 (d) $\log K_c = \frac{nE_{\text{cell}}^\circ}{0.059}$ at 298 K.

C9. In a galvanic cell, the salt bridge

- (a) does not participate chemically in the cell reaction
 (b) stops the diffusion of ions from one electrode to another
 (c) is necessary for the occurrence of the cell reaction
 (d) ensures mixing of the two electrolytic solution.

(JEE Advance 2014)

C10. During electrolysis of molten NaCl, some water is added, what will happen?

- (a) Electrolysis will stop.
 (b) Hydrogen will be evolved.
 (c) Some amount of caustic soda will be formed.
 (d) A fire is likely.

(W.B. J.E.E. 2017)

Answers

- C1.** (b), (d) **C2.** (b), (c) **C3.** (a), (c) **C4.** (b), (c) **C5.** (a), (c) **C6.** (a), (d)
C7. (a), (b) **C8.** (b), (c) **C9.** (a), (b), (c) **C10.** (b), (c), (d)

D
MULTIPLE CHOICE QUESTIONS
based on the given passage/comprehension
Passage I.

Fuel cells convert the energy produced during the combustion of fuels directly into electrical energy. Probably the most successful fuel cell so far is hydrogen-oxygen fuel cell, which has been used in spacecraft. The electrodes consist of porous screens of titanium coated with a layer of platinum catalyst. Concentrated KOH or NaOH solution is placed between the electrodes to serve as electrolyte. Hydrogen and oxygen gases are bubbled through the porous electrodes into the electrolyte solution.

The following electrode reactions occur :

At anode : $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

At cathode : $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Overall reaction : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

In this cell, the gaseous materials are consumed and continuously supplied. The thermodynamic properties of fuel cell reaction at 25°C are :

$\Delta H^\circ = -285.8\text{ kJ mol}^{-1}$, $\Delta G^\circ = -237.2\text{ kJ mol}^{-1}$, $E^\circ = 1.23\text{ V}$

Answer the following questions :

D1. The value of ΔS° for the fuel cell reaction at 25°C is

- (a) 1944 JK^{-1} (b) -163 JK^{-1}
 (c) -1630 JK^{-1} (d) 1.944 k JK^{-1}

Answers

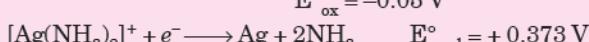
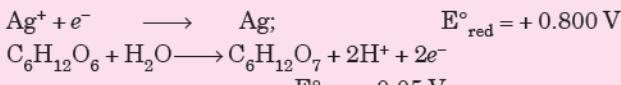
- Passage I.** **D1.** (b)

Competition File

- D2.** If the potential of the half cell reaction at cathode is, $E^\circ = 0.41\text{V}$, then E° for the half cell reaction at anode is
 (a) 1.64 V (b) 0.82 V
 (c) -0.82 V (d) -1.64 V
- D3.** The volume of H_2 when combined with excess O_2 in the fuel cell at 25°C and 1 atm needed to produce 47.4 kJ of work under ideal conditions is
 (a) 4.89 L (b) 2.45 L
 (c) 7.35 L (d) 2.0 L
- D4.** If the concentrations of OH^- ions in the cell are doubled, the cell potential will
 (a) become double (b) be reduced to $1/2$
 (c) become four times (d) remain unchanged
- D5.** The thermodynamic efficiency of H_2-O_2 fuel cell is
 (a) 9.5% (b) 89%
 (c) 83% (d) 95%

Passage II.

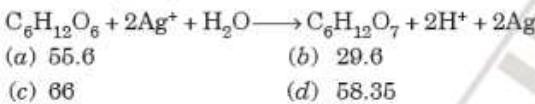
Tollen's test is given by aldehydes



$$\text{use } \left(\frac{F}{RT} \right) = 38.9\text{ V}^{-1}$$

Answer the following questions :

- D6.** Calculate ($\ln K$) for



- D7.** On adding NH_3 , pH of the solution increases to 11 then identify the effect on potential of half cell.

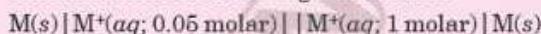
- $$(a) E_{\text{ox}}^\circ \text{ increased by } E_{\text{ox}}^\circ \text{ by } 0.65\text{ V}$$
- $$(b) E_{\text{ox}}^\circ \text{ decreased by } E_{\text{ox}}^\circ \text{ by } 0.65\text{ V}$$
- $$(c) E_{\text{red}}^\circ \text{ increased by } E_{\text{red}}^\circ \text{ by } 0.65\text{ V}$$
- $$(d) E_{\text{red}}^\circ \text{ decreased by } E_{\text{red}}^\circ \text{ by } 0.65\text{ V}$$

- D8.** NH_3 is used in this reaction rather than any other base. What is the correct reason for this ?

- $$(a) [\text{Ag}(\text{NH}_3)_2]^+ \text{ is a weaker oxidising agent than } \text{Ag}^+.$$
- $$(b) \text{NH}_3 \text{ prevents the decomposition of gluconic acid.}$$
- $$(c) \text{Ag precipitates gluconic acid as its silver salt.}$$
- $$(d) \text{NH}_3 \text{ changes the standard reduction potential of } [\text{Ag}(\text{NH}_3)_2]^+$$

Passage III.

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is



For the above electrolytic cell the magnitude of the cell potential $|E_{\text{cell}}| = 70\text{ mV}$.

Answer the following questions :

- D9.** For the above cell

- $$(a) E_{\text{cell}} < 0; \Delta G > 0 \quad (b) E_{\text{cell}} > 0; \Delta G < 0$$
- $$(c) E_{\text{cell}} < 0; \Delta G^\circ > 0 \quad (d) E_{\text{cell}} > 0; \Delta G^\circ < 0$$

(I.I.T.J.E.E. 2010)

- D10.** If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be

- $$(a) 35\text{ mV} \quad (b) 70\text{ mV}$$
- $$(c) 140\text{ mV} \quad (d) 700\text{ mV}$$

(I.I.T.J.E.E. 2010)

Passage IV.

The electrochemical cell shown below is a concentration cell. $\text{M} \mid \text{M}^{2+}$ (saturated solution of a sparingly soluble salt, MX_2) || $\text{M}^{2+}(0.001 \text{ mol dm}^{-3}) \mid \text{M}$

The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V .

Answer the following questions :

- D11.** The value of ΔG (kJ mol^{-1}) for the given cell is
 (take $1\text{F} = 96500\text{ C mol}^{-1}$)

- $$(a) -5.7 \quad (b) 5.7$$
- $$(c) 11.4 \quad (d) -11.4$$

(I.I.T.J.E.E. 2012)

- D12.** The solubility product (K_{sp} ; $\text{mol}^3 \text{dm}^{-9}$) of MX_2 at 298 K based on the information available for the given concentration cell is
 (take $2.303 \times R \times 298/\text{F} = 0.059\text{ V}$)

- $$(a) 1 \times 10^{-15} \quad (b) 4 \times 10^{-15}$$
- $$(c) 1 \times 10^{-12} \quad (d) 4 \times 10^{-12}$$

(I.I.T.J.E.E. 2012)

Answers

Passage I. D2. (c) D3. (a) D4. (d) D5. (c)

Passage II. D6. (d) D7. (a) D8. (a)

Passage III. D9. (b) D10. (c)

Passage IV. D11. (d) D12. (b)

Competition File

Assertion Reason Type Questions

The questions given below consist of an Assertion and a Reason. Use the following key to choose the appropriate answer.

- (a) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
 - (b) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.
 - (c) If assertion is CORRECT but reason is INCORRECT.
 - (d) If assertion is INCORRECT but reason is CORRECT.
 - (e) If both assertion and reason are INCORRECT.
- 1. Assertion :** Equivalent conductance of all electrolytes decreases with increasing concentration.
Reason : Lesser number of ions are available per gram equivalent at higher concentration.
- 2. Assertion :** Iron is protected from corrosion by connecting magnesium metal with it.
Reason : Iron acts as a cathode and magnesium as anode which gradually disappears.
- 3. Assertion :** Chromium is used for coating iron.
Reason : Chromium is non-corroding metal which forms a protective layer on iron.

- 4. Assertion :** Zinc can liberate H₂ from aqueous solution of HCl.
Reason : Zinc has +ve reduction potential.
- 5. Assertion :** Copper sulphate solution can be kept in a zinc vessel.
Reason : The position of zinc is higher than copper in the electrochemical series.
- 6. Assertion :** For CH₃COOH, the molar conductance of 0.1 M CH₃COOH and equivalent conductance of 0.1 N CH₃COOH is same.
Reason : These do not depend upon concentration.
- 7. Assertion :** 0.1 M NH₄OH at 25°C has more conductance than at 50°C.
Reason : Conductance of a weak electrolyte decreases with increase in temperature.
- 8. Assertion :** E° for Mn³⁺ | Mn²⁺ is more positive than Cr³⁺ | Cr²⁺.
Reason : The third ionisation energy of Mn is larger than that of Cr. (A.I.I.M.S. 2006)
- 9. Assertion :** According to Kohlrausch law the molar conductivity of a strong electrolyte at infinite dilution is sum of molar conductivities of its ions.
Reason : The current carried by cation and anion is always equal. (A.I.I.M.S. 2007)

Answers

1. (c) 2. (a) 3. (c) 4. (c) 5. (d) 6. (c) 7. (e) 8. (b) 9. (c)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as p, q, r and s. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

If the correct matches are A-q, B-p, B-s, C-r, C-s and D-q, then the correctly bubbled matrix will look like the following:

	p	q	r	s
A	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>
B	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>
C	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>
D	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>

1. Match the electrochemical behaviour of metals in Column I with the examples listed in Column II.

- | Column I | Column II |
|---|--------------------------------------|
| (A) can liberate H ₂ from dil HCl
(B) cannot liberate H ₂ from dil HCl
(C) metals more active than zinc
(D) metals less reactive than zinc | (p) Mg
(q) Al
(r) Cu
(s) Fe |
2. Match the type of cell in Column I with the electrolyte used in the cell listed in Column II.

Column I	Column II
(A) Lead storage cell	(p) Potassium hydroxide
(B) Nickel-cadmium cell	(q) Ammonium chloride
(C) Fuel cell	(r) Aqueous H ₂ SO ₄
(D) Dry cell	(s) Zinc chloride

3. Match the units in Column I with the quantity given in Column II.

Column I	Column II
(A) m ⁻¹	(p) Molar conductivity
(B) S m ² mol ⁻¹	(q) S
(C) S m ⁻¹	(r) Cell constant
(D) Conductance	(s) Conductivity

Answers

- (1) : (A) – (p) (q) (s) (B) – (r) (C) – (p) (q) (D) – (r) (s)
(2) : (A) – (r) (B) – (p) (C) – (p) (D) – (q) (s)
(3) : (A) – (r) (B) – (p) (C) – (s) (D) – (q)

Competition File

Matching Type Questions

Each question has matching lists. The codes for the lists have the choices (a), (b), (c) and (d) out of which only one is correct.

1. The standard reduction potential data at 25°C is given below.

$$E^\circ(\text{Fe}^{3+}, \text{Fe}^{2+}) = +0.77 \text{ V}; E^\circ(\text{Fe}^{2+}, \text{Fe}) = -0.44 \text{ V}$$

$$E^\circ(\text{Cu}^{2+}, \text{Cu}) = +0.34 \text{ V}; E^\circ(\text{Cu}^+, \text{Cu}) = +0.52 \text{ V}$$

$$E^\circ[\text{O}_{2(g)} + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}] = +1.23 \text{ V};$$

$$E^\circ[\text{O}_{2(g)} + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-] = +0.40 \text{ V}$$

$$E^\circ(\text{Cr}^{3+}, \text{Cr}) = -0.74 \text{ V}; E^\circ(\text{Cr}^{2+}, \text{Cr}) = -0.91 \text{ V}$$

Match E° of the redox pair in List I with the values given in List II and select the correct answer using the code given below the lists:

List I		List II		
P.	$E^\circ(\text{Fe}^{3+}, \text{Fe})$	1.	-0.18 V	
Q.	$E^\circ(4\text{H}_2\text{O} \rightleftharpoons 4\text{H}^+ + 4\text{OH}^-)$	2.	-0.4 V	
R.	$E^\circ(\text{Cu}^{2+} + \text{Cu} \rightarrow 2\text{Cu}^+)$	3.	-0.04 V	
S.	$E^\circ(\text{Cr}^{3+}, \text{Cr}^{2+})$	4.	-0.83 V	

	P	Q	R	S
(a)	4	1	2	3
(b)	2	3	4	1
(c)	1	2	3	4
(d)	3	4	1	2

(JEE Advance 2013)

Answers

1. (d)

Integer type or Numerical Value Type Questions

Integer Types: The answer to each of the following question is a single-digit-integer ranging from 0 to 9.

