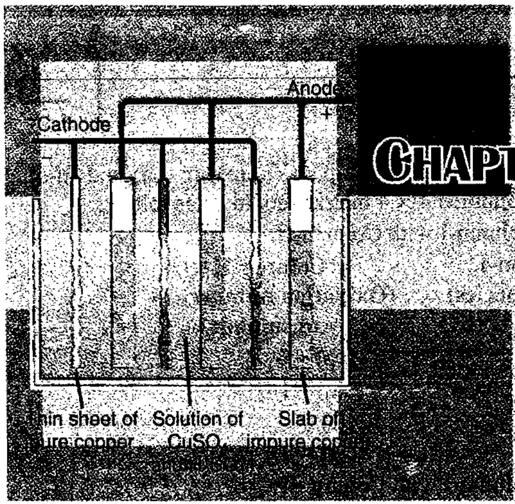

CHAPTER 12

ELECTROCHEMISTRY

SECTION I : ELECTROLYTES AND ELECTROLYSIS

12.1 INTRODUCTION

Electrochemistry deals with the interactions of electrical energy with chemical species. It is broadly divided into two categories, namely (i) production of chemical change by electrical energy (phenomenon of electrolysis) and (ii) conversion of chemical energy into electrical energy, *i.e.*, generation of electricity by spontaneous redox reactions. In this chapter both of these aspects will be described. All electrochemical reactions involve transfer of electrons and are, therefore, oxidation-reduction (redox) reactions.

Substances which allow the passage of electric current through them are called **electrical conductors** or simply conductors. Those which do not allow the flow of electric current through them are termed **insulators.** Electrical conductors are of two types:

(i) Metallic or electronic conductors: Conductors which transfer electric current by transfer of electrons, without transfer of any matter, are known as **metallic or electronic conductors.** Metals such as copper, silver, aluminium, etc., non-metals like carbon (graphite—an allotropic form of carbon) and various alloys belong to this class. These materials contain electrons which are relatively free to move. The passage of current through these materials has no observable effect other than a rise in their temperature.

(ii) Electrolytic conductors: Conductors like aqueous solutions of acids, bases and salts in which the flow of electric current is accompanied by chemical decomposition are known as **electrolytic conductors.** The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed **electrolytes.**

The substances whose aqueous solutions do not conduct electric current are called **non-electrolytes.** Solutions of cane sugar, glycerine, alcohol, etc., are examples of non-electrolytes.

In order to pass the current through an electrolytic conductor (aqueous solution or fused electrolyte), two rods or plates (metallic conductors) are always needed which are connected with the terminals of a battery. These rods or plates are known as **electrodes.** The electrode through which the current enters the electrolytic solution is called the **anode** (positive electrode) while the electrode through which the current leaves the electrolytic solution is known as **cathode** (negative electrode). The electrolytic solution conducts electricity not by virtue of flow of electrons as in metallic conductors but as a result of movement of charged particles called **ions** towards the respective oppositely charged electrodes. The ions which carry positive charge and move towards cathode are termed **cations** while ions carrying negative charge which move towards anode are called **anions.** When these ions reach the boundary between a metallic and an electrolytic conductor, electrons are being either attached to or removed from the ions. Removal of electrons is termed **oxidation** (de-electronation) which occurs at anode while addition of electrons is called **reduction** (electronation) that takes place at cathode. Hence, flow of electrons through the outer circuit from anode to cathode across the boundary is accompanied by oxidation and reduction.

Distinction between metallic and electrolytic conduction

Metallic conduction	Electrolytic conduction
1. Electric current flows by movement of electrons.	Electric current flows by movement of ions.
2. No chemical change occurs.	Ions are oxidised or reduced at the electrodes.
3. It does not involve the transfer of any matter.	It involves transfer of matter in the form of ions.
4. Ohm's law is followed.	Ohm's law is followed.
5. Resistance increases with increase of temperature.	Resistance decreases with increase of temperature.
6. Faraday's law is not followed.	Faraday's law is followed.

The process of chemical decomposition of an electrolyte by passage of electric current through its solution is called electrolysis.

Or

Chemical change (oxidation and reduction) occurring at electrodes when electric current is passed through electrolytic solution is called electrolysis.

Molecules of an electrolyte when dissolved in water split up into ions, *i.e.*, into cations and anions. On passing current, these ions move towards oppositely charged electrodes. On reaching the electrodes the ions lose their charge either by accepting electrons or losing electrons and thereby deposited at the respective electrodes or undergo a secondary change. For example, when electric current is passed through a solution of hydrochloric acid, the H^+ ions move towards cathode and Cl^- ions move towards anode.

$$HCl \rightleftharpoons H^+ + Cl^-$$

Cathode	Anode
$H^+ + e^- \longrightarrow H$	$Cl^- \longrightarrow Cl + e^-$
$2H \longrightarrow H_2$	$2Cl \longrightarrow Cl_2$
(Reduction)	(Oxidation)

The decomposition of HCl into H_2 and Cl_2 as a result of passage of current is termed electrolysis of HCl. It is, thus, a process in which electric current brings the chemical change.

The device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical change is done is known as **electrolytic cell.** An electrolytic cell consists of a vessel for the electrolytic solution or fused electrolyte and two metallic electrodes immersed in the reaction material which are connected to a source of electric current. The metallic electrodes which do not react with ions or final products are called **inert electrodes.** Inert electrodes are usually used in an electrolytic cell.

12.2 PREFERENTIAL DISCHARGE THEORY

If an electrolytic solution consists of more than two ions and the electrolysis is done, it is observed that all the ions are not discharged at the electrodes simultaneously but certain ions are liberated at the electrodes in preference to others. This is explained by **preferential discharge theory.** It states that if more than one type of ions are attracted towards a particular electrode, then the one discharged is the ion which requires least energy. The potential at which the ion is discharged or deposited on the appropriate electrode is termed the discharge or deposition potential. The values of discharge potential are different for different ions. For example, the discharge potential of H^+ ions is lower than Na^+ ions when platinum or most of the other metals* are used as cathodes. Similarly, discharge potential of Cl^- ions is lower than that of OH^- ions. This can be explained by some examples given below:

(i) Electrolysis of sodium chloride solution

The solution of sodium chloride besides Na^+ and Cl^- ions possesses H^+ and OH^- ions due to ionisation of water. However, the number is small as water is a weak electrolyte. When potential difference is established across the two electrodes, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. At cathode H^+ ions are discharged in preference to Na^+ ions as the discharge potential of H^+ ions is lower than Na^+ ions. Similarly at anode, Cl^- ions are discharged in preference to OH^- ions.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode	At anode
$H^+ + e^- \longrightarrow H$	$Cl^- \longrightarrow Cl + e^-$
$2H \longrightarrow H_2$	$2Cl \longrightarrow Cl_2$

Thus, Na^+ and OH^- ions remain in solution and the solution when evaporated yields crystals of sodium hydroxide.

(ii) Electrolysis of copper sulphate solution using platinum electrodes

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode	At anode
$Cu^{2+} + 2e^- \longrightarrow Cu$	$2OH^- \longrightarrow H_2O + O + 2e^-$
	$O + O \longrightarrow O_2$

Copper is discharged at cathode as Cu^{2+} ions have lower discharge potential than H^+ ions. OH^- ions are discharged at anode as these have lower discharge potential than SO_4^{2-} ions. Thus, copper is deposited at cathode and oxygen gas is evolved at anode.

(iii) Electrolysis of sodium sulphate solution using inert electrodes

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode	At anode
$H^+ + e^- \longrightarrow H$	$2OH^- \longrightarrow H_2O + O + 2e^-$
$2H \longrightarrow H_2$	$O + O \longrightarrow O_2$

Hydrogen is discharged at cathode as H^+ ions have lower discharge potential than Na^+ ions. OH^- ions are discharged at anode as these have lower discharge potential than SO_4^{2-} ions. Thus, hydrogen is evolved at cathode and oxygen is evolved at anode, *i.e.*, the net reaction describes the electrolysis of water. The ions of Na_2SO_4 conduct the current through the solution and take no part in the overall chemical reaction.

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*When Hg is used as a cathode, Na^+ ions have lower discharge potential than H^+ ions.

The decreasing order of discharge potential or the increasing order of deposition of some of the ions is given below:

For cations: $K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, H^+, Cu^{2+}, Hg^{2+}, Ag^+$

For anions: $SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$

(iv) Electrolysis of copper sulphate solution using copper electrodes

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

At cathode, copper is deposited.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

At anode, the copper of the electrode is oxidised to Cu^{2+} ions or SO_4^{2-} ions dissolve equivalent amount of copper of the anode.

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

or $$Cu + SO_4^{2-} \longrightarrow CuSO_4 + 2e^-$$

Thus, during electrolysis, copper is transferred from anode to cathode.

(v) Electrolysis of silver nitrate solution using silver electrodes

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

At cathode, silver is deposited.

$$Ag^+ + e^- \longrightarrow Ag$$

At anode, the silver of the electrode is oxidised to Ag^+ ions which go into the solution or NO_3^- ions dissolve equivalent amount of silver of the electrode.

$$Ag \longrightarrow Ag^+ + e^-$$

$$Ag + NO_3^- \longrightarrow AgNO_3 + e^-$$

Table 12.1 Some More Examples of Electrolysis

Electrolyte	Electrode	Cathodic reaction	Anodic reaction
Aqueous acidified $CuCl_2$ solution	Pt	$Cu^{2+} + 2e^- \longrightarrow Cu$	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Molten $PbBr_2$	Pt	$Pb^{2+} + 2e^- \longrightarrow Pb$	$2Br^- \longrightarrow Br_2 + 2e^-$
Sodium chloride solution	Hg	$2Na^+ + 2e^- \longrightarrow 2Na$	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Silver nitrate solution	Pt	$Ag^+ + e^- \longrightarrow Ag$	$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$
Sodium nitrate solution	Pt	$2H^+ + 2e^- \longrightarrow H_2$	$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

12.3 FARADAY'S LAWS OF ELECTROLYSIS

The relationship between the quantity of electric charge passed through an electrolyte and the amount of the substance deposited at the electrodes was presented by Faraday in 1834, in the form of laws of electrolysis.

(i) Faraday's first law

When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation:

$$W \propto Q$$

A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs,

$$Q = \text{current in amperes} \times \text{time in seconds}$$
$$= I \times t$$

So, $$W \propto I \times t$$

or $$W = Z \times I \times t$$

where, Z is a constant, known as **electrochemical equivalent,** and is characteristic of the substance deposited.

When a current of one ampere is passed for one second, *i.e.*, one coulomb $(Q = 1)$, then

$$W = Z$$

Thus, **electrochemical equivalent** can be defined as the **mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second.** For example, when a charge of one coulomb is passed through silver nitrate solution, the amount of silver deposited is 0.001118 g. This is the value of electrochemical equivalent of silver.

(ii) Faraday's second law

When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses.

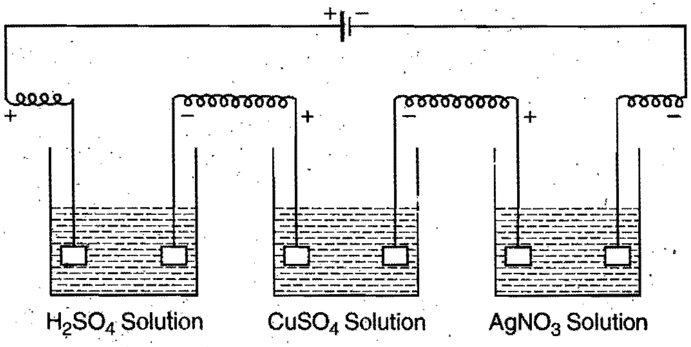


Fig. 12.1 Voltameters arranged in series

The law can be illustrated by passing same quantity of electric current through three voltameters containing solutions of H_2SO_4, $CuSO_4$ and $AgNO_3$ respectively as shown in Fig. 12.1. In the first voltameter, hydrogen and oxygen will be liberated; in the second, copper will be deposited and in the third, silver will be deposited.

$$\frac{\text{Mass of hydrogen}}{\text{Mass of copper}} = \frac{\text{Equivalent mass of hydrogen}}{\text{Equivalent mass of copper}}$$

or
$$\frac{\text{Mass of copper}}{\text{Mass of silver}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}$$

or
$$\frac{\text{Mass of silver}}{\text{Mass of hydrogen}} = \frac{\text{Equivalent mass of silver}}{\text{Equivalent mass of hydrogen}}$$

It is observed that by passing one coulomb of electric charge,

$$\text{Hydrogen evolved} = 0.00001036 \text{ g},$$
$$\text{Copper deposited} = 0.0003292 \text{ g},$$
and
$$\text{Silver deposited} = 0.001118 \text{ g}$$

These masses are in the ratio of their equivalent masses. From these masses, the amount of electric charge required to deposit one equivalent of hydrogen or copper or silver can be calculated.

$$\text{For hydrogen} = \frac{1}{0.00001036} \approx 96500 \text{ coulomb}$$

$$\text{For copper} = \frac{31.78}{0.0003292} \approx 96500 \text{ coulomb}$$

$$\text{For silver} = \frac{107.88}{0.001118} \approx 96500 \text{ coulomb}$$

This follows that 96500 coulomb of electric charge will deposit one g-equivalent of any substance. 96500 coulomb is termed as one **Faraday** and is denoted by F.

Again according to first law,

$$W = Z \times Q$$

When, $Q = 96500$ coulomb, W becomes gram equivalent mass (E).

Thus,
$$E = Z \times 96500$$

or
$$Z = \frac{E}{96500}$$

$$\frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Fundamental unit of charge: As one g-equivalent of an ion is liberated by 96500 coulomb, it follows that charge carried by one g-equivalent of an ion is 96500 coulomb. If the valency of an ion is 'n', then one mole of these ions will carry a charge of nF coulomb. One g-mole of an ion contains 6.02×10^{23} ions. Then,

$$\text{The charge carried by an ion} = \frac{nF}{6.02 \times 10^{23}} \text{ coulomb}$$

For $n = 1$,

$$\text{The fundamental unit of charge} = \frac{F}{6.02 \times 10^{23}}$$

i.e.,
$$\frac{96500}{6.02 \times 10^{23}} \approx 1.6 \times 10^{-19} \text{ coulomb}$$

or
$$1 \text{ coulomb}^{*} = 6.24 \times 10^{18} \text{ electrons}$$

The rate of flowing of electric charge through a conductor is called the electric current.

$$\text{Electric current} = \frac{\text{Electric charge}}{\text{Time}}$$

$$1 \text{ ampere} = \frac{1 \text{ coulomb}}{1 \text{ second}}$$

Volt is a unit of electrical potential difference. It is defined as potential energy per unit charge.

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}} = \frac{1 \text{ newton} \times 1 \text{ metre}}{1 \text{ ampere} \times 1 \text{ second}}$$

$$\begin{aligned}\text{Electrical energy} &= \text{Potential difference} \times \text{Quantity of charge}\\ &= V \times Q\\ &= V \times I \times t \qquad (I = \text{ampere};\ t = \text{second})\\ &= \text{watt-second}\end{aligned}$$

Faraday's Law for Gaseous Electrolytic Product

We know that,
$$\begin{aligned}W &= ZQ\\ &= ZIt\end{aligned}$$

$$W = \frac{ItE}{96500} \qquad \text{... (i)}$$

where,
$$Z = E/96500$$

Equation (i) is used to calculate the mass of solid substance dissolved or deposited at an electrode.

For the gases, we use

$$V = \frac{ItV_e}{96500} \qquad \text{....(ii)}$$

***Coulomb:** It is the unit of electric charge. It is the amount of charge that moves past any given point in a circuit when a current of 1 ampere is supplied for one second.

1 coulomb = 1 ampere-second

It is also defined as the amount of charge which is required to deposit by electrolysis 0.001118 g of silver from a solution of silver nitrate.

An electron has 1.6×10^{-19} coulomb of negative charge. Hence, one coulomb of charge is carried by 6.24×10^{18} electrons. 1 mole of electrons carry a charge of 96500 coulomb. This quantity of charge is called **Faraday.**

Charge carried by 1 mole of electrons

$$\begin{aligned}&= (6.023 \times 10^{23})\,(1.6 \times 10^{-19})\\ &= 96368 \text{ coulomb}\\ &\approx 96500 \text{ coulomb}\end{aligned}$$

where, V = Volume of gas evolved at STP at an electrode
V_e = Equivalent volume
= Volume of gas evolved at an electrode at STP by 1 faraday charge

Illustration

O_2: $M = 32,\ E = 8$

$$32\text{ g } O_2 \equiv 22.4\text{ L at STP}$$
$$8\text{ g } O_2 \equiv 5.6\text{ L at STP}$$

$\left[\begin{array}{l} M = \text{Molecular mass} \\ E = \text{Equivalent mass} \end{array}\right]$

Thus, V_e of $O_2 = 5.6\text{ L}$

H_2: $M = 2,\ E = 1$

$$2\text{ g } H_2 \equiv 22.4\text{ L at STP}$$
$$1\text{ g } H_2 \equiv 11.2\text{ L at STP}$$

Thus, V_e of $H_2 = 11.2\text{ L}$

Cl_2: $M = 71,\ E = 35.5$

$$71\text{ g } Cl_2 \equiv 22.4\text{ L at STP}$$
$$35.5\text{ g } Cl_2 \equiv 11.2\text{ L at STP}$$

Thus, V_e of $Cl_2 = 11.2\text{ L}$

12.4 APPLICATIONS OF ELECTROLYSIS

The phenomenon of electrolysis has wide applications. The important ones are:

(1) Determination of equivalent masses of elements: According to second law of electrolysis when the same quantity of electric current is passed through solutions of salts of two different metals taken in two different cells, the amounts of the metals deposited on the cathodes of the two cells are proportional to their equivalent masses of the respective metals. If the amounts of the metals deposited on the cathodes be W_A and W_B respectively, then

$$\frac{W_A}{W_B} = \frac{\text{Equivalent mass of } A}{\text{Equivalent mass of } B}$$

Knowing the equivalent mass of one metal, the equivalent mass of the other metal can be calculated from the above relationship. The equivalent masses of those non-metals which are evolved at anodes can also be determined by this method.

(2) Electrometallurgy: The metals like sodium, potassium, magnesium, calcium, aluminium, etc., are obtained by electrolysis of fused electrolytes.

Fused electrolyte	Metal isolated
$NaCl + CaCl_2 + KF$	Na
$CaCl_2 + CaF_2$	Ca
Al_2O_3 + cryolite	Al
$MgCl_2$ (35%) + NaCl (50%) + $CaCl_2$ (15%)	Mg
NaOH	Na
$KCl + CaCl_2$	K

(3) Manufacture of non-metals: Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

(4) Electro-refining of metals: The metals like copper, silver, gold, aluminium, tin, etc., are refined by electrolysis.

(5) Manufacture of compounds: Compounds like NaOH, KOH, Na_2CO_3, $KClO_3$, white lead, $KMnO_4$, etc., are manufactured by electrolysis.

(6) Electroplating: The process of coating an inferior metal with a superior metal by electrolysis is known as **electroplating.**

The aims of electroplating are:

(i) To prevent the inferior metal from corrosion.
(ii) To make it more attractive in appearance.

The object to be electroplated is made the cathode and block of the metal to be deposited is made the anode in an electrolytic bath containing a solution of a salt of the anodic metal. On passing electric current in the cell, the metal of the anode dissolves out and is deposited on the cathode-article in the form of a thin film. The following are the requirements for fine coating:

(i) The surface of the article should be free from greasy matter and its oxide layer. The surface is cleaned with chromic acid or detergents.
(ii) The surface of the article should be rough so that the metal deposited sticks permanently.
(iii) The concentration of the electrolyte should be so adjusted as to get smooth coating.
(iv) Current density must be the same throughout.

For electroplating	Anode	Cathode	Electrolyte
With copper	Cu	Object	$CuSO_4$ + dilute H_2SO_4
With silver	Ag	Object	$KAg(CN)_2$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$KAu(CN)_2$
With zinc	Zn	Iron objects	$ZnSO_4$
With tin	Sn	Iron objects	$SnSO_4$

Thickness of Coated Layer

Let the dimensions of metal sheet to be coated be (a cm × b cm).

Thickness of coated layer = c cm

Volume of coated layer = $(a \times b \times c)\text{ cm}^3$

Mass of the deposited substance = volume × density

$$= (a \times b \times c) \times d\text{ g}$$

$$\therefore \quad (a \times b \times c) \times d = \frac{I \times t \times E}{96500}$$

Using above relation we may calculate the thickness of coated layer.

Note: Sometimes radius of atom of deposited metal is given instead of density, *e.g.*,

Radius of silver atom $= 10^{-8}$ cm

Atomic mass of Ag $= 108$

Mass of single silver atom $= \dfrac{108}{6.023 \times 10^{23}}$ g

Volume of single atom $= \dfrac{4}{3} \times \pi R^3$

$$= \frac{4}{3} \times 3.14 \times (10^{-8})^3 \text{ cm}^3$$

$$\text{Density of Ag} = \frac{\text{Mass of single atom}}{\text{Volume of single atom}}$$

$$= \frac{108 / 6.023 \times 10^{23}}{\frac{4}{3} \times 3.14 \times (10^{-8})^3} = 42.82 \text{ g / cm}^3$$

Current Efficiency

Sometimes the ammeter shows false current due to mechanical fault. In this case,

$$\% \text{ current efficiency} = \frac{\text{Actual current}}{\text{Ammeter current}} \times 100$$

[**Note :** The conditions for the operating electrolytic cell are: $\Delta G > 0$ and $E < 0$]

SOME SOLVED EXAMPLES

Example 1. *Find the charge in coulomb on* 1 *g-ion of* N^{3-}.

Solution: Charge on one ion of N^{3-}

$$= 3 \times 1.6 \times 10^{-19} \text{ coulomb}$$

$$\text{one g-ion} = 6.02 \times 10^{23} \text{ ions}$$

Thus, charge on one g-ion of N^{3-}

$$= 3 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23}$$

$$= 2.89 \times 10^5 \text{ coulomb}$$

Example 2. *How much charge is required to reduce* (*a*) 1 *mole of* Al^{3+} *to Al and* (*b*) 1 *mole of* MnO_4^- *to* Mn^{2+}?

Solution: (a) The reduction reaction is:

$$\underset{1 \text{ mole}}{Al^{3+}} + \underset{3 \text{ mole}}{3e^-} \longrightarrow Al$$

Thus, 3 mole of electrons are needed to reduce 1 mole of Al^{3+}.

$$Q = 3 \times F$$

$$= 3 \times 96500 = 289500 \text{ coulomb}$$

(b) The reduction reaction is:

$$\underset{1 \text{ mole}}{MnO_4^-} + 8H^+ + \underset{5 \text{ mole}}{5e^-} \longrightarrow Mn^{2+} + 4H_2O$$

$$Q = 5 \times F$$

$$= 5 \times 96500 = 482500 \text{ coulomb}$$

Example 3. *How much electric charge is required to oxidise* (*a*) 1 *mole of* H_2O *to* O_2 *and* (*b*) 1 *mole of* FeO *to* Fe_2O_3?

Solution: (a) The oxidation reaction is:

$$\underset{1 \text{ mole}}{H_2O} \longrightarrow \frac{1}{2} O_2 + 2H^+ + \underset{2 \text{ mole}}{2e^-}$$

$$Q = 2 \times F$$

$$= 2 \times 96500 = 193000 \text{ coulomb}$$

(b) The oxidation reaction is:

$$FeO + \frac{1}{2} H_2O \longrightarrow \frac{1}{2} Fe_2O_3 + H^+ + e^-$$

$$Q = F = 96500 \text{ coulomb}$$

Example 4. *Exactly* 0.4 *faraday electric charge is passed through three electrolytic cells in series, first containing* $AgNO_3$, *second* $CuSO_4$ *and third* $FeCl_3$ *solution. How many grams of each metal will be deposited assuming only cathodic reaction in each cell?*

Solution: The cathodic reactions in the cells are respectively,

$$\underset{\substack{1 \text{ mole} \\ 108 \text{ g}}}{Ag^+} + \underset{\substack{1 \text{ mole} \\ 1 \text{ F}}}{e^-} \longrightarrow Ag$$

$$\underset{\substack{1 \text{ mole} \\ 63.5 \text{ g}}}{Cu^{2+}} + \underset{\substack{2 \text{ mole} \\ 2 \text{ F}}}{2e^-} \longrightarrow Cu$$

and

$$\underset{\substack{1 \text{ mole} \\ 56 \text{ g}}}{Fe^{3+}} + \underset{\substack{3 \text{ mole} \\ 3 \text{ F}}}{3e^-} \longrightarrow Fe$$

Hence, Ag deposited $= 108 \times 0.4 = 43.2$ g

$$\text{Cu deposited} = \frac{63.5}{2} \times 0.4 = 12.7 \text{ g}$$

and

$$\text{Fe deposited} = \frac{56}{3} \times 0.4 = 7.47 \text{ g}$$

Example 5. *An electric current of* 100 *ampere is passed through a molten liquid of sodium chloride for* 5 *hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.*

Solution: The reaction taking place at anode is:

$$\underset{71.0 \text{ g}}{2Cl^-} \longrightarrow \underset{\substack{71.0 \text{ g} \\ 1 \text{ mole}}}{Cl_2} + \underset{2 \times 96500 \text{ coulomb}}{2e^-}$$

$$Q = I \times t = 100 \times 5 \times 60 \times 60 \text{ coulomb}$$

The amount of chlorine liberated by passing $100 \times 5 \times 60 \times 60$ coulomb of electric charge

$$= \frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole}$$

Volume of Cl_2 liberated at NTP $= 9.3264 \times 22.4 = 208.91$ L

Example 6. *A* 100 *watt,* 110 *volt incandescent lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What mass of cadmium will be deposited by the current flowing for* 10 *hours?*

Solution: We know that,

$$\text{Watt} = \text{ampere} \times \text{volt}$$

$$100 = \text{ampere} \times 110$$

$$\text{Ampere} = \frac{100}{110}$$

$$\text{Quantity of charge} = \text{ampere} \times \text{second}$$

$$= \frac{100}{110} \times 10 \times 60 \times 60 \text{ coulomb}$$

The cathodic reaction is:

$$\underset{112.4 \text{ g}}{Cd^{2+}} + \underset{2 \times 96500 \text{ C}}{2e^-} \longrightarrow Cd$$

Mass of cadmium deposited by passing $\frac{100}{110}\times 10\times 60\times 60$ coulomb charge

$$=\frac{112.4}{2\times 96500}\times\frac{100}{110}\times 10\times 60\times 60=19.0598\text{ g}$$

Example 7. *In an electrolysis experiment, a current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold salt and the second cell contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode in the second cell. Also calculate the magnitude of the current in ampere.*

Solution: We know that,

$$\frac{\text{Mass of Au deposited}}{\text{Mass of Cu deposited}}=\frac{\text{Eq. mass of Au}}{\text{Eq. mass of Cu}}$$

$$\text{Eq. mass of Au}=\frac{197}{3}\ ;\ \text{Eq. mass of Cu}=\frac{63.5}{2}$$

Mass of copper deposited

$$=9.85\times\frac{63.5}{2}\times\frac{3}{197}\text{ g}=4.7625\text{ g}$$

Let Z be the electrochemical equivalent of Cu.

$$E=Z\times 96500$$

or $$Z=\frac{E}{96500}=\frac{63.5}{2\times 96500}$$

Applying $$W=Z\times I\times t$$

$$t=5\text{ hour}=5\times 3600\text{ second}$$

$$4.7625=\frac{63.5}{2\times 96500}\times I\times 5\times 3600$$

or $$I=\frac{4.7625\times 2\times 96500}{63.5\times 5\times 3600}=0.804\text{ ampere}$$

Example 8. *How long has a current of 3 ampere to be applied through a solution of silver nitrate to coat a metal surface of 80 cm^2 with 0.005 mm thick layer? Density of silver is 10.5 g/cm^3.*

Solution: Mass of silver to be deposited

= volume × density

= Area × thickness × density

Given: Area $=80\text{ cm}^2$, thickness $=0.0005$ cm and density $=10.5\text{ g/cm}^3$

$$\text{Mass of silver to be deposited}=80\times 0.0005\times 10.5=0.42\text{ g}$$

Applying to silver $$E=Z\times 96500$$

$$Z=\frac{108}{96500}\text{ g}$$

Let the current be passed for t seconds.

We know that, $$W=Z\times I\times t$$

So, $$0.42=\frac{108}{96500}\times 3\times t$$

or $$t=\frac{0.42\times 96500}{108\times 3}=125.09\text{ second}$$

Example 9. *What current strength in ampere will be required to liberate 10 g of chlorine from sodium chloride solution in one hour?*

Solution: Applying $E=Z\times 96500$ (E for chlorine = 35.5),

$$35.5=Z\times 96500$$

or $$Z=\frac{35.5}{96500}\text{ g}$$

Now, applying the formula

$$W=Z\times I\times t$$

where, $W=10\text{ g}$, $Z=\frac{35.5}{96500}$, $t=60\times 60=3600$ second

$$I=\frac{10\times 96500}{35.5\times 3600}=7.55\text{ ampere}$$

Example 10. *0.2964 g of copper was deposited on passage of a current of 0.5 ampere for 30 minutes through a solution of copper sulphate. Calculate the atomic mass of copper. (1 faraday = 96500 coulomb)*

Solution: Quantity of charge passed

$$=0.5\times 30\times 60=900\text{ coulomb}$$

900 coulomb deposit copper = 0.2964 g

$$96500\text{ coulomb deposit copper}=\frac{0.2964}{900}\times 96500=31.78\text{ g}$$

Thus, 31.78 is the equivalent mass of copper.

$$\text{At. mass}=\text{Eq. mass}\times\text{Valency}$$

$$=31.78\times 2=63.56$$

Example 11. *19 g of molten $SnCl_2$ is electrolysed for some time using inert electrodes until 0.119 g of Sn is deposited at the cathode. No substance is lost during electrolysis. Find the ratio of the masses of $SnCl_2 : SnCl_4$ after electrolysis.*

Solution: The chemical reaction occurring during electrolysis is:

$$\underset{2\times 190\text{ g}}{2SnCl_2}\longrightarrow\underset{261\text{ g}}{SnCl_4}+\underset{119\text{ g}}{Sn}$$

119 g of Sn is deposited by the decomposition of 380 g of $SnCl_2$.

So, 0.119 g of Sn is deposited by the decomposition of

$$\frac{380}{119}\times 0.119=0.380\text{ g of }SnCl_2$$

Remaining amount of $SnCl_2=(19-0.380)=18.62$ g

380 g of $SnCl_2$ produce = 261 g of $SnCl_4$

So, 0.380 g of $SnCl_2$ produce $= \frac{261}{380} \times 0.380 = 0.261$ g of $SnCl_4$

Thus, the ratio $SnCl_2 : SnCl_4 = \frac{18.62}{0.261}$, *i.e.*, 71.34 : 1

Example 12. *A current of* 2.68 *ampere is passed for one hour through an aqueous solution of copper sulphate using copper electrodes. Calculate the change in mass of cathode and that of the anode.* (*At. mass of copper* = 63.5)

Solution: The electrode reactions are:

$$\underset{1\text{ mole}}{Cu^{2+}} + \underset{2\times 96500\text{ C}}{2e^-} \longrightarrow Cu \text{ (Cathode)}$$

$$Cu \longrightarrow Cu^{2+} + 2e^- \text{ (Anode)}$$

Thus, cathode increases in mass as copper is deposited on it and the anode decreases in mass as copper from it dissolves.

Charge passed through cell = 2.68 × 60 × 60 coulomb

$$\text{Copper deposited or dissolved} = \frac{63.5}{2 \times 96500} \times 2.68 \times 60 \times 60$$

$$= 3.174 \text{ g}$$

Increase in mass of cathode = Decrease in mass of anode

$$= 3.174 \text{ g}$$

Example 13. *An ammeter and a copper voltameter are connected in series through which a constant current flows. The ammeter shows* 0.52 *ampere. If* 0.635 *g of copper is deposited in one hour, what is the percentage error of the ammeter?* (*At. mass of copper* = 63.5)

Solution: The electrode reaction is:

$$\underset{1\text{ mole}}{Cu^{2+}} + \underset{2\times 96500\text{ C}}{2e^-} \longrightarrow Cu$$

63.5 g of copper deposited by passing charge

$$= 2 \times 96500 \text{ coulomb}$$

0.635 g of copper deposited by passing charge

$$= \frac{2 \times 96500}{63.5} \times 0.653 \text{ coulomb}$$

$$= 2 \times 965 \text{ coulomb}$$

$$= 1930 \text{ coulomb}$$

We know that,

$$Q = I \times t$$

$$1930 = I \times 60 \times 60$$

$$I = \frac{1930}{3600} = 0.536 \text{ ampere}$$

$$\therefore \quad \text{Percentage error} = \frac{(0.536 - 0.52)}{0.536} \times 100 = 2.985$$

Example 14. *A current of* 3.7 *ampere is passed for* 6 *hours between platinum electrodes in* 0.5 *litre of a* 2 *M solution of* $Ni(NO_3)_2$. *What will be the molarity of the solution at the end of electrolysis? What will be the molarity of the solution if nickel electrodes are used?* (1*F* = 96500 *coulomb*; *Ni* = 58.7)

Solution: The electrode reaction is:

$$\underset{1\text{ mole}}{Ni^{2+}} + \underset{2\times 96500\text{ C}}{2e^-} \longrightarrow Ni$$

Quantity of electric charge passed

$$= 3.7 \times 6 \times 60 \times 60 \text{ coulomb} = 79920 \text{ coulomb}$$

Number of moles of $Ni(NO_3)_2$ decomposed or nickel deposited

$$= \frac{1}{2 \times 96500} \times 79920 = 0.4140$$

Number of moles of $Ni(NO_3)_2$ present before electrolysis

$$= 0.5 \times 2 = 1.0$$

Number of moles of $Ni(NO_3)_2$ present after electrolysis

$$= (1.0 - 0.4140) = 0.586$$

Since, 0.586 moles are present in 0.5 litre,

$$\text{Molarity of the solution} = 2 \times 0.586 = 1.72\,M$$

When nickel electrodes are used, anodic nickel will dissolve and get deposited at the cathode. The molarity of the solution will, thus, remain unaffected.

Example 15. *An acidic solution of* Cu^{2+} *salt containing* 0.4 *g of* Cu^{2+} *is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with volume of solution kept at* 100 *mL and the current at* 1.2 *amp. Calculate the gases evolved at NTP during the entire electrolysis.*

Solution: $0.4 \text{ g of } Cu^{2+} = \frac{0.4}{31.75} = 0.0126 \text{ g-equivalent}$

At the same time, the oxygen deposited at anode

$$= 0.0126 \text{ g-equivalent}$$

$$= \frac{8}{32} \times 0.0126 = 0.00315 \text{ g-mole}$$

After the complete deposition of copper, the electrolysis will discharge hydrogen at cathode and oxygen at anode.

The amount of charge passed = 1.2 × 7 × 60 = 504 coulomb

$$\text{So, Oxygen liberated} = \frac{1}{96500} \times 504 = 0.00523 \text{ g-equivalent}$$

$$= \frac{8}{32} \times 0.00523 = 0.001307 \text{ g-mole}$$

Hydrogen liberated = 0.00523 g-equivalent

$$= \frac{1}{2} \times 0.00523 = 0.00261 \text{ g-mole}$$

$$\text{Total gases evolved} = (0.00315 + 0.001307 + 0.00261) \text{ g-mole}$$

$$= 0.007067 \text{ g-mole}$$

Volume of gases evolved at NTP

$$= 22400 \times 0.007067 \text{ mL}$$

$$= 158.3 \text{ mL}$$

Example 16. *A current of* 1.70 *ampere is passed through* 300 *mL of* 0.160 *M solution of zinc sulphate for* 230 *seconds with a current efficiency of* 90 *per cent. Find out the molarity of* Zn^{2+} *ions after the deposition of zinc. Assume the volume of the solution to remain constant during electrolysis.* **(IIT 1991)**

Solution: Amount of charge passed = 1.70 × 230 coulomb

$$\text{Amount of actual charge passed} = \frac{90}{100} \times 1.70 \times 230$$

$$= 351.9 \text{ coulomb}$$

No. of moles of Zn deposited by passing 351.9 coulomb of charge

$$= \frac{1}{2 \times 96500} \times 351.9 = 0.000182$$

Molarity of Zn^{2+} ions after deposition of zinc

$$= \left[0.160 - \frac{0.000182 \times 1000}{300}\right] M$$

$$= 0.154\ M$$

Example 17. *Calculate the electricity that would be required to reduce* 12.3 *g of nitrobenzene to aniline, if the current efficiency for the process is* 50 *per cent. If the potential drop across the cell is* 3.0 *volt, how much energy will be consumed?*

[AIPMT (Mains) 2008]

Solution: The reduction reaction is:

$$\underset{\substack{123\,g \\ 1\text{ mole}}}{C_6H_5NO_2} + \underset{\substack{6\,g \\ 3\text{ mole}}}{3H_2} \longrightarrow C_6H_5NH_2 + 2H_2O$$

Hydrogen required for reduction of $\frac{12.3}{123}$ or 0.1 mole of nitrobenzene $= 0.1 \times 3 = 0.3$ mole

Amount of charge required for liberation of 0.3 mole of hydrogen $= 2 \times 96500 \times 0.3 = 57900$ coulomb

Actual amount of charge required as efficiency is 50%

$$= 2 \times 57900 = 115800 \text{ coulomb}$$

$$\text{Energy consumed} = 115800 \times 3.0 = 347400 \text{ J}$$

$$= 347.4 \text{ kJ}$$

Example 18. *An aqueous solution of sodium chloride on electrolysis gives $H_2(g)$, $Cl_2(g)$ and NaOH according to the reaction:*

$$2Cl^-(aq.) + 2H_2O \longrightarrow 2OH^-(aq.) + H_2(g) + Cl_2(g)$$

A direct current of 25 *ampere with a current efficiency* 62% *is passed through* 20 *L of NaCl solution* (20% *by mass*). *Write down the reactions taking place at the anode and cathode. How long will it take to produce* 1 *kg of Cl_2? What will be the molarity of the solution with respect to hydroxide ion? Assume no loss due to evaporation.* (IIT 1992)

Solution: Reactions at anode and cathode are:

$$2Cl^- \longrightarrow Cl_2 + 2e^- \quad \text{(at anode)}$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad \text{(at cathode)}$$

$$1 \text{ kg of } Cl_2 = \frac{1000}{71.0} = 14.08 \text{ mole}$$

Charge to produce one mole of $Cl_2 = 2 \times 96500$ coulomb

Charge to produce 14.08 mole of $Cl_2 = 2 \times 96500 \times 14.08$ coulomb

$$\text{Effective current} = \frac{62}{100} \times 25.0 = 15.5 \text{ ampere}$$

$$\text{Time} = \frac{\text{Charge}}{\text{Current}} = \frac{2 \times 96500 \times 14.08}{15.5}$$

$$= 175318.7 \text{ second} = 48.699 \text{ hour}$$

OH^- ions produced $= 2 \times$ moles of Cl_2

$$= 2 \times 14.08 = 28.16 \text{ mole}$$

$$\text{Molarity} = \frac{\text{Mole}}{\text{Volume}} = \frac{28.16}{20} = 1.408\ M$$

Example 19. *Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following reaction:*

$$CrO_3 + 6H^+ + 6e^- \longrightarrow Cr + 3H_2O$$

Calculate the mass of chromium plated out by 24000 *coulomb. How long will it take to plate out* 1.5 g *of chromium using* 12.5 *ampere current?* (IIT 1993)

Solution:

$$CrO_3 + 6H^+ + \underset{6 \times 96500\text{ C}}{6e^-} \longrightarrow \underset{\substack{1\text{ mole} \\ 52\text{ g}}}{Cr} + 3H_2O$$

Mass of chromium plated out by 24000 coulomb charge

$$= \frac{52}{6 \times 96500} \times 24000 = 2.155 \text{ g}$$

Charge required for plating out 1.5 g of chromium

$$= \frac{6 \times 96500}{52} \times 1.5 = 16701.92 \text{ coulomb}$$

$$\text{Time} = \frac{\text{Charge}}{\text{Current}} = \frac{16701.92}{12.5} = 1336.15 \text{ second}$$

$$= 22.27 \text{ minute}$$

Example 20. *After electrolysis of a sodium chloride solution with inert electrodes for a certain period of time,* 600 *mL of the solution was left which was found to be* 1 *N in NaOH. During the same period* 31.75 *g of copper was deposited in the copper voltameter in series with the electrolytic cell. Calculate the percentage theoretical yield of NaOH obtained.*

Solution: Equivalent mass of NaOH = 40

$$\text{Amount of NaOH formed} = \frac{40}{1000} \times 600 = 24 \text{ g}$$

31.75 g of Cu = 1 g-equivalent of Cu.

During the same period, 1 g-equivalent of NaOH should have been formed.

1 g-equivalent of NaOH = 40 g

$$\% \text{ yield} = \frac{24}{40} \times 100 = 60$$

Example 21. *Peroxy disulphuric acid ($H_2S_2O_8$) can be prepared by electrolytic oxidation of H_2SO_4 as:*

$$2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$$

Oxygen and hydrogen are by products. In such an electrolysis 9.72 *litre of H_2 and* 2.35 *litre of O_2 were generated at NTP. What is the mass of peroxy disulphuric acid formed?*

Solution:

Anodic reaction: $2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$

$$2H_2O \longrightarrow 4H^+ + O_2 + 2e^-$$

Cathodic reaction: $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

Total equivalent of $H_2S_2O_8$ + equivalent of oxygen

$$= \text{Equivalent of } H_2$$

$$9.72 \text{ litre } H_2 = \frac{9.72}{11.2} = 0.868 \text{ equivalent}$$

$$2.35 \text{ litre } O_2 = \frac{2.35}{5.6} = 0.42 \text{ equivalent}$$

$$\text{Equivalent of } H_2S_2O_8 = (0.868 - 0.420) = 0.448$$

$$\text{Mass of } H_2S_2O_8 = 0.448 \times \frac{194}{2} = 43.456 \text{ g}$$

Example 22. *Cadmium amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. Find how long a current of 5 ampere should be passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2 g mercury. At. mass of Cd = 112.40.*

Solution: 2 g Hg require Cd to prepare 12% amalgam

$$= \frac{12}{88} \times 2 = 0.273 \text{ g}$$

$$\begin{array}{llll} Cd^{2+} & + & 2e^- & \longrightarrow Cd \\ \text{1 mole} & & 2 \times 96500 \text{ C} & \\ 112.40 \text{ g} & & & \end{array}$$

Charge required to deposit 0.273 g of Cd

$$= \frac{2 \times 96500}{112.40} \times 0.273 \text{ coulomb}$$

$$\text{Charge} = \text{ampere} \times \text{second}$$

$$\text{Second} = \frac{2 \times 96500 \times 0.273}{112.40 \times 5} = 93.75$$

Example 23. *Assume that impure copper contains iron, gold and silver as impurities. After passing a current of 140 ampere for 482.5 second, the mass of anode decreased by 22.260 g and the cathode increased in mass by 22.011 g. Estimate the percentage of iron and copper originally present.*

Solution: The increase at the cathode is due to copper only. Hence, there is 22.011 g of copper and rest impurities of iron, gold and silver.

$$\text{Mass of impurities} = (22.260 - 22.011) = 0.249 \text{ g}$$

At anode, only copper and iron are oxidised; the gold and silver collect below anode in the form of anodic mud.

$$\underset{\text{(Copper and iron)}}{M} \longrightarrow M^{2+} + 2e^-$$

$$\text{No. of moles of metal oxidised} = \frac{140 \times 482.5}{2 \times 96500} = 0.35$$

$$\text{No. of moles of copper} = \frac{22.011}{63.5} = 0.3466$$

$$\text{No. of moles of iron} = (0.35 - 0.3466) = 0.0034$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Amount of energy used in the passage of 1 amp current for 100 sec under a potential of 115 V is:

(a) 20 kJ (b) 11.5 kJ (c) 115 kJ (d) 0.115 kJ

[Ans. (b)]

[Hint: $Q = I \times t = 1 \times 100 = 100$ C

$$\text{Energy} = \text{charge} \times \text{potential}$$
$$= 100 \times 115 = 11500 \text{ J} = 11.5 \text{ kJ}]$$

2. One litre of 1 *M* $CuSO_4$ solution is electrolysed. After passing 2*F* charge, the molarity of $CuSO_4$ will be:

(a) *M*/2 (b) *M*/4 (c) *M* (d) zero

[Ans. (d)]

[Hint: 2*F* charge will deposit 2 equivalent or 1 mole of copper

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Thus, all the copper from $CuSO_4$ solution will be deposited and molarity of remaining $CuSO_4$ solution will be zero.]

3. The time required to coat a metal surface of 80 cm^2 with 5×10^{-3} cm thick layer of silver (density 1.05 g/cm^3) by passing a current of 3 amp through silver nitrate solution is:

(a) 115 sec (b) 125 sec (c) 135 sec (d) 145 sec

[Ans. (b)]

[Hint:

Mass of silver in coated layer = volume × density

$$= (80 \times 5 \times 10^{-3}) \times 1.05 \text{ g}$$
$$= 0.42 \text{ g}$$

$$\because \quad W = \frac{ItE}{96500}$$

$$\therefore \quad t = \frac{W \times 96500}{I \times E} = \frac{0.42 \times 96500}{3 \times 108} = 125.09 \text{ sec}]$$

4. 4.5 g of aluminium (At. mass = 27 amu) is deposited at cathode from Al^{3+} solution by a 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: **[CBSE (PMT) 2005]**

(a) 44.8 L (b) 22.4 L (c) 11.2 L (d) 5.6 L

[Ans. (d)]

[Hint: Number of equivalents of aluminium deposited

$$= \frac{4.5}{9} = 0.5$$

∴ Number of equivalents of H_2 will also be 0.5.

Volume of H_2 gas at STP = Number of equivalents × Equivalent volume

$$= 0.5 \times 11.2 = 5.6 \text{ L}]$$

5. Cost of electricity for the production of *x* L H_2 at NTP at cathode is Rs *x*; then cost of production of *x* L O_2 at NTP at anode will be : (assume 1 mole of electrons as one unit of electricity)

(a) 2*x* (b) 4*x* (c) 16*x* (d) 32*x*

[Ans. (a)]

[Hint: $\dfrac{\text{Volume of } H_2}{\text{Volume of } O_2} = \dfrac{\text{Equivalent volume of } H_2}{\text{Equivalent volume of } O_2}$

$$\frac{x}{\text{Volume of } O_2} = \frac{11.2}{5.6} = 2$$

$$\text{Volume of } O_2 = \frac{x}{2}$$

Thus, $\frac{x}{2}$ L O_2 requires Rs x for its production,

i.e., x L O_2 will require Rs $2x$ for the production.]

6. What current is to be passed for 0.25 sec for deposition of certain weight of metal which is equal to its electrochemical equivalent? **[AMU (Medical) 2006]**

(a) 4 A (b) 100 A (c) 200 A (d) 2 A

[**Ans.** (a)]

[**Hint:**
$$W = ZIt$$
$$\frac{W}{Z} = It$$
$$1 = It = I \times 0.25$$
$$I = 4 \text{ amp.}]$$

7. If the aqueous solutions of the following salts are electrolysed for 1 hour with 10 ampere current, which solution will deposit the maximum mass of the metal at cathode? The atomic weights are: Fe = 56, Zn = 65, Ag = 108, Hf = 178 and W = 184. **[PMT (Kerala) 2006]**

(a) $ZnSO_4$ (b) $FeCl_3$ (c) $HfCl_4$ (d) WCl_6

(e) $AgNO_3$

[**Ans.** (e)]

[**Hint:** Greater is the equivalent mass of the metal more will be the amount deposited at cathode.

Compound	Equivalent mass of metals
$ZnSO_4$	$65/2 = 32.5$
$FeCl_3$	$56/3 = 18.66$
$HfCl_4$	$178/4 = 44.5$
WCl_6	$184/6 = 30.66$
$AgNO_3$	$108/1 = 108$

∴ Maximum amount of silver will be deposited at cathode.]

8. When a quantity of electricity is passed through $CuSO_4$ solution, 0.16 g of copper gets deposited. If the same quantity of electricity is passed through acidulated water, then the volume of H_2 liberated at STP will be: (given atomic weight of Cu = 64) **(KCET 2006)**

(a) 4 cm^3 (b) 56 cm^3 (c) 604 cm^3 (d) 8 cm^3

[**Ans.** (b)]

[**Hint:** Number of equivalents of copper deposited $= \frac{0.16}{32} = 0.005$

Volume of H_2 gas at STP $= 11.2 \times 0.005$
$= 0.056$ litre $= 56 \text{ cm}^3$]

9. Number of faraday's required to generate one gram atom of magnesium from molten $MgCl_2$ is: **[PMT (MP) 2007]**

(a) 1 (b) 2 (c) 3 (d) 4

[**Ans.** (b)]

[**Hint:** $Mg^{2+} + 2e^- \longrightarrow Mg$

1 mole of Mg atom requires 2 mole of electrons, *i.e.*, 2 faraday of charge.]

10. A direct current deposits 54 g of silver (Atomic mass = 108) during electrolysis. How much aluminium (Atomic mass = 27) would be deposited from aluminium chloride solution by the same amount of electricity? **[PMT (Kerala) 2008]**

(a) 4.5 g (b) 5.4g (c) 54g (d) 2.7g

(e) 27g

[**Ans.** (a)]

[**Hint:** Equivalent mass of silver = 108

Equivalent mass of aluminium in $(AlCl_3) = \frac{27}{3} = 9$

$$\frac{W_{Ag}}{W_{Al}} = \frac{E_{Ag}}{E_{Al}}$$
$$\frac{54}{W_{Al}} = \frac{108}{9}$$
$$W_{Al} = 4.5 \text{ g}]$$

SECTION II : CONDUCTANCE AND CONDUCTORS

12.5 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

In order to explain the properties of electrolytic solutions, Arrhenius put forth, in 1884, a comprehensive theory which is known as theory of **electrolytic dissociation** or **ionic theory.** The main points of the theory are:

(i) An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called ions. Positively charged ions are termed cations and negatively charged as anions.

$$AB \longrightarrow A^+ + B^-$$

$$NaCl \longrightarrow Na^+ + Cl^-$$

$$\underset{\text{Electrolyte}}{K_2SO_4} \longrightarrow \underbrace{2K^+ + SO_4^{2-}}_{\text{Ions}}$$

In its modern form, the theory assumes that solid electrolytes are composed of ions which are held together by electrostatic forces of attraction. When an electrolyte is dissolved in a solvent, these forces are weakened and the electrolyte undergoes dissociation into ions. The ions are solvated.

$$A^+B^- \longrightarrow A^+ + B^-$$

or
$$A^+B^- + aq. \longrightarrow A^+(aq.) + B^-(aq.)$$

(ii) The process of splitting of the molecules into ions of an electrolyte is called **ionisation.** The fraction of the total number of molecules present in solution as ions is known as **degree of ionisation** or **degree of dissociation.** It is denoted by 'α'

$$\alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$$

It has been observed that all electrolytes do not ionise to the same extent. Some are almost completely ionised while others are feebly ionised. The degree of ionisation depends on a number of factors (see 12.6).

(iii) Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionised and non-ionised molecules, *i. e.*,

$$AB \rightleftharpoons A^+ + B^-$$

Applying the law of mass action to above equilibrium

$$\frac{[A^+][B^-]}{[AB]} = K$$

K is known as ionisation constant. The electrolytes having high value of K are termed **strong electrolytes** and those having low value of K as **weak electrolytes.**

(iv) When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged, *i. e.*, electrolysis occurs.

The ions are discharged always in equivalent amounts, no matter what their relative speeds are.

(v) The electrolytic solution is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always.

$AB \rightleftharpoons A^+ + B^-$ (Both ions are equal)

$NaCl \rightleftharpoons Na^+ + Cl^-$ (Both ions are equal)

$AB_2 \rightleftharpoons A^{2+} + 2B^-$ (Anions are double that of cations)

$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$ (Anions are double that of cations)

$A_2B \rightleftharpoons 2A^+ + B^{2-}$ (Cations are double that of anions)

$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$ (Cations are double that of anions)

(vi) The properties of electrolytes in solution are the properties of ions present in solution. For example, acidic solution always contains H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^+ ions and OH^- ions respectively.

(vii) The ions act like molecules towards depressing the freezing point, elevating the boiling point, lowering the vapour pressure and establishing the osmotic pressure.

(viii) The conductivity of the electrolytic solution depends on the nature and number of ions as the current is carried through solution by the movement of ions.

Evidences in Favour of Ionic Theory

A large number of experimental observations are available which support Arrhenius theory. A few of them are given below:

(i) **Ions present in solid electrolytes:** X-ray diffraction studies have shown that electrolytes are composed of ions. For example, a crystal of NaCl does not contain NaCl units but Na^+ and Cl^- ions. Each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion in turn is surrounded by six Na^+ ions. The whole system is composed of equal number of Na^+ and Cl^- ions. The ionic compounds behave as good conductors in fused state. It can only be possible if ions are already present in ionic solids.

(ii) Ohm's law applicability: The electrolytic solutions like metallic conductors obey Ohm's law, *i. e.*, the strength of the current flowing through a conductor is directly proportional to potential difference (E) applied across the conductor and is inversely proportional to the resistance of the conductor. Mathematically,

$$I = E/R$$

This can only be possible if ions are already present in the solution and no part of the current is used in splitting up the molecules into ions. The current has only directive effect on the ions.

(iii) Ionic reactions: Evidence for the existence of ions in aqueous solutions of electrolytes is furnished by well known reactions in inorganic chemistry. A white precipitate of silver chloride is obtained whenever Ag^+ ions come in contact with chloride ions.

$$Ag^+ + NO_3^- + Na^+ + Cl^- \longrightarrow \underset{\text{ppt.}}{AgCl} + Na^+ + NO_3^-$$

But no precipitation occurs when $AgNO_3$ solution is added to CCl_4, $CHCl_3$ or C_2H_5Cl as these substances being non-electrolytes do not furnish Cl^- ions in solution.

An acid which gives all tests of H^+ ions in aqueous solution, does not give the same tests when dissolved in any organic solvent because no ionisation of the acid occurs in the organic solvent to furnish H^+ ions.

(iv) Heat of neutralization: When one gram-equivalent of a strong acid is neutralized by one gram-equivalent of a strong base, the heat evolved is always the same, *i. e.*, 13.7 kcal. This can be explained on the basis of Arrhenius theory that an acid furnished H^+ ions and base OH^- ions when dissolved in water and the process of neutralisation involves the common reaction.

$$H^+ + OH^- \rightleftharpoons H_2O + 13.7\,\text{kcal}$$

Thus, heat of neutralisation is actually the heat of formation of H_2O from H^+ and OH^- ions.

(v) Abnormal colligative properties: The abnormal behaviour towards colligative properties as observed in the case of electrolytes can be explained on the basis of ionic theory. When an electrolyte is dissolved in water, the number of particles in the solution is always more than the number of molecules actually dissolved due to ionisation. The van't Hoff factor,

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

is always more than one, *i. e.*, $i = 1 + (n - 1)\alpha$ where, 'n' is the number of ions produced by the ionisation of one molecule of the electrolyte and 'α' is the degree of ionisation.

(vi) Colour of solutions: The colour of the electrolytes in solution, if any, is due to their ions. The $CuSO_4$ is blue in solution due to the presence of Cu^{2+} ions. Potassium permanganate ($KMnO_4$) is purple in solution due to the presence of MnO_4^- ions.

(vii) Explanation of some other phenomena: Ionic theory provides satisfactory explanations regarding various phenomena such as electrolysis, conductivity, salt hydrolysis, solubility product, etc.

Limitations of Arrhenius Theory

(i) Ostwald's dilution law which is based on Arrhenius theory is not applicable to strong electrolytes.

(ii) Strong electrolytes conduct electricity in fused state, *i.e.*, in absence of water. This is in contradiction of Arrhenius theory according to which the presence of solvent is a must for ionisation.

(iii) Arrhenius theory assumes independent existence of ions but fails to account for the factors which influence the mobility of the ions.

12.6 FACTORS PERTAINING TO DEGREE OF IONISATION

The degree of ionisation of an electrolyte in solution depends upon the following factors:

(i) Nature of solute: When the ionisable parts of a molecule of a substance are held more by covalent bonding than by electrovalent bonding, less ions are furnished in solution. Such substances are termed weak electrolytes. H_2S, HCN, NH_4OH, CH_3COOH are examples of this class. NaCl, $Ba(NO_3)_2$, KOH, etc., are strong electrolytes, in which the transfer of electrons seems to be more or less complete, furnish ions immediately when dissolved. Strong electrolytes are almost completely ionised in solution.

(ii) Nature of solvent: The main function of the solvent is to weaken the electrostatic forces of attraction between the two ions and separate them. The force of attraction holding the ions together in any medium is expressed as:

$$F = \frac{1}{K}\frac{q_1 q_2}{r^2}$$

where, K is the dielectric constant of medium.

Any solvent which has high value of dielectric constant has the capacity of separating ions. Water is considered to be the best solvent as it has the highest dielectric constant. The dielectric constants of some of the solvents are given below at 25°C.

Water	Methyl alcohol	Ethyl alcohol	Acetone
81	35	27	21

(iii) Dilution: The extent of ionisation of an electrolyte is inversely proportional to the concentration of its solution. Thus, degree of ionisation increases with the increase of dilution of the solution, *i.e.*, decreasing the concentration of the solution.

(iv) Temperature: The degree of ionisation increases with the increase of temperature. This is due to the fact that at higher temperature molecular speed is increased which overcomes the forces of attraction between the ions.

12.7 ELECTROLYTIC CONDUCTANCE

The conductance is the property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance, *i.e.*,

$$\text{Conductance} = \frac{1}{\text{Resistance}} = \frac{1}{R} \quad \text{... (i)}$$

It is expressed in the unit called reciprocal ohm (ohm^{-1} or mho) or siemens.

Specific Conductance or Conductivity

The resistance of any conductor varies directly as its length (l) and inversely as its cross-sectional area (a), *i.e.*,

$$R \propto \frac{l}{a} \text{ or } R = \rho\frac{l}{a} \quad \text{... (ii)}$$

where, ρ is called the specific resistance.

