7. ELECTROCHEMISTRY

1. ELECTROCHEMISTRY

Electrochemistry is the study of production of electricity from the energy released during a spontaneous chemical reaction and the use of electrical energy to bring about non-spontaneous chemical transformations.

2. ELECTROCHEMICAL CELLS

A spontaneous chemical process is the one which can take place on its own and in such a process the Gibb's energy of the system decreases. It is this energy that gets converted to electrical energy.The reverse process is also possible in which we can make non-spontaneous processes occur by supplying external energy in the form of electrical energy. These inter conversions are carried out in equipments called Electrochemical Cells.

3. TYPES

Electrochemical Cells are of two types:

3.1 Galvanic Cells

Converts chemical energy into electrical energy

3.2 Electrolytic Cells

Converts electrical energy into chemical energy.

4. GALVANIC CELL

Cell energy is extracted from a spontaneous chemical process or reaction and it is converted to electric current.

For example, Daniell Cell is a Galvanic Cell in which Zinc and Copper are used for the redox reaction to take place.

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

Oxidation Half : $Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2e^{-}$

Reduction Half : $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$

Zn is the reducing agent and Cu^{2+} is the oxidising agent.The half cells are also known as **Electrodes.** The oxidation half is known as **Anode** and the reduction half is called **Cathode**. Electrons flow from anode to cathode in the external circuit. Anode is assigned **negative polarity** and cathode is assigned **positive polarity**. In Daniell Cell, Zn acts as the anode and Cu acts as the cathode.

5. ELECTROLYTIC CELL

These electrodes are dipped in and electrolytic solution containing cations and anions. On supplying current the ions move towards electrodes of opposite polarity and simultaneous reduction and oxidation takes place.

5.1 Preferential Discharge of ions

Where there are more than one cation or anion the process of discharge becomes competitive in nature. Discharge of any ion requires energy and in case of several ions being present the discharge of that ion will take place first which requires the energy.

6. ELECTRODE POTENTIAL

It may be defined as the tendency of an element, when it is placed in contact with its own ions to either lose or gain electrons and in turn become positively or negatively charged.

The electrode potential will be named as oxidation or reduction potential depending upon whether oxidation or reduction has taken place.

$$M(s) \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} M^{n+}(aq) + ne^{-}$$

$$M^{n+}(aq) + ne^{-} \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} M(s)$$

6.1 Characteristics

(a) Both oxidation and reduction potentials are equal in magnitude but opposite in sign.

(b) It is not a thermodynamic property, so values of E are not additive.

7. STANDARD ELECTRODE POTENTIAL (E^{o})

It may be defined as the electrode potential of an electrode determined relative to standard hydrogen electrode under standard conditions. The standard conditions taken are :

(i) 1M concentration of each ion in the solution.

(ii) A temperature of 298 K.

(iii) 1 bar pressure for each gas.

8. ELECTROCHEMICAL SERIES

The half cell potential values are standard values and are represented as the standard reduction potential values as shown in the table at the end which is also called Electrochemical Series.

9. CELL POTENTIAL OR EMF OF A CELL

The difference between the electrode potentials of two half cells is called cell potential. It is known as electromotive force (EMF) of the cell if no current is drawn from the cell.

$$E_{cell} = E_{cathode} + E_{anode}$$

For this equation we take oxidation potential of anode and reduction potential of cathode.

Since anode is put on left and cathode on right, it follows therefore,

$$= E_R + E_L$$

For a Daniel cell, therefore

$$E^o_{cell} = E^o_{Cu^{2+}/Cu} - E^o_{Zn/Zn^{+2}} = 0.34 + (0.76) = 1.10\,V$$

10. CELL DIAGRAM OR REPRESENTATION OF A CELL

The following conventions or notations are applied for writing the cell diagram in accordance with IUPAC recommendations. The Daniel cell is represented as follows :

$$Zn(s)\,|\,Zn^{2+}(C_1)\,||\,Cu^{2+}(C_2)\,|\,Cu\,(s)$$

(a) Anode half cell is written on the left hand side while cathode half cell on right hand side.

(b) A single vertical line separates the metal from aqueous solution of its own ions.

$$\underset{\text{Anodic chamber}}{Zn(s)\,|\,Zn^{2+}(aq)}; \qquad \underset{\text{Cathodic chamber}}{Cu^{2+}(aq)\,|\,Cu(s)}$$

(c) A double vertical line represents salt bridge

(d) The molar concentration (C) is placed in brackets after the formula of the corresponding ion.

(e) The value of e.m.f. of the cell is written on the extreme right of the cell. For example,

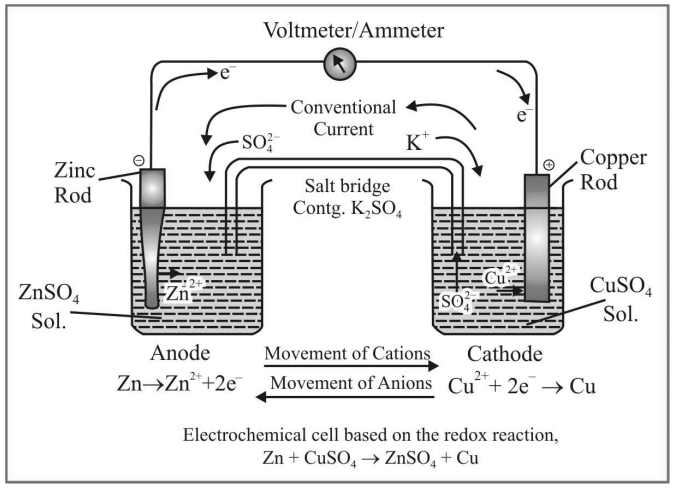
$$Zn(s)\,|\,Zn^{2+}(1\,M)\,||\,Cu^{2+}(1\,M)\,|\,Cu \quad EMF = +1.1V$$

(f) If an inert electrode like platinum is involved in the construction of the cell, it may be written along with the working electrode in bracket say for example, when a zinc anode is connected to a hydrogen electrode.

$$Zn(s)\,|\,Zn^{2+}(C_1)\,||\,H^+(C_2)\,|\,H_2\,|\,(Pt)(s)$$

11. SALT BRIDGE

Salt bridge is used to maintain the charge balance and to complete the circuit by facilitating the flow of ions through it. It contains a gel in which an inert electrolyte like Na_2SO_4 or KNO_3 etc are mixed. Negative ions flow to the anode and positive ions flow to the cathode through the salt bridge and charge balance is maintained and cell keeps on functioning.



Electrochemical cell based on the redox reaction, $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

12. SPONTANEITY OF A REACTION

$$\Delta G = -nFE_{CELL}$$

For a spontaneous cell reaction ΔG should be negative and cell potential should be positive.

If we take standard value of cell potential in the above equation we will obtain standard value of ΔG as well.

$$\Delta G^o = -nFE^0_{CELL}$$

13. TYPES OF ELECTRODES

13.1 Metal-Metal Ion electrodes

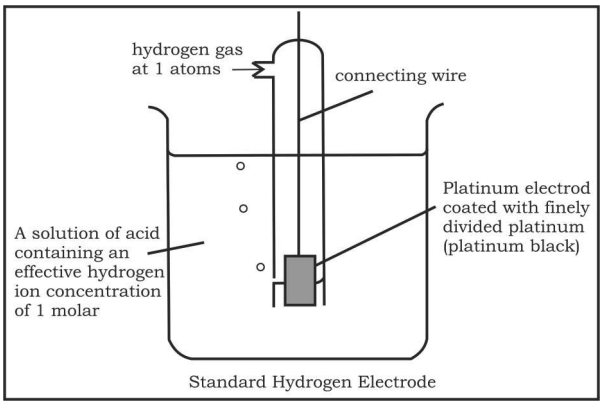
A metal rod/plate is dipped in an electrolyte solution containing metal ions. There is a potential difference between these two phases and this electrode can act as a cathode or anode both.

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

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

13.2 Gas Electrodes

Electrode gases like H_2, Cl_2 etc are used with their respective ions. For example, H_2 gas is used with a dilute solution of HCl (H^+ ions). The metal should be inert so that it does not react with the acid.



Anode: $H_2 \longrightarrow 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$

The hydrogen electrode is also used as the standard to measure other electrode potentials. Its own potential is set to 0 V as a reference. When it is used as a reference the concentration of dil HCl is taken as 1 M and the electrode is called "Standard Hydrogen Electrode (SHE)".

13.3 Metal-Insoluble salt electrode

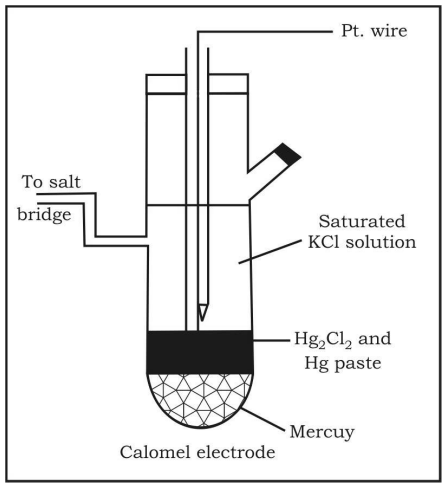
We use salts of some metals which are sparingly soluble with the metal itself as electrodes. For example, if we use AgCl with Ag there is a potential gap between these two phases which can be identified in the following reaction:

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$$

This electrode is made by dipping a silver rod in a solution containing AgCl(s) and Cl^- ions.

13.4 Calomel Electrode

Mercury is used with two other phases, one is a calomel paste (Hg_2Cl_2) and electrolyte containing Cl^- ions.



Cathode :

$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$

Anode :

$2Hg(l) + 2Cl^-(aq) \longrightarrow Hg_2Cl_2(s) + 2e^-$

This electrode is also used as another standard to measure other potentials. Its standard form is also called **Standard Calomel Electrode (SCE)**.

13.5 Redox Electrode

In these electrodes two different oxidation states of the same metal are used in the same half cell. For example, Fe^{2+} and Fe^{3+} are dissolved in the same container and an inert electrode of platinum is used for the electron transfer. Following reactions can take place:

Anode: $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

Cathode: $Fe^{3+} + e^- \longrightarrow Fe^{2+}$

14. NERNST EQUATION

It relates electrode potential with the concentration of ions.