1. The number of metals which can liberate H₂ from dil HCl is :



2. The e.m.f. of the cell



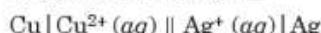
is 2.651 V. The standard e.m.f. of the cell is 2.71 V. The value of x is

3. The number of Faradays of electricity required to deposit 81 g of Al from electrolysis of AlCl₃ is

4. In an electrolysis of acidulated water, 4.48 L of hydrogen was produced by passing a current of 2.14 A. How many hours, the current was passed?

5. Two litres of 0.5 M KMnO₄ solution have to be completely reduced in acidic medium. The number of Faradays of electricity required will be

6. The e.m.f. of the cell



is 0.46 V. The e.m.f. for the cell reaction :



is 0.46y V. The value of y is

7. A cell consists of two hydrogen electrodes. The negative electrode is in contact with a solution having pH = 6. The positive electrode is in contact with a solution of pH = x. Calculate the value of x if the e.m.f. of the cell is found to be 0.118 V at 298 K.

8. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda_x^\circ = \lambda_y^\circ$, the difference in their pK_a values, pK_a(HX) - pK_a(HY), is (consider degree of ionization of both acids to be << 1)

(JEE Advance 2015)

9. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross-section of 1 cm². The conductance of this solution was found to be 5×10^{-7} S. The pH of the solution is 4. The value of limiting molar conductivity (Λ_m°) of this weak monobasic acid in aqueous solution is Z × 10² S cm² mol⁻¹. The value of Z is

(JEE Advance 2017)

Answers

1. 5. 2. 3.

3. 9.

4. 5.

5. 5

6. 1

7. 4

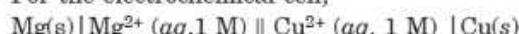
8. 3

9. 6

Competition File

Numerical Value Type: Give the correct numerical value (in decimal notation truncated/rounded off to the second decimal place)

10. For the electrochemical cell,



the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of x is

(Given, $\frac{F}{R} = 11500 \text{ K V}^{-1}$, where F is the Faraday constant and R is the gas constant, $\ln(10) = 2.30$)

(JEE Advance 2018)

Answers

10. 10.00 11. -11.62



NCERT

11. Consider an electrochemical cell:

$\text{A(s)} \mid \text{A}^{n+}(\text{aq}, 2\text{ M}) \parallel \text{B}^{2n+}(\text{aq}, 1\text{ M}) \mid \text{B(s)}$. the value of ΔH° for the cell reaction is twice that of ΔG° at 300 K. If the emf of the cell is zero, ΔS° (in $\text{JK}^{-1} \text{ mol}^{-1}$) of the cell reaction per mole of B formed at 300 K is

(Given : $\ln(2) = 0.7$, R (universal gas constant) = $8.3 \text{ J K}^{-1} \text{ mol}^{-1}$. H, S and G are enthalpy, entropy and Gibbs energy, respectively).

(JEE Advance 2018)

Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

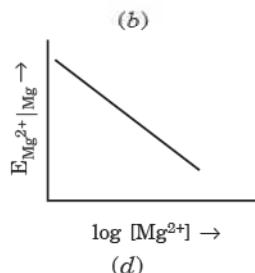
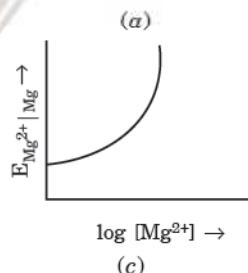
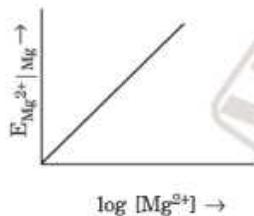
1. Which cell will measure standard electrode potential of copper electrode?

- (a) $\text{Pt(s)} \mid \text{H}_2(\text{g}, 0.1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1\text{ M}) \parallel \text{Cu}^{2+}(\text{aq}, 1\text{ M}) \mid \text{Cu}$
- (b) $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1\text{ M}) \parallel \text{Cu}^{2+}(\text{aq}, 2\text{ M}) \mid \text{Cu}$
- (c) $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1\text{ M}) \parallel \text{Cu}^{2+}(\text{aq}, 1\text{ M}) \mid \text{Cu}$
- (d) $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(\text{aq}, 0.1\text{ M}) \parallel \text{Cu}^{2+}(\text{aq}, 1\text{ M}) \mid \text{Cu}$

2. Electrode potential for Mg electrode varies according to the equation

$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^\circ - \frac{0.059}{2} \log \frac{1}{[\text{Mg}^{2+}]}. \text{ The graph of } E_{\text{Mg}^{2+}/\text{Mg}}$$

vs $\log [\text{Mg}^{2+}]$ is



3. Which of the following statement is correct?

- (a) E_{cell} and $\Delta_r G$ of cell reaction both are extensive properties.
- (b) E_{cell} and $\Delta_r G$ of cell reaction both are intensive properties.
- (c) E_{cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property.
- (d) E_{cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property.

4. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called _____.

- (a) Cell potential
- (b) Cell emf
- (c) Potential difference
- (d) Cell voltage

Answers

1. (c) 2. (b) 3. (c) 4. (b)

Competition File

5. Which of the following statement is **not** correct about an inert electrode in a cell?
 (a) It does not participate in the cell reaction.
 (b) It provides surface either for oxidation or for reduction reaction.
 (c) It provides surface for conduction of electrons.
 (d) It provides surface for redox reaction.
6. An electrochemical cell can behave like an electrolytic cell when _____.
 (a) $E_{\text{cell}} = 0$ (b) $E_{\text{cell}} > E_{\text{ext}}$
 (c) $E_{\text{ext}} > E_{\text{cell}}$ (d) $E_{\text{cell}} = E_{\text{ext}}$
7. Which of the statements about solutions of electrolytes is not correct?
 (a) Conductivity of solution depends upon size of ions.
 (b) Conductivity depends upon viscosity of solution.
 (c) Conductivity does not depend upon solvation of ions present in solution.
 (d) Conductivity of solution increases with temperature.
8. Using the data given below find out the strongest reducing agent.
- $$E^\ominus_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V} \quad E^\ominus_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$$
- $$E^\ominus_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V} \quad E^\ominus_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$$
- (a) Cl^- (b) Cr (c) Cr^{3+} (d) Mn^{2+}
9. Use the data given in Q.8 and find out which of the following is the strongest oxidising agent.
 (a) Cl^- (b) Mn^{2+} (c) MnO_4^- (d) Cr^{3+}
10. Using the data given in Q.8 find out in which option the order of reducing power is correct.
 (a) $\text{Cr}^{3+} < \text{Cl}^- < \text{Mn}^{2+} < \text{Cr}$
 (b) $\text{Mn}^{2+} < \text{Cl}^- < \text{Cr}^{3+} < \text{Cr}$
 (c) $\text{Cr}^{3+} < \text{Cl}^- < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$
 (d) $\text{Mn}^{2+} < \text{Cr}^{3+} < \text{Cl}^- < \text{Cr}$
11. Use the data given in Q.8 and find out the most stable ion in its reduced form.
 (a) Cl^- (b) Cr^{3+} (c) Cr (d) Mn^{2+}
12. Use the data of Q.8 and find out the most stable oxidised species.
 (a) Cr^{3+} (b) MnO_4^- (c) $\text{Cr}_2\text{O}_7^{2-}$ (d) Mn^{2+}
13. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is _____.
 (a) 1F (b) 6F (c) 3F (d) 2F
14. The cell constant of a conductivity cell _____.
 (a) changes with change of electrolyte.
 (b) changes with change of concentration of electrolyte.
 (c) changes with temperature of electrolyte.
 (d) remains constant for a cell.
15. While charging the lead storage battery _____.
 (a) PbSO_4 anode is reduced to Pb.
 (b) PbSO_4 cathode is reduced to Pb.
 (c) PbSO_4 cathode is oxidised to Pb.
 (d) PbSO_4 anode is oxidised to PbO_2 .
16. $\Lambda_m^0(\text{NH}_4\text{OH})$ is equal to _____.
 (a) $\Lambda_m^0(\text{NH}_4\text{OH}) + \Lambda_m^0(\text{NH}_4\text{Cl}) - \Lambda_m^0(\text{HCl})$
 (b) $\Lambda_m^0(\text{NH}_4\text{Cl}) + \Lambda_m^0(\text{NaOH}) - \Lambda_m^0(\text{NaCl})$
 (c) $\Lambda_m^0(\text{NH}_4\text{Cl}) + \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NaOH})$
 (d) None of these
17. In the electrolysis of aqueous sodium chloride solution which of the half cell reaction will occur at anode?
 (a) $\text{Na}^+(aq) + e^- \longrightarrow \text{Na}(s)$; $E_{\text{cell}}^\ominus = -2.71 \text{ V}$
 (b) $2\text{H}_2\text{O}(l) \longrightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$; $E_{\text{cell}}^\ominus = 1.23 \text{ V}$
 (c) $\text{H}^+(aq) + e^- \longrightarrow \frac{1}{2}\text{H}_2(g)$; $E_{\text{cell}}^\ominus = 0.00 \text{ V}$
 (d) $\text{Cl}^-(aq) \longrightarrow \frac{1}{2}\text{Cl}_2(g) + e^-$; $E_{\text{cell}}^\ominus = 1.36 \text{ V}$

Multiple Choice Questions (Type-II)

Note : In the following questions two or more than two options may be correct.

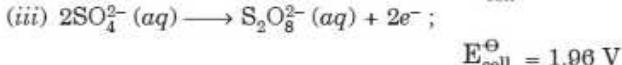
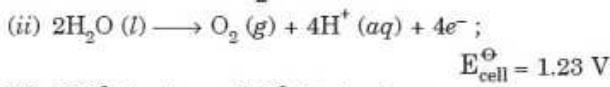
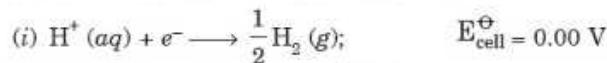
18. The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that _____.
 (a) this redox couple is a stronger reducing agent than the H^+/H_2 couple.
 (b) this redox couple is a stronger oxidising agent than H^+/H_2 .
 (c) Cu can displace H_2 from acid.
 (d) Cu cannot displace H_2 from acid.

Answers

- | | | | | | | | | | |
|---------|---------|---------|--------------|--------|---------|---------|---------|---------|---------|
| 5. (d) | 6. (c) | 7. (c) | 8. (b) | 9. (c) | 10. (b) | 11. (d) | 12. (a) | 13. (c) | 14. (d) |
| 15. (a) | 16. (b) | 17. (b) | 18. (b), (d) | | | | | | |

Competition File

19. $E_{\text{cell}}^{\ominus}$ for some half cell reactions are given below. On the basis of these mark the correct answer.



- (a) In dilute sulphuric acid solution, hydrogen will be reduced at cathode.
- (b) In concentrated sulphuric acid solution, water will be oxidised at anode.
- (c) In dilute sulphuric acid solution, water will be oxidised at anode.
- (d) In dilute sulphuric acid solution, SO_4^{2-} ion will be oxidised to tetrathionate ion at anode.

20. $E_{\text{cell}}^{\ominus} = 1.1 \text{ V}$ for Daniel cell. Which of the following expressions are correct description of state of equilibrium in this cell?

(a) $1.1 = K_c$ (b) $\frac{2.303RT}{2F} \log K_c = 1.1$

(c) $\log K_c = \frac{2.2}{0.059}$ (d) $\log K_c = 1.1$

21. Conductivity of an electrolytic solution depends on _____.

- (a) nature of electrolyte.
- (b) concentration of electrolyte.

- (c) power of AC source.
- (d) distance between the electrodes.

22. $\Lambda_m^0 \text{ H}_2\text{O}$ is equal to _____.

- (a) $\Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{NaOH}) - \Lambda_m^0(\text{NaCl})$
- (b) $\Lambda_m^0(\text{HNO}_3) + \Lambda_m^0(\text{NaNO}_3) - \Lambda_m^0(\text{NaOH})$
- (c) $\Lambda_m^0(\text{HNO}_3) + \Lambda_m^0(\text{NaOH}) - \Lambda_m^0(\text{NaNO}_3)$
- (d) $\Lambda_m^0(\text{HN}_3\text{OH}) + \Lambda_m^0(\text{HCl}) - \Lambda_m^0(\text{NH}_3\text{Cl})$

23. What will happen during the electrolysis of aqueous solution of CuSO_4 by using platinum electrodes?

- (a) Copper will deposit at cathode.
- (b) Copper will deposit at anode.
- (c) Oxygen will be released at anode.
- (d) Copper will dissolve at anode.