If $l = 1$ cm and $a = 1\ cm^2$, then

$$R = \rho \quad \text{... (iii)}$$

The specific resistance is, thus, defined as the resistance of one centimetre cube of a conductor.

The reciprocal of specific resistance is termed the **specific conductance** or it is the conductance of one centimetre cube of a conductor.

It is denoted by the symbol κ. Thus,

$$\kappa = \frac{1}{\rho}, \quad \kappa = \text{kappa—The specific conductance} \quad \text{... (iv)}$$

Specific conductance is also called conductivity.

From eq. (ii), we have

$$\rho = \frac{a}{l}\cdot R \text{ or } \frac{1}{\rho} = \frac{l}{a}\cdot\frac{1}{R}$$

$$\kappa = \frac{l}{a}\times C \qquad \left(\frac{l}{a} = \text{cell constant}\right)$$

or Specific conductance = conductance × cell constant

In the case of electrolytic solutions, the specific conductance is defined as the conductance of a solution of definite dilution enclosed in a cell having two electrodes of unit area separated by one centimetre apart as shown in Fig. 12.2.

The unit of specific conductance is $ohm^{-1}\ cm^{-1}$.

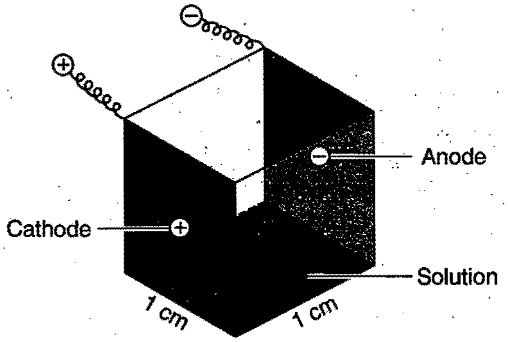


Fig. 12.2 Representation of specific conductance

Equivalent Conductance

One of the factors on which the conductance of an electrolytic solution depends, is the concentration of the solution. In order to obtain comparable results for different electrolytes, it is necessary to take equivalent conductances.

Equivalent conductance is defined as the conductance of all the ions produced by **one gram-equivalent** of an electrolyte in a given solution. It is denoted by Λ.

To understand the meaning of equivalent conductance, imagine a rectangular trough with two opposite sides made of metallic conductor (acting as electrodes) exactly 1 cm apart, If $1\ cm^3$ (1 mL)

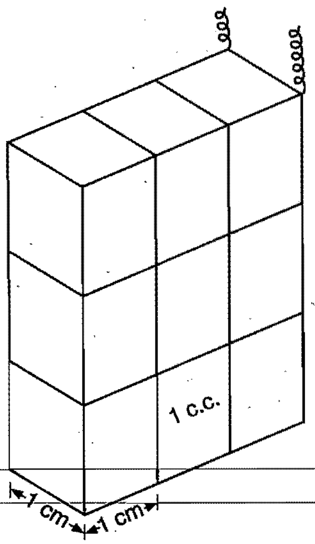


Fig. 12.3

solution containing 1 gram-equivalent of an electrolyte is placed in this container and conductance is measured.

According to definitions,

Conductance = Specific conductance (κ)

= Equivalent conductance (Λ)

If the solution is diluted to say ($9\,\text{cm}^3$) (9 mL), the conductance of the solution will be the same but specific conductance becomes 1/9 th as it contains nine cubes. The conductance is also equal to the equivalent conductance because the solution still has 1 g-equivalent of the electrolyte. This is shown in Fig. 12.3. Thus,

Equivalent conductance $(\Lambda) = 9 \times \kappa$

In general,

$$\Lambda = \kappa \times V \qquad \text{... (v)}$$

where, V is the volume in mL containing 1 g-equivalent of the electrolyte.

In case, if the concentration of the solution is c g-equivalent per litre, then the volume containing 1 g-equivalent of the electrolyte will be $1000/c$.

So, equivalent conductance,

$$\Lambda = \kappa \times \frac{1000}{c} \qquad \text{... (vi)}$$

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

where, N = normality

The unit of equivalent conductance is $\text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$.

Molar Conductance

The molar conductance is defined as the conductance of all the ions produced by ionisation of **1 g-mole** of an electrolyte when present in V mL of solution. It is denoted by μ.

$$\text{Molar conductance } \mu = \kappa \times V \qquad \text{... (vii)}$$

where, V is the volume in mL containing 1 g-mole of the electrolyte. If c is the concentration of the solution in g-mole per litre, then

$$\mu = \kappa \times \frac{1000}{c}$$

Its unit is $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

$$\text{Equivalent conductance} = \frac{\text{Molar conductance}}{n}$$

where, $$n = \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

Measurement of Conductance

It is now known to us that when the solution of an electrolyte is taken between two parallel electrodes of cross-sectional area 'a' and 'l' cm apart, then the specific conductance, κ, should be:

$$\kappa = \frac{l}{a} \cdot \frac{1}{R}$$

Thus, knowing the values of R, l and a, the specific conductance can be measured. The resistance of the solution between two parallel electrodes is determined by using Wheatstone bridge method. The diagram of the apparatus is shown in Fig. 12.4. AB is a uniform wire and X is a sliding contact which moves over it. C is the conductivity cell containing the solution of the electrolyte and S represents the source of alternating current. R is the resistance box and T is a headphone to detect the flow of current. A suitable resistance is taken out from the resistance box and the sliding contact X is moved on the wire to search a point of minimum sound in the headphone. At this point, the bridge is balanced.

$$\frac{\text{Resistance of solution}}{\text{Resistance from resistance box}} = \frac{\text{Resistance } XB}{\text{Resistance } XA} = \frac{\text{Length } XB}{\text{Length } XA}$$

Thus, resistance of solution can be determined. Reciprocal of this resistance gives the conductance of solution.

Direct current (DC) cannot be used because it produces two complications.

(i) Change in the concentration of the solution occurs due to electrolysis which will change the resistance.

(ii) Polarisation at the electrodes sets in which also changes the resistance.

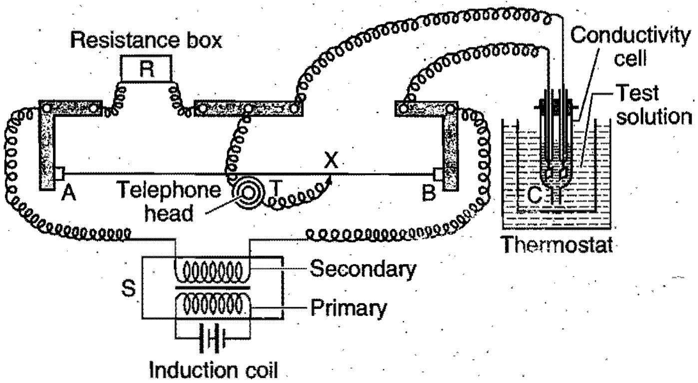


Fig. 12.4 Determination of conductivity

Thus, an alternating current (AC) is used to overcome the above complications.

The solution whose conductance is to be measured is taken in a special type of cell known as conductivity cell. Various types of cells are shown in Fig. 12.5. The electrodes consist of platinum discs coated with finely divided platinum black and welded to platinum wires fused in two glass tubes. The glass tubes contain mercury and are firmly fixed in the cover of cells. Contact with the platinum is made by dipping the copper wires of the circuit in the mercury contained in the tubes. As the conductivity changes with temperature, the cell is usually placed in a constant temperature bath during the experiment. Cells with long paths are used for concentrated solutions and cells with short paths and large electrodes are used for dilute solutions.

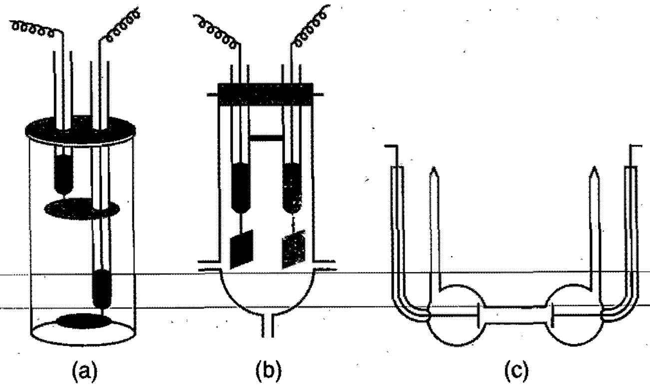


Fig. 12.5 Conductance cells

Cell Constant

Since, the electrodes are not exactly 1 unit apart and may not possess a surface area of 1 square unit, the measured resistance does not give the specific conductance of the solution. Actual measurements of l and a being inconvenient, an indirect method is employed to determine the value of $\frac{l}{a}$ which is a constant quantity for a particular cell and is known as cell constant. We know that,

$$\frac{\text{Specific conductance}}{\text{Conductance}} = \frac{l}{a} = \text{Cell constant}$$

The resistance of cell, *i.e.*, conductance is measured when filled with a standard solution (say $N/10\,\text{KCl}$ solution) at a given temperature. The standard values of specific conductance of KCl solutions of various concentrations at different temperatures are known. Thus, the cell constant is calculated by using the above equation. The same cell constant applies to a measurement with any other solution.

The determination of specific conductance of an electrolytic solution, thus, consists of two steps:

Step I: Determination of cell constant by using a standard KCl solution of known concentration in the conductivity cell.

Step II: Determination of resistance of the given solution using the same cell. The reciprocal of this gives the value of conductance.

Multiplication of conductance and cell constant gives the value of specific conductance of the solution.

In order to determine equivalent conductance or molar conductance, the concentration of the experimental solution should be known. In conductance measurements, the solutions are always prepared in **conductivity water** which has no conductance due to dissolved impurities. It is prepared by distilling a number of times the distilled water to which a little $KMnO_4$ and KOH have been added in a hard glass distillation assembly. Such water has very low conductance of the order of 4.3×10^{-8} ohm^{-1}. For ordinary purposes, double distilled water may be used.

Effect of Dilution on Equivalent Conductance

The value of equivalent conductance increases with dilution. This is due to the fact that degree of ionisation increases with dilution thereby increasing the total number of ions in solution. Solution which contains large number of ions compared to another solution of the same concentration at the same temperature has more conductance and is said to be **stronger electrolyte.** The one which has relatively small number of ions is called a **weak electrolyte.** The number of ions from an electrolyte depends on the degree of dissociation. The curve (Fig. 12.6) shows the variation of the equivalent conductance of some electrolytes with dilution. It shows that electrolytes behave in two ways on dilution:

(i) Electrolytes like KCl have high value of conductance even at low concentration and there is no rapid increase in their equivalent conductance on dilution. Such electrolytes are termed **strong electrolytes.** In the case of strong electrolytes, there is a tendency for equivalent conductance to approach a limiting value when the concentration approaches zero. When the whole of the electrolyte has ionised, further addition of the water does not bring any change in the value of equivalent conductance. This stage is called infinite dilution. The equivalent conductance has a limiting value at infinite dilution and is represented by Λ_∞.

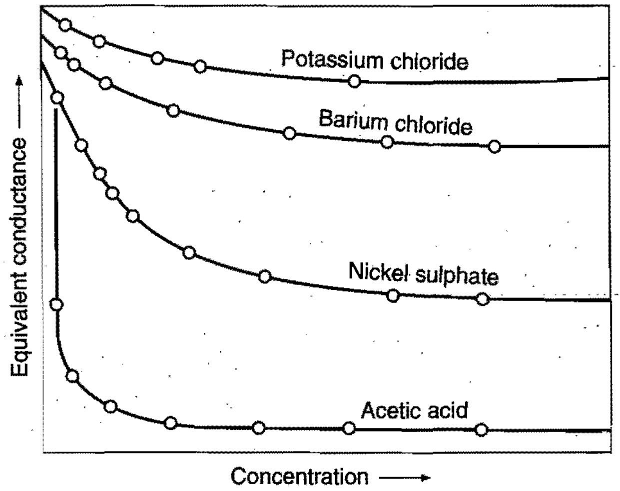


Fig. 12.6 Conductance curve

(ii) Electrolytes like acetic acid have a low value at high concentration and there is a rapid increase in the value of equivalent conductance with dilution. Such electrolytes are termed **weak electrolytes.** There is no indication that a limiting value of equivalent conductance can be attained even when the concentration approaches zero. Thus, graphically, Λ_∞ of weak electrolytes cannot be obtained.

It is thus concluded that equivalent conductance of electrolytes whether strong or weak increases with dilution and reaches to a maximum or limiting value which is termed Λ_∞ (equivalent conductance at infinite dilution). Λ_∞ in the case of strong electrolytes can be obtained by extrapolation of the graph of equivalent conductance to zero concentration but in the case of weak electrolytes it cannot be obtained accurately. An indirect method for obtaining Λ_∞ for weak electrolytes has been given by Kohlrausch.

12.8 KOHLRAUSCH'S LAW

"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", *i.e.*, anions and cations. Thus,

$$\Lambda_\infty = \lambda_a + \lambda_c$$

The λ_c and λ_a are called the ionic conductances of cation and anion at infinite dilution respectively. The ionic conductances are proportional to their ionic mobilities. Thus, at infinite dilution,

$$\lambda_c = ku_c$$

and $$\lambda_a = ku_a$$

where, u_c and u_a are ionic mobilities of cation and anion respectively at infinite dilution. The value of k is equal to 96500 C, *i.e.*, one Faraday.

Thus, assuming that increase in equivalent conductance with dilution is due to increase in the degree of dissociation of the electrolyte; it is evident that the electrolyte achieves the degree of dissociation as unity when it is completely ionised at infinite dilution. Therefore, at any other dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

Degree of dissociation

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{\text{Equivalent conductance at a given concentration}}{\text{Equivalent conductance at infinite dilution}}$$

Calculation of absolute ionic mobilities: It has been experimentally found that ionic conductance is directly proportional to ionic mobilities.

$$\lambda_+ \propto u_+$$

$$\lambda_- \propto u_-$$

where, u_+ and u_- are ionic mobilities of cations and anions.

$$\lambda_+ = Fu_+ \quad \text{where, } F = \text{Faraday}$$

$$\lambda_- = Fu_- \qquad = 96500 \text{ coulomb}$$

$$\text{Ionic mobility} = \frac{\text{Ionic velocity}}{\text{Potential gradient}}$$

$$= \frac{\text{Ionic velocity (cm/ sec)}}{\text{Potential difference (volt)/ electrode separation}}$$

Relation between Equivalent and Molar Conductance at Infinite Dilution

$$\Lambda^\infty = \frac{1}{z^+}\lambda_+^\infty + \frac{1}{z^-}\lambda_-^\infty \qquad \text{... (i)}$$

where, z^+ and z^- are corresponding charges on the ions,

e.g., $$\Lambda_{BaCl_2}^\infty = \frac{1}{2}\lambda_{Ba^{2+}}^\infty + \frac{1}{1}\lambda_{Cl^-}^\infty \qquad \text{... (ii)}$$

$$\Lambda_{AlCl_3}^\infty = \frac{1}{3}\lambda_{Al^{3+}}^\infty + \frac{1}{1}\lambda_{Cl^-}^\infty \qquad \text{... (iii)}$$

$$\Lambda_{Al_2(SO_4)_3}^\infty = \frac{1}{3}\lambda_{Al^{3+}}^\infty + \frac{1}{2}\lambda_{SO_4^{2-}}^\infty \qquad \text{... (iv)}$$

Molar Conductance at Infinite Dilution

$$\Lambda_m^\infty \text{ or } \mu^\infty = \text{Molar conductance at infinite dilution}$$

$$= m\lambda_+^\infty + n\lambda_-^\infty$$

where, m and n are number of ions formed.

$$\mu_{Al_2(SO_4)_3}^\infty = 2\lambda_{Al^{3+}}^\infty + 3\lambda_{SO_4^{2-}}^\infty = 6\Lambda_{Al_2(SO_4)_3}^\infty$$

$$\mu_{BaCl_2} = \lambda_{Ba^{2+}}^\infty + 2\lambda_{Cl^-}^\infty = 2\Lambda_{BaCl_2}^\infty$$

12.9 THEORY OF WEAK ELECTROLYTES

(i) Weak electrolytes are not completely ionized when dissolved in a polar medium like water. There exists equilibrium between ions and unionised molecules.

$$AB \rightleftharpoons A^+ + B^-$$

(ii) Concept of chemical equilibrium and law of mass action can be applied to ionic equilibrium also.

$$\begin{array}{lccc} & AB & \rightleftharpoons & A^+ \; + \; B^- \\ t = 0 & C & & 0 \qquad 0 \\ t_{\text{eq.}} & C - C\alpha & & C\alpha \quad C\alpha \end{array}$$

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K = \frac{C\alpha^2}{1-\alpha} \qquad \text{... (i)}$$

For weak electrolytes, $\alpha << 1$

$\therefore$ $$(1-\alpha) \approx 1$$

Thus, equation (i) can be written as:

$$K = C\alpha^2$$

$$\alpha = \sqrt{\frac{K}{C}} \qquad \text{... (ii)}$$

From eq. (ii), it is clear that on dilution concentration decreases, as a result of which degree of ionisation 'α' increases. At high degree of ionisation both equivalent and molar conductance increase.

(iii) Degree of ionisation can be calculated as:

$$\alpha = \frac{\Lambda_e^C}{\Lambda_e^\infty} = \frac{\Lambda_m^C}{\Lambda_m^\infty} \qquad \text{... (iii)}$$

Λ_e^C, Λ_m^C = Equivalent and molar conductance at concentration 'C'

$\Lambda_e^\infty, \Lambda_m^\infty$ = Equivalent and molar conductance at infinite dilution.

Substituting the values of 'α' from eq. (iii) in eq. (i), we get

$$K = \frac{C \times \left(\dfrac{\Lambda_e^C}{\Lambda_e^\infty}\right)^2}{1 - \dfrac{\Lambda_e^C}{\Lambda_e^\infty}} = \frac{C(\Lambda_e^C)^2}{\Lambda_e^\infty(\Lambda_e^\infty - \Lambda_e^C)} \qquad \text{... (iv)}$$

Similarly,

$$K = \frac{C(\Lambda_m^C)^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m^C)} \qquad \text{... (v)}$$

Equations (iv) and (v) are called **Ostwald equations.**

Example 24. 1.0 *N solution of a salt surrounding two platinum electrodes* 2.1 *cm apart and* 4.2 *sq cm in area was found to offer a resistance of* 50 *ohm. Calculate the equivalent conductivity of the solution.*

Solution: Given, $l = 2.1\,\text{cm}, a = 4.2\,\text{sq cm}, R = 50\,\text{ohm}$

$$\text{Specific conductance, } \kappa = \frac{l}{a}\cdot\frac{1}{R}$$

or

$$\kappa = \frac{2.1}{4.2}\times\frac{1}{50} = 0.01\,\text{ohm}^{-1}\,\text{cm}^{-1}$$

$$\text{Equivalent conductivity} = \kappa \times V$$

V = the volume containing 1 g-equivalent = 1000 mL

So, $\text{Equivalent conductivity} = 0.01 \times 1000$

$$= 10\,\text{ohm}^{-1}\,\text{cm}^2\,\text{eq}^{-1}$$

Example 25. *Specific conductance of a decinormal solution of KCl is* $0.0112\,ohm^{-1}\,cm^{-1}$. *The resistance of a cell containing the solution was found to be 56. What is the cell constant?*

Solution: We know that,

$$\text{Sp. conductance} = \text{Cell constant} \times \text{Conductance}$$

or

$$\text{Cell constant} = \frac{\text{Sp. conductance}}{\text{Conductance}}$$

$$= \text{Sp. conductance} \times \text{Resistance}$$

$$= 0.0112 \times 56 = 0.6272\,\text{cm}^{-1}$$

Example 26. *The specific conductivity of* 0.02 *M KCl solution at* 25° *C is* $2.768 \times 10^{-3}\,ohm^{-1}\,cm^{-1}$. *The resistance of this solution at* 25° *C when measured with a particular cell was* 250.2 *ohm. The resistance of* 0.01 *M* $CuSO_4$ *solution at* 25° *C measured with the same cell was* 8331 *ohm. Calculate the molar conductivity of the copper sulphate solution.*

Solution:

$$\text{Cell constant} = \frac{\text{Sp. cond. of KCl}}{\text{Conductance of KCl}}$$

$$= \frac{2.768 \times 10^{-3}}{1/250.2}$$

$$= 2.768 \times 10^{-3} \times 250.2$$

For 0.01 M $CuSO_4$ solution

$$\text{Sp. conductivity} = \text{Cell constant} \times \text{Conductance}$$

$$= 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$$

$$\text{Molar conductance} = \text{Sp. cond.} \times \frac{1000}{C}$$

$$= \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100} = 8.312\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$$

Example 27. *The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are* 126.45, 426.16 *and* 91.0 $ohm^{-1}\,cm^2\,eq^{-1}$, *respectively, at* 25° *C. Calculate the equivalent conductance of acetic acid at infinite dilution.*

Solution: According to Kohlrausch's law,

$$\Lambda_{\infty CH_3COONa} = \lambda_{CH_3COO^-} + \lambda_{Na^+} = 91.0 \qquad \text{... (i)}$$

$$\Lambda_{\infty HCl} = \lambda_{H^+} + \lambda_{Cl^-} = 426.16 \qquad \text{... (ii)}$$

$$\Lambda_{\infty NaCl} = \lambda_{Na^+} + \lambda_{Cl^-} = 126.45 \qquad \text{... (iii)}$$

Adding eqs. (i) and (ii) and subtracting eq. (iii),

$$\lambda_{CH_3COO^-} + \lambda_{Na^+} + \lambda_{H^+} + \lambda_{Cl^-} - \lambda_{Na^+} - \lambda_{Cl^-}$$

$$= 91.0 + 426.16 - 126.45$$

$$\lambda_{CH_3COO^-} + \lambda_{H^+} = \Lambda_{\infty CH_3COOH} = 390.7\,\text{ohm}^{-1}\,\text{cm}^2\,\text{eq}^{-1}$$

Example 28. *The equivalent conductivity of* $N/10$ *solution of acetic acid at* 25° *C is* $14.3\,ohm^{-1}\,cm^2\,eq^{-1}$. *Calculate the degree of dissociation of* CH_3COOH *if* $\Lambda_{\infty CH_3COOH}$ *is* 390.71.

Solution:

$$\Lambda_{\infty CH_3COOH} = 390.71\,\text{ohm}^{-1}\,\text{cm}^2\,\text{eq}^{-1}$$

$$\Lambda_{CH_3COOH} = 14.3\,\text{ohm}^{-1}\,\text{cm}^2\,\text{eq}^{-1}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{14.3}{390.71}$$

$$= 0.0366, \textit{ i.e., } 3.66\% \text{ dissociated}$$

Example 29. *A decinormal solution of NaCl has specific conductivity equal to* 0.0092. *If ionic conductances of* Na^+ *and* Cl^- *ions at the same temperature are* 43.0 *and* 65.0 ohm^{-1} *respectively, calculate the degree of dissociation of NaCl solution.*

Solution: Equivalent conductance of $N/10$ NaCl solution

$$\Lambda_v = \text{Sp. conductivity} \times \text{dilution}$$

$$= 0.0092 \times 10{,}000 = 92\,\text{ohm}^{-1}$$

$$\Lambda_\infty = \lambda_{Na^+} + \lambda_{Cl^-}$$

$$= 43.0 + 65.0 = 108\,\text{ohm}^{-1}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{92}{108} = 0.85$$

Example 30. *At* 18° *C, the conductivities at infinite dilution of* NH_4Cl, *NaOH and NaCl are* 129.8, 217.4 *and* 108.9 *mho respectively. If the equivalent conductivity of* $N/100$ *solution of* NH_4OH *is* 9.93 *mho, calculate the degree of dissociation of* NH_4OH *at this dilution.*

Solution:

$$\Lambda_{\infty NH_4Cl} = \lambda_{NH_4^+} + \lambda_{Cl^-} = 129.8 \qquad \text{... (i)}$$

$$\Lambda_{\infty NaOH} = \lambda_{Na^+} + \lambda_{OH^-} = 217.4 \qquad \text{... (ii)}$$

$$\Lambda_{\infty NaCl} = \lambda_{Na^+} + \lambda_{Cl^-} = 108.9 \qquad \text{... (iii)}$$

Adding eqs. (i) and (ii) and subtracting eq. (iii),

$$\lambda_{NH_4^+} + \lambda_{Cl^-} + \lambda_{Na^+} + \lambda_{OH^-} - \lambda_{Na^+} - \lambda_{Cl^-} =$$

$$\lambda_{NH_4^+} + \lambda_{OH^-} = 129.8 + 217.4 - 108.9$$

$$\Lambda_{\infty NH_4OH} = 238.3\,\text{mho}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{9.93}{238.3} = 0.04167$$

or 4.17 % dissociated.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

11. If the equivalent conductance of 1 M benzoic acid is 12.8 ohm^{-1} cm^2 eq^{-1} and if the conductance of benzoate ion and H^+ ions are 42 and 288.42 ohm^{-1} cm^2 eq^{-1} respectively, its degree of dissociation is: **(DPMT 2005)**

(a) 39% (b) 3.9%

(c) 0.35% (d) 0.039%

[Ans. (b)]

[Hint: $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{12.8}{(42 + 288.42)} = 0.0387$

Percentage dissociation = $0.0387 \times 100 \approx 3.9\%$]

12. Equivalent conductances of NaCl, HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and 91 ohm^{-1} cm^2 eq^{-1} respectively. The equivalent conductance of CH_3COOH at infinite dilution would be:

(a) 101.38 ohm^{-1} cm^2 eq^{-1} (b) 253.62 ohm^{-1} cm^2 eq^{-1}

(c) 390.71 ohm^{-1} cm^2 eq^{-1} (d) 678.90 ohm^{-1} cm^2 eq^{-1}

[Ans. (c)]

[Hint: $\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COONa} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$

$= 91 + 426.16 - 126.45$

$= 390.71\ ohm^{-1}\ cm^2\ eq^{-1}$]

13. The specific conductance of saturated solution of AgCl is found to be 1.86×10^{-6} ohm^{-1} cm^{-1} and that of water is 6×10^{-8} ohm^{-1} cm^{-1}. The solubility of AgCl is ....

Given, $\Lambda^\circ_{AgCl} = 137.2\ ohm^{-1}\ cm^2\ eq^{-1}$

(a) 1.7×10^{-3} M (b) 1.3×10^{-5} M

(c) 1.3×10^{-4} M (d) 1.3×10^{-6} M

[Ans. (b)]

[Hint: $\kappa_{AgCl} = \kappa_{AgCl\ (Solution)} - \kappa_{H_2O}$

$= 1.86 \times 10^{-6} - 6 \times 10^{-8} = 1.8 \times 10^{-6}\ ohm^{-1}\ cm^{-1}$

$$\Lambda^\circ_{AgCl} = \kappa \times \frac{1000}{S}$$

$$\therefore \quad S = \frac{\kappa \times 1000}{\Lambda^\circ_{AgCl}} = \frac{1.8 \times 10^{-6} \times 1000}{137.2} = 1.31 \times 10^{-5}\ M]$$

14. The specific conductivity of $N/10$ KCl solution at 20°C is 0.0212 ohm^{-1} cm^{-1} and the resistance of the cell containing this solution at 20°C is 55 ohm. The cell constant is:

(a) 4.616 cm^{-1} (b) 1.166 cm^{-1}

(c) 2.173 cm^{-1} (d) 3.324 cm^{-1}

[Ans. (b)]

[Hint: $\kappa = C \times \frac{l}{A}$

$$\frac{l}{A} = \kappa \times \frac{1}{C} = \kappa \times R = 0.0212 \times 55 = 1.166\ cm^{-1}]$$

15. The resistance of 1 N solution of CH_3COOH is 250 ohm; when measured in a cell of cell constant 1.15 cm^{-1}. The equivalent conductance will be:

(a) 4.6 ohm^{-1} cm^2 eq^{-1} (b) 9.2 ohm^{-1} cm^2 eq^{-1}

(c) 18.4 ohm^{-1} cm^2 eq^{-1} (d) 0.023 ohm^{-1} cm^2 eq^{-1}

[Ans. (a)]

[Hint: $\kappa = C \times \frac{l}{A} = \frac{1}{250} \times 1.15 = 4.6 \times 10^{-3}\ ohm^{-1}\ cm^{-1}$

$$\Lambda_e = \kappa \times \frac{1000}{N} = 4.6 \times 10^{-3} \times \frac{1000}{1} = 4.6\ ohm^{-1}\ cm^2\ eq^{-1}]$$

16. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 ohm. 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 520 ohm. The molar conductivity of 0.02 M solution of the electrolyte will be: **(AIEEE 2006)**

(a) 124×10^{-4} S m^2 mol^{-1} (b) 1240×10^{-4} S m^2 mol^{-1}

(c) 1.24×10^{-4} S m^2 mol^{-1} (d) 12.4×10^{-4} S m^2 mol^{-1}

[Ans. (a)]

[Hint:

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

$$1.29 = \frac{1}{100} \times \frac{l}{A}$$

$$\frac{l}{A} = 129\ m^{-1}$$

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

$$= \left(\frac{1}{R} \times \frac{l}{A}\right) \times \frac{1000}{M}$$

$$= \left(\frac{1}{520} \times 129\right) \times \frac{1000}{0.02} \times 10^{-6}$$

$$= 124 \times 10^{-4}\ S\ m^2\ mol^{-1}]$$

17. If the molar conductance values of Ca^{2+} and Cl^- at infinite dilution are respectively 118.88×10^{-4} m^2 mho mol^{-1} and 77.33×10^{-4} m^2 mho mol^{-1} then that of $CaCl_2$ is:

(in m^2 mho mol^{-1}) **(VITEEE 2007)**

(a) 118.88×10^{-4} (b) 154.66×10^{-4}

(c) 273.54×10^{-4} (d) 196.21×10^{-4}

[Ans. (c)]

[Hint: $\Lambda^\circ_m\ CaCl_2 = \lambda^\circ Ca^{2+} + 2\lambda^\circ Cl^-$

$= (118.88 \times 10^{-4}) + 2(77.33 \times 10^{-4})$

$= 273.54 \times 10^{-4}\ m^2\ mho\ mol^{-1}$]

18. The molar conductivities of KCl, NaCl and KNO_3 are 152, 128 and 111 S cm^2 mol^{-1} respectively. What is the molar conductivity of $NaNO_3$? **(VITEEE 2008)**

(a) 101 S cm^2 mol^{-1} (b) 87 S cm^2 mol^{-1}

(c) – 101 S cm^2 mol^{-1} (d) – 391 S cm^2 mol^{-1}

[Ans. (b)]

[Hint: $\Lambda^\circ_{NaNO_3} = \Lambda^\circ_{NaCl} + \Lambda^\circ_{KNO_3} - \Lambda^\circ_{KCl}$

$= 128 + 111 - 152 = 87\ S\ cm^2\ mol^{-1}$]

SECTION III : ELECTROCHEMICAL CELL

12.10 ELECTROCHEMICAL CELL

Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge. Electrochemical cells are of two types:

(a) Electrolytic cell
(b) Galvanic or voltaic cell

(a) Electrolytic Cell

It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

(b) Galvanic or Voltaic Cell

It is a device in which a redox reaction is used to convert chemical energy into electrical energy, *i.e.*, electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called **half-cells.** When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

12.11 DANIELL CELL

It is designed to make use of the spontaneous redox reaction between zinc and cupric ions to produce an electric current (Fig. 12.7). It consists of two half-cells. The half-cell on the left contains a zinc metal electrode dipped in $ZnSO_4$ solution. The half-cell on the right consists of copper metal electrode in a solution of $CuSO_4$. The half-cells are joined by a salt bridge that prevents the mechanical mixing of the solution.

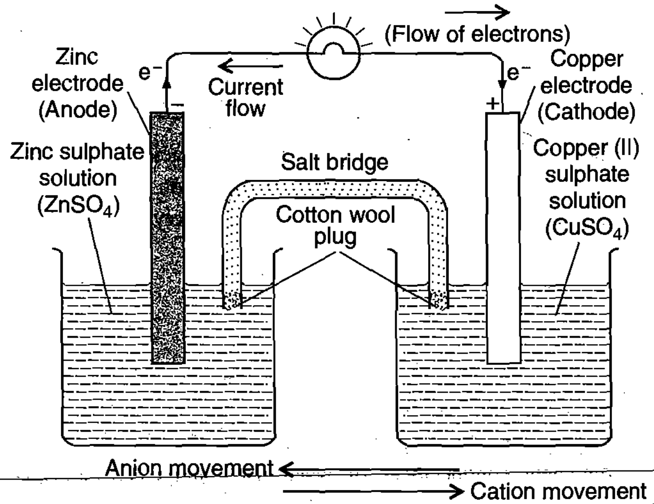


Fig. 12.7 Daniell cell

When the zinc and copper electrodes are joined by a wire, the following observations are made:

(i) There is a flow of electric current through the external circuit.
(ii) The zinc rod loses its mass while the copper rod gains in mass.
(iii) The concentration of $ZnSO_4$ solution increases while the concentration of copper sulphate solution decreases.
(iv) The solutions in both the compartments remain electrically neutral.

During the passage of electric current through external circuit, electrons flow from the zinc electrode to the copper electrode. At the zinc electrode, the zinc metal is oxidised to zinc ions which go into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode where they are used in the reduction of Cu^{2+} ions to metallic copper which is deposited on the electrode. Thus, the overall redox reaction is:

$$Zn(s) + Cu^{2+}(aq.) \longrightarrow Cu(s) + Zn^{2+}(aq.)$$

Thus, indirect redox reaction leads to the production of electrical energy. At the zinc rod, oxidation occurs. It is the anode of the cell and is negatively charged while at copper electrode, reduction takes place; it is the cathode of the cell and is positively charged.

Thus, the above points can be summed up as:

(i) Voltaic or Galvanic cell consists of two **half-cells.** The reactions occurring in half-cells are called **half-cell reactions.** The half-cell in which oxidation occurs is called **oxidation half-cell** and the reaction taking place in it is called **oxidation half-cell reaction.** Similarly, the half-cell in which reduction occurs is called **reduction half-cell** and the reaction taking place in it is called **reduction half-cell reaction.**
(ii) The electrode where oxidation occurs is called anode and the electrode where reduction occurs is termed cathode.
(iii) Electrons flow from anode to cathode in the external circuit.
(iv) Overall ion movement during the operation of the galvanic cell shows that negative ions (anions) move away from cathode where they are present in excess, towards anode, where they are needed to balance the charge of the positive ions (cations) formed. Similarly, cations move away from the anode where they are in excess, towards the cathode, where they balance the anions left in excess.

Example : An $Au(NO_3)_3$ solution containing a gold electrode is connected by means of salt bridge to a $PbCl_2$ solution containing lead electrode. The cell can be correctly represented as,

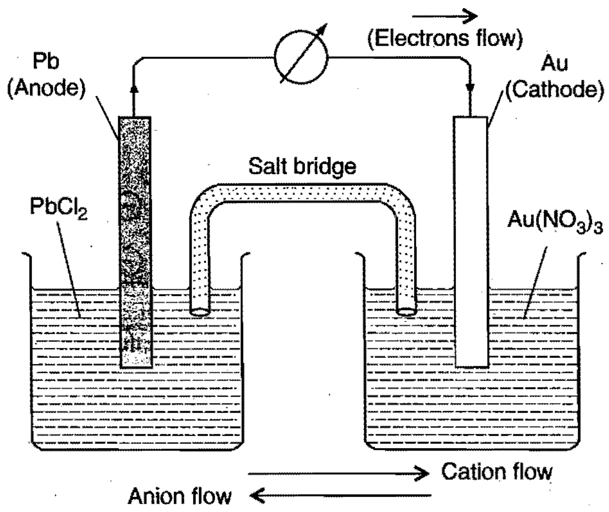


Fig. 12.8

Difference in electrolytic cell and galvanic cell

	Electrolytic cell	Galvanic cell
1.	Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
2.	Anode is positive electrode. Cathode is negative electrode.	Anode is negative electrode. Cathode is positive electrode.
3.	Ions are discharged on both the electrodes.	Ions are discharged only on the cathode.
4.	If the electrodes are inert, concentration of the electrolyte decreases when the electric current is circulated.	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are joined by a wire.
5.	Both the electrodes can be fitted in the same compartment.	The electrodes are fitted in different compartments.

(v) Chemical energy is converted into electrical energy.

(vi) The net reaction is the sum of two half-cell reactions. The reactions in Daniell cell can be represented as:

Oxidation half reaction, $\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq.) + 2e^-$

Reduction half reaction, $\mathrm{Cu}^{2+}(aq.) + 2e^- \longrightarrow \mathrm{Cu}(s)$

Net reaction $\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq.) \longrightarrow \mathrm{Zn}^{2+}(aq.) + \mathrm{Cu}(s)$

Electrode Signs

The signs of the anode and cathode in the voltaic or galvanic cells are opposite to those in the electrolytic cells (Fig. 12.9).

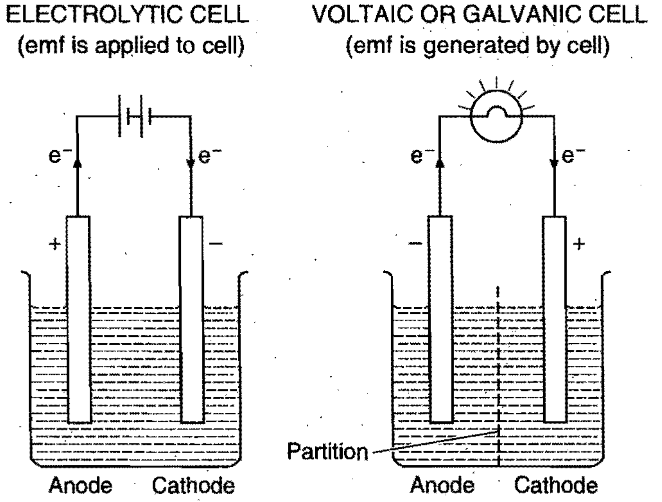


Fig. 12.9

	Electrolytic cell		Voltaic or Galvanic cell	
	Anode	Cathode	Anode	Cathode
Sign	+	−	−	+
Electron flow	out	in	out	in
Half reaction	oxidation	reduction	oxidation	reduction

12.12 SALT BRIDGE AND ITS SIGNIFICANCE

Salt bridge is usually an inverted U-tube filled with concentrated solution of inert electrolytes. An inert electrolyte is one whose ions are neither involved in any electrochemical change nor do they react chemically with the electrolytes in the two half-cells. Generally salts like KCl, $\mathrm{KNO_3}$, $\mathrm{NH_4NO_3}$, etc., are used. For the preparation of salt bridge, gelatin or agar-agar is dissolved in a hot concentrated aqueous solution of an inert electrolyte and the solution thus formed is filled in the U-tube. On cooling the solution sets in the form of a gel in the U-tube. The ends of the U-tube are plugged with cotton wool as to minimise diffusion effects. This is used as a salt bridge.

Significance of salt bridge: The following are the functions of the salt bridge:

(i) It connects the solutions of two half-cells and completes the cell circuit.

(ii) It prevents transference or diffusion of the solutions from one half-cell to the other.

(iii) It keeps the solutions in two half-cells electrically neutral. In anodic half-cell, positive ions pass into the solution and there shall be accumulation of extra positive charge in the solution around the anode which will prevent the flow of electrons from anode. This does not happen because negative ions are provided by salt bridge. Similarly, in cathodic half-cell, negative ions will accumulate around cathode due to deposition of positive ions by reduction. To neutralise these negative ions, sufficient number of positive ions are provided by salt bridge. Thus, salt bridge maintains electrical neutrality.

(iv) It prevents liquid-liquid junction-potential, *i.e.*, the potential difference which arises between two solutions when in contact with each other.

A broken vertical line or two parallel vertical lines in a cell reaction indicates the salt bridge.

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+} \parallel \mathrm{Cu}^{2+} \mid \mathrm{Cu}$$

Salt bridge can be replaced by a porous partition which allows the migration of ions without allowing the solutions to intermix.

12.13 REPRESENTATION OF AN ELECTROCHEMICAL CELL (Galvanic Cell)

The following universally accepted conventions are followed in representing an electrochemical cell:

(i) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.

(ii) A vertical line or semicolon (;) indicates a contact between two phases. The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution. Both are separated by a vertical line or a semicolon. For example,

$$\text{Zn} \mid \text{Zn}^{2+} \text{ or } \text{Zn}; \text{Zn}^{2+}$$

The molar concentration or activity of the solution is written in brackets after the formula of the ion. For example,

$$\text{Zn} \mid \text{Zn}^{2+}(1\,M) \text{ or } \text{Zn} \mid \text{Zn}^{2+}(0.1\,M)$$

(iii) The cathode of the cell is represented by writing the cation of the electrolyte first and then metal. Both are separated by a vertical line or semicolon. For example,

$$\text{Cu}^{2+} \mid \text{Cu} \text{ or } \text{Cu}^{2+}; \text{Cu} \text{ or } \text{Cu}^{2+}(1\,M) \mid \text{Cu}$$

(iv) The salt bridge which separates the two half-cells is indicated by two parallel vertical lines.

(v) Sometimes negative and positive signs are also put on the electrodes.

The Daniell cell can be represented as:

$$\overset{-}{\text{Zn}} \mid \text{ZnSO}_4(aq.) \parallel \text{CuSO}_4(aq.) \mid \overset{+}{\text{Cu}}$$

Anode Salt bridge Cathode

Oxidation half-cell Reduction half-cell

or $$\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$$

or $$\text{Zn} \mid \text{Zn}^{2+}(1\,M) \parallel \text{Cu}^{2+}(1\,M) \mid \text{Cu}$$

12.14 ELECTRODE POTENTIAL

When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called **electrode potential.** For example, when a plate of zinc is placed in a solution having Zn^{2+} ions, it becomes negatively charged with respect to solution and thus a potential difference is set-up between zinc plate and the solution. This potential difference is termed the electrode potential of zinc. Similarly, when copper is placed in a solution having Cu^{2+} ions, it becomes positively charged with respect to solution. A potential difference is set-up between the copper plate and the solution. The potential difference thus developed is termed as electrode potential of copper. The potential difference is established due to the formation of electrical double layer at the interface of metal and the solution. The development of negative charge (as on zinc plate) or positive charge (as on copper plate) can be explained in the following manner. When a metal rod is dipped in its salt solution, two changes occur:

$$M(s) \longrightarrow M^{n+}(aq.) + ne^-$$

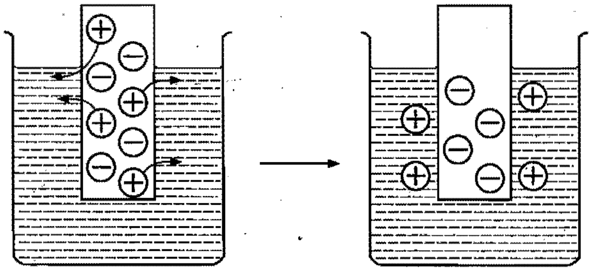


Fig. 12.10 (a)

$$M^{n+}(aq.) + ne^- \longrightarrow M(s)$$

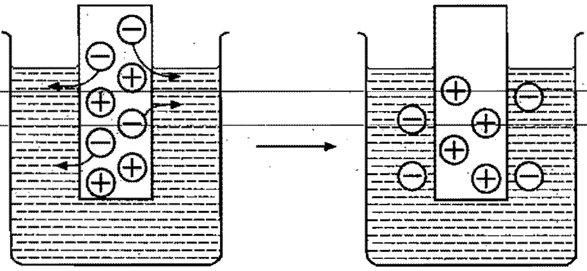


Fig. 12.10 (b)

(a) Oxidation : Metal ions pass from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode.

(b) Reduction : Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode.

(i) The conversion of metal atoms into metal ions by the attractive force of polar water molecules.

$$M \longrightarrow M^{n+} + ne^-$$

The metal ions go into the solution and the electrons remain on the metal making it negatively charged. The tendency of the metal to change into ions is known as **electrolytic solution pressure.**

(ii) Metal ions start depositing on the metal surface leading to a positive charge on the metal.

$$M^{n+} + ne^- \longrightarrow M$$

This tendency of the ions is termed **osmotic pressure.**

In the beginning, both these changes occur with different speeds but soon an equilibrium is established.

$$M \rightleftharpoons M^{n+} + ne^-$$

In practice, one effect is greater than the other, if first effect is greater than the second, the metal acquires a negative charge with respect to solution and if the second is greater than the first, it acquires positive charge with respect to solution, thus in both the cases a potential difference is set-up.

The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons, *i.e.*, it is a measure of the relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons). The magnitude of potential depends on the following factors:

(i) Nature of the electrode,
(ii) Concentration of the ions in solution,
(iii) Temperature.

Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types:

(i) Oxidation potential: When electrode is negatively charged with respect to solution, *i.e.*, it acts as anode. Oxidation occurs.

$$M \longrightarrow M^{n+} + ne^-$$

(ii) Reduction potential: When electrode is positively charged with respect to solution, *i.e.*, it acts as cathode. Reduction occurs.

$$M^{n+} + ne^- \longrightarrow M$$

It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as **reference electrode.** The emf of the resulting cell is measured experimentally. The emf of the cell is equal to the sum of potentials on the two electrodes.

Emf of the cell = $E_{\text{Anode}} + E_{\text{Cathode}}$
= Oxidation potential of anode
+ Reduction potential of cathode

Knowing the value of reference electrode, the value of other electrode can be determined.

12.15 STANDARD ELECTRODE POTENTIAL

In order to compare the electrode potentials of various electrodes, it is necessary to specify the concentration of the ions present in solution in which the electrode is dipped and the temperature of the half-cell. The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 *M*) at 25° C (298 K) is called **standard electrode potential.**

According to the IUPAC convention, the reduction potential alone can be called as the electrode potential (E°), *i.e.*, the given value of electrode potential can be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential. Standard reduction potential of an electrode means that reduction reaction is taking place at the electrode. If the reaction is reversed and written as oxidation reaction, the numerical value of electrode potential will remain same but the sign of standard potential will have to be reversed. Thus,

Standard reduction potential = – Standard oxidation potential

or Standard oxidation potential = – Standard reduction potential

12.16 REFERENCE ELECTRODE (Standard Hydrogen Electrode, SHE or NHE)

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and sealed in a glass tube as to make contact with the outer circuit through mercury. The platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in an acid solution which has H^+ ion concentration 1 *M*. Pure hydrogen gas is circulated at one atmospheric pressure. A part of the gas is adsorbed and the rest escapes through holes. This gives an equilibrium between the adsorbed hydrogen and hydrogen ions in the solution.

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

The temperature of the cell is maintained at 25° C. By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly ± 0.000... volt.

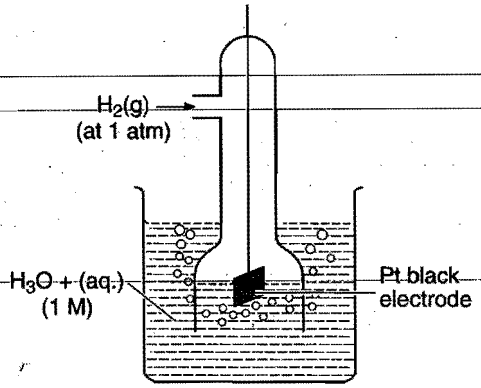


Fig. 12.11 Hydrogen electrode

The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. When this half-cell is connected with any other half-cell, a voltaic cell is constituted. The hydrogen electrode can act as cathode or anode with respect to other electrode.

SHE half reaction	Electrode potential
$H_2 \longrightarrow 2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^- \longrightarrow H_2$	0.0 V (Cathode)

12.17 MEASUREMENT OF ELECTRODE POTENTIAL

The measurement of electrode potential of a given electrode is made by constituting a voltaic cell, *i.e.*, by connecting it with a standard hydrogen electrode (SHE) through a salt bridge. 1 *M* solution is used in hydrogen half-cell and the temperature is maintained at 25° C. The emf of the cell is measured either by a calibrated potentiometer or by a high resistance voltmeter, *i.e.*, a valve voltmeter. The reading of the voltmeter gives the electrode potential of the electrode in question with respect to the hydrogen electrode. The standard electrode potential of a metal may be determined as it is the potential difference in volt developed in a cell consisting of two electrodes: the pure metal is in contact with a molar solution of one of its ions and the standard hydrogen electrode.

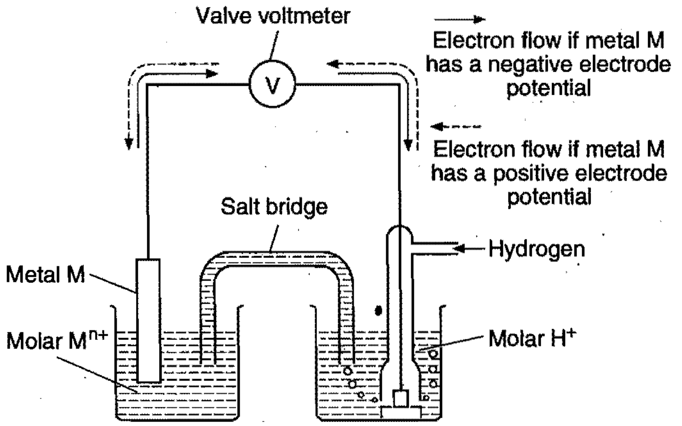


Fig. 12.12

(i) Determination of standard electrode potential of Zn/Zn^{2+} electrode: A zinc rod is dipped in 1 *M* zinc sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge. Both the electrodes are connected with a voltmeter as shown in Fig. 12.13. The deflection of the voltmeter indicates that current is flowing from hydrogen electrode to metal electrode or the electrons are moving from zinc rod to hydrogen electrode. The zinc electrode acts as an anode and the hydrogen electrode as cathode and the cell can be represented as

$$\underset{\text{Anode }(-)}{\underline{Zn \mid Zn^{2+}(aq.)}} \,||\, \underset{\text{Cathode }(+)}{\underline{2H^+(aq.) \mid H_2(g)}}$$

$$\underset{\text{(Oxidation)}}{Zn \longrightarrow Zn^{2+} + 2e^-} \; ; \underset{\text{(Reduction)}}{2H^+ + 2e^- \longrightarrow H_2 \uparrow}$$

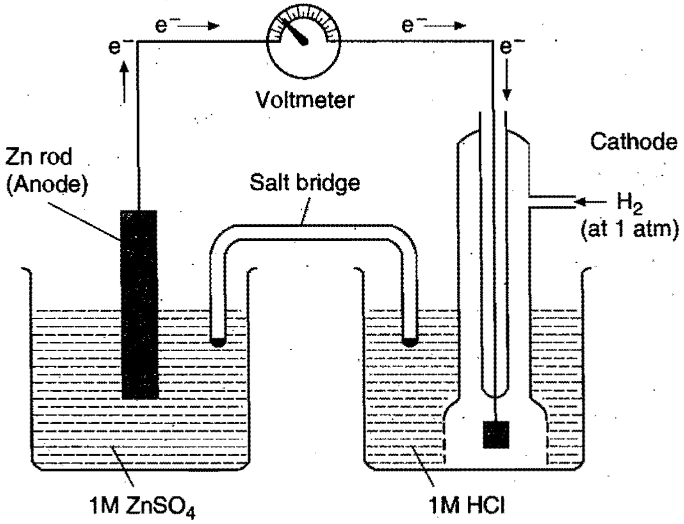


Fig. 12.13 Zn–H_2 electrochemical cell

The emf of the cell is 0.76 volt

$$E^\circ_{\text{Cell}} = E^\circ_{\text{Anode}} + E^\circ_{\text{Cathode}}$$

$$0.76 = E^\circ_{\text{Anode}} + 0 \text{ or } E^\circ_{\text{Anode}} = +0.76\text{ V}$$

As the reaction on the anode is oxidation, *i.e.*,

$$Zn \longrightarrow Zn^{2+} + 2e,$$

E°_{Anode} is the standard oxidation potential of zinc. This potential is given the positive sign.

$$E^\circ_{\text{ox}}(Zn/Zn^{2+}) = +0.76\text{ volt}$$

So, standard reduction potential of Zn, *i.e.*, $E^\circ(Zn^{2+}/Zn)$

$$= -E^\circ_{\text{ox}} = -(+0.76)$$

$$= -0.76\text{ volt}$$

The emf of such a cell gives the positive value of standard oxidation potential of metal *M*. The standard reduction potential (E°) is obtained by reversing the sign of standard oxidation potential.

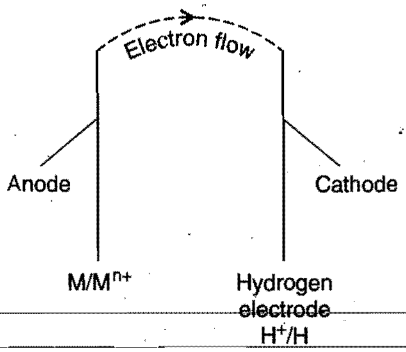


Fig. 12.14

(ii) Determination of standard electrode potential of Cu^{2+}/Cu, electrode: A copper rod is dipped in 1 *M* solution of $CuSO_4$. It is combined with hydrogen electrode through a salt bridge. Both the electrodes are joined through a voltmeter. The deflection of the voltmeter indicates that current is flowing from copper electrode towards hydrogen electrode, *i.e.*, the electrons are moving from hydrogen electrode to copper electrode. The hydrogen electrode acts as an anode and the copper electrode as a cathode. The cell can be represented as

$$\underset{\text{Anode }(-)}{H_2(g) \mid 2H^+(aq.)} \,||\, \underset{\text{Cathode }(+)}{Cu^{2+}(aq.) \mid Cu}$$

$$\underset{\text{Oxidation}}{H_2 \longrightarrow 2H^+ + 2e^-} \; ; \underset{\text{Reduction}}{Cu^{2+} + 2e^- \longrightarrow Cu}$$

The emf of the cell is 0.34 volt.

$$E^\circ_{\text{Cell}} = E^\circ_{\text{Anode}} + E^\circ_{\text{Cathode}}$$

$$0.34 = 0 + E^\circ_{\text{Cathode}}$$

Since, the reaction on the cathode is reduction, *i.e.*, $Cu^{2+} + 2e^- \longrightarrow Cu$, E°_{Cathode} is the standard reduction potential of copper. This is given the + ve sign.

E°, *i.e.*, standard reduction potential of $Cu^{2+}/Cu = 0.34$ volt

So, E°_{ox} (standard oxidation potential of copper) $= -0.34$ volt

The emf of such a cell gives positive value of reduction potential of metal electrode. The standard oxidation potential of this electrode is obtained by reversing the sign of standard reduction potential.

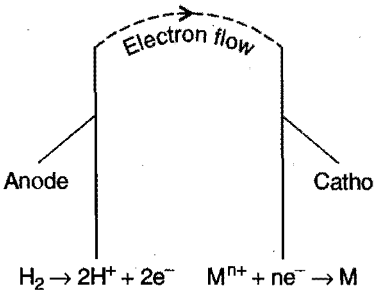


Fig. 12.15

It is thus concluded that at the metal electrode which acts as anode with respect to hydrogen electrode (cathode), the reduction potential is given the minus sign and at the metal electrode which acts as cathode with respect to hydrogen electrode (anode), the reduction potential is given the positive sign.

The standard electrode potentials (oxidation or reduction) of various elements can be measured by combining the electrode in question with a standard hydrogen electrode and measuring the emf of the cell constituted.

12.18 EMF OF A GALVANIC CELL

Every galvanic or voltaic cell is made up of two half-cells, the oxidation half-cell (anode) and the reduction half-cell (cathode). The potentials of these half-cells are always different. On account of this difference in electrode potentials, the electric current moves from the electrode at higher potential to the electrode at lower potential, *i.e.*, from cathode to anode. The direction of the flow of electrons is from anode to cathode.

$$\text{Anode} \underset{\text{Flow of current}}{\overset{\text{Flow of electrons}}{\rightleftarrows}} \text{Cathode}$$

The difference in potentials of the two half-cells is known as the electromotive force **(emf) of the cell or cell potential.**

The emf of the cell or cell potential can be calculated from the values of electrode potentials of the two half-cells constituting the cell. The following three methods are in use:

(i) When oxidation potential of anode and reduction potential of cathode are taken into account:

$$E^\circ_{\text{cell}} = \text{Oxidation potential of anode} + \text{Reduction potential of cathode}$$

$$= E^\circ_{\text{ox}}\ (\text{anode}) + E^\circ_{\text{red}}\ (\text{cathode})$$

(ii) When reduction potentials of both electrodes are taken into account:

$$E^\circ_{\text{cell}} = \text{Standard Reduction potential of cathode} - \text{Standard Reduction potential of anode}$$

$$= E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$$

$$= E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

(iii) When oxidation potentials of both electrodes are taken into account:

$$E^\circ_{\text{cell}} = \text{Oxidation potential of anode} - \text{Oxidation potential of cathode}$$

$$= E^\circ_{\text{ox}}\ (\text{anode}) - E^\circ_{\text{ox}}\ (\text{cathode})$$

Difference between emf and potential difference: The potential difference is the difference between the electrode potentials of the two electrodes of the cell under any condition while emf is the potential generated by a cell when there is zero electron flow, *i.e.*, it draws no current. The points of difference are given ahead:

Emf	Potential difference
1. It is the potential difference between two electrodes when no current is flowing in the circuit.	It is the difference of the electrode potentials of the two electrodes when the cell is under operation.
2. It is the maximum voltage that the cell can deliver.	It is always less than the maximum value of voltage which the cell can deliver.
3. It is responsible for the steady flow of current in the cell.	It is not responsible for the steady flow of current in the cell.

12.19 REVERSIBLE AND IRREVERSIBLE CELLS

Daniell cell has the emf value 1.09 volt. If an opposing emf exactly equal to 1.09 volt is applied to the cell, the cell reaction,

$$\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Cu} + \text{Zn}^{2+}$$

stops but if it is increased infinitesimally beyond 1.09 volt, the cell reaction is reversed.

$$\text{Cu} + \text{Zn}^{2+} \longrightarrow \text{Zn} + \text{Cu}^{2+}$$

Such a cell is termed a **reversible cell.** Thus, the following are the two main conditions of reversibility:

(i) The chemical reaction of the cell stops when an exactly equal opposing emf is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the opposing emf is slightly greater than that of the cell.