Thus, the reduction potential increases with the increase in the concentration of ions. For a general electrochemical reaction of the type.

$$aA + bB \xrightarrow{ne^-} cC + dD$$

Nernst equation can be given as

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

$$E_{cell} = E^{o}_{cell} - \frac{2303}{nF} RT \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Substituting the values of R and F we get

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{at 298 K}$$

15. APPLICATIONS OF NERNST EQUATION

15.1 Equilibrium Constant from Nernst Equation

For a Daniel cell, at equilibrium

$$E_{cell} = 0 = E^{o}_{cell} - \frac{2.303\,RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

or $$E^{o}_{cell} = \frac{2.303\,RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium, $\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c$

$$E^{o}_{cell} = \frac{2.303\,RT}{2F} \log K_c$$

$$E^{o}_{cell} = \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log K_c$$

$$= \frac{0.0591}{2} \log K_c$$

In general, $E^{o}_{cell} = \frac{0.0591}{n} \log K_c$

or, $$\log K_C = \frac{n E^{o}_{cell}}{0.0591}$$

16. CONCENTRATION CELLS

If two electrodes of the same metal are dipped separately into two solutions of the same electrolyte having different concentrations and the solutions are connected through salt bridge, such cells are known as concentration cells. For example

$$H_2 | H^+(c_1) \| H^+(c_2) | H_2$$

$$Cu | Cu^{+2}(c_1) \| Cu^{2+}(c_2) | Cu$$

These are of two types :

16.1 Electrode concentration cells

$$H_2(P_1) | H^+(C) \| H^+(C) | H_2(P_2)$$

$$E_{cell} = 0 - \frac{0.059}{n} \log \frac{P_2}{P_1}$$

where $p_2 < p_1$ for spontaneous reaction

16.2 Electrolyte concentration cell

The EMF of concentration cell at 298 K is given by $Zn | Zn^{2+}(c_1) \| Zn^{2+}(c_2) | Zn$

$$E_{cell} = \frac{0.0591}{n_1} \log \frac{c_2}{c_1},$$

where $c_2 > c_1$ for spontaneous reaction

17. CASES OF ELECTROLYSIS

17.1 Electrolysis of molten sodium chloride

$$2NaCl(l) \rightleftharpoons 2Na^+(l) + 2Cl^-(l)$$

The reactions occurring at the two electrodes may be shown as follows :

At cathode :

$2Na^+ + 2e^- \rightarrow 2Na$ **$E^0 = -2.71$ V**

At anode :

$2Cl^- \rightarrow Cl_2 + 2e^-$ **$E^0 = -1.36$V**

Overall reaction :

$$2Na^+(l) + 2\,Cl^-(l) \xrightarrow{\text{Electrolysis}} 2Na(l) + Cl_2(g)$$

$$\text{or } 2NaCl(l) \xrightarrow{\text{Electrolysis}} 2Na(l) + Cl_2(g)$$

At cathode At anode

17.2 Electrolysis of an aqueous solution of sodium chloride

$NaCl\,(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$

(almost completely ionized)

$H_2O\,(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

(only slightly ionized)

At cathode :

$\mathbf{2Na^+ + 2e^- \longrightarrow 2Na \qquad E^0 = -2.71V}$

$\mathbf{2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad E^0 = -0.83V}$

Thus H_2 gas is evolved at cathode value Na^+ ions remain in solution.

At anode :

$\mathbf{2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad E^0 = -1.23V}$

$\mathbf{2Cl^- \longrightarrow Cl_2 + 2e^- \qquad E^0 = -1.36V}$

Thus, Cl_2 gas is evolved at the anode by **over voltage** concept while OH^- ions remain in the solution.

18. BATTERIES

When Galvanic cells are connected in series to obtain a higher voltage the arrangement is called Battery.

18.1 Primary Batteries

Primary cells are those which can be used so long the active materials are present. Once they get consumed the cell will stop functioning and cannot be re-used. Example Dry Cell or Leclanche cell and Mercury cell.

18.2 Dry cell

Anode : Zn container

Cathode : Carbon (graphite) rod surrounded by powdered MnO_2 and carbon.

Electrolyte : NH_4Cl and $ZnCl_2$

Reaction :

Anode : $\mathbf{Zn \longrightarrow Zn^{2+} + 2e^-}$

Cathode : $\mathbf{MnO_2 + NH_4^+ + e^- \longrightarrow MnO\,(OH) + NH_3}$

The standard potential of this cell is 1.5 V and it falls as the cell gets discharged continuously and once used it cannot be recharged.

18.3 Mercury cells

These are used in small equipments like watches, hearing aids.

Anode : Zn – Hg Amalgam

Cathode : Paste of HgO and carbon

Electrolyte : Paste of KOH and ZnO

Anode : $\mathbf{Zn\,(Hg) + 2OH^- \longrightarrow ZnO\,(s) + H_2O + 2e^-}$

Cathode : $\mathbf{HgO\,(s) + H_2O + 2e^- \longrightarrow Hg\,(\mathit{l}) + 2OH^-}$

Overall Reaction : $\mathbf{Zn\,(Hg) + HgO\,(s) \longrightarrow ZnO\,(s) + Hg\,(\mathit{l})}$

The cell potential is approximately 1.35V and remains constant during its life.

18.4 Secondary Batteries

Secondary cells are those which can be recharged again and again for multiple uses. e.g. lead storage battery and Ni – Cd battery.

18.5 Lead Storage Battery

Anode : Lead (Pb)

Cathode : Grid of lead packed with lead oxide (PbO_2)

Electrolyte : 38% solution of H_2SO_4

Discharging Reactions

Anode: $\mathbf{Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-}$

Cathode: $\mathbf{PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(\mathit{l})}$

Overall Reaction : $\mathbf{Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(\mathit{l})}$

To recharge the cell, it is connected with a cell of higher potential and this cell behaves as an electrolytic cell and the reactions are reversed. Pb(s) and PbO_2(s) are regenerated at the respective electrodes.These cells deliver an almost consistent voltage.

Recharging Reaction : $\mathbf{2PbSO_4(s) + 2H_2O(\mathit{l}) \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)}$

19. FUEL CELLS

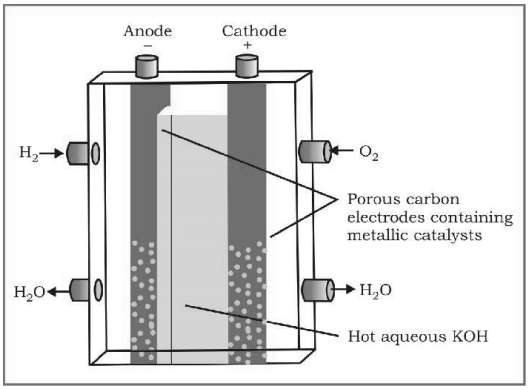
A fuel cell differs from an ordinary battery in the sense that the reactants are not contained inside the cell but are

externally supplied from an external reservoir. Fuel cell is used in space vehicles and in this cell the two gases are supplied from external storages. In this cell carbon rods are used as electrodes with KOH as the electrolyte.

Cathode : $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Anode : $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

overall Reaction : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$



20. CORROSION

It involves a redox reaction and formation of an electrochemical cell on the surface of iron or any other metal.

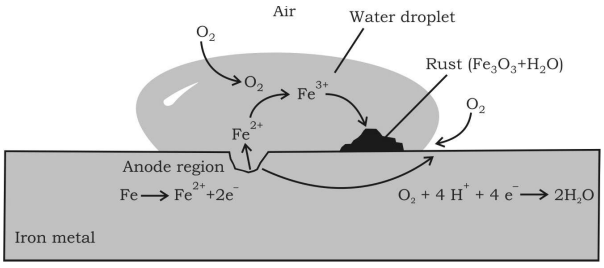
At one location oxidation of iron takes place (anode) and at another location reduction of oxygen to form water takes place (cathode). First Fe gets oxidised to Fe^{2+} and then in the presence of oxygen it forms Fe^{3+} which then reacts with water to form rust which is represented by $Fe_2O_3.xH_2O$.

Anode : $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$ $E^\circ = +0.44$ V

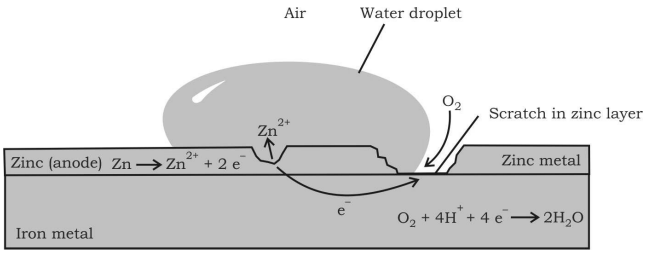
Cathode : $O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$ $E^\circ = 1.23$ V

Overall R × N :

$2Fe(s) + O_2(q) + 4H^+ \rightarrow 2Fe^{2+} + + 2H_2O$ $E^\circ_{cell} = 1.67$ M



Rusting of iron can be avoided by painting it or by coating it with some other metals like Zinc. The latter process is known as **Galvanisation**. As the tendency of Zn to get oxidised is more than iron it gets oxidised in preference and iron is protected. This method of protecting one metal by the other is also called **Cathodic Protection.**



21. CONDUCTANCE (G)

It is the reciprocal of resistance and may be defined as the ease with which the electric current flows through a conductor.

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

SI unit is Siemen (S).

$$1\ S = 1\ ohm^{-1}\ (mho)$$

22. CONDUCTIVITY (κ)

It is the reciprocal of resistivity (ρ).

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{\ell}{A} = G \times \frac{\ell}{A}$$

Now if $\ell = 1$ cm and $A = 1$ cm^2, then $\kappa = G$.

Hence, conductivity of an electrolytic solution may be defined as the conductance of a solution of 1 cm length with area of cross-section equal to 1 cm^2.