24. What will happen during the electrolysis of aqueous solution of CuSO_4 in the presence of Cu electrodes?

- (a) Copper will deposit at cathode.
- (b) Copper will dissolve at anode.
- (c) Oxygen will be released at anode.
- (d) Copper will deposit at anode.

25. Conductivity, is equal to _____.

(a) $\frac{1}{R} \frac{l}{a}$ (b) $\frac{G^*}{R}$ (c) Λ_m (d) $\frac{l}{a}$

26. Molar conductivity of ionic solution depends on _____.

- (a) temperature
- (b) distance between electrodes
- (c) concentration of electrolytes in solution
- (d) surface area of electrodes

27. For the given cell, $\text{Mg}|\text{Mg}^{2+}||\text{Cu}^{2+}|\text{Cu}$

- (a) Mg is cathode
- (b) Cu is cathode
- (c) The cell reaction is $\text{Mg} + \text{Cu}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Cu}$
- (d) Cu is the oxidising agent

Answers

- | | | | | | |
|--------------|--------------|--------------|--------------|--------------|--------------|
| 19. (a), (c) | 20. (b), (c) | 21. (a), (b) | 22. (a), (b) | 23. (a), (c) | 24. (a), (b) |
| 25. (a), (b) | 26. (a), (c) | 27. (b), (c) | | | |

Matching Type Questions

Note : Match the items of Column I and Column II in the following questions:

28. Match the terms given in Column I with the units given in Column II.

Column I	Column II
(a) Λ_m	(i) S cm^{-1}
(b) $E_{\text{cell}}^{\ominus}$	(ii) m^{-1}
(c) κ	(iii) $\text{S cm}^2 \text{ mol}^{-1}$
(d) G^*	(iv) V

29. Match the terms given in Column I with the items given in Column II.

Column I	Column II
(a) Λ_m	(i) intensive property
(b) $E_{\text{cell}}^{\ominus}$	(ii) depends on number of ions / volume
(c) G	(iii) extensive property
(d) $\Delta_r G_{\text{cell}}$	(iv) increases with dilution

30. Match the items of Column I and Column II.

Column I	Column II
(a) Lead storage battery	(i) maximum efficiency
(b) Mercury cell	(ii) prevented by galvanisation
(c) Fuel cell	(iii) gives steady potential
(d) Rusting	(iv) Pb is anode, PbO_2 is cathode

28. (a) — (iii); (b) — (iv); (c) — (i); (d) — (ii).

30. (a) — (iv); (b) — (iii); (c) — (i); (d) — (ii).

29. (a) — (iv); (b) — (i); (c) — (ii); (d) — (iii).

Competition File

31. Match the items of Column I and Column II.

Column I	Column II
(a) G	(i) I_t
(b) Λ_m	(ii) $\frac{\Lambda_c}{\Lambda_m}$
(c) α	(iii) $\frac{\kappa}{c}$
(d) Q	(iv) $\frac{G^*}{R}$

32. Match the items of Column I and Column II.

Column I	Column II
(a) Lechlanche cell	(i) cell reaction $2H_2 + O_2 \rightarrow 2H_2O$
(b) Ni-Cd cell	(ii) does not involve any ion in solution and is used in hearing aids.
(c) Fuel cell	(iii) rechargeable
(d) Mercury cell	(iv) reaction at anode, $Zn \rightarrow Zn^{2+} + 2e^-$ (v) converts energy of combustion into electrical energy

33. Match the items of Column I and Column II on the basis of data given below:

$$E_{F_2|F^-}^{\circ} = 2.87V, E_{Li^+|Li}^{\circ} = -3.5V,$$

$$E_{Au^{3+}|Au}^{\circ} = 1.4V, E_{Br_2|Br^-}^{\circ} = 1.09V$$

Column I	Column II
(a) F_2	(i) metal is the strongest reducing agent
(b) Li	(ii) metal ion which is the weakest oxidising agent
(c) Au^{3+}	(iii) non metal which is the best oxidising agent
(d) Br^-	(iv) unreactive metal
(e) Au	(v) anion that can be oxidised by Au^{3+}
(f) Li^+	(vi) anion which is the weakest reducing agent
(g) F ⁻	(vii) metal ion which is an oxidising agent

Answers

31. (a) — (iv); (b) — (iii); (c) — (ii); (d) — (i).

33. (a) — (iii); (b) — (i); (c) — (vii); (d) — (v); (e) — (iv); (f) — (ii); (g) — (vii, vi).

32. (a) — (iv); (b) — (iii); (c) — (i, v); (d) — (ii).

Assertion and Reason Type Questions

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Both assertion and reason are true and the reason is the correct explanation of assertion.
- (b) Both assertion and reason are true and the reason is not the correct explanation of assertion.
- (c) Assertion is true but the reason is false.
- (d) Both assertion and reason are false.
- (e) Assertion is false but reason is true.

34. Assertion : Cu is less reactive than hydrogen.

Reason : $E_{Cu^{2+}|Cu}^{\circ}$ is negative.

35. Assertion : E_{Cell}° should have a positive value for the cell to function.

Reason : $E_{cathode} < E_{anode}$

36. Assertion : Conductivity of all electrolytes decreases on dilution.

Reason : On dilution number of ions per unit volume decreases.

37. Assertion : Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

Reason : For weak electrolytes degree of dissociation increases with dilution of solution.

38. Assertion : Mercury cell does not give steady potential.

Reason : In the cell reaction, ions are not involved in solution.

39. Assertion : Electrolysis of NaCl solution gives chlorine at anode instead of O_2 .

Reason : Formation of oxygen at anode requires overvoltage.

40. Assertion : For measuring resistance of an ionic solution an AC source is used.

Reason : Concentration of ionic solution will change if DC source is used.

41. Assertion : Current stops flowing when $E_{Cell} = 0$.

Reason : Equilibrium of the cell reaction is attained.

42. Assertion : $E_{Ag^+|Ag}^{\circ}$ increases with increase in concentration of Ag^+ ions.

Reason : $E_{Ag^+|Ag}^{\circ}$ has a positive value.

43. Assertion : Copper sulphate can be stored in zinc vessel.

Reason : Zinc is less reactive than copper.

Answers

34. (c)

35. (c)

36. (a)

37. (a)

38. (e)

39. (a)

40. (a)

41. (a)

42. (b)

43. (d)

Competition File

Hints & Explanations for Difficult Objective Type Questions

A. Topicwise multiple choice questions

A1. (a) : $\kappa = \text{Conductance} \times \text{cell constant}$
 Since $\kappa = \text{Conductance}$
 $\therefore \text{Cell constant} = 1.$

$$\begin{aligned}\text{A3. (c) : } \kappa &= \frac{1}{R} \times \text{Cell constant} \\ &= \frac{1}{250} \times 1.15\end{aligned}$$

$$\therefore \Lambda = \frac{\kappa \times 1000}{C} = \frac{1}{250} \times \frac{1.15 \times 1000}{0.1} = 46.$$

$$\begin{aligned}\text{A4. (a) : } \Lambda_m^{\infty}(\text{BaCl}_2) &= \Lambda^{\infty}(\text{Ba}^{2+}) + 2\Lambda^{\infty}(\text{Cl}^-) \\ &= 127.32 + 2 \times 76.34 \\ &= 280 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{A5. (a) : } \Lambda_m &= \frac{\kappa \times 1000}{M} \\ &= \frac{1.06 \times 10^{-2} \times 1000}{0.1} \\ &= 1.06 \times 10^2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{A6. (c) : } \Lambda^{\circ}(\text{NaBr}) &= \Lambda^{\circ}(\text{NaCl}) + \Lambda^{\circ}(\text{KBr}) - \Lambda^{\circ}(\text{KCl}) \\ &= 126 + 152 - 150 \\ &= 128 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

$$\begin{aligned}\text{A7. (c) : } \Lambda(\text{ClCH}_2\text{COOH}) &= \Lambda(\text{ClCH}_2\text{COONa}) + \Lambda(\text{HCl}) - \Lambda(\text{NaCl}) \\ &= 224 + 203 - 38.2 \\ &= 388.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}.\end{aligned}$$

$$\begin{aligned}\text{A8. (b) : } \Lambda^{\circ}(\text{CH}_3\text{COOH}) &= (\lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \lambda_{\text{Na}^+}^{\circ}) + (\lambda_{\text{H}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}) - (\lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}) \\ &= 90 + 425 - 125 = 390 \text{ mho cm}^2 \text{ mol}^{-1} \\ \text{Degree of dissociation} &= \frac{\Lambda^{\circ}}{\Lambda^{\circ}} = \frac{7.8}{390} = 0.02.\end{aligned}$$

$$\begin{aligned}\text{A9. (d) : } \Lambda_m^{\circ}(\text{HCOOH}) &= \lambda^{\circ}_{\text{H}^+} + \lambda^{\circ}_{\text{HCOO}^-} = 347 + 53 \\ &= 400 \text{ S cm}^2 \text{ mol}^{-1} ; C = 0.025 \text{ M}\end{aligned}$$

$$\Lambda_m^{\circ} = 40 \text{ S cm}^2 \text{ mol}^{-1} ; C = 0.025 \text{ M}$$

$$\alpha = \frac{\Lambda_m^{\circ}}{\Lambda_m^{\circ}} = \frac{40}{400} = 0.1$$

$$\begin{aligned}K_a &= \frac{c \alpha^2}{1-\alpha} = c \alpha^2 \\ &= 0.025 \times (0.1)^2 = 2.5 \times 10^{-4}.\end{aligned}$$

$$\begin{aligned}\text{A10. (b) : } K &= \frac{c \alpha^2}{1-\alpha} \approx c \alpha^2 \\ 2.5 \times 10^{-5} &= 0.01 \alpha^2\end{aligned}$$

$$\begin{aligned}\alpha &= \sqrt{\frac{2.5 \times 10^{-5}}{0.01}} = 5 \times 10^{-2} \\ \alpha &= \frac{\Lambda^{\circ}}{\Lambda^{\infty}} \\ \Lambda^{\infty} &= \frac{\Lambda^{\circ}}{\alpha} = \frac{19.6}{5 \times 10^{-2}} = 392\end{aligned}$$

$$\begin{aligned}\text{A13. (a) : } E &= E^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]} \\ E^{\circ} &= E^{\circ}_{(\text{Pb}^{2+}/\text{Pb})} - E^{\circ}_{(\text{Zn}^{2+}/\text{Zn})} \\ &= -0.126 - (-0.763) = 0.637 \text{ V} \\ E &= 0.637 - \frac{0.059}{2} \log \frac{(0.1)}{(0.1)} \\ &= 0.637 \text{ V}.\end{aligned}$$

A14. (a) : The electrode reaction is:
 $\text{Zn}^{2+}(aq) + 2e^- \longrightarrow \text{Zn}(s)$

$$\begin{aligned}E &= E^{\circ} - \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{2+}]} \\ [\text{Zn}^{2+}] &= 0.1 \times \frac{20}{100} = 0.02 \text{ M}, E^{\circ} = -0.76 \text{ V}\end{aligned}$$

$$\begin{aligned}\therefore E &= -0.76 - \frac{0.059}{2} \log \frac{1}{0.02} \\ &= -0.76 - \frac{0.059}{2} \log 50 \\ &= -0.76 - \frac{0.059}{2} \times 1.70 \\ &= -0.76 - 0.05 = -0.81 \text{ V}\end{aligned}$$

$$\text{A17. (b) : } E = E^{\circ} - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Ag}^{+}]^2}$$

Increase in conc. of Sn^{2+} will decrease E.