Any other cell which does not obey the above two conditions is termed as **irreversible.** A cell consisting of zinc and copper electrodes dipped into the solution of sulphuric acid is irreversible. Similarly, the cell

$$\text{Zn} \mid \text{H}_2\text{SO}_4(aq.) \mid \text{Ag}$$

is also irreversible because when the external emf is greater than the emf of the cell, the cell reaction,

$$\text{Zn} + 2\text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2$$

is not reversed but the cell reaction becomes

$$2\text{Ag} + 2\text{H}^+ \longrightarrow 2\text{Ag}^+ + \text{H}_2$$

12.20 SOME OTHER REFERENCE ELECTRODES

Since, a standard hydrogen electrode is difficult to prepare and maintain, it is usually replaced by other reference electrodes, which are known as secondary reference electrodes. These are convenient to handle and are prepared easily. Two important secondary reference electrodes are described here.

(i) **Calomel electrode:** It consists of mercury at the bottom over which a paste of mercury-mercurous chloride is placed. A solution of potassium chloride is then placed over the paste. A platinum wire sealed in a glass tube helps in making the electrical contact. The electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode to make a complete cell.

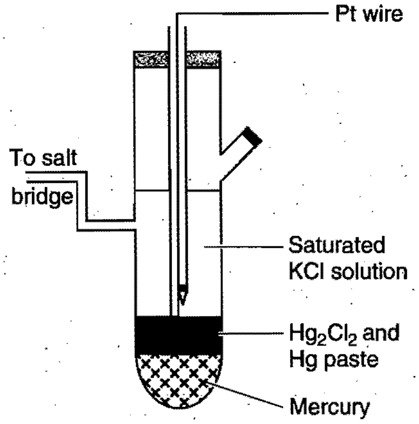


Fig. 12.16 Calomel electrode

The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode (SCE) and if the potassium chloride solution is 1 *N*, the electrode is known as normal calomel electrode (NCE) while for 0.1 *N* potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE). The electrode reaction when the electrode acts as cathode is:

$$\frac{1}{2}\mathrm{Hg_2Cl_2} + e^- \rightleftharpoons \mathrm{Hg} + \mathrm{Cl^-}$$

The reduction potentials of the calomel electrodes on hydrogen scale at 298 K are as follows:

Saturated KCl	0.2415 V
1.0 *N* KCl	0.2800 V
0.1 *N* KCl	0.3338 V

The electrode potential of any other electrode on hydrogen scale can be measured when it is combined with calomel electrode. The emf of such a cell is measured. From the value of electrode potential of calomel electrode, the electrode potential of the other electrode can be evaluated.

(ii) Silver-silver chloride electrode: This is another widely used reference electrode. It is reversible and stable and can be combined with cells containing chlorides without inserting liquid junctions.

Silver chloride is deposited electrolytically on a silver or platinum wire and it is then immersed in a solution containing chloride ions. Its standard electrode potential with respect to the standard hydrogen electrode is 0.2224 V at 298 K. The electrode is represented as:

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{Cl^-}$$

The electrode reaction is:

$$\mathrm{AgCl} + e^- \longrightarrow \mathrm{Ag} + \mathrm{Cl^-}$$

12.21 PREDICTION FOR OCCURRENCE OF A REDOX REACTION

Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative. The free energy is related to cell emf in the following manner:

$$\Delta G^\circ = -nFE^\circ$$

where, n is the number of electrons involved, F is the value of Faraday and E° is the cell emf. ΔG can be negative if E° is positive.

When E° is positive, the cell reaction is spontaneous and serves as a source of electrical energy.

To predict whether a particular redox reaction will occur or not, write down the redox reaction into two half reactions, one involving oxidation reaction and the other involving reduction reaction. Write the oxidation potential value for oxidation reaction and reduction potential value for reduction reaction. Add these two values, if the algebraic summation gives a positive value, the reaction will occur, otherwise not.

[**Note :** The true conditions for operating voltaic cells are :

$$\Delta G < 0, \; E > 0]$$

12.22 ELECTRODE AND CELL POTENTIALS—NERNST EQUATION

The electrode potential and the emf of the cell depend upon the nature of the electrode, temperature and the activities (concentrations) of the ions in solution. The variation of electrode and cell potentials with concentration of ions in solution can be obtained from thermodynamic considerations. For a general reaction such as

$$m_1A + m_2B + \ldots \rightleftharpoons n_1X + n_2Y + \ldots \quad \ldots \text{(i)}$$

occurring in the cell, the Gibbs free energy change is given by the equation

$$\Delta G = \Delta G^\circ + 2.303RT \log_{10} \frac{a_X^{n_1} \times a_Y^{n_2} \ldots}{a_A^{m_1} \times a_B^{m_2} \ldots} \quad \ldots \text{(ii)}$$

where, '*a*' represents the activities of reactants and products under a given set of conditions and ΔG° refers to free energy change for the reaction when the various reactants and products are present at standard conditions. The free energy change of a cell reaction is related to the electrical work that can be obtained from the cell, *i.e.*, $\Delta G = -nFE_{\text{cell}}$ and $\Delta G^\circ = -nFE^\circ$. On substituting these values in eq. (ii), we get

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + 2.303RT \log_{10} \frac{a_X^{n_1} \times a_Y^{n_2} \ldots}{a_A^{m_1} \times a_B^{m_2} \ldots} \quad \ldots \text{(iii)}$$

or $$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF} \log_{10} \frac{a_X^{n_1} \times a_Y^{n_2} \ldots}{a_A^{m_1} \times a_B^{m_2} \ldots} \quad \ldots \text{(iv)}$$

This equation is known as Nernst equation.

Putting the values of $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$, $T = 298$ K and $F = 96500$ C, eq. (iv) reduces to

$$E = E^\circ - \frac{0.0591}{n} \log_{10} \frac{a_X^{n_1} \times a_Y^{n_2} \ldots}{a_A^{m_1} \times a_B^{m_2} \ldots} \quad \ldots \text{(v)}$$

$$= E^\circ - \frac{0.0591}{n} \log_{10} \frac{[\text{Products}]}{[\text{Reactants}]} \quad \ldots \text{(vi)}$$

Potential of single electrode (Anode): Consider the general oxidation reaction,

$$M \longrightarrow M^{n+} + ne^-$$

Applying Nernst equation,

$$E_{\text{ox}} = E^\circ_{\text{ox}} - \frac{0.0591}{n} \log_{10} \frac{[M^{n+}]}{[M]}$$

where, E_{ox} is the oxidation potential of the electrode (anode), E°_{ox} is the standard oxidation potential of the electrode.

[**Note:** The concentration of pure solids and liquids are taken as unity.]

$$E_{\text{ox}} = E^\circ_{\text{ox}} - \frac{0.0591}{n} \log_{10} [M^{n+}]$$

Let us consider a Daniell cell to explain the above equations. The concentrations of the electrolytes are not 1 *M*.

$$\text{Zn}(s) + \text{Cu}^{2+}(aq.) \rightleftharpoons \text{Zn}^{2+}(aq.) + \text{Cu}(s)$$

$$\text{Zn}(s) \mid \text{Zn}^{2+}(aq) \parallel \text{Cu}^{2+}(aq.) \mid \text{Cu}$$

Potential at zinc electrode (Anode)

$$E_{\text{ox}} = E^\circ_{\text{ox}} - \frac{0.0591}{n} \log_{10} [\text{Zn}^{2+}]$$

Potential at copper electrode (Cathode)

$$E_{\text{red}} = E^\circ_{\text{red}} + \frac{0.0591}{n} \log_{10} [\text{Cu}^{2+}]$$

Emf of the cell

$$\begin{aligned} E_{\text{cell}} &= E_{\text{ox}} + E_{\text{red}} \\ &= (E^\circ_{\text{ox}} + E^\circ_{\text{red}}) - \frac{0.0591}{n} \log_{10} \left[\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}}\right] \\ &= E^\circ_{\text{cell}} - \frac{0.0591}{n} \log_{10} \left[\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}}\right] \end{aligned}$$

The value of $n = 2$ for both zinc and copper.

Let us consider an example, in which the values of *n* for the two ions in the two half-cells are not same. For example, in the cell

$$\text{Cu} \mid \text{Cu}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$$

The cell reaction is:

$$\text{Cu}(s) + 2\text{Ag}^+ \longrightarrow \text{Cu}^{2+} + 2\text{Ag}$$

The two half-cell reactions are:

$$\text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^-$$

$$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$$

The second equation is multiplied by 2 to balance the number of electrons.

$$2\text{Ag}^+ + 2e^- \longrightarrow 2\text{Ag}$$

$$E_{\text{ox}} = E^\circ_{\text{ox}} - \frac{0.0591}{2} \log_{10} [\text{Cu}^{2+}]$$

$$E_{\text{red}} = E^\circ_{\text{red}} + \frac{0.0591}{2} \log_{10} [\text{Ag}^+]^2$$

$$\begin{aligned} E_{\text{cell}} = E_{\text{ox}} + E_{\text{red}} &= E^\circ_{\text{ox}} + E^\circ_{\text{red}} - \frac{0.0591}{2} \log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \\ &= E^\circ_{\text{cell}} - \frac{0.0591}{2} \log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \end{aligned}$$

SOME SOLVED EXAMPLES

Example 31. *Construct the cells in which the following reactions are taking place. Which of the electrodes shall act as anode (negative electrode) and which one as cathode (positive electrode)?*

(*a*) $Zn + CuSO_4 = ZnSO_4 + Cu$

(*b*) $Cu + 2AgNO_3 = Cu(NO_3)_2 + 2Ag$

(*c*) $Zn + H_2SO_4 = ZnSO_4 + H_2$

(*d*) $Fe + SnCl_2 = FeCl_2 + Sn$

Solution: It should always be kept in mind that the metal which goes into solution in the form of its ions undergoes oxidation and thus acts as negative electrode (anode) and the element which comes into the free state undergoes reduction and acts as positive electrode (cathode):

(a) In this case Zn is oxidised to Zn^{2+} and thus acts as anode (negative electrode) while Cu^{2+} is reduced to copper and thus acts as cathode (positive electrode). The cell can be represented as

$$\text{Zn} \mid \text{ZnSO}_4 \parallel \text{CuSO}_4 \mid \text{Cu}$$

or

$$\underset{\text{Anode }(-)}{\text{Zn} \mid \text{Zn}^{2+}} \parallel \underset{\text{Cathode }(+)}{\text{Cu}^{2+} \mid \text{Cu}}$$

(b) In this case Cu is oxidised to Cu^{2+} and Ag^+ is reduced to Ag. The cell can be represented as

$$\text{Cu} \mid \text{Cu(NO}_3)_2 \parallel \text{AgNO}_3 \mid \text{Ag}$$

or

$$\underset{\text{Anode }(-)}{\text{Cu} \mid \text{Cu}^{2+}} \parallel \underset{\text{Cathode }(+)}{\text{Ag}^+ \mid \text{Ag}}$$

(c) In this case, Zn is oxidised to Zn^{2+} and H^+ is reduced to H_2. The cell can be represented as:

$$\text{Zn} \mid \text{ZnSO}_4 \parallel \text{H}_2\text{SO}_4 \mid \text{H}_2(\text{Pt})$$

or

$$\underset{\text{Anode }(-)}{\text{Zn} \mid \text{Zn}^{2+}} \parallel \underset{\text{Cathode }(+)}{2\text{H}^+ \mid \text{H}_2(\text{Pt})}$$

(d) Here, Fe is oxidised to Fe^{2+} and Sn^{2+} is reduced to Sn. The cell can be represented as:

$$\text{Fe} \mid \text{FeCl}_2 \parallel \text{SnCl}_2 \mid \text{Sn}$$

or

$$\underset{\text{Anode }(-)}{\text{Fe} \mid \text{Fe}^{2+}} \parallel \underset{\text{Cathode }(+)}{\text{Sn}^{2+} \mid \text{Sn}}$$

Note : Oxidation potential is $E^\circ_{M/M^{n+}}$ while reduction potential is represented as $E^\circ_{M^{n+}/M}$. The value of $E^\circ_{\text{Zn/Zn}^{2+}}$ (oxidation potential of Zn) is + 0.76 volt and the value of $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ (reduction potential of copper) is + 0.34 volt. The electrode having lower value of reduction potential acts as an anode while that having higher value of reduction potential acts as cathode.

Example 32. *Consider the reaction,*

$$2Ag^+ + Cd \longrightarrow 2Ag + Cd^{2+}$$

The standard electrode potentials for $Ag^+ \longrightarrow Ag$ *and* $Cd^{2+} \longrightarrow Cd$ *couples are* 0.80 *volt and* – 0.40 *volt respectively.*

(*i*) *What is the standard potential* $E°$ *for this reaction?*

(*ii*) *For the electrochemical cell, in which this reaction takes place which electrode is negative electrode?*

Solution: (i) The half reactions are:

$$2Ag^+ + \underset{\substack{\text{Reduction}\\ \text{(Cathode)}}}{2e^-} \longrightarrow 2Ag,$$

$$E^\circ_{Ag^+/Ag} = 0.80 \text{ volt} \qquad \text{(Reduction potential)}$$

$$Cd \longrightarrow \underset{\substack{\text{Oxidation}\\ \text{(Anode)}}}{Cd^{2+}} + 2e^-,$$

$$E^\circ_{Cd^{2+}/Cd} = -0.40 \text{ volt} \quad \text{(Reduction potential)}$$

or $$E^\circ_{Cd/Cd^{2+}} = +0.40 \text{ volt}$$

$$E° = E^\circ_{Cd/Cd^{2+}} + E^\circ_{Ag^+/Ag} = 0.40 + 0.80 = 1.20 \text{ volt}$$

(ii) The negative electrode is always the electrode whose reduction potential has smaller value or the electrode where oxidation occurs. Thus, Cd electrode is the negative electrode.

Example 33. *Consider the cell,*

$$Zn \mid Zn^{2+}(aq.)(1.0M) \parallel Cu^{2+}(aq.)(1.0M) \mid Cu$$

The standard electrode potentials are:

$$Cu^{2+} + 2e^- \longrightarrow Cu(aq.); \qquad E° = 0.350 \text{ volt}$$

$$Zn^{2+} + 2e^- \longrightarrow Zn(aq.); \qquad E° = -0.763 \text{ volt}$$

(*i*) *Write down the cell reaction.*

(*ii*) *Calculate the emf of the cell.*

Solution: (i) Reduction potential of Zn is less than copper, hence Zn acts as anode and copper as cathode.

At anode $\quad Zn \longrightarrow Zn^{2+} + 2e^- \quad$ (Oxidation)

At cathode $\quad Cu^{2+} + 2e^- \longrightarrow Cu \quad$ (Reduction)

Cell reaction $\quad Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

(ii) $$E^\circ_{cell} = E^\circ_{Zn/Zn^{2+}} + E^\circ_{Cu^{2+}/Cu}$$

= Oxi. potential of zinc + Red. potential of copper

$$E^\circ_{Zn^{2+}/Zn} = -0.763 \text{ (Reduction potential)}$$

$$E^\circ_{Zn/Zn^{2+}} = +0.763 \text{ (Oxidation potential)}$$

and $$E^\circ_{Cu^{2+}/Cu} = 0.350 \quad \text{(Reduction potential)}$$

So, $$E^\circ_{cell} = 0.763 + 0.350 = 1.113 \text{ volt}$$

Example 34. *Write the electrode reactions and the net cell reactions for the following cells. Which electrode would be the positive terminal in each cell?*

(*a*) $Zn \mid Zn^{2+} \parallel Br^-, Br_2 \mid Pt$ (*b*) $Cr \mid Cr^{3+} \parallel I^-, I_2 \mid Pt$

(*c*) $Pt \mid H_2, H^+ \parallel Cu^{2+} \mid Cu$ (*d*) $Cd \mid Cd^{2+} \parallel Cl^-, AgCl \mid Ag$

Solution:

(a) Oxidation half reaction, $\quad Zn \longrightarrow Zn^{2+} + 2e^-$

Reduction half reaction, $Br_2 + 2e^- \longrightarrow 2Br^-$

Net cell reaction $\quad Zn + Br_2 \longrightarrow Zn^{2+} + 2Br^-$

Positive terminal—Cathode Pt

(b) Oxidation half reaction, $\quad [Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$

Reduction half reaction, $[I_2 + 2e^- \longrightarrow 2I^-] \times 3$

Net cell reaction $\quad 2Cr + 3I_2 \longrightarrow 2Cr^{3+} + 6I^-$

Positive terminal—Cathode Pt

(c) Oxidation half reaction, $\quad H_2 \longrightarrow 2H^+ + 2e^-$

Reduction half reaction, $Cu^{2+} + 2e^- \longrightarrow Cu$

Net cell reaction $\quad H_2 + Cu^{2+} \longrightarrow Cu + 2H^+$

Positive terminal—Cathode Cu

(d) Oxidation half reaction, $\quad Cd \longrightarrow Cd^{2+} + 2e^-$

Reduction half reaction,

$$[AgCl + e^- \longrightarrow Ag + Cl^-] \times 2$$

Net cell reaction $\quad Cd + 2AgCl \longrightarrow Cd^{2+} + 2Ag + 2Cl^-$

Positive terminal—Cathode Ag

Example 35. *Will Fe be oxidised to* Fe^{2+} *by reaction with* 1.0 *M HCl?* $E°$ *for* $Fe/Fe^{2+} = +0.44$ *volt.*

Solution: The reaction will occur if Fe is oxidised to Fe^{2+}.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

Writing two half reactions,

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \text{Oxidation;} \; E^\circ_{Fe/Fe^{2+}} = 0.44 \text{ volt}$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad \text{Reduction;} \; E^\circ_{H^+/H} = 0.0 \text{ volt}$$

Adding; emf = 0.44 volt

Since, emf is positive, the reaction shall occur.

Example 36. *The values of* $E°$ *of some of the reactions are given below:*

$$I_2 + 2e^- \longrightarrow 2I^-; \qquad E° = +0.54 \text{ volt}$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^-; \qquad E° = +1.36 \text{ volt}$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}; \qquad E° = +0.76 \text{ volt}$$

$$Ce^{4+} + e^- \longrightarrow Ce^{3+}; \qquad E° = +1.60 \text{ volt}$$

$$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}; \qquad E° = +0.15 \text{ volt}$$

On the basis of the above data, answer the following questions:

(*a*) *Whether* Fe^{3+} *oxidises* Ce^{3+} *or not?*

(*b*) *Whether* I_2 *displaces chlorine from KCl?*

(*c*) *Whether the reaction between* $FeCl_3$ *and* $SnCl_2$ *occurs or not?*

Solution: (a) Chemical reaction,

$$Fe^{3+} + Ce^{3+} \longrightarrow Ce^{4+} + Fe^{2+}$$

Two half reactions,

$Fe^{3+} + e \longrightarrow Fe^{2+}$; Reduction; $E° = 0.76$ volt

$Ce^{3+} \longrightarrow Ce^{4+} + e^-$; Oxidation; $E°_{ox} = -1.60$ volt

Adding; emf = − 0.84 volt

Since, emf is negative, the reaction does not occur, *i.e.*, Fe^{3+} does not oxidise Ce^{3+}.

(b) Chemical reaction,

$$I_2 + 2KCl = 2KI + Cl_2$$

Half reactions,

$I_2 + 2e^- \longrightarrow 2I^-$; Reduction; $E° = 0.54$ volt

$2Cl^- \longrightarrow Cl_2 + 2e^-$; Oxidation; $E°_{ox} = -1.36$ volt

Adding; emf = − 0.82 volt

Since, emf is negative, the reaction does not occur, *i.e.*, I_2 does not displace Cl_2 from KCl.

(c) Chemical reaction,

$$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$$

Half reactions,

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$; Reduction; $E° = 0.76$ volt

$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$; Oxidation; $E° = -0.15$ volt

Adding; emf = + 0.61 volt

Since, emf is positive, the reaction will occur.

Example 37. *Calculate the electrode potential at a copper electrode dipped in a* 0.1 *M solution of copper sulphate at* 25° *C. The standard electrode potential of* Cu^{2+}/Cu *system is* 0.34 *volt at* 298 *K.*

Solution: We know that, $E_{red} = E°_{red} + \frac{0.0591}{n} \log_{10}[\text{ion}]$

Putting the values of $E°_{red} = 0.34$ V, $n = 2$ and $[Cu^{2+}] = 0.1\,M$

$$E_{red} = 0.34 + \frac{0.0591}{2}\log_{10}[0.1]$$

$$= 0.34 + 0.02955 \times (-1)$$

$$= 0.34 - 0.02955 = 0.31045 \text{ volt}$$

Example 38. *What is the single electrode potential of a half-cell for zinc electrode dipping in* 0.01 *M* $ZnSO_4$ *solution at* 25° *C? The standard electrode potential of* Zn/Zn^{2+} *system is* 0.763 *volt at* 25° *C.*

Solution: We know that, $E_{ox} = E°_{ox} - \frac{0.0591}{n}\log_{10}[\text{ion}]$

Putting the value of $E°_{ox} = 0.763$ V, $n = 2$ and $[Zn^{2+}] = 0.01$ *M*,

$$E_{ox} = 0.763 - \frac{0.0591}{2}\log_{10}[0.01]$$

$$= 0.763 - 0.02955 \times (-2)$$

$$= (0.763 + 0.0591) \text{ volt} = 0.8221 \text{ volt}$$

Example 39. *The standard oxidation potential of zinc is* 0.76 *volt and of silver is* − 0.80 *volt. Calculate the emf of the cell:*

$$Zn \mid \underset{0.25\,M}{Zn(NO_3)_2} \parallel \underset{0.1\,M}{AgNO_3} \mid Ag$$

at 25° *C.*

Solution: The cell reaction is

$$Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$$

$E°_{ox}$ of Zn = 0.76 volt

$E°_{red}$ of Ag = 0.80 volt

$E°_{cell} = E°_{ox}$ of Zn + $E°_{red}$ of Ag = 0.76 + 0.80 = 1.56 volt

We know that, $E_{cell} = E°_{cell} - \frac{0.0591}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$

$$= E°_{cell} - \frac{0.0591}{2}\log\frac{0.25}{0.1 \times 0.1}$$

$$= 1.56 - \frac{0.0591}{2} \times 1.3979$$

$$= (1.56 - 0.0413) \text{ volt}$$

$$= 1.5187 \text{ volt}$$

Alternative method: First of all, the single electrode potentials of both the electrodes are determined on the basis of given concentrations.

$$E_{ox\,(\text{Zinc})} = E°_{ox} - \frac{0.0591}{2}\log 0.25$$

$$= 0.76 + 0.0177 = 0.7777 \text{ volt}$$

$$E_{red\,(\text{Silver})} = E°_{red} + \frac{0.0591}{1}\log 0.1$$

$$= 0.80 - 0.0591 = 0.7409 \text{ volt}$$

$$E_{cell} = E_{ox\,(\text{Zinc})} + E_{red\,(\text{Silver})}$$

$$= 0.7777 + 0.7409 = 1.5186 \text{ volt}$$

Example 40. *The emf* ($E°$) *of the following cells are:*

$Ag \mid Ag^+(1M) \parallel Cu^{2+}(1M) \mid Cu$; $E° = -0.46$ *volt*

$Zn \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu$; $E° = +1.10$ *volt*

Calculate the emf of the cell:

$$Zn \mid Zn^{2+}(1M) \parallel Ag^+(1M) \mid Ag$$

Solution: $Zn \mid Zn^{2+}(1\,M) \parallel Ag^+(1\,M) \mid Ag$

$$E_{cell} = E_{ox\,(Zn/Zn^{2+})} + E_{red\,(Ag^+/Ag)}$$

With the help of the following two cells, the above equation can be obtained:

$Ag \mid Ag^+(1\,M) \parallel Cu^{2+}(1\,M) \mid Cu$; $E° = -0.46$ volt

or $Cu \mid Cu^{2+}(1\,M) \parallel Ag^+(1\,M) \mid Ag$; $E°$ will be + 0.46 volt or $$+0.46 = E_{\text{ox (Cu/Cu}^{2+})} + E_{\text{red (Ag}^{+}/\text{Ag)}} \quad \text{... (i)}$$

$$\text{Zn} \mid \text{Zn}^{2+}(1\,M) \parallel \text{Cu}^{2+} \mid \text{Cu};\ E^{\circ} = +1.10\ \text{volt}$$

$$+1.10 = E_{\text{ox (Zn/Zn}^{2+})} + E_{\text{red (Cu}^{2+}/\text{Cu)}} \quad \text{... (ii)}$$

Adding eqs. (i) and (ii),

$$+1.56 = E_{\text{ox (Cu/Cu}^{2+})} + E_{\text{red (Ag}^{+}/\text{Ag)}} + E_{\text{ox (Zn/Zn}^{2+})} + E_{\text{red (Cu}^{2+}/\text{Cu)}}$$

Since, $E_{\text{ox (Cu/Cu}^{2+})} = -E_{\text{red (Cu}^{2+}/\text{Cu)}}$

So, $+1.56 = E_{\text{ox (Zn/Zn}^{2+})} + E_{\text{red (Ag}^{+}/\text{Ag)}}$

Thus, the emf of the following cell is

$$\text{Zn} \mid \text{Zn}^{2+}(1\,M) \parallel \text{Ag}^{+}(1\,M) \mid \text{Ag is } +1.56\ \text{volt}$$

Example 41. *Calculate the emf of the cell.*

$$Mg(s) \mid Mg^{2+}(0.2\,M) \parallel Ag^{+}(1 \times 10^{-3}) \mid Ag$$

$$E^{\circ}_{Ag^{+}/Ag} = +0.8\,volt,\ E^{\circ}_{Mg^{2+}/Mg} = -2.37\,volt$$

What will be the effect on emf if concentration of Mg^{2+} *ion is decreased to* 0.1 *M?*

Solution: $E^{\circ}_{\text{Cell}} = E^{\circ}_{\text{Cathode}} - E^{\circ}_{\text{Anode}}$

$$= 0.80 - (-2.37) = 3.17\ \text{volt}$$

Cell reaction, $\text{Mg} + 2\text{Ag}^{+} \longrightarrow 2\text{Ag} + \text{Mg}^{2+}$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{\text{Mg}^{2+}}{[\text{Ag}^{+}]^{2}}$$

$$= 3.17 - \frac{0.0591}{2}\log\frac{0.2}{[1 \times 10^{-3}]^{2}}$$

$$= 3.17 - 0.1566 = 3.0134\ \text{volt}$$

when $\text{Mg}^{2+} = 0.1\,M$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2}\log\frac{0.1}{(1 \times 10^{-3})^{2}}$$

$$= (3.17 - 0.1477)\ \text{volt}$$

$$= 3.0223\ \text{volt}$$

Example 42. *To find the standard potential of* M^{3+}/M *electrode, the following cell is constituted:*

$$Pt \mid M \mid M^{3+}(0.0018\,mol^{-1}L) \parallel Ag^{+}(0.01\,mol^{-1}L) \mid Ag$$

The emf of this cell is found to be 0.42 *volt. Calculate the standard potential of the half reaction* $M^{3+} + 3e^{-} \longrightarrow M$. $E^{\circ}_{Ag^{+}/Ag} = 0.80\,volt$.

Solution: The cell reaction is

$$M + 3\text{Ag}^{+} \longrightarrow 3\text{Ag} + M^{3+}$$

Applying Nernst equation,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{3}\log\frac{[M^{3+}]}{[\text{Ag}^{+}]^{3}}$$

$$0.42 = E^{\circ}_{\text{cell}} - \frac{0.0591}{3}\log\frac{(0.0018)}{(0.01)^{3}} = E^{\circ}_{\text{cell}} - 0.064$$

$$E^{\circ}_{\text{cell}} = (0.42 + 0.064) = 0.484\ \text{volt}$$

$$E^{\circ}_{\text{Cell}} = E^{\circ}_{\text{Cathode}} - E^{\circ}_{\text{Anode}}$$

or $$E^{\circ}_{\text{Anode}} = E^{\circ}_{\text{Cathode}} - E^{\circ}_{\text{Cell}}$$

$$= (0.80 - 0.484) = 0.32\ \text{volt}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. The oxidation potential of hydrogen electrode at pH = 10 and $\text{pH}_2 = 1$ atm is:

(a) 0.51 V (b) 0.00 V (c) + 0.59 V (d) 0.059 V

[Ans. (c)]

[Hint: $E_{\text{ox}} = E^{\circ}_{\text{ox}} - \dfrac{0.0591}{n}\log\dfrac{[\text{H}^{+}]}{\text{pH}_2}$

$$= 0 - \frac{0.0591}{1}\log\frac{10^{-10}}{1} = 0.59\ \text{V}\,]$$

20. The value of equilibrium constant for a feasible cell reaction is:

(a) < 1 (b) = 1 (c) > 1 (d) zero

[Ans. (c)]

[Hint: $K = \text{antilog}\left(\dfrac{nE^{\circ}}{0.0591}\right)$

For feasible cell, E° is positive; hence from the above equation, $K > 1$ for feasible cell reaction.]

21. E° for the electrochemical cell

$$\text{Zn}(s) \mid \text{Zn}^{2+}\ 1\,M\,(aq.) \parallel \text{Cu}^{2+}\ 1\,M\,(aq.) \mid \text{Cu}(s)$$

is 1.10 V at 25°C. The equilibrium constant for the cell reaction,

$$\text{Zn}(s) + \text{Cu}^{2+}(aq.) \rightleftharpoons \text{Zn}^{2+}(aq.) + \text{Cu}(s)$$

will be:

(a) 10^{-37} (b) 10^{37}

(c) 10^{-39} (d) 10^{39}

[Ans. (b)]

[Hint: $K = \text{antilog}\left[\dfrac{nE^{\circ}}{0.0591}\right]$

$$= \text{antilog}\left[\frac{2 \times 1.10}{0.0591}\right] = 1.67 \times 10^{37}\,]$$

22. The value of the reaction quotient Q, for the cell

$$\text{Zn}(s) \mid \text{Zn}^{2+}(0.01\,M) \parallel \text{Ag}^{+}\,(1.25\,M) \mid \text{Ag}(s)$$

is:

(a) 156 (b) 125

(c) 1.25×10^{-2} (d) 6.4×10^{-3}

[Ans. (d)]

[Hint: $\text{Zn}(s) \longrightarrow \text{Zn}^{2+} + 2e^{-}$ (Anodic process)

$2\text{Ag}^{+} + 2e^{-} \longrightarrow 2\text{Ag}(s)$ (Cathodic process)

$\text{Zn}(s) + 2\text{Ag}^{+} \rightleftharpoons 2\text{Ag}(s) + \text{Zn}^{2+}$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^{+}]^{2}} = \frac{0.01}{(1.25)^{2}} = 6.4 \times 10^{-3}\,]$$

23. Calculate the emf of the following concentration cell at 25°C:

$Ag(s) | AgNO_3\ (0.01\ M) || AgNO_3\ (0.05\ M) | Ag(s)$

(a) – 0.414 V (b) 0.828 V

(c) 0.414 V (d) 0.0414 V

[**Ans.** (d)]

[**Hint:** $E = E^\circ - \frac{0.0591}{n} \log_{10} Q$

($\because E^\circ = 0$ for all concentration cells)

$$= 0 - \frac{0.0591}{1} \log_{10}\left(\frac{0.01}{0.05}\right) = 0.0414 \text{ V}]$$

24. The equilibrium constant of the reaction:

$Cu(s) + 2Ag^+(aq.) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$

$E^\circ = 0.46$ V at 298 K is: [CBSE (Med.) 2007]

(a) 2.0×10^{10} (b) 4.0×10^{10}

(c) 4.0×10^{15} (d) 2.4×10^{10}

[**Ans.** (c)]

[**Hint:** $K = \text{antilog}\left[\frac{nE^\circ}{0.059}\right] = \text{antilog}\left[\frac{2 \times 0.46}{0.059}\right]$

$= \text{antilog } 15.593$

$= 3.9 \times 10^{15}$

$\approx 4 \times 10^{15}$]

25. The cell reaction of a cell is:

$Mg(s) + Cu^{2+}(aq.) \rightleftharpoons Cu(s) + Mg^{2+}(aq.)$

If the standard reduction potentials of Mg and Cu are – 2.37 and + 0.34 V respectively. The emf of the cell is: [JEE (WB) 2007]

(a) 2.03 V (b) – 2.03 V (c) + 2.71 V (d) – 2.71 V

[**Ans.** (c)]

[**Hint:** $E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$

$= E^\circ_{\text{Reduced species}} - E^\circ_{\text{Oxidised species}}$

$= 0.34 - (-2.37) = +2.71$ V]

26. 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+}? [PMT (Kerala) 2008]

(a) + 1.006 V (b) – 1.006 V

(c) + 0.77 V (d) – 0.77 V

(e) – 0.652 V

[Ans. (c)]

[**Hint:** $E^\circ = \frac{0.059}{n} \log_{10} K$

$= \frac{0.059}{2} \log_{10} 10^8 = 0.236$

$E^\circ_{\text{Cell}} = E^\circ_{\text{Reduced species}} - E^\circ_{\text{Oxidised species}}$

$0.236 = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.54$

$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$V]

12.23 ELECTROCHEMICAL SERIES

By measuring the potentials of various electrodes *versus* standard hydrogen electrode (SHE), a series of standard electrode potentials has been established. When the electrodes (metals and non-metals) in contact with their ions are arranged on the basis of the values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the **electrochemical** or **electromotive** or **activity series** of the elements.

By international convention, the standard potentials of electrodes are tabulated for reduction half reactions, indicating the tendencies of the electrodes to behave as cathodes towards SHE. Those with positive E° values for reduction half reactions do in fact act as cathodes *versus* SHE, while those with negative E° values of reduction half reactions behave instead as anodes *versus* SHE. The electrochemical series is shown in the given table:

Standard Aqueous Electrode Potentials at 25° C
'The Electrochemical Series'

Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E°, volt
Li	$Li^+ + e^- = Li$	– 3.05
K	$K^+ + e^- = K$	– 2.925
Ca	$Ca^{2+} + 2e^- = Ca$	– 2.87
Na	$Na^+ + e^- = Na$	– 2.714
Mg	$Mg^{2+} + 2e^- = Mg$	– 2.37
Al	$Al^{3+} + 3e^- = Al$	– 1.66
Zn	$Zn^{2+} + 2e^- = Zn$	– 0.7628
Cr	$Cr^{3+} + 3e^- = Cr$	– 0.74
Fe	$Fe^{2+} + 2e^- = Fe$	– 0.44
Cd	$Cd^{2+} + 2e^- = Cd$	– 0.403
Ni	$Ni^{2+} + 2e^- = Ni$	– 0.25
Sn	$Sn^{2+} + 2e^- = Sn$	– 0.14
H_2	$2H^+ + 2e^- = H_2$	0.00
Cu	$Cu^{2+} + 2e^- = Cu$	+ 0.337
I_2	$I_2 + 2e^- = 2I^-$	+ 0.535
Ag	$Ag^+ + e^- = Ag$	+ 0.799
Hg	$Hg^{2+} + 2e^- = Hg$	+ 0.885
Br_2	$Br_2 + 2e^- = 2Br^-$	+ 1.08
Cl_2	$Cl_2 + 2e^- = 2Cl^-$	+ 1.36
Au	$Au^{3+} + 3e^- = Au$	+ 1.50
F_2	$F_2 + 2e^- = 2F^-$	+ 2.87

↓ Increasing tendency to accept electrons
Increasing strength as oxidising agent

↑ Increasing strength as reducing agent
Increasing tendency to lose electrons

Characteristics of Electrochemical Series

(i) The negative sign of standard reduction potential indicates that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode. For example, standard reduction potential of zinc is – 0.76 volt. When zinc electrode is joined with SHE, it acts as anode (–ve electrode), *i.e.*, oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

(ii) The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

(iii) The substances which are stronger oxidising agents than H^+ ion are placed below hydrogen in the series.

(iv) The metals on the top (having high negative values of standard reduction potentials) have the tendency to lose electrons readily. These are active metals. The activity of metals decreases from top to bottom. The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active non-metals. The activity of non-metals increases from top to bottom.

Applications of Electrochemical Series

(i) Reactivity of metals: The activity of the metal depends on its tendency to lose electron or electrons, *i.e.*, tendency to form cation (M^{n+}). This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active.

The chemical reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series. For example,

(a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(b) Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.

(c) Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(ii) Electropositive character of metals: The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups:

(a) Strongly electropositive metals: Metals having standard reduction potential near about –2.0 volt or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.

(b) Moderately electropositive metals: Metals having values of reduction potentials between 0.0 and about –2.0 volt are moderately electropositive. Al, Zn, Fe, Ni, Co, etc., belong to this group.

(c) Weakly electropositive metals: The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. Cu, Hg, Ag, etc., belong to this group.

(iii) Displacement reactions:

(a) To predict whether a given metal will displace another, from its salt solution: A metal higher in the series will displace the metal from its solution which is lower in the series, *i.e.*, **the metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential.** A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

(b) Displacement of one non-metal from its salt solution by another non-metal: A non-metal higher in the series (towards bottom side), *i.e.*, having high value of reduction potential will displace another non-metal with lower reduction potential, *i.e.*, occupying position above in the series. The non-metals which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the ions of the non-metal having low value of reduction potential. Thus, Cl_2 can displace bromine and iodine from bromides and iodides.

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$2I^- \longrightarrow I_2 + 2e^- \qquad \text{(Oxidation)}$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \qquad \text{(Reduction)}$$

[The activity or electronegative character or oxidising nature of the non-metal increases as the value of reduction potential increases.]

(c) Displacement of hydrogen from dilute acids by metals: The metal which can provide electrons to H^+ ions present in dilute acids for reduction, evolve hydrogen from dilute acids.

$$Mn \longrightarrow Mn^{n+} + ne^- \qquad \text{(Oxidation)}$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad \text{(Reduction)}$$

The metal having negative values of reduction potential possess the property of losing electron or electrons.

- **Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.**

The metals which are below hydrogen in electrochemical series like Cu, Hg, Au, Pt, etc., do not evolve hydrogen from dilute acids.

(d) Displacement of hydrogen from water: Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series.

Alkali and alkaline earth metals liberate hydrogen from cold water but Mg, Zn and Fe liberate hydrogen from hot water or steam.

(iv) Reducing power of metals: Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential, more is the tendency to lose electron or electrons. **Thus, reducing nature decreases from top to bottom in the electrochemical series.** The power of the reducing agent increases as the standard reduction potential becomes more and more negative.

Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron.

Element	Na	Zn	Fe
Reduction potential	−2.71	− 0.76	− 0.44

$$\xrightarrow[\text{Reducing nature decreases}]{\qquad\qquad\qquad}$$

Alkali and alkaline earth metals are strong reducing agents.

(v) **Oxidising nature of non-metals:** Oxidising nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. **Thus, oxidising nature increases from top to bottom in the electrochemical series.** The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive.

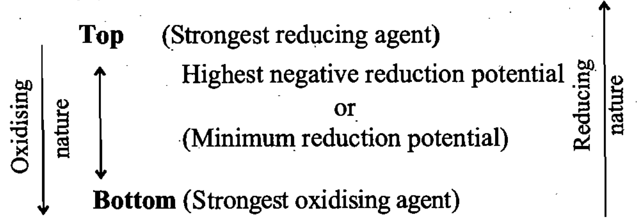
F_2 (Fluorine) is a stronger oxidant than Cl_2, Br_2 and I_2.

Cl_2 (Chlorine) is a stronger oxidant than Br_2 and I_2.

Element	I_2	Br_2	Cl_2	F_2
Reduction potential	+0.53	+1.06	+1.36	+2.85

$$\xrightarrow[\text{Oxidising nature increases}]{\qquad\qquad\qquad}$$

Thus, in electrochemical series



Top (Strongest reducing agent)

Highest negative reduction potential

or

(Minimum reduction potential)

Bottom (Strongest oxidising agent)

Highest positive value of reduction potential

(vi) **Thermal stability of metallic oxides:** The thermal stability of the metal oxide depends on its electropositive nature. As the electropositivity decreases from top to bottom, the thermal stability of the oxide also decreases from top to bottom. The oxides of metals having high positive reduction potentials are not stable towards heat. The metals which come below copper form unstable oxides, *i.e.*, these are decomposed on heating.

$$Ag_2O \xrightarrow{\text{Heat}} 2Ag + \frac{1}{2}O_2$$

$$2HgO \xrightarrow{\text{Heat}} 2Hg + O_2$$

$$\left.\begin{array}{l} BaO \\ Na_2O \\ Al_2O_3 \end{array}\right] \xrightarrow{\text{Heat}} \text{No decomposition}$$

(vii) **Products of electrolysis:** In case, two or more types of positive and negative ions are present in solution, during electrolysis certain ions are discharged or liberated at the electrodes in preference to others. **In general, in such competition the ion which is stronger oxidising agent (high value of standard reduction potential) is discharged first at the cathode.** The increasing order of deposition of few cations is:

$$K^+, Ca^{2+}, Na^+, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{2+}, H^+, Cu^{2+}, Ag^+, Au^{3+}$$

$$\xrightarrow[\text{Increasing order of deposition}]{\qquad\qquad\qquad\qquad\qquad\qquad}$$

Similarly, the anion which is stronger reducing agent (low value of standard reduction potential) is liberated first at the anode.

The increasing order of discharge of few anions is:

$$SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$$

$$\xrightarrow[\text{Increasing order of discharge}]{\qquad\qquad\qquad\qquad}$$

Thus, when an aqueous solution of NaCl containing Na^+, Cl^-, H^+ and OH^- ions is electrolysed, H^+ ions are discharged at cathode and Cl^- ions at the anode, *i.e.*, H_2 is liberated at cathode and chlorine at anode.

When an aqueous solution of $CuSO_4$ containing Cu^{2+}, SO_4^{2-}, H^+ and OH^- ions is electrolysed, Cu^{2+} ions are discharged at cathode and OH^- ions at the anode.

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \text{(Cathodic reaction)}$$

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \qquad \text{(Anodic reaction)}$$

Cu is deposited on cathode while O_2 is liberated at anode.

(viii) **Latimer diagram:** Redox chemistry of an element can be understand by comparing the standard electrode potentials of the various oxidation states of the element. Latimer diagram showing relative stabilities of different oxidation states are given below :

Acid Medium

$$Fe \xrightarrow{E^\circ_{Fe/Fe^{2+}} = +0.44\text{ V}} Fe^{2+} \xrightarrow{E^\circ_{Fe^{2+}/Fe^{3+}} = -0.77\text{ V}} Fe^{3+}$$

Alkaline Medium

$$Fe \xrightarrow{E^\circ_{Fe/Fe^{2+}} = +0.88\text{ V}} Fe^{2+} \xrightarrow{E^\circ_{Fe^{2+}/Fe^{3+}} = +0.56\text{ V}} Fe^{3+}$$

In acid medium, the positive value of $E^\circ_{Fe/Fe^{2+}}$ indicates that iron will dissolve in acid medium to form Fe^{2+} ion; since $E^\circ_{Fe^{2+}/Fe^{3+}}$ is negative, hence +2 state of iron will be more state than +3 state in acid medium.

When the potential on right of a species is more positive (less negative) than that on the left, then the species will tend to undergo disproportionation.

Example :

Alkaline Medium

$$Cl^- \xrightarrow{E^\circ_{Cl^-/Cl_2} = -1.35\text{ V}} \frac{1}{2}Cl_2 \xrightarrow{E^\circ_{Cl_2/ClO^-} = -0.4\text{ V}} ClO^-$$

Thus, Cl_2 will undergo disproportionation into Cl^- and ClO^- ions in basic medium.

$$Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$$

(ix) **Corrosion of metals:** Corrosion is defined as the deterioration of a substance because of its reaction with its environment. This is also defined as the process by which metals have the tendency to go back to their combined state, *i.e.*, reverse of extraction of metals.

Thus, the process of weathering away of the metal due to attack of the atmospheric gases on the surface of the metal *resulting into the formation of compounds such as oxides, sulphates, sulphides, carbonates, etc., is called corrosion.*

The process of corrosion of iron is called rusting. Rust is chemically the hydrated oxide of iron having the formula $Fe_2O_3 \cdot xH_2O$. Other examples of corrosion of metals are tarnishing of silver and those of copper and bronze etc. Corrosion of copper and bronze forms a green coating on the surface. The corrosion of metals, particularly iron, causes damage to buildings, dams, bridges, etc., and we lose a lot of money every year.

Mechanism of Corrosion : Corrosion is a redox process by which metals are oxidised by oxygen in presence of moisture. The mechanism can be understood by taking the example of rusting of iron. The theory of rusting is called **electrochemical theory.** In this theory the process of rusting can be explained on the basis of formation of electrochemical cell on the surface of an iron object.

Rusting of iron involves the following steps :

Step 1 : The water vapours present in contact with iron surface have dissolved CO_2 and O_2 from air.

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(l)$$

Thus, the surface of iron is covered with an aqueous solution of carbonic acid, which undergoes dissociation to a small extent.

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-} \quad \text{(Ionisation of carbonic acid)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(Ionisation of water)}$$

Step 2 : Second step involves oxidation of iron. Oxidation of metal takes place at the point of strain. For example, a steel nail first corrodes at the tip and head. The tip of the nail acts as anode where iron is oxidised to ferrous ion.

$$Fe(s) \longrightarrow Fe^{2+} + 2e^- \quad \text{(Anodic process, oxidation)} \quad \ldots\text{(i)}$$

$$(E^\circ_{Fe^{2+}/Fe} = -0.44 \text{ volt})$$

Step 3 : The electrons flow along the nail to the areas containing impurities which act as cathode where oxygen (dissolved in water) is reduced to hydroxyl ions.

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-$$

$$\text{(Cathodic process, reduction)}$$

$$(E^\circ_{red} = 1.23 \text{ volt})$$

The process of reduction involves the following two steps :

First of all H^+ ions are reduced to hydrogen atoms.

$$H^+ + e^- \longrightarrow [H] \quad \ldots\text{(ii)}$$

These hydrogen atoms combine with oxygen dissolved in water or from air.

$$4[H] + O_2 \longrightarrow 2H_2O \quad \ldots\text{(iii)}$$

Combining (ii) and (iii), we get

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O(l) \quad \ldots\text{(iv)}$$

$$(E^\circ_{red} = 1.23 \text{ volt})$$

Adding equations (i) and (iv), we get, the overall reactions of microcells established on the surface of iron.

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

$$(E^\circ_{cell} = 1.67 \text{ volt})$$

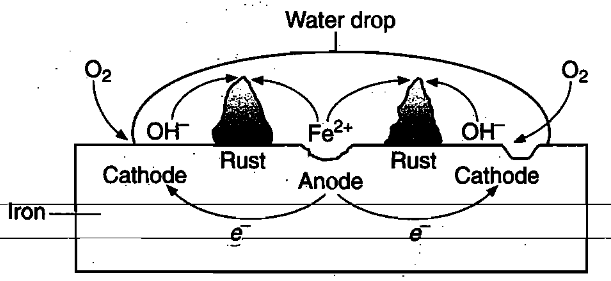
Step 4 : The ferrous ions (Fe^{2+}) formed in the previous step reacts with dissolved oxygen or oxygen from air to form ferric oxide (Fe_2O_3).

$$4Fe^{2+} + O_2 + 4H_2O \longrightarrow 2Fe_2O_3 + 8H^+(aq)$$

Hydration of ferric oxide gives rust.

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3 \cdot xH_2O$$

The process of rusting may be diagrammatically represented as in Fig. 12.17.



Oxidation : $Fe(s) \longrightarrow Fe^{2+}(aq.) + 2e^-$

Reduction : $O_2 + 4H^+(aq.) + 4e^- \longrightarrow 2H_2O(l)$

Atmospheric $4Fe^{2+} + O_2 + 4H_2O(l) \longrightarrow 2Fe_2O_3(s) + 8H^+(aq.)$

Oxidation $Fe_2O_3 + xH_2O \longrightarrow \underset{\text{Rust}}{Fe_2O_3 . xH_2O}$

Fig. 12.17 Rusting of iron

Factors Affecting Corrosion

1. Standard reduction potential : Lesser is the standard reduction potential, greater is the tendency of corrosion. In other words, more is the reactivity of metal, greater is the tendency of corrosion.

2. Strains and corrosion : Corrosion of metals occurs more readily at points of strain, bend, nick and scratches.

3. Impurity of metal and corrosion : Presence of impurity in metals increases the probability of their corrosion. Pure metals, *e.g.*, pure iron does not undergo rusting.

4. Salinity of water and corrosion : If water is saline, it helps in the flow of current in microelectrochemical cells on the surface of iron and hence, increases the process of corrosion.

5. Pollution and corrosion : The acidic oxides like CO_2, SO_2, NO_2 etc., present in air act as catalysts for corrosion. It should be noted that if iron is placed in vacuum, it does not undergo rusting.

Prevention of Rusting : Prevention of rusting is not only important from the point of view of economy but also from the point of view of safety. Prevention of corrosion not only saves money but also prevents accidents due to collapse of bridges and buildings.

Some important methods for preventing corrosion are described below:

1. Using antirust solution : Alkaline phosphate and alkaline chromate solutions are the commonly used antirust solutions. Alkaline phosphates tend to form an insoluble film of iron phosphate on the surface of iron, thereby protecting it from corrosion. In addition, the alkaline nature of an antirust solution decreases the availability of H^+ ions which facilitate the oxidation of Fe to Fe^{2+}. These solutions are used to prevent rusting of radiators of cars and water coolers.

2. Barrier protection : It is one of the simplest methods of preventing corrosion. In this method a barrier or coating is applied to prevent the surface of the metallic object from come in contact with the atmosphere. This can be achieved by the following methods :

(i) Oil paints on the surface of metal prevents its contact with moist air.

(ii) By applying grease or oil on the surface of iron tools and other objects, rusting can be prevented.

(iii) Nichrome (Ni + Cr) plating on the surface of iron also acts as a barrier between metal and atmosphere.

(iv) Bisphenol is an important chemical which can be applied on the surface of the metal to avoid its corrosion.

3. Sacrificial protection : In this method, the surface of iron is coated with a more active metal than iron. This active metal loses electrons, *i.e.*, undergo oxidation in preference to iron and hence, prevents the rusting of iron. So, long as the surface of iron is covered with such metals the corrosion of iron is prevented. If the surface is scratched or the coating is broken, even then the rusting of iron does not start.

Zinc metal is the most stable metal to cover iron surfaces. **The process of coating the iron surface by zinc is called galvanization.** Zinc metal present on the surface of iron forms a thin protective layer of basic zinc carbonate, *i.e.*, $ZnCO_3 \cdot Zn(OH)_2$ due to the reaction between zinc, oxygen, CO_2 and moisture in air.

$$Zn^{2+} + 2e^- \longrightarrow Zn(s); \qquad E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ volt}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe(s); \qquad E^\circ_{Fe^{2+}/Fe} = -0.44 \text{ volt}$$

(Zinc will undergo oxidation in preference to iron.)

Since, standard reduction potential of zinc is less than iron, hence, iron will not undergo corrosion (oxidation) even when the zinc coating is broken due to scratches or some other mechanical stress.

Sometimes an iron surface is coated with tin metal and this process is known as **tinning** or tin plating. This method is not as effective as **galvanization.**

$$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s); \quad E^\circ_{Sn^{2+}/Sn} = -0.14 \text{ volt}$$

$$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s); \quad E^\circ_{Fe^{2+}/Fe} = -0.44 \text{ volt}$$

(Iron will undergo oxidation in preference to tin.)

Tinning is effective in checking the rusting of iron so long as the surface of iron is fully covered by tin. Once the tin coating is broken or scratched then rusting will start because standard reduction potential of iron is less than that of tin.

4. Electrical or Cathodic protection : If a buried steel pipe is connected to an active metal, *i.e.*, highly electropositive metal, say magnesium, a voltaic cell is formed; the active metal is the anode and iron becomes the cathode. Wet soil or moisture forms the electrolyte and the electrode reactions are :

$$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-; \quad E^\circ_{Mg^{2+}/Mg} = -2.37\text{ V}$$

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq); \quad E^\circ_{red} = 1.23\text{ V}$$

Overall: $$2Mg(s) + O_2(g) + 2H_2O(l) \longrightarrow 2Mg^{2+} + 4OH^-; \quad E^\circ_{cell} = 3.60\text{ V}$$

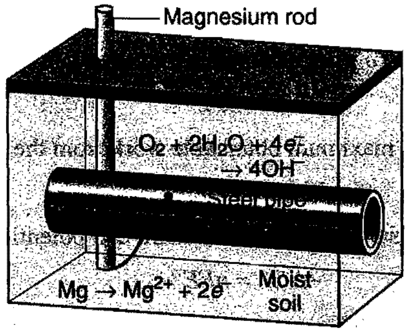


Fig. 12.18 Cathodic protection of a buried steel pipe

As the cathode, the iron containing steel pipe is protected from oxidation. Of course, the magnesium rod is eventually consumed and must be replaced, but this is cheaper than digging up the pipe line. This method is used to prevent the rusting of submarines and base line of oil refineries.

(x) Extraction of metals: A more electropositive metal can displace a less electropositive metal from its salt's solution. This principle is applied for the extraction of Ag and Au by cyanide process. Silver from the solution containing sodium argento cyanide, $NaAg(CN)_2$, can be obtained by the addition of zinc as it is more electropositive than Ag.

$$2NaAg(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2Ag$$

Concept of Equilibrium in Electrochemical Cell

In an electrochemical cell a reversible redox process takes place, *e.g.*, in Daniell cell:

$$Zn(s) + Cu^{2+}(aq.) \rightleftharpoons Zn^{2+}(aq.) + Cu(s)$$

(1) At equilibrium mass action ratio becomes equal to equilibrium constant,

i.e., $Q = K_e$

(2) Oxidation potential of anode = − Reduction potential of cathode

i.e., emf = Oxidation potential of anode + Reduction potential of cathode = 0

Cell is fully discharged.

According to Nernst equation:

$$E = E^\circ - \frac{0.0591}{n}\log_{10} Q \text{ at } 25^\circ\text{C}$$

At equilibrium, $E = 0,\ Q = K$

$$0 = E^\circ - \frac{0.0591}{n}\log_{10} K$$

$$K = \text{antilog}\left[\frac{nE^\circ}{0.0591}\right]$$

Work done by the Cell

Let *n* faraday charge be taken out of a cell of emf *E*; then work done by the cell will be calculated as:

$$\text{Work} = \text{Charge} \times \text{Potential}$$
$$= nFE$$

Work done by the cell is equal to decrease in free energy.

$$-\Delta G = nFE$$

Similarly, maximum obtainable work from the cell will be

$$W_{\max} = nFE^\circ$$

where, E° = standard emf or standard cell potential.

$$-\Delta G^\circ = nFE^\circ$$

The Relationship among K, ΔG° and E° Cell

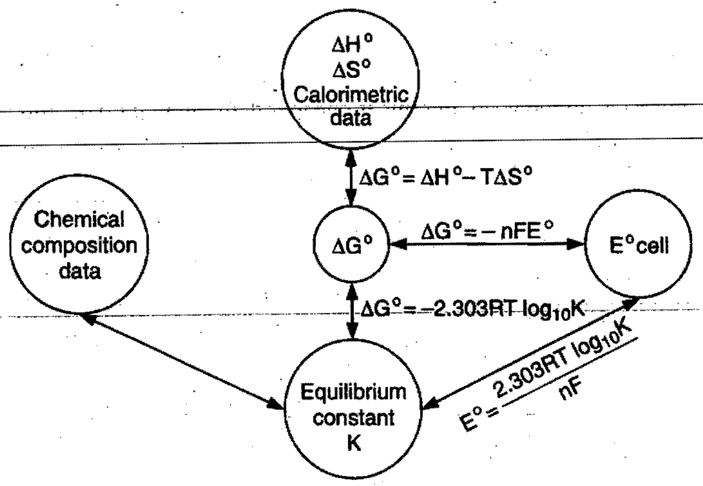


Fig. 12.19

Heat of Reaction in an Electrochemical Cell

Let n faraday charge flows out of a cell of emf E,

Then $$-\Delta G = nFE \qquad \text{... (i)}$$

Gibbs-Helmholtz equation from thermodynamics may be given as:

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad \text{... (ii)}$$

From equations (i) and (ii), we get

$$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_P = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$$

Here, $\left(\frac{\partial E}{\partial T}\right)_P$ = Temperature coefficient of cell

Case I: When $\left(\frac{\partial E}{\partial T}\right)_P = 0$, then $\Delta H = -nFE$

Case II: When $\left(\frac{\partial E}{\partial T}\right) > 0$, then $nFE > \Delta H$, *i.e.*, process inside the cell is endothermic.

Case III: When $\left(\frac{\partial E}{\partial T}\right) < 0$, then $nFE < \Delta H$, *i.e.*, process inside the cell is exothermic.

12.24 PRIMARY VOLTAIC CELL (The Dry Cell)

In this cell, once the chemicals have been consumed, further reaction is not possible. It cannot be regenerated by reversing the current flow through the cell using an external direct current source of electrical energy. The most common example of this type is dry cell.

The container of the dry cell is made of zinc which also serves as one of the electrodes. The other electrode is a carbon rod in the centre of the cell. The zinc container is lined with a porous paper. A moist mixture of ammonium chloride, manganese dioxide, zinc chloride and a porous inert filler occupy the space between the paper lined zinc container and the carbon rod. The cell is sealed with a material like wax.

As the cell operates, the zinc is oxidised to Zn^{2+}

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{(Anode reaction)}$$

The electrons are utilized at carbon rod (cathode) as the ammonium ions are reduced.

$$2NH_4^+ + 2e^- \longrightarrow 2NH_3 + H_2 \quad \text{(Cathode reaction)}$$

The cell reaction is

$$Zn + 2NH_4^+ \longrightarrow Zn^{2+} + 2NH_3 + H_2$$

Hydrogen is oxidised by MnO_2 in the cell.

$$2MnO_2 + H_2 \longrightarrow 2MnO(OH)$$

Ammonia produced at cathode combines with zinc ions to form complex ion.

$$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$$

E_{cell} is 1.6 volt.

Alkaline dry cell is similar to ordinary dry cell. It contains potassium hydroxide. The reactions in alkaline dry cell are:

$$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^- \quad \text{(Anode reaction)}$$

$$2MnO_2 + 2H_2O + 2e^- \longrightarrow 2MnO(OH) + 2OH^- \quad \text{(Cathode reaction)}$$

$$Zn + 2MnO_2 + 2H_2O \longrightarrow Zn(OH)_2 + 2MnO(OH) \quad \text{(Overall)}$$

E_{cell} is 1.5 volt.