23. FACTORS AFFECTING ELECTROLY CONDUCTANCE

23.1 Electrolyte

An electrolyte is a substance that dissociates in solution to produce ions and hence conducts electricity in dissolved or molten state.

Examples : HCl, NaOH, KCl (Strong electrolytes).

CH_3–COOH, NH_4OH (Weak electrolytes).

The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The following factors govern the flow of electricity through a solution of electrolyte.

(i) **Nature of electrolyte or interionic attractions :** Lesser the solute-solute interactions, greater will be the freedom of movement of ions and higher will be the conductance.

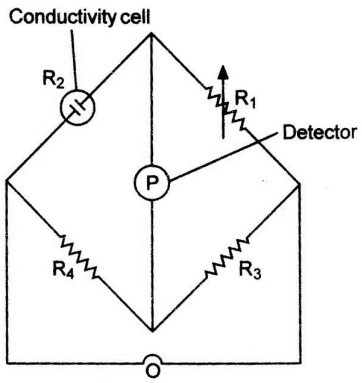
(ii) **Solvation of Ions :** Larger the magnitude of solute-solvent interactions, greater is the extent of solvation and lower will be the electrical conductance.

(iii) **The nature of solvent and its viscosity :** Larger the solvent-solvent interactions, larger will be viscosity and more will be the resistance offered by the solvent to flow of ions and hence lesser will be the electrical conductance.

(iv) **Temperature :** As the temperature of electrolytic solution rises solute-solute, solute-solvent and solvent-solvent interactions decreases, this results in the increase of electrolytic conductance.

24. MEASUREMENT OF CONDUCTANCE

As we know, $\kappa = \frac{1}{R} \times \frac{\ell}{A}$ The value of κ could be known, if we measure *l*, A and R. The value of the resistance of the solution R between two parallel electrodes is determined by using **'Wheatstones' bridge method** (Fig.)



Wheatstone Bridge

It consists of two fixed resistance R_3 and R_4, a variable resistance R_1 and the conductivity cell having the unknown resistance R_2. The bridge is balanced when no current passes through the detector. Under these conditions,

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \quad \text{or} \quad R_2 = \frac{R_1 R_4}{R_3}$$

25. MOLAR CONDUCTIVITY (Λ_m)

It may be defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte placed between two large electrodes at one centimeter apart.

Mathematically,

$$\Lambda_m = \kappa \times V, \quad \Lambda_m = \frac{\kappa \times 1000}{C}$$

where, V is the volume of solution in cm^3 containing 1 mole of electrolyte and C is the molar concentration.

Units : $\Lambda_m = \frac{\kappa \times 1000}{C} = \frac{S\ cm^{-1}}{mol\ cm^{-3}}$

$= ohm^{-1}\ cm^2\ mol^{-1}$ or $S\ cm^2\ mol^{-1}$

26. EQUIVALENT CONDUCTIVITY (Λ_{eq})

It is conducting power of one equivalent of electrolyte placed between two large electrodes at one centimeter apart.

Mathematically :

$$\Lambda_{eq} = \kappa \times v =$$

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

Where, v is the volume of solution in cm^3 containing 1 equivalent of electrolyte and N is normality.

Units :

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

$$= \frac{S\ cm^{-1}}{equivalent\ cm^{-3}} = \text{or} \quad \frac{Ohm^{-1}\ cm^2\ equivalent^{-1}}{S\ cm^2\ equivalent^{-1}}$$

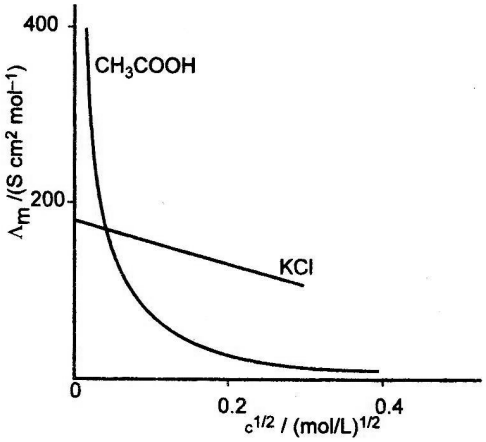
27. VARIATION OF CONDUCTIVITY AND MOLAR CONDUCTIVITY WITH DILUTION

Conductivity decreases with decrease in concentration, this is because the number of ions per unit volume that carry the current in the solution decreases on dilution.

Molar conductivity $(\Lambda_m = \kappa \times V)$ increases with decrease in concentration. This is because the total volume V of solution containing one mole of electrolyte also increases.

It has been found that the decrease in κ on dilution of a solution is more than compensated by increases in its volume.

Graphic representation of the variation of Λ_m vs $\sqrt{c}$



28. LIMITING MOLAR CONDUCTIVITY (Λ_m)

The value of molar conductivity when the concentration approaches zero is known as limiting molar conductivity or molar conductivity at infinite dilution. It is possible to determine the molar conductivity at infinite dilution $\left(\Lambda_m^o\right)$ in case of strong electrolyte by extrapolation of curve of Λ_m vs$\sqrt{c}$. On contrary, the value of molar conductivity of weak electrolyte at infinite dilution cannot be determined by extapolation of the curve as the curve becomes almost parallel to y-axis when concentration approaches to zero.

The mathematical relationship between Λ_m and Λ_m^o for strong electrolyte was developed by Debye, Huckel and Onsagar. In simplified form the equation can be given as

$$\Lambda_m = \Lambda_m^\infty - b\ c^{1/2}$$

where Λ_m^∞ is the molar conductivity at infinite dilution and b is a constant which depends on the nature of the solvent and temperature.

29. KOHLRAUSCH'S LAW

It states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. In general, if an electrolyte on dissociation gives v_+ cations and v_- anions then its limiting molar conductivity is given by

$$\Lambda_m^\infty = v_+\lambda_+^o + v_-\lambda_-^o$$

Here, λ_+^o and λ_-^o are the limiting molar conductivities of cations and anions respectively.

30. APPLICATIONS OF KOHLRAUSCH'S LAW

30.1 (i) Calculation of molar conductivities of weak electrolyte at infinite dilution

For example, molar conductivity of acetic acid at infinite dilution can be obtained from the knowledge of molar conductivities at infinite dilution of strong electrolyte like HCl, CH_3COONa and NaCl as illustrated below.

$$\Lambda^o_{m(CH_3-COOH)} = \lambda^o_{CH_3-COO^\ominus} + \lambda^o_{H^+}$$

$$= \left[\lambda^o_{CH_3-COO^-} + \lambda^o_{Na^+}\right] + \left[\lambda^o_{H^+} + \lambda_{Cl^-}\right] - \left[\lambda^o_{Na^+} + \lambda^o_{Cl^-}\right]$$

i.e. $\Lambda^o_{m(CH_3-COOH)} = \Lambda^o_{m(CH_3-COONa)} + \Lambda^o_{m(HCl)} - \Lambda^o_{m(NaCl)}$

30.2 (ii) Determination of Degree of Dissociation of Weak Electrolytes

Degree of dissociation $(\alpha) = \dfrac{\Lambda_m^c}{\Lambda_m^o}$

30.3 (iii) Determination of Dissociation Constant (K) of Weak Electrolytes:

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

also $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^\infty}$

$\therefore$ $K = \dfrac{c\left(\Lambda_m^c/\Lambda_m^\infty\right)^2}{1-\Lambda_m^c/\Lambda_m^\infty} = \dfrac{C\left(\Lambda_m^c\right)^2}{\Lambda_m^\infty\left(\Lambda_m^\infty - \Lambda_m^c\right)}$

31. USE OF ΔG IN RELATING EMF VALUES OF HALF CELL REACTIONS

When we have two half cell reactions such that on adding them we obtain another half cell reaction then their emfs cannot be added directly. But in any case thermodynamic functions like ΔG can be added and emf values can be related through them. Consider the following three half cell reactions:

$$Fe^{2+} + 2e^- \rightarrow Fe \quad E_1$$

$$Fe^{3+} + 3e^- \rightarrow Fe \quad E_2$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E_3$$

We can easily observe that the third reaction can be obtained by subtracting the first reaction from the second. But the same relation does not apply on the emf values. That is, $E_3 \neq E_2 - E_1$. But the ΔG values can be related according to the reactions. That is,

$$\Delta G_3 = \Delta G_2 - \Delta G_1$$

$$-n_3FE_3 = -n_2FE_2 + n_1FE_1$$

$$-E_3 = -3E_2 + 2E_1$$

$$\Rightarrow \mathbf{E_3 = 3E_2 - 2E_1}$$

NOTE

We should always remember that emf values are additive only when two half cell reactions are added to give a complete balanced cell reaction. In any other case we will be using ΔG values to obtain relations between emf values.

32. FORMULAE

1. $R = \rho\left(\frac{\ell}{A}\right) = \rho \times$ Cell constant

where, R = Resistance

A = Area of cross-section of the electrodes.

ρ = Resistivity

2. $\kappa = \frac{1}{R} \times$ cell constant

where, κ = Conductivity or specific conductance

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

where, Λ_m = Molar conductivity

M = Molarity of the solution.

4. $\Lambda_m^\infty (A_x B_y) = x\,\Lambda_m^\infty (A^{y+}) + y\,\Lambda_m^\infty (B^{x-})$

where, Λ_m^∞ = Molar conductivity at infinite dilution x and y are the number of cations and anions produced by one formula unit of the electrolyte on complete dissociation.

5. $\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty}$

where, α = Degree of dissociation

Λ_m^c = Molar conductivity at a given concentration

6. For a weak binary electrolyte AB

$$K = \frac{c\alpha^2}{1-\alpha} = \frac{c\left(\Lambda_m^c\right)^2}{\Lambda_m^\infty\left(\Lambda_m^\infty - \Lambda_m^c\right)}$$

where, K = Dissociation constant

$$E_{cell}^o = E_{cathode}^o + E_{anode}^o$$

$$= E^o \text{ Right} + E^o \text{ left}$$

7. Nernst equation for a general electrochemical reaction

$$aA + bB \xrightarrow{ne^-} cC + dD$$

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

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

$$E_{cell} = E_{cell}^o - \frac{0.059}{n} \log \frac{[A]^a[B]^b}{[C]^c[D]^d} \quad \text{at 298 K}$$

8. $\log K_c = \frac{n}{0.0591} E_{cell}^o$

where, K_c = Equilibrium constant.