A18. (c) : This can be obtained in terms of Gibbs free energies

$$\begin{aligned}\text{Cu}^{2+} + e^- &\longrightarrow \text{Cu}^+ \quad E_1^{\circ} = +0.15 \text{ V} \\ \therefore \Delta G_1^{\circ} &= -1 \times F \times 0.15 \text{ V} = -0.15 \text{ F}\end{aligned}$$

$$\begin{aligned}\text{Cu}^+ + e^- &\longrightarrow \text{Cu} \quad E_2^{\circ} = +0.50 \text{ V} \\ \therefore \Delta G_2^{\circ} &= -1 \times F \times 0.50 = -0.50 \text{ F}\end{aligned}$$

$$\text{Now Cu}^{2+} + 2e^- \longrightarrow \text{Cu} \quad E_3^{\circ} = ?$$

$$\therefore \Delta G_3^{\circ} = -2 \times F \times E_3^{\circ} = -2E_3^{\circ} \text{ F}$$

$$\text{Now } \therefore \Delta G_3^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$$

$$-2E_3^{\circ} \text{ F} = -0.15 \text{ F} - 0.50 \text{ F} = -0.65 \text{ F}$$

$$\therefore E_3^{\circ} = \frac{0.65}{2} = 0.325 \text{ V}.$$

Competition File

A19. (a) : $E_1 = E^\ominus - \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]_1}$

On dilution

$$\begin{aligned} E_2 &= E^\ominus - \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]_2} \\ &= E^\ominus - \frac{0.059}{2} \log \frac{1}{0.1 [Zn^{2+}]_1} \\ E_2 - E_1 &= -\frac{0.059}{2} \log \frac{1}{0.1 [Zn^{2+}]_1} \\ &\quad + \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]_1} \\ &= \frac{0.059}{2} \log 0.1 \\ &= \frac{0.059}{2} \times (-1) = -0.0295 \\ \text{or} \quad &= -30 \text{ mV} \end{aligned}$$

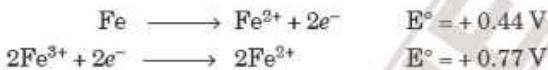
A20. (d) : $E_{\text{cell}}^\circ = E_{(\text{Ag}^+|\text{Ag})}^\circ - E_{(\text{Cu}^{2+}|\text{Cu})}^\circ$
 $0.46 = 0.80 - E_{(\text{Cu}^{2+}|\text{Cu})}^\circ$
 $\therefore E_{(\text{Cu}^{2+}|\text{Cu})}^\circ = 0.80 - 0.46 = 0.34 \text{ V}$

A22. (c) : $\text{Al}|\text{Al}^{3+}||\text{Cu}^{2+}|\text{Cu}$

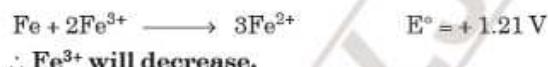
$$\begin{aligned} E_{\text{cell}}^\circ &= E_{(\text{Cu}^{2+}|\text{Cu})}^\circ - E_{(\text{Al}^{3+}|\text{Al})}^\circ \\ 2.00 &= 0.34 - E_{(\text{Al}^{3+}|\text{Al})}^\circ \end{aligned}$$

$$\therefore E^\circ(\text{Al}^{3+}|\text{Al}) = 0.34 - 2.0 = -1.66 \text{ V}$$

A23. (b) : For e.m.f. to be positive, the following half cell reactions will occur:



Overall reaction:



A24. (d) : Subtracting eqn. (ii) from eqn (i)



$$E = E^\ominus - \frac{0.059}{1} \log \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}(s)]}$$

At equilibrium, $E = 0$ and $[\text{AgCl}(s)] = 1$

$$\begin{aligned} E^\circ &= 0.059 \log [\text{Ag}^+][\text{Cl}^-] \\ &= 0.059 \log K_{sp} \end{aligned}$$

$$\therefore 0.059 \log K_{sp} = -0.58$$

$$\log K_{sp} = -0.831$$

$$\therefore K_{sp} = 1.48 \times 10^{-10}.$$

A25. (a) : For the given cell, $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

$$E = E^\ominus - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\therefore E_1 = E^\ominus - \frac{0.059}{2} \log \frac{0.01}{1.0} = E^\circ + 0.059$$

$$E_2 = E^\ominus - \frac{0.059}{2} \log \frac{1.0}{0.01} = E^\circ - 0.059$$

$$\therefore E_1 > E_2$$

A26. (d) : $E = E^\ominus - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$

$$E^\ominus = E^\ominus_{(\text{Cu}^{2+}|\text{Cu})} - E^\ominus_{(\text{Zn}^{2+}|\text{Zn})}$$

$$E^\ominus = 0.34 - (-0.76) = 1.10 \text{ V}$$

$$\begin{aligned} E &= 1.10 - \frac{0.059}{2} \log \frac{0.1}{0.01} \\ &= 1.10 - 0.295 = 1.0705 \text{ V.} \end{aligned}$$

A27. (a) : $E^\ominus = E^\ominus_{(\text{Fe}^{3+}|\text{Fe}^{2+})} - E^\ominus_{(\text{Sn}^{2+}|\text{Sn})}$
 $= 0.77 - (-0.14) = 0.91 \text{ V.}$

A28. (b) : $\begin{array}{ll} \text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe} & E^\ominus_1 = -0.414 \text{ V} \\ \text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+} & E^\ominus_2 = 0.771 \text{ V} \end{array}$

The required equation can be obtained as:



$$E_{\text{cell}}^\ominus = E_c^\ominus - E_a^\ominus = 0.771 - (-0.441) = 1.212 \text{ V}$$

A29. (c) : 96500 \times 3 coulomb of electricity is required to deposit 27 g of Al

No. of coulombs required to deposit 90 g of Al

$$= \frac{96500 \times 3}{27} \times 90 = 965000$$

$$\text{or} \quad = 9.65 \times 10^5 \text{ C.}$$

A30. (a) : 2.977 g of metal require = 10800 C

$$\begin{array}{ll} 106.4 \text{ g of metal require} & = \frac{10800}{2.977} \times 106.4 \\ & = 3.86 \times 10^5 \text{ C} \end{array}$$

$$\text{Valency} = \frac{3.86 \times 10^5}{96500} = 4$$

A31. (b) : 96500 \times 3 = 289500 = 2.89 \times 10⁵ C

A32. (c) : $\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}$

197 g of Au is obtained by charge = 96500 \times 3 C

1.234 g of Au is obtained by charge

$$\begin{aligned} &= \frac{96500 \times 3 \times 1.234}{197} \\ &= 1813.4 \text{ C} \end{aligned}$$

Now $A \times t = \text{C}$

$$3 \times t = 1813.4$$

$$\begin{aligned} \text{or} \quad t &= \frac{1813.4}{3} = 604 \text{ s} \\ &= 10 \text{ min } 4 \text{ s.} \end{aligned}$$

A33. (a) : $\frac{\text{Wt. of Ag deposited}}{\text{Wt. of O}_2 \text{ produced}} = \frac{108}{8}$
 $\frac{0.108}{\text{Wt. of O}_2} = \frac{108}{8}$

Competition File

$$\therefore \text{Wt. of O}_2 = \frac{0.108 \times 8}{108} = 8 \times 10^{-3} \text{ g}$$

$$\text{Vol. of O}_2 = \frac{22400}{32} \times 8 \times 10^{-3} = 5.6 \text{ cm}^3.$$

$$= 5(-394.4) + 6(-237.2) - (-8.2) - 8 \times 0 \\ = -1972 - 1423.2 + 8.2 - 0 \\ = -3387 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = -nFE^\circ$$

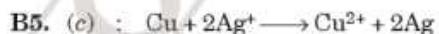
$$\text{or } E^\circ = -\frac{\Delta G^\circ}{nF} \text{ where } n = 32$$

$$\therefore E^\circ = -\frac{-3387 \times 10^3}{32 \times 96500} = 1.0968 \text{ V.}$$

$$\text{B4. (d) : } \alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{8}{400} = 2 \times 10^{-2}$$

Dissociation constant, $K = C\alpha^2$

$$K = \frac{1}{32} \times (2 \times 10^{-2})^2 = 1.25 \times 10^{-5}$$



$$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 0.46 \\ = -88780 \text{ J} = -89 \text{ kJ.}$$

B6. (c) : In strong electrolytes, number of ions remain constant, so equivalent conductance increases due to increase in ionic mobility.

B7. (c) : Higher the reduction potential, lower is the reducing power. Therefore, correct order is $Z > X > Y$.

$$\text{B8. (d) : } \Delta G^\circ = -nFE^\circ$$

$$E^\circ < 0, \Delta G^\circ = -RT \ln K_{eq}.$$

$$\Delta G^\circ > 0 \text{ and } K_{eq} < 1.$$

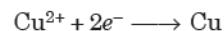
$$\text{B9. (b) : Cu}^{2+} + e^- \longrightarrow \text{Cu} \quad E_1^\circ = 0.15 \text{ V} \quad \dots(i)$$

$$\therefore \Delta G_1^\circ = -nFE_1^\circ = -1 \times F \times 0.15$$

$$\text{Cu}^+ + e^- \longrightarrow \text{Cu} \quad E_2^\circ = 0.50 \text{ V} \quad \dots(ii)$$

$$\Delta G_2^\circ = -nFE_2^\circ = -1 \times F \times 0.50$$

Adding eqn. (i) and (ii)



$$\Delta G^\circ = -nFE^\circ = -2 \times FE^\circ$$

$$-2 \times F \times E^\circ = -1 \times F \times 0.15 + (-1 \times F \times 0.50)$$

$$E^\circ = \frac{0.15 + 0.50}{2} = 0.325 \text{ V.}$$

$$\text{B10. (b) : } E_{cell}^\circ = E^\circ(\text{Sn}^{4+} \mid \text{Sn}^{2+}) - E^\circ(\text{Cr}^{3+} \mid \text{Cr}) \\ = 0.15 - (-0.74) = 0.89 \text{ V.}$$

$$\text{B11. (d) : } \Lambda_m^0(\text{NH}_4\text{OH})$$

$$= \Lambda_m^0(\text{NH}_4\text{Cl}) + \Lambda_m^0(\text{NaOH}) - \Lambda_m^0(\text{NaCl})$$

A35. (d) : Gram equivalents of H^+ = Gram equivalents of Al^{3+}

$$\text{No. of gm equivalents of Al}^{3+} = \frac{4.5}{9} = 0.5$$

$$\text{No. of gm equivalents of H}^+ = \text{No. of mol of H}^+$$

$$\therefore \text{Mass of H}^+ = 0.5 \times 1 = 0.5 \text{ g}$$

$$\text{Now, } 2 \text{ g of H}_2 \text{ at STP} = 22.4 \text{ L}$$

$$0.5 \text{ g of H}_2 \text{ at STP} = \frac{22.4 \times 0.5}{2} = 5.6 \text{ L}$$



Therefore, charge required for ZnSO_4 , AlCl_3 and AgNO_3 solutions is 2F , 3F and 1F respectively.

Thus, the ratio is 2:3:1.

$$\text{A41. (a) : } \Delta G = -nFE_{cell}^\circ$$

$$= (-2) \times (96500 \text{ C}) \times (1.23 \text{ V}) \\ = -237390 \text{ J mol}^{-1}$$

$$\text{or } = -237.390 \text{ kJ mol}^{-1}$$

$$\text{Efficiency} (\eta) = \frac{\Delta G}{\Delta H} \times 100$$

$$= \frac{-237.390}{285.8} \times 100 = 83\%$$

B from competitive examinations

B1. (b) : Efficiency of a fuel cell (η) = $\Delta G/\Delta H$

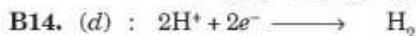


$$\Delta G^\circ = 5\Delta_f G^\circ(\text{CO}_2) + 6\Delta_f G^\circ(\text{H}_2\text{O}) \\ - \Delta_f G^\circ(\text{C}_5\text{H}_{12}) - 8\Delta_f G^\circ(\text{O}_2)$$

Competition File

B12. (a) : Degree of ionization = $\frac{\Lambda_m}{\Lambda_m''} \times 100 = \frac{9.54 \times 100}{23.8}$
 $= 4.008\%$

B13. (c) : $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
 $= 0.34 - (-0.76) = 1.10\text{V}$



$$\begin{aligned} E(\text{H}^+, \frac{1}{2}\text{H}_2) &= E^\circ - \frac{0.059}{2} \log \frac{1}{[\text{H}^+]^2} \\ &= 0 - \frac{0.059}{2} \log \frac{1}{(10^{-10})^2} \\ &= -\frac{0.059}{2} \times 20 = -0.59\text{V} \end{aligned}$$

Oxidation potential = **0.59 V**

B15. (c) : Change in oxidation number from MnO_4^{2-} to MnO_4^- is from +6 to +7. Therefore, 1 electron is lost in the process.