Button cell : The button cells are usually pallet type flat in construction and look like a button in shape. Owing to their small sizes, they are used in small electronic devices like hearing aids, electronic watches etc. These cells are basically primary cells. Mercuric oxide button cell is the most commonly used button cell. In this cell, zinc anode and mercuric oxide plus carbon paste cathode is used. The electrolyte is a paste of ZnO and KOH.

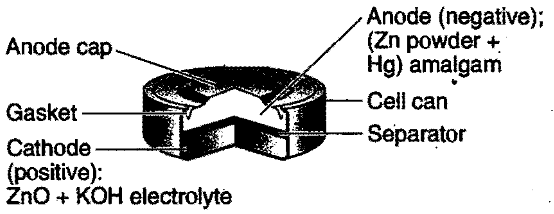


Fig. 12.20

The cell process is given below :

Anode : $\underset{\text{(Amalgam)}}{Zn} + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

Cathode: $HgO(s) + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

Overall : $\underset{\text{Amalgam}}{Zn} + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

The potential of this cell is approximately 1.35 volt and it remains constant during its life because overall reaction does not involve any ion whose concentration can change during the process.

12.25 SECONDARY VOLTAIC CELL (Lead Storage Battery)

The cell in which original reactants are regenerated by passing direct current from external source, *i.e.*, it is recharged, is called secondary cell. Lead storage battery is the example of this type.

It consists of a group of lead plates bearing compressed spongy lead, alternating with a group of lead plates bearing lead dioxide, PbO_2. These plates are immersed in a solution of about 30% H_2SO_4. When the cell discharges, it operates as a voltaic cell. The spongy lead is oxidised to Pb^{2+} ions and lead plates acquire a negative charge.

$$Pb \longrightarrow Pb^{2+} + 2e^- \qquad \text{(Anode reaction)}$$

Pb^{2+} ions combine with sulphate ions to form insoluble lead sulphate, $PbSO_4$, which begins to coat lead electrode.

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \qquad \text{(Precipitation)}$$

The electrons are utilised at PbO_2 electrode.

$$PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O \qquad \text{(Cathode reaction)}$$

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \qquad \text{(Precipitation)}$$

Overall cell reaction is:

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$$

E_{cell} is 2.041 volt.

When a potential slightly greater than the potential of battery is applied, the battery can be recharged.

$$2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 2H_2SO_4$$

After many repeated charge-discharge cycles, some of the lead sulphate falls to the bottom of the container, the sulphuric acid concentration remains low and the battery cannot be recharged fully.

Nickel-Cadmium storage cell : It is also a common storage battery. It is more expensive than the lead storage battery but it is light, therefore, used in calculators, portable power tools, etc.

It is a voltaic cell consisting of an anode of cadmium and a cathode of hydrated nickel oxide on nickel. The electrolyte in the cell is aqueous solution of potassium hydroxide. Electrode processes are given below :

Anode: $Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2 + 2e^-$

Cathode: $NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$

$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2 + Ni(OH)_2$$

In the recharging of the cell the process is reversed.

$$Cd(OH)_2 + Ni(OH)_2 \longrightarrow Cd(s) + NiO_2(s) + 2H_2O(l)$$

12.26 FUEL CELL

Fuel cells are another means by which chemical energy may be converted into electrical energy. The main disadvantage of a primary cell is that it can deliver current for a short period only. This is due to the fact that the quantity of oxidising agent and reducing agent is limited. But the energy can be obtained indefinitely from a fuel cell as long as the outside supply of fuel is maintained. One of the examples is the hydrogen-oxygen fuel cell. The cell consists of three compartments separated by a porous electrode. Hydrogen gas is introduced into one compartment and oxygen gas is fed into another compartment. These gases then diffuse slowly through the electrodes and react with an electrolyte that is in the central compartment. The electrodes are made of porous carbon and the electrolyte is a resin containing concentrated aqueous sodium hydroxide solution. Hydrogen is oxidised at anode and oxygen is reduced at cathode. The overall cell reaction produces water. The reactions which occur are:

Anode $[H_2(g) + 2OH^-(aq.) \longrightarrow 2H_2O(l) + 2e^-] \times 2$

Cathode $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq.)$

Overall $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

This type of cells are used in space-crafts. Fuel cells are efficient and pollution free.

Thermodynamic efficiency of fuel cells is the ratio of the electrical free energy to the enthalpy of the reaction.

$$\eta = \frac{\Delta G}{\Delta H}$$

12.27 CONCENTRATION CELLS

If two plates of the same metal are dipped separately into two solutions of the same electrolyte and are connected with a salt bridge, the whole arrangement is found to act as a galvanic cell. In general, there are two types of concentration cells:

(i) Electrode concentration cells: In these cells, the potential difference is developed between two like electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gas pressures in the same solution of hydrogen ions constitute a cell of this type.

$$\underset{\text{Anode}}{\underline{\text{Pt, H}_2\ (\text{Pressure } p_1)}}\ |\text{H}^+|\ \underset{\text{Cathode}}{\underline{\text{H}_2\ (\text{Pressure } p_2)\ \text{Pt}}}$$

If $p_1 > p_2$, oxidation occurs at LHS electrode and reduction occurs at RHS electrode.

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{(p_1)}{(p_2)} \quad \text{at } 25^\circ \text{C}$$

In the amalgam cells, two amalgams of the same metal at two different concentrations are immersed in the same electrolytic solution.

$$M(\text{Hg}\ C_1)\ |M^{n+}|\ \text{Zn}(\text{Hg}\ C_2)$$

The emf of the cell is given by the expression

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_1}{C_2} \quad \text{at } 25^\circ \text{C}$$

(ii) Electrolyte concentration cells: In these cells, electrodes are identical but these are immersed in solutions of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the start the emf of the cell is maximum and it gradually falls to zero. Such a cell is represented in the following manner:

(C_2 is greater than C_1).

$$M\ |\ M^{n+}(C_1)\ ||\ M^{n+}(C_2)\ |\ M$$

or

$$\underset{\text{Anode}}{\underline{\text{Zn}\ |\ \text{Zn}^{2+}(C_1)}}\ ||\ \underset{\text{Cathode}}{\underline{\text{Zn}^{2+}(C_2)\ |\ \text{Zn}}}$$

The emf of the cell is given by the following expression:

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_{2\,(\text{RHS})}}{C_{1\,(\text{LHS})}} \quad \text{at } 25^\circ \text{C}$$

The concentration cells are used to determine the solubility of sparingly soluble salts, valency of the cation of the electrolyte and transition point of the two allotropic forms of a metal used as electrodes, etc.

SOME SOLVED EXAMPLES

Example 43. *A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of* 10^{-6} *M hydrogen ions. The emf of the cell is* 0.118 *volt at* 25° *C. Calculate the concentration of hydrogen ions at the positive electrode.*

Solution: The cell may be represented as

$$\text{Pt}\ |\ \text{H}_2\ (1\ \text{atm})\ |\ \underset{10^{-6}\ M}{\text{H}^+}\ ||\ \underset{CM}{\text{H}^+}\ |\ \text{H}_2\ (1\ \text{atm})\ |\ \text{Pt}$$

Anode	Cathode
(–ve)	(+ ve)
$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{[\text{H}^+]^2_{\text{Cathode}}}{[10^{-6}]^2}$$

$$0.118 = (0.0591) \log \frac{[\text{H}^+]}{10^{-6}}$$

$$\log \frac{[\text{H}^+]_{\text{Cathode}}}{10^{-6}} = \frac{0.118}{0.0591} = 2$$

$$\frac{[\text{H}^+]_{\text{Cathode}}}{10^{-6}} = 10^2$$

$$[\text{H}^+]_{\text{Cathode}} = 10^{-6} \times 10^2 = 10^{-4}\ M$$

Example 44. *The emf of the cell*

$$Ag\ |\ AgI \text{ in } 0.05\ M\ KI\ |\ Sol.\ NH_4NO_3\ |\ 0.05\ M\ AgNO_3\ |\ Ag$$

is 0.788 *volt at* 25° *C. The activity coefficient of KI and silver nitrate in the above solution is* 0.90 *each. Calculate (i) the solubility product of AgI and (ii) the solubility of AgI in pure water at* 25° *C.*

Solution: Ag^+ ion concentration on AgNO_3 side

$$= 0.9 \times 0.05 = 0.045\ M$$

Similarly I^- ion concentration in 0.05 M KI solution

$$= 0.05 \times 0.9 = 0.045\ M$$

$$E_{\text{cell}} = \frac{0.0591}{1} \log \frac{[\text{Ag}^+]_{\text{RHS}}}{[\text{Ag}^+]_{\text{LHS}}} = 0.0591 \log \frac{0.045}{[\text{Ag}^+]_{\text{LHS}}}$$

or

$$\log \frac{0.045}{[\text{Ag}^+]_{\text{LHS}}} = \frac{0.788}{0.0591} = 13.33$$

$$[\text{Ag}^+]_{\text{LHS}} = \frac{0.045}{2.138 \times 10^{13}}$$

$$= 2.105 \times 10^{-15}\ M$$

$$\text{Solubility product of AgI} = [\text{Ag}^+][\text{I}^-]$$

$$= 2.105 \times 10^{-15} \times 0.045$$

$$= 9.472 \times 10^{-17}$$

$$\text{Solubility of AgI} = \sqrt{\text{Solubility product of AgI}}$$

$$= \sqrt{9.472 \times 10^{-17}}$$

$$= 9.732 \times 10^{-9}\ \text{g mol L}^{-1}$$

$$= 9.732 \times 10^{-9} \times 143.5\ \text{g L}^{-1}$$

$$= 1.396 \times 10^{-6}\ \text{g L}^{-1}$$

Example 45. *The observed emf of the cell,*

$$Pt\ |\ H_2\ (1\ atm)\ |\ H^+(3 \times 10^{-4}\ M)\ ||\ H^+(M_1)\ |\ H_2\ (1\ atm)\ |\ Pt$$

is 0.154 *V. Calculate the value of* M_1 *and pH of cathodic solution.*

Solution:

$$E_{\text{cell}} = 0.0591 \log \frac{M_1}{3 \times 10^{-4}}$$

or

$$\log \frac{M_1}{3 \times 10^{-4}} = \frac{0.154}{0.0591} = 2.6058$$

$$\frac{M_1}{3\times 10^{-4}} = 4.034\times 10^{2}$$

$$M_1 = 4.034\times 10^{2}\times 3\times 10^{-4}\ M$$

$$= 0.121M$$

$$pH = -\log[H^+] = -\log 0.121 = 0.917$$

Example 46. *Calculate the emf of the following cell at 25° C:*

$$Pt\ \underset{2\ atm}{H_2}\ |HCl|\ \underset{10\ atm}{H_2}\ Pt$$

Solution: $E_{cell} = \frac{0.0591}{2}\log\frac{p_1}{p_2}$

$$= \frac{0.0591}{2}\log\frac{2}{10}$$

$$= -0.0206\ \text{volt}$$

Example 47. *In a fuel cell H_2 and O_2 react to produce electricity. In the process H_2 gas is oxidised at the anode and O_2 is reduced at the cathode. If 67.2 litre of H_2 at NTP reacts in 15 minute, what is the average current produced? If the entire current is used for electro-deposition of Cu from Cu^{2+}, how many g of Cu are deposited?*

Solution: Reaction at anode of fuel cell,

$$\underset{\substack{1\ \text{mole}\\ 22.4\ \text{L}}}{H_2(g)} \longrightarrow 2H^+ + \underset{\substack{2\ \text{mole}\\ 2\ \text{F}}}{2e^-}$$

$$67.2\ \text{L of } H_2 \text{ correspond} = \frac{2\times 96500}{22.4}\times 67.2\ \text{coulomb}$$

$$\text{Time} = 15\times 60\ \text{second}$$

$$\text{Average current} = \frac{2\times 96500\times 67.2}{22.4\times 15\times 60} = 643.3\ \text{amp}$$

$$\text{Mass of copper deposited by } \frac{2\times 96500}{22.4}\times 67.2\ \text{coulomb}$$

$$= \frac{63.5}{2\times 96500}\times\frac{2\times 96500\times 67.2}{22.4}$$

$$= 190.5\ \text{g}$$

Example 48. *Neglecting the liquid-liquid junction potential, calculate the emf of the following cell at 25° C:*

$$H_2(1\ atm)|\ 0.5\ M\ HCOOH\ ||\ 1M\ CH_3COOH\ |\ (1\ atm)\ H_2$$

K_a for HCOOH and CH_3COOH are 1.77×10^{-4} and 1.8×10^{-5} respectively.

Solution: $[H^+]$ in HCOOH $= \sqrt{C\times K_a} = \sqrt{0.5\times 1.77\times 10^{-4}}$

$$= 0.9407\times 10^{-2}\ M$$

$$[H^+] \text{ in } CH_3COOH = \sqrt{C\times K_a} = \sqrt{1\times 1.8\times 10^{-5}}$$

$$= 4.2426\times 10^{-3}\ M$$

$$E_{cell} = 0.0591\log\frac{[H^+]_{RHS}}{[H^+]_{LHS}} = 0.0591\log\frac{4.2426\times 10^{-3}}{0.9407\times 10^{-2}}$$

$$= -0.0204\ \text{volt}$$

Example 49. *During the discharge of a lead storage battery, density of H_2SO_4 fell from 1.294 to 1.139 g/mL. Sulphuric acid of density 1.294 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 litre of the acid and volume remains practically constant during discharge. Calculate ampere-hour of which the battery must have been used. The charging and discharging reactions are:*

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^- \qquad (charging)$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O\ (discharging)$$

Solution:

$$\text{Weight of solution before discharge} = 3500\times 1.294$$

$$= 4529\ \text{g}$$

$$\text{Weight of } H_2SO_4 \text{ before discharge} = \frac{39}{100}\times 4529$$

$$= 1766.31\ \text{g}$$

$$\text{Weight of solution after discharge} = 3500\times 1.139$$

$$= 3986.5\ \text{g}$$

$$\text{Weight of } H_2SO_4 \text{ after discharge} = \frac{20}{100}\times 3986.5$$

$$= 797.3\ \text{g}$$

Loss in mass of H_2SO_4 during discharge

$$= 1766.31 - 797.3 = 969.01\ \text{g}$$

Now from first law of electrolysis,

$$W = \frac{Q\times E}{96500}$$

$$969.01 = \frac{Q\times 98}{96500}$$

$$Q = 954178.21\ \text{coulomb}$$

$$\text{Ampere-hour} = \frac{\text{Coulomb}}{3600} = \frac{954178.21}{3600}$$

$$= 265.04\ \text{ampere-hour}$$

12.28 COMMERCIAL PRODUCTION OF CHEMICALS

The wide applications of electrolysis have been listed in section 12.4 of this chapter. A large number of chemicals are produced by electrolysis. A few of these are described below:

1. Manufacture of sodium

Sodium is obtained on large scale by two processes:

(i) Castner's process: In this process, electrolysis of fused sodium hydroxide is carried out at 330°C using iron as cathode and nickel as anode.

$$2NaOH \rightleftharpoons 2Na^+ + 2OH^-$$

At cathode: $2Na^+ + 2e \longrightarrow 2Na$

At anode: $4OH^- \longrightarrow 2H_2O + O_2 + 4e$

During electrolysis, oxygen and water are produced. Water formed at the anode gets partly evaporated and is partly broken down and hydrogen is discharged at cathode.

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode: $2H^+ + 2e \longrightarrow 2H \longrightarrow H_2 \uparrow$

(ii) Down's process: Now-a-days sodium metal is manufactured by this process. It involves the electrolysis of fused sodium chloride containing calcium chloride and potassium fluoride using iron as cathode and graphite as anode at about 600°C (Fig. 12.21).

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At cathode: $Na^+ + e \longrightarrow Na$

At anode: $2Cl^- \longrightarrow Cl_2 + 2e$

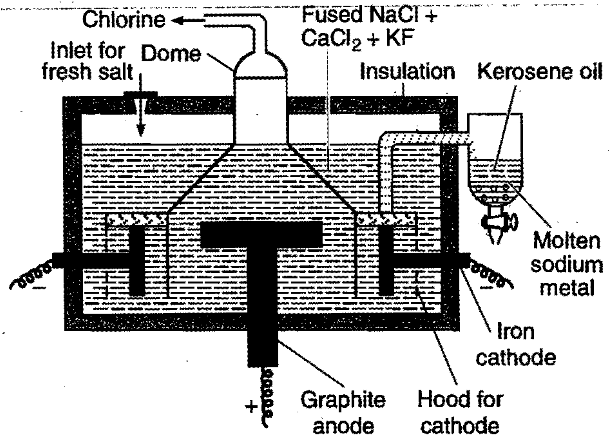


Fig. 12.21 Down's cell for extraction of sodium

The electrolysis of pure NaCl presents the following difficulties:

(a) The fusion temperature of NaCl is high, *i.e.*, 803°C. At this temperature both sodium and chlorine are corrosive.

(b) Sodium forms a metallic fog at this temperature.

To remove above difficulties, the fusion temperature is reduced to 600°C by adding $CaCl_2$ and KF. This is a cheaper method and **chlorine is obtained as a byproduct.** The sodium obtained is of high purity (about 99.5%).

2. Sodium hydroxide (Caustic soda), NaOH

Caustic soda is manufactured by the electrolysis of aqueous solution of sodium chloride in an electrolytic cell.

Principle: A sodium chloride solution contains Na^+, H^+, Cl^- and OH^- ions.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

On passing electricity, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. The discharge potential of H^+ ions is less than Na^+ ions, thus hydrogen ions get discharged easily and hydrogen is liberated. Similarly, at anode Cl^- ions are easily discharged as their discharge potential is less than that of OH^- ions. Cl_2 gas is, therefore, liberated at anode.

The solution on electrolysis becomes richer in Na^+ and OH^- ions.

Since, chlorine reacts with sodium hydroxide solution even in the cold forming sodium chloride and sodium hypochlorite, it is necessary that chlorine should not come in contact with sodium hydroxide during electrolysis.

$$2NaOH + Cl_2 \longrightarrow NaCl + NaClO + H_2O$$

To overcome this problem, the anode is separated from the cathode in the electrolytic cell either by using a porous diaphragm or by using a mercury cathode.

(i) Porous diaphragm process (Nelson cell process): Nelson cell consists of a perforated steel tube lined inside with asbestos. The tube acts as a cathode (Fig. 12.22).

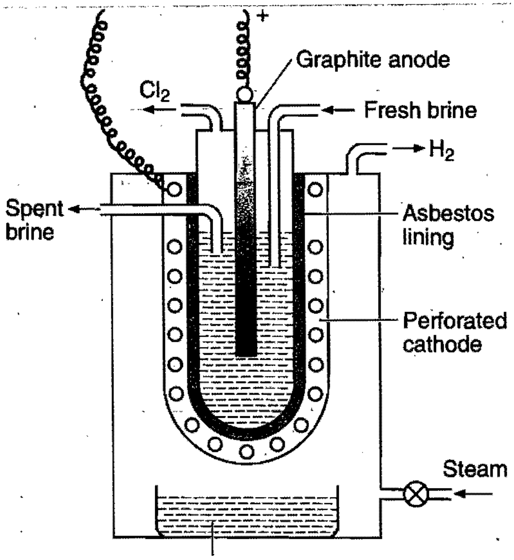


Fig. 12.22 Nelson cell

It is suspended in a steel tank. A graphite rod dipped in sodium chloride solution serves as anode. On passing electric current, chlorine is liberated at the anode and let out through the outlet. Sodium ions penetrate through the asbestos and reach the cathode where hydrogen and OH^- ions are formed by reduction of water. Sodium ions combine with OH^- ions to form NaOH which is collected in the outer tank while hydrogen is drawn off through the outlet. The steam blown during the process keeps the electrolyte warm and helps to keep perforation clear.

$$NaCl \rightleftharpoons Na^+ + Cl^- \quad \text{(in solution)}$$

At cathode: $2H_2O + 2e \rightleftharpoons H_2 + 2OH^-$

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

At anode: $2Cl^- \longrightarrow Cl_2 + 2e$

The solution containing NaOH and NaCl as impurity is taken out and evaporated to dryness.

(ii) Castner-Kellner cell: This is the common cell in which mercury is used as cathode. The advantage of using Hg as a cathode is that the discharge potential of Na^+ ions is less than that of H^+ ions. Na^+ ions get discharged on mercury and the sodium so deposited combines with mercury to form sodium amalgam. The cell consists of a large rectangular trough divided into three compartments by slate partitions which do not touch the bottom of the cell but dipping in mercury as shown in the Fig. 12.23.

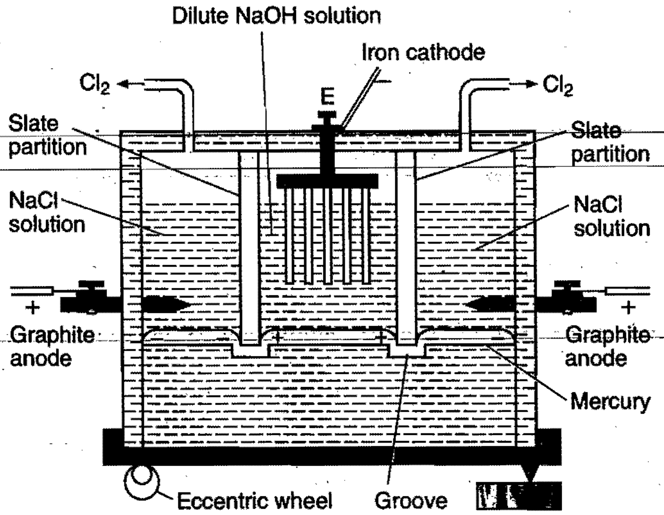


Fig. 12.23 Castner-Kellner cell

The mercury can flow from one compartment into other but the solution kept in one compartment cannot flow into other. Sodium chloride solution is placed in the two outer compartments and a dilute solution of sodium hydroxide in the inner compartment. Two graphite electrodes which act as anodes are fixed in the outer compartments and a series of iron rods fitted in the inner compartment acts as cathode. Mercury in the outer compartments acts as cathode while in the inner compartment it acts as anode by induction. The cell is kept rocking with the help of an eccentric wheel.

When electricity is circulated, sodium chloride in the outer compartments is electrolysed. Chlorine is evolved at the graphite anode while Na^+ ions are discharged at the Hg cathode. The liberated sodium forms amalgam with mercury.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At anode: $2Cl^- \longrightarrow 2Cl + 2e \longrightarrow Cl_2$

At cathode: $Na^+ + e \longrightarrow Na$

$$Na + Hg \longrightarrow \text{Amalgam}$$

The sodium amalgam thus formed comes in the inner compartment due to rocking. Here, the sodium amalgam acts as the anode and iron rods acts as cathode.

At anode: $\text{Na-amalgam} \longrightarrow Na^+ + Hg + e$

At cathode: $2H_2O + 2e \longrightarrow H_2\uparrow + 2OH^-$

The concentrated solution of sodium hydroxide (about 20%) is taken out from the inner compartment and evaporated to dryness to get solid NaOH.

(iii) Kellner-Solvay cell: This is the modified cell. This cell has no compartments. The flowing mercury as shown in Fig. 12.24 acts as cathode. A number of graphite rods dipping in sodium chloride solution act as anode. A constant level of sodium chloride solution is maintained in the cell. On electrolysis chlorine gas is liberated and Na^+ ions are discharged at cathode (mercury). Sodium discharged dissolves in Hg and forms amalgam. This amalgam flows out in a vessel containing water. Sodium hydroxide is formed with evolution of hydrogen.

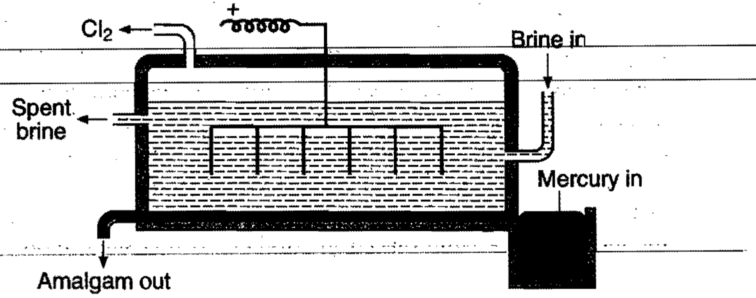


Fig. 12.24 Kellner-Solvay cell

Preparation of pure sodium hydroxide: Commercial sodium hydroxide is purified with the help of alcohol. Sodium hydroxide dissolves in alcohol while impurities like NaCl, Na_2CO_3, Na_2SO_4, etc., remain insoluble. The alcoholic filtrate is distilled. The alcohol distills off while pure solid sodium hydroxide is left behind.

3. Manufacture of aluminium

Aluminium is manufactured from pure bauxite ore by electrolysis. The bauxite ore usually contains impurities such as iron oxide, silica, etc. These impurities are first removed by the application of the following methods in order to get pure alumina, *i. e.*, pure bauxite ore:

(a) Hall's process; (b) Baeyer's process; (c) Serpeck's process.

Electrolytic reduction of pure alumina: The electrolysis of pure alumina faces two difficulties: (i) Pure alumina is a bad conductor of electricity and (ii) The fusion temperature of pure alumina is about 2000°C and at this temperature when the electrolysis is carried of the fused mass, the metal formed vapourises as the boiling point of aluminium is 1800°C.

The above difficulties are overcome by using a mixture containing alumina, cryolite (Na_3AlF_6) and fluorspar (CaF_2) in the ratio of 20 : 60 : 20. The fusion temperature of this mixture is 900°C and it is a good conductor of electricity.

The electrolysis is carried out in an iron box lined inside with gas carbon which acts as cathode. The anode consists of carbon rods which dip in the fused mixture of the electrolyte from above. The fused electrolyte is covered with a layer of coke (Fig. 12.25).

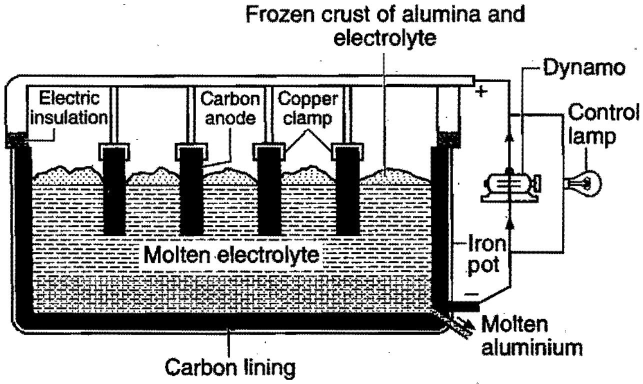


Fig. 12.25

The current passed through the cell serves two purposes: (i) Heating of the electrolyte: The temperature of the cell is automatically maintained at 900 – 950°C. (ii) Electrolysis: On passing current, aluminium is discharged at cathode. Aluminium being heavier than the electrolyte sinks to the bottom and is tapped out periodically from a tapping hole. Oxygen is liberated at anode. It attacks the carbon rods forming CO and CO_2. The process is continuous. When the concentration of the electrolyte decreases, the resistance of the cell increases. This is indicated by the glowing of a lamp placed in parallel. At this stage more of alumina is added.

The exact mechanism of the electrolysis is not yet known. Two concepts have been proposed.

First concept: AlF_3 from cryolite ionises as:

$$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$$

Al^{3+} ions are discharged at cathode and F^- ions at anode.

$$Al^{3+} + 3e \longrightarrow Al \text{ (at cathode)}$$

$$2F^- \longrightarrow F_2 + 2e \text{ (at anode)}$$

The liberated fluorine reacts with alumina to form AlF_3 and O_2. The oxygen attacks the carbon anodes to form CO and CO_2.

$$Al_2O_3 + 3F_2 \longrightarrow 2AlF_3 + \frac{3}{2}O_2$$

$$2C + O_2 \longrightarrow 2CO$$

$$C + O_2 \longrightarrow CO_2$$

Anodes are replaced frequently.

Second concept: Alumina (Al_2O_3) ionises as:

$$Al_2O_3 \rightleftharpoons \underset{\text{Cathode}}{Al^{3+}} + \underset{\text{Anode}}{AlO_3^{3-}}$$

$$Al^{3+} + 3e \longrightarrow Al \text{ (at cathode)}$$

At anode AlO_3^- is oxidised.

$$4AlO_3^{3-} \longrightarrow 2Al_2O_3 + 3O_2 + 12e \text{ (at anode)}$$

Thus, the overall chemical reaction taking place during electrolysis is,

$$2Al_2O_3 \longrightarrow 4Al + 3O_2$$

Aluminium of 99.8% purity is obtained from this process.

Refining of aluminium by Hoope's electrolytic method: Aluminium is further purified by Hoope's process. The electrolytic cell consists of an iron box lined inside with carbon. The cell consists of three layers which differ in specific gravities. The upper layer is of pure aluminium which acts as cathode. The middle layer consists of a mixture of the fluorides of Al, Ba and Na. The lowest layer consists of impure aluminium which acts as anode. The middle layer works as electrolyte.

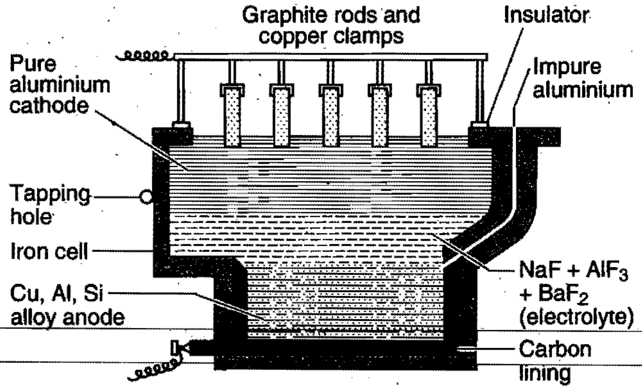


Fig. 12.26

The graphite rods are dipped in pure aluminium and Cu-Al alloy rods at the bottom of impure aluminium work as conductors. On electrolysis, aluminium is deposited at the cathode from the middle layer and an equivalent amount of aluminium is taken up by the middle layer from the bottom layer (impure aluminium). Therefore, aluminium is transferred from bottom to the top layer through middle layer while impurities are left behind. Aluminium thus obtained is 99.98%.

4. Isolation of fluorine

Fluorine presented many difficulties in its isolation. It remained a difficult problem in chemistry for many years and after a hard labour of many chemists for about 75 years it could be isolated finally by **Moissan** in 1886. **The reasons for its late discovery were its high reactivity and non-conducting nature of hydrofluoric acid.** Fluorine attacked the material of the vessels used for its isolation. Carbon vessel was attacked with formation of CF_4 and platinum vessel was reduced to chocolate powder. The vessels of other metals were also affected. Platinum and carbon could not be used as electrodes. Another difficulty experienced was that when the electrolysis of aqueous hydrofluoric acid was carried out, hydrogen and oxygen (ozone) were obtained and when anhydrous hydrofluoric acid was tried it was found to be a bad conductor of electricity.

Moissan finally solved the problem and isolated fluorine by the electrolysis of anhydrous hydrofluoric acid in the presence of potassium hydrogen fluoride using Pt-Ir alloy vessel at −23°C. The electrodes used were also of Pt-Ir alloy.

Modern methods of isolation: In modern methods, fluorine is prepared by electrolysis of a fused fluoride (usually potassium hydrogen fluoride, KHF_2). The electrolytic cells are made of copper, nickel or monel metal. The anode is generally of graphite and the fluorine set free contains some carbon tetrafluoride.

Reactions in the electrolytic cell

$$KHF_2 \longrightarrow KF + HF$$

$$\Downarrow$$

$$K^+ + F^-$$

Cathode	Anode
$K^+ + e \rightarrow K$	$F^- \rightarrow F + e$
$K + HF \rightarrow KF + H$	$2F \rightarrow F_2$
$2H \rightarrow H_2$	

The following precautions should be taken in the preparation of fluorine:

(i) The electrolyte must be completely dry. In presence of moisture, the evolved fluorine reacts with moisture to form O_2 and O_3.

(ii) The parts of the apparatus which come in contact with fluorine must be free from oil and grease.

(iii) The vessel in which fluorine is collected should also be absolutely dry.

(iv) The gas must be made free from HF before storing by passing through sodium fluoride (NaF), otherwise HF will attack the vessel.

Note: HF is more corrosive and reactive than fluorine.

Dennis method: The electrolytic cell used in this method consists of a V-shaped copper tube (5 cm in diameter) fitted with copper caps. Graphite electrodes through these caps are sealed and insulated in the tube by bakelite cement which is not affected by fluorine. The cell is covered with an insulating layer of asbestos cement over which is wound a resistance wire for electrical heating. The tube is thickly lagged to prevent the loss of heat.

The electrolyte consists of fused potassium hydrogen fluoride which has already been dried for 48 hours at 130°C. The electrolyte is kept in fused state by electrical heating externally. For electrolysis, a current of 5 ampere and 12 volt is used. On electrolysis fluorine is liberated at anode. To make the liberated fluorine free from HF vapours, it is passed through copper U-tubes containing sodium fluoride.

$$NaF + HF \longrightarrow NaHF_2$$

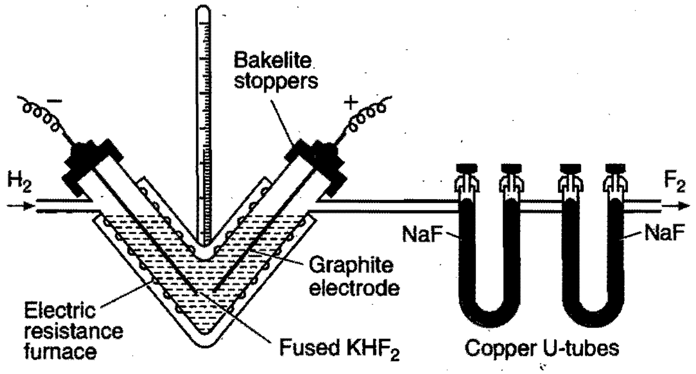


Fig. 12.27

The following difficulty is experienced in this method:

The liberated fluorine at anode does not escape fast enough due to narrow exit. The escape is further hindered due to frothing in the electrolyte. There are, thus, chances of mixing of H_2 and F_2 which may result in explosion. To avoid this, a modified apparatus has been devised by Whytlaw-Gray.

Whytlaw-Gray method: It consists of a copper cell wound with resistance wire for electrical heating. The pure graphite anode is enclosed in a copper cylinder which is perforated at the bottom (Fig. 12.28). The electrolysis of fused KHF_2 is carried out in this cell. The escape of fluorine is fast enough and thus no frothing in the electrolyte occurs. There are no chances of mixing of H_2 and F_2 in this cell.

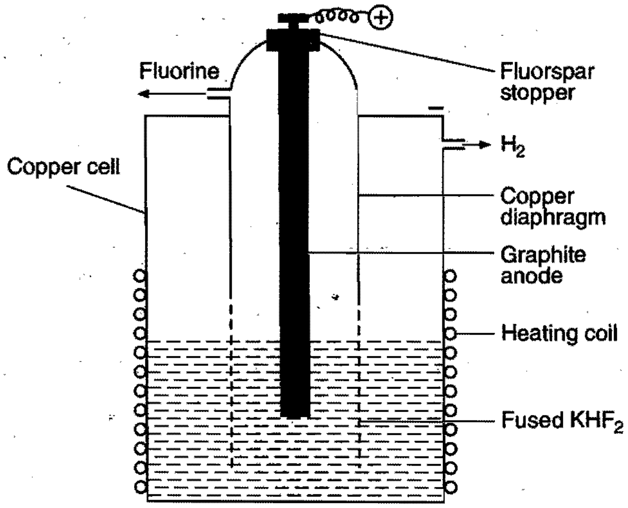


Fig. 12.28

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *Anodic oxidation of ammonium hydrogen sulphate produces ammonium persulphate.*

$$NH_4HSO_4 \longrightarrow NH_4SO_4^- + H^+$$

$$2NH_4SO_4^- \longrightarrow (NH_4)_2S_2O_8 + 2e^- \ (Anodic\ oxidation)$$

$$2H^+ + 2e^- \longrightarrow H_2 \ (Cathodic\ reduction)$$

Hydrolysis of ammonium persulphate forms H_2O_2.

$$(NH_4)_2S_2O_8 + 2H_2O \longrightarrow 2NH_4HSO_4 + H_2O_2$$

Current efficiency in electrolytic process is 60%. Calculate the amount of current required to produce 85 g of H_2O_2 per hour. Hydrolysis reaction shows 100% yield.

Solution: Given,

$$\underset{228\,g}{(NH_4)_2S_2O_8} + H_2O \longrightarrow 2NH_4HSO_4 + \underset{34\,g}{H_2O_2}$$

$\because$ 34 g H_2O_2 is produced by 228 g $(NH_4)_2S_2O_8$

$\therefore$ 85 g H_2O_2 will be produced by $\frac{228}{24} \times 85$ g $(NH_4)_2S_2O_8$

$$= 570\,g$$

Equivalent mass of $(NH_4)_2S_2O_8$ may be calculated using the following reaction:

$$2NH_4SO_4^- \longrightarrow (NH_4)_2S_2O_8 + 2e$$

$$\text{Equivalent mass of } (NH_4)_2S_2O_8 = \frac{\text{Mol. mass}}{2} = \frac{228}{2} = 114$$

From first law of electrolysis,

$$W = \frac{ItE}{96500}$$

$$570 = \frac{I \times 3600 \times 114}{96500}$$

$$I = 134.0277 \text{ ampere}$$

Given that, current efficiency is 60%, the actual amount of current

$$= \frac{100}{60} \times 134.0277$$

$$= 223.379 \text{ ampere}$$

Example 2. *In a zinc manganese dioxide dry cell, the anode is made up of zinc and cathode of a carbon rod surrounded by a mixture of MnO_2, carbon, NH_4Cl and $ZnCl_2$ in aqueous base.*

The cathodic reaction may be represented as:

$$2MnO_2(s) + Zn^{2+} + 2e^- \longrightarrow ZnMn_2O_4(s)$$

Let there be 8 g MnO_2 in the cathodic compartment. How many days will the dry cell continue to give a current of 4×10^{-3} ampere?

Solution: When MnO_2 will be used up in cathodic process, the dry cell will stop to produce current.

Cathodic process:

$$2\overset{+4}{Mn}O_2(s) + Zn^{2+} + 2e^- \longrightarrow Zn\overset{+3}{Mn}_2O_4$$

$$\text{Equivalent mass of } MnO_2 = \frac{\text{Molecular mass}}{\text{Change in oxidation state}}$$

$$= \frac{87}{1} = 87$$

From first law of electrolysis,

$$W = \frac{ItE}{96500}$$

$$8 = \frac{4 \times 10^{-3} \times t \times 87}{96500}$$

$$t = 2218390.8 \text{ second}$$

$$= \frac{2218390.8}{3600 \times 24} = 25.675 \text{ day}$$

Example 3. *Ten gram of a fairly concentrated solution of cupric sulphate is electrolysed using 0.01 faraday of electricity. Calculate:*

(i) *The mass of the resulting solution;*

(ii) *The number of equivalents of acid or alkali in the solution.*

Solution: Electrode process during electrolysis of aqueous $CuSO_4$ may be given as:

$$Cu^{2+} + 2e^- \longrightarrow Cu \ (\text{Cathode})$$

$$2OH^- \longrightarrow H_2O + \tfrac{1}{2}O_2 + 2e^- \ (\text{Anode})$$

Mass of copper deposited at cathode by 0.01 faraday charge

$= 0.01 \times 31.75$

$= 0.3175$ g

(Here, 31.75 is the equivalent mass of Cu^{2+}.)

Mass of oxygen evolved by 0.01 faraday charge

$= 0.01 \times 8 = 0.08$ g

Total weight loss from solution $= 0.3175 + 0.08 = 0.3975$ g

Mass of resulting solution $= 10 - 0.3975$

$= 9.6025$ g

After deposition of Cu^{2+} and OH^- ions at the respective electrodes, H_2SO_4 will prevail in the solution. 0.01 faraday of electricity will result in 0.01 equivalent of acid.

Example 4. *A current of 40 microampere is passed through silver nitrate solution for 16 minutes using platinum electrodes. 50% of the cathode is occupied by a single atom thick silver layer. Calculate the total surface area of the cathode if one silver atom occupies 5.5×10^{-16} cm^2 surface area.*

Solution: Mass of silver deposited may be calculated according to Faraday's first law of electrolysis.

$$W = \frac{ItE}{96500}$$

$$= \frac{40\times10^{-6}\times60\times16\times108}{96500}$$

$$= 42.976\times10^{-6}\ \text{g}$$

Total number of deposited 'Ag' atoms

$$= \frac{42.976\times10^{-6}}{108}\times6.023\times10^{23}$$

$$= 2.3967\times10^{17}\ \text{atoms}$$

Surface occupied by deposited silver

= number of silver atoms × area occupied by a single atom

$= 2.3967\times10^{17}\times5.5\times10^{-16}$

$= 131.818\ \text{cm}^2$

Since, deposited silver occupies 50% of total area of cathode, hence,

Total surface area of cathode $= 2\times131.818$

$$= 263.636\ \text{cm}^2$$

Example 5. *A pin of 2 cm length and 0.4 cm diameter was placed in $AgNO_3$ solution through which a 0.2 ampere current was passed for 10 minute to deposit silver on the pin. The pin was used by a surgeon in lachrymal duct operation. The density of silver and electrochemical equivalent are 1.05×10^4 kg m^{-1} and 1.118×10^{-6} kg/coulomb respectively. What is the thickness of silver deposited on the pin? Assume that the tip of the pin contains negligible mass of silver?*

Solution: From Faraday's first law,

$$W = ZIt$$

$$= 1.118\times10^{-6}\times0.2\times10\times60 = 1.34\times10^{-4}\ \text{kg}$$

$$V = \frac{W}{d} = \frac{1.34\times10^{-4}}{1.05\times10^{4}} = 1.277\times10^{-8}\ \text{m}^3$$

$$= 1.277\times10^{-2}\ \text{cm}^3 \qquad \text{... (i)}$$

Surface area of pin $= 2\pi rh$

$$= 2\times3.14\times0.2\times2$$

$$= 2.512\ \text{cm}^2$$

Surface area may be treated as that of a rectangle of length 'h' and breadth $2\pi r$. Let the thickness of the coating be 'd' cm. Then

Volume of the occupied metal $= 2.512\times d\ \text{cm}^3$ ... (ii)

From equations (i) and (ii), we get

$$1.277\times10^{-2} = 2.512\times d$$

$$d = 0.5083\times10^{-2}\ \text{cm}$$

$$= 5.083\times10^{-5}\ \text{metre}$$

Example 6. *The specific conductivity of a saturated solution of silver chloride is 2.30×10^{-6} mho cm^{-1}, at 25° C. Calculate the solubility of silver chloride at 25° C if $\lambda_{Ag^+} = 61.9$ mho cm^2 mol^{-1} and $\lambda_{Cl^-} = 76.3$ mho cm^2 mol^{-1}.*

Solution: Let the solubility of AgCl be s gram mole per litre

$$\text{Dilution} = \frac{1000}{S}$$

$$\Lambda^{\infty}_{AgCl} = \lambda_{Ag^+} + \lambda_{Cl^-}$$

$$= 61.9 + 76.3$$

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

$$\text{Sp. conductivity}\times\text{dilution} = \Lambda^{\infty}_{AgCl} = 138.2$$

$$2.30\times10^{-6}\times\frac{1000}{S} = 138.2$$

$$S = \frac{2.30\times10^{-3}}{138.2} = 1.66\times10^{-5}\ \text{mol per litre}$$

$$= 1.66\times10^{-5}\times143.5\ \text{gL}^{-1}$$

$$= 2.382\times10^{-3}\ \text{gL}^{-1}$$

Example 7. *Resistance of a solution (A) is 50 ohm and that of solution (B) is 100 ohm, both solutions being taken in the same conductivity cell. If equal volumes of solutions (A) and (B) are mixed, what will be the resistance of the mixture, using the same cell? Assume that there is no increase in the degree of dissociation of (A) and (B) on mixing.*

Solution: Let us suppose κ_1 and κ_2 are the specific conductances of solutions 'A' and 'B' respectively and cell constant is 'y'. We know that,

Specific conductance = Conductance × Cell constant

For (A), $\kappa_1 = \frac{1}{50}\times y$

For (B), $\kappa_2 = \frac{1}{100}\times y$

When equal volumes of (A) and (B) are mixed, the volume becomes double. Then,

$$\text{Specific conductance of mixture} = \frac{\kappa_1+\kappa_2}{2}$$

$$\therefore \quad \frac{\kappa_1+\kappa_2}{2} = \frac{1}{R}\times y$$

$$\frac{1}{2}\left[\frac{y}{50}+\frac{y}{100}\right] = \frac{1}{R}\times y$$

$$\frac{1}{100}+\frac{1}{200} = \frac{1}{R}$$

$$R = 200/3 = 66.66\ \text{ohm}$$

Example 8. *A big irregular shaped vessel contained water, specific conductance of which was 2.56×10^{-5} mho cm^{-1}. 500 g of NaCl was then added to the water and the specific conductance after the addition of NaCl was found to be*

3.1×10^{-5} mho cm^{-1}. Find the capacity of the vessel if it was fully filled with water. (Λ^{∞} NaCl $= 149.9$ ohm^{-1} cm^{2} eq^{-1})

Solution: Let us suppose the volume of vessel is V mL

Volume containing 1 equivalent

$$= \frac{\text{Volume}}{\text{Mass / equivalent mass}}$$

$$= \frac{V}{500/58.5} = \frac{V}{8.547}$$

Specific conductance of NaCl

$$= \text{Specific conductance of NaCl solution} - \text{Specific conductance of water}$$

$$= 3.1\times10^{-5} - 2.56\times10^{-5}$$

$$= 0.54\times10^{-5} \text{ mho cm}^{-1}$$

$\Lambda = \kappa \times$ volume containing 1 equivalent of electrolyte ...(i)

For very dilute solution, when the big vessel is fully filled

$$\Lambda^{\infty}_{\text{NaCl}} = 149.9 \text{ ohm}^{-1}\text{ cm}^{2}\text{ eq}^{-1}$$

Thus, from eq. (i),

$$149.9 = 0.54\times10^{-5}\times\frac{V}{8.547}$$

$$V = 237258.38 \text{ L}$$

Example 9. *A 0.05 N solution of a salt occupying a volume between two platinum electrodes separated by a distance of 1.72 cm and having an area of 4.5 cm^{2} has a resistance of 250 ohm. Calculate the equivalent conductance of the solution.*

Solution:

Specific conductance = conductance × cell constant

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

$$= \frac{1}{R}\times\frac{l}{A}$$

$$= \frac{1}{250}\times\frac{1.72}{4.5}$$

$$= 1.5288\times10^{-3} \text{ ohm}^{-1}\text{ cm}^{-1}$$

$$\Lambda_{e} = \kappa\times\frac{1000}{N}$$

$$= 1.5288\times10^{-3}\times\frac{1000}{0.05}$$

$$= 30.56 \text{ ohm}^{-1}\text{ cm}^{2}\text{ eq}^{-1}$$

Example 10. *At 18°C, the mobilities of NH_4^+ and ClO_4^- ions are 6.6×10^{-4} and 5.7×10^{-4} cm^{2} volt^{-1} sec^{-1} at infinite dilution. Calculate the equivalent conductance of ammonium chlorate solution.*

Solution: $\Lambda^{\infty}_{NH_4ClO_4} = \lambda^{\infty}_{NH_4^+} + \lambda^{\infty}_{ClO_4^-}$

$$= (U^{\infty}_{NH_4^+} + U^{\infty}_{ClO_4})F$$

$$= (6.6\times10^{-4} + 5.7\times10^{-4})\times96500$$

$$= 118.69 \text{ ohm}^{-1}\text{ cm}^{2}\text{ eq}^{-1}$$

Example 11. *For the cell reaction,*

$$Mg\,|\,Mg^{2+}(aq.)\,||\,Ag^{+}(aq.)\,|\,Ag$$

calculate the equilibrium constant at 25°C and maximum work that can be obtained by operating the cell.

$$E^{\circ}_{Mg^{2+}/Mg} = -2.37 \text{ volt} \text{ and } E^{\circ}_{Ag^{+}/Ag} = +0.80 \text{ volt}$$

Solution: $E^{\circ}_{\text{cell}} = 0.80 + 2.37 = 3.17$ volt

$$\log K_c = \frac{nE^{\circ}_{\text{cell}}}{0.0591}$$

$$= \frac{2\times3.17}{0.0591} = 107.2758$$

$$K_c = 1.89\times10^{107}$$

$$-\Delta G = \text{maximum work}$$

$$= nFE^{\circ} = 2\times96500\times3.17$$

$$= 611810 \text{ J}$$

Example 12. *Zinc granules are added in excess to 500 mL of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potentials of Zn^{2+}/Zn and Ni^{2+}/Ni are −0.75 and −0.24 volt respectively, find out the concentration of Ni^{2+} ions in solution at equilibrium.* (IIT 1991)

Solution: The reaction to be considered is,

$$\text{Zn}(s) + \text{Ni}^{2+}(aq.) \rightleftharpoons \text{Zn}^{2+}(aq.) + \text{Ni}(s)$$

The cell involving this reaction would be,

$$\text{Zn}(s)\,|\,\text{Zn}^{2+}(aq.)\,||\,\text{Ni}^{2+}(aq.)\,|\,\text{Ni}(s)$$

$$E^{\circ}_{\text{cell}} = -0.24 + 0.75 = 0.51 \text{ volt}$$

$$\log K_{\text{eq}} = \frac{nFE^{\circ}}{2.303\,RT} = \frac{nE^{\circ}}{0.0591} = \frac{2\times0.51}{0.0591} = 17.25$$

So, $K_{\text{eq}} = 1.78\times10^{17}$

Let x be the concentration of Ni^{2+} that have been reduced to nickel at equilibrium.

$$\underset{(1.0-x)}{\text{Zn}(s) + \text{Ni}^{2+}(aq.)} \rightleftharpoons \underset{x}{\text{Zn}^{2+}(aq.)} + \text{Ni}(s)$$

$$K_{\text{eq}} = \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} = \frac{x}{(1-x)} = 1.78\times10^{17}$$

$$x \approx 1.0\,M$$

So, $(1-x) = [\text{Ni}^{2+}] = \dfrac{1.0}{1.78\times10^{17}} = 5.6\times10^{-18}\,M$

Example 13. *The standard reduction potential of Cu^{2+}/Cu and Ag^{+}/Ag electrodes are 0.337 and 0.799 volt* *respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of Ag^+ will the emf of the cell at 25° C be zero if concentration of Cu^{2+} is 0.01 M?* (IIT 1990)

Solution: Given, $E^\circ_{Cu^{2+}/Cu} = 0.337$ volt and $E^\circ_{Ag^+/Ag} = 0.799$ volt. The standard emf will be positive if Cu / Cu^{2+} is anode and Ag^+ / Ag is cathode. The cell can be represented as:

$$Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$$

The cell reaction is,

$$Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$

E°_{cell} = Oxid. potential of anode + Red. potential of cathode

$$= -0.337 + 0.799$$

$$= 0.462 \text{ volt}$$

Applying the Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

When, $E_{cell} = 0$

$$E^\circ_{cell} = \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

or

$$\log\frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{0.462 \times 2}{0.0591} = 15.6345$$

$$\frac{[Cu^{2+}]}{[Ag^+]^2} = 4.3102 \times 10^{15}$$

$$[Ag^+]^2 = \frac{0.01}{4.3102 \times 10^{15}}$$

$$= 0.2320 \times 10^{-17}$$

$$= 2.320 \times 10^{-18}$$

$$[Ag^+] = 1.523 \times 10^{-9}\ M$$

Example 14. *The standard reduction potential for the half- cell having reaction,*

$$NO_3^-(aq.) + 2H^+(aq.) + e^- \longrightarrow NO_2(g) + H_2O$$

is 0.78 volt.

(i) Calculate the reduction potential in 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. (IIT 1993)

Solution: (i) Applying the formula,

$$E_{red} = E^\circ_{red} + \frac{0.0591}{n}\log[H^+]^2$$

$$= 0.78 + \frac{0.0591}{2}\log 8^2$$

$$= 0.78 + 0.0591 \times 3 \times 0.3010$$

$$= 0.833 \text{ volt}$$

(ii)

$$E_{red} = 0.78 + \frac{0.0591}{2}\log(10^{-7})^2$$

[For neutral solution $[H^+] = 10^{-7}\ M$]

$$= 0.78 - 0.0591 \times 7$$

$$= 0.367 \text{ volt}$$

Example 15. *The emf of a cell corresponding to the reaction,*

$$Zn + 2H^+(aq.) \longrightarrow Zn^{2+}(0.1M) + H_2(g)\ 1\,atm$$

is 0.28 volt at 25° C. Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.

$$E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ volt} \quad and \quad E^\circ_{H^+/H_2} = 0$$

Solution: $E^\circ_{cell} = 0.76$ volt

Applying Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}][H_2]}{[H^+]^2}$$

$$0.28 = 0.76 - \frac{0.0591}{2}\log\frac{(0.1) \times 1}{[H^+]^2}$$

$$\log\frac{0.1}{[H^+]^2} = \frac{2 \times 0.48}{0.0591}$$

$\log 0.1 - \log[H^+]^2 = 16.2436$ [Since, $-\log[H^+] = \text{pH}$]

$$2\,\text{pH} = 16.2436 - \log 0.1$$

$$\text{pH} = \frac{17.2436}{2} = 8.6218$$

Example 16. *Calculate the solubility product constant of AgI from the following values of standard electrode potentials.*

$$E^\circ_{Ag^+/Ag} = 0.80 \text{ volt} \quad and \quad E^\circ_{I/AgI/Ag} = -0.15 \text{ volt} \quad at\ 25° C.$$

Solution: Solubility product of AgI = $[Ag^+][I^-]$

[**Note:** See chapter 10 for solubility product.]

Two half reactions for the cell are:

$Ag \longrightarrow Ag^+ + e^-$ Anode (Oxidation)

$AgI + e^- \longrightarrow Ag + I^-$ Cathode (Reduction)

Cell reaction $AgI \longrightarrow Ag^+ + I^-$

Applying Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{1}\log\frac{[Ag^+][I^-]}{[AgI]}$$

At equilibrium, $E_{cell} = 0$ and $[AgI] = 1$

So, $\log[Ag^+][I^-] = \dfrac{E^\circ_{cell}}{0.0591}$

$$E^\circ_{cell} = -0.80 - 0.15 = -0.95 \text{ volt}$$

$$\log[Ag^+][I^-] = -\frac{0.95}{0.0591} = -16.0744$$

Solubility product of AgI $= 8.4\times10^{-17}$

Example 17. *The standard reduction potential of Ag^+/Ag electrode at 298K is 0.799 volt. Given for AgI, $K_{sp} = 8.7\times10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of the $I^-/AgI/Ag$ electrode.* (IIT 1994)

Solution: In the saturated solution of AgI, the half-cell reactions are:

$$AgI + e^- \longrightarrow Ag + I^- \quad \text{Cathode (Reduction)}$$

$$Ag \longrightarrow Ag^+ + e^- \quad \text{Anode (Oxidation)}$$

$$\text{Cell reaction} \quad AgI \longrightarrow Ag^+ + I^-$$

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + 0.0591\log[Ag^+]$$

$$[Ag^+][I^-] = K_{sp}(AgI) = [Ag^+]^2 = [I^-]^2$$

So, $[Ag^+]^2 = 8.7\times10^{-17}$

$$[Ag^+] = \sqrt{8.7\times10^{-17}} = 9.3\times10^{-9}$$

Substituting the value of $E^\circ_{Ag^+/Ag}$ and $[Ag^+]$ in the above equation.

$$E_{Ag^+/Ag} = 0.799 - 0.0591\log(9.3\times10^{-9})$$
$$= 0.324 \text{ volt}$$
$$E^\circ_{cell} = 0.0591\log K_{sp}(AgI)$$
$$= 0.0591\log(8.7\times10^{-17})$$
$$= -0.95 \text{ volt}$$

$$E^\circ_{cell} = \text{Oxid. pot. of anode} + \text{Red. pot. of cathode}$$

$$\text{Red. pot. of cathode } E^\circ_{I^-/AgI/Ag} = -0.95 - (-0.799)$$
$$= -0.95 + 0.799$$
$$= -0.151 \text{ volt}$$

Example 18. *Calculate the pH of the following half-cells solutions:*

(*a*) *$PtH_2(1\,atm)|H^+(HCl)$; $E = 0.25$ volt*

(*b*) *$PtH_2(1\,atm)|H^+(H_2SO_4)$; $E = 0.3$ volt*

Solution: (a) $H_2 \longrightarrow 2H^+ + 2e$

$$E_{H_2/H^+} = E^\circ_{H_2/H^+} - \frac{0.0591}{2}\log\frac{[H^+]^2}{P_{H_2}}$$

$$= 0.0 - 0.0591\log\frac{[H^+]}{1}$$

$$0.25 = 0.0591\,\text{pH}$$

$$\text{pH} = \frac{0.25}{0.0591} = 4.23$$

(b) $$E_{H_2/H^+} = E^\circ_{H_2/H^+} - \frac{0.0591}{2}\log\frac{[H^+]^2}{P_{H_2}}$$

$$= 0.0 - 0.0591\log\frac{[H^+]}{1}$$

$$0.3 = 0.0591\,\text{pH}$$

$$\text{pH} = \frac{0.3}{0.0591} = 5.076$$

Example 19. *The emf of the cells obtained by combining zinc and copper electrodes of the Daniell cell with calomel electrodes are 1.083 volt and – 0.018 volt respectively at 25°C. If the reduction potential of normal calomel electrode is + 0.28 volt, find the emf of the Daniell cell.*

Solution: For the cell Zn electrode || Calomel electrode

E_{cell} = Oxid. pot. of Zn electrode + Red. pot. of calomel electrode

So, oxid. pot. of Zn electrode = 1.083 – 0.28 = 0.803 volt

For the cell,

Cu electrode || Calomel electrode

E_{cell} = Oxid. pot. of Cu electrode + Red. pot. of calomel electrode

So, oxid. pot. of Cu electrode = – 0.018 – 0.28 = – 0.298 volt

For the Daniell cell,

Zn electrode || Cu electrode

E_{cell} = Oxid. pot. of Zn electrode + Red. pot. of copper electrode
= 0.803 + 0.298 = 1.101 volt

Example 20. *The Edison storage cell is represented as:*

$$Fe(s)|FeO(s)|KOH(aq.)|Ni_2O_3(s)|Ni(s)$$

The half-cell reactions are:

$$Ni_2O_3(s) + H_2O(l) + 2e^- \longrightarrow 2NiO(s) + 2OH^-; \quad E^\circ = +0.40 \text{ volt}$$

$$FeO(s) + H_2O(l) + 2e^- \longrightarrow Fe(s) + 2OH^-; \quad E^\circ = -0.87 \text{ volt}$$

(*a*) *What is the cell reaction?*

(*b*) *What is the emf of the cell? How does it depend on the concentration of KOH?*

(*c*) *What is the maximum amount of energy that can be obtained from one mole of Ni_2O_3?* (IIT 1994)

Solution: Actual half reactions are:

$$Fe + 2OH^- \longrightarrow FeO + H_2O + 2e^- \quad \text{Anode (Oxidation)}$$

$$Ni_2O_3 + H_2O + 2e^- \longrightarrow 2NiO + 2OH^- \quad \text{Cathode (Reduction)}$$

Thus, the cell reaction is:

(a) $Fe + Ni_2O_3 \longrightarrow FeO + 2NiO$

(b) $$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[NiO]^2[FeO]}{[Fe][Ni_2O_3]} = E^\circ_{cell}$$

$$\left[\text{Since, } \frac{[NiO]^2[FeO]}{[Fe][Ni_2O_3]} = 1 \text{ as all are solids}\right]$$

$$= 0.87 + 0.40 = 1.27 \text{ volt}$$

The emf of the cell is independent of KOH concentration.