9. $\Delta_r G^o = -nFE_{cell}^o$ (Creterion of spontaneity)

$\Delta_r G^o = -2.303RT \log K_c$

where, $\Delta_r G^o$ = Standard Gibbs energy of the reaction.

10. $Q = I \times t$

where Q = Quantity of charge in coulombs

I = Current in amperes

t = Time in seconds

11. $m = Z \times I \times t$

where m = mass of the substance liberated at the electrodes

Z = Electrochemical equivalent.

where E = Equivalent weight = E/96500

STANDARD REDUCTION POTENTIALS AT 298 K. IN ELECTROCHEMICAL ORDER

$H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$	+3.0
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	+2.07
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+2.05
$Ag^{2+} + e^- \rightarrow Ag^+$	+1.98
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.78
$Au^+ + e^- \rightarrow Au$	+1.69
$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$	+1.67
$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	+1.63
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$	+1.60
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.51
$Au^{3+} + 3e^- \rightarrow Au$	+1.40
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33
$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	+1.24
$O_2 + 4H^+ 4e^- \rightarrow 2H_2O$	+1.23
$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	+1.23
$MNO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Pu^{4+} + e^- \rightarrow Pu^{3+}$	+0.97
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+0.96
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+0.92
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	+0.89
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.86
$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	+0.80
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+0.79
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	+0.76
$Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-}$	+0.62
$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$	+0.60
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.56
$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$Cu^+ + e^- \rightarrow Cu$	+0.52
$I_3^- + 2e^- \rightarrow 3I^-$	+0.53
$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$	+0.49
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	+0.45
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40
$ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$	+0.36
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	+0.36
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.27
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22
$Bi + 3e^- \rightarrow Bi$	+0.20
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.16
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
$AgBr + e^- \rightarrow Ag + Br^-$	+0.07
$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
$2H^+ + 2e^- \rightarrow H_2$	0, by definition
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.04
$O_2\ H_2O + 2e^- \rightarrow HO_2^- + OH^-$	−0.08
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$In^+ + e^- \rightarrow In$	−0.14
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$AgI + e^- \rightarrow Ag + I^-$	−0.15
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$In^{3+} + 3e^- \rightarrow In$	−0.34
$Tl^+ e^- \rightarrow Tl$	−0.34
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.36

$Ti^{3+} + e^- \rightarrow Ti^{2+}$	-0.37
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$In^{2+} + e^- \rightarrow In^+$	-0.40
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.41
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$In^{3+} + 2e^- \rightarrow In^+$	-0.44
$S + 2e^- \rightarrow S^{2-}$	-0.48
$In^{3+} + e^- \rightarrow In^{2+}$	-0.49
$U^{4+} + e^- \rightarrow U^{3+}$	-0.61
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	-0.81
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$Cr^{2+} + 2e^- \rightarrow Cr$	-0.91
$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$V^{2+} + 2e^- \rightarrow V$	-1.19
$Ti^{2+} + 2e^- \rightarrow Ti$	-1.63
$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$U^{3+} + 3e^- \rightarrow U$	-1.79
$Sc^{3+} + 3e^- \rightarrow Sc$	-2.09
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.36
$Ce^{3+} + 3e^- \rightarrow Ce$	-2.48
$La^{3+} + 3e^- \rightarrow La$	-2.52
$Na^+ + e^- \rightarrow Na$	-2.71
$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
$Sr^{2+} + 2e^- \rightarrow Sr$	-2.89
$Ba^{2+} + 2e^- \rightarrow Ba$	-2.91
$Ra^{2+} + 2e^- \rightarrow Ra$	-2.92
$Cs^+ + e^- \rightarrow Cs$	-2.92
$Rb^+ + e^- \rightarrow Rb$	-2.93
$K^+ + e^- \rightarrow K$	-2.93
$Li^+ + e^- \rightarrow Li$	-3.05

REDUCTION POTENTIALS IN ALPHABETICAL ORDER

$Ag^+ + e^- \rightarrow Ag$	$+0.80$
$Ag^{2+} + e^- \rightarrow Ag^+$	$+1.98$
$AgBr + e^- \rightarrow Ag + Br^-$	$+0.0713$
$AgCl + e^- \rightarrow Ag + Cl^-$	$+0.22$
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	$+0.45$
$AgF + e^- \rightarrow Ag + F^-$	$+0.78$
$AgI + e^- \rightarrow Ag + I^-$	-0.15
$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$Au^+ + e^- \rightarrow Au$	$+1.69$
$Au^{3+} + 3e^- \rightarrow Au$	$+1.40$
$Ba^{2+} + 2e^- \rightarrow Ba$	$+2.91$
$Be^{2+} + 2e^- \rightarrow Be$	-1.85
$Bi^{3+} + 3e^- \rightarrow Bi$	$+0.20$
$Br_2 + 2e^- \rightarrow 2Br^-$	$+1.09$
$BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	$+0.76$
$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	-0.81
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$Ce^{3+} + 3e^- \rightarrow Ce$	-2.48
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	$+1.61$
$Cl_2 + 2e^- \rightarrow 2Cl^-$	$+1.36$
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	$+0.89$
$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	$+1.23$
$ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$	$+0.36$
$Co^{2+} + 2e^- \rightarrow Co$	-0.28
$Co^{3+} + e^- \rightarrow Co^{2+}$	$+1.81$
$Cr^{2+} + 2e^- \rightarrow Cr$	-0.91
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	$+1.33$
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.41

$Cs^+ e^- \rightarrow Cs$	-2.92
$Cu^+ + e^- \rightarrow Cu$	$+0.52$
$Cu^{2+} + 2e^- \rightarrow Cu$	$+0.34$
$Cu^{2+} + e^- \rightarrow Cu^+$	$+0.16$
$F_2 + 2e^- \rightarrow 2F^-$	$+2.87$
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$Fe^{3+} + 3e^- \rightarrow Fe$	-0.04
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$+0.77$
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	$+0.36$
$2H^+ + 2e^- \rightarrow H_2$	0, by definition
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$	$+1.60$
$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	$+1.63$
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	$+1.78$
$H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$	$+3.0$
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	$+0.79$
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	$+0.27$
$Hg^{2+} + 2e^- \rightarrow Hg$	$+0.86$
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	$+0.92$
$Hg_2SO_4 + 2e- \rightarrow 2Hg + SO_4^{2-}$	$+0.62$
$I_2 + 2e^- \rightarrow 2I^-$	$+0.54$
$I_3^- + 2e^- \rightarrow 3I^-$	$+0.53$
$In^+ + e^- \rightarrow In$	-0.14
$In^{2+} + e^- \rightarrow In^+$	-0.40
$In^{3+} + 2e^- \rightarrow In^+$	-0.44
$In^{3+} + 3e^- \rightarrow In$	-0.34
$In^{3+} + e^- \rightarrow In^{2+}$	-0.49
$K^+ + e^- \rightarrow K$	-2.93
$La^{3+} + 3e^- \rightarrow La$	-2.52
$Li+ e^- \rightarrow Li$	-3.05
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.36
$Mn^{2+} + 2e^- \rightarrow M_n$	-1.18
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	$+1.51$
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	$+1.23$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	$+1.51$
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	$+0.56$
$MnO_4^- + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$	$+0.60$
$Na^+ + e^- \rightarrow Na$	-2.71
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$	$+0.49$
$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	-0.80
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	$+0.96$
$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$	$+0.10$
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$+0.40$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$+1.23$
$O_2 + e^- \rightarrow O_2^-$	-0.56
$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	-0.08
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	$+2.07$
$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	$+1.24$
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$	$+1.67$
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.36
$Pt^{2+} + 2e^- \rightarrow Pt$	$+1.20$
$Pu^{4+} + e^- \rightarrow Pu^{3+}$	$+0.97$
$Ra^{2+} + 2e^- \rightarrow Ra$	-2.92
$Rb^+ + e^- \rightarrow Rb$	-2.93
$S + 2e^- \rightarrow S^{2-}$	-0.48
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	$+2.05$
$SC^{3+} + 3e^- \rightarrow Sc$	-2.09
$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	$+0.15$
$Sr^{2+} + 2e^- \rightarrow Sr$	-2.89
$Ti^{2+} + 2e^- \rightarrow Ti$	-1.63
$Ti^{3+} + e^- \rightarrow Ti^{2+}$	-0.37
$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
$Tl^+ + e^- \rightarrow Tl$	-0.34
$U^{3+} + 3e^- \rightarrow U$	-1.79
$U^{4+} + e^- \rightarrow U^{3+}$	-0.61
$V^{2+} + 2e^- \rightarrow V$	-1.19
$V^{3+} + e^- \rightarrow V^{2+}$	-0.26
$Zn^{2+} + 2e- \rightarrow Zn$	-0.76

SOLVED EXAMPLES

Example – 1

Give the relationship between equivalent and molar conductance ?

Sol. $\Lambda_m = \kappa \times \frac{1000}{\text{Molarity}}$ and $\Lambda_{eq} = \kappa \times \frac{1000}{\text{Normality}}$

$\therefore \quad \frac{\Lambda_m}{\Lambda_{eq}} = \frac{\text{Normality}}{\text{Molarity}}$

Example – 2

Can nickel spatula be used to stir a copper sulphate solution ? Support your answer with a reason

$E^o_{Ni^{2+}/Ni} = -0.25$ V, $E^o_{Cu^{2+}/Cu} = +0.34$ V.

Sol. $E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$E^o_{cell} = E^o_{Cu^{2+}/Cu} - E^o_{Ni^{2+}/Ni} = +0.34 \text{ V} - (-0.25) = +0.59 \text{ V}$

As E^o_{cell} is +ve, ΔG = – ve, because $\Delta G = -nE^o F$, i.e, reaction will take place. Therefore, we cannot stir a copper sulphate solution with nickel spatula.