Charge required by 1 mol MnO_4^{2-} = 1 F

Charge required by 0.1 mol MnO_4^{2-} = 0.1 F
 $= 9650\text{ C}$

B16. (d) : At STP, 22,400 mL of oxygen = 32 g

$$5600 \text{ mL of oxygen} = \frac{32 \times 5600}{22,400} = 8 \text{ g}$$

∴ Weight of O_2 deposited = 8 g

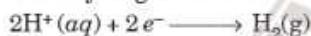
According to Faraday's second law,

$$\frac{\text{Wt. of O}_2 \text{ deposited}}{\text{Wt. of Ag deposited}} = \frac{\text{Equivalent wt. of oxygen}}{\text{Equivalent wt. of silver}}$$

$$\text{or } \frac{8\text{g}}{\text{Wt. of Ag deposited}} = \frac{8}{108}$$

or Wt. of silver deposited = 108 g

B18. (c) : For a hydrogen electrode



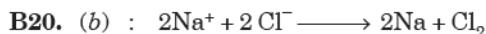
$$E = E^\circ - \frac{0.059}{2} \log \frac{p(\text{H}_2)}{[\text{H}^+]^2}$$

In pure water at 298K, $[\text{H}^+] = 10^{-7}$

$$\therefore E = 0 - \frac{0.059}{2} \log \frac{p(\text{H}_2)}{[10^{-7}]^2} = \frac{0.059}{2} \log \frac{p(\text{H}_2)}{10^{-14}}$$

∴ E will be zero when $p(\text{H}_2) = 10^{-14}$ atm

B19. (b) : $\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{5.76 \times 10^{-3} \times 1000}{0.5}$
 $= 11.52 \text{ S cm}^2 \text{ mol}^{-1}$



$$\text{Amount of Cl}_2 \text{ produced} = 0.1 \times 71 = 7.1 \text{ g}$$

71 g of Cl_2 is produced by electricity = $2 \times 96500\text{C}$

$$\begin{aligned} 7.1 \text{ g of Cl}_2 \text{ is produced by electricity} &= \frac{2 \times 96500}{71} \times 7.1 \\ &= 19300 \text{ C} \end{aligned}$$

Now, quantity of electricity $Q = I \times t$

$$19300 \text{ C} = 3 \times t$$

$$t = \frac{19300}{3} = 6433.3 \text{ s}$$

= 107.2 min. $\approx 110 \text{ min.}$

B21. (c) : $Q = I \times t = 1 \times 60 = 60 \text{ C}$

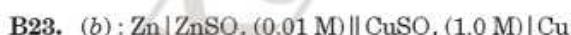
Charge on $1e^- = 1.6 \times 10^{-19}\text{C}$

$\therefore 1.6 \times 10^{-19}\text{C} = 1 \text{ electron}$

$$1\text{C} = \frac{1}{1.6 \times 10^{-19}} \text{ electrons}$$

$$60 \text{ C} = \frac{1}{1.6 \times 10^{-19}} \times 60 \text{ electrons}$$

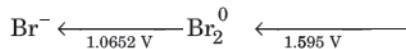
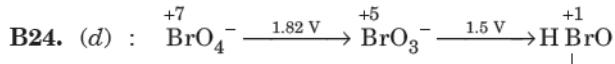
$$= 3.75 \times 10^{20} \text{ electrons}$$



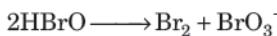
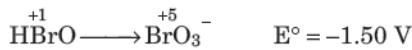
$$\begin{aligned} E_1 &= E_0 - \frac{0.059}{2} \log \frac{0.01}{1} \\ &= E_0 - \frac{0.059}{2} \log \frac{1}{100} \\ &= E_0 + 0.059 \end{aligned}$$

When concentrations are changed

$$\begin{aligned} E_2 &= E_0 - \frac{0.059}{2} \log \frac{1}{0.01} \\ &= E_0 - \frac{0.059}{2} \log 100 \\ &= E_0 - 0.059 \\ \therefore E_1 &> E_2 \end{aligned}$$



HBrO undergoes oxidation as well as reduction and e.m.f. of the cell is +ve.



$$E^\circ_{\text{cell}} = 1.595 - 1.50 = 0.095 \text{ V}$$

Since E°_{cell} is positive, the reaction is spontaneous.

B25. (c) : $E^\circ_{\text{cell}} = \frac{0.059}{n} \log K_c \quad \therefore n = 2$

$$E^\circ_{\text{cell}} = \frac{0.059}{2} \log 1 \times 10^8$$

$$= \frac{0.059}{2} \times 8 = 0.236 \text{ V}$$

$$E^\circ_{\text{cell}} = E^\circ(\text{Fe}^{3+}|\text{Fe}) - E^\circ(\text{I}_2|\text{I}^-)$$

$$0.236 = E^\circ(\text{Fe}^{3+}|\text{Fe}) - 0.54$$

$$\therefore E^\circ(\text{Fe}^{3+}|\text{Fe}) = 0.236 + 0.54 = 0.776 \text{ V.}$$

Competition File

B26. (b) : Applying Nernst equation,

$$E = E^\circ - \frac{0.059}{2} \log \frac{1}{[Ni^{2+}]}$$

After dilution

$$\begin{aligned} E &= E^\circ - \frac{0.059}{2} \log \frac{1}{[Ni^{2+}] / 10} \\ &= E^\circ - \frac{0.059}{2} \log \frac{1}{[Ni^{2+}]} - \frac{0.059}{2} \log 10 \\ &= E^\circ - \frac{0.059}{2} \log \frac{1}{[Ni^{2+}]} - 0.0295 \end{aligned}$$

Hence, reduction potential decreases by
0.0295 V = 29.5 mV = **30 mV**.

B27. (c) : According to Faraday's second law

$$\frac{\text{Weight of O}_2 \text{ liberated}}{\text{Weight of Mg deposited}} = \frac{\text{Equivalent weight of O}_2}{\text{Equivalent weight of Mg}}$$

$$\text{or } \frac{x}{0.150} = \frac{8}{12}$$

$$\text{or } x = \frac{8}{12} \times 0.150 = 0.1 \text{ g}$$

At S.T.P., volume of 32 g oxygen is 22,400 cm³
 \therefore Volume of 0.1 g oxygen at S.T.P. is

$$\frac{22,400}{32} \times 0.1 = 70 \text{ cm}^3$$

B28. (c) : Applying

$$\begin{aligned} E^\circ(I^- | AgI | Ag) &= E^\circ(Ag^+ | Ag) + 0.059 K_{sp}(AgI) \\ \log K_{sp}(AgI) &= \frac{E^\circ(I^- | AgI | Ag) - E^\circ(Ag^+ | Ag)}{0.059} \\ &= \frac{-0.152 - 0.8}{0.059} = -16.13 \end{aligned}$$

B29. (c) : Conductivity = $\frac{\text{Cell constant}}{\text{Resistance}}$

$$\text{Cell constant} = 1.20 \times 100 = 120 \text{ m}^{-1}$$

$$\text{Conductivity of 0.2 M solution} = \frac{129}{520} = 0.248 \text{ S m}^{-1}$$

$$\begin{aligned} \text{Molar conductivity} &= \frac{0.248 \times 10^{-3}}{0.2} \\ &= 12.4 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}. \end{aligned}$$

B30. (b) : $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

When the cell is completely discharged, $E_{cell} = 0$

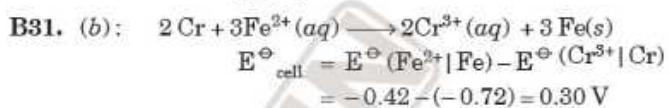
$$0 = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\text{or } E^\circ_{cell} = \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

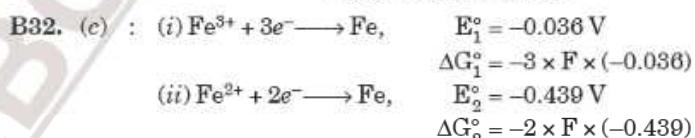
$$1.10 = \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\log \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1.10 \times 2}{0.059} = 37.3$$

$$\therefore \frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37.3}$$



$$\begin{aligned} E &= E^\circ_{cell} - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} \\ &= 0.30 - \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3} \\ &= 0.30 - \frac{0.059}{6} \times \log 10^4 \\ &= 0.30 - \frac{0.059}{6} \times 4 \\ &= 0.30 - 0.039 = \mathbf{0.26 \text{ V}}. \end{aligned}$$

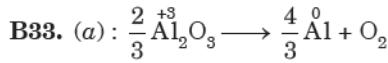


Required reaction is



Subtracting eqn. (ii) from eqn (i) gives the required equation so that

$$\begin{aligned} \Delta G_3^\circ &= \Delta G_1^\circ - \Delta G_2^\circ \\ -1 \times F \times E_3^\circ &= -3 \times F \times (-0.036) - (-2 \times F \times -0.439) \\ -E_3^\circ &= 0.108 - 0.878 \\ E_3^\circ &= -0.108 + 0.878 \\ &= \mathbf{0.77 \text{ V}}. \end{aligned}$$



$$\text{No. of electrons involved} = \frac{2}{3} (3 \times 2) = 4$$

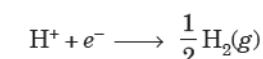
$$\Delta G^\circ = -nFE^\circ$$

$$966 \times 10^3 = -4 \times 96500 \times E^\circ$$

$$\therefore E^\circ = \frac{966 \times 10^3}{4 \times 96500} = -2.5 \text{ V}$$

Thus, minimum potential difference required = 2.50 V

B34. (a) : Pt | H₂(g) | H⁺(aq)



$$E = E^\circ - \frac{0.059}{1} \log \frac{p(H_2)^{1/2}}{[H^+]}$$

$$E = E^\circ - \frac{0.059}{1} \log \frac{(2)^{1/2}}{1} = -\text{ve.}$$

Competition File

B35. (a) : $\kappa = 1.3 \text{ S m}^{-1} = 1.3 \times 10^{-2} \text{ S cm}^{-1}$

$$\kappa = \frac{1}{R} \left(\frac{l}{a} \right)$$

$$1.3 \times 10^{-2} = \frac{1}{50} \left(\frac{l}{a} \right)$$

$$\therefore \left(\frac{l}{a} \right) = 1.3 \times 10^{-2} \times 50 = 65.0 \times 10^{-2} \text{ cm}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

$$\kappa = \frac{1}{R} \left(\frac{l}{a} \right) = \frac{1}{260} \times 65.0 \times 10^{-2}$$

$$\begin{aligned}\Lambda_m &= \frac{1}{260} \times \frac{65.0 \times 10^{-2} \times 1000}{0.4} \\ &= 6.25 \text{ S mol}^{-1} \text{ cm}^2 \\ &= 6.25 \times 10^{-4} \text{ S mol}^{-1} \text{ m}^2.\end{aligned}$$

B36. (c) : The element with high negative value of standard reduction potential is good reducing agent and can be easily oxidised. Therefore, X should have higher negative value of standard reduction potential than Y so that it will be oxidised to X^{2+} by reducing Y^{2+} to Y. Therefore,



$$\text{or } E^\circ_{\text{cell}} = -0.23 - (-0.76) = +0.53 \text{ V}$$

Since E°_{cell} is +ve, the reaction is spontaneous.

B37. (d) : Mn^{2+} is the strongest oxidising agent because it has highest reduction potential value.

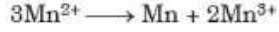
B38. (b) : $\text{Mn}^{2+} + 2e^- \longrightarrow \text{Mn}; \quad E^\circ = -1.18 \text{ V}$

$$\Delta G_1^\circ = -2F(-1.18) = 2.36 \text{ V} \quad \dots(i)$$

$$\text{Mn}^{3+} + e^- \longrightarrow \text{Mn}^{2+}; \quad E^\circ = +1.51 \text{ V} \quad \dots(ii)$$

$$\Delta G_2^\circ = -F(1.51) = -1.51 \text{ F} \quad \dots(ii)$$

$$\text{Eq. (i)} - 2 \times \text{Eq. (ii)}$$



$$\begin{aligned}\Delta G_3^\circ &= \Delta G_1^\circ - 2\Delta G_2^\circ \\ &= [2.36 - 2 \times (-1.51)] \text{ F} \\ &= 5.38 \text{ F}\end{aligned}$$

$$\text{But } \Delta G_3^\circ = -2F E^\circ$$

$$\therefore E^\circ = -2.69 \text{ V}$$

Since E° value is negative, the reaction will not occur.