(c) Maximum amount of electrical energy

$$= nFE^\circ$$

$$= 2 \times 96500 \times 1.27$$

$$= 245.11 \text{ kJ}$$

Example 21. *The normal oxidation potential of zinc referred to the standard hydrogen electrode is 0.76 volt and that of copper is – 0.34 volt at 25° C. When excess of zinc is added to a solution of copper sulphate, the zinc displaces copper till equilibrium is reached. What is the ratio of concentration of* Zn^{2+} *to* Cu^{2+} *ions at equilibrium?*

Solution: The reaction is,

$$Zn + CuSO_4 \longrightarrow Cu + ZnSO_4$$

or
$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

At equilibrium, $E_{cell} = 0$

$$E^\circ_{cell} = \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

or
$$\log \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{2 \times E^\circ_{cell}}{0.0591}$$

$$(E^\circ_{cell} = 0.76 + 0.34 = 1.10 \text{ volt})$$

$$= \frac{2 \times 1.10}{0.0591} = 37.225$$

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.679 \times 10^{37} : 1$$

Example 22. *An excess of liquid mercury is added to an acidified solution of* 1.0×10^{-3} *M* Fe^{3+}. *It is found that 5% of* Fe^{3+} *remains at equilibrium at 25°C. Calculate* $E^\circ_{Hg_2^{2+}/Hg}$ *assuming that the only reaction that occurs is*

$$2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+}$$

(Given, $E_{Fe^{3+}/Fe^{2+}} = 0.77$ *volt).* (IIT 1995)

Solution:

$$\begin{array}{lcccccc} & 2Hg & + & 2Fe^{3+} & \longrightarrow & Hg_2^{2+} & + \; 2Fe^{2+} \\ \text{At equilibrium, } & \text{excess} & & \frac{10^{-3} \times 5}{100} & & \frac{10^{-3} \times 95}{2 \times 100} & \frac{10^{-3} \times 95}{100} \end{array}$$

At equilibrium, $E_{cell} = 0$

$$0 = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Hg_2^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2}$$

$$= (E^\circ_{Hg/Hg_2^{2+}} + E^\circ_{Fe^{3+}/Fe^{2+}}) - \frac{0.0591}{2} \log \frac{\left(\frac{10^{-3} \times 95}{2 \times 100}\right)\left(\frac{10^{-3} \times 95}{100}\right)^2}{\left(\frac{10^{-3} \times 5}{100}\right)^2}$$

$$E^\circ_{Hg/Hg_2^{2+}} = -0.77 + \frac{0.0591}{2} \log \frac{(95)^3 \times 10^{-5}}{25 \times 2}$$

$$= -(0.77 + 0.0226)$$

$$= -0.7926 \text{ volt}$$

$$E^\circ_{Hg_2^{2+}/Hg} = +0.7926 \text{ volt}$$

Example 23. *Prove that for two half reactions having potentials* E_1 *and* E_2 *which are combined to yield a third half reaction, having a potential* E_3,

$$E_3 = \frac{n_1E_1 + n_2E_2}{n_3}$$

Solution:
$$\Delta G_3 = \Delta G_1 + \Delta G_2$$

$$-n_3FE_3 = -n_1FE_1 - n_2FE_2$$

or
$$n_3E_3 = n_1E_1 + n_2E_2$$

or
$$E_3 = \frac{n_1E_1 + n_2E_2}{n_3}$$

Example 24. *What is the standard potential of the* Tl^{3+}/Tl *electrode?*

$$Tl^{3+} + 2e^- \longrightarrow Tl^+; \quad E^\circ = 1.26 \text{ volt}$$

$$Tl^+ + e^- \longrightarrow Tl; \quad E^\circ = -0.336 \text{ volt}$$

Solution:

$$Tl^{3+} + 2e^- \longrightarrow Tl^+; \quad nFE^\circ = 2 \times 1.26 \times F = 2.52F$$

$$Tl^+ + e^- \longrightarrow Tl; \quad nFE^\circ = 1 \times (-0.336) \times F = -0.336F$$

Adding

$$Tl^{3+} + 3e^- \longrightarrow Tl; \quad E^\circ = \frac{2.52F - 0.336F}{nF} = \frac{2.184}{3}$$

$$= 0.728 \text{ volt}$$

Example 25. *Calculate the minimum mass of NaOH required to be added in RHS to consume all the* H^+ *present in RHS of the cell of emf + 0.701 volt at 25°C before its use. Also report the emf of the cell after addition of NaOH.*

$$Zn \mid \underset{0.1\,M}{Zn^{2+}} \parallel \underset{1\,litre}{HCl} \mid \underset{1\,atm}{Pt(H_2g)}; \quad E^\circ_{Zn/Zn^{2+}} = 0.760\,V$$

Solution: The cell reaction is,

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

Applying Nernst equation,

$$E_{\text{cell}} = E^\circ - \frac{0.0591}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

$$0.701 = 0.760 - \frac{0.0591}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

So, $\log\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = \frac{0.0591\times 2}{0.0591} = 2$

or $\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = 10^2$

$$[\text{H}^+]^2 = \frac{0.1}{10^2} = 10^{-3}$$

$$[\text{H}^+] = 0.0316\ \text{mol L}^{-1}$$

Thus, 0.0316 mol/litre of NaOH is required to neutralise H^+ ions.

$$\text{Mass of NaOH} = 0.0316 \times \text{Mol. mass of NaOH}$$
$$= 0.0316 \times 40 = 1.264\ \text{g}$$

After addition of NaOH, the solution becomes neutral, *i.e.*, the concentration of H^+ ions in cathodic solution becomes 10^{-7}.

Applying again Nernst equation,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

$$= 0.760 - \frac{0.0591}{2}\log\frac{0.1}{(10^{-7})^2} = 0.3759\ \text{volt}$$

Example 26. *For the galvanic cell,*

$$Ag \mid AgCl(s), KCl\,(0.2\,M) \mid\mid KBr\,(0.001\,M), AgBr(s) \mid Ag$$

Calculate the emf generated and assign correct polarity to each electrode for the spontaneous process after taking into account the cell reaction at 25° C.

Given, $K_{sp\,AgCl} = 2.8\times 10^{-10}$; $K_{sp\,AgBr} = 3.3\times 10^{-13}$ **(IIT 1992)**

Solution:

$$E_{\text{cell}} = E_{\text{Oxid. pot. LHS electrode}} + E_{\text{Red. pot. RHS electrode}}$$

$$= E^\circ_{\text{Oxid. pot. Ag/Ag}^+} - 0.0591\log[\text{Ag}^+]_{\text{LHS}} + E^\circ_{\text{Red. pot. Ag}^+/\text{Ag}} + 0.0591\log[\text{Ag}^+]_{\text{RHS}}$$

$$= 0.0591\log\frac{[\text{Ag}^+]_{\text{RHS}}}{[\text{Ag}^+]_{\text{LHS}}} \quad [\text{Since, } E^\circ_{\text{Ag/Ag}^+} + E^\circ_{\text{Ag}^+/\text{Ag}} = 0]$$

$$= 0.0591\log\frac{\dfrac{K_{\text{sp AgBr}}}{[\text{Br}^-]}}{\dfrac{K_{\text{sp AgCl}}}{[\text{Cl}^-]}}$$

$$= 0.0591\log\frac{3.3\times 10^{-13}}{0.001}\times\frac{0.2}{2.8\times 10^{-10}}$$

$$= -\,0.0371\ \text{volt}$$

The cell potential is negative; therefore, the cell reaction is non-spontaneous. For spontaneous reaction emf should be positive. Therefore, the correct cell reaction is

$$\underset{\text{Anode}}{\text{Ag} \mid \text{AgBr}; \text{KBr}} \mid\mid \underset{\text{Cathode}}{\text{KCl, AgCl} \mid \text{Ag}}$$

Example 27. *The following electrochemical cell has been set-up,*

$$Pt(1) \mid Fe^{3+}, Fe^{2+}\,(a=1) \mid\mid Ce^{4+}, Ce^{3+}\,(a=1)\,Pt(2)$$

$$E^\circ(Fe^{3+}/Fe^{2+}) = 0.77\ V;\ E^\circ(Ce^{4+}/Ce^{3+}) = 1.61\,V$$

If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time? **(IIT 2000)**

Solution: Current will flow from higher reduction potential electrode to lower reduction potential electrode, *i.e.*, from Pt(2) electrode to Pt(1) electrode.

$$E^\circ_{\text{cell}} = 1.61 - 0.77 = 0.84\ \text{volt}$$

Example 28. *Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.* **(IIT 2000)**

Solution: Number of faraday passed through the aqueous solution of CuSO_4

$$= \frac{I\times t}{96500} = \frac{(2\times 10^{-3})\times 16\times 60}{96500} = 1.98\times 10^{-5}$$

Thus, number of equivalents of CuSO_4 involved in electrolysis from 1 litre solution

$$= 4\times 1.98\times 10^{-5} = 7.92\times 10^{-5}$$

Since, after electrolysis, the absorbance reduces to 50% hence, initial number of equivalents of CuSO_4 per litre

$$= 2\times 7.92\times 10^{-5}$$
$$= 1.584\times 10^{-4}$$

or Normality of CuSO_4 solution $= 1.584\times 10^{-4}\ N$.

Example 29. *A silver electrode is immersed in saturated $Ag_2SO_4(aq.)$. The potential difference between silver and the standard hydrogen electrode is found to be 0.711 V. Determine $K_{sp}(Ag_2SO_4)$. (Given, $E^\circ_{Ag^+/Ag} = 0.799\,V$)* **(IIT 2000)**

Solution: The cell may be represented as:

$$\text{Pt}(\text{H}_2\ 1\,\text{atm}) \mid \text{H}^+(1\,M) \mid\mid \text{Ag}^+(\text{salt}) \mid \text{Ag}(s)$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{H}^+/\text{H}_2}$$

$$= 0.799 - 0 = 0.799\ \text{V}$$

Given, emf of the cell = 0.711 V

$$H_2 + 2Ag^+ \longrightarrow 2Ag + 2H^+$$

$$Q = \frac{[Ag]^2[H^+]^2}{[H_2][Ag^+]^2} = \frac{1^2 \times 1^2}{1 \times [Ag^+]^2} = \frac{1}{[Ag^+]^2}$$

Applying Nernst equation,

$$E = E^\circ - \frac{0.0591}{n}\log_{10} Q$$

or $$0.711 = 0.799 - \frac{0.0591}{2}\log_{10}\frac{1}{[Ag^+]^2}$$

$$[Ag^+] = 0.03243 \text{ mol L}^{-1}$$

$$\underset{}{Ag_2SO_4} \rightleftharpoons \underset{0.03243}{2Ag^+} + \underset{0.016215}{SO_4^{2-}}$$

$$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (0.03243)^2 \times (0.016215) = 1.705 \times 10^{-5}.$$

Example 30. *Calculate the equilibrium constant for the reaction,*

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

Given, $E^\circ_{Ce^{4+}/Ce^{3+}} = 1.44\ V$ *and* $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.68\ V$

(IIT (July) 1997)

Solution: $$E^\circ_{cell} = \frac{0.059}{1}\log K_c$$

$$E^\circ_{cell} = E^\circ_{Fe^{2+}/Fe^{3+}} + E^\circ_{Ce^{4+}/Ce^{3+}}$$

$$= -0.68 + 1.44 = 0.76\text{ V}$$

$$\log_{10} K_c = \frac{0.76}{0.059} = 12.8814$$

$$K_c = 7.6 \times 10^{12}$$

Example 31. *Find the solubility product of a saturated solution of* Ag_2CrO_4 *in water at 298 K if the emf of the cell*

$$Ag \mid Ag^+ \text{ (satd. } Ag_2CrO_4 \text{ soln.)} \mid\mid Ag^+ (0.1\,M) \mid Ag$$

is 0.164 V at 298 K. (IIT 1998)

Solution: $$E_{cell} = \frac{0.059}{1}\log\frac{[Ag^+]_{RHS}}{[Ag^+]_{LHS}}$$

$$0.164 = \frac{0.059}{1}\log\frac{0.1}{[Ag^+]_{LHS}}$$

or $$[Ag^+]_{LHS} = 1.66 \times 10^{-4}\ M$$

So, $$[CrO_4^{2-}] = \frac{1.66 \times 10^{-4}}{2}$$

$$K_{sp(Ag_2CrO_4)} = [Ag^+]^2[CrO_4^{2-}]$$

$$= (1.66 \times 10^{-4})^2\left(\frac{1.66 \times 10^{-4}}{2}\right)$$

$$= 2.287 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3}$$

Example 32. *The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 25°C*

$$PtH_2(g) \mid HCl(aq.) \mid\mid AgCl(s) \mid Ag(s)$$

(*i*) *Write cell reaction.*

(*ii*) *Calculate* ΔH° *and* ΔS° *for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.*

(*iii*) *Calculate the solubility of AgCl in water at 25°C. Given the standard reduction potential of the* Ag^+ / Ag *couple is 0.80 volt at 25°C.* (IIT 2001)

Solution: (i) Electrode process:

$$\tfrac{1}{2}H_2 \longrightarrow H^+ + e^- \qquad \text{(Anode)}$$

$$AgCl + e^- \longrightarrow Ag + Cl^- \qquad \text{(Cathode)}$$

$$\tfrac{1}{2}H_2 + AgCl \rightleftharpoons H^+ + Ag + Cl^-$$

(ii) We know that, $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$

$$-22195 = \Delta H^\circ - 288 \times \Delta S^\circ$$

$$-20265 = \Delta H^\circ - 308 \times \Delta S^\circ$$

On solving, $\Delta S^\circ = -96.5\text{ J}, \Delta H^\circ = 49.987\text{ kJ}$

(iii) $$E = E^\circ - \frac{0.0591}{n}\log_{10} Q$$

At equilibrium, $E = 0, Q = K = [Ag^+][Cl^-]$

$$0 = (0.8 - 0.22) + \frac{0.0591}{1}\log K_{sp}$$

$$\frac{(-0.8 + 0.22)}{0.0591} = \log K_{sp}$$

$$K_{sp} = 1.47 \times 10^{-10}$$

Solubility, $$S = \sqrt{K_{sp}}$$

$$= \sqrt{1.47 \times 10^{-10}} = 1.21 \times 10^{-5}\ M$$

Example 33. *Two students use same stock solution of* $ZnSO_4$ *and a solution of* $CuSO_4$*. The emf of one cell is 0.03 V higher than that of other. The concentration of* $CuSO_4$ *in the cell with higher emf value is 0.5 M. Find out the concentration of* $CuSO_4$ *in the other cell.* $\left(\dfrac{2.303\,RT}{F} = 0.06\right)$ (IIT 2003)

Solution: Student I.

$$Zn(s) \mid ZnSO_4\ (C_1) \mid\mid 0.5\,M\ CuSO_4 \mid Cu(s)$$

$$E_1 = E^\circ - \frac{0.06}{2}\log\frac{C_1}{0.5} \qquad \text{...(i)}$$

Student II. $Zn(s) \mid ZnSO_4(C_1) \mid\mid CuSO_4\ (C_2) \mid Cu(s)$

$$E_2 = E^\circ - \frac{0.06}{2}\log\frac{C_1}{C_2} \qquad \text{...(ii)}$$

$$E_1 - E_2 = \frac{0.06}{2}\left[\log\frac{C_1}{C_2} - \log\frac{C_1}{0.5}\right]$$

$$0.03 = \frac{0.06}{2}\left[\log\left(\frac{0.5}{C_2}\right)\right]$$

$$1 = \log\frac{0.5}{C_2}$$

$$C_2 = 0.05\,M$$

Example 34. *Find the equilibrium constant for the reaction,*

$$In^{2+} + Cu^{2+} \rightleftharpoons In^{3+} + Cu^{+} \text{ at } 298\,K$$

Given: $E_{Cu^{2+}/Cu^{+}} = 0.15V$; $E^{\circ}_{In^{2+}/In^{+}} = -0.4$ *volt*

$E^{\circ}_{In^{3+}/In^{+}} = -0.42$ *volt* (IIT 2004)

Solution: The given reversible reaction can be obtained as,

$$Cu^{2+} + e^{-} \longrightarrow Cu^{+}; \quad \Delta G^{\circ} = -0.15F \quad \because \Delta G^{\circ} = -nFE^{\circ}$$

$$In^{2+} + e^{-} \longrightarrow In^{+}; \quad \Delta G^{\circ} = +0.40F$$

$$In^{+} \longrightarrow In^{3+} + 2e^{-}; \Delta G^{\circ} = -0.84F$$

$$\overline{Cu^{2+} + In^{2+} \rightleftharpoons In^{3+} + Cu^{+}; \quad \Delta G^{\circ} = -0.59\,F}$$

$$-nFE^{\circ} = -0.59\,F$$

$$E^{\circ} = 0.59 \text{ volt}$$

Equilibrium constant can be calculated as,

$$K = \text{antilog}\left[\frac{nE^{\circ}}{0.059}\right]$$

$$= \text{antilog}\left[\frac{1 \times 0.59}{0.059}\right] = 10^{10}$$

Example 35. *In which direction can the reaction,*

$$2Hg\,(l) + 2Ag^{+}(aq.) \rightleftharpoons 2Ag(s) + Hg_2^{2+}(aq.)$$

proceed spontaneously at the following concentrations of the ions participating in the reactions (i) and (ii)?

(*i*) $[Ag^{+}] = 10^{-4}$ *mol* L^{-1} *and* $[Hg_2^{2+}] = 10^{-1}$ *mol* L^{-1}

(*ii*) $[Ag^{+}] = 10^{-1}$ *mol* L^{-1} *and* $[Hg_2^{2+}] = 10^{-4}$ *mol* L^{-1}

Given: $E^{\circ}_{Hg_2^{2+}/Hg} = 0.79\,V$; $E^{\circ}_{Ag^{+}/Ag} = 0.80\,V$

[CBSE (Mains) Medical 2006]

Solution: (i) $Q = \dfrac{[Hg_2^{2+}]}{[Ag^{+}]^2} = \dfrac{10^{-1}}{[10^{-4}]^2} = 10^{7}$

$$E^{\circ} = E^{\circ}_{Ag^{+}/Ag} - E^{\circ}_{Hg_2^{2+}/Hg}$$

$$= 0.80 - 0.79 = 0.01\,V$$

$$E = E^{\circ} - \frac{0.059}{n}\log Q$$

$$= 0.01 - \frac{0.059}{2}\log 10^{7}$$

$$= -0.1965\,V$$

Negative value shows that the reaction will proceed from right to left, *i. e.*, in backward direction.

(ii) $Q = \dfrac{[Hg_2^{2+}]}{[Ag^{+}]^2} = \dfrac{10^{-4}}{[10^{-1}]^2} = 10^{-2}$

$$n = 2$$

$$E^{\circ} = 0.01 \text{ volt}$$

$$E = E^{\circ} - \frac{0.059}{n}\log_{10} Q$$

$$= 0.01 - \frac{0.059}{2}\log_{10} 10^{-2}$$

$$= 0.01 + 0.059\,V$$

$$= 0.069\,V$$

Since, the value of cell potential is positive, the reaction will proceed spontaneously in forward direction.

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Electrochemistry is a branch of physical chemistry which deals with the relationship between chemical energy and electrical energy and how one can be converted into another. The subject is divided into two categories: (i) use of electrical energy to produce chemical changes (electrolysis) and (ii) conversion of chemical energy into electrical energy (production of electricity by spontaneous redox reactions).

2. Conductors are the substances which allow the passage of electric current through them. Those which do not allow the flow of electric current through them are called **insulators.** Conductors are of two types:

(a) Metallic or electronic conductors are those which remain unchanged as current flows through them. These conductors transfer electric current by transfer of electrons without transfer of matter. Metals such as Cu, Ag, Al, Pt, etc., non- metals like carbon (graphite) and various alloys belong to this class.

(b) Electrolytic conductors are the conductors like aqueous solutions of acids, bases and salts or substance in molten state which allow the flow of electric current with chemical decomposition. These conductors are termed as **electrolytes.** The substances whose aqueous solutions do not conduct electric current are called **non-electrolytes.**

To pass the current through an electrolytic conductor, two metallic rods or plates are required. These are termed **electrodes.** The electrode which is connected with the positive terminal of battery or through which electric current enters the solution is termed **anode** and the electrode which is connected with negative terminal of battery or through which electric current leaves the solution is termed **cathode.** Actually the anode is the electrode where oxidation occurs and the cathode is the electrode where reduction takes place.

3. **Electrolysis** is the process of chemical decomposition of an electrolyte by passage of electric current through its aqueous solution or molten state. Molecules of the electrolyte when dissolved in water split up into cations and anions. On passing electric current these ions move towards their respective electrodes. On reaching electrodes these ions lose their charge either by losing or accepting electrons and thereby deposited at the respective electrodes or undergo a secondary change. The device in which electrolysis is carried out is known as **electrolytic cell.**

4. **Preferential discharge theory:** If more than one type of ion is attracted towards a particular electrode, then the ion discharged is the one which requires least energy.

The decreasing order of the discharge potential or the increasing order of deposition for the cations and anions is as follows:

Cations : $K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, H^+, Cu^{2+}, Ag^+, Au^{3+}$.

Anions : $SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$.

5. **Faraday's laws of electrolysis:** These present the relationship between the quantity of electric charge and the amount of the substance deposited at the electrode. These were given by Faraday in 1834.

(i) **First law:** When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge which flows through the electrolyte.

Mathematically, $W \propto Q$

or $W = ZQ = Z \times I \times t$

where, Z is a constant, known as electrochemical equivalent, I is the current in amperes and t is the time in seconds. When $Q = 1$ coulomb or one ampere of current is passed for 1 second, $W = Z$. Z is thus the mass of the substance deposited by one coulomb.

(ii) **Second law:** When the same quantity of current is passed through different electrolytes, the masses of different substances deposited on the electrodes will be in the ratio of their equivalent masses. For example, if same quantity of current is passed through copper sulphate and silver nitrate solutions, then

$$\frac{\text{Mass of copper deposited}}{\text{Mass of silver deposited}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}$$

One gram equivalent of any substance is deposited by passing same amount of charge, *i.e.*, 96500 coulomb (1 faraday).

$$E = Z \times 96500$$

or $$Z = \frac{E}{96500}$$

The charge carried by an ion $= \dfrac{nF}{6.02 \times 10^{23}}$ coulomb

When, $n = 1$,

The fundamental unit of charge $= \dfrac{F}{6.02 \times 10^{23}} = \dfrac{96500}{6.02 \times 10^{23}}$

$$= 1.6 \times 10^{-19} \text{ coulomb}$$

$$1 \text{ coulomb} = 6.24 \times 10^{18} \text{ electrons}$$

Charge on one mole of electrons

$$= 6.02 \times 10^{23} \times 1.6 \times 10^{-19}$$

$$\approx 96500 \text{ coulomb}$$

Applications of electrolysis: (i) Determination of equivalent masses of elements (ii) Electrometallurgy (iii) Manufacture of non-metals (iv) Electroplating of metal (v) Manufacture of compounds (vi) Electroplating—The process of coating an inferior metal with a superior metal by electrolysis.

6. **Arrhenius theory of electrolytic dissociation:** It was put forward by Arrhenius in 1884 to explain the properties of electrolytic solutions. The main points of the theory are:

(i) An electrolyte, when dissolved in water, breaks up into two types of charged particles called ions. The ion carrying positive charge is called **cation** and the ion carrying negative charge is called **anion.**

$$AB \rightleftharpoons A^+ \text{ (cation)} + B^- \text{ (anion)}$$

(ii) The process of splitting of the molecules of the electrolyte into ions is called **ionisation.** The fraction of the total number of molecules present in solution as ions is known as **degree of ionisation.**

It is denoted by 'α'.

$$\alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules dissolved}}$$

The degree of ionisation depends upon: (a) Nature of solute (b) Nature of solvent (c) Dilution and temperature.

(iii) Ions present in solution constantly reunite to form neutral molecules; thus, there is a state of dynamic equilibrium between ionised and unionised molecules.

$$AB \rightleftharpoons A^+ + B^-$$

$$\frac{[A^+][B^-]}{[AB]} = K \text{ (ionisation constant)}$$

(iv) The ions are discharged always in equivalent amounts when current is passed through electrolytic solution no matter what their relative speeds are.

(v) The electrolytic solution is always neutral in nature as the total charge on cations is equal to the total charge on anions. However, it is not necessary that the number of cations and anions should be always equal.

(vi) The properties of electrolytes in solution are the properties of ions present in the solution.

(vii) The ions act as molecules for colligative properties.

(viii) The conductivity of the solution depends on the nature and number of ions.

Evidences in favour of Arrhenius theory: (i) Ohm's law applicability: No part of the current is used in splitting up the molecules into ions. (ii) X-ray studies have shown that ions are present in solid electrolytes. The ionic compounds in molten state behave as good conductors. (iii) Ionic reactions are observed in the case of electrolytes. (iv) Constant value of heat of neutralisation. (v) Abnormal colligative properties in the case of electrolytes. (vi) Colour of compounds in solution. (vii) This theory explains satisfactorily various phenomena such as electrolysis, conductivity, salt hydrolysis, etc.

7. **Conductivity** is the property of the conductor which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance.

$$\text{Conductivity} = \frac{1}{\text{Resistance}} = \frac{1}{R}$$

It is expressed as ohm^{-1} or mho.

Specific conductivity is defined as the reciprocal of specific resistance, *i.e.*, it is the conductance of 1 cm^3 of a conductor. It is represented by the symbol κ.

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

where, l = distance between electrodes and a = area of cross-section of electrode.

In the case of electrolytic solutions, specific conductance is the conductance of a solution of definite dilution enclosed in a cell having two electrodes of unit area separated by one centimetre. The units of specific conductance are $\text{ohm}^{-1}\ \text{cm}^{-1}$. The ratio of l/a is called **cell constant.**

Equivalent conductance: Conductivity of a solution containing 1g equivalent of the electrolyte. It is denoted by 'Λ'. If the concentration of solution is C g equivalent per litre, then

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

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

where, V is the volume in mL containing 1g equivalent of the electrolyte. The unit of equivalent conductance is $\text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$.

Molar conductance: Conductance of a solution containing 1 g mole of an electrolyte. If V is volume in mL containing 1g mole, then

$$\text{Molar conductance}, \mu = \kappa \times V$$

If C is the concentration of the solution in g mole per litre, then

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

Its unit is $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

$$\text{Equivalent conductance} = \frac{\text{Molar conductance}}{n}$$

where, $$n = \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

8. **Kohlrausch's law:** At infinite dilution, each ion makes a definite contribution towards equivalent conductance of the electrolyte. The value of equivalent conductance at infinite dilution for any electrolyte is the sum of conductances at infinite dilution of its constituent ions. Thus,

$$\Lambda_\infty = \Lambda_a + \Lambda_c$$

Λ_a and Λ_c are called the ionic conductances of anion and cation at infinite dilution respectively. It can be used to determine degree of dissociation.

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{\text{Equivalent conductance at given concentration}}{\text{Equivalent conductance at infinite dilution}}$$

9. **Galvanic or Voltaic or Electrochemical cell:** It is the device in which chemical energy is converted into electrical energy. In this cell a redox reaction is carried out in an indirect manner and the decrease in free energy during the chemical process appears as electrical energy.

The common galvanic cell, dry cell and the lead storage battery are the devices for converting chemical energy into electrical energy. Daniell cell is the typical example of galvanic cell. It consists of two half-cells, one containing zinc electrode dipping in solution of zinc sulphate (1 M) and another containing copper electrode dipping in solution of copper sulphate (1 M). Zinc electrode acts as anode. At this electrode oxidation occurs. $Zn \rightarrow Zn^{2+} + 2e^-$. Copper electrode acts as cathode. At this electrode reduction occurs, $Cu^{2+} + 2e^- \rightarrow Cu$. When the two half-cells are connected by a salt bridge and the metal electrodes are joined externally, the electrons from zinc electrode (–ve electrode) move towards copper electrode (+ve electrode), *i.e.*, current flows from cathode to anode. The cell reaction is:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Salt-bridge allows the flow of current by completing the circuit and maintains electrical neutrality. It also prevents liquid-liquid junction potential.

A galvanic cell is represented in the following manner:

LHS	Salt-bridge	RHS
Anode (–ve)		Cathode (+ve)
$Zn \mid Zn^{2+}$ (1 M)		Cu^{2+} (1 M) $\mid Cu$
Oxidation half-cell		Reduction half-cell
$Zn \rightarrow Zn^{2+} + 2e^-$		$Cu^{2+} + 2e^- = Cu$

10. **Electrode potential:** When a metal is placed in a solution of its ions, the metal either acquires a positive charge or negative charge with respect to solution. On account of this a definite potential is developed between the metal and the solution. This potential difference is termed **electrode potential.** The magnitude of potential depends on the nature of electrode, concentration of ions and temperature. It is a measure of the tendency of the metal to lose or gain electrons or a measure of the relative tendency to undergo oxidation or reduction. Depending on the nature of the metal electrode, the electrode potential is of two types:

(i) Oxidation potential: When electrode is negatively charged with respect to solution, *i.e.*, oxidation occurs and the electrode acts as anode

$$M \rightarrow M^{n+} + ne^-$$

(ii) Reduction potential: When electrode is positively charged with respect to solution, *i.e.*, reduction occurs and the electrode acts as cathode,

$$M^{n+} + ne^- \rightarrow M$$

Standard electrode potential: The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 *M*) at 25°C is called standard electrode potential.

It is not possible to measure the absolute value of single electrode potential directly. Only difference in potential of two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as **reference electrode.** The emf of the resulting cell is measured experimentally.

$$\text{Emf of the cell} = E_{\text{Anode}} + E_{\text{Cathode}}$$

$$= \text{Oxid. pot. of anode} + \text{Red. pot. of cathode}$$

Knowing the value of reference electrode, the value of other electrode can be determined.

Standard reduction potential = – (Standard oxidation potential)

Standard oxidation potential = – (Standard reduction potential)

11. Reference electrode (Standard hydrogen electrode, SHE): It is a primary standard electrode. It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and sealed in a glass tube as to make contact with outer circuit through mercury. The platinum strip and glass tube is surrounded by another glass tube which has an inlet for hydrogen gas and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in acid solution which has H^+ ion concentration 1 *M*. Pure hydrogen gas is circulated at 1 atmospheric pressure. The temperature of the cell is maintained at 25°C. By international agreement, the standard hydrogen electrode is arbitrarily assigned a potential of exactly ± 0.000... volt. This electrode can act as cathode or anode with respect to other electrode.

The electrode whose electrode potential is to be determined is connected with SHE and emf of such a cell is determined which is taken as the electrode potential of the given electrode. The metal electrode which acts as anode with respect to hydrogen electrode, the **oxidation potential** of the electrode is given positive sign and the metal electrode which acts as cathode with respect to hydrogen electrode, the reduction potential is given the positive sign.

12. Emf of a cell: The difference in potentials of two half-cells is known as the emf of the cell.

$$E^\circ_{\text{Cell}} = \text{Red. pot. cathode} - \text{Red. pot. anode } (E^\circ_{\text{right}} - E^\circ_{\text{left}})$$

$$= \text{Red. pot. cathode} + \text{Oxid. pot. anode}$$

$$= \text{Oxid. potential anode} - \text{Oxid. potential cathode}$$

13. Some more reference electrodes: Since, a hydrogen electrode is difficult to prepare and maintain, it is usually replaced by other reference electrodes which are known as **secondary** reference electrodes. These are convenient to handle and prepared easily. Calomel electrode and silver-silver chloride are used as reference electrodes. The potentials of these electrodes are fixed on hydrogen scale but their values depend on strong electrolyte concentration.

14. Reversible and irreversible cells: A cell is said to be reversible if the following two conditions are fulfilled:

(i) The chemical reaction of the cell stops when an exactly equal external emf is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the external emf is slightly higher than that of the cell.

Any other cell which does not obey the above two conditions is termed as irreversible. Daniell cell is reversible but $\text{Zn}\,|\,H_2SO_4\,|\,\text{Ag}$ cell is irreversible in nature.

15. Prediction for occurrence of a redox reaction: Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative.

$\Delta G^\circ = -nFE^\circ$ where, '*n*' is the number of electrons involved, *F* is the value of faraday and E° is the cell emf. ΔG° can be negative if E° is positive.

When E° is positive, the cell reaction will be spontaneous and serves as a source of electrical energy.

16. Nernst equation: The potential of an electrode changes with the change in concentration of ions in solution in contact with the electrode. Increase in concentration of cations results in an increase of reduction potential of an electrode.

Consider $M^{n+} + ne^- \rightarrow M$

$$E_{\text{red}} = E^\circ_{\text{red}} - \frac{2.303RT}{nF}\log\frac{[\text{reduced form}]}{[\text{oxidised form}]}$$

At 25°C, $\dfrac{2.303RT}{F} = 0.0591$

and the concentration of metal is unity.

$$E_{\text{red}} = E^\circ_{\text{red}} + \frac{0.0591}{n}\log[M^{n+}]$$

Similarly, consider the electrode where oxidation occurs.

$$M \rightarrow M^{n+} + ne^-$$

$$E_{\text{oxid.}} = E^\circ_{\text{oxid.}} - \frac{0.0591}{n}\log[M^{n+}]$$

Cell potential depends on the potential of anode and cathode.

$$E_{\text{Cell}} = E_{\text{Anode}} + E_{\text{Cathode}}$$

$$= \text{Oxid. pot. of anode} - \text{Red. pot. of cathode}$$

$$= E^\circ_{\text{oxid.}} - \frac{0.0591}{n}\log[\text{Anodic ion conc.}]$$

$$+ E^\circ_{\text{red}} - \frac{0.0591}{n}\log[\text{Cathodic ion conc.}]$$

$$= E^\circ_{\text{oxid.}} + E^\circ_{\text{red}} - \frac{0.0591}{n}\log\frac{[\text{Anodic ion conc.}]}{[\text{Cathodic ion conc.}]}$$

$$= E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

or

$$= E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{ion}]_{\text{LHS}}}{[\text{ion}]_{\text{RHS}}}$$

17. Electrochemical series: When the electrodes (metals and non-metals) in contact with their ions are arranged on the basis of values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the electrochemical or activity series of the elements.

Characteristics of Electrochemical Series

(i) The negative sign of reduction potential indicates that an electrode when joined with SHE acts as anode. Similarly the positive sign of reduction potential indicates that the electrode joined with SHE acts as cathode.

(ii) The substances which act as stronger reducing agents than hydrogen are placed above hydrogen in series. All those which have positive values of reduction potentials and placed below hydrogen are weaker reducing agents than hydrogen.

(iii) The substances which are stronger oxidising agents are placed below hydrogen in the series.

(iv) The metals at the top have the tendency to lose electrons readily. The activity of metals decreases from top to bottom while that of non-metals increases from top to bottom.

(v) A metal higher in the series will displace the metal from its solution which is lower in the series.

(vi) A non-metal higher in the series (towards bottom side) having high value of reduction potential will displace another non-metal with lower reduction potential.

(vii) The metals occupying top positions in the series readily liberate hydrogen from dilute acids.

(viii) Iron and metals above iron are capable of liberating hydrogen from water.

(ix) The oxides of metals having low reduction potentials are thermally stable while the oxides of metals having high reduction potentials are thermally not stable.

18. Relation between emf and equilibrium constant:

$$\Delta G^\circ = -2.303RT \log K$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

So,

$$nFE^\circ_{\text{cell}} = 2.303\,RT \log K$$

$$E^\circ_{\text{cell}} = \frac{2.303RT}{nF} \log K$$

$$= \frac{0.0591}{n} \log K \qquad (T = 298\text{ K})$$

19. Primary cells are those which have definite life and become dead over a time. These cannot be recharged. Examples are dry cell, mercury cell, etc.

Secondary cells are the cells which can be recharged by passing direct current through them. Lead storage battery and nickel-cadmium cell are examples of secondary cells. Lead storage battery consists of spongy lead as anode, a grid of lead packed with PbO_2 as cathode and an aqueous solution of H_2SO_4 (38% by mass or 20% H_2SO_4 of specific gravity 2.15) as electrolyte.

Reaction during discharging	**Reaction during charging**
$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$ Voltage 2.0 volt. The concentration of H_2SO_4 decreases during discharging.	$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$

Name of cell	**Anode**	**Cathode**	**Electrolyte used**
Dry cell	Zn	Graphite	MnO_2 + C (around cathode) $NH_4Cl + ZnCl_2$ (around anode)
Mercury cell	Zn	Graphite	HgO + KOH (moist)
Lead storage battery	Pb	PbO_2	H_2SO_4 (38% by mass)
Lithium battery	Li	Metal sulphide	$LiClO_4$ in organic solvent
Ni-Cad cell	Cd	NiO	KOH solution
Fuel cell (H_2-O_2)	Porous carbon (with catalyst)	Porous carbon (with catalyst)	Conc. NaOH or KOH (*aq*.)

20. Fuel cell: The cells which convert chemical energy of fuels directly into electrical energy are known as fuel cells. One of such cells is fuel cell (H_2-O_2) in which electrical energy is generated by the use of H_2 and O_2. In fuel cell NaOH is used as an electrolyte and hydrogen gas is diffused at the anode made of porous carbon. At the cathode oxygen is diffused through a porous carbon. The following chemical reactions occur:

(i) At anode, $H_2 \rightarrow 2H$

$$2H + 2OH^- \rightarrow 2H_2O + 2e^-$$

(ii) At cathode, $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Net cell reaction $2H_2 + O_2 \rightarrow 2H_2O + \text{energy}$

Fuel cells are quite efficient, and free from pollution. These are used in spacecrafts.

21. Concentration cells: If two plates of the same metal are dipped separately into two solutions of the same electrolyte and are connected with a salt bridge, the whole arrangement is found to acts as galvanic cell. Such cells are known as concentration cells. These are of two types:

(i) Electrode concentration cells

$$\text{Pt, } H_2 \text{ (pressure } p_1) \,|\, H^+ \,|\, H_2 \text{ (pressure } p_2\text{), Pt}$$

If $p_1 > p_2$ oxidation occurs at LHS electrode and reduction occurs at RHS electrode.

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{(p_1)}{(p_2)} \text{ at } 25°\text{C}$$

(ii) Electrolyte concentration cells

$$M \,|\, M^{n+} (C_1) \,||\, M^{n+} (C_2) \,|\, M$$

$$\text{Zn} \,|\, \text{Zn}^{n+} (C_1) \,||\, \text{Zn}^{n+} (C_2) \,|\, \text{Zn}$$

C_2 is higher than C_1.

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1} \text{ at } 25°\text{C}$$

Questions

1. Match the List-I with List-II and List-III:

List-I (Quantity)	List-II (Symbol)	List-III (Unit)
(a) Conductivity	(p) Λ_m	(u) mho cm^{-1}
(b) Cell constant	(q) κ	(v) cm^{-1}
(c) Molar conductance	(r) Λ_e	(w) $ohm^{-1}\ cm^2\ mol^{-1}$
(d) Equivalent conductance	(s) l/A	(x) $ohm^{-1}\ cm^2\ eq^{-1}$

2. Match the salts in the Column-I with their use in Column-II:

Column-I	Column-II
(a) Hg_2Cl_2	(p) Salt bridge
(b) Agar-agar	(q) Calomel electrode
(c) 0.1 N KCl	(r) Used in ice cream
(d) Quinhydrone	(s) Redox electrode

3. Match the Column-I with Column-II:

Column-I (Term)	Column-II (Relation)
(a) α (Degree of ionisation)	(p) λ^+/Λ
(b) t_+ (Transport number)	(q) Λ_m^c/Λ_m^0
(c) Fraction of a mole undergoing ionization	(r) $U^+/U^+ + U^-$
(d) NaCl	(s) Λ_e^c/Λ_e^0
	(t) $\Lambda_m = \Lambda_e$

4. Match the physical quantities in the List-I with their units in List-II:

List-I	List-II
(a) Resistance	(p) ohm
(b) Resistivity	(q) volt amp^{-1}
(c) Conductivity	(r) ohm m
(d) Specific conductance	(s) $ohm^{-1}\ m^{-1}$

5. Match the Column-I with Column-II:

Column-I	Column-II
(a) Specific conductance, κ	(p) $\Lambda_m^c / \Lambda_m^\circ$
(b) Molar conductance, Λ_m	(q) Decreases with dilution
(c) Resistance of electrolyte solution R	(r) Increases with dilution
(d) Degree of ionization of weak electrolyte, α	(s) Increases with increase in the distance between parallel plates

6. Match Column-I with Column-II:

Column-I (Combination of half-cell reactions)	Column-II (Potential of overall process)
(a) $6OH^- + Br^- \rightleftharpoons BrO_3^- + 3H_2O + 6e^-$ $E^\circ = -0.61$ V $2OH^- + Br^- \rightleftharpoons BrO^- + H_2O + 2e^-$ $E^\circ = -0.76$ V $\underline{4OH^- + BrO^- \rightleftharpoons BrO_3^- + 2H_2O + 4e^-}$ $E^\circ = ?$	(p) $E^\circ = 0.56$ V
(b) $H_2SO_3 + 4H^+ + 4e^- \rightleftharpoons S + 3H_2O$ $E^\circ = 0.45$ V $SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_2SO_3 + H_2O$ $E^\circ = 0.17$ V $\underline{SO_4^{2-} + 8H^+ + 6e^- \rightleftharpoons S + 4H_2O}$ $E^\circ = ?$	(q) $E^\circ = -0.535$V
(c) $ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O$ $E^\circ = +1.45$ V $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\circ = +1.36$ V $\underline{ClO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Cl_2 + 3H_2O}$ $E^\circ = ?$	(r) $E^\circ = +0.36$ V
(d) $Zn^{2+}_{(aq)} + 2e \longrightarrow Zn(s)$ $E^\circ = -0.76$ V $Ag^+ + e^- \longrightarrow Ag(s)$ $E^\circ = +0.80$ V $\underline{Zn(s) + 2Ag^+ \rightleftharpoons Zn^{2+}(aq) + 2Ag(s)}$ $E^\circ = ?$	(s) $E^\circ = +1.47$ V

7. Match the Column-I with Column-II:

Column-I	Column-II
(a) Concentration cell	(p) Fe is oxidised by Ni_2O_3
(b) Edison cell	(q) Zinc anode
(c) Mercury cell	(r) HgO cathode
(d) Dry cell	(s) $E^\circ = 0$

8. Match the Column-I with Column-II:

Column-I (Electrode)	Column-II (Type)
(a) Calomel	(p) Reference
(b) Glass	(q) Redox
(c) Hydrogen	(r) Membrane
(d) Quinhydrone	(s) Gas

9. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Kohlrausch law	(p) $\Lambda_m / \Lambda_m^\circ$
(b) Λ_m	(q) $\frac{1}{R} \times \frac{1}{A}$
(c) κ (kappa)	(r) $\Lambda_m^\circ Ca_3(PO_4)_2 = 3\lambda^\circ Ca^{2+} + 2\lambda^\circ PO_4^{3-}$
(d) α	(s) $\kappa \times \frac{1000}{M}$

10. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) $E^\circ = 0$	(p) Cell is discharged
(b) $E = 0$	(q) $Q = K$
(c) $\Delta G = 0$	(r) 96500 coulomb
(d) 1 Faraday	(s) 1 mol electrons
	(t) Concentration cell

Answers

1. (a—q, u), (b—s, v), (c—p, w), (d—r, x)
2. (a—q), (b—p, r), (c—p), (d—s)
3. (a—q, s), (b—p, r), (c—q, s), (d—t)
4. (a—p, q), (b—r), (c—s), (d—s)
5. (a—q), (b—r), (c—q, s), (d—p, r)
6. (a—q), (b—r), (c—s), (d—p)
7. (a—s), (b—p), (c—q, r), (d—q)
8. (a—p), (b—r), (c—s), (d—q)
9. (a—r), (b—s), (c—q), (d—p)
10. (a—t), (b—p, q), (c—p, q), (d—r, s)

• PRACTICE PROBLEMS •

1. How many coulombs are required for the following reductions?

(i) 1 mole of Ag^+ ions to Ag

(ii) 1 mole of Cu^{2+} ions to Cu

(iii) 1 mole of MnO_4^- ions to MnO_4^{2-}

[**Ans.** (i) 96500 coulomb (ii) 193000 coulomb (iii) 96500 coulomb]

2. How many faradays are needed to reduce 2 gram-mole of Cu^{2+} to Cu metal?

[**Ans.** 4 faraday]

3. How many faradays are released when 12.7 g of copper metal is changed into copper ions?

[**Ans.** 0.4 faraday]

[**Hint:** $\underset{\substack{1\text{ mole}\\63.5}}{Cu} \longrightarrow Cu^{2+} + \underset{\substack{2\text{ mole}\\2F}}{2e^-}$]

4. Calculate the number of coulombs required to deposit 40.5 g Al when the electrode reaction is:

$$Al^{3+} + 3e^- \longrightarrow Al$$

[**Ans.** 4.34×10^5 coulomb]

5. Calculate the number of coulombs required to deposit 50 g of silver at cathode from silver nitrate solution. (Atomic mass of silver = 108)

[**Ans.** 44675.9 coulomb]

6. How much electric charge is required to produce 20.0 g of calcium from molten $CaCl_2$?

[**Ans.** 96500 coulomb]

7. If 3 faradays of electricity are passed through an iron (II) bromide solution, how many grams of iron metal will be deposited? (At. mass of iron = 56)

[**Ans.** 84 g]

8. A certain quantity of electricity deposits 0.54 g of Ag from silver nitrate solution. What volume of hydrogen will be liberated by the same quantity of electricity at 27°C and 750 mm of Hg pressure?

[**Hint:** $\dfrac{\text{Mass of } H_2}{\text{Mass of Ag}} = \dfrac{\text{Eq. mass of } H_2}{\text{Eq. mass of Ag}}$

$$\text{Mass of } H_2 = \frac{1 \times 0.54}{108} = 0.005 \text{ g}$$

$$\text{Volume of } H_2 = \frac{0.005 \times 0.0821 \times 300 \times 760}{2 \times 750} \quad \left(V = \frac{w}{M} \cdot \frac{RT}{P}\right)$$

$$= 0.06234 \text{ litre}]$$

9. In the electrolysis of an aqueous cupric bromide solution, how many grams of bromine are formed on passing a current of 1 ampere for 16 minutes and 5 seconds? Write the anode and the cathode half reactions.

[**Ans.** 0.80 g; cathode reaction $Cu^{2+} + 2e^- \longrightarrow Cu$;
anode reaction $2Br^- \longrightarrow Br_2 + 2e^-$]

10. A current of 1.5 amperes is passed through a solution of a salt of a bivalent metal for 30 minutes. Increase in mass of cathode is 0.8898 g. Find the atomic mass of the metal.

[**Ans.** 63.6]

11. A lead storage battery is discharged in which the following electrode reaction takes place:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(l) \longrightarrow 2PbSO_4 + 2H_2O$$

The original volume in electrolyte is 1 litre. During discharge the concentration of H_2SO_4 changes from 34.6% by weight (density 1.261 g/mL) to 27% by weight. How many faradays have left the anodic half-cell? Water produced during electrolysis is used up.

[**Ans.** 1.254 faraday]

12. The chemical reaction given below:

$$Cl_2(g) + SO_2(g) + 2H_2O(l) \longrightarrow 2Cl^-(aq.) + 3H^+(aq.) + HSO_4^-(aq.)$$

proceeds readily in aqueous acid solution.

(i) Give the half-cell reactions.

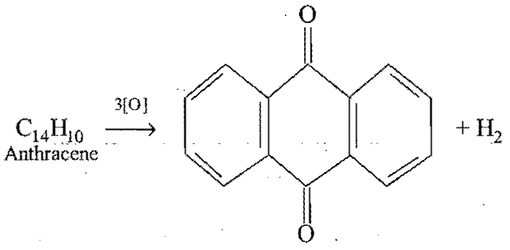
(ii) If a fully charged cell initially held 1 mole of Cl_2, for how many days could it sustain a current of 0.05 ampere, assuming the cell becomes non-operative when 90% of initial Cl_2 has been used up?

[**Ans.** 40.2 days]

13. A current of 80 microampere is passed through a solution of $AgNO_3$ for 32 minutes using platinum electrodes. A uniform single atom thick layer is deposited covering 86% of the cathode surface. If total surface area of cathode is 601.7 cm^2, calculate the area covered by one Ag atom.

[**Ans.** 5.4×10^{-16} cm^2]

14. Anthracene can be electrolytically oxidised to anthraquinone.



Anthraquinone

What mass of anthraquinone can be produced by the passage of 1 ampere current for an hour at 100% efficiency?

[**Ans.** 1.2932 g]

15. Dal lake has water 8.2×10^{12} litre approximately. A power reactor produces electricity at the rate of 1.5×10^6 coulomb per second at an appropriate voltage. How much time would it take to electrolyse the lake?

[**Ans.** 1.9 million year]

16. How many grams of H_2 and O_2 are produced during the electrolysis of water by a 1.30 ampere current for 5 hours? What volumes of dry gases are produced at NTP?

[**Ans.** 0.242 g H_2; 1.94 g O_2; 2.72 litre H_2; 1.36 litre O_2]

17. How many coulombs of electricity would be required to reduce the iron in 36.0 g of potassium hexacyano ferrate(III), $K_3Fe(CN)_6$, to metallic iron?
[**Ans.** 3.17×10^4 coulomb]
[**Hint:** Iron in the complex is Fe^{3+}.

$$\underset{1\text{ mole}}{K_3Fe(CN)_6} + \underset{3 \times 96500\text{ C}}{3e^-} \longrightarrow 3K^+ + 6CN^- + Fe\,]$$

18. What current strength in ampere will be required to liberate 5 g of iodine from potassium iodide solution in 30 minutes?
[**Ans.** 2.11 ampere]

19. The mass of copper deposited from a solution of copper sulphate by a uniform current of 0.25 ampere flowing for one hour is 0.295 g. Find the equivalent mass of copper. (1 faraday = 96500 coulomb)
[**Ans.** 31.75]

20. The solution of a salt of a metal of atomic mass 112 was electrolysed for 15 minutes with a current of 1.5 ampere. The mass of the metal deposited was 0.788 g. Find the valency of the metal.
[**Ans.** 2]

21. If a monovalent metal ion carries 1.6×10^{-19} coulomb of electricity, what is the amount of electricity carried by one gram molecular mass of the metal ions?
[**Ans.** 9.6336×10^4 coulomb]

22. Calculate approximately how much current is necessary to produce oxygen gas at the rate of 1 mL per second?
[**Ans.** 17.23 ampere]
[**Hint:** 1 g-equivalent of oxygen or $\frac{22400}{4}$ mL is liberated by 96500 coulomb.]

23. 0.5 faraday of electricity was required to deposit all the copper in 500 mL of a copper sulphate solution. What is the normality of the copper sulphate solution?
[**Ans.** Normality = 1 N.]

24. Copper is deposited at an electrode according to the reaction $Cu^{2+} \xrightarrow{+2e^-} Cu$. When a current of 1.34 ampere was passed through a solution of copper sulphate for 10 hours, 15.885 g of copper was deposited.
(i) How many coulombs of electricity were passed through the solution?
(ii) How many moles of copper were deposited?
(iii) How many coulombs are required for the deposition of 1 mole of copper?
(iv) If the charge on an electron is 1.6×10^{-19} coulomb, calculate the value of Avogadro's number.
[**Ans.** (i) 482.40 coulomb (ii) 0.25 mol (iii) 2×96500 coulomb (iv) 6.03×10^{23}]

25. Calculate the mass and volume at NTP of hydrogen and chlorine that will be formed by passing 10,000 coulomb of charge through an aqueous solution of potassium chloride. The cell reaction is:

$$2KCl + 2HOH \longrightarrow 2KOH + Cl_2 + H_2$$

[**Ans.** 0.1036 g H_2, volume 1.063 litre; 3.678 g Cl_2, volume 1.1603 litre]

26. Three electrolytic cells A, B and C containing electrolytes zinc sulphate, silver nitrate and copper sulphate respectively, were connected in series. A steady current of 1.50 ampere was passed through them until 1.45 g of silver was deposited at the cathode of cell B. How long did the current flow? What masses of copper and zinc were deposited?
(At. mass: Cu = 63.5, Zn = 65.4, Ag = 107.8)
[**Ans.** 865 second; 0.427 g Cu; 0.44 g Zn]

27. An electric current passing for 6 minutes through a dilute H_2SO_4 solution gave 40 mL of the electrolytic gas ($H_2 + O_2$) measured at NTP. What was the average value of current?
[**Ans.** 0.638 ampere]
[**Hint:** 96500 coulomb give 11.2 litre of H_2 and 5.6 litre of O_2, *i.e.*, 16.8 litre of electrolytic gas at NTP.]

28. The same quantity of electricity that liberated 2.158 g silver was passed through a solution of a gold salt and 1.314 g of gold was deposited. The equivalent mass of silver is 107.9. Calculate the equivalent mass of gold. What is the oxidation state of gold in this gold salt? (At. mass of gold = 197)
[**Ans.** Eq. mass = 65.7; Oxidation state = 3]

29. Calculate the volume of Cl_2 at NTP produced during electrolysis of $MgCl_2$ which produces 6.50 g Mg.
(At. mass of Mg = 24.3)
[**Ans.** 5.99 litre]

30. How long does it take to deposit 100 g of Al from an electrolytic cell containing Al_2O_3 using a current of 125 ampere?
[**Ans.** 8577.8 second]

31. 10g fairly concentrated solution of $CuSO_4$ is electrolysed using 1.01 faraday of electricity. Calculate the mass of the resulting solution.
[**Ans.** 9.6025 g]

32. The density of copper is 8.94 g mL^{-1}. Find out the number of coulombs needed to plate an area $10 \times 10\text{ cm}^2$ to a thickness of 10^{-2} cm using $CuSO_4$ solution as electrolyte. (At. mass of Cu = 63.6)
[**Ans.** 27129.2 coulomb]

33. What mass of Ag (At. mass 108) could be plated on a spoon from electrolysis of $AgNO_3$ solution by one ampere current for 10 minutes? (Dhanbad 1990)
[**Ans.** 0.6715 g]

34. If a current of 0.3 ampere is drawn from a Daniell cell for 1 hour, what would be the change in mass of electrodes? (At. mass of Cu = 63.5 and Zn = 65.37)
[**Ans.** 0.356 g Cu deposited, 0.366 g of Zn dissolves]

35. An element A (At. mass 112) and an element B (At. mass 27) form chlorides. Solutions of these chlorides are electrolysed separately and it is found that when the same quantity of electricity is passed, 5.6 g of A was deposited while in the other cell only 0.9 g of B was deposited. What is the valency of A if the valency of B is 3? (Dhanbad 1991)
[**Ans.** 2]

36. How many coulombs must be applied to a cell for the electrolytic production of 245 g $NaClO_4$ from $NaClO_3$. The anode efficiency for the desired reaction is 60%.
[**Ans.** 6.43×10^5 coulomb]

37. Calculate the mass of Hg_2Cl_2 which can be prepared by the reduction of mercury(II) ions in the presence of chloride ions by the passage of 5.0 ampere current for 3.0 hours.

[**Ans.** 132.34 g]

[**Hint:** $\underset{}{2Hg^{2+}} + 2Cl^- + \underset{2\,F}{2e^-} \longrightarrow \underset{1\text{ mole}}{Hg_2Cl_2}$]

38. How long will it take for a uniform current of 6.0 ampere to deposit 78.0 g gold from a solution of $AuCl_4^-$? What mass of chlorine gas will be formed simultaneously at the anode in the electrolytic cell?

[**Ans.** 19104 second; chlorine liberated = 42.17 g]

[**Hint:** $AuCl_4^- + \underset{3\,F}{3e^-} \longrightarrow \underset{1\text{ mole}}{Au} + 4Cl^-$ (Cathode)

$2Cl^- \longrightarrow \underset{1\text{ mole}}{Cl_2} + \underset{2\,F}{2e^-}$ (Anode)]

39. How long will it take 5 ampere of current to deposit 2 g of copper from a solution of copper sulphate?
(Given, CE of copper = 32, F = 96500 coulomb)
(Ranchi 1996)

[**Ans.** 20.1 minute]

40. The amount of lactic acid, $HC_3H_5O_3$, produced in a sample of muscle tissue was analysed by reaction with hydroxide ion. Hydroxide ion was produced in the sample mixture by electrolysis. The cathode reaction was,

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq.)$$

Hydroxide ion reacts with lactic acid as soon as it is produced. The end point of the reaction is detected with an acid-base indicator. It required 115 seconds for a current of 15.6 mA to reach end point. How many grams of lactic acid (a monoprotic acid) were present in the sample?