Example – 3

State two advantages of H_2—O_2 fuel cell over ordinary cell.

Sol. The two advantages of H_2—O_2 fuel cell over ordinary cell are :

(i) They do not cause any pollution.

(ii) They have high efficiency of 60-70%.

Example – 4

What is galvanisation ?

Sol. The process of coating zinc over iron is called galvanisation.

Example – 5

Which type of a metal can be used in cathodic protection of iron against rusting ?

Sol. A metal which is more electropositive than iron such as Al, Zn, Mg can be used in cathode protection of iron against rusting.

Example – 6

Write the chemical equations for all the steps involved in the rusting of iron, Give any one method to prevent rusting of iron.

Sol. **Anode:** $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$, $E^o_{Fe^{2+}/Fe} = -0.44$ V

Cathode : $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$,

$E^o_{H^+/O_2/H_2O} = 1.23$ V

Overall reaction

$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-] \times 2$

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

$2Fe + O_2 + 4H^+(aq) \longrightarrow 2Fe^{2+} + 2H_2O$ $E^o_{cell} = 1.67$V

Further $4Fe^{2+}(aq) + O_2(g) + 4H_2O(l) \longrightarrow 2Fe_2O_3 + 8H^+(aq)$

$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3 . xH_2O$

Hydrated ferric oxide (Rust)

Galvanisation is used to prevent rusting of iron.

Example – 7

The following chemical reaction is occurring in an electrochemical cell.

$Mg(s) + 2Ag^+(0.0001\text{ M}) \longrightarrow Mg^{2+}(0.10\text{M}) + 2Ag(s)$

The E^o electrode values are

$Mg^{2+}/Mg = -2.36$ V

$Ag^+/Ag = 0.81$ V

For this cell calculate/write

(a) (i) E^o value for the electrode $2Ag^+/2Ag$.

(ii) Standard cell potential E^o_{cell}.

(b) Cell potential $(E)_{cell}$

(c) (i) Symbolic representation of the above cell.

(ii) Will the above cell reaction be spontaneous ?

Sol. (a) (i) $E^o_{Ag^+/Ag} = 0.81$V

(ii) $E^o_{cell} = E^o_{cathode} + E^o_{anode}$

$= E^o_{Ag^+/Ag} + E^o_{Mg/Mg^{+2}} = 0.81 + 2.36$

$E^o_{cell} = 3.17\,V$

(b) At anode : $Mg \longrightarrow Mg^{2+} + 2e^-$

A cathode : $Ag^+ + e^- \longrightarrow Ag \quad] \times 2$

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

$$E_{cell} = E^o_{cell} - \frac{0.059}{n}\log\frac{\left[Mg^{2+}\right]}{\left[Ag^+\right]^2}$$

$$= 3.17 - \frac{0.059}{2}\log\frac{0.1}{\left(10^{-4}\right)^2}$$

$= 3.17 - 0.0295 \log 10^7$

$= 3.17 - 0.0295 \times 7 = 3.17 - 0.21$

$E_{cell} = 2.96\,V$

(c) (i) $Mg\,|\,Mg^{2+}(0.1\,M)\,||\,Ag^+(0.0001M)\,|\,Ag$

(ii) Yes, as the cell potential is positive.

Example – 8

(a) Current of 1.50 A was passed through an electrolytic cell containing $AgNO_3$ solution with inert electrodes. The weight of Ag deposited was 1.50g. How long did the current flow ?

(b) Write the reactions taking place at the anode and cathode in the above cell if inert electrodes are used.

(c) Give reactions taking place at the two electrodes if these are made up of Ag.

Sol. (a) According to Faraday's first law, charge required to deposit 1.50 g.

$$Ag = \frac{96500}{108} \times 1.50 = 1331.70 \text{ coulombs}$$

$$\text{Time taken} = \frac{1331.70}{1.50} = 893.5\,s$$

(b) Inert electrodes

Anode: $2H_2O(\ell) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode : $Ag^+(aq) + e^- \longrightarrow Ag(s)$

(c) Ag electrodes

Anode : $Ag(s) \longrightarrow Ag^+(aq) + e^-$

Cathode : $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Example – 9

Explain Kohlrausch's law of independent migration of ions. Mention one application of Kohlrausch's law.

Sol. **Kohlrausch's law of independent migration of ions:** The molar conductivity of an electrolyte at infinite dilution is the sum of the individual contributions of the anion and cation of the electrolyte.

$$\Lambda^0 = v_+ \lambda^0_+ + v_- \lambda^0_-$$

where, λ^0_+ and λ^0_- are the limiting molar conductivities of the cation and anion respectively and v_+ and v_- are the number of cations and anions formed from a formula unit of the electrolyte. For example, one formula unit of $Al_2(SO_4)_3$ gives two Al^{3+} ions and three sulphate ions. Therefore,

$$\Lambda^o_{m(Al_2(SO_4)_3)} = 2\lambda^o_{Al^{3+}} + 3\lambda^o_{SO_4^{2-}}$$

Application : It can be used to determine molar conductivity of weak electrolytes at infinite dilution :

Consider acetic acid as the example of a weak electrolyte.

$$\Lambda^o_{m(CH_3COONa)} = \lambda^o_{CH_3COO^-} + \lambda^o_{Na^+}$$

$$\Lambda^o_{m(HCl)} = \lambda^o_{H^+} + \lambda^o_{Cl^-}$$

$$\Lambda^o_{m(NaCl)} = \lambda^o_{Na^+} + \lambda^o_{Cl^-}$$

From (i) + (ii) – (iii) we get

$$\lambda^o_{CH_3COO^-} + \lambda^o_{Na^+} + \lambda^o_{H^+} + \lambda^o_{Cl^-} - \lambda^o_{Na^+} - \lambda^o_{Cl^-}$$

$$= \lambda^o_{CH_3COO^-} + \lambda^o_{H^+} = \Lambda^o_{CH_3COOH}$$

Example – 10

The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Sol. $A = \pi r^2 = 3.14 \times 0.5^2\,cm^2 = 0.785\,cm^2 = 0.785 \times 10^{-4}\,m^2$,

$l = 50\,cm = 0.5\,m$

$$R = \frac{\rho \ell}{A} \text{ or } \rho = \frac{RA}{\ell} = \frac{5.55 \times 10^3 \Omega \times 0.785}{50 \text{ cm}} =$$

$$= 87.135 \, \Omega \, \text{cm}$$

$$\text{Conductivity} = \kappa = \frac{1}{\rho} = \left(\frac{1}{87.135}\right) \text{S cm}^{-1} = 0.01148 \text{ S cm}^{-1}$$

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{c}$$

$$= \frac{0.01148 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.05 \text{ mol L}^{-1}} = 229.6 \text{ S cm}^2 \text{ mol}^{-1}$$

Example – 11

The measured resistance of a conductance cell containing 7.5×10^{-3} M solution of KCl at 25°C was 1005 ohms. Calculate (a) specific conductance (b) molar conductance of the solution. Cell constant = 1.25 cm^{-1}.

Sol. Specific conductance $(\kappa) = \frac{1}{R} \times$ cell constant

$$= \frac{1}{1005 \, \Omega} \times 1.25 \text{ cm}^{-1} = 0.001244 \, \Omega^{-1} \text{ cm}^{-1}$$

Molar conductance $(\Lambda_m) = \frac{\kappa \times 1000}{\text{Molarity}}$

$$= \frac{0.001244 \, \Omega^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{7.5 \times 10^{-3} \text{ mol L}^{-1}}$$

$$= 165.87 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}.$$

Example – 12

Λ_m for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ_m^0 for HAc.

Sol. $\Lambda^0_{m(HAc)} = \lambda^o_{H^+} + \lambda^o_{Ac} = \lambda^o_{H^+} + \lambda^o_{Cl^-} + \lambda^o_{Ac^-} + \lambda^o_{Na^+} - \lambda^o_{Cl^-} - \lambda^o_{Na^+}$

$= \Lambda^o_{m(HCl)} + \Lambda^o_{m(NaAc)} - \Lambda^o_{m(NaCl)}$

$= (425.9 + 91.0 - 126.4) \text{ S cm}^2 \text{ mol}^{-1}$

$= 390.5 \text{ S cm}^2 \text{ mol}^{-1}$.

Example – 13

The conductivity of 0.0011028 mol L^{-1} acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate its dissociation constant if Λ^o_m for acetic acid is 390.5 S cm^2 mol^{-1}.

Sol. $\Lambda_m = \frac{\kappa}{c} = \frac{4.95 \times 10^{-5} \text{ S cm}^{-1}}{0.001028 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$

$= 44.88 \text{ S cm}^2 \text{ mol}^{-1}$

$\alpha = \frac{\Lambda_m}{\Lambda^o_m} = \frac{44.88 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.115$

$K = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028 \text{ mol L}^{-1} \times (0.115)^2}{0.115}$

$= 1.65 \times 10^{-5} \text{ mol L}^{-1}$

Example – 14

A cell is prepared by dipping copper rod in 1 M copper sulphate solution and zinc rod in 1 M zinc sulphate solution. The standard reduction potentials of copper and zinc are 0.34 V and – 0.76 V respectively.

(i) What will be the cell reaction?

(ii) What will be the standard electromotive force (EMF) of the cell ?

(iii) Which electrode will be positive ?

(iv) How will the cell be represented ?

Sol. (i) The cell reaction can be

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

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

The EMF comes out to be positive for the 1st reaction. Hence, the cell reaction is

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

(ii) $E^o_{cell} = E^o_{cathode} + E^o_{anode} = E^o_{Cu^{2+}/Cu} + E^o_{Zn/Zn^{+2}}$

$= 0.34 + 0.76 = 1.10 \text{ V}$

(iii) reduction takes place on copper electrode. Hence it is positive

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

Example – 15

Represent the cell in which the following reaction takes place

$Mg(s) + 2Ag^{+}(0.0001\ M) \rightarrow Mg^{2+}(0.130\ M) + 2\,Ag\ 9\,(s)$

Calculate its $E_{(cell)}$ if $E^{o}_{(cell)} = 3.17$ V.