B39. (d) : According to Debye Huckel Onsager equation,

$$\Lambda_c = \Lambda_\infty - A\sqrt{C}$$

$$\text{Here } A = B$$

$$\therefore \Lambda_c = \Lambda_\infty - B\sqrt{C}$$

B40. (b) : For 0.2 M solution

$$\kappa = \frac{1}{R} \times \frac{l}{A} \text{ or } 1.4 = \frac{1}{50} \times \frac{l}{A}$$

$$\text{or } \frac{l}{A} = 50 \times 1.4 = 70 \text{ m}^{-1} = 0.70 \text{ cm}^{-1}$$

For 0.5 M solution

$$\kappa = \frac{1}{R} \times \frac{l}{A} = \frac{1}{280} \times 0.70$$

$$= 2.5 \times 10^{-3} \text{ S cm}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$$

$$= \frac{2.5 \times 10^{-3} \times 1000}{0.5} = 5 \text{ S cm}^2 \text{ mol}^{-1}$$

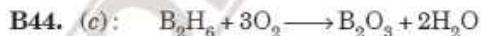
$$= 5 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$



2F of electricity deposit 1 mol of Cu

∴ Mass of Cu deposited = 63.5 g

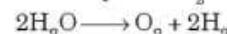
B43. (a) : E° for $\text{Cr}^{3+} \mid \text{Cr}$ is minimum and therefore, it can be readily oxidised. Hence, it is a strongest reducing agent.



$$\text{Moles of B}_2\text{H}_6 = \frac{27.66}{27.6} = 1 \text{ mol}$$

1 mole of B_2H_6 requires 3 mole of O_2 for complete burning

Electrolysis of H_2O



1 mole of O_2 is produced from 2 mole of H_2O

Amount of H_2O required to produce 3 mole of $\text{O}_2 = 6$ mole

No. of Faradays required = $6 \times 2 = 12 \text{ F}$

$$12 \times 96500 \text{ C} = I \times t$$

$$12 \times 96500 \text{ C} = 100 \times t$$

$$\text{or } t = \frac{12 \times 96500}{100} = 11580 \text{ s}$$

$$\text{or } \frac{11580}{3600} = 3.21 \text{ hr}$$

B45. (d) : Cell reaction is



$$E = E^\circ - \frac{2.303RT}{2F} \log \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2 p_{\text{H}_2}}$$

$$0.62 = 0.80 - \frac{0.06}{2} \log \frac{1}{[\text{Ag}^+]^2}$$

$$0.62 = 0.80 + \frac{2 \times 0.06}{2} \log [\text{Ag}^+]$$

$$0.06 \log [\text{Ag}^+] = 0.62 - 0.80 = -0.18$$

$$\log [\text{Ag}^+] = \frac{-0.18}{0.06} = -3$$

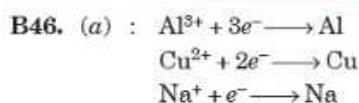
$$[\text{Ag}^+] = 10^{-3}$$

$$\text{Moles of Ag}^+ \text{ in } 100 \text{ mL} = \frac{10^{-3} \times 100}{1000} = 10^{-4}$$

$$\text{Weight of Ag}^+ \text{ in } 100 \text{ mL} = 10^{-4} \times 108 = 0.0108 \text{ g}$$

$$\% \text{ of Ag in } 1.08 \text{ g alloy} = \frac{0.0108}{1.08} \times 100 = 1\%$$

Competition File



Thus, 1F of electricity will deposit $\frac{1}{3}$ mol of Al, $\frac{1}{2}$ mol of Cu and 1 mol of Na. Hence, mole ratio of Al, Cu, Na deposited at respected cathodes is :

$$\frac{1}{3} : \frac{1}{2} : 1 = 2 : 3 : 6.$$

B47. (e) : $E = E^\circ - \frac{0.059}{n} \log \frac{1}{[\text{M}^{n+}]}$

Lower the concentration of M^{n+} , lower is the reduction potential.

Thus, standard reduction potential is
 $\text{Q} > \text{R} > \text{S} > \text{P}$



$$E = E^\circ - \frac{0.059}{n} \log \frac{1}{[\text{H}^+]} \\ = 0 - \frac{0.059}{1} \text{ pH} = 0 - 0.059 \times 10 = -0.59 \text{ V.}$$

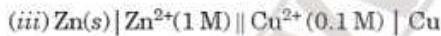
B49. (b) : $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$



$$E_1 = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \left(\frac{0.1}{1} \right) \\ = E_{\text{cell}}^\circ + \frac{0.059}{2}.$$



$$E_2 = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \left(\frac{1.0}{1.0} \right) \\ = E_{\text{cell}}^\circ.$$

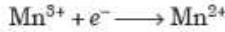


$$E_3 = E_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{1.0}{0.1} \\ = E_{\text{cell}}^\circ - \frac{0.059}{2}.$$

$$\therefore E_1 > E_2 > E_3.$$

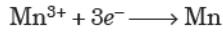


$$\Delta G^\circ = -nFE^\circ = 2.36 \text{ F} \quad \dots(i)$$



$$\Delta G^\circ = -nFE^\circ = -1.51 \text{ F} \quad \dots(ii)$$

Adding eq. (i) and (ii)



$$\Delta G^\circ = 2.36 \text{ F} + (-1.51 \text{ F}) = 0.85 \text{ F}$$

$$\Delta G^\circ = -nFE^\circ$$

$$0.85 \text{ F} = -3 \times F \times E^\circ$$

$$\text{or } E^\circ = -\frac{0.85}{3} = -0.28 \text{ V.}$$

B51. (c) : The oxidation states of X and Y are X^{3+} and Y^{2+}

Atomic masses are in the ratio = 1 : 2

Since equivalent mass = Atomic mass / Valency

$$\text{Equivalent masses} = \frac{1}{3} : \frac{2}{2} \text{ or } 1 : 3.$$

B52. (d) : $\alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$

$$\therefore \Lambda_m = \alpha \times \Lambda_m^\infty = \frac{2}{100} \times 400 \\ = 8.0 \text{ S cm}^2 \text{ g equiv}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{C}$$

$$8.0 = \frac{\kappa \times 1000}{0.1}$$

$$\text{or } \kappa = \frac{8.0 \times 0.1}{1000} = 8 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$$

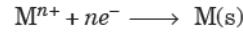
$$\text{Now } \kappa = \frac{1}{R} \times \text{Cell constant}$$

$$\text{or } R = \frac{\text{Cell constant}}{\kappa}$$

$$= \frac{0.4 \text{ cm}^{-1}}{8 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}} = 500 \text{ ohm}$$

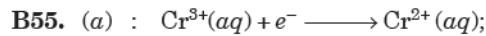
B53. (b) : $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ = 0.25 - 0.52 = -0.27 \text{ V}$

B54. (c) : Metals get deposited on cathode after undergoing reduction;

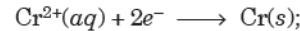


Higher the reduction potential, more is the tendency to get reduced.

Hence, correct order Ag, Hg, Cu.



$$\Delta G^\circ = -1 \times F \times -0.424 = 0.424 \text{ F} \quad \dots(i)$$



$$\Delta G^\circ = -2 \times F \times (-0.9000) = 1.8 \text{ F} \quad \dots(ii)$$

Adding eq. (i) and (ii)



$$\Delta G^\circ = -nFE^\circ$$

$$\text{or } E^\circ = -\frac{2.224 \text{ F}}{3 \text{ F}} = -0.741 \text{ V}$$

B56. (d) : $\Lambda_m^\infty [(\text{COO}^-)_2 \text{Na}^+ \text{K}^+] = \Lambda_m^\infty (\text{COO}^-)_2 + \Lambda_m^\infty (\text{Na}^+) \\ + \Lambda_m^\infty (\text{K}^+)$
 $= 148.2 + 50.1 + 73.5 = 271.8 \text{ S cm}^2 \text{ mol}^{-1}$

$$\Lambda_{\text{equiv}}^\infty = \frac{\Lambda_m^\infty}{\text{Total charge on cation or anion}}$$

$$\therefore \Lambda_{\text{equiv}}^\infty = \frac{271.8}{2} = 135.9 \text{ S cm}^2 \text{ mol}^{-1}$$

B57. (d) : Quantity of electricity = $I \times t$

$$= 9.65 \times 5 \times 60 \times 60$$

$$= 173,700 \text{ C}$$

Competition File

$$\text{Faraday of electricity} = \frac{173,700}{96500} = 1.8 \text{ F}$$

$$2\text{Cl}^- - 2e^- \longrightarrow \text{Cl}_2$$

1F of electricity liberates 35.5 g or 11.2 L of Cl_2 at S.T.P.
 \therefore Volume of Cl_2 liberated by 1.8 F electricity
 $= 1.8 \times 11.2 = 20.16 \text{ L}$

B58.(d) : $\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{150}{500} = 0.3$

$$K_a = \frac{ca^2}{1-\alpha} = \frac{0.007(0.3)^2}{(1-0.3)}$$

$$= \frac{0.007 \times 0.09}{0.7} = 9 \times 10^{-4} \text{ M}$$

B59. (d) : Decreases by 60 mV

B60. (d) : For a sparingly soluble salt

$$\text{Solubility} = \frac{\kappa \times 1000}{\Lambda_m^\circ}$$

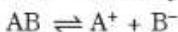
$$\kappa = 1.85 \times 10^{-5} \text{ Sm}^{-1} = 1.85 \times 10^{-7} \text{ S cm}^{-1}$$

$$\Lambda_m^\circ = 140 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1} = 140 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Solubility} = \frac{1.85 \times 10^{-7} \times 1000}{140}$$

$$= 1.321 \times 10^{-6} \text{ mol L}^{-1}$$

For an electrolyte AB,



If s is the solubility, then

$$K_{sp} = s^2 = (1.321 \times 10^{-6})^2$$

$$= 1.745 \times 10^{-12} \text{ mol}^2 \text{ L}^{-2}$$

B61. (a) : $E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^4}$

$$1.067 = 1.33 - \frac{0.0591}{6} \log \frac{(15 \times 10^{-3})^2}{(4.5 \times 10^{-3})[\text{H}^+]^4}$$

$$1.067 = 1.33 - 0.0098 \log \frac{50 \times 10^{-3}}{[\text{H}^+]^4}$$

$$0.0098 \log \frac{50 \times 10^{-3}}{[\text{H}^+]^4} = 1.33 - 1.067 = 0.263 \text{ V}$$

$$\log \frac{50 \times 10^{-3}}{[\text{H}^+]^4} = \frac{0.263}{0.0098} = 26.83$$

$$\log(50 \times 10^{-3}) - \log[\text{H}^+]^{14} = 26.83$$

$$-1.3 - 14 \log[\text{H}^+] = 26.83$$

$$-14 \log[\text{H}^+] = 26.83 + 1.3 = 28.13$$

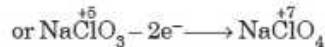
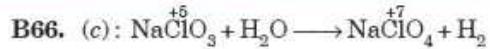
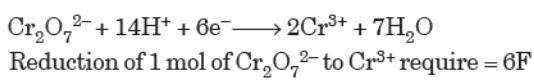
$$\text{or } -\log[\text{H}^+] = \frac{28.13}{14} = 2.01$$

$$\therefore \text{pH} = 2$$

B62. (c) : During charging, Pb^{2+} ions of PbSO_4 are reduced to Pb on cathode:



B65. (d) : In acidic medium

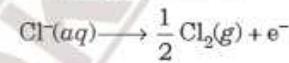


2 moles of electrons or 2 Faradays charge produce 1 mole of NaClO_4 .

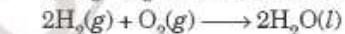
\therefore 3 Faradays of charge will produce = $\frac{1}{2} \times 3 = 1.5$ moles of NaClO_4

B67. (b) : Lower the reduction potential, more easily it is oxidised and stronger is the reducing agent. Thus, zinc having lowest reduction potential is the strongest reducing agent.

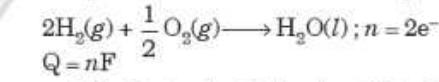
B68. (a) : During electrolysis of aqueous NaCl, the reaction occurring at anode is



B69. (c) : In $\text{H}_2 - \text{O}_2$ fuel cell, net reaction is



Since cell is supplied with 1 mole of H_2 and 10 moles of O_2 , H_2 is the limiting reagent. Therefore, 1 mole of H_2 will react with 0.5 mole of O_2



and $Q = I \times t$, $I = 96.5 \text{ mA} = 96.5 \times 10^{-3} \text{ A}$

$$2 \times 96500 = 96.5 \times 10^{-3} \times t$$

$$\text{or } t = \frac{2 \times 96500}{96.5 \times 10^{-3}} = 2 \times 10^6 \text{ s}$$

B71. (a) : $\text{Zn} | \text{Zn}^{2+}(0.1 \text{ M}) || \text{Cu}^{2+}(0.01 \text{ M}) | \text{Cu}$

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+}|\text{Cu}} - E^\circ_{\text{Zn}^{2+}|\text{Zn}}$$

$$= 0.34 - (-0.76) = 1.10 \text{ V}$$

$$E = E^\circ - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 1.10 - \frac{0.059}{2} \log \frac{(0.1)}{(0.01)}$$

$$= 1.0 - 0.0295 = 1.07 \text{ V}$$

Since, E of the cell is positive, the reaction is spontaneous.