[**Ans.** 1.674×10^{-3} g]

[**Hint:** No. of moles of lactic acid = No. of moles of OH^- used
= No. of faraday used in electrolysis

$$\text{Number of faraday used} = \frac{I \times t}{96500} = \frac{15.6 \times 10^{-3} \times 115}{96500}$$

$$= 1.86 \times 10^{-5}$$

Mass of lactic acid = Number of moles × Molecular mass

$$= 1.86 \times 10^{-5} \times 90$$

$$= 1.674 \times 10^{-3} \text{ g}]$$

41. In what direction, can the reaction:

$$2NaCl + Fe_2(SO_4)_3 \rightleftharpoons 2FeSO_4 + Cl_2 + Na_2SO_4$$

proceed spontaneously?
(Given: $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\,V$; $E^\circ_{Cl^-/Cl_2} = 1.36\,V$)
(BCECE 2005)

[**Ans.** Forward]

42. How many faradays of electricity will be required to completely electrolyse one mole of molten Al_2O_3 to produce Al metal and O_2 gas? **[JEE (West Bengal) 2005]**

[**Ans.** 3 F]

43. The resistance of 0.01 N solution at 25°C is 200 ohm. Cell constant of the conductivity cell is unity. Calculate the equivalent conductance of the solution.

[**Ans.** 500 $ohm^{-1}\,cm^2\,eq^{-1}$]

44. A conductivity cell was filled with 0.01 M solution of KCl which was known to have a specific conductivity of 0.1413 $ohm^{-1}\,m^{-1}$ at 298 K. Its measured resistance at 298 K was 94.3 ohm. When the cell was filled with 0.02 M $AgNO_3$ solution, its resistance was 50.3 ohm. Calculate (i) cell constant and (ii) the specific conductance of $AgNO_3$ solution.

[**Ans.** 13.32 m^{-1}; $2.648 \times 10^{-1}\,ohm^{-1}\,m^{-1}$]

45. A conductance cell was calibrated by filling it with a 0.02 M solution of potassium chloride. (specific conductance = 0.2768 $ohm^{-1}\,m^{-1}$) and measuring the resistance at 298 K which was found to be 457.3 ohm. The cell was then filled with a calcium chloride solution containing 0.555 g of $CaCl_2$ per litre. The measured resistance was 1050 ohm. Calculate the molar conductivity of $CaCl_2$ solution.

[**Ans.** 0.0241 mho $m^2\,mol^{-1}$]

[**Hint:** Determine cell constant with KCl data. Its value is 126.6 m^{-1}.

$$\text{Sp. cond. of } CaCl_2 \text{ soln.} = \text{Cell const.} \times \frac{1}{\text{Resistance}}$$

$$= 126.6 \times \frac{1}{1050} = 0.1206\ ohm^{-1}\,m^{-1}$$

$$\text{Molar conductance} = \frac{\text{Sp. cond.}}{\text{Conc.}}$$

$$\text{Conc.} = \frac{0.555}{111.0} = 0.005\ mol\ dm^{-3} = 5\ mol\ m^{-3}]$$

46. The molar conductivities at infinite dilution of KCl, KNO_3 and $AgNO_3$ at 298 K are 0.01499 mho $m^2\,mol^{-1}$, 0.01250 mho $m^2\,mol^{-1}$ and 0.01334 mho $m^2\,mol^{-1}$ respectively. What is the molar conductivity of AgCl at infinite dilution at this temperature?

[**Ans.** 0.01383 mho $m^2\,mol^{-1}$]

47. The electrodes in a conductivity cell have area $1.2 \times 10^{-4}\,m^2$ and they are fixed 3×10^{-3} m apart. A solution containing 200 g equivalent of the electrolyte per m^3 of the solution has a resistance of 60 ohm at 298 K. Calculate the equivalent conductivity of the solution.

[**Ans.** 2.09×10^{-2} mho $m^2\,eq^{-1}$]

48. The molar conductivities of NH_4^+ ion and Cl^- ion are 73.5 mho $cm^2\,mol^{-1}$ and 76.2 mho $cm^2\,mol^{-1}$ respectively. The specific conductivity of 0.1 M NH_4Cl is 1.288×10^{-2} mho cm^{-1}. What is the dissociation constant of NH_4Cl?

[**Ans.** 0.86]

49. The specific conductivity of a saturated solution of silver chloride at 18°C is 1.24×10^{-6} mho after subtracting that of water. Ionic conductances at infinite dilution of Ag^+ and Cl^- ions at this temperature are 53.8 and 65.3 respectively. Calculate the solubility of silver chloride in gram per litre.

[**Ans.** 1.494×10^{-3} g per litre]

50. Given:

$$\lambda^\infty [\tfrac{1}{2} Mg^{2+}] = 53.06 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$
$$\lambda^\infty [\tfrac{1}{2} SO_4^{2-}] = 80 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$
$$\lambda^\infty [\tfrac{1}{3} Al^{3+}] = 63 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Calculate the values of $\Lambda_m^\infty [Al_2(SO_4)_3]$ and $\Lambda^\infty [MgSO_4]$.

[**Ans.** 858 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, 266.12 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$]

51. Hydrofluoric acid is a weak acid. At 25°C, the molar conductivity of 0.002 M HF is 176.2 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. If its $\Lambda_m^\infty = 405.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, calculate its degree of dissociation and equilibrium constant at the given concentration.

[**Ans.** $\alpha = 0.435, K = 6.7 \times 10^{-4}$]

52. For mercury at 0°C specific conductance,

$$\kappa = 1.062963 \times 10^6 \text{ S/m}.$$

(a) If the resistance of a cell containing mercury is 0.243166 ohm, what is the cell constant of the cell?

(b) If the same cell is filled with KCl solution at 0°C, the resistance of the cell is 3.966×10^4 ohm. What is the conductivity of KCl solution?

(c) If the average cross-sectional area of the cell is 0.9643 mm^2, what is the effective distance between the electrodes?

[**Ans.** (a) 2.58476×10^5 S/m; (b) 6.517 S/m; (c) 0.2492 m]

53. The mobility of the NH_4^+ ions is $7.623 \times 10^{-8} \text{ m}^2/\text{Vs}$. Calculate:

(a) the molar conductivity of NH_4^+ ion;

(b) velocity of the ion if 15 volt are applied across the electrodes 25 cm apart.

[**Ans.** (a) $73.55 \times 10^{-4} \text{ S m}^2/\text{mol}$; (b) 4.574 μm/s]

54. Construct electric cells for the following reactions:

(a) $Fe + Cu^{2+} \longrightarrow Cu + Fe^{2+}$

(b) $Cu + 2Ag^+ \longrightarrow 2Ag + Cu^{2+}$

(c) $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

(d) $Cd + I_2 \longrightarrow Cd^{2+} + 2I^-$

(e) $2Fe^{3+} + 2Cl^- \longrightarrow 2Fe^{2+} + Cl_2$

[**Ans.** (a) $Fe \mid Fe^{2+} \parallel Cu^{2+} \mid Cu$

(b) $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$

(c) $Pt \mid Fe^{2+}, Fe^{3+} \parallel H^+, Cr_2O_7^{2-}, Cr^{3+} \mid Pt$

(d) $Cd \mid Cd^{2+} \parallel I^-, I_2 \mid Pt$

(e) $Pt \mid Cl_2, Cl^- \parallel Fe^{3+}, Fe^{2+} \mid Pt$]

55. Predict whether the following reaction will occur spontaneously or not:

$$Co^{2+} + Sn \longrightarrow Co + Sn^{2+}$$

$$E^\circ_{Co/Co^{2+}} = 0.277 \text{ volt and } E^\circ_{Sn/Sn^{2+}} = 0.136 \text{ volt}$$

[**Ans.** No; E°_{cell} is negative = − 0.141 volt]

56. An iron wire is immersed in a solution containing $ZnSO_4$ and $NiSO_4$. 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: $E^\circ_{Zn^{2+}/Zn} = -0.76$ volt; $E^\circ_{Fe^{2+}/Fe} = -0.44$ volt and $E^\circ_{Ni^{2+}/Ni} = -0.25$ volt.

[**Ans.** Iron reduces Ni^{2+} ions as the E°_{cell} in this case has positive value.]

57. Can a solution of 1 M $CuSO_4$ be stored in a vessel made of nickel metal?

Given: $E^\circ_{(Ni^{2+};\, Ni)} = -0.25$ volt

$E^\circ_{(Cu^{2+};\, Cu)} = 0.34$ volt

Ans. No; The reaction takes place between $CuSO_4$ and nickel as E°_{cell} is positive.]

58. Answer whether, under standard conditions, the following reactions are possible or not:

(i) Will copper reduce Ag^+ to Ag? Given: $E^\circ_{Ag^+/Ag} = 0.799$ volt; $E^\circ_{Cu^{2+}/Cu} = -0.337$ volt

(ii) Will Fe^{3+} be reduced to Fe^{2+} by Sn^{2+} ion? Given:

$Fe^{3+} \mid Fe^{2+} = 0.771$ volt;

$Sn^{2+} \mid Sn^{4+} = -0.250$ volt

(iii) Would you use a silver spoon to stir a solution of $Cu(NO_3)_2$?

[**Ans.** (i) Yes, E°_{cell} $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$ is positive (+ 0.462 volt)

(ii) Yes, E°_{cell} $Pt \mid Sn^{4+}, Sn^{2+} \parallel Fe^{3+}, Fe^{2+} \mid Pt$ is positive (+0.621 volt)

(iii) Yes, the reaction does not occur.]

59. The electrode potentials of two half reactions are as follows:

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$; $E^\circ = +0.76$ volt

$Ce^{4+} + e^- \longrightarrow Ce^{3+}$; $E^\circ = +1.60$ volt

Giving reason, describe if Ce^{3+} can be oxidised by Fe^{3+}.

[**Hint:** $Ce^{3+} + Fe^{3+} \longrightarrow Ce^{4+} + Fe^{2+}$

$Ce^{3+} \longrightarrow Ce^{4+} + e^-$ (oxidation); $E^\circ = -1.60$ volt

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ (reduction); $E^\circ = +0.76$ volt

Adding both, E° of the reaction = − 0.84 volt

The oxidation of Ce^{3+} by Fe^{3+} is not possible.]

60. Calculate the standard reduction potential of Ni^{2+}/Ni electrode when the emf of the cell

$$Ni \mid Ni^{2+} (1\,M) \parallel Cu^{2+} (1\,M) \mid Cu$$

is 0.59 volt and $E^\circ_{Cu^{2+}/Cu} = +0.34$ volt

[**Ans.** − 0.25 volt]

61. Calculate the half-cell potential at 298 K for the reaction,

$$Zn^{2+} + 2e^- \longrightarrow Zn$$

if $[Zn^{2+}] = 0.1\,M$ and $E^\circ = -0.76$ volt.

[**Ans.** − 0.789 volt]

62. A galvanic cell consists of a metallic zinc plate immersed in 0.1 M $Zn(NO_3)_2$ solution. Calculate the emf of the cell at 25°C. Write the chemical equations for the electrode reactions and represent the cell. (Given: $E^\circ_{Zn^{2+}/Zn} = -0.76$ volt and $E^\circ_{Pb^{2+}/Pb} = -0.13$ volt)

[**Ans.** $Zn \longrightarrow Zn^{2+} + 2e^-$, $Pb^{2+} + 2e^- \longrightarrow Pb$

$$Zn \mid \underset{0.1\,M}{Zn^{2+}} \parallel \underset{0.02\,M}{Pb^{2+}} \mid Pb$$

$E^\circ_{cell} = 0.63$ volt $E_{cell} = 0.609$ volt]

63. Calculate the cell potential of the cell at 25°C having the cell reaction:

$$2Ag^+ + Cu \rightleftharpoons 2Ag + Cu^{2+}$$

(Given that, $[Ag^+] = 1.0 \times 10^{-3}\,M$,

$[Cu^{2+}] = 1.0 \times 10^{-4}\,M$, $E^\circ_{cell} = 0.46$ volt)

[**Ans.** 0.40 volt]

64. Calculate the E and E° of the cell

$$Ni \mid Ni^{2+} \parallel Cu^{2+} \mid Cu$$

from the following half-cell reactions:

$Ni^{2+} + 2e^- \longrightarrow Ni$; $E^\circ = -0.25$ volt

$Cu^{2+} + 2e^- \longrightarrow Cu$; $E^\circ = +0.34$ volt

(Given: $[Ni^{2+}] = 1\,M$ and $[Cu^{2+}] = 10^{-3}\,M$)

[**Ans.** $E^\circ_{cell} = 0.59$ volt; $E_{cell} = 0.5015$ volt]

65. Use E° values to calculate ΔG° for the reaction

$$Fe^{2+} + Ag^+ \longrightarrow Fe^{3+} + Ag$$

$E^\circ_{Ag^+/Ag} = 0.80$ volt and $E^\circ_{Pt/Fe^{3+}, Fe^{2+}} = 0.77$ volt

[**Ans.** -2895 J]

[**Hint:** $E^\circ_{cell} = 0.03$ volt, $\Delta G^\circ = -nFE^\circ_{cell}$]

66. A piece of zinc metal is dipped in a 0.1 M solution of zinc salt. The salt is dissociated to the extent of 20%. Calculate the electrode potential of Zn^{2+}/Zn.

(Given: $E^\circ_{Zn^{2+}/Zn} = -0.76$ volt.)

[**Ans.** -0.8102 volt]

[**Hint:** $[Zn^{2+}] = 0.1 \times 0.2 = 0.02\,M$

$Zn^{2+} + 2e^- \longrightarrow Zn$ (Reduction)

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} + \frac{0.0591}{2} \log_{10} [Zn^{2+}]\,]$$

67. Estimate the concentration limit beyond which the half-cell potential of $Cu^{2+} \mid Cu$ will be zero.

$$E^\circ_{Cu^{2+}/Cu} = 0.34 \text{ volt}$$

[**Ans.** 3.1×10^{-12} mol L^{-1}]

[**Hint:** $E^\circ_{Cu^{2+}/Cu} = \frac{0.0591}{2} \log [Cu^{2+}]$]]

68. Calculate equilibrium constant for the following reaction:

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

$E^\circ_{Zn/Zn^{2+}} = 0.765$ volt; $E^\circ_{Cu^{2+}/Cu} = 0.347$ volt

[**Ans.** 1.862×10^{37}]

69. For the cell reaction,

$$Ni \mid Ni^{2+} \parallel Ag^+ \mid Ag$$

Calculate the equilibrium constant at 25°C. How much maximum work would be obtained by the operation of this cell?

[**Ans.** 3.98×10^{35}, Max. work = 202650 J]

70. Calculate the emf of the cell

$$Cr \mid Cr^{3+}\,(0.1\,M) \parallel Fe^{2+}\,(0.01\,M) \mid Fe$$

(Given: $E^\circ_{Cr^{3+}/Cr} = -0.75$ volt; $E^\circ_{Fe^{2+}/Fe} = -0.45$ volt)

[**Ans.** 0.261 volt]

71. Calculate the equilibrium constant for the reaction,

$$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow 2Ag(s) + Zn^{2+}(aq.) + 2OH^-(aq.)$$

when $E^\circ_{cell} = 1.11$ at 298 K.

[**Ans.** $K_c = 3.499 \times 10^{37}$]

72. The standard reduction potential of $Ag^+ \mid Ag$ electrode is 0.80 volt. Calculate the standard electrode potential of $Cl^- \mid AgCl \mid Ag$ at 25°C. Given solubility product, $K_{sp}(AgCl) = 1.8 \times 10^{-10}$.

[**Hint:** Apply

$E^\circ_{cell} = 0.0591 \times \log [Ag^+][Cl^-] = 0.0591 \log K_{sp}(AgCl)$

$E^\circ_{cell} = -0.576$ volt

E°_{cell} = Oxid. pot. anode + Red. pot. cathode

Red. pot. cathode $[Cl^- \mid AgCl \mid Ag] = -0.576 - (-0.80)$

$= -0.576 + 0.80 = 0.224$ volt]

73. Derive Nernst equation for the cell.

$$Ni(s) \mid Ni^{2+}\,(aq.\,0.1\,M) \parallel Ag^+\,(aq.\,0.1\,M) \mid Ag(s)$$

and also find its cell potential. Given:

$E^\circ_{Ag^+/Ag} = 0.80$ volt and $E^\circ_{Ni^{2+}/Ni} = -0.25$ volt

[**Hint:** Cell reaction,

$Ni + 2Ag^+ \longrightarrow 2Ag + Ni^{2+}$; $E^\circ_{cell} = 1.05$ volt

Nernst equation, $E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$

$\doteq (1.05 - 0.0295)$ volt

$= 1.02$ volt]

74. Determine the equilibrium constant of the following reaction at 298 K:

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

(Given: $E^\circ_{Sn^{4+}/Sn^{2+}} = 0.15$ volt, $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$ volt)

[**Ans.** $K = 1.0 \times 10^{21}$]

[**Hint:** Calculate E°_{cell}. The value is 0.621 volt.

Apply $E^\circ_{cell} = \frac{0.0591}{2} \log K$]

75. The zinc-silver oxide cell is used in hearing aids and electric watches. From the following data:

$Zn^{2+} + 2e^- \longrightarrow Zn$; $E^\circ = -0.76$ volt

$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$; $E^\circ = 0.334$ volt

Answer the following:

(a) Construct the cell and what will be its emf ?

(b) What is its cell reaction and what will be ΔG° value of this cell reaction?

(c) Name the species which undergo oxidation and reduction when the cell is in operation.

[**Ans.** (a) Cell $Zn \mid Zn^{2+} \parallel OH^- \mid Ag_2O \mid Ag$

$$E^\circ_{cell} = 1.104 \text{ volt}$$

(b) Cell reaction,

$$Ag_2O + H_2O + Zn \longrightarrow 2Ag + Zn^{2+} + 2OH^-$$

$$\Delta G^\circ = -nFE^\circ_{cell} = -2 \times 96500 \times 1.104 = -213072 \text{ J}$$

(c) Zinc is oxidised to Zn^{2+} and Ag_2O is reduced to Ag.]

76. An excess of Hg was added to 10^{-3} M acidified solution of Fe^{3+} ions. It was found that only 4.6% of the ions remained as Fe^{3+} at equilibrium at 25°C. Calculate E° for $2Hg / Hg_2^{2+}$ at 25°C for

$$2Hg + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$$

[**Ans.** -0.7912 volt]

77. The emf of the cell,

$$Ag \mid AgI \; (0.05) \, M \, KI \parallel (0.05) \, M \, AgNO_3 \mid Ag$$

is 0.788 volt. Calculate the solubility product of AgI.

[**Ans.** 1.10×10^{-16}]

78. At equimolar concentrations of Fe^{2+} and Fe^{3+}, what must $[Ag^+]$ be so that the voltage of the galvanic cell made from Ag^+/Ag and Fe^{3+}/Fe^{2+} electrodes equals zero? The reaction is $Fe^{2+} + Ag^+ \rightleftharpoons Fe^{3+} + Ag$. Determine the equilibrium constant at 25°C for the reaction. (Given: $E^\circ_{Ag^+/Ag} = 0.799$ volt and $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$ volt)

[**Hint:** $E^\circ_{cell} = E^\circ_{Fe^{2+}/Fe^{3+}} + E^\circ_{Ag^+/Ag}$

$$= -0.771 + 0.799 = 0.028 \text{ volt}$$

At equilibrium, $E_{cell} = 0$

$$0 = E^\circ_{cell} - \frac{0.0591}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]}$$

$$= E^\circ_{cell} - 0.0591 \log \frac{1}{[Ag^+]}$$

$$[Ag^+] = 0.34$$

$$\log K = \frac{nE^\circ}{0.0591}$$

$$K = 3.0]$$

79. Using Nernst equation for the cell reaction,

$$Pb + Sn^{2+} \longrightarrow Pb^{2+} + Sn$$

Calculate the ratio $\frac{[Pb^{2+}]}{[Sn^{2+}]}$ for which $E_{cell} = 0$.

(Given: $E^\circ_{Pb/Pb^{2+}} = 0.13$ volt and $E^\circ_{Sn^{2+}/Sn} = -0.14$ volt)

[**Ans.** $\frac{[Pb^{2+}]}{[Sn^{2+}]} = 0.5$]

80. Determine the potential of a Daniell cell, initially containing 1.00 L each of 1.0 M copper(II) ion and 1.0 M zinc(II) ion, after passage of 10^5 coulomb charge. The E° of the Daniell cell is 1.10 volt.

[**Ans.** 1.09 volt]

[**Hint:** By passage of 10^5 coulomb charge, zinc ion concentration increases by 0.518 mole while copper ion concentration decreases by 0.518 mole.

Thus, $[Zn^{2+}] = 1.518\,M$ and $[Cu^{2+}] = 0.482\,M$

(Now apply Nernst equation)]

81. Calculate the standard potential for the reaction,

$$Hg_2Cl_2 + Cl_2 \longrightarrow 2Hg^{2+} + 4Cl^-$$

(Given:

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-; \quad E^\circ = 0.270 \text{ volt}$$

$$Hg_2^{2+} \longrightarrow 2Hg^{2+} + 2e^-; \quad E^\circ = -0.92 \text{ volt}$$

$$2Hg \longrightarrow Hg_2^{2+} + 2e^-; \quad E^\circ = -0.79 \text{ volt}$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^-; \quad E^\circ = 1.36 \text{ volt})$$

Ans. -0.08 volt]

[**Hint:** First determine E° for

$$Hg_2Cl_2 \longrightarrow 2Hg^{2+} + 2Cl^- + 2e^- \text{ electrode.}$$

It comes to -1.44 volt.

This electrode is now coupled with $Cl_2 + 2e^- \longrightarrow 2Cl^-$ electrode.]

82. Given:

$$Cu^{2+} + e^- \longrightarrow Cu^+; \quad E^\circ = 0.15 \text{ volt}$$

$$Cu^+ + e^- \longrightarrow Cu; \quad E^\circ = 0.5 \text{ volt}$$

Calculate potential for $Cu^{2+} + 2e^- \longrightarrow Cu$.

[**Ans.** 0.325 volt]

83. What is the standard electrode potential for the electrode MnO_4^-/MnO_2 in solution?

(Given: $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51$ volt, $E^\circ_{MnO_2/Mn^{2+}} = 1.23$ volt)

[**Ans.** 1.7 volt]

[**Hint:**

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O; \; E^\circ = 1.51 \text{ volt}$$

$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O; \; E^\circ = 1.23 \text{ volt}$$

Subtracting

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O; \; E^\circ = ?$$

$$E^\circ = \frac{5 \times 1.51 - 2 \times 1.23}{3} = \frac{7.55 - 2.46}{3} = \frac{5.09}{3} = 1.70 \text{ volt}]$$

84. What ratio of Pb^{2+} to Sn^{2+} concentration is needed to reverse the following cell reaction?

$$Sn(s) + Pb^{2+}(aq.) \longrightarrow Sn^{2+}(aq.) + Pb(s)$$

$$E^\circ_{Sn^{2+}/Sn} = -0.136 \text{ volt} \quad \text{and} \quad E^\circ_{Pb^{2+}/Pb} = -0.126 \text{ volt}$$

[**Ans.** $\frac{[Pb^{2+}]}{[Sn^{2+}]} < 0.458$]

85. For the cell $Mg \mid Mg^{2+} \parallel Ag^+ \mid Ag$, calculate the equilibrium constant at 25°C and the maximum work that can be obtained during the operation of the cell.

(Given: $E^\circ_{Mg/Mg^{2+}} = 2.37$ volt and $E^\circ_{Ag^{2+}/Ag} = 0.80$ volt)

[**Ans.** $K = 2.86 \times 10^{107}$; $W_{max} = 6.118 \times 10^5$ J]

86. Determine the potential for the cell:

$$\mathrm{Pt} \mid \mathrm{Fe}^{2}, \mathrm{Fe}^{3+} \parallel \mathrm{Cr_2O_7^{2-}}, \mathrm{Cr}^{3+}, \mathrm{H}^+ \mid \mathrm{Pt}$$

in which $[\mathrm{Fe}^{2+}]$ and $[\mathrm{Fe}^{3+}]$ are $0.5M$ and $0.75M$ respectively and $[\mathrm{Cr_2O_7^{2-}}]$, $[\mathrm{Cr}^{3+}]$ and $[\mathrm{H}^+]$ are $2M$, $4M$ and $1M$ respectively. Given:

$$\mathrm{Fe}^{3+} + e^- \longrightarrow \mathrm{Fe}^{2+}; \qquad E^\circ = 0.770 \text{ volt}$$

$$14\mathrm{H}^+ + 6e^- + \mathrm{Cr_2O_7^{2-}} = 2\mathrm{Cr}^{3+} + 7\mathrm{H_2O}; \qquad E^\circ = 1.35 \text{ volt}$$

[**Ans.** 0.56 volt]

87. For the measurement of the solubility product of AgCl the following cell is constructed:

$$\mathrm{Ag} \mid \mathrm{AgCl} \parallel \mathrm{KCl}\ (0.1\ M) \parallel \mathrm{AgNO_3}\ (0.1\ M) \mid \mathrm{Ag}$$

The emf of the cell is 0.45 volt. In the cell, KCl is dissociated to the extent of 83% and $\mathrm{AgNO_3}$ is dissociated to the extent of 86%. Calculate the solubility product of AgCl at 298 K.

[**Ans.** 1.735×10^{-10}]

[**Hint:** $E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0591 \log \dfrac{[\mathrm{Ag}^+]_{\text{Anode}}}{[\mathrm{Ag}^+]_{\text{Cathode}}}$]

88. Excess of AgCl is added to 0.1 M solution of KBr at 298 K. Calculate the equilibrium concentrations of Br^- and Cl^- ions.

$E^\circ_{\mathrm{Cl^-/AgCl/Ag}} = 0.222$ volt $\quad E^\circ_{\mathrm{Br^-/AgBr/Ag}} = 0.095$ volt

[**Ans.** $[\mathrm{Cl}^-] = 0.09929$ mol L^{-1}, $[\mathrm{Br}^-] = 0.00071$ mol L^{-1}]

[**Hint:** $\mathrm{AgCl} + \mathrm{Br}^- \rightleftharpoons \mathrm{AgBr} + \mathrm{Cl}^-$

At equilibrium $\quad (0.1 - x) \qquad x$

Apply $\quad \log K = \dfrac{E^\circ_{\text{cell}}}{0.0591}$

or $\quad \log \dfrac{x}{(0.1 - x)} = \dfrac{E^\circ_{\text{cell}}}{0.0591}$]

89. The emf of the cell $\underset{a\,=\,0.1}{\mathrm{Cu} \mid \mathrm{CuSO_4}} \parallel \underset{x}{\mathrm{CuSO_4}} \mid \mathrm{Cu}$ is -0.03 V at 25°C. Calculate the activity of copper sulphate solution in the right hand side electrode.

[**Ans.** 0.009616 mol L^{-1}]

[**Hint:** Apply $E = (E^\circ_{\mathrm{Cu}} - E^\circ_{\mathrm{Cu}}) - \dfrac{0.0591}{2} \log \dfrac{0.1}{x}$]

90. The cell, $\quad \mathrm{Pt} \mid \mathrm{H_2}\ (1\ \mathrm{atm}) \parallel \mathrm{H}^+\ (\mathrm{pH} = x) \mid$ normal calomel electrode, has an emf of 0.67 volt as 25°C. Calculate the pH of the solution. The oxidation potential of calomel electrode on the hydrogen scale is -0.28 volt.

[**Ans.** pH = 6.61]

91. The emf of the cell,

$$\mathrm{Ag} \mid \mathrm{AgI}, \mathrm{KI}\ (0.05\ M) \parallel \mathrm{AgNO_3}\ (0.05\ M) \mid \mathrm{Ag}$$

is 0.788 volt. Calculate the solubility product of AgI.

[**Ans.** 1.101×10^{-16}]

92. The standard reduction potential for $\mathrm{Cu}^{2+}/\mathrm{Cu}$ is + 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $\mathrm{Cu(OH)_2}$ is 1.0×10^{-19}.

[**Ans.** -0.22 V] **(IIT 1996)**

93. Calculate the potential of a cell in which H electrode is immersed in a solution of pH 3.5 and in a solution of pH 10.7.

[**Ans.** 0.4255 volt]

94. Calculate the emf of the cell,

$$\mathrm{Cl_2}\ (1\ \mathrm{atm}) \mid \mathrm{NaCl}\ (aq.) \mid \mathrm{Cl_2}\ (0.1\ \mathrm{atm})$$

[**Ans.** -0.0295 volt]

95. The standard free energy change for the reaction,

$$\mathrm{H_2}(g) + 2\mathrm{AgCl}(s) \longrightarrow 2\mathrm{Ag}(s) + 2\mathrm{H}^+(aq.) + 2\mathrm{Cl}^-(aq.)$$

is -10.26 kcal mol^{-1} at 25°C. A cell using the above reaction is operated at 25°C under $P_{\mathrm{H_2}} = 1$ atm, $[\mathrm{H}^+]$ and $[\mathrm{Cl}^-] = 0.1$. Calculate the emf of the cell.

[**Ans.** 0.340 volt]

96. For the reaction, $\mathrm{Fe}^{3+} + 3e^- \rightleftharpoons \mathrm{Fe}$. E° is -0.036 volt and the standard electrode potential for $\mathrm{Fe}^{3+} + e^- \rightleftharpoons \mathrm{Fe}^{2+}$ is 0.771 volt. Calculate the E° for $\mathrm{Fe}^{2+} + 2e^- \rightleftharpoons \mathrm{Fe}$.

[**Ans.** -0.4395 volt]

97. The standard reduction potential at 25°C of the reaction $2\mathrm{H_2O} + 2e^- \longrightarrow \mathrm{H_2} + 2\mathrm{OH}^-$ is -0.8277 volt. Calculate the equilibrium constant for the reaction,

$$2\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH}^- \text{ at } 25^\circ\mathrm{C}$$

[**Ans.** $\approx 10^{14}$]

[**Hint:**

$\mathrm{H_2O} + e^- \longrightarrow \frac{1}{2}\mathrm{H_2} + \mathrm{OH}^-$ (Cathode); $E^\circ = -0.8277$ volt

$\mathrm{H_2O} + \frac{1}{2}\mathrm{H_2} \longrightarrow \mathrm{H_3O^+} + e^-$ (Anode); $E^\circ = 0$

E° for the cell $= -0.8277$ volt

Apply now $\quad E^\circ = \dfrac{0.0591}{n} [\log K] \qquad (n = 1)$]

98. Calculate the emf of the following cell:

$$\mathrm{Pt}(\mathrm{H_2}\ 1\ \mathrm{atm}) \mid \mathrm{CH_3CH_2COOH}\ (0.15\ M) \parallel 0.01\ M\ \mathrm{NH_4OH} \mid \mathrm{H_2}\ (1\ \mathrm{atm})\ \mathrm{Pt}$$

K_a for $\mathrm{CH_3CH_2COOH} = 1.4 \times 10^{-5}$

K_b for $\mathrm{NH_4OH} = 1.8 \times 10^{-5}$

[**Ans.** -0.4603 volt]

[**Hint:** $[\mathrm{H}^+]$ in $\mathrm{CH_3CH_2COOH} = \sqrt{C \times K_a} = \sqrt{0.15 \times 1.4 \times 10^{-5}}$

$= 1.449 \times 10^{-3}$

$[\mathrm{OH}^-]$ in $\mathrm{NH_4OH} = \sqrt{C \times K_b} = \sqrt{0.01 \times 1.8 \times 10^{-5}} = 0.4242 \times 10^{-3}$

$$[\mathrm{H}^+] \text{ in } \mathrm{NH_4OH} = \frac{10^{-14}}{0.4242 \times 10^{-3}} = 2.3573 \times 10^{-11}$$

$$E_{\text{cell}} = 0.0591 \log \frac{[\mathrm{H}^+]_{\text{RHS}}}{[\mathrm{H}^+]_{\text{LHS}}}]$$

99. Calculate equilibrium constant for

$$\mathrm{I_2} + \mathrm{I}^- \rightleftharpoons \mathrm{I_3^-}$$

at 298 K from the following information:

$\mathrm{I_2}(aq.) + 2e^- \longrightarrow 2\mathrm{I}^-; \qquad E^\circ = 0.6197$ volt

$\mathrm{I_3^-} + 2e^- \longrightarrow 3\mathrm{I}^-; \qquad E^\circ = 0.5355$ volt

[**Ans.** 706.9]

[**Hint:** $\mathrm{I_2} + 2e^- \longrightarrow 2\mathrm{I}^-; \qquad E^\circ = 0.6197$ volt

$3\mathrm{I}^- \longrightarrow \mathrm{I_3^-} + 2e^-; \quad E^\circ = -0.5355$ volt

$\mathrm{I_2} + \mathrm{I}^- \rightleftharpoons \mathrm{I_3^-}; \qquad E^\circ = 0.6197 - 0.5355$

$= 0.0842$ volt

$$K = \text{antilog}\left[\frac{nE^\circ}{0.0591}\right] = \text{antilog}\left[\frac{2 \times 0.0842}{0.0591}\right] = 706.9]$$

100. A lead storage battery has initially 200 g of lead and 200 g of PbO_2, plus excess H_2SO_4. How long could this cell deliver a current of 10 amp, without recharging, if it was possible to operate it so that the reaction goes to completion?

[Ans. 4.48 hour]

101. $Zn(s) + 2AgCl(s) \rightleftharpoons ZnCl_2\ (0.555\ M) + 2Ag(s)$

$$E_{0^\circ C} = 1.015 \text{ volt} \left(\frac{dE}{dT}\right)_P = -4.02 \times 10^{-4} \text{ volt per degree.}$$

Find $\Delta G, \Delta S$.

[Ans. $\Delta G = -195.895$ kJ, $\Delta S = -18.55$ cal]

[Hint: We know that,

$$\Delta H = nF\left[T\left(\frac{dE}{dT}\right)_P - E\right]$$

$$= 2 \times 96500\,[-273 \times 4.02 \times 10^{-4} - 1.015]$$

$$= -217075.98 \text{ joule} = -217.075 \text{ kJ}$$

$$\Delta G = -nFE = -2 \times 96500 \times 1.015 = -195895 \text{ J}$$

$$= -195.895 \text{ kJ}$$

$$\Delta G = \Delta H - T\Delta S$$

$$-195.895 = -217.075 - 273 \times \Delta S$$

$$\Delta S = -0.07758 \text{ kJ} = -77.58 \text{ J} = -18.55 \text{ cal}]$$

102. Calculate the equilibrium constant for the reaction,

$$2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$$

The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for Fe^{3+}/Fe^{2+} and I_3^-/I^- couples. **(IIT 1998)**

[Ans. 6.26×10^7]

103. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as the per reaction,

$$Mn^{2+}(aq.) + 2H_2O \longrightarrow MnO_2 + 2H^+(aq.) + H_2$$

Passing a current of 27 A for 24 hours gives one kg of MnO_2. What is the value of current efficiency? Write the reactions taking place at the cathode and at the anode. **[IIT (May) 1997]**

[Hint: Apply $w = \dfrac{E \times i \times t}{96500}$

$$1000 = \frac{87 \times i \times 24 \times 60 \times 60}{2 \times 96500}$$

$$i = 25.6 \text{ ampere}$$

$$\text{Current efficiency} = \frac{25.6}{27.0} \times 100 = 94.8\%$$

Reactions:

Anode: $Mn^{2+} \longrightarrow Mn^{4+} + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$]

104. Calculate the number of kWh of electricity is necessary to produce 1 metric ton (1000 kg) of aluminium by Hall process in a cell operating at 15 V.

[Ans. 4.47×10^4 kWh]

105. What will be the value of Λ for a 0.001 M aqueous NH_3 solution?

$K_b = 1.6 \times 10^{-5}$ and $\Lambda_0 = 2.38 \times 10^{-2}$ ohm^{-1} m^2 mol^{-1}

[Ans. 2.998×10^{-3} ohm^{-1} cm^2 mol^{-1}]

[Hint: $K_b = C\alpha^2$

$$1.6 \times 10^{-5} = 0.001 \times \alpha^2$$

$$\alpha = 0.126$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty};$$

(Λ_m^c = molar conductance at concentration 'c' and Λ_m^∞ = molar conductance at infinite dilution)

$$0.126 = \frac{\Lambda_m^c}{2.38 \times 10^{-2}}$$

$$\Lambda_m^c = 2.998 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}]$$

106. A weak monobasic acid is 5% dissociated in 0.01 mol dm^{-3} solution. The limiting molar conductivity at infinite dilution is 4.00×10^{-2} ohm^{-1} m^2 mol^{-1}. Calculate the conductivity of a 0.05 mol dm^{-3} solution of the acid.

[Ans. 8.92×10^{-4} ohm^{-1} cm^2 mol^{-1}]

[Hint: Dissociation constant of acid $K_a = C\alpha^2$

$$= 0.01 \times (0.05)^2$$

$$= 2.5 \times 10^{-5}$$

$$K_a = C\alpha^2$$

$$2.5 \times 10^{-5} = 0.05 \times \alpha^2$$

$$\alpha = 0.0223$$

We know that, $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^\infty}$

$$0.0223 = \frac{\Lambda_m^c}{4 \times 10^{-2}}$$

$$\Lambda_m^c = 8.92 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}]$$

107. 1.05 g of a lead ore containing impurity of Ag was dissolved in quantity of HNO_3 and the volume was made 350 mL. A Ag electrode was dipped in the solution and E_{cell} of,

$$Pt(H_2) \mid H^+(1\ M) \parallel Ag^+ \mid Ag$$

was 0.503 V at 298 K. Calculate % of lead in the ore.

$$E^\circ_{Ag^+/Ag} = 0.80 \text{ V}$$

[Ans. 0.0339%]

[Hint: Anode $\frac{1}{2}H_2(g) \longrightarrow H^+(1\ M) + e^-$

Cathode $Ag^+(x) + e^- \longrightarrow Ag(s)$

$$\frac{1}{2}H_2(g) + Ag^+(x) \rightleftharpoons Ag(s) + H^+(1\ M) \qquad (n = 1)$$

$$E^\circ = 0.80 - 0 = 0.80 \text{ volt}$$

$$Q = \frac{[H^+]}{[Ag^+]} = \frac{1}{x}$$

$$E = E^\circ - \frac{0.0591}{n}\log_{10} Q$$

$$0.503 = 0.80 - \frac{0.0591}{1}\log_{10}\left(\frac{1}{x}\right)$$

$$x = 9.43 \times 10^{-6}\ M$$

Number of moles of Ag^+ in 350 mL

$$= \frac{MV}{1000} = \frac{9.43 \times 10^{-6} \times 350}{1000}$$

$$= 3.3 \times 10^{-6}$$

$$\text{Mass of Ag} = 3.3 \times 10^{-6} \times 108 = 3.56 \times 10^{-4}\ \text{g}$$

$$\%\ \text{Ag in the ore} = \frac{3.56 \times 10^{-4}}{1.05} \times 100 = 0.0339\%]$$

108. Calculate E° of the following half-cell reaction at 298 K:

$$Ag(NH_3)_2^+ + e^- \longrightarrow Ag + 2NH_3$$

$$Ag^+ + e^- \longrightarrow Ag; \qquad E^\circ_{Ag^+/Ag} = 0.80\ \text{V}$$

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3; \qquad K = 6 \times 10^{-8}$$

[**Ans.** 0.373 volt]

[**Hint:** Anode $Ag(s) \longrightarrow Ag^+ + e^-; \quad E^\circ = 0.80$ volt

Cathode $[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag(s) + 2NH_3; E^\circ = v$ volt

$$\underline{Ag(s) + [Ag(NH_3)_2]^+ \rightleftharpoons Ag(s) + Ag^+ + 2NH_3}$$

$$Q = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+} = 6 \times 10^{-8} \qquad (n = 1)$$

$$E^\circ_{cell} = (v - 0.80)$$

At equilibrium, $E = 0$

$$\therefore \qquad E = E^\circ - \frac{0.0591}{n} \log Q$$

$$0 = (v - 0.80) - \frac{0.0591}{1} \log (6 \times 10^{-8})$$

$$v = 0.373 \text{ volt}]$$

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. An electrolyte is a substance which:
(a) conducts electricity
(b) decomposes on heating
(c) is acidic in nature
(d) when dissolved in water, dissociates into ions

2. The theory of ionisation was presented by:
(a) Faraday (b) Arrhenius (c) Ostwald (d) Rutherford

3. Dissociation of an electrolyte in water into negative and positive ions is called:
(a) ionisation (b) electrolysis
(c) decomposition (d) hydrolysis

4. Degree of ionisation is equal to:
(a) total number of moles of the electrolyte present in solution
(b) total number of moles of the electrolyte dissociated into ions
(c) number of moles dissociated /total number of moles dissolved
(d) total number of moles dissolved/number of moles dissociated

5. Conductivity of aqueous solution of an electrolyte depends on:
(a) molecular mass of the electrolyte
(b) boiling point of solvent
(c) degree of ionisation
(d) volume of the solvent

6. Degree of ionisation does not depend on:
(a) nature of the solvent
(b) nature of the electrolyte
(c) dilution
(d) molecular mass of the electrolyte

7. Substances which give good conducting aqueous solution are called:
(a) weak electrolytes (b) strong electrolytes
(c) non-electrolytes (d) catalysts

8. The number of ions given by one molecule of $K_4Fe(CN)_6$ after complete dissociation is:
(a) 5 (b) 11 (c) 2 (d) 10

9. The amount of electricity required to produce one mole of copper from copper sulphate solution will be : **(VITEEE 2008)**
(a) 1 faraday (b) 2.33 faraday
(c) 2 faraday (d) 1.33 faraday

[**Hint :** $Cu^{2+} + 2e^- \longrightarrow Cu\ (s)$

1 mole copper requires 2 mole electron, *i.e.*, 2 faraday charge.]

10. The process in which chemical change occurs on passing electricity is termed:
(a) ionisation (b) neutralisation
(c) electrolysis (d) hydrolysis

11. Which of the following condition is correct for operation of electrolytic cell?
(a) $\Delta G = 0, E = 0$ (b) $\Delta G < 0, E > 0$
(c) $\Delta G > 0, E < 0$ (d) $\Delta G > 0, E > 0$

12. Which one is the correct equation that represents the first law of electrolysis?
(a) $mZ = ct$ (b) $m = cZt$ (c) $mc = Zt$ (d) $c = mZt$

13. When one coulomb of electricity is passed through an electrolytic solution, the mass deposited on the electrode is equal to:
(a) equivalent weight (b) molecular weight
(c) electrochemical equivalent (d) one gram

14. One faraday is equal to:
(a) 9650 coulomb (b) 10,000 coulomb
(c) 19640 coulomb (d) 96500 coulomb

15. When one faraday of electric current is passed, the mass deposited is equal to:
(a) one gram equivalent (b) one gram mole
(c) electrochemical equivalent (d) half gram equivalent

16. On passing one faraday of electricity through a dilute solution of an acid, the volume of hydrogen obtained at NTP is:
(a) 22400 mL (b) 1120 mL
(c) 2240 mL (d) 11200 mL

17. w g of copper is deposited in a copper voltameter when an electric current of 2 ampere is passed for 2 hours. If one ampere of electric current is passed for 4 hours in the same voltameter, copper deposited will be:
(a) w (b) $w/2$ (c) $w/4$ (d) $2w$

18. Copper sulphate solution is electrolysed between two platinum electrodes. A current is passed until 1.6 g of oxygen is liberated at anode. The amount of copper deposited at the cathode during the same period is:
(a) 6.36 g (b) 63.6 g (c) 12.7 g (d) 3.2 g

19. When electricity is passed through a solution of $AlCl_3$, 13.5 g of Al is discharged. The amount of charge passed is:
(a) 1.5 F (b) 0.5 F (c) 1.0 F (d) 2.0 F

20. When the same electric current is passed through the solution of different electrolytes in series, the amounts of elements deposited on the electrodes are in the ratio of their:
(a) atomic numbers (b) atomic masses
(c) specific gravities (d) equivalent masses

21. Faraday's laws of electrolysis are related to:
(a) atomic number of the cation
(b) atomic number of the anion
(c) equivalent mass of the electrolyte
(d) speed of the cation

22. The specific conductance of a 0.01 M solution of KCl is 0.0014 ohm^{-1} cm^{-1} at 25°C. Its equivalent conductance is:
(a) 14 (b) 140 (c) 1.4 (d) 0.14

23. The equivalent conductivity of 0.1 N CH_3COOH at 25°C is 80 and at infinite dilution 400 ohm^{-1}. The degree of dissociation of CH_3COOH is:
(a) 1 (b) 0.2 (c) 0.1 (d) 0.5

24. The number of electrons involved when one faraday of electricity is passed through an electrolytic solution is:
(a) 96500 (b) 8×10^6 (c) 12×10^{16} (d) 6×10^{23}

25. One faraday of charge was passed through the electrolytic cells placed in series containing solutions of Ag^+, Ni^{2+} and Cr^{3+} respectively. The amount of Ag (At. mass 108), Ni (At. mass 59) and Cr (At. mass 52) deposited will be:

	Ag	Ni	Cr
(a)	108 g	29.5 g	17.5 g
(b)	108 g	59.0 g	52.0 g
(c)	108 g	108.0 g	108.0 g
(d)	108 g	117.5 g	166.0 g

26. One faraday of electricity will liberate one gram mole of the metal from the solution of:
(a) $BaCl_2$ (b) $CuSO_4$
(c) $AlCl_3$ (d) NaCl

27. Strong electrolytes are those which:
(a) dissolve readily in water
(b) conduct electricity
(c) dissociate into ions even at high concentration
(d) dissociate into ions at high dilution

28. The extent of ionisation increases:
(a) with increase in concentration of the electrolyte
(b) on decreasing temperature of solution
(c) on addition of excess of water
(d) on stirring the solution vigorously

29. Molten sodium chloride conducts electricity due to the presence of:
(a) free electrons (b) free ions
(c) free molecules (d) free atoms of Na and Cl

30. When NaCl is dissolved in water, the sodium ion is:
(a) oxidised (b) reduced
(c) hydrolysed (d) hydrated

31. A solution of sodium sulphate in water is electrolysed using platinum electrodes. The products at cathode and anode are respectively:
(a) H_2, O_2 (b) O_2, H_2
(c) O_2, Na (d) O_2, SO_2

32. The electric conduction of a salt solution in water depends on the:
(a) shape of molecules (b) size of its molecules
(c) size of solvent molecules (d) extent of its ionisation

33. In electroplating, the article to be electroplated serves as:
(a) cathode (b) electrolyte
(c) anode (d) conductor

34. The amount of electricity that can deposit 108 g of silver from silver nitrate solution is: **(AFMC 1993)**
(a) 1 ampere (b) 1 coulomb
(c) 1 faraday (d) 2 ampere

35. A certain current liberated 0.504 g of hydrogen in 2 hours. How many grams of copper can be liberated by the same current flowing for the same time in $CuSO_4$ solution?
(a) 12.7 g (b) 15.9 g (c) 31.8 g (d) 63.5 g

36. If the specific resistance of a solution of concentration C g equivalent $litre^{-1}$ is R, then its equivalent conductance is:
(a) $\frac{100R}{C}$ (b) $\frac{RC}{1000}$ (c) $\frac{1000}{RC}$ (d) $\frac{C}{1000R}$

37. If the specific conductance and conductance of a solution are same, then its cell constant is equal to:
(a) 1 (b) 0 (c) 10 (d) 100

38. On increasing the dilution, the specific conductance: **(Jiwaji 1990)**
(a) increases (b) decreases
(c) remains constant (d) none of these

39. The distance between two electrodes of a cell is 2.5 cm and area of each electrode is 5 cm^2. The cell constant is: **(Jabalpur 1990)**
(a) 2 (b) 12.5 (c) 7.5 (d) 0.5

40. At 25°C, the molar conductances at infinite dilution for the strong electrolytes NaOH, NaCl and $BaCl_2$ are 248×10^{-4}, 126×10^{-4} and 280×10^{-4} Sm^2 mol^{-1} respectively. $\Lambda^\circ_m Ba(OH)_2$ in S m^2 mol^{-1}: **(EAMCET 2009)**
(a) 52.4×10^{-4} (b) 524×10^{-4}
(c) 402×10^{-4} (d) 262×10^{-4}

[**Hint :** $\Lambda^\circ_m Ba(OH)_2 = \Lambda^\circ_m BaCl_2 + 2\Lambda^\circ_m NaOH - 2\Lambda^\circ_m NaCl$
$= 280 \times 10^{-4} + 2 \times 248 \times 10^{-4} - 2 \times 126 \times 10^{-4}$
$= 524 \times 10^{-4} S\ m^2\ mol^{-1}$]

41. The electrochemical cell stops working after some time because : **(VITEEE 2008)**
(a) electrode potential of both the electrodes becomes zero
(b) electrode potential of both the electrodes becomes equal
(c) one of the electrodes is eaten away
(d) the cell reaction gets reversed

42. Which reaction will take place at cathode when fused calcium chloride is electrolysed?
(a) $Ca^{2+} + 2e^- \longrightarrow Ca$ (b) $Cl^- \longrightarrow Cl + e^-$
(c) $Ca^{2+} - 2e^- \longrightarrow Ca$ (d) $Cl^- - e^- \longrightarrow Cl$

43. In electrolysis oxidation takes place at:
(a) both the electrodes (b) cathode
(c) anode (d) in the solution

44. The equation representing the process by which standard reduction potential of zinc can be defined is:
(a) $Zn^{2+}(s) + 2e^- \longrightarrow Zn$
(b) $Zn(g) \longrightarrow Zn^{2+}(g) + 2e^-$
(c) $Zn^{2+}(g) + 2e^- \longrightarrow Zn$
(d) $Zn^{2+}(aq.) + 2e^- \longrightarrow Zn(s)$

45. The measured potential for,

$$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$$

does not depend upon:
(a) raising the temperature
(b) increasing the concentration of Mg^{2+} ions
(c) making the magnesium plate bigger
(d) purity of magnesium plate

46. All cells do not contain:
(a) an anode (b) a cathode
(c) ions (d) a porous partition

47. When lead accumulator is charged, it is:
(a) an electrolytic cell (b) a galvanic cell
(c) a Daniell cell (d) none of these

48. The standard electrode potentials for the reactions,

$$Ag^+(aq.) + e^- \longrightarrow Ag(s)$$
$$Sn^{2+}(aq.) + 2e^- \longrightarrow Sn(s)$$

at 25°C are 0.80 volt and – 0.14 volt respectively. The emf of the cell,

$$Sn \mid Sn^{2+}(1\,M) \parallel Ag^+(1\,M) \mid Ag$$

is:
(a) 0.66 volt (b) 0.80 volt (c) 1.08 volt (d) 0.94 volt

49. The cathodic reaction in electrolysis of dilute H_2SO_4 with platinum electrode is:
(a) oxidation
(b) reduction
(c) both oxidation and reduction
(d) neutralization

50. Strongest reducing agent is:
(a) K (b) Mg (c) Al (d) I

51. The metal oxide which decomposes on heating, is:
(a) ZnO (b) HgO (c) Al_2O_3 (d) CuO

52. The reaction, $\frac{1}{2}H_2(g) + AgCl(s) = H^+(aq.) + Cl^-(aq.) + Ag(s)$ occurs in the galvanic cell: **(AFMC 2009)**
(a) $Ag \mid AgCl(s) \mid KCl\ (soln.) \parallel AgNO_3\ (soln.) \mid Ag$
(b) $Pt \mid H_2(g) \mid HCl\ (soln.) \parallel AgNO_3\ (soln.) \mid Ag$
(c) $Pt \mid H_2(g) \mid HCl\ (soln.) \parallel AgCl(s) \mid Ag$
(d) $Pt \mid H_2(g) \mid KCl\ (soln.) \parallel AgCl(s) \mid Ag$

53. The standard oxidation potentials, $E°$, for the half reactions are as,

$Zn \longrightarrow Zn^{2+} + 2e^-$; $E° = +0.76$ volt
$Fe \longrightarrow Fe^{2+} + 2e^-$; $E° = +0.41$ volt

The emf of the cell, $Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$ is: **[CET (Karnataka) 2009]**
(a) + 0.35 volt (b) – 0.35 volt
(c) +1.17 volt (d) –1.17 volt

54. The standard reduction potentials at 25°C for the following half reactions are given against each;

$Zn^{2+}(aq.) + 2e^- \rightleftharpoons Zn(s)$; – 0.762
$Cr^{3+}(aq.) + 3e^- \rightleftharpoons Cr(s)$; – 0.740
$2H^+ + 2e^- \rightleftharpoons H_2(g)$; 0.00
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$; 0.77

Which is the strongest reducing agent? **(VITEEE 2007)**
(a) Zn (b) Cr
(c) $H_2(g)$ (d) $Fe^{2+}(aq.)$

55. Hydrogen gas will not reduce heated:
(a) cupric oxide (b) ferric oxide
(c) stannic oxide (d) aluminium oxide

56. A solution containing one mole per litre of each $Cu(NO_3)_2$; $AgNO_3$; $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The values of standard electrode potentials (reduction potentials) are $Ag/Ag^+ = 0.80$ volt, $2Hg/Hg_2^{2+} = 0.79$ volt, $Cu/Cu^{2+} = +0.24$ volt, $Mg/Mg^{2+} = -2.37$ volt. With increasing voltage, the sequence of deposition of metals on the cathode will be: **[PMT (Kerala) 2004]**
(a) Ag, Hg, Cu (b) Cu, Hg, Ag
(c) Ag, Hg, Cu, Mg (d) Mg, Cu, Hg, Ag

57. Four colourless salt solutions are placed in separate test tubes and a strip of copper is dipped in each. Which solution finally turns blue?
(a) $Pb(NO_3)_2$ (b) $AgNO_3$ (c) $Zn(NO_3)_2$ (d) $Cd(NO_3)_2$

58. Red hot carbon will remove oxygen from the oxide *XO* and *YO* but not from *ZO*. *Y* will remove oxygen from *XO*. Use this evidence to deduce the order of activity of the three metals *X*, *Y* and *Z* putting the most active first:
(a) *XYZ* (b) *ZYX* (c) *YXZ* (d) *ZXY*

59. Which of the following metals does not give the following reaction?

$$M + \text{Water} \longrightarrow \text{Oxide or hydroxide} + H_2$$

(a) Iron (b) Sodium (c) Mercury (d) Magnesium

60. Which is the best reducing agent?

(a) F^- (b) Cl^- (c) Br^- (d) I^-

61. If a spoon of copper metal is placed in a solution of ferrous sulphate:

(a) Cu will precipitate out
(b) iron will precipitate
(c) Cu and Fe will precipitate
(d) no reaction will take place

62. Among Na, Hg, S, Pt and graphite, which can be used as electrodes in electrolytic cells having aqueous solutions?

(a) Hg and Pt (b) Hg, Pt and graphite
(c) Na and S (d) Na, Hg and S

63. The most reactive metal among the following is:

(a) Al (b) Ni (c) Pb (d) Cu

64. Which of the following metals is most readily corroded in moist air?

(a) Copper (b) Iron
(c) Silver (d) Nickel

65. Which one will liberate Br_2 from KBr?

(a) HI (b) I_2 (c) Cl_2 (d) SO_2

66. Which one of the following is not the correct representation?

(a) E°_{cell} = Red. pot. of cathode + Oxid. pot. of anode
(b) E°_{cell} = Red. pot. of cathode − Oxid. pot. of anode
(c) E°_{cell} = Red. pot. of cathode − Red. pot. of anode
(d) E°_{cell} = Oxid. pot. of cathode + Oxid. pot. of anode

67. Which of the following represents the potential of silver wire dipped into 0.1 M $AgNO_3$ solution at 25°C ?

(a) $E^\circ_{\text{red.}}$ (b) $(E^\circ_{\text{red.}} + 0.059)$
(c) $(E^\circ_{\text{oxid.}} - 0.059)$ (d) $(E^\circ_{\text{red.}} - 0.059)$

68. If the solution of the $CuSO_4$ in which copper rod is immersed is diluted to 10 times, the electrode potential:

(a) increases by 0.030 volt (b) decreases by 0.030 volt
(c) increases by 0.059 volt (d) decreases by 0.0059 volt

69. A solution of Cu(II) sulphate is reacted with KCl and KI. In which case will the Cu^{2+} be reduced to Cu^+?

(a) In both the cases
(b) When reacted with KCl
(c) When reacted with KI
(d) In both the cases but in presence of H^+

70. From the electrochemical series, it can be concluded that:

(a) Zn^{2+} will liberate H_2 from 1 M HCl
(b) Ag metal reacts spontaneously with Zn^{2+}
(c) Zn metal will liberate H_2 from 1 M HCl
(d) Ag metal will liberate H_2 from 1 M HCl

71. The potential of a hydrogen electrode at pH = 1 is:

(a) 0.059 volt (b) 0 volt
(c) −0.059 volt (d) 0.59 volt

72. Which is not true for a standard hydrogen electrode?

(a) The hydrogen ion concentration is 1 M
(b) Temperature is 25°C
(c) Pressure of hydrogen is 1 atmosphere
(d) It contains a metallic conductor which does not absorb hydrogen

73. The electrode potential becomes equal to standard electrode potential when reactants and products ratio is:

(a) equal to 1 (b) greater than 1
(c) less than 1 (d) none of these

74. For the half-cell reaction,

$$Au^{3+} + 3e^- \longrightarrow Au$$

the value of n used in Nernst equation is:

(a) 3 (b) 2 (c) 1 (d) 3 × 96500

75. When a piece of sodium metal is dropped in water, a reaction takes place to yield hydrogen because:

(a) sodium loses electrons
(b) sodium acts as an oxidising agent
(c) water loses electrons
(d) water acts as a reducing agent

76. Which one is the wrong statement about electrochemical series?

(a) Active metals have negative reduction potentials
(b) Active non-metals have positive reduction potentials
(c) Metals above hydrogen liberate hydrogen from acids
(d) Metals below hydrogen are strong reducing agents

77. The reduction potential values are given below:

$Al^{3+}/Al = -1.67$ volt, $Mg^{2+}/Mg = -2.34$ volt,
$Cu^{2+}/Cu = +0.34$ volt, $I_2/2I^- = +0.53$ volt.

Which one is the best reducing agent?