Sol. The cell can be written as $Mg \mid Mg^{2+}(0.130\ M) \parallel Ag^{+}(0.0001\ M) \mid Ag$

$$E_{(cell)} = E^{o}_{(cell)} - \frac{RT}{nF}\ln\frac{\left[Mg^{2+}\right]}{\left[Ag^{+}\right]^2} = E^{o}_{(cell)} - \frac{2.303\,RT}{2F}\log\frac{\left[Mg^{2+}\right]}{\left[Ag^{+}\right]}$$

$$= 3.17\,V - \frac{0.059\,V}{2}\log\frac{0.130}{(0.0001)^2}$$

$$= 3.17\,V - 0.21\,V = 2.96\,V$$

Example – 16

A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential $\left(E^{o}_{Zn^{2+}/Zn} = -0.76\,V\right)$.

Sol. The electrode reaction written as reduction reaction is

$$Zn^{2+} + 2e^{-} \rightarrow Zn\ (n = 2)$$

Applying Nernst equation, we get

$$E_{Zn^{2+}/Zn} = E^{o}_{Zn^{2+}/Zn} - \frac{0.0591}{2}\log\frac{1}{\left[Zn^{2+}\right]}$$

As 0.1 M $ZnSO_4$ solution is 95% dissociated, this means that in the solution,

$$\left[Zn^{2+}\right] = \frac{95}{100}\times 0.1\,M = 0.095\,M$$

$$\therefore \quad E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2}\log\frac{1}{0.095}$$

$$= -0.76 - 0.02955\,(\log 1000 - \log 95)$$

$$= -0.76 - 0.02955\,(3 - 1.9777)$$

$$= -0.76 - 0.03021$$

$$= -0.79021\ V$$

Example – 17

Calculate the potential (emf) of the cell

$Cd \mid Cd^{2+}(0.10\,M) \parallel H^{+}(0.20\,M) \mid Pt, H_2(0.5\,atm)$

(Given E^{o} for $Cd^{2+}/Cd = -0.403$ V, $R = 8.14\ JK^{-1}\,mol^{-1}$, $F = 96{,}500\ C\,mol^{-1}$).

Sol. The cell reaction is

$$Cd + 2H^{+}(0.20\ M) \rightarrow Cd^{2+}(0.10\ M) + H_2(0.5\ atm)$$

$$E^{o}_{cell} = E^{o}_{H^{+}/1/2H_2} - E^{o}_{Cd^{2+}/Cd} = 0 - (-0.403) = 0.403\ V$$

Applying Nernst equation to the cell reaction,

$$E_{cell} = E^{o}_{cell} - \frac{2.303\ RT}{nF}\log\frac{\left[Cd^{2+}\right]\times P_{H_2}}{\left[H^{+}\right]^2}$$

$$= 0.403 - \frac{2.303\times 8.314\times 298}{2\times 96{,}500}\log\frac{0.1\times 0.5}{(0.2)^2}$$

$$= 0.403 - 0.003 = 0.400\ V$$

Example – 18

Calculate the equilibrium constant of the reaction

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)\ \ E^{o}_{cell} = 0.46\,V$$

Sol.
$$E^{o}_{cell} = \frac{0.059\,V}{2}\log K_c = 0.46\,V$$

or
$$\log K_c = \frac{0.46\,V\times 2}{0.059\,V} = 15.6 \Rightarrow K_c = \text{Antilog } 15.6$$

$$K_c = 3.92\times 10^{15}$$

Example – 19

Calculate the standard free energy change and maximum work obtainable for the reaction occurring in the cell : (Daniell cell).

$$Zn(s) \mid Zn^{2+}(1\ M) \parallel Cu^{2+}(1\ M) \mid Cu(s)$$

[Given $E^{o}_{Zn^{2+}/Zn} = -0.76\,V, E^{o}_{Cu^{2+}/Cu}$

$= +0.34\,V,\ F = 96{,}500\ C\,mol^{-1}$]

Also calculate the equilibrium constant for the reaction.

Sol. (i)
$$E^{o}_{cell} = E^{o}_{Cu^{2+}/Cu} + E^{o}_{Zn/Zn^{+2}} = 0.34 + 0.76$$

$$= 1.10\,V$$

The reaction taking place in the Daniell cell is

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

For this reaction, n = 2

$$\Delta G^o = -nFE^o_{cell}$$

$$= -2 \times 96500\ C\ mol^{-1} \times 1.10\ V$$

$$= -212300\ CV\ mol^{-1}$$

$$= -212300\ J\ mol^{-1}\ (1\ CV = 1\ J)$$

$$= -212.300\ kJ\ mol^{-1}$$

Thus, the maximum work that can be obtained from the Daniel cell = 212.3 kJ.

(ii) $\Delta G^o = -RT\ In\ K_c = -2.303\ RT \log K_c$

$\therefore$ $-212300 = -2.303 \times 8.14 \times 298 \times \log K_c$

or $$\log K_c = \frac{212300}{2.303 \times 8.314 \times 298} = 37.2704$$

$\therefore$ $K_c = Antilog\ 37.2074 = 1.6 \times 10^{37}$

Example – 20

Calculate the equilibrium constant, K_c for the reaction.

$3Sn^{4+} + 2Cr \rightarrow 3Sn^{2+} + 2Cr^{3+}$

Given $E^o = 0.885$ V.

Sol. $$E^o_{cell} = \frac{0.059}{n} \log K_c,\ n = 6$$

$$0.885 = \frac{0.059}{6} \log K_c$$

$$\log K_c = \frac{6 \times 0.885}{0.059}$$

$K_c = Antilog\ 90 = 1 \times 10^{90}$

Example – 21

Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation:

$CrO_3(aq) + 6H^+(aq) + 6e^- \rightarrow Cr(s) + 3H_2O$

Calculate (i) how many grams of chromium will be plated out by 24,000 coulombs and (ii) how long will it take to plate out 1.5 g of chromium by using 12.5 amp current ? (At. mass of Cr = 52).

Sol. (i) $6 \times 96,500$ coulomb deposit Cr = 1 mole = 52 g

$\therefore$ 24,000 coulomb deposit $Cr = \frac{52 \times 24000}{6 \times 965000} g = 2.1554\ g$

(ii) 52 g of Cr is deposited by electricity = 6×96500 C

$\therefore$ 1.5 g require electricity $= \frac{6 \times 96500}{52} \times 1.5\ C = 16071\ C$

$\therefore$ Time for which the current is required to be passed

$$= \frac{16071.9}{12.5\ A} = 1336\ s.$$

Example – 22

(a) Calculate the equilibrium constant for the reaction

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

If $E^o_{Cd^{2+}/Cd} = -0.403\ V$

$E^o_{Zn^{2+}/Zn} = -0.763\ V$

(b) When a current of 0.75A is passed through a $CuSO_4$ solution for 25 min, 0.369 g of copper is deposited at the cathode. Calculate the atomic mass of copper.

(c) Tarnished silver contains Ag_2S. Can this tarnish be removed by placing tarnished silver ware in an aluminium pan containing an inert electrolytic solution such as NaCl. The standard electrode potential for half reaction:

$Ag_2S(s) + 2e^- \longrightarrow 2Ag(s) + S^{2-}$ is –0.71V

and for $Al^{3+} + 3e^- \longrightarrow 2Al(s)$ is – 1.66 V

Sol. (a) $E^o_{cell} = E^o_c + E^o_a = -0.403 + 0.763 = 0.360\ V$

As $$\log Kc = \left(\frac{nE^o_{cell}}{0.059}\right) = \left(\frac{2 \times 0.360}{0.059}\right)$$

$$= \left(\frac{0.720}{0.059}\right) = 12.20$$

$K_c = antilog\ (12.20) = 1.585 \times 10^{12}$

(b) M = Z I t

$$0.369 = \frac{x}{2 \times 96500} \times 0.75 \times 25 \times 60$$

(x = molar mass of copper)

x = 63.3 g/mol

(c) E^{o}_{cell} for reaction of tarnished silver ware with aluminium pan is $(-0.71\ V) + 1.66\ V$ i.e., $+0.95\ V$

Tarnished silver ware, therefore, can be cleaned by placing it in an aluminium pan as E^{o}_{cell} is positive.

Example – 23

(a) Calculate the standard free energy change for the following reaction at 25°C.

$$Au\,(s) + Ca^{2+}(aq, 1M) \longrightarrow Au^{3+}(aq, 1M) + Ca(s)$$

$$E^{o}_{Au^{3+}/Au} = +1.50\ V,\ E^{o}_{Ca^{2+}/Ca} = -2.87\ V$$

Predict whether the reaction will be spontaneous or not at 25°C. Which of the above two half cells will act as an oxidizing agent and which one will be a reducing agent?

(b) The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if Λ^{o}_{m} for acetic acid is 390. 5 S cm^2/mol.

Sol. (a) $E^{o}_{cell} = (-2.87\ V) - (1.50\ V) = -4.37\ V$

$$\Delta G^{o}_{cell} = -6 \times 96500 \times -4.37\ V = +2530.230\ kJ/mol$$

Since $\Delta_r G^{o}$ is positive, reaction is non-spontaneous.

Au^{3+}/Au half cell will be a reducing agent, Ca^{2+}/Ca half cell will be an oxidising agent.

(b) $\Lambda^{c}_{m} = K \times \dfrac{1000}{\text{molarity}}$

K = Specific conductance

$$= \frac{4\times10^{-5}\ S/cm \times 1000}{0.001} = 40\ S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^{o}_{m}} = \frac{40}{390.5} = 0.103$$

$$K_c = \frac{C\alpha^2}{1-\alpha} = \frac{0.001\times(0.103)^2}{1-0.103} = 1.19\times10^{-5}$$

Example – 24

(a) Depict the galvanic cell in which the following reaction takes place :

$$Zn\,(s) + 2Ag^{+}(aq) \longrightarrow Zn^{2+}(aq) + 2Ag\,(s)$$

Also indicate that in this cell

(i) which electrode is negatively charged.

(ii) what are the carrier of the current in the cell.

(iii) what is the individual reaction at each electrode.