B72. (c) : $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$

For depositing 1 mole of Al, electricity required = 3F

B73. (b) : $E^\circ = E^\circ_{\text{red}(\text{cathode})} - E^\circ_{\text{red}(\text{anode})}$

$$= E^\circ_{\text{Fe}^{2+}|\text{Fe}} - E^\circ_{\text{Zn}^{2+}|\text{Zn}}$$

$$= -0.41 - (-0.76) = 0.35 \text{ V}$$

B74. (a) : $\Lambda_m = \frac{\kappa (\text{Specific conductance}) \times 1000}{M}$

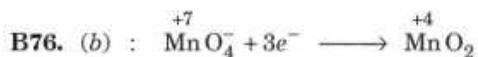
or $\frac{\Lambda_m}{\kappa} = \frac{1000}{0.01} = 10^5 \text{ cm}^3 \text{ mol}^{-1}$

Competition File

B75. (d) : $\log K = \frac{nFE^\circ_{\text{cell}}}{2.303RT} = \frac{nE^\circ_{\text{cell}}}{0.059}$

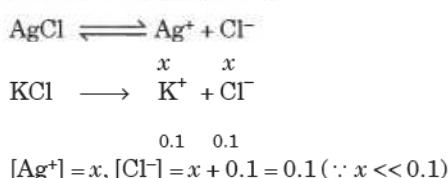
$$= \frac{2 \times 0.3}{0.0591} = 10.15 \approx 10$$

$K = 10^{10}$



Charge required for reduction of 1 mol of MnO_4^-
 $= 3F$

B77. (a) : If x is the solubility of AgCl



For precipitation to start

$$\begin{aligned} K_{sp} &= [\text{Ag}^+] [\text{Cl}^-] \\ 1.8 \times 10^{-10} &= x \times 0.1 \\ x &= \frac{1.8 \times 10^{-10}}{0.1} = 1.8 \times 10^{-9} \\ \text{Mass of AgCl} &= 1.8 \times 10^{-9} \times 143.5 \\ &= 2.58 \times 10^{-7} \text{ g} \end{aligned}$$

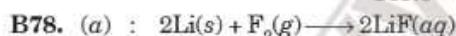
Quantity of electricity required to deposit $2.58 \times 10^{-7} \text{ g AgCl}$

1 mol or 143.5 g of AgCl is deposited by 96500 C

$2.58 \times 10^{-7} \text{ g of AgCl is deposited by} =$

$$\frac{96500 \times 2.58 \times 10^{-7}}{143.5}$$

Now, $Q = It$ or $t = \frac{Q}{I}$
or $t = \frac{96500 \times 2.58 \times 10^{-7}}{143.5 \times 1 \times 10^{-6}} = 173.4 \text{ s.}$



$$\begin{aligned} E^\circ_{\text{cell}} &= 5.92 \text{ V} \\ E &= E^\circ_{\text{cell}} - \frac{0.059}{2} \log [\text{LiF}]^2 \\ &= 5.92 - \frac{0.059}{2} \log(2)^2 \\ &= 5.92 - \frac{0.059}{2} \times 2 \log 2 \\ &= 5.92 - 0.059 \times 0.3010 = 5.90 \text{ V} \end{aligned}$$

B79. (a) : $\alpha = \frac{\Lambda_m^\circ}{\Lambda_m^c}$

$$= \frac{240}{420} = \frac{12}{21}$$

$$\alpha = \frac{i-1}{n-1} = \frac{i-1}{2-1} = \frac{12}{21}$$

$$i = \frac{12}{21} + 1 = \frac{33}{21}$$

$$\Delta T_b = i K_b m$$

$$= \frac{33}{21} \times 0.52 \times 3 = 2.45 \text{ K}$$

$$\text{Boiling point of solution} = 373.15 + 2.45 \\ = 375.6 \text{ K}$$



$$\begin{aligned} E &= E^\ominus - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]} \\ &= E^\ominus - \frac{0.059}{2} \log \frac{10^{-2}}{10^{-3}} \end{aligned}$$

$$0.2905 = E^\ominus - \frac{0.059}{2}$$

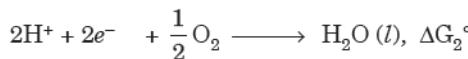
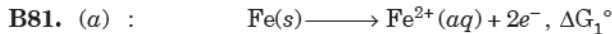
$$E^\ominus = 0.2905 + \frac{0.059}{2} = 0.32$$

Now $E^\ominus = \frac{0.059}{2} \log K$

$$0.32 = \frac{0.059}{2} \log K$$

$$\log K = \frac{0.32}{0.059} / 0.0295$$

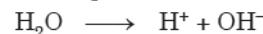
$$\therefore K = 10^{0.32/0.0295}$$



Applying $\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$

$$\begin{aligned} \Delta G_3^\circ &= -2F \times 0.44 + (-2F \times 1.23) \\ &= -2 \times 96500 \times 0.44 - 2 \times 96500 \times 1.23 \\ &= -322310 \text{ J} \end{aligned}$$

or $\Delta G_3^\circ = -322.3 \text{ kJ}$



0.5 mol of H_2 is liberated by 96500 C

0.01 mol of H_2 will be liberated by

$$= \frac{96500}{0.5} \times 0.01 = 1930 \text{ C}$$

$$Q = I \times t$$

or $t = \frac{Q}{I} = \frac{1930 \text{ C}}{10 \times 10^{-3} \text{ A}}$
 $= 193000 \text{ sec} = 19.3 \times 10^{-4} \text{ s}$

Competition File

B83. (d) :

$$\begin{aligned} E &= E^\circ - \frac{0.059}{4} \log \frac{[\text{Fe}^{2+}]^2}{p_{\text{O}_2} \times [\text{H}^+]^4} \\ &= 1.67 - \frac{0.059}{4} \log \frac{(10^{-3})^2}{0.1 \times (10^{-3})^4} \\ &= 1.67 - \frac{0.059}{4} \log 10^7 \\ &= 1.67 - 0.10 = 1.57. \end{aligned}$$

B85. (d) : Pt(s) | H₂(g)(1 bar) | H⁺(aq), (1M) || M⁴⁺(aq), M²⁺(aq) | Pt(s)

The cell reaction is: H₂ + M⁴⁺(aq) → 2H⁺(aq) + M²⁺(aq)

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[\text{H}^+]^2 [\text{M}^{2+}(\text{aq})]}{p_{\text{H}_2} \cdot [\text{M}^{4+}(\text{aq})]} \\ E_{\text{cell}}^\circ &= E_{\text{M}^{4+}|\text{M}^{2+}}^\circ - E_{\text{H}^+|\text{H}_2}^\circ = 0.151 - 0 = 0.151 \text{ V} \\ [\text{H}^+] &= 1, E_{\text{cell}} = 0.092 \text{ V}, p_{\text{H}_2} = 1 \text{ bar}, n = 2 \\ \therefore 0.092 &= 0.151 - \frac{0.059}{2} \log \frac{[\text{l}]^2 [\text{M}^{2+}(\text{aq})]}{[\text{l}] [\text{M}^{4+}(\text{aq})]} \\ 0.092 - 0.151 &= -\frac{0.059}{2} \log \frac{[\text{M}^{2+}(\text{aq})]}{[\text{M}^{4+}(\text{aq})]} \\ -0.059 &= -\frac{0.059}{2} \log \frac{[\text{M}^{2+}(\text{aq})]}{[\text{M}^{4+}(\text{aq})]} \end{aligned}$$

or $\log \frac{[\text{M}^{2+}(\text{aq})]}{[\text{M}^{4+}(\text{aq})]} = 2$

or $\frac{[\text{M}^{2+}(\text{aq})]}{[\text{M}^{4+}(\text{aq})]} = 10^2 = 10^x \quad \text{or} \quad x = 2$

B86. (a) : Zn(s) + Cu²⁺(aq) → Zn²⁺(aq) + Cu(s)

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ \Delta G &= \Delta G^\circ + 2.303 RT \ln Q \\ Q &= \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{10}{1} \\ \Delta G^\circ &= -nF E_{\text{cell}}^\circ = -2 \times F \times 1.1 \\ \therefore \Delta G &= -2 \times F \times 1.1 + 2.303 RT \ln \frac{10}{1} \\ &= 2.303 RT - 2.2 F. \end{aligned}$$

D. mcq based on passage/comprehension

D1. (b) : $\Delta G = \Delta H - T\Delta S$

or $\Delta S = \frac{\Delta H - \Delta G}{T}$

$$\begin{aligned} &= \frac{-285.8 - (-237.2)}{298} = \frac{-48.6}{298} \\ &= -0.163 \text{ kJ K}^{-1} \text{ mol}^{-1} \\ &= -163 \text{ J K}^{-1} \text{ mol}^{-1}. \end{aligned}$$

D2. (c) : $E_{\text{cell}}^\circ = E_{\text{(cathode)}}^\circ - E_{\text{(anode)}}^\circ$

$$1.23 = 0.41 - E_{\text{(anode)}}^\circ$$

$$\therefore E_{\text{(anode)}}^\circ = -0.82 \text{ V}$$

D3. (a) : Under ideal conditions, electrical work
 $= \Delta G = -237.2 \text{ kJ mol}^{-1}$

Moles of H₂ needed

$$= \frac{-47.4}{-237.2} = 0.2$$

Vol. of H₂ needed at 25°C and 1 atm.

$$\begin{aligned} &= \frac{nRT}{p} \\ &= \frac{0.2 \times 0.082 \times 298}{1} \\ &= 4.89 \text{ L} \end{aligned}$$

D4. (d) : Since the cell reaction does not involve OH⁻ ions concentration, E[⊖]_{cell} will remain unchanged.

D5. (c) : Thermodynamic efficiency

$$\begin{aligned} &= \frac{\Delta G}{\Delta H} = \frac{-nFE}{\Delta H} \\ &= \frac{-2 \times 96500 \times 1.23}{-285.8 \times 10^3} \\ &= 0.83 \text{ or } 83\% \end{aligned}$$

D6. (d) : $E_{\text{cell}}^\ominus = E_{\text{R}}^\ominus - E_{\text{L}}^\ominus$

$$\begin{aligned} &= 0.8 - 0.05 \\ &= 0.75 \text{ V} \end{aligned}$$

$$\begin{aligned} \Delta G_{\text{cell}}^\ominus &= -2FE_{\text{cell}}^\ominus \\ &= -RT \ln K \\ \ln K &= \frac{2F}{RT} \times 0.75 \\ &= 2 \times 38.9 \times 0.75 \\ &= 58.35 \end{aligned}$$

D7. (a) : $E = E^\ominus - \frac{RT}{2F} \ln [\text{H}^+]^2$

$$\begin{aligned} &= E^\ominus - \frac{2}{38.9 \times 2} \ln [\text{H}^+] \\ &= E^\ominus + \frac{2.303}{38.9} \text{ pH} \\ \text{or} \quad E &= E^\ominus + \frac{2.303}{38.9} \times 11 \\ &= E^\ominus + 0.65 \\ E - E^\ominus &= 0.65 \text{ V.} \end{aligned}$$

D8. (a) : Because $E_{\text{Ag}^+|\text{Ag}}^\ominus > E_{[\text{Ag}(\text{NH}_3)_2]^+|\text{Ag}}^\ominus$

D9. (b) : $\text{M}^+ \xrightarrow{(1\text{M})} \text{M}^+ \xrightarrow{(0.05\text{M})}$

Applying Nernst equation

$$E = E^\circ - \frac{0.059}{1} \log \frac{0.05}{1}$$

$$E = -\frac{0.059}{1} \log (5 \times 10^{-2}) = 0.076$$

E = +ve or > 0, ΔG = -ve or < 0

Competition File

D10. (c) : $\frac{E_1}{E_2} = \frac{\log 0.05}{\log 0.0025}$

$$\frac{E_1}{E_2} = \frac{\log 5 \times 10^{-2}}{\log 25 \times 10^{-4}} = \frac{-1.3}{-2.6} = \frac{1}{2}$$

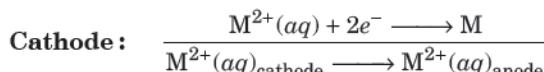
Now $E_1 = 70$ (given)

$$\frac{70}{E_2} = \frac{1}{2} \quad \therefore E_2 = 70 \times 2 = 140 \text{ mV}$$

D11. (d) : $\Delta G = -nFE_{\text{cell}}$
 $= -2 \times 96500 \times 0.059$
 $= -11387 \text{ J mol}^{-1}$
 or $= -11.4 \text{ kJ mol}^{-1}$