(a) Al (b) Mg
(c) Cu (d) I_2

78. From the values given in question No. 77, which one is the best oxidising agent?

(a) Al (b) Mg (c) I_2 (d) Cu

79. When iron is rusted, it is:

(a) reduced (b) oxidised
(c) evaporated (d) decomposed

80. Galvanization of iron denotes coating with:

(a) Cu (b) Sn (c) Zn (d) Al

81. The standard electrode potentials of four elements A, B, C and D are −3.05, 1.66, −0.40 and 0.80 volt. The highest chemical activity will be shown by:

(a) A (b) B (c) C (d) D

82. Which of the following methods does not liberate hydrogen?

(a) Zn + H_2SO_4 (dil.) (b) Mg + H_2SO_4 (dil.)
(c) Cu + H_2SO_4 (dil.) (d) Zn + HCl (dil.)

83. A depolarizer used in dry cell is:

(a) ammonium chloride (b) manganese dioxide
(c) potassium oxide (d) sodium phosphate

84. The oxide which can be reduced by hydrogen is:

(a) Na_2O (b) CaO (c) K_2O (d) CuO

85. The reference electrode is made from which of the following?

(a) $ZnCl_2$ (b) $CuSO_4$ (c) Hg_2Cl_2 (d) $HgCl_2$

86. Given, standard electrode potentials;

$$Fe^{3+} + 3e^- \longrightarrow Fe; \qquad E^\circ = -0.036 \text{ volt}$$
$$Fe^{2+} + 2e^- \longrightarrow Fe; \qquad E^\circ = -0.440 \text{ volt}$$

The standard electrode potential E° for $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ is: **[AMU (Medical) 2007; AIEEE 2009]**

(a) -0.476 volt (b) -0.404 volt
(c) 0.440 volt (d) -0.772 volt

[**Hint:** Apply $\Delta G = -nFE$

$Fe^{2+} + 2e^- \longrightarrow Fe \quad \Delta G = -2 \times F \times (-0.440 \text{ V}) = 0.88F$ ...(i)

$Fe^{3+} + 3e^- \longrightarrow Fe \quad \Delta G = -3 \times F \times (-0.036) = 0.108F$ ...(ii)

Subtracting eq. (i) from eq. (ii),

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}; \quad \Delta G = 0.108F - 0.880F = -0.772F$$

$$E^\circ \text{ for the reaction} = -\frac{\Delta G}{nF} = -\frac{(-0.772F)}{1 \times F} = 0.772 \text{ volt}]$$

87. K, Ca and Li metals may be arranged in the decreasing order of their standard electrode potentials as:

(a) K, Ca and Li (b) Li, K and Ca
(c) Li, Ca and K (d) Ca, Li and K

88. In a galvanic cell energy changes occur like:

(a) chemical energy ⟶ electrical energy
(b) electrical energy ⟶ chemical energy
(c) chemical energy ⟶ internal energy
(d) internal energy ⟶ electrical energy

89. The reaction is spontaneous if the cell potential is:

(a) positive (b) negative
(c) zero (d) infinite

90. Is the reaction, $2Al + 3Fe^{2+} \rightleftharpoons 2Al^{3+} + 2Fe$ possible?

(a) No, because standard oxidation potential of Al < Fe
(b) Yes, because standard oxidation potential of Al > Fe
(c) Cannot be predicted
(d) Yes, because aluminium is a strong oxidising agent

91. In an experimental set-up for the measurement of emf of a half-cell using a reference electrode and a salt bridge, when the salt bridge is removed, the voltage:

(a) does not change (b) increases to maximum
(c) decreases half the value (d) drops to zero

92. More electronegative elements have:

(a) negative reduction potential
(b) tendency to lose electrons
(c) positive reduction potential
(d) positive oxidation potential

93. Which metal will be deposited in the galvanic cell?

$$Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$$

(a) Cu (b) Ag
(c) Both (d) None of these

94. In the cell $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$, the negative electrode is:

(a) Cu (b) Cu^{2+} (c) Zn (d) Zn^{2+}

95. Which of the following gains electrons more easily?

(a) Na^+ (b) Zn^{2+}
(c) Al^{3+} (d) H^+

96. The potential of a hydrogen electrode at pH 10 is:

(a) 0.51 volt (b) 0 volt
(c) -0.591 volt (d) 0.059 volt

97. The emf of the cell,

$$Ni \mid Ni^{2+} (1.0\,M) \parallel Ag^+ (1.0\,M) \mid Ag$$

(E° for $Ni^{2+}/Ni = -0.25$ volt, E° for $Ag^+/Ag = 0.80$ volt) is given by:

(a) $-0.25 + 0.80 = 0.55$ volt
(b) $-0.25 - (+0.80) = -1.05$ volt
(c) $0 + 0.80 - (-0.25) = +1.05$ volt
(d) $-0.80 - (-0.25) = -0.55$ volt

98. The reaction for the cell,

$$Zn \mid Zn^{2+} (1.0\,M) \parallel Cd^{2+} (1.0\,M) \mid Cd$$

is:

(a) $Cd \longrightarrow Cd^{2+} + 2e^-$
(b) $Zn^{2+} \longrightarrow Zn - 2e^-$
(c) $Cd + Zn^{2+} \longrightarrow Cd^{2+} + Zn$
(d) $Zn + Cd^{2+} \longrightarrow Cd + Zn^{2+}$

99. The position of some metals in the electrochemical series in decreasing electropositive character is given as Mg > Al > Zn > Cu > Ag. What will happen if a copper spoon is used to stir a solution of aluminium nitrate?

(a) The spoon will get coated with aluminium
(b) An alloy of aluminium and copper is formed
(c) The solution becomes blue
(d) There is no reaction

100. The half-cell reaction is the one that:

(a) takes place at one electrode
(b) consumes half a unit of electricity
(c) involves half a mole of electrolyte
(d) goes half way to completion

Which Nernst equation is true to find out the potential of non-standard electrochemical cell from the following ?

$$Fe(s) \mid Fe^{2+} (xM) \parallel I^- (aq.) \mid I_2(s)\,(Pt)$$

[CET (Gujarat) 2008]

(a) $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.592}{n} \log_{10} [Fe^{2+}][I^-]^2$

(b) $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0592}{n} \log_{10} [Fe^{2+}][I^-]^2$

(c) $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0592}{n} \log_{10} [Fe^{2+}][I^-]$

(d) $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0592}{nF} \log_{10} \dfrac{[Fe^{2+}][I^-]^2}{[Fe][I_2]}$

102. During the electrolysis of fused NaCl, which reaction occurs at anode?

(a) Chloride ions are oxidised
(b) Sodium ions are oxidised
(c) Chloride ions are reduced
(d) Sodium ions are reduced

103. $E^\circ(Ni^{2+}/Ni) = -0.25$ volt, $E^\circ(Au^{3+}/Au) = 1.50$ volt. The emf of the voltaic cell,

$$Ni \mid Ni^{2+}\,(1.0\,M) \parallel Au^{3+}\,(1.0\,M) \mid Au$$

is:

(a) 1.25 volt (b) −1.75 volt (c) 1.75 volt (d) 4.0 volt

104. Which of the following does not occur at cathode?

(a) $Ag^+ \longrightarrow Ag - e^-$ (b) $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

(c) $Cu^{2+} + 2e^- \longrightarrow Cu$ (d) $2H^+ \longrightarrow H_2 - 2e^-$

105. The strong oxidising agent has:

(a) high value of reduction potential

(b) high value of oxidation potential

(c) low value of reduction potential

(d) high tendency to lose electrons

106. The passage of electricity in the Daniell cell when Zn and Cu electrodes are connected is from:

(a) Cu to Zn in the cell

(b) Cu to Zn outside the cell

(c) Zn to Cu outside the cell

(d) Zn to Cu in the cell

107. Which of the following can be used as an electrode?

(a) A glass rod (b) A wooden stick

(c) A nail (d) A soda straw

108. H^+ ions are reduced at platinum electrode prior to:

(a) Zn^{2+} (b) Cu^{2+} (c) Ag^+ (d) I_2

109. Which of the following statements is wrong?

(a) F_2 is the strongest oxidising agent as its reduction potential is high

(b) Li is the weakest reducing agent as its reduction potential is low

(c) Li is the strongest reducing agent as its oxidation potential is high

(d) F^- ion does not show reducing property

110. Out of Cu, Ag, Fe and Zn, the metal which can displace all others from their salt solution is:

(a) Ag (b) Cu (c) Fe (d) Zn

111. When the electric current is passed through a cell having an electrolyte, the positive ions move towards cathode and negative ions towards the anode. If the cathode is pulled out of the solution:

(a) the positive and negative ions will move towards anode

(b) the positive ions will start moving towards the anode while negative ions will stop moving

(c) the negative ions will continue to move towards anode while positive ions will stop moving

(d) the positive and negative ions will start moving randomly

112. The oxidation potentials of Zn, Cu, Ag, H_2 and Ni are 0.76, − 0.34, − 0.80, 0 and 0.25 volt respectively. Which of the following reactions will provide maximum voltage? **[PET (Kerala) 2007]**

(a) $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$

(b) $Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$

(c) $H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu$

(d) $H_2 + Ni^{2+} \longrightarrow 2H^+ + Ni$

(e) $Zn(s) + 2H^+(aq.) \rightleftharpoons Zn^{2+}(aq.) + H_2(g)$

113. Which one of the following will increase the voltage of the cell?

$$Sn + 2Ag^+ \longrightarrow Sn^{2+} + 2Ag$$

(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

114. A chemist wants to produce $Cl_2(g)$ from molten NaCl. How many grams could be produced if he uses a steady current of 2 ampere for 2.5 minutes?

(a) 3.55 g (b) 1.775 g (c) 0.110 g (d) 0.1775 g

115. In the electrolysis of $CuCl_2$ solution, the mass of cathode increased by 6.4 g. What occurred at copper anode?

(a) 0.224 litre of Cl_2 was liberated

(b) 1.12 litre of oxygen was liberated

(c) 0.05 mole Cu^{2+} passed into the solution

(d) 0.1 mole Cu^{2+} passed into the solution

116. Consider the reaction,

$$Cl_2(g) + 2Br^-(aq.) \longrightarrow 2Cl^-(aq.) + Br_2$$

The emf of the cell, when $[Cl^-] = [Br_2] = [Br^-] = 0.01\,M$ and Cl_2 gas is at 1 atm pressure, will be: (E° for the above reaction is 0.29 volt)

(a) 0.54 volt (b) 0.35 volt (c) 0.24 volt (d) − 0.29 volt

117. If λ_c°, λ_a° and λ° refer to equivalent conductance of a cation, an anion and equivalent conductance of the salt at infinite dilution, then according to Kohlrausch's law:

(a) $\lambda^\circ = \lambda_c^\circ + \lambda_a^\circ$ (b) $\lambda^\circ = \lambda_c^\circ - \lambda_a^\circ$

(c) $\lambda^\circ = \lambda_a^\circ - \lambda_c^\circ$ (d) $\lambda^\circ = \lambda_c^\circ / \lambda_a^\circ$

118. How much silver will be obtained by that quantity of current which displaces 5.6 litre of H_2? **[PMT (Pb.) 1993]**

(a) 54 g (b) 13.5 g (c) 20 g (d) 108 g

119. The specific conductance of a salt of 0.01 M concentration is 1.061×10^{-4}. Molar conductance of the same solution will be: **[PMT (Pb.) 1993]**

(a) 1.061×10^{-4} (b) 1.061 (c) 10.61 (d) 106.1

120. What is the number of coulombs required for the conversion of one mole of MnO_4^- to one mole of Mn^{2+}? **[MBBS (Orissa) 1993]**

(a) 5×96500 (b) 3×96500 (c) 96500 (d) 9650

121. Which of the following solutions of NaCl will have the highest specific conductance?

(a) 0.001 N (b) 0.1 N (c) 0.01 N (d) 1.0 N

122. The equivalent conductance of a 1 N solution of an electrolyte is nearly:

(a) 10^3 times its specific conductance

(b) 10^{-3} times its specific conductance

(c) 100 times its specific conductance

(d) the same as its specific conductance

123. Zinc is coated over iron to prevent rusting of iron because:

(a) it is cheaper than iron (b) $E^\circ_{(Zn^{2+}/Zn)} = E^\circ_{(Fe^{2+}/Fe)}$

(c) $E^\circ_{(Zn^{2+}/Zn)} < E^\circ_{(Fe^{2+}/Fe)}$ (d) $E^\circ_{(Zn^{2+}/Zn)} > E^\circ_{(Fe^{2+}/Fe)}$

124. Free energy change (ΔG) is related to the emf of the cell (E)

(a) $E = -nF\,\Delta G$ (b) $\Delta G = -nFE$

(c) $\Delta G = -\frac{RT}{n} F \log E$ (d) $\Delta G = -\frac{nF}{RT} \log E$

125. The standard reduction potentials at 25°C of Li^+/Li, Ba^{2+}/Ba, Na^+/Na and Mg^{2+}/Mg are – 3.05, – 2.73, – 2.71 and – 2.37 volt respectively. Which one of the following is the strongest oxidising agent?

(a) Na^+ (b) Li^+

(c) Ba^{2+} (d) Mg^{2+}

126. Three faradays of electricity was passed through an aqueous solution of iron(II) bromide. The mass of iron metal (At. mass 56) deposited at the cathode is: **(EAMCET 1991)**

(a) 56 g (b) 84 g (c) 112 g (d) 168 g

127. The standard electrode potentials of Zn, Ag and Cu are – 0.76, 0.80 and 0.34 volt respectively; then:

(a) Ag can oxidise Zn and Cu

(b) Ag can reduce Zn^{2+} and Cu^{2+}

(c) Zn can reduce Ag^+ and Cu^{2+}

(d) Cu can oxidise Zn and Ag

128. The standard emf for the cell reaction,

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

is 1.10 volt at 25°C. The emf for the cell reaction when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solutions are used at 25°C is: **(MLNR 1994)**

(a) 1.10 volt (b) 0.110 volt

(c) – 1.10 volt (d) – 0.110 volt

129. Three mole of electrons are passed through three solutions in succession containing $AgNO_3$, $CuSO_4$ and $AuCl_3$ respectively. The ratio of amounts of cations reduced at cathode will be:

(a) 1 : 2 : 3 (b) 2 : 1 : 3

(c) 3 : 2 : 1 (d) 6 : 3 : 2

130. In the electrolysis of an aqueous solution of NaOH, 2.8 litre of oxygen gas at NTP was liberated at anode. How much of hydrogen gas was liberated at cathode?

(a) 2.8 litre (b) 5.6 litre

(c) 11.2 litre (d) 22.4 litre

131. Two half-cells have potentials – 0.44 and 0.799 volt respectively. These two are coupled to make a galvanic cell. Which of the following will be true?

(a) Electrode of half-cell potential – 0.44 V will act as anode

(b) Electrode of half-cell potential – 0.44 V will act as cathode

(c) Electrode of half-cell potential 0.799 V will act as anode

(d) Electrode of half-cell potential – 0.44 V will act as a positive terminal

132. When a lead storage battery is charged:

(a) PbO_2 dissolves

(b) the lead electrode becomes coated with lead sulphate

(c) sulphuric acid is regenerated

(d) the amount of acid decreases

133. An example of a simple fuel cell is:

(a) lead storage battery (b) $H_2 — O_2$ cell

(c) Daniell cell (d) Lechlanche cell

134. For the cell reaction,

$$Mg(s) + 2Ag^+(aq.) \rightleftharpoons Mg^{2+}(aq.) + 2Ag(s).$$

E°_{cell} is +3.17 V at 298 K. The value of E_{cell}, ΔG° and Q at Ag^+ and Mg^{2+} concentrations of 0.001 M and 0.02 M respectively are: **(ISAT 2010)**

(a) 3.04 V, –605.8 kJ mol^{-1}, 20000

(b) 3.04 V, 611.8 kJ mol^{-1}, 20000

(c) 3.13 V, –604 kJ mol^{-1}, 20

(d) 3.04 V, –611.8 kJ, 20000

[**Hint:** $E^\circ = +3.17$ V, $n = 2$

$$Q = \frac{[Mg^{2+}]}{[Ag^+]^2} = \frac{0.02}{[0.001]^2} = 20000$$

$$\Delta G^\circ = -nFE^\circ$$
$$= -2 \times 96500 \times 3.17$$
$$= -611.8\text{ kJ}$$
$$E = E^\circ - \frac{0.059}{n}\log_{10} Q$$
$$= 3.17 - \frac{0.059}{2}\log(20000)$$
$$= +3.04\text{ V}$$]

135. Which of the following statements is correct?

(a) The temperature coefficient of electrolytic conductance is positive

(b) The temperature coefficient of electrolytic resistance is negative

(c) The resistance of an electrolyte decreases with decreasing temperature

(d) The resistance of electrolytic conductors is independent of temperature

136. Kohlrausch's law states that at: **[CBSE (PMT) 2008]**

(a) infinite dilution, each ion makes definite contribution to conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte

(b) infinite dilution, each ion makes definite contribution to the equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte

(c) finite dilution, each ion makes definite contribution to the equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte

(d) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte

137. Which one of the following conditions will increase the voltage of the cell represented by the equation?

$Cu(s) + 2Ag^+(aq.) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$ **(KCET 2006)**

(a) Increase in the dimension of Cu electrode

(b) Increase in the dimension of Ag electrode

(c) Increase in the concentration of Cu^{2+} ion

(d) Increase in the concentration of Ag^+ ion

[**Hint:** Cell voltage will increase, either by increasing the concentration of Cu^{2+} ion or by decreasing the concentration of Ag^+.

$$Q = \frac{[Cu^{2+}]}{[Ag^{+}]}$$

Lesser is the value of Q, greater is the cell voltage.]

138. Which of the following reactions occurs at cathode during charging of storage battery? **(MGIMS 2007)**

(a) $Pb^{2+} + 2e^{-} \longrightarrow Pb$

(b) $Pb \longrightarrow Pb^{2+} + 2e^{-}$

(c) $Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

(d) $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^{+} + SO_2^{2-} + 2e^{-}$

139. The amount of silver deposited on passing 2F of electricity through aqueous solution of $AgNO_3$ is: **(MHT-CET 2007)**

(a) 54 g (b) 108 g (c) 216 g (d) 324 g

140. Statements:

(i) Unit of specific conductivity is $ohm^{-1}\ cm^{-1}$.

(ii) Specific conductivity of strong electrolytes decreases on dilution.

(iii) The amount of an ion discharged during electrolysis does not depend upon resistance.

(iv) The unit of electrochemical equivalence is g/coulomb.

(a) All are correct

(b) All are wrong

(c) Only (i), (ii) and (iv) are correct

(d) Only (ii), (iii) and (iv) are correct

141. Which among the following expressions is/are not correct?

(a) $\mu^{\infty} = \gamma_{+}\lambda_{+}^{\infty} + \gamma_{-}\lambda_{-}^{\infty}$

(b) $\lambda^{\infty} = \frac{1}{n^{+}}\lambda_{+}^{\infty} + \frac{1}{n^{-}}\lambda_{-}^{\infty}$

(c) $\lambda_{\text{cation}}^{\infty} = \mu_{\text{cation}}^{\infty} \times \text{faraday}$

(d) $\lambda_{\text{anion}}^{\infty} = \mu_{\text{cation}}^{\infty} \times \text{faraday}$

142. For the electrochemical cell, $M \mid M^{+} \parallel X^{-} \mid X$, $E^{\circ}_{M^{+}/M} = 0.44$ V and $E^{\circ}_{X/X^{-}} = 0.33$ V. From this data we can deduce that: **[IIT (Screening) 2000]**

(a) $M + X \longrightarrow M^{+} + X^{-}$ is the spontaneous reaction

(b) $M^{+} + X^{-} \longrightarrow M + X$ is the spontaneous reaction

(c) $E_{\text{cell}} = 0.77$ V

(d) $E_{\text{cell}} = -0.77$ V

143. For the cell reaction,

$$\underset{(C_1)}{Cu^{2+}(aq.)} + Zn(s) \longrightarrow \underset{(C_2)}{Zn^{2+}(aq.)} + Cu(s)$$

the change in free energy (ΔG) at a given temperature is a function of: **(CBSE 1998)**

(a) $\ln C_1$ (b) $\ln\left(\frac{C_2}{C_1}\right)$

(c) $\ln(C_1 + C_2)$ (d) $\ln C_2$

144. The standard reduction potential values of three metallic cations X, Y and Z are 0.52, –3.03 and –1.18 V respectively. The order of reducing powers of the corresponding metals is: **(IIT 1998)**

(a) $Y > Z > X$ (b) $X > Y > Z$

(c) $Z > Y > X$ (d) $Z > X > Y$

145. A gas 'X' at 1 atm is bubbled through a solution containing a mixture of 1 M Y^{-} and 1 M Z^{-} at 25°C. If the reduction potential of $Z > Y > X$, then: **(IIT 1999)**

(a) Y will oxidise X and not Z

(b) Y will oxidise Z and not X

(c) Y will oxidise both Z and X

(d) Y will reduce both X and Z

146. The number of coulombs required for the deposition of 107.87 g of silver is: **[PMT (MP) 1998]**

(a) 48250 (b) 10000 (c) 96500 (d) 19300

147. At 25°C, the standard emf of a cell having reaction involving two electrons change is found to be 0.295 V. The equilibrium constant of the reaction is: **(IIT 1999)**

(a) 29.5×10^{-2} (b) 10

(c) 1×10^{10} (d) 29.5×10^{10}

148. The emf of the cell in which the following reaction,

$$Zn(s) + Ni^{2+}(0.1\ M) \longrightarrow Zn^{2+}(1.0\ M) + Ni(s)$$

occurs, is found to 0.5105 V at 298 K. The standard emf of the cell is: **(IIT 1998)**

(a) 0.4810 V (b) 0.5696 V

(c) – 0.5105 V (d) 0.5400 V

[Hint: $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{2}\log\frac{1}{0.1}$]

149. The molar conductances of NaCl, HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and 91 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively. The molar conductance of CH_3COOH at infinite dilution is: **[CBSE 1997; DCE 2009]**

(a) 201.28 $ohm^{-1}\ cm^2\ mol^{-1}$ (b) 390.71 $ohm^{-1}\ cm^2\ mol^{-1}$

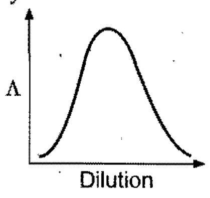
(c) 698.28 $ohm^{-1}\ cm^2\ mol^{-1}$ (d) 540.48 $ohm^{-1}\ cm^2\ mol^{-1}$

150. The specific conductance of a 0.1 N KCl solution at 23°C is 0.0112 $ohm^{-1}\ cm^{-1}$. The resistance of the cell containing the solution at the same temperature was found to be 55 ohm. The cell constant will be: **(CBSE 1999)**

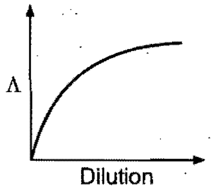
(a) 0.142 cm^{-1} (b) 0.918 cm^{-1}

(c) 1.12 cm^{-1} (d) 0.616 cm^{-1}

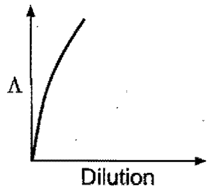
151. Which of the following plots represents correctly variation of equivalent conductance (Λ) with dilution for a strong electrolyte?



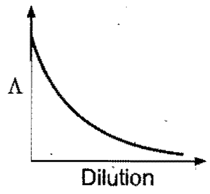
(a)



(b)



(c)



(d)

152. The standard reduction potential for Cu^{2+}/Cu and Cu^{2+}/Cu^{+} are 0.337 V and 0.153 V respectively. The standard electrode potential of Cu^{+}/Cu half cell is: **[AMU (PMT) 2009; CBSE (PMT) 2009]**

(a) 0.184 V (b) 0.827 V
(c) 0.521 V (d) 0.490 V

153. Solubility of a sparingly soluble salt S, specific conductance κ and the equivalent conductance Λ_0 are related as: **[IAS (Pre.) 1997]**

(a) $S = \frac{1000}{\kappa}\Lambda_0$ (b) $S = \kappa\Lambda_0$
(c) $S = \frac{\kappa}{1000\Lambda_0}$ (d) $S = \frac{1000\kappa}{\Lambda_0}$

154. $2Ag^{+}(aq.) + Cu(s) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$
$(E^{\circ}_{cell} = +0.46\ V)$
Which change will increase potential the most?

(a) Doubling the $[Ag^{+}]$
(b) Halving the $[Cu^{2+}]$
(c) Doubling the size of Cu electrode
(d) Halving the size of Ag electrode

155. As a lead storage battery is charged: **[PMT (MP) 1993, 2000]**

(a) lead dioxide dissolves
(b) sulphuric acid is regenerated
(c) lead electrode becomes coated with lead sulphate
(d) the concentration of sulphuric acid decreases

156. In the electrochemical reaction,

$$2Fe^{3+} + Zn \longrightarrow Zn^{2+} + 2Fe^{2+}$$

increasing the concentration of Fe^{2+}: **[CEE (Kerala) 2000]**

(a) increases the cell emf
(b) increases the current flow
(c) decreases the cell emf
(d) alters the pH of the solution

157. In the cell reaction,

$$Cu(s) + 2Ag^{+}(aq.) \longrightarrow Cu^{2+}(aq.) + 2Ag(s).$$

$E^{\circ}_{cell} = 0.46$ V. By doubling the concentration of Cu^{2+}, E°_{cell} is: **[MEE (Kerala) 2000]**

(a) doubled
(b) halved
(c) increased but less than double
(d) decreased by a small fraction

158. The conductivity of 0.01 mol/dm^3 aqueous acetic acid at 300 K is 19.5×10^{-5} ohm^{-1} cm^{-1} and the limiting molar conductivity of acetic acid at the same temperature is 390 ohm^{-1} cm^2 mol^{-1}. The degree of dissociation of acetic acid is: **[IAS (Pre.) 1995]**

(a) 0.5 (b) 0.05 (c) 5×10^{-3} (d) 5×10^{-7}

159. The ionization constant of a weak electrolyte is 25×10^{-6} while the equivalent conductance of its 0.01 M solution is 19.6 s cm^2 eq^{-1}. The equivalent conductance of the electrolyte at infinite dilution (in s cm^2 eq^{-1}) will be: **[IAS (Pre.) 1998]**

(a) 250 (b) 196
(c) 392 (d) 384

160. What is the amount of chlorine evolved when 2 ampere of current is passed for 30 minutes in an aqueous solution of NaCl? **(BHU 1998; AIIMS 1999)**

(a) 66 g (b) 1.32 g
(c) 33 g (d) 99 g

161. When 9.65 coulomb of electricity is passed through a solution of silver nitrate (Atomic mass of Ag = 108 g mol^{-1}), the amount of silver deposited is: **(KCET 2000)**

(a) 16.2 mg (b) 21.2 mg
(c) 10.8 mg (d) 6.4 mg

162. The quantity of electricity needed to deposit 127.08 g of copper is: **[CET (Pb.) 2000; PET (MP) 2004]**

(a) 1 faraday (b) 4 coulomb
(c) 4 faraday (d) 1 ampere

163. The charge required to deposit 9 g of Al from Al^{3+} solution is (At. wt. of Al = 27.0): **[MEE (Kerala) 2000]**

(a) 3216.3 C (b) 96500 C (c) 9650 C (d) 32163 C

164. The emf of the cell $Ni|Ni^{2+}(1.0\ M)\,||\,Au^{3+}(1.0\ M)|Au$ is (E° for $Ni^{2+}|Ni = -0.25$ V; E° for $Au^{3+}|Au = 1.5$ V): **[CET (Pb.) 2000; PMT (MP) 2[illegible]**

(a) +1.25 V (b) +1.75 V (c) −1.25 V (d) −1.75 V

165. For the reduction of silver ions with copper metal, the standard cell potential was found to be +0.46 V at 25°C. The value of standard Gibbs energy, ΔG° will be: ($F = 96500$ C mol^{-1}) **(AIPMT 2010)**

(a) −89 kJ (b) −89 J
(c) −44.5 kJ (d) −98 kJ

166. In electrolysis of NaCl when Pt electrode is taken then H_2 is liberated at cathode while with Hg cathode it forms sodium amalgam: **[CBSE (PMT) 2002]**

(a) Hg is more inert than Pt
(b) more voltage is required to reduce H^{+} at Hg than at Pt
(c) Na is dissolved in Hg while it does not dissolve in Pt
(d) concentration of H^{+} ions is larger when Pt electrode is taken

167. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because: **[CBSE (PMT) 2002]**

(a) Zn acts as oxidising agent when reacts with HNO_3
(b) HNO_3 is weaker acid than H_2SO_4 and HCl
(c) in electrochemical series, Zn is above hydrogen
(d) NO_3^{-} is reduced in preference to hydronium ion

168. A current is passed through two voltameters connected in series. The first voltameter contains XSO_4 $(aq.)$ while the second voltameter contains Y_2SO_4 $(aq.)$. The relative atomic masses of X and Y are in the ratio 2 : 1. The ratio of the mass of X liberated to the mass of Y liberated is:

(a) 1 : 1 (b) 1 : 2
(c) 2 : 1 (d) none of these

169. Which of the following reactions is possible at anode? **(AIEEE 2002)**

(a) $2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^{+}$
(b) $F_2 \longrightarrow 2F^{-}$
(c) $\frac{1}{2}O_2 + 2H^{+} \longrightarrow H_2O$
(d) None of the above

170. When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are: **(AIEEE 2002)**

	Cathode	**Anode**
(a)	Pure zinc	Pure copper
(b)	Impure sample	Pure copper
(c)	Impure zinc	Impure sample
(d)	Pure copper	Impure sample

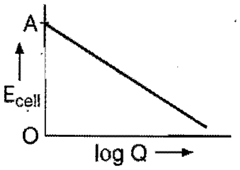
171. Conductivity (Unit Siemen's 'S') is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then the unit of constant of proportionality is: **(AIEEE 2002)**

(a) $S\ \text{m mol}^{-1}$ (b) $S\ \text{m}^2\ \text{mol}^{-1}$

(c) $S^{-2}\ \text{m}^2\ \text{mol}$ (d) $S^2\ \text{m}^2\ \text{mol}^{-2}$

172. $Zn(s) + Cu^{2+}(aq.) \rightleftharpoons Cu(s) + Zn^{2+}(aq.)$

Reaction quotient $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$, variation E_{cell} with Q is of the ne with $OA = 1.10$ volt. $E_{cell} = 1.1591$ volt when:



(a) $[Cu^{2+}]/[Zn^{2+}] = 0.01$ (b) $[Zn^{2+}]/[Cu^{2+}] = 0.01$

$[Zn^{2+}]/[Cu^{2+}] = 0.1$ (d) $[Zn^{2+}]/[Cu^{2+}] = 1$

173. In which of the following cells will the emf be independent of the activity of the chloride ions?

(a) $Zn\ |\ ZnCl_2(aq.)\ |\ Pt(Cl_2)$

(b) $Zn\ |\ ZnCl_2(aq.)\ ||\ KCl(aq.)\ |\ AgCl(s), Ag(s)$

(c) $Ag, AgCl(s)\ |\ KCl(aq.)\ |\ Pt(Cl_2)$

(d) $Hg, Hg_2Cl_2(s)\ |\ KCl(aq.)\ ||\ AgNO_3(aq.)\ |\ Ag(s)$

174. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half-cell reactions and their standard potentials are given below:

$MnO_4^-(aq.) + 8H^+(aq.) + 5e^- \longrightarrow Mn^{2+}(aq.) + 4H_2O(l);$ $E^\circ = 1.51$ volt

$Cr_2O_7^{2-}(aq.) + 14H^+(aq.) + 6e^- \longrightarrow 2Cr^{3+}(aq.) + 7H_2O(l);$ $E^\circ = 1.38$ volt

$Fe^{3+}(aq.) + e^- \longrightarrow Fe^{2+}(aq.);$ $E^\circ = 0.77$ volt

$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq.);$ $E^\circ = 1.40$ volt

Identify the only incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$: **(IIT 2002)**

(a) MnO_4^- can be used in aqueous HCl

(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl

(c) MnO_4^- can be used in aqueous H_2SO_4

(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

175. The standard reduction potential E°, for the half reaction are:

$Zn \longrightarrow Zn^{2+} + 2e^-;$ $E^\circ = 0.76$ V

$Cu \longrightarrow Cu^{2+} + 2e^-;$ $E^\circ = 0.34$ V

The emf for the cell reaction, $Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$ is: **[Bihar CECE (Pre.) 2004]**

(a) 0.42 V (b) − 0.42 V

(c) − 1.1 V (d) + 1.1 V

176. In a galvanic cell, the electrons flow from: **(KCET 2004)**

(a) anode to cathode through the solution

(b) cathode to anode through the solution

(c) anode to cathode through the external circuit

(d) cathode to anode through the external circuit

177. The standard emf of a galvanic cell involving cell reaction with $n = 2$ is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be:

Given: $F = 96500\ \text{C mol}^{-1}$; $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$ **[CBSE (PMT) 2004; AIEEE 2004]**

(a) 2×10^{11} (b) 4×10^{12}

(c) 1×10^2 (d) 1×10^{10}

178. The emf of the cell,

$Zn\ |\ Zn^{2+}\ (0.01\ M)\ ||\ Fe^{2+}\ (0.001\ M)\ |\ Fe$

at 298 K is 0.2905 V then the value of equilibrium constant for the cell reaction is: **[IIT (S) 2004]**

(a) $e^{0.32/0.0295}$ (b) $10^{0.32/0.0295}$

(c) $10^{0.26/0.0295}$ (d) $10^{0.32/0.0591}$

179. The standard emf of the following electrodes are;

$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77$ V; $E^\circ_{Sn^{2+}/Sn} = -0.14$ V

under standard conditions, the potential for the reaction,

$Sn(s) + 2Fe^{3+}(aq.) \longrightarrow 2Fe^{2+}(aq.) + Sn^{2+}(aq.)$ is: **(AIEEE 2004)**

(a) 1.68 V (b) 1.40 V (c) 0.91 V (d) 0.63 V

180. The highest electrical conductivity of the following aqueous solutions is of: **(AIEEE 2005)**

(a) 0.1 M acetic acid (b) 0.1 M chloroacetic acid

(c) 0.1 M fluoroacetic acid (d) 0.1 M difluoroacetic acid

181. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (Atomic mass = 27 amu; 1 faraday = 96500 coulomb). The cathode reaction is:

$$Al^{3+} + 3e^- \longrightarrow Al$$

To prepare 5.12 kg of aluminium metal by this method we would require: **(AIEEE 2005)**

(a) 5.49×10^7 C of electricity (b) 1.83×10^7 C of electricity

(c) 5.49×10^4 C of electricity (d) 5.49×10^{10} C of electricity

182. During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are: **(AIEEE 2005)**

(a) Sn and Ag (b) Pb and Zn

(c) Ag and Au (d) Fe and Ni

183. When an acid cell is charged, then: **(AFMC 2005)**

(a) voltage of the cell increases

(b) electrolyte of the cell dilutes

(c) resistance of the cell increases
(d) none of the above

184. How many coulombs of electricity are required for the reduction of 1 mole of MnO_4^- to Mn^{2+}? **[PMT (Kerala) 2005]**

(a) 96500 C (b) 1.93×10^5 C
(c) 4.83×10^5 C (d) 9.65×10^6 C
(e) 5.62×10^5 C

185. The standard electrode potential of Ag^+/Ag is + 0.80 V and of Cu^{2+}/Cu is + 0.34 V. These electrodes are connected through a salt bridge and if: **[PET (Kerala) 2005]**

(a) copper electrode acts as cathode, then E°_{cell} is + 0.46 volt
(b) silver electrode acts as anode, then E°_{cell} is – 0.34 volt
(c) copper electrode acts as anode, then E°_{cell} is + 0.46 volt
(d) silver electrode acts as cathode, then E°_{cell} is – 0.34 volt
(e) silver electrode acts as anode, then E°_{cell} is + 1.14 volt

186. The half-cell reaction for the corrosion,

$$2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O; \quad E^\circ = 1.23 \text{ V}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe(s); \quad E^\circ = -0.44 \text{ V}$$

Find the ΔG° (in kJ) for the overall reaction: **[IIT (S) 2005]**

(a) – 76 kJ (b) – 322 kJ (c) – 161 kJ (d) – 152 kJ

[**Hint:**
$$Fe(s) \longrightarrow Fe^{2+} + 2e^-; \ \Delta G_1^\circ$$
$$2H^+ + 2e^- + \frac{1}{2}O_2 \longrightarrow H_2O(l); \quad \Delta G_2^\circ$$
$$\overline{Fe(s) + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O; \ \Delta G_3^\circ}$$

Applying $\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$

$$\begin{aligned}\Delta G_3^\circ &= (-2F \times 0.44) + (-2F \times 1.23)\\ &= (-2 \times 96500 \times 0.44) + (-2 \times 96500 \times 1.23)\\ &= -322310 \text{ J} = -322 \text{ kJ}\end{aligned}$$
]

187. What is the cell reaction occurring in Daniell cell (galvanic cell)? **[CET (J&K) 2006]**

(a) $Cu(s) + ZnSO_4(aq.) \longrightarrow CuSO_4(aq.) + Zn(s)$
(b) $Zn(s) + CuSO_4(aq.) \longrightarrow Cu(s) + ZnSO_4(aq.)$
(c) $Ni(s) + ZnSO_4(aq.) \longrightarrow NiSO_4(aq.) + Zn(s)$
(d) $2Na(s) + CdSO_4(aq.) \longrightarrow Na_2SO_4(aq.) + Cd(s)$

188. What are the units of equivalent conductivity of a solution? **[CET (J&K) 2006]**

(a) mho cm^{-1} (b) ohm cm^{-1} g $equiv^{-1}$
(c) mho cm^{-2} g $equiv^{-1}$ (d) mho cm^2 g $equiv^{-1}$

189. The amount of copper deposited by one faraday current will be maximum in an acidic solution of one litre of: **[PMT (Kerala) 2006]**

(a) $1M\ Cu_2Cl_2$ (b) $2M\ Cu(NO_3)_2$
(c) $5M\ CuSO_4$ (d) $5M\ Cu_3(PO_4)_2$
(e) $10M\ CuF_2$

[**Hint:** Greater is the equivalent mass, more is the amount deposited by 1 F charge.]

190. The reduction potential values of M, N and O are +2.46 V, – 1.13 V, – 3.13 V respectively. Which of the following orders is correct regarding their reducing property? **[JEE (Orissa) 2006]**

(a) $O > N > M$ (b) $O > M > N$
(c) $M > N > O$ (d) $M > O > N$

191. The molar conductivities of Λ°_{NaOAc} and Λ°_{HCl} at infinite dilution in water at 25°C are 91 and 426.2 S cm^2 mol^{-1} respectively. To calculate, Λ°_{HOAc}, the additional value required is: **(AIEEE 2006)**

(a) $\Lambda^\circ_{H_2O}$ (b) Λ°_{KCl}
(c) Λ°_{NaOH} (d) Λ°_{NaCl}

[**Hint:** $\Lambda^\circ_{HOAc} = \Lambda^\circ_{NaOAc} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$]

192. The equivalent conductances at infinite dilution of HCl and NaCl are 426.15 and 126.15 mho cm^2 g eq^{-1} respectively. It can be said that the mobility of: **[CET (Gujarat) 2006]**

(a) H^+ ions is much more than that of Cl^- ions
(b) Cl^- ions is much more than that of H^+ ions
(c) H^+ ions is much more than that of Na^+ ions
(d) Na^+ ions is much more than that of H^+ ions

193. The tendencies of the electrodes made up of Cu, Zn and Ag to release electrons when dipped in their respective salt solutions decrease in the order: **(VITEEE 2006)**

(a) Zn > Ag > Cu (b) Cu > Zn > Ag
(c) Zn > Cu > Ag (d) Ag > Cu > Zn

194. The electrode reaction that takes place at the anode of $CH_4 — O_2$ fuel cell is: **(VITEEE 2006)**

(a) $2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O$
(b) $CH_4 + 2H_2O \longrightarrow CO_2 + 8H^+ + 8e^-$
(c) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
(d) $2H^+ + 2e^- \longrightarrow H_2$

195. The cell,

$$Zn(s) | Zn^{2+} (1M || Cu^{2+} (1M) | Cu(s) \quad (E^\circ_{cell} = +1.10 \text{ V})$$

was allowed to be completely discharged at 298K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is: **(AIEEE 2007)**

(a) 9.65×10^4 (b) antilog (24.08)
(c) 37.3 (d) $10^{37.3}$

[**Hint:**
$$E = E^\circ - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$
$$0 = 1.10 - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$
$$\log \frac{[Zn^{2+}]}{[Cu^{2+}]} = 37.3$$
$$\therefore \quad \frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37.3}$$
]

196. The efficiency of a cell is given by: **[CBSE (Med.) 2007]**

(a) $\frac{\Delta G}{\Delta S}$ (b) $\frac{\Delta G}{\Delta H}$
(c) $\frac{\Delta S}{\Delta G}$ (d) $\frac{\Delta H}{\Delta G}$

197. An electric current of 1 amp is passed through acidulated water for 160 minutes and 50 seconds. What is the volume of the hydrogen liberated at the anode (as reduced to NTP)? **(SCRA 2007)**

(a) 1.12 litre (b) 2.24 litre (c) 11.2 litre (d) 22.4 litre

[**Hint:** $V = \dfrac{I + V_e}{96500}$

$= \dfrac{1 \times 9650 \times 11.2}{96500} = 1.12$ litre]

198. The resistance of $N/10$ solution is found to be 2.5×10^3 ohm. The equivalent conductance of the solution is (cell constant $= 1.25\ \text{cm}^{-1}$): **[PMT (Kerala) 2007]**

(a) $2.5\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$ (b) $5\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$

(c) $2.5\ \text{ohm}^{-1}\ \text{cm}^{-2}\ \text{equiv}^{-1}$ (d) $5\ \text{ohm}^{-1}\ \text{cm}^{-2}\ \text{equiv}^{-1}$

(e) $1.25\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$

199. For strong electrolytes, the plot of molar conductance *versus* $\sqrt{C}$ is: **(VITEEE 2007)**

(a) parabolic (b) linear

(c) sinusoidal (d) circular

200. How long (in hours) must a current of 5 ampere be maintained to electroplate 60 g of calcium from molten $CaCl_2$? **(VITEEE 2007)**

(a) 27 hours (b) 8.3 hours (c) 11 hours (d) 16 hours

201. Emf of hydrogen electrode in term of pH is (at 1 atm pressure): **(MHT-CET 2007)**

(a) $E_{H_2} = \dfrac{RT}{F} \times \text{pH}$ (b) $E_{H_2} = \dfrac{RT}{F}\dfrac{1}{\text{pH}}$

(c) $E_{H_2} = \dfrac{2.303RT}{F}\ \text{pH}$ (d) $E_{H_2} = -0.0591\ \text{pH}$

202. The rusting of iron is catalysed by which of the following? **(MGIMS 2007)**

(a) Fe (b) O_2 (c) Zn (d) H^+

203. On the basis of $E°$ values, the strongest oxidising agent is :

$$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e^- \qquad E° = -0.35\ \text{V}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \qquad E° = -0.77\ \text{V}$$

[CBSE (PMT) 2008]

(a) Fe^{3+} (b) $[Fe(CN)_6]^{3-}$

(c) $[Fe(CN)_6]^{4-}$ (d) Fe^{2+}

204. Given $E°_{Cr^{3+}/Cr} = -0.72\ \text{V}, E°_{Fe^{2+}/Fe} = -0.42\ \text{V}$

The potential for the cell, $Cr|Cr^{3+}(0.1M)\,||\,Fe^{2+}(0.01M)|Fe$ is: **(AIEEE 2008)**

(a) – 0.26 V (b) 0.26 V (c) 0.339 V (d) – 0.339 V

[**Hint:** $E°_{\text{cell}} = -0.42 - (-0.72) = +0.30\ \text{V}$

$2Cr(s) + 3Fe^{2+}(0.01M) \rightleftharpoons 2Cr^{3+}(0.1M) + 3Fe(s)$

$$Q = \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} = \frac{[0.1]^2}{[0.01]^2} = 10^4$$

According to Nernst equation,

$$E = E° - \frac{0.059}{n}\log_{10} Q$$

$$= 0.30 - \frac{0.059}{6}\log 10^4 \qquad (\because\ n = 6)$$

$= 0.261$ V]

205. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mole of H_2 gas at the cathode is: (1 faraday = 96500 C mol^{-1}) **(IIT 2008)**

(a) 9.65×10^4 sec (b) 19.3×10^4 sec

(c) 28.95×10^4 sec (d) 38.6×10^4 sec

[**Hint:** Mass of 0.01 mol H_2 = 0.02 g

$$W = \frac{ItE}{96500}$$

$$0.02 = \frac{10 \times 10^{-3} \times t \times 1}{96500}$$

$t = 19.3 \times 10^4$ sec]

206. The emf of a cell containing sodium/copper electrodes is 3.05 V, if the electrode potential of copper electrode is + 0.34 V, the electrode potential of sodium is: **[Comed (Karnataka) 2008]**

(a) – 2.71 V (b) + 2.71 V (c) – 3.71 V (d) + 3.71 V

207. What is the number of moles of oxygen gas evolved by electrolysis of 180 g of water? **(SCRA 2009)**

(a) 2.5 (b) 5.0 (c) 7.5 (d) 10.0

208. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows :

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2;\ \Delta_rG = +966\ \text{kJ mol}^{-1}$$

The potential difference needed for the electrolytic reduction of Al_2O_3 at 500°C is at least : **(AIEEE 2010)**

(a) 2.5 V (b) 5.0 V (c) 4.5 V (d) 3.0 V

[**Hint:** In the given reaction,

$$\frac{2}{3}[2Al^{3+}] + 4e \longrightarrow \frac{4}{3}Al \quad (n = 4)$$

$$\therefore \quad \Delta G = -nFE$$

$$E = -\frac{\Delta G}{nF} = -\frac{966 \times 1000}{4 \times 96500}$$

$= -2.5$ V]

Set–2: The questions given below may have more than one correct answers

1. What is the difference between galvanic cell and electrolytic cell?

(a) In galvanic cell, electrical energy is produced while in electrolytic cell electrical energy is consumed

(b) In galvanic cell, anode is (–)ve while in electrolytic cell anode is (+)ve

(c) In galvanic cell, cathode is (+)ve while in electrolytic cell anode is (–)ve

(d) All are correct

2. $Ag\,|\,Ag^+, KI\,||\,AgI\,|\,Ag$ emf is E, then K_{sp} of AgI is given as:

(a) $K_{sp} = \dfrac{nF}{2.303RT}\log E°$ (b) $\ln K_{sp} = nF\left[\dfrac{\delta E°}{\delta T} - E°\right]$

(c) $\ln K_{sp} = \dfrac{nF}{E°}$ (d) $\log K_{sp} = \dfrac{nFE°}{2.303RT}$

3. A hydrogen electrode is placed in a buffer solution of acetic acid and sodium acetate in the ratio $y : x$ and $x : y$ has electrode potential values E_1 and E_2 volts respectively. pK_a value for acetic acid is:

(a) $\frac{E_1 + E_2}{0.118}$ (b) $\frac{E_2 - E_1}{0.118}$

(c) $\frac{-(E_1 + E_2)}{0.118}$ (d) $\frac{E_1 - E_2}{0.118}$

(E_1 and E_2 are oxidation potentials)

4. For which electrolyte $\alpha = \frac{\lambda_v}{\lambda_\infty}$ doesn't hold good?

(a) CH_3OH (b) $HClO_4$

(c) HCOOH (d) $NaNH_2$

5. The main factors which affect corrosion are:

(a) position of metal in electrochemical series

(b) presence of CO_2 in water

(c) presence of impurities in metal

(d) presence of protective coating

6. Which is correct about silver plating?

(a) Anode—pure Ag

(b) Cathode—object to be electroplated

(c) Electrolyte—$Na[Ag(CN)_2]$

(d) Electrolyte—$AgNO_3$

7. Lead storage battery contains:

(a) Pb rod as anode

(b) Pb rod as cathode

(c) Pb plates coated with PbO_2 act as cathode

(d) electrolyte is H_2SO_4

8. During the electrolysis of $AgNO_3$ (using Pt electrodes) concentration around cathode as well as anode falls from 4*M* to 3*M*. What will happen if this happened with Ag electrodes?

(a) Result will remain same

(b) Concentration around cathode will fall from 4*M* to 3*M* but around anode will increase from 4*M* to 5*M*

(c) Reverse of statement (b)

(d) Concentration increases from 4*M* to 5*M* on both the electrodes

9. Emf of the cell $Pt \cdot H_2$ (1 atm) | $H^+(aq.)$ || AgCl|Ag is 0.27 V and 0.26 V at 25°C and 35°C. Heat of reaction occurring inside the cell at 25°C is:

(a) – 54.8 kJ (b) 26.05 kJ

(c) – 26.05 kJ (d) + 54.8 kJ

10. Given that,

$$Ni^{2+}/Ni = 0.25\ V,\ Cu^{2+}/Cu = 0.34\ V,$$
$$Ag^+/Ag = 0.80\ V \text{ and } Zn^{2+}/Zn = -0.76\ V$$

which of the following reactions under standard condition will not take place in the specified direction?

(a) $Ni^{2+}(aq.) + Cu(s) \longrightarrow Ni(s) + Cu^{2+}(aq.)$

(b) $Cu(s) + 2Ag^+(aq.) \longrightarrow Cu^{2+}(aq.) + 2Ag(s)$

(c) $Cu(s) + 2H^+(aq.) \longrightarrow Cu^{2+}(aq.) + H_2(g)$

(d) $Zn(s) + 2H^+(aq.) \longrightarrow Zn^{2+}(aq.) + 3H_2(g)$

11. Which of the following statements is/are correct?

(a) One faraday is the charge carried by one mole of electrons

(b) If same quantity of electricity flows through the solutions of 0.1 *M* $AgNO_3$ and 0.1 *M* $CuSO_4$ solutions, same weight of silver and copper will be deposited

(c) Electrochemical equivalent has the units of grams per coulomb

(d) Passage of one faraday of electricity produces one gram equivalent of the substance at the electrode

12. Which of the following statements is/are not correct?

(a) Zn-Cu cell is called Daniell cell

(b) Rust is Fe_2O_3

(c) Saline water slows down rusting

(d) Pure metals undergo corrosion faster than impure metals

13. In electrolysis of very dilute NaOH solution using platinum electrodes:

(a) H_2 is evolved at cathode

(b) H_2 is produced at anode

(c) Na is obtained at cathode

(d) O_2 is produced at anode

14. We observe blue colour if:

(a) Cu electrode is placed in the $AgNO_3$ solution

(b) Cu electrode is placed in the $ZnSO_4$ solution

(c) Cu electrode is placed in the dil. HNO_3

(d) Cu electrode is placed in dil. H_2SO_4

15. In which of the following cell (s); $E_{cell} = E^\circ_{cell}$?

(a) $Cu(s) \mid Cu^{2+}(0.01\ M) \parallel Ag^+(0.1\ M) \mid Ag(s)$

(b) $Pt(H_2) \mid pH = 1 \parallel Zn^{2+}(0.01\ M) \mid Zn(s)$

(c) $Pt(H_2) \mid pH = 1 \parallel Zn^{2+}(1\ M) \mid Zn(s)$

(d) $Pt(H_2) \mid H^+ = 0.01\ M \parallel Zn^{2+}(0.01\ M) \mid Zn(s)$

16. Rusting on the surface of iron involves:

(a) $Fe(s) \longrightarrow Fe^{2+}(aq.) + 2e^-$ (at anodic site)

(b) $O_2(g) + 4H^+(aq.) + 4e^- \longrightarrow 2H_2O(l)$ (at cathodic site)

(c) $4Fe^{2+}(aq.) + O_2(g) + 4H_2O(l) \longrightarrow 2Fe_2O_3(s) + 8H^+$

(d) $Fe_2O_3(s) + xH_2O(l) \longrightarrow Fe_2O_3 \cdot xH_2O$

17. Fuel cell involves following reaction(s):

(a) $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq.)$ (at cathode)

(b) $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq.)$ (at anode)

(c) $2H_2(g) + 4OH^-(aq.) \longrightarrow 4H_2O(l) + 4e^-$ (at anode)

(d) $2H_2(g) + 4OH^-(aq.) \longrightarrow 4H_2O(l) + 4e^-$ (at cathode)

18. In the following question, more than one of the answers given may be correct. Select the correct answers and mark it according to the code:

Codes: **[BHU (Mains) 2008]**

(a) 1, 2 and 3 are correct (b) 1 and 2 are correct

(c) 2 and 4 are correct (d) 1 and 3 are correct

[**Hint:** In a cell $Zn(s) \mid Zn^{2+} \parallel H^+ \mid H_2(Pt)$; the addition of H_2SO_4 to the cathode compartment, will:

1. decrease *E*
2. increase *E*
3. shift equilibrium to left
4. shift equilibrium to right]

19. For the reduction of NO_3^- in an aqueous solution, $E°$ is 0.96 V. Values of $E°$ for some metal ions are given below :

$$V^{2+}_{(aq)} + 2e^- \longrightarrow V \qquad E° = -1.19\text{ V}$$
$$Fe^{3+}_{(aq)} + 3e^- \longrightarrow Fe \qquad E° = -0.04\text{ V}$$
$$Au^{3+}_{(aq)} + 3e^- \longrightarrow Au \qquad E° = +1.40\text{ V}$$
$$Hg^{2+}_{(aq)} + 2e^- \longrightarrow Hg \qquad E° = +0.86\text{ V}$$

The pair(s) of metal that is(are) oxidised by NO_3^- in aqueous solution is(are) : **(IIT 2009)**

(a) V and Hg (b) Hg and Fe
(c) Fe and Au (d) Fe and V

[**Hint :** $E^\circ_{M^{n+}/M}$ for V, Fe and Hg are lower than that of NO_3^-, so, NO_3^- will oxidise V, Fe and Hg.]

Assertion-Reason TYPE QUESTIONS

The questions given below consist of an **'Assertion' (A)** and **'Reason' (R)**. Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
(c) If (A) is correct, but (R) is incorrect.
(d) If (A) is incorrect, but (R) is correct.

1. (A) When acidified zinc sulphate solution is electrolysed between zinc electrodes, it is zinc that is deposited at the cathode and hydrogen evolution does not take place.
(R) The electrode potential of zinc is more negative than hydrogen as the over voltage for the hydrogen evolution on zinc is quite large.

2. (A) In electrolysis, the quantity of electricity needed for depositing 1 mole of silver is different from that required for 1 mole of copper.
(R) The molecular weights of silver and copper are different. **(AIIMS 1996)**

3. (A) Equivalent conductance of all electrolytes decreases with increasing concentration.
(R) Lesser number of ions are available per gram equivalent at higher concentration. **(AIIMS 1999)**

4. (A) Zinc displaces copper from copper sulphate solution.
(R) The $E°$ is Zn of – 0.76 volt and that of copper is +0.34 volt. **(AIIMS 1999)**

5. (A) An electrochemical cell can be set-up only if the redox reaction is spontaneous.
(R) A reaction is spontaneous if free energy change is negative.

6. (A) If an aqueous solution of NaCl is electrolysed, the product obtained at the cathode is H_2 gas and not Na.
(R) Gases are liberated faster than the metals.

7. (A) Specific conductance decreases with dilution whereas equivalent conductance increases.
(R) On dilution, number of ions per cc decreases but total number of ions increases considerably.

8. (A) The cell constant of a cell depends upon the nature of the material of the electrodes.
(R) The observed conductance of a solution depends upon the nature of the material of the electrodes.

9. (A) The ratio of specific conductivity to the observed conductance does not depend upon the concentration of the solution taken in the conductivity cell.
(R) Specific conductivity decreases with dilution whereas observed conductance increases with dilution.

10. (A) Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.
(R) Kohlrausch's law helps to find the molar conductivity of a weak electrolyte at infinite dilution.

11. (A) One coulomb of electric charge deposits weight equal to the electrochemical equivalent of the substance.
(R) One faraday deposits one mole of the substance.

12. (A) If standard reduction potential for the reaction, $Ag^+ + e^- \longrightarrow Ag$ is 0.80 volt, then for the reaction, $2Ag^+ + 2e^- \longrightarrow 2Ag$, it will be 1.60 volt.
(R) If concentration of Ag^+ ions is doubled, the electrode potential is also doubled.

13. (A) Gold chloride ($AuCl_3$) solution cannot be stored in a vessel made of copper, iron, nickel, chromium, zinc or tin.
(R) Gold is very precious metal.

14. (A) In the Daniell cell, if concentrations of Cu^{2+} and Zn^{2+} ions are doubled, the emf of the cell will be doubled.
(R) If the concentration of ions in contact with the metals is doubled, the electrode potential is doubled.

15. (A) $H_2 + O_2$ fuel cell gives a constant voltage throughout its life.
(R) In this fuel cell, H_2 reacts with OH^- ions, yet the overall concentration of OH^- ions does not change.

16. (A) Presence of CO_2 in the air accelerates corrosion.
(R) CO_2 is a poisonous gas.