(b) Write the Nernst equation and determine the e.m.f. of the following cell at 298 K:

$$Mg\,(s)\,|\,Mg^{2+}(0.001\ M)\,\|\,Cu^{2+}(0.0001\ M)\,|\,Cu\,(s)$$

(Given : $E^{o}_{Mg^{2+}/Mg} = -2.375\ V,\ E^{o}_{Cu^{2+}/Cu} = +0.34\ V$)

Sol. (a) $Zn\ |\ Zn^{2+}$ (conc.) $\|\ Ag^{+}$ (conc) $|\ Ag$

(i) Zn electrode is negatively charged.

(ii) Current carriers of cell are

- electrons in external wire
- Zn^{2+} ions in anodic half cell.
- Ag^{+} ions in cathodic half cell.
- Ions of salt bridge, i.e., K^{+} and Cl^{-}.

(iii) At anode $Zn \longrightarrow Zn^{2+} + 2e^{-}$

At cathode $2Ag^{+} + e^{-} \longrightarrow 2Ag$

(b) $Mg \longrightarrow Mg^{2+} + 2e^{-}$

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

$$Mg + Cu^{2+} \longrightarrow Cu + Mg^{2+}$$

Nernst equation

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{n}\log\frac{\left[Mg^{2+}\right]}{\left[Cu^{2+}\right]}$$

$$E_{cell} = \left(E^{o}_{Cu^{2+}/Cu} + E^{o}_{Mg/Mg^{+2}}\right) - \frac{0.059}{2}\log\frac{\left[Mg^{2+}\right]}{\left[Cu^{2+}\right]}$$

$$= 0.34 + (2.375) - \frac{0.059}{2} \log \frac{10^{-3}}{10^{-4}}$$

$$= 0.34 + 2.375 - 0.0295 \log 10$$

$$E_{cell} = 2.6855 \text{ V}$$

$$E_{cell} = 2.685 \text{ V}$$

Example – 25

(a) Define molar conductivity of a substance and describe how weak and strong electrolytes' molar conductivity changes with concentration of solute. How is such change explained ?

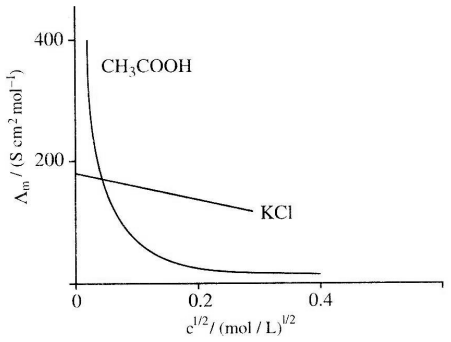
(b) A voltaic cell is set up at 25 °C with the following half cells:

$Ag^+ (0.001 \text{ M}) \,|\, Ag$ and $Cu^{2+} (0.10 \text{ M}) \,|\, Cu$

What would be the voltage of this cell ?

$(E^o_{cell} = 0.46 \text{ V})$

Sol. Molar Conductivity (Λ_m) : It may be defined as the conductance of a solution containing 1 mole of electrolyte such that the entire solution is placed in between two electrodes one centimetre apart.



$$\Lambda_m = k \times v$$

or

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

Molar conductivity increases with decrease in concentration or increase in dilution as number of ions as well as mobility of ions increased with dilution.

For strong electrolytes, the number of ions do not increase appreciably on dilution and only mobility or ions increases due to decrease in interionic attractions. Therefore, Λ_m increases a little as shown in graph by a straight line.

For weak electrolytes, the number of ions as well as mobility of ions increases on dilution which results in a very large increase in molar conducvity especially near infinite dilutuion as shown by curve in the figure.

At anode : $Cu(s) \longrightarrow Cu^{2+}(aq) + 2\bar{e}$

At cathode : $2Ag^+(aq) + 2\bar{e} \longrightarrow 2Ag(s)$

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

Here, $$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

Here, $E^o_{cell} = 0.46$ V, n = 2

$[Ag^+] = 0.001\text{M} = 1 \times 10^{-3}$ M, $[Cu^{2+}] = 0.1$ M

$$E_{cell} = 0.46 - \frac{0.0591}{2} \log \frac{0.1}{(10^{-3})^2}$$

$$E_{cell} = 0.46 - \frac{0.0591}{2} \log 10^5 = 0.46 - \frac{0.0591}{2} \times 5 \log 10$$

$$E_{cell} = 0.46 - 0.0591 \times 2.5 \times 1 = 0.46 - 0.14775 = 0.31225 \text{V}$$

$$E_{cell} = 0.312 \text{ V}$$

Example – 26

(a) State the relationship amongst cell constant of cell, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solute related to conductivity of its solution ?

(b) A voltaic cell is set up at 25°C with the following half-cells:

$Al \,|\, Ag^{3+} (0.001 \text{ M})$ and $Ni \,|\, Ni^{2+} (0.50 \text{ M})$

Calculate the cell voltage

$\left[E^o_{Ni^{+2}|Ni} = -0.25 \text{ V},\ E^o_{Al^{3+}|Al} = -1.66 \text{ V}\right]$

Sol. (a) $\kappa = \frac{1}{R} \times \left(\frac{l}{A}\right)$

where, κ = Conductivity

$\frac{1}{A}$ = Cell constant

R = Resistance

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

where, Λ_m = Molar conductivity

κ = Conductivity

M = Molarity of Solution

(b) At anode : $Al(s) \longrightarrow Al^{3+}(aq) + 3\bar{e}] \times 2$

At cathode : $Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)] \times 3$

$$2Al(s) + 3Ni^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + Ni(s)$$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{\left[Al^{3+}\right]^2}{\left[Ni^{2+}\right]^3}$$

Here, $n = 6$, $[Al^{3+}] = 0.001\ M = 1 \times 10^{-3}\ M$,

$[Ni^{2+}] = 0.5M$

$E^o_{cell} = 1.41V$

$$E^o_{cell} = 1.41V - \frac{0.0591}{6} \log \frac{(10^{-3})^2}{(0.5)^3} = 1.41 - \frac{0.0591}{6} \log \frac{10^{-6}}{0.125}$$

$$= 1.41 - \frac{0.0591}{6} \log(10^{-6} \times 8) = 1.41 - \frac{0.0591}{6}(\log 10^{-6} + \log 2^3)$$

$$= 1.41 - \frac{0.0591}{6}(-6 \log 10 + 3 \log 2) = 1.41 - \frac{0.0591}{6}(-6 + 3 \times 0.3010)$$

$$= 1.41 - \frac{0.0591}{6}(-5.097) = 1.41 + \frac{0.3012}{6}$$

$= 1.41 + 0.0502 = 1.4602V$

$E_{cell} = 1.46\ V$

Example – 27

(a) What type of a cell is the lead storage battery ? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery while operating.

(b) A voltaic cell is set up at 25°C with the half-cells Al | Al^{3+} (0.001 M) and Ni | Ni^{2+} (0.50 M). Write the equation for the reaction that occurs when the cell genrates an electric current and determine the cell potential.

(Given : $E^o_{Ni^{2+}|Ni} = -0.25\ V$, $E^o_{Al^{3+}|Al} = -1.66V$).

Sol. (a) The lead storage battery is a secondary cell.

The cell reactions when the battery is in use are given below

At anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

At cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

$\longrightarrow PbSO_4(s) + 2H_2O(\ell)$

Overall cell reaction: $Pb(s) + 2H_2SO_4(aq) \longrightarrow$

$PbSO_4(s) + 2H_2O(\ell)$

(b) $2Al(s) + 3Ni^{+2}(aq) \rightarrow 3Ni(s) + 2Al^{+3}(aq)$

$E^o_{cell} = 1.41\ V$

$$E_{cell} = 1.41 - \frac{0.0591}{6} \log \left[\frac{(10^{-3})^2}{(0.5)^3}\right]$$

$= 1.46\ V$

Example – 28

(a) Express the relationship amongst cell constant, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solute related to conductivity of its solution.

(b) Calculate the equilibrium constant for the reaction.

$$Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$$

(Given : $E^o_{Cd^{2+}|Cd} = -0.40\ V$, $E^o_{Fe^{2+}|Fe} - 0.44\ V$).

Sol. (a) Conductivity $(\kappa) = \frac{1}{\text{Resistance } (R)} \times$ Cell constant (G)

$$\Lambda_m = \frac{\kappa \times 1000}{M}, \text{ where, } \Lambda_m = \text{Molar conductivity}$$

(b) $Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$

$$\log k_c = n\frac{E^o_{cell}}{0.059}$$

Here, $n = 2$

$$E^o_{cell} = E^o_{cathode} + E^o_{anode}$$

$$= E^o_{Cd^{2+}/Cd} + E^o_{Fe/Fe^{+2}}$$

$$= -0.4 + 0.44$$

$$E^o_{cell} = 0.04\,V$$

$$\log k_c = \frac{2 \times 0.04}{0.059} = \frac{0.08}{0.059}$$

$$\log k_c = 1.3536$$

$$k_c = \text{Antilog } 1.3536$$

$$k_c = 22.57$$

Example – 29

(a) Define the term molar conductivity. How is it related to conductivity of the related solution?

(b) One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. Its other half-cell consists of zinc electrode dipping in 1.0 M solution of $Zn(NO_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver nitrate solution used.

$$(E^o_{Zn^{2+}/Zn} = -0.76\,V,\ E^o_{Ag^{2+}/Ag} = +0.80\,V)$$

Sol.

(a) **Molar conductivity** (Λ_m) : It may be defined as the conductivity of one molar electrolytic solution placed between two electrodes one centimetre apart and have enough area of cross section to hold entire volume.