D12. (b) : M | M²⁺(aq) (saturated solution)

$$|| \text{M}^2+(aq)(0.001 \text{ M}) | 1 \text{ M}$$



$$E = E^\circ - \frac{0.059}{2} \log \frac{[\text{M}^2+(aq)]_{\text{anode}}}{[\text{M}^2+(aq)]_{\text{cathode}}}$$

$$0.059 = 0 - \frac{0.059}{2} \log \frac{[\text{M}^2+(aq)]_{\text{anode}}}{10^{-3}}$$

$$-2 = \log \frac{[\text{M}^2+(aq)]_{\text{anode}}}{10^{-3}}$$

$$-2 = 3 \log [\text{M}^2+(aq)]_{\text{anode}}$$

or $10^{-2} = 10^3 [\text{M}^2+(aq)]_{\text{anode}}$

$$\therefore [\text{M}^2+(aq)]_{\text{anode}} = \frac{10^{-2}}{10^3} = 10^{-5}$$

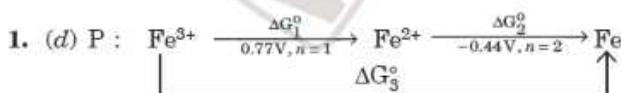
For MX₂, MX₂ ⇌ M²⁺ + 2X⁻

If s is the solubility, then

$$[\text{M}^{2+}] = s, [\text{X}^-] = 2s$$

$$\begin{aligned} K_{sp} &= [\text{M}^{2+}][\text{X}^-]^2 \\ &= s \times (2s)^2 = 4s^3 \\ &= 4 \times (10^{-5})^3 = 4 \times 10^{-15} \text{ dm}^{-9} \text{ mol}^3 \end{aligned}$$

Matching Type Questions



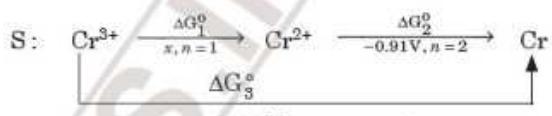
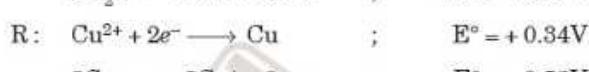
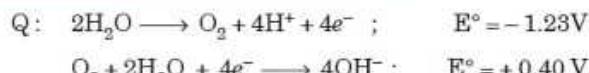
$$xV, n = 3$$

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$3 \times xF = 1 \times 0.77 \times F + 2(-0.44) \times F$$

$$3x = 0.77 - 0.88$$

$$x = -\frac{0.11}{3} = -0.037 = -0.04 \text{ V}$$



$$-0.74 \text{ V}, \quad n = 3$$

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

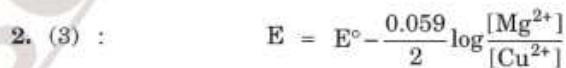
$$-3F \times 0.74 = 1F \times x + 2F \times (-0.91)$$

$$x = -2.22 + 1.82$$

$$\text{or} = -0.40 \text{ V}$$

Integer Type or Numerical Value Type Questions

1. (5) : Zn, K, Al, Na, Ni



$$2.651 = 2.71 - \frac{0.059}{2} \log \frac{0.1}{(1.0 \times 10^{-x})}$$

$$2.651 - 2.71 = -\frac{0.059}{2} \log \frac{0.1}{(1.0 \times 10^{-x})}$$

$$-0.059 = -\frac{0.059}{2} \log \frac{0.1}{(1.0 \times 10^{-x})}$$

$$2 = \log 0.1 - \log (1.0 \times 10^{-x})$$

$$2 = -1 - \log (1.0 \times 10^{-x})$$

$$\log (1.0 \times 10^{-x}) = -3$$

$$\log 1.0 - x \log 10 = -3$$

$$\therefore -x = -3$$

$$\text{or} \quad x = 3$$

3. (9) : Al³⁺ + 3e⁻ → Al

For depositing 1 mol or 27 g Al, electricity required = 3F

For depositing 81 g, electricity required = $\frac{3 \times 81}{27} = 9 \text{ F}$

4. (5) : 2H⁺ + 2e⁻ → H₂

22.4 L of H₂ is produced by = 2 × 96500 C

4.48 L of H₂ is produced by = $\frac{2 \times 96500 \times 4.48}{22.4} = 38600 \text{ C}$

Now 38600 C = 2.14 A × t(s)

$$t = \frac{38600}{2.14} = 18037 \text{ s}$$

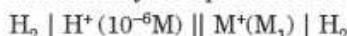
$$\text{or} \quad t = \frac{18037}{3600} = 5 \text{ hr.}$$

Competition File

5. (5) : 2 L of 0.5 M KMnO_4 solution will contain $2 \times 0.5 = 1.0$ mol of KMnO_4 . Reduction of KMnO_4 is
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
 Thus, 1 mol of MnO_4^- requires 5F of electricity.

6. (1) : Electrode potential does not change with change in stoichiometric coefficients of electrode reactions.

7. (4) : The cell may be represented as



$$\begin{aligned} E &= E^\circ - \frac{0.059}{1} \log \frac{[\text{H}^+]_{\text{anode}}}{[\text{H}^+]_{\text{cathode}}} \\ 0.118 &= 0 - \frac{0.059}{1} \log \frac{(10^{-6})}{\text{M}_1} \\ \log \frac{(10^{-6})}{\text{M}_1} &= -\frac{0.118}{0.059} = -2 \end{aligned}$$

$$\begin{aligned} \frac{10^{-6}}{\text{M}_1} &= 10^{-2} \\ \therefore \quad \text{M}_1 &= \frac{10^{-6}}{10^{-2}} = 10^{-4} \text{M} \end{aligned}$$

$$\therefore \quad x = 4$$

8. (3) : Given : $\lambda^\circ_{\text{X}^-} = \lambda^\circ_{\text{Y}^-}$

Adding $\lambda^\circ_{\text{H}^+}$ on both sides

$$\lambda^\circ_{\text{X}^-} + \lambda^\circ_{\text{H}^+} = \lambda^\circ_{\text{Y}^-} + \lambda^\circ_{\text{H}^+}$$

or $\Lambda^\circ_{\text{HX}} = \Lambda^\circ_{\text{HY}}$... (i)

Degree of dissociation is given as

$$\alpha_{\text{HX}} = \frac{\Lambda^\circ_{\text{HX}}}{\Lambda^\circ_{\text{HX}}} \quad \text{and} \quad \alpha_{\text{HY}} = \frac{\Lambda^\circ_{\text{HY}}}{\Lambda^\circ_{\text{HY}}}$$

$$\text{or} \quad \frac{\alpha_{\text{HX}}}{\alpha_{\text{HY}}} = \frac{\Lambda^\circ_{\text{HX}}}{\Lambda^\circ_{\text{HY}}} \times \frac{\Lambda^\circ_{\text{HY}}}{\Lambda^\circ_{\text{HX}}} = \frac{\Lambda^\circ_{\text{HX}}}{\Lambda^\circ_{\text{HY}}} \quad \dots (\text{ii})$$

$$\text{But} \quad \Lambda^\circ_{\text{HX}} = \frac{1}{10} \Lambda^\circ_{\text{HY}} = 0.1 \Lambda^\circ_{\text{HY}}$$

$$\therefore \quad \alpha_{\text{HX}} = 0.1 \alpha_{\text{HY}}$$

$$\text{Now} \quad K_a(\text{HX}) = \frac{c\alpha_{\text{HX}}^2}{1-\alpha_{\text{HX}}} = c\alpha_{\text{HX}}^2 \quad \dots (\text{iii})$$

$$= 0.01 \times (0.1 \alpha_{\text{HY}})^2 \quad \dots (\text{iii})$$

$$K_a(\text{HY}) = c\alpha_{\text{HY}}^2 = 0.1 (\alpha_{\text{HY}})^2 \quad \dots (\text{iv})$$

Dividing eq. (iii) by eq. (iv)

$$\frac{K_a(\text{HX})}{K_a(\text{HY})} = \frac{0.01 \times 0.01 \alpha_{\text{HY}}^2}{0.1 \alpha_{\text{HY}}^2} = 10^{-3}$$

Taking log

$$\log K_a(\text{HX}) - \log K_a(\text{HY}) = -3$$

$$-pK_a(\text{HX}) + pK_a(\text{HY}) = -3$$

$$\text{or} \quad pK_a(\text{HX}) - pK_a(\text{HY}) = 3$$

9. (6) : Refer Advanced Level Problems, Problem 2.
 (page 21)

10. (10) : Refer Advanced Level Problems, Problem 8
 (page 45).

11. (-11.62) : Refer Advanced Level Problems, Problem 11
 (page 51).

NCERT Exemplar Problems : MCQs Type-I

1. (c) : $\text{Pt}(s) | \text{H}_2(g, 1 \text{ bar}) | \text{H}^+(aq, 1 \text{ M}) \parallel \text{Cu}^{2+}(aq, 1 \text{ M}) | \text{Cu}$ represents correct cell for measuring standard electrode potential of copper.

2. (b) : $E_{(\text{Mg}^{2+}|\text{Mg})}$ increases with increase in $\log [\text{Mg}^{2+}]$ and at $\log [\text{Mg}^{2+}] = 0$, the value is equal to $E^\circ_{(\text{Mg}^{2+}|\text{Mg})}$.

3. (c) : E_{cell} is an intensive property and $\Delta_s G$ is an extensive property.

5. (d) : It provides surface either for oxidation or for reduction reaction and not for a redox reaction.

6. (c) : When E_{ext} becomes larger than E_{cell} , the electrochemical cell behaves as an electrolytic cell.

7. (c) : Conductivity also depends upon the extent of solvation of ions in the solution.

8. (b) : $\text{Cr}^{3+} | \text{Cr}$ has the least reduction potential and therefore, it can be easily oxidised. Hence Cr acts as strongest reducing agent.

9. (c) : MnO_4^- can be easily reduced to Mn^{2+} and therefore, MnO_4^- acts as the strongest oxidising agent.

11. (d) : Mn^{2+} is most stable ion in reduced form because MnO_4^- acts as the strongest oxidising agent.

12. (a) : Cr^{3+} is most stable oxidised species because Cr acts as the strongest reducing agent.

13. (c) : $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$

Quantity of charge required for one mole = 3F

15. (a) : While charging the lead storage battery,
 $2\text{PbSO}_4(s) + 2\text{H}_2\text{O} \xrightarrow{\text{Charge}} \text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4$ at anode

17. (b) : At anode, the standard reduction potential of water is slightly less than that of $\text{Cl}^-(aq)$ and therefore, it has more chances of getting oxidised.

NCERT Exemplar Problems : MCQs Type-II

20. (b), (c) : $\frac{2.303RT}{2F} \log K_c = E^\circ = 1.1 \text{ V}$

$$\log K_c = \frac{nE^\circ}{0.059} = \frac{2 \times 1.1}{0.059}$$

22. (a), (b) : because $\Lambda_m^\circ(\text{H}_2\text{O}) = \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{OH}^-)$

25. (a), (b) : Conductivity, $\kappa = \frac{1}{R} \cdot \frac{l}{a}$

$$\text{or } \kappa = \frac{1}{R} \cdot G^*, \text{ where } G^* \text{ is cell constant and is equal to } \frac{l}{a}$$



Unit Practice Test

for Board Examination

Time allowed : 2 Hrs.

Maximum Marks : 35

1. Give the units of conductivity and molar conductivity. (1)
2. Write the overall cell reaction for lead storage battery. (1)
3. Define Faraday's second law of electrolysis. (1)
4. What is the role of $ZnCl_2$ in a dry cell ? (1)
5. Out of copper and zinc vessels, which vessel would be suitable for storing 1M HCl? (1)
6. Predict the products of electrolysis in each of the following : (2)
 - (i) An aqueous solution of $AgNO_3$ with silver electrode.
 - (ii) A dilute solution of H_2SO_4 with platinum electrodes.
7. How much electricity is required in Coulombs to produce 40 g of Al from molten Al_2O_3 ? (2)
8. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm $^{-1}$. Calculate its molar conductivity. If Λ_m° for acetic acid is 390.5 S cm 2 mol $^{-1}$, what would be its dissociation constant? (2)
9. Write cell reactions which occur in lead storage battery (2)
 - (i) When battery is in use
 - (ii) When the battery is on charging.
10. Give two points of differences between emf and potential difference . (2)
11. Write the Nernst equation and calculate e.m.f. of the following cell at 298 K : (3)

$$Sn(s) | Sn^{2+}(0.050M) \parallel H^+(0.020\text{ M}) | H_2(1\text{ atm}) Pt.$$
12. Explain the following : (3)
 - (i) Electrical protection for preventing rusting of iron pipes in underground water.
 - (ii) Can you store copper sulphate solution in a zinc pot or not?
 - (iii) Effect of dilution on molar conductivity.
13. Write the chemical equations for all the steps involved in the rusting of iron. Explain why does alkaline medium inhibits the rusting of iron. (3)
14. State Kohlrausch law of independent migration of ions. Mention one application of the law. (3)
15. List main differences between electrochemical cells and electrolytic cells ? (3)
16. (a) The cell in which the following reaction occurs : (3)

$$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2$$
 has $E_{cell}^\circ = 0.236$ V at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

 (b) What are fuel cells ? Give one example.

 (c) Give the units of cell constant. (5)

► To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part I of the book.