17. (A) For the Daniell cell, $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$ with $E_{cell} = 1.1$ volt, the application of opposite potential greater than 1.1 V results into flow of electrons from cathode to anode.
(R) Zn is deposited at anode and Cu is dissolved at cathode. **(AIIMS 2006)**

18. (A) A current of 96.5 ampere is passed into aqueous $AgNO_3$ solution for 100 second. The weight of silver deposited is 10.8 g. (Atomic weight of Ag = 108)
(R) The mass of a substance deposited during the electrolysis of an electrolyte is inversely proportional to the quantity of electricity passing through the electrolyte. **[EAMCET (Engg.) 2006]**

19. (A) According to Kohlrausch's law, the molar conductance of a strong electrolyte at infinite dilution is sum of molar conductivities of its ions.
(R) The current carried by cation and anion is always equal. **(AIIMS 2007)**

20. (A) The cell potential of mercury cell is 1.35 V, which remains constant.
(R) In mercury cell, the electrolyte is a paste of KOH and ZnO. **(AIIMS 2008)**

Answers : OBJECTIVE QUESTIONS

Set–1

1. (d)	**2.** (b)	**3.** (a)	**4.** (c)	**5.** (c)	**6.** (d)	**7.** (b)	**8.** (a)
9. (c)	**10.** (c)	**11.** (c)	**12.** (b)	**13.** (c)	**14.** (d)	**15.** (a)	**16.** (d)
17. (a)	**18.** (a)	**19.** (a)	**20.** (d)	**21.** (c)	**22.** (b)	**23.** (b)	**24.** (d)
25. (a)	**26.** (d)	**27.** (c)	**28.** (c)	**29.** (b)	**30.** (d)	**31.** (a)	**32.** (d)
33. (a)	**34.** (c)	**35.** (b)	**36.** (c)	**37.** (a)	**38.** (b)	**39.** (d)	**40.** (b)
41. (b)	**42.** (a)	**43.** (c)	**44.** (d)	**45.** (c)	**46.** (d)	**47.** (d)	**48.** (d)
49. (d)	**50.** (a)	**51.** (b)	**52.** (c)	**53.** (a)	**54.** (a)	**55.** (d)	**56.** (a)
57. (b)	**58.** (b)	**59.** (c)	**60.** (d)	**61.** (d)	**62.** (b)	**63.** (a)	**64.** (b)
65. (c)	**66.** (b)	**67.** (d)	**68.** (b)	**69.** (c)	**70.** (c)	**71.** (c)	**72.** (d)
73. (a)	**74.** (a)	**75.** (a)	**76.** (d)	**77.** (b)	**78.** (c)	**79.** (b)	**80.** (c)
81. (a)	**82.** (c)	**83.** (b)	**84.** (d)	**85.** (c)	**86.** (d)	**87.** (b)	**88.** (a)
89. (a)	**90.** (b)	**91.** (d)	**92.** (c)	**93.** (b)	**94.** (c)	**95.** (d)	**96.** (c)
97. (c)	**98.** (d)	**99.** (d)	**100.** (a)	**101.** (b)	**102.** (a)	**103.** (c)	**104.** (b)
105. (a)	**106.** (b)	**107.** (c)	**108.** (a)	**109.** (b)	**110.** (d)	**111.** (d)	**112.** (b)
113. (c)	**114.** (c)	**115.** (d)	**116.** (b)	**117.** (a)	**118.** (a)	**119.** (c)	**120.** (a)
121. (d)	**122.** (a)	**123.** (c)	**124.** (b)	**125.** (d)	**126.** (b)	**127.** (c)	**128.** (a)
129. (d)	**130.** (b)	**131.** (a)	**132.** (c)	**133.** (b)	**134.** (d)	**135.** (d)	**136.** (a)
137. (d)	**138.** (a)	**139.** (c)	**140.** (a)	**141.** (d)	**142.** (b)	**143.** (b)	**144.** (a)
145. (a)	**146.** (c)	**147.** (c)	**148.** (d)	**149.** (b)	**150.** (d)	**151.** (b)	**152.** (c)
153. (d)	**154.** (a)	**155.** (b)	**156.** (c)	**157.** (d)	**158.** (b)	**159.** (c)	**160.** (b)
161. (c)	**162.** (c)	**163.** (b)	**164.** (b)	**165.** (b)	**166.** (b)	**167.** (d)	**168.** (a)
169. (a)	**170.** (d)	**171.** (a)	**172.** (b)	**173.** (c)	**174.** (a)	**175.** (d)	**176.** (c)
177. (d)	**178.** (b)	**179.** (c)	**180.** (d)	**181.** (a)	**182.** (c)	**183.** (a)	**184.** (c)
185. (c)	**186.** (b)	**187.** (b)	**188.** (d)	**189.** (a)	**190.** (a)	**191.** (d)	**192.** (c)
193. (c)	**194.** (b)	**195.** (d)	**196.** (b)	**197.** (a)	**198.** (b)	**199.** (b)	**200.** (d)
201. (d)	**202.** (d)	**203.** (a)	**204.** (b)	**205.** (b)	**206.** (a)	**207.** (b)	**208.** (a)

Set–2

1. (d)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (a, b, c, d)	**6.** (a, b, c)	**7.** (a, c, d)	**8.** (b)
9. (a)	**10.** (a, c)	**11.** (a, c, d)	**12.** (b, c, d)	**13.** (a, d)	**14.** (a, c)	**15.** (a, b)	**16.** (a, b, c, d)
17. (a, c)	**18.** (c)	**19.** (a, b, d)					

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (a)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (b)	**6.** (c)	**7.** (c)	**8.** (d)
9. (b)	**10.** (b)	**11.** (c)	**12.** (d)	**13.** (b)	**14.** (d)	**15.** (a)	**16.** (c)
17. (b)	**18.** (c)	**19.** (c)	**20.** (b)				

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

1. When aluminium oxide (Al_2O_3) is electrolysed for the production of aluminium metal. For a given quantity of electricity, the number of moles of aluminium obtained if the volume of O_2 gas obtained is 201.6 litre measured at NTP, is:

(a) 9 (b) 6 (c) 12 (d) 4.5

[**Hint:** Number of equivalents of oxygen $= \frac{201.6}{5.6} = 36$

(Equivalent volume of oxygen = 5.6 litre at NTP)

∴ Number of equivalents of Al = 36

$$\text{Mass of aluminium} = 36 \times 9 \text{ g}$$

$$\text{Number of moles of aluminium} = \frac{36 \times 9}{27} = 12]$$

2. A smuggler could not carry gold by depositing iron on the gold surface since:

(a) gold is denser

(b) iron rusts

(c) gold has higher reduction potential than iron

(d) gold has lower reduction potential than iron

3. On electrolysis, which of the following does not give out oxygen?

(a) Acidic water using Pt electrode

(b) Fused NaOH using Pt electrode

(c) Dilute H_2SO_4 using Pt electrode

(d) Dilute H_2SO_4 using Cu electrode

4. During electrolysis of a solution of $AgNO_3$, 9650 coulomb of charge pass through the electrolytic cell; the mass of silver deposited on the cathode will be:

(a) 21.6 g (b) 108 g (c) 10.8 g (d) 1.08 g

5. An electrolytic cell contains a solution of Ag_2SO_4 and has platinum electrodes. A current is passed until 1.6 g of O_2 has been liberated at anode. The amount of silver deposited at cathode will be:

(a) 108 g (b) 1.6 g (c) 0.8 g (d) 21.60 g

[**Hint:** Number of equivalents of oxygen $= \frac{1.6}{8} = 0.2$

∴ Number of equivalents of Ag deposited = 0.2

Mass of Ag deposited $= 0.2 \times 108 = 21.6$ g]

6. In the process of electroplating, *m* g of silver is deposited when 4 ampere of current flows for 2 minutes. The amount (in g) of silver deposited by 6 ampere of current flowing for 40 seconds will be:

(a) $4m$ (b) $\frac{m}{2}$ (c) $\frac{4m}{3}$ (d) $3m$

[**Hint:**

$$\frac{W_1}{W_2} = \frac{Q_1}{Q_2}$$

$$\frac{W_1}{W_2} = \frac{I_1 \times t_1}{I_2 \times t_2}$$

$$\frac{m}{W_2} = \frac{4 \times 2 \times 60}{6 \times 40}$$

$$W_2 = \frac{m}{2} \text{ g}]$$

7. If four moles of electrons are transferred from anode to cathode in an experiment on electrolysis of water, then total volume of the two gases produced at STP will be:

(a) 224 L (b) 72.6 L (c) 67.2 L (d) 89.4 L

[**Hint:** Equivalent volume of H_2 = 11.2 L

Equivalent volume of O_2 = 5.6 L

Volume of H_2 and O_2 evolved by 4 moles electrons or 4 faraday charge $= 4 \times 11.2 + 4 \times 5.6 = 67.2$ L]

8. When one faraday of electricity is passed through three electrolytic cells containing Ag^+, Ni^{2+} and Cr^{3+} ions respectively, the deposited Ag (At. mass = 108), Ni (At. mass = 59) and Cr (At. mass = 52) are:

	Ag	Ni	Cr
(a)	108 g	29.5 g	17.3 g
(b)	108 g	59 g	52 g
(c)	108 g	108 g	17.3 g
(d)	108 g	29.5 g	166 g

[**Hint:** Equivalent mass of Ag $= \frac{108}{1} = 108$

Equivalent mass of Ni $= \frac{59}{2} = 29.5$

Equivalent mass of Cr $= \frac{52}{3} = 17.3$

∴ Amount of these metals deposited by 1 faraday charge will be: 108 g Ag, 29.5 g Ni and 17.3 g Cr respectively.]

9. Which of the following reactions occur at the cathode during the charging of lead storage battery?

(a) $Pb^{2+} + 2e^- \longrightarrow Pb$

(b) $Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

(c) $Pb \longrightarrow Pb^{2+} + 2e^-$

(d) $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

10. A current of 2.6 amp was passed through $CuSO_4$ solution for 6 minutes and 20 seconds. The amount of copper deposited is:

(a) 0.3175 g (b) 0.0031 g (c) 6.35 g (d) 3.175 g

[**Hint:** $W = \frac{ItE}{96500} = \frac{2.6 \times 380 \times 31.75}{96500} \approx 0.32$ g]

11. In the electrolysis of fused salt, the weight of the substance deposited on an electrode will not depend on:

(a) temperature of the bath

(b) current intensity

(c) time of electrolysis

(d) electrochemical equivalent of the ions

12. When an aqueous solution of sodium chloride is electrolysed using platinum electrodes, the ions discharged at the electrodes are:

(a) sodium and hydrogen (b) sodium and chloride
(c) hydrogen and chloride (d) hydroxyl and chloride

13. How many coulombs are required for the oxidation of 1 mole of H_2O_2 to O_2?
(a) 9.65×10^4 C (b) 93000 C
(c) 1.93×10^5 C (d) 19.3×10^2 C

[**Hint:**
$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$
$$\begin{aligned} 1 \text{ mol } H_2O_2 &\equiv 2 \text{ mol } e^- \\ &\equiv 2 \times 96500 \text{ C} \\ &\equiv 193000 \text{ C} \\ &= 1.93 \times 10^5 \text{ C} \end{aligned}$$
]

14. A current of 2 amp when passed for 5 hours through a molten salt deposits 22.2 g of metal of atomic mass 177. The oxidation state of the metal in the metal salt is:
(a) +1 (b) +2 (c) +3 (d) +4

[**Hint:**
$$W = \frac{ItE}{96500}$$
$$E = \frac{W \times 96500}{It} = \frac{22.2 \times 96500}{2 \times 5 \times 3600} = 59.5$$
$$\text{Equivalent mass} = \frac{\text{Atomic mass}}{\text{Oxidation state}}$$
$$59.5 = \frac{177}{n}$$
$$\therefore \quad n \approx 3$$
]

15. When water is electrolysed, hydrogen and oxygen gases are produced. If 1.008 g of H_2 is liberated at cathode, what mass of O_2 is formed at the anode?
(a) 32 g (b) 16 g (c) 8 g (d) 4 g

[**Hint:**
$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$
$$\frac{1.008}{W_2} = \frac{1.008}{8}$$
$$\therefore \quad W_2 = 8 \text{ g}$$
where, E_1 and E_2 are equivalent mass of hydrogen and oxygen respectively.]

16. The cell potential (E) and the free energy change (ΔG) accompanying an electrochemical reaction are related by:
(a) $\Delta G = nF \log E$ (b) $\Delta G = nFE$
(c) $-\Delta G = nFE$ (d) $-\Delta G = nF \log E$

17. The units of conductivity are:
(a) siemens^{-1} cm^{-1} (b) siemens cm
(c) siemens cm^{-1} (d) siemens cm^{-2} mol^{-1}

18. The calomel electrode used as a reference electrode contains:
(a) PbO_2-$PbSO_4$ mixture (b) $HgCl_2$
(c) Hg_2Cl_2 (d) $ZnCl_2$

19. KCl is used in salt bridge because:
(a) it forms a good jelly with agar-agar
(b) it is a strong electrolyte
(c) it is a good conductor of electricity
(d) the transference number of K^+ and Cl^- ions are almost equal

[**Hint:** Only those electrolytes are used in salt bridge whose ions have same transference number in agar-agar gel.]

20. The increase in the equivalent conductance of a salt solution on dilution is due to increase in the:
(a) attraction between the ions
(b) degree of ionization of the salt
(c) molecular attraction
(d) association of the salt

21. When 96500 coulombs of electricity are passed through nickel sulphate solution, the amount of nickel deposited will be:
(a) 1 mol (b) 0.5 mol (c) 0.1 mol (d) 2 mol

[**Hint:** 1 faraday deposits 1 equivalent of nickel.
1 equivalent of Ni = 1/2 mole of nickel.]

22.
$$Al^{3+}(aq.) + 3e^- \longrightarrow Al(s); \; E^\circ = -1.66 \text{ V}$$
$$Cu^{2+}(aq.) + 2e^- \longrightarrow Cu(s); \; E^\circ = +0.34 \text{ V}$$
What voltage is produced under standard conditions by combining the half reactions with these standard electrode potentials?
(a) 1.32 V (b) 2.00 V (c) 2.30 V (d) 4.34 V

[**Hint:** The cell will be:
$$Al(s) \mid Al^{3+}(aq.) \parallel Cu^{2+}(aq.) \mid Cu(s)$$
$$\begin{aligned} E^\circ_{\text{Cell}} &= E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}} \\ &= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Al^{3+}/Al} \\ &= +0.34 - (-1.66) = +2.00 \text{ V} \end{aligned}$$
]

23. For which of these oxidation/reduction pairs will the reduction potential vary with pH?
I. AmO_2^{2+}/AmO_2^{+} II. AmO_2^{2+}/Am^{4+} III. Am^{4+}/Am^{2+}
(a) I only (b) II only
(c) I and II only (d) I, II and III

[**Hint:** $4H^+ + AmO_2^{2+} + 2e^- \longrightarrow Am^{4+} + 2H_2O$
It includes H^+ ions; hence the electrode potential depends on pH.]

24. $2Ag^+(aq.) + Cu(s) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$
The standard potential E° for this reaction is 0.46 V. Which change will increase the potential the most?
(a) Doubling the $[Ag^+]$
(b) Halving the $[Cu^{2+}]$
(c) Doubling the size of the Cu(s) electrode
(d) Decreasing the size of the Ag electrode by one-half

25. $10Cl^-(aq.) + 2MnO_4^-(aq.) + 16H^+(aq.) \rightleftharpoons 5Cl_2(g) + 2Mn^{2+}(aq.) + 8H_2O(l)$
The value of E° for this reaction is 0.15 V. What is the value of the equilibrium constant (K) for this reaction?
(a) 2.4×10^{25} (b) 4.9×10^{12} (c) 1.2×10^5 (d) 3.4×10^2

[**Hint:**
$$\begin{aligned} K &= \text{antilog}\left[\frac{nE^\circ}{0.059}\right] \\ &= \text{antilog}\left[\frac{10 \times 0.15}{0.059}\right] \\ &\approx 2.4 \times 10^{25} \end{aligned}$$
]

26. What takes place when zinc metal is added to an aqueous solution containing magnesium nitrate and silver nitrate?

1. Zn is oxidised
2. Mg^{2+} is reduced
3. Ag^+ is reduced
4. No reaction takes place

(a) 1 and 2 only (b) 1 and 3 only
(c) 1, 2 and 3 only (d) 4 only

27. In the galvanizing process, iron is coated with zinc. The resulting chemical protection is most similar to that provided when:

(a) a magnesium bar is connected to an iron pipe
(b) an iron can is plated with tin
(c) copper pipes are connected using lead solder
(d) a copper pipe is covered with epoxy paint

28. What is the sign of ΔG° and the value of K for an electrochemical cell for which $E^\circ_{cell} = 0.80\,V$?

	ΔG°	K
(a)	–	> 1
(b)	+	> 1
(c)	+	< 1
(d)	–	< 1

29. Consider a voltaic cell based on these half-cells:

$$Ag^+(aq.) + e^- \longrightarrow Ag(s);\ E^\circ = +0.80\,V$$
$$Cd^{2+}(aq.) + 2e^- \longrightarrow Cd(s);\ E^\circ = -0.40\,V$$

Identify the anode and give the voltage of this cell under standard conditions.

(a) Ag; $E_{cell} = 0.40\,V$ (b) Ag; $E_{cell} = 2.00\,V$
(c) Cd; $E_{cell} = 1.20\,V$ (d) Cd; $E_{cell} = 2.00\,V$

[**Hint:** Anode has lower standard reduction potential; thus Cd will be considered as anode.

$$E^\circ_{Cell} = E_{Cathode} - E_{Anode}$$
$$= E_{Ag^+/Ag} - E^\circ_{Cd^{2+}/Cd}$$
$$= 0.80 - (-0.40) = 1.20\ V\,]$$

30. If the E°_{cell} for a given reaction has a negative value, which 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) $\Delta G^\circ < 0;\ K_{eq} < 1$

31. Which of the following solutions is used as an anti-rusting solution?

(a) Na_2SO_4 (b) Na_3PO_4 (c) Na_3BO_3 (d) Na_2S

32. The pressure of hydrogen gas is increased from 1 atm to 100 atm. Keeping the H^+ (1 *M*) constant, the voltage of the hydrogen half-cell at 25°C will be:

(a) 0.059 V (b) 0.59 V (c) 0.0295 V (d) 0.118 V

33. Efficiency of the following cell is 84%.

$$A(s) + B^{2+}(aq.) \rightleftharpoons A^{2+}(aq.) + B(s);\ \Delta H = -285\,kJ$$

Then the standard electrode potential of the cell will be:

(a) 1.20 V (b) 2.40 V (c) 1.10 V (d) 1.24 V

[**Hint:** Efficiency $= \dfrac{\Delta G^\circ}{\Delta H^\circ} = \dfrac{-nFE^\circ}{\Delta H^\circ}$

$$0.84 = -\frac{2 \times E^\circ \times 96500}{-285 \times 1000}$$
$$E^\circ = +1.24\ V\,]$$

34. A chemical reaction will be spontaneous if:

(a) E°_{cell} is positive (b) ΔG° is negative
(c) reaction quotient, $Q < K$ (d) E°_{oxid} is negative

35. Match the List-I with List-II :

List-I (Electrode)	**List-II (Type)**
1. Calomel	(A) Reference
2. Glass	(B) Redox
3. Hydrogen	(C) Membrane
4. Quinhydrone	(D) Gas

Codes:

(a)	1–A	2–C	3–D	4–B
(b)	1–B	2–A	3–D	4–C
(c)	1–C	2–B	3–A	4–D
(d)	1–D	2–A	3–C	4–B

36. The conductivity of saturated solution of $BaSO_4$ is 3.06×10^{-6} mho cm^{-1} and its equivalent conductance is 1.53 mho cm^2 eq^{-1}. The K_{sp} for $BaSO_4$ will be:

(a) $4 \times 10^{-12}\,M$ (b) $4 \times 10^{6}\,M$
(c) $4 \times 10^{-12}\,M^2$ (d) $4 \times 10^{-6}\,M^2$

37. The standard reduction potential of hydrogen is zero because:

(a) it is assumed
(b) hydrogen is easiest to oxidise
(c) hydrogen has single electron
(d) hydrogen is electronegative

In the following three questions, three statements I, II and III are given. Mark:

(a) if all the statements are correct
(b) if II and III are correct
(c) if I and III are correct
(d) if only II is correct **[BHU (Mains) 2007]**

38. I. Conductance of electrolyte solution increases with temperature.
II. Resistivity is reciprocal of molar conductivity of electrolyte.
III. Cell constant has unit cm^{-1}.

(a) (b) (c) (d)

39. I. The conductivity of molten NaCl is due to movement of Na^+ and Cl^- ions.
II. Solid NaCl is also conductor of electricity.
III. Molten sodium is a good conductor because of mobile electrons.

(a) (b) (c) (d)

40. I. Cathode is –ve terminal both in electrochemical and electrolytic cells.
II. Reduction occurs at cathode both in galvanic as well as electrolytic cells.
III. Chemical charge in electrolytic cell is non-spontaneous.

(a) (b) (c) (d)

41. In an experiment, 0.04 F was passed through 400 mL of a 1 *M* solution of NaCl. What would be the pH of the solution after the electrolysis? **[PMT (Kerala) 2007]**

(a) 8 (b) 10 (c) 13 (d) 6

(e) 9

[**Hint:** Electrolysis of *aq.* NaCl gives hydrogen gas at cathode and oxygen gas at anode, the electrolyte solution contains NaOH after electrolysis.

Number of equivalents of NaOH formed = 0.04

Normality, $N = \frac{0.04 \times 1000}{400} = 0.1$

$$[OH^-] = 0.1M$$

$$pOH = 1 \qquad \therefore \; pH = 13]$$

42. An alloy of Pb-Ag weighing 1.08 g was dissolved in dilute HNO_3 and the volume made to 100 mL. A silver electrode was dipped in the solution and the emf of the cell set-up $Pt(s), H_2(g) \mid H^+(1M) \parallel Ag^+(aq.) \mid Ag(s)$ was 0.62 V. If E°_{cell} is 0.80 V, what is the percentage of Ag in the alloy? (At 25°C, $RT/F = 0.06$) **[PET (Kerala) 2007]**

(a) 25 (b) 2.50 (c) 10 (d) 1

(e) 50

[**Hint:** Overall cell reaction is:

$$H_2(g) + 2Ag^+ \rightleftharpoons 2Ag(s) + 2H^+(aq.)$$

$$E = E^\circ - \frac{0.06 \times 2.303}{2} \log \frac{[H^+]^2}{[Ag^+]^2 \, pH_2}$$

$$0.62 = 0.80 + \frac{2 \times 0.06 \times 2.303}{2} \log [Ag^+]$$

$$[Ag^+] = 0.05\,M$$

Number of moles of Ag^+ in 100 mL

$$= \frac{MV}{1000} = \frac{0.05 \times 100}{1000} = 0.005$$

Mass of silver = 0.005 × 108 g

Percentage of Ag in 1.08 g of alloy $= \frac{0.005 \times 108 \times 100}{1.08} = 50\%$]

43. Select the correct statements about dry cell:

(a) It is also called Leclanche cell

(b) It is also called Daniell cell

(c) Electrolyte used is moist paste of NH_4Cl and $ZnCl_2$

(d) Cathodic process is:

$$2MnO_2(s) + 2NH_4^+(aq.) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$$

44. Given the standard oxidation potentials,

$$Fe \xrightarrow{+0.4\,V} Fe^{2+}(aq.) \xrightarrow{-0.8\,V} Fe^{3+}(aq.)$$

$$Fe \xrightarrow{+0.9\,V} Fe(OH)_2 \xrightarrow{0.6\,V} Fe(OH)_3$$

It is easier to oxidise Fe^{2+} to Fe^{3+} in:

(a) acid medium

(b) alkaline medium

(c) neutral medium

(d) both in acidic and alkaline mediums

[**Hint:** $E^\circ_{Fe^{2+}/Fe^{3+}}$ is positive in alkaline solution, therefore, it is easier to oxidise Fe^{2+} to Fe^{3+} in alkaline medium.]

45. Dipping iron article into a strongly alkaline solution of sodium phosphate: **(VITEEE 2008)**

(a) does not affect the article

(b) forms $Fe_2O_3 \cdot xH_2O$ on the surface

(c) forms iron phosphate film

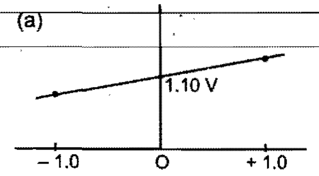
(d) forms ferric hydroxide

46. For the redox process,

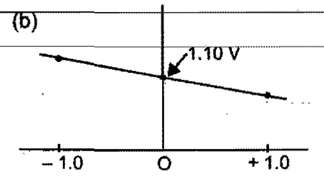
$$Zn(s) + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu(s) \; E^\circ_{cell} = +1.10\,V$$

which graph correctly represents E_{cell} (*Y*-axis) as a function of $\log \frac{[Zn^{2+}]}{[Cu^{2+}]}$ (*X*-axis)?

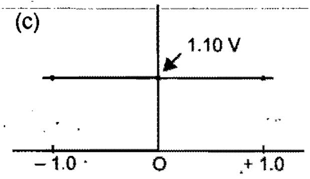
(a)



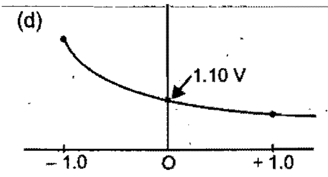
(b)



(c)



(d)



47. A fuel cell involves combustion of the butane at 1 atm and 298 K

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$$

$$\Delta G^\circ = -2746 \text{ kJ/mol}$$

what is E° of a cell ?

(a) + 4.74 V (b) + 0.547 V (c) + 1.09 V (d) + 4.37 V

[**Hint :** In the reaction

$$\overset{-10+10}{C_4H_{10}}(g) + \frac{13}{2}O_2(g) \longrightarrow \overset{+4\,-4}{4CO_2}(g) + 5H_2O(l)$$

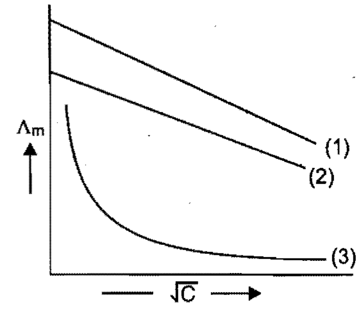
Change in oxidation number of carbon = + 16 – (– 10) = + 26

∴ Number of electrons involved in cell process will be 26.

$$E^\circ = \frac{-\Delta G^\circ}{nF} = -\frac{(-2746) \times 1000}{26 \times 96500}$$

$$= +1.09\text{ V}]$$

48. Molar conductance Λ_m is plotted agains $\sqrt{C}$ (mol litre^{-1}) for three electrolytes (NaCl, HCl, NH_4OH)



which of the following is correct ?

	1	2	3
(a)	NaCl	HCl	NH_4OH
(b)	HCl	NaCl	NH_4OH
(c)	NH_4OH	NaCl	HCl
(d)	NH_4OH	HCl	NaCl

49. In the concentration cell

$$\text{Pt}(\text{H}_2)\left|\begin{matrix}\text{H}A\ (0.1\,M)\\ \text{Na}A\ (1M)\end{matrix}\right|\left|\begin{matrix}\text{H}A\ (1\,M)\\ \text{Na}A\ (1M)\end{matrix}\right|(\text{H}_2)\ \text{Pt}$$

(pK_a of HA = 4)
Cell potential will be:
(a) 0.03 V (b) 0.06 V (c) – 0.06 V (d) – 0.03 V

[Hint : $E_{\text{cell}} = \frac{0.0591}{1}\log_{10}\frac{[\text{H}^+]\ \text{Cathode}}{[\text{H}^+]\ \text{Anode}}$

$$E_{\text{cell}} = 0.06\ [\text{pH Anode} - \text{pH Cathode}] \qquad \ldots(1)$$

$$\text{pH Anode} = pK_a + \log\overline{[\text{H}A]} = 4 + \log\frac{0.1}{1} = 3$$

$$\text{pH Cathode} = 4 \quad (\text{from eq. 1})$$

$$E_{\text{cell}} = -\ 0.06\ \text{V}]$$

50. In the following process of disproportionation:

$$\underset{\text{Chlorate ion}}{2\text{ClO}_3^-} \rightleftharpoons \text{ClO}_2^- + \underset{\text{Per chlorate ion}}{\text{ClO}_4^-} \qquad \begin{aligned} E^\circ_{\text{ClO}_4^-/\text{ClO}_3^-} &= +\ 0.36\ \text{V}\\ E^\circ_{\text{ClO}_3^-/\text{ClO}_2^-} &= +\ 0.33\ \text{V}\end{aligned}$$

Initial concentration of chlorate ion was 0.1 M. The equilibrium concentration of per chlorate ion will be :
(a) 0.19 V (b) 0.1 M (c) 0.024 M (d) 0.019 M

[Hint :

$$\text{ClO}_3^-(aq.) + \text{H}_2\text{O}(l) \longrightarrow \text{ClO}_4^-(aq.) + 2\text{H}^+(aq.) + 2e^-$$

$$2\text{H}^+ + \text{ClO}_3^-(aq.) + 2e^- \longrightarrow \text{ClO}_2^-(aq.) + \text{H}_2\text{O}(l)$$

$$2\text{ClO}_3^-(aq.) \rightleftharpoons \text{ClO}_2^-(aq.) + \text{ClO}_4^-(aq.)$$

$$E^\circ_{\text{cell}} = 0.33 - 0.36 = -\ 0.03\ \text{V}$$

$$E = E^\circ - \frac{0.059}{n}\log Q$$

At equilibrium, $E = 0, \quad n = 2, \quad Q = K$

$$0 = -\ 0.03 - \frac{0.059}{2}\log K$$

$$\log K = -\ 1$$

$$K = \frac{1}{10} \qquad \ldots(1)$$

$$2\text{ClO}_3^-(aq.) \rightleftharpoons \text{ClO}_2^-(aq.) + \text{ClO}_4^-(aq.)$$

t_0	0.1	0	0
$t_{\text{eq.}}$	$0.1 - 2x$	x	x

$$K = \frac{x \times x}{(0.1 - 2x)^2} = \frac{1}{10}$$

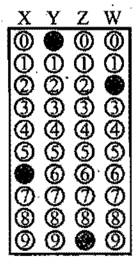
$$x = 0.019]$$

Answers

1. (c)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (d)	**6.** (b)	**7.** (c)	**8.** (a)
9. (d)	**10.** (a)	**11.** (a)	**12.** (c)	**13.** (c)	**14.** (c)	**15.** (c)	**16.** (c)
17. (c)	**18.** (c)	**19.** (d)	**20.** (b)	**21.** (b)	**22.** (b)	**23.** (b)	**24.** (a)
25. (a)	**26.** (b)	**27.** (a)	**28.** (a)	**29.** (c)	**30.** (a)	**31.** (b)	**32.** (d)
33. (d)	**34.** (a, b, c, d)	**35.** (a)	**36.** (d)	**37.** (a)	**38.** (c)	**39.** (c)	**40.** (b)
41. (c)	**42.** (e)	**43.** (a, c, d)	**44.** (b)	**45.** (c)	**46.** (b)	**47.** (c)	**48.** (b)
49. (c)	**50.** (d)						

Integer Answer TYPE QUESTIONS

This section contains 10 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. How many grams of water will be electrolysed by 96500 coulomb charge?
2. Number of faradays required to convert 1 mole of $Cr_2O_7^{2-}$ into Cr^{3+} ions is :
3. At what pH the potential of hydrogen electrode will be 0.059 V?
4. The ratio of $\left(\frac{\Lambda_m}{\Lambda_e}\right)$ for $Ca_3(PO_4)_2$ will be equal to :
5. $I_2(s)/I^-$ (0.1 M) half-cell is connected to $H^+(aq)/(H_2$ 1 atm) Pt half-cell and its cell potential is found to be 0.7714 V. If $E^\circ_{I_2/I^-} = 0.535$ V, the pH of H^+ / H_2 half-cell will be :
6. If an aqueous solution of NaCl is electrolysed using platinum electrode by a current of 5 amp, then what volume of Cl_2 gas in litres at STP will be produced?
7. Charge of 6.24×10^{18} electrons will be (in coulomb) :
8. A current of 2 amp when passed for 5 hour through a molten salt deposits 22.2 g of metal of atomic mass 177. The positive oxidation state of the metal in the metal salt is :
9. $$Cr(s) \mid Cr^{3+} \parallel Fe^{2+} \mid Fe(s)$$
   In above cell, the value of n in the Nernst equation:
   i.e., $E = E^\circ - \frac{0.059}{n}\log_{10} Q$ will be :
10. In the Nernst Equation,
    $$E = E^\circ - \frac{2.303RT}{nF}\log_{10} Q$$
    Q will be equal to the equilibrium constant K_C, when the cell potential E is equal to :

Answers

1. (9) 2. (6) 3. (1) 4. (6) 5. (3) 6. (7) 7. (1) 8. (3)
9. (6) 10. (0)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

In a lead storage battery, Pb (anode) and PbO_2 (cathode) are used. Concentrated H_2SO_4 is used as electrolyte. The battery holds 3.5 litre acid with it. In the discharge process, the density of acid fell from 1.294 to 1.139 g/mL. The sulphuric acid of density 1.294 g mL^{-1} is 39% by mass and that of density 1.139 g/mL is 20% by mass.

Answer the following questions:

1. Equivalent mass of sulphuric acid in lead storage battery is:
   (a) 49 (b) 98
   (c) 24.5 (d) none of these
2. Normalities of sulphuric acid before and after discharge are:
   (a) 5.15, 2.32 (b) 2.32, 5.15 (c) 5.15, 5.15 (d) 2.32, 2.32
3. The number of ampere-hours for which the battery must have been used is:
   (a) 26504 amp-hrs (b) 2650.4 amp-hrs
   (c) 265.04 amp-hrs (d) 26.504 amp-hrs
4. The amount of charge which the battery must have been used is:
   (a) 9.88 F (b) 8.98 F (c) 8.89 F (d) 7.88 F
5. Which of the following takes place in discharge process at anode?
   (a) $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$
   (b) $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$
   (c) $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$
   (d) $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$

• Passage 2

Electrolysis is the process in which electrical energy is converted to chemical energy. In electrolytic cell, oxidation takes place at anode and reduction at cathode. Electrode process depends on the electrode taken for electrolysis. Amount of substance liberated at an electrode is directly proportional to the amount of charge passed through it. The mass of substance liberated at electrode is calculated using the following relation:

$$m = \frac{ItE}{96500}$$

Here, E represents the equivalent mass and 96500 C is called the Faraday constant. Faraday (96500 C) is the charge of 1 mole electron, i.e., 6.023×10^{23} electrons; it is used to liberate one gram equivalent of the substance.

Answer the following questions:

1. The platinum electrodes were immersed in a solution of cupric sulphate ($CuSO_4$) and electric current is passed through the solution. After sometime, it was observed that the colour of copper sulphate disappeared with evolution of a gas at the electrode. The colourless solution contains:
   (a) platinum sulphate (b) copper nitrate
   (c) copper sulphate (d) sulphuric acid
2. The passage of current liberates H_2 at cathode and Cl_2 at anode. The solution is:
   (a) copper chloride in water (b) NaCl in water
   (c) mercuric chloride in water (d) $AuCl_3$ in water
3. On electrolysis of dilute sulphuric acid using platinum electrodes, the product obtained at the anode will be:
   (a) hydrogen (b) oxygen
   (c) hydrogen sulphide (d) sulphur oxide
4. How many faradays are required to reduce 1 mol BrO_3^- to Br^-?
   (a) 3 (b) 5 (c) 6 (d) 4
5. Calculate the volume of gas liberated at the anode at STP during the electrolysis of a $CuSO_4$ solution by a current of 1 A passed for 16 minutes and 5 seconds:
   (a) 224 mL (b) 56 mL (c) 112 mL (d) 448 mL

   [**Hint:** At anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$
   (Oxygen gas is evolved)
   Equivalent volume V_e of oxygen = 5.6 litre
   $$\therefore \quad V = \frac{ItV_e}{96500} = \frac{1 \times 965 \times 5.6 \times 10^3}{96500} = 56 \text{ mL}]$$
6. The quantity of electricity required to liberate 112 cc hydrogen at S.T.P from acidified water is: **[Comed (Karnataka) 2008]**
   (a) 965 C (b) 9650 C (c) 96500 C (d) 4825 C

• Passage 3

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:

$$M(s) \mid M^+(aq.\ 0.05\ molar) \parallel M^+\ (aq;\ 1\ molar) \mid M(s)$$

For the above electrolytic cell, the magnitude of the cell potential $|E_{cell}| = 70\ mV$.

Answer the following questions:

1. For the above cell
   (a) $E_{cell} < 0; \Delta G > 0$ (b) $E_{cell} > 0; \Delta G < 0$
   (c) $E_{cell} < 0; \Delta G^\circ > 0$ (d) $E_{cell} > 0; \Delta G^\circ < 0$
2. 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 mV (b) 70 mV
   (c) 140 mV (d) 700 mV **[IIT 2010]**

[**Hint:** 1 (b) Electrolyte concentration cell will be spontaneous when the concentration in cathodic half cell is greater than that of anodic half cell. Thus, the given cell is spontaneous hence

$$\Delta G < 0, \ E_{cell} > 0$$

2. (c) $E^\circ_{cell} = 0$, for every concentration cell

$$E = 0 - \frac{0.059}{n} \log \frac{[M^+]_{anode}}{[M^+]_{cathode}}$$
$$= -\frac{0.059}{1} \log[0.0025]$$
$$= +153 \text{ mV}$$

It is close to 140 mV.]

• Passage 4

The driving force ΔG diminishes to zero on the way to equilibrium, just as in any other spontaneous process. Both ΔG and the corresponding cell potential $\left(E = -\frac{\Delta G}{nF}\right)$ are zero when the redox reaction comes to equilibrium. The Nernst equation for the redox process of the cell may be given as:

$$E = E^\circ - \frac{0.059}{n}\log Q$$

The key to the relationship is the standard cell potential E°, derived from the standard free energy change as:

$$E^\circ = -\frac{\Delta G^\circ}{nF}$$

At equilibrium, the Nernst equation is given as:

$$E^\circ = \frac{0.059}{n}\log K$$

Answer the following questions:

1. On the basis of information available for the reaction:

$$\frac{4}{3}\text{Al} + \text{O}_2 \longrightarrow \frac{2}{3}\text{Al}_2\text{O}_3;\quad \Delta G = -827\ \text{kJ/mol of O}_2$$

the minimum emf required to carry out an electrolysis of Al_2O_3 is:
(Given: 1 F = 96500 C)
(a) 2.14 V (b) 4.28 V (c) 6.42 V (d) 8.56 V

[**Hint:** $\text{Al} \longrightarrow \text{Al}^{3+} + 3e^-$

$$\frac{4}{3}\text{ mol Al} \equiv \frac{4}{3}\times 3\text{ mol }e^-$$

$$\equiv 4\text{ mol }e^-$$

i.e., $n = 4$

$$\Delta G = -nFE$$

$$-827 \times 1000 = -4 \times 96500 \times E$$

$$E = 2.14\text{ V}]$$

2. The equilibrium constant K_c will be equal to Q, when:
(a) $E = E^\circ$ (b) $RT/nF = 1$
(c) $E = 0$ (d) $E^\circ = 1$

3. The nature of graph of E°_{cell} against $\log K_c$ is a/an:
(a) straight line (b) parabola
(c) hyperbola (d) elliptical curve

4. The equilibrium constant K_c for the reaction:
$\text{Cu}(s) + 2\text{Ag}^+(aq.) \rightleftharpoons \text{Cu}^{2+}(aq.) + 2\text{Ag}(s)$ ($E^\circ_{\text{cell}} = 0.46$ V)
will be:
(a) antilog 15.6 (b) antilog 2.5
(c) antilog 1.5 (d) antilog 12.2

5. E for the electrochemical cell,
$\text{Zn}(s) \mid \text{Zn}^{2+}(1\,M)\,aq. \parallel \text{Cu}^{2+}(1\,M)\,aq. \mid \text{Cu}(s)$ is 1.10 volt at 25°C.
The equilibrium constant for the cell reaction:

$$\text{Zn}(s) + \text{Cu}^{2+}(aq.) \rightleftharpoons \text{Cu}(s) + \text{Zn}^{2+}(aq.)$$

will be:
(a) 10^{-37} (b) 10^{37} (c) 10^{-39} (d) 10^{39}

• Passage 5

Conductors allow the passage of electric current through them. Metallic and electrolytic are the two types of conductors. Current carriers in metallic and electrolytic conductors are free electrons and free ions respectively. Specific conductance or conductivity of the electrolyte solution is given by the following relation:

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

where, $c = 1/R$ is the conductance and l/A is the cell constant. Molar conductance (Λ_m) and equivalence conductance (Λ_e) of an electrolyte solution are calculated using the following similar relations:

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

$$\Lambda_e = \kappa \times \frac{1000}{N}$$

where, M and N are the molarity and normality of the solution respectively. Molar conductance of strong electrolyte depends on concentration:

$$\Lambda_m = \Lambda^\circ_m - b\sqrt{c}$$

where, Λ°_m = molar conductance at infinite dilution
c = concentration of the solution
b = constant

The degrees of dissociation of weak electrolytes are calculated as:

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{\Lambda_e}{\Lambda^\circ_e}$$

Answer the following questions:

1. Which of the following decreases on dilution of electrolyte solution?
(a) Equivalent conductance (b) Molar conductance
(c) Specific conductance (d) Conductance

2. The correct order of equivalent conductances at infinite dilution of LiCl, NaCl and KCl is:
(a) LiCl > NaCl > KCl (b) KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl (d) LiCl > KCl > NaCl

3. For which of the following electrolytic solutions Λ_m and Λ_e are equal?
(a) $BaCl_2$ (b) KCl (c) $Al_2(SO_4)_3$ (d) $CaCl_2$

4. The conductance of a solution of an electrolyte is equal to that of its specific conductance. The cell constant of the conductivity cell is equal to:
(a) resistance (b) faraday
(c) zero (d) unity

5. Which of the following equality holds good for the strong electrolytes?
(a) $\Lambda = \Lambda^\circ$ as $c \to 1$ (b) $\Lambda = \Lambda^\circ$ as $c \to 0$
(c) $\Lambda = \Lambda^\circ$ as $c \to \infty$ (d) $\Lambda = \Lambda^\circ$ as $c \to \sqrt{b}$

• Passage 6

At infinite dilution, when the dissociation of electrolyte is complete, each ion makes a definite contribution towards the molar conductance of electrolyte, irrespective of the nature of the other ion with which it is associated.

The molar conductance of an electrolyte at infinite dilution can be expressed as the sum of the contributions from its individual ions.

$$A_xB_y \longrightarrow xA^{y+} + yB^{x-}$$

$$\Lambda^\circ_m(A_xB_y) = x\lambda^\circ_{A^{y+}} + y\lambda^\circ_{B^{x-}}$$

where, x and y are the number of cations and anions respectively.

The degree of ionisation 'α' of weak electrolyte can be calculated as:

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$$

Answer the following questions:

1. The ionic conductances of Al^{3+} and SO_4^{2-} ions at infinite dilution are x and y ohm^{-1} cm^2 mol^{-1} respectively. If Kohlrausch's law is valid, then molar conductance of aluminium sulphate at infinite dilution will be:
(a) $3x + 2y$ (b) $3y + 2x$ (c) $2x + 2y$ (d) $3x + 3y$

2. The molar conductances at infinite dilution for electrolytes BA and CA are 140 and 120 ohm^{-1} cm^2 mol^{-1}. If the molar conductance at infinite dilution of BX is 198 ohm^{-1} cm^2 mol^{-1}, then at infinite dilution, the molar conductance of CX is:
(a) 178 (b) 198 (c) 218 (d) 130

[**Hint:** $\Lambda^\circ_{CX} = \Lambda^\circ_{CA} + \Lambda^\circ_{BX} - \Lambda^\circ_{AB}$
$= 120 + 198 - 140 = 178$]

3. The molar conductance of 0.001 M acetic acid is 50 ohm^{-1} cm^2 mol^{-1}. The maximum value of molar conductance of acetic acid is 250 ohm^{-1} cm^2 mol^{-1}. What is the degree of dissociation (α) of acetic acid?
(a) 0.5 (b) 0.2 (c) 0.3 (d) 0.4

4. Which of the following solutions will have highest value of the molar conductance of CH_3COOH?
(a) 1 M CH_3COOH (b) 0.5 M CH_3COOH
(c) 0.3 M CH_3COOH (d) 0.1 M CH_3COOH

5. The unit of molar conductance of an electrolyte solution will be:
(a) ohm^{-1} cm^2 mol^{-1} (b) mho cm^2 mol^{-1}
(c) S cm^2 mol^{-1} (d) ohm^{-1} cm^{-1} mol^{-1}

• Passage 7

The potential associated with each electrode is known as electrode potential. If the concentration of each species taking part in the electrode reaction is unity (if any appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298 K, then the potential of each electrode is said to be the standard electrode potential. By convention, the standard electrode potential of hydrogen electrode is 0.0 volt. The electrode potential value for each electrode process is a measure of relative tendency of the active species in the process to remain in the oxidised/reduced form. A negative E° means that the redox couple is a stronger reducing agent than the H^+/H_2 couple. A positive E° means that the redox couple is a weaker reducing agent than the H^+/H_2 couple. The metal with greater positive value of standard reduction potential forms the oxide of greater thermal stability.

Answer the following questions:

1. Given the standard reduction potentials,
$E^\circ_{K^+/K} = -2.93$ V, $E^\circ_{Ag^+/Ag} = +0.80$ V, $E^\circ_{Hg^{2+}/Hg} = 0.79$ V
$E^\circ_{Mg^{2+}/Mg} = -2.37$ V, $E^\circ_{Cr^{3+}/Cr} = -0.74$ V.
The correct increasing order of reducing power is:
(a) K > Mg > Cr > Hg > Ag (b) Ag > Hg > Cr > Mg > K
(c) Mg > K > Cr > Hg > Ag (d) Cr > Hg > K > Mg > Ag

2. Which of the following oxides will be thermally most stable?
(a) ZnO (b) MgO (c) Cu_2O (d) Ag_2O

3. Which of the following reactions is not correct?
(a) $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$
(b) $Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$
(c) $Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$
(d) $Cu + H_2SO_4 \longrightarrow CuSO_4 + H_2$

4. Which of the following couples will have highest value of emf ?
(a) $Mg \mid Mg^{2+} \parallel Ag^+ / Ag$ (b) $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$
(c) $Zn \mid Zn^{2+} \parallel Ag^+ / Ag$ (d) $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$

5. Which of the following metals will not displace hydrogen from water?
(a) Mg (b) Zn (c) Sn (d) Ag

• Passage 8

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (Atomic mass : Na = 23; Hg = 200; 1 Faraday = 96500 coulombs). **(IIT 2007)**

Answer the following questions:

1. The total number of moles of chlorine gas evolved is:
(a) 0.5 (b) 1.0 (c) 2.0 (d) 3.0

[**Hint:** Number of moles of NaCl $= \frac{MV}{1000} = \frac{4 \times 500}{1000} = 2$

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

2 mol Cl^- ions give 1 mol Cl_2]

2. If the cathode is a Hg electrode, the maximum weight (in g) of amalgam formed from this solution is:
(a) 200 (b) 225 (c) 400 (d) 446

[**Hint:** Electrolysis gives 2 mol sodium at cathode. Thus, amalgam (Na / Hg) will contain 2 mol of each sodium and Hg.
Mass of amalgam $= 2 \times 200 + 2 \times 23 = 446$]

3. The total charge (in coulombs) required for complete electrolysis is:
(a) 24125 (b) 48250 (c) 96500 (d) 193000

[**Hint:** 2 mol electrons will be required, therefore, required charge will be 2 faraday or 193000 coulombs.]

Answers

Passage 1.	1. (b)	2. (a)	3. (c)	4. (a)	5. (c)	
Passage 2.	1. (d)	2. (b)	3. (b)	4. (c)	5. (b)	6. (a)
Passage 3.	1. (b)	2. (b)	3. (a)	4. (d)	5. (a)	
Passage 4.	1. (a)	2. (c)	3. (a)	4. (a)	5. (b)	
Passage 5.	1. (c)	2. (b)	3. (b)	4. (d)	5. (b)	
Passage 6.	1. (b)	2. (a)	3. (b)	4. (d)	5. (a, b, c)	
Passage 7.	1. (a)	2. (d)	3. (d)	4. (a)	5. (d)	
Passage 8.	1. (b)	2. (d)	3. (d)			

SELF ASSESSMENT

ASSIGNMENT NO. 12

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. The specific conductance (κ) of an electrolyte of 0.1N concentration is related to equivalent conductance (Λ_e) by the following formula: **[CET (J&K) 2007]**
(a) $\Lambda_e = \kappa$ (b) $\Lambda_e = 10\kappa$
(c) $\Lambda_e = 100\kappa$ (d) $\Lambda_e = 10000\kappa$

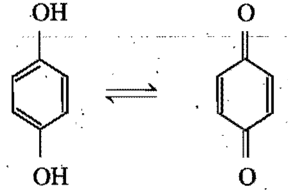
2. The standard E°_{red} values of A, B and C are $+0.68$ V, -2.54 V, -0.50 V respectively. The order of their reducing power is: **(MHT-CET 2007)**
(a) $A > B > C$ (b) $A > C > B$ (c) $C > B > A$ (d) $B > C > A$

3. In the electrochemical reaction,
$$2Fe^{3+} + Zn \longrightarrow Zn^{2+} + 2Fe^{2+},$$
increasing the concentration of Fe^{2+}: **[JEE (WB) 2007]**
(a) increasing the cell emf
(b) increasing the current flow
(c) decrease the cell emf
(d) alter the pH of the solution

4. Fully charged lead storage battery contains 1.5 L of 5 M H_2SO_4. If 2.5 amp of current is taken from the cell for 965 minutes, then what will be the molarity of remaining H_2SO_4? Assume that volume of battery fluid to be constant:
(a) 4 M (b) 3.5 M (c) 2 M (d) 4.25 M

5. In a hydrogen-oxygen, 67.2 litre of H_2 at STP is used in 15 minutes. What is the average current produced?
(a) 549.4 amp (b) 643.33 amp
(c) 965 amp (d) 129.8 amp

6. The cell reaction involving quinhydrone electrode is:



$+ 2H^+ + 2e^-$; $E^\circ = 1.30$ volt

What will be the electrode potential at pH = 3 ?
(a) 1.48 V (b) 1.20 V (c) 1.10 V (d) 1.30 V

[Hint: $E = E^\circ - \dfrac{0.0591}{2}\log[H^+]^2$
$= 1.30 + 0.0591 \times 3 = 1.48$ V]

7. The standard reduction potential E° for OCl^- / Cl^- and for $Cl^- / 1/2Cl_2$ are 0.86 V and -1.10 volt respectively. The E° value of $OCl^- / 1/2Cl_2$ will be:
(a) $+1.96$ V (b) -1.96 V (c) $+0.24$ V (d) -0.24 V

[Hint:
$$OCl^- + H_2O + e^- \longrightarrow Cl^- + 2OH^- \qquad E^\circ_{\text{red}} = 0.86 \text{ V}$$
$$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^- \qquad E^\circ_{\text{oxi.}} = -1.10 \text{ V}$$
$$OCl^- + H_2O \longrightarrow \frac{1}{2}Cl_2 + 2OH^- \qquad E^\circ = 0.86 + (-1.10)$$
$$= -0.24 \text{ V}]$$

8. The standard reduction potential for the following two reactions are given:
$AgCl + e^- \longrightarrow Ag(s) + Cl^- (aq.)$; $E^\circ = 0.22$ V ...(i)
$Ag^+ (aq.) + e^- \longrightarrow Ag(s)$ $E^\circ = 0.80$ V ...(ii)
The solubility product of AgCl under standard condition will be:
(a) 1.613×10^{-5} M^2 (b) 1.535×10^{-8} M^2
(c) 3.213×10^{-10} M^2 (d) 1.535×10^{-10} M^2

[**Hint:** From eqs. (i) and (ii),

$AgCl(s) \rightleftharpoons Ag^+ + Cl^-; E^\circ = 0.22 - 0.80 = -0.58$ V

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log [Ag^+][Cl^-]$$

$$0 = -0.58 - \frac{0.0591}{2} \log [Ag^+][Cl^-]$$

$$K_{sp} = [Ag^+].[Cl^-] = 1.535 \times 10^{-10}\ M^2]$$

9. The equilibrium constant for the reaction,

$$Cu(s) + Cu^{2+}(aq.) \rightleftharpoons 2Cu^+(aq.)$$

$E^\circ_{Cu^{2+}/Cu} = 0.34$ V $\quad E^\circ_{Cu^{2+}/Cu} = 0.15$ V

(Given: log 3.72 = 0.571)

(a) 3.72×10^{-6} (b) 3.72×10^{-5}

(c) 3.72×10^{-7} (d) 3.72×10^{-8}

10. Cations absorb 6.023×10^{22} electrons for their reduction. How many equivalents of the ion are reduced?

(a) 0.1 (b) 0.01 (c) 0.001 (d) 0.0001

SECTION-II

Multiple Answers Type Objective Questions

11. In an electrolytic cell:

(a) anode is positively charged

(b) cathode is negatively charged

(c) oxidation takes place at anode

(d) reduction takes place at cathode

12. One gram equivalent of a substance is liberated at an electrode by:

(a) 6.023×10^{23} electrons

(b) 96500 C

(c) 1 amp current for 1 second

(d) 1 amp current for 96500 sec

13. If 9 gm H_2O is electrolysed completely with the current of 50% efficiency then:

(a) 96500 charge is required

(b) 2×96500 C charge is required

(c) 5.6 L of O_2 at STP will be formed

(d) 11.2 L of O_2 at STP will be formed

14. A galvanic cell involves the following reaction:

$Zn(s) + 2Ag^+(aq.) \rightleftharpoons Zn^{2+}(aq.) + 2Ag(s)$

Select the correct statements among the following:

(a) Zinc is negatively charged

(b) The given redox process is spontaneous

(c) $Ag^+ + e^- \longrightarrow Ag$, takes place at anode

(d) $Zn(s) \longrightarrow Zn^{2+} + 2e^-$, takes place at cathode

15. Given that,

$$E^\circ_{Ni^{2+}/Ni} = -0.25 \text{ V}, \quad E^\circ_{Cu^{2+}/Cu} = +0.34 \text{ V}$$

$$E^\circ_{Ag^+/Ag} = +0.80 \text{ V} \quad E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ V}$$

Which of the following redox processes will not take place in specified direction?

(a) $Ni^{2+}(aq.) + Cu(s) \longrightarrow Ni(s) + Cu^{2+}(aq.)$

(b) $Cu(s) + 2Ag^+(aq.) \longrightarrow Cu^{2+}(aq.) + 2Ag(s)$

(c) $Cu(s) + 2H^+(aq.) \longrightarrow Cu^{2+}(aq.) + H_2(g)$

(d) $Zn(s) + 2H^+(aq.) \longrightarrow Zn^{2+}(aq.) + H_2(g)$

SECTION-III

Assertion-Reason Type Questions

This section contains 6 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.

(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.

(c) Statement-1 is true; statement-2 is false.

(d) Statement-1 is false; statement-2 is true.

16. **Statement-1:** During the electrolysis of water, two faraday of charge will produce a total of 33.6 litre of gases at STP at electrodes.

Because

Statement-2: In the electrolysis of water, two faraday of charge will produce half mole of H_2 gas and one fourth mole of O_2 gas.

17. **Statement-1:** Aqueous solution of $CuSO_4$ turns colourless on complete electrolysis using platinum electrode.

Because

Statement-2: $CuSO_4$ is converted to $Cu(OH)_2$ on electrolysis.

18. **Statement-1:** Sodium ions are discharged at a mercury cathode in preference to hydrogen ion.

Because

Statement-2: Na^+ is stronger reducing agent than H^+.

19. **Statement-1:** KCl and NH_4Cl cannot be used in salt bridge of a cell containing Ag^+, Hg_2^{2+} and Tl^+ ions.

Because

Statement-2: Cell will be destroyed due to precipitation of metal chlorides.

20. **Statement-1:** The voltage of mercury cell remains constant for its life time.

Because

Statement-2: Overall cell reaction does not involve any ion.

21. **Statement-1:** In alkaline version of dry cell, NH_4Cl is replaced by KOH.

Because

Statement-2: Zinc container does not undergo corrosion in alkaline medium.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	●	○	○
d	○	○	○	●

22. Match the Column-I with Column-II:

Column-I	Column-II
(a) Nickel-Cadmium cell	(p) Used in auto vehicles
(b) Lithium battery	(q) Secondary cell
(c) $H_2 - O_2$ cell	(r) Fuel cell
(d) Lead storage battery	(s) Used in Apollo space craft

23. Match the Column-I with Column-II:

Column-I	Column-II
(a) Specific conductance, κ	(p) $\Lambda_m^c / \Lambda_m^\circ$
(b) Molar conductance, Λ_m	(q) Decreases with dilution
(c) Resistance of electrolyte solution, R	(r) Increases with dilution
(d) Degree of ionization of weak electrolyte, α	(s) Increases with increase in the distance between parallel plates

24. Match the Column-I with Column-II:

Column-I	Column-II
(a) Concentration cell	(p) Fe is oxidised by Ni_2O_3
(b) Edison cell	(q) Zinc anode
(c) Mercury cell	(r) HgO cathode
(d) Dry cell	(s) $E^\circ = 0$

SECTION-V

Linked Comprehension Type Questions

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential (E°) of two half-cells reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values.

$$I_2 + 2e^- \longrightarrow 2I^- \quad ; \quad E^\circ = 0.54$$
$$Cl_2 + 2e^- \longrightarrow 2Cl^- \quad ; \quad E^\circ = 1.36$$
$$Mn^{3+} + e^- \longrightarrow Mn^{2+} \quad ; \quad E^\circ = 1.50$$
$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \quad ; \quad E^\circ = 0.77$$
$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \quad ; \quad E^\circ = 1.23$$

(IIT 2007)

Answer the following questions:

25. Among the following, identify the correct statement:

(a) Chloride ion is oxidised by O_2

(b) Fe^{2+} is oxidised by iodine

(c) Iodide ion is oxidised by chlorine

(d) Mn^{2+} is oxidised by chlorine

[**Hint:** Species with greater reduction potential, oxidises other with lower reduction potential.]

26. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because:

(a) O_2 oxidises Mn^{2+} to Mn^{3+}

(b) O_2 oxidises both Mn^{2+} and Fe^{2+}

(c) Fe^{3+} oxidises H_2O to O_2

(d) Mn^{3+} oxidises H_2O to O_2

[**Hint:** Mn^{3+} oxidises H_2O to O_2 because the standard reduction potential of ($Mn^{3+} \longrightarrow Mn^{2+}$) is greater than that of ($O_2 \longrightarrow H_2O$).]

Answers

1. (d) **2.** (d) **3.** (c) **4.** (a) **5.** (b) **6.** (a) **7.** (d) **8.** (b)
9. (c) **10.** (a) **11.** (a, b, c, d) **12.** (a, b, d) **13.** (b, c) **14.** (a, b) **15.** (a, c) **16.** (c)
17. (c) **18.** (b) **19.** (a) **20.** (a) **21.** (a) **22.** (a-q) (b-q) (c-r,s) (d-p,q)
23. (a-q) (b-r) (c-q,s) (d-p,r) **24.** (a-s) (b-p) (c-q,r) (d-q) **25.** (c) **26.** (d)