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

where, κ = Conductivity

c = Concentration of solution in mol L^{-1}

(b) At anode : $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

At cathode : $Ag^+(aq) + e^- \longrightarrow Ag(s)] \times 2$

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

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Ag^+]^2}$$

Here, $n = 2$, $[Zn^{2+}] = 1$ M

$$E^o_{cell} = E^o_{Ag^+/Ag} + E^o_{Zn/Zn^{+2}} = 0.80V + 0.76V$$

$$E^o_{cell} = 1.56\,V$$

$$1.48 = 1.56 - \frac{0.0591}{2}\log\frac{1}{[Ag^+]^2}$$

$$-0.08 = -\frac{0.0591}{2}\log\frac{1}{[Ag^+]^2}$$

$$\log\frac{1}{[Ag^+]^2} = \frac{0.16}{0.0591} = 2.7072 = 2.7072$$

$$\log 1 - \log[Ag^+]^2 = 2.7072$$

$$0 - 2\log[Ag^+] = 2.7072$$

$$\log[Ag^+] = -1.3536 = \bar{2}.6464$$

$$[Ag^+] = \text{Anti log}(\bar{2}.6464) = 4.43 \times 10^{-2}\,M$$

$$[Ag^+] = 0.044\,M$$

Example – 30

(a) Corrosion is essentially an electrochemical phenomenon. Explain the reactions occurring during corrosion of iron kept in an open atmosphere.

(b) Calculate the equilibrium constant for the equilibrium reaction.

$$Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$$

(Given : $E^o_{Cd^{2+}/Cd} = -0.40\,V$, $E^o_{Fe^{2+}/Fe} = -0.44V$)

Sol. (a) At anode : Oxidation of Fe atoms takes place

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad E^o_{Fe^{2+}/Fe} = -0.44\,V$$

At cathode : Reduction of oxygenin the presence of H^+ ions. The H^+ ions are produced by either H_2O or H_2CO_3 (formed by dissolution of CO_2 in moisture)

$$2H^+(aq) + 2e^- \longrightarrow 2H$$

$$2H + \frac{1}{2}O_2(g) \longrightarrow H_2O$$

Net reaction at cathodic area

$$2H^+(aq) + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O$$

$$E^o_{H^+/O_2/H_2O} = 1.23\,V$$

The overall reaction

$$Fe(s) + 2H^+(aq) + \frac{1}{2}O_2(g) \longrightarrow Fe^{2+}(aq) + H_2O(\ell)$$

$$E^o_{cell} = 1.67\,V$$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3 . xH_2O$).

(b) $Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$

$$\log k_c = n\frac{E^o cell}{0.059}$$

Here, n = 2

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= E^o_{Cd^{2+}/Cd} - E^o_{Fe^{2+}/Fe} = -40 - (-0.44)$$

$E^o_{cell} = 0.04V$

$$\log k_c = \frac{2 \times 0.04}{0.059} = \frac{0.08}{0.059}$$

$\log k_c = 1.3536$

k_c = Antilog 1.3536

$k_c = 22.57$

Example – 31

Two half cell reactions of an electrochemical cell are given below :

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}$

$(aq) + 4H_2O(\ell), E^o = 1.51\,V$

$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-, E^o = +0.15\,V$

Construct the redox equation from the two half cell reactions and predict if this reaction favours formation of reactants or product shown in the quation

Sol. **At cathode** : $MnO_4^-(aq) + 8H^+ + 5e^- \longrightarrow Mn^{2+}$

$(aq) + 4H_2O(\ell)] \times 2 \quad E^o = +1.15V$

At anode: $Sn^{2+} \longrightarrow Sn^{4+}(aq) + 2e^-] \times 5\ E^o = +0.15\,V$

Overall reaction :

$$2MnO_4^-(aq) + 5Sn^{2+}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}$$

$$(aq) + 5Sn^4(aq) + 8H_2O\,(\ell)$$

$$E^o_{Sn^{4+}/Sn^{2+}} = -E^o_{Sn^{2+}/Sn^{4+}} = -0.15V$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{MnO_4^-/Mn^{2+}} - E^o_{Sn^{4+}/Sn^{2+}}$$

$$= 1.51 - (-0.15)$$

$$E^o_{cell} = 1.66\,V$$

As E^o_{cell} is +ve therefore the reaction will take place in forward direction, i.e., favours the formation of products.

Example – 32

(a) Account for the following

(i) Alkaline medium inhibits the rusting of iron

(ii) Iron does not rust even if the zinc coating is broken in a galvanized iron pipe.

(b) $Cu^{2+} + 2e^- \rightarrow Cu\ ; E^o = +0.34\,V$

$Ag^+ + e^- \rightarrow Ag; E^o = +0.80\,V$

(i) Construct a galvanic cell using the above data.

(ii) For what concentration of Ag^+ ions will the emf of the cell be zero at 25°C, if the concentration of Cu^{2+} is 0.01 M? [log 3.919 = 0.593]

Sol. (a) (i) The alkalinity of the solution prevents the availability of H^+ ions.

(ii) Zinc is more electropositive than iron. Therefore, zinc coating acts anode and the exposed iron portions act as cathode. If zinc coating is broken, zinc undergoes corrosion, protecting iron from rusting. No attack occurs on iron till all the zinc is corroded.

(b) At anode $Cu \rightarrow Cu^{2+} + 2e^-$

At cathode $[Ag^+ + e^- \rightarrow Ag] \times 2$

$$Cu + 2\,Ag^+ \rightarrow Cu^{2+} + 2Ag$$

Cell representation

$$Cu \mid Cu^{2+}\,(conc.) \parallel Ag^+\,(conc.) \mid Ag$$

$$E_{cell} = E^o_{cell} - \frac{0.059}{n}\log\frac{\left[Cu^{+2}\right]}{\left[Ag^+\right]^2}$$

$$O = (0.80 - 0.34) - \frac{0.059}{2}\log\left[\frac{0.01}{x^2}\right]$$

$$15.59 = \log\left(\frac{0.01}{x^2}\right)$$

$$x = 1.597 \times 10^{-9}\ M$$

$$[Ag^+] = 1.597 \times 10^{-9} M$$

Example – 33

(a) State advantages of H_2-O_2 fuel cell over ordinary cell.

(b) Silver is electrodeposited on a metallic vessel of total surface area 500 cm^2 by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited.

[Given: Density of silver = 10.5 g cm^{-3}, Atomic mass of silver = 108 amu, F = 9,500 C mol^{-1}]

Sol. (a) **Advantages Fuels Cells:**

1. It is a pollution-free device since no harmful products are formed.
2. This is very efficient cell. Its efficiency is about 75% which is considerably higher than conventional cells.
3. These cells are light in weight as compared to electrical generators to produce corresponding quantity of power.
4. It is a continuous source of energy if the supply of gases is maintained.

(b) **Mass of silver deposited**

$$m = z\,I\,t.$$

$$= \frac{108}{96500} \times 0.5 \times 2 \times 3600$$

$$m = 4.029\ g$$

$$d = \frac{m}{v} \Rightarrow v = \frac{m}{d}$$

$$V = \frac{4.029}{10.5} = 0.3837\ cm^3$$

Let the thickness of silver deposited be x cm.

$\therefore \quad V = A \times x$

$\Rightarrow \quad x = \frac{V}{A}$

$$x = \frac{0.3837}{500}$$

$\therefore \quad x = 7.67 \times 10^{-4}$ cm.

Example – 34

(a) Give reasons for the following:

(i) Rusting of iron is quicker in saline water than in ordinary water.

(ii) Resistance of a conductivity cell filled with 0.1 M KCl solution is 100 ohm.If the resistance of the same cell when filled with 0.02 M KCl solution is 520 ohms, calculate the conductivity and molar conductivity of 0.02 M KCl solution.

(Conductivity of 0.1 M KCl solution is 1.29 Sm^{-1}).

Sol. (a) (i) It is because in saline water, there is more H^+ ions. Greater the number of H^+ ions, quicker the rusting.

(ii) Due to higher reduction potential of hydrogen we get hydrogen at cathode.

(b) $\kappa = \frac{1}{R} \times$ cell constant

$\Rightarrow$ cell constant = $\kappa \times R$

$= 1.29\ Sm^{-1} \times 100$ ohm

$= 129\ m^{-1} = 1.29\ cm^{-1}$

For second solution

$$\kappa = \frac{1}{R} \times \text{ cell constant}$$

$$\kappa = \frac{1}{520} \times 1.29 = 2.48 \times 10^{-3} \text{ S cm}^{-1}$$

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

$$= \frac{2.48 \times 10^{-3} \times 1000}{0.02} = \frac{248}{2}$$

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

Example – 35

(a) Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write overall reaction.

($E^\circ_{Na^+/Na} = -2.71$ V; $E^\circ_{H_2O/H_2} = -0.83$ V, $E^\circ_{Cl_2/2Cl^-} =$ +1.36 V; $E^\circ_{H^+ + O_2/H_2O} = 1.23$ V)

(b) Calculate the emf of the cell of $Zn / Zn^{2+}(0.1\text{ M}) \| Cd^{2+}(0.01\text{ M}) / Cd$ at 298 K,

[Given $E^\circ_{Zn^{2+}/Zn} = -0.76$ V and $E^\circ_{Cd^{2+}/Cd} = -0.40$ V]

Sol. (a) Because of higher reduction potential of water, water is reduced in preference to sodium at therefore instea of deposition of sodium metal, hydrogen is discharged at cathode.

$$H_2O(\ell) + 2e^- \longrightarrow H_2(g) + 2OH^-$$

$$2Cl^- \longrightarrow Cl_2(g)$$

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

At anode Cl_2 gas is liberated because of overpotential of oxygen.

(b)
$$\left.\begin{array}{l} Zn \longrightarrow Zn^{2+} + 2e^- \\ Cd^{2+} + 2e^- \longrightarrow Cd \end{array}\right\} \text{Half cell reactions}$$

$Zn + Cd^{2+} \rightarrow Zn^{2+} + Cd\}$ cell reaction

$$E^\circ_{cell} = E^\circ_{cathode} + E^\circ_{anode}$$

$$= 0.76 - 0.40 = 0.36 \text{ V}$$

$$E = E^\circ_{cell} - \frac{0.0591}{n} \log Q$$

$$= 0.36 - \frac{0.0591}{2} \log \left[\frac{Zn^{+2}}{Cd^{+2}}\right]$$

$$= 0.36 - \frac{0.0591}{2} \log \left[\frac{0.1}{0.01}\right] = 0.33\text{V}$$

Example – 36

Three iron sheets have been coated separately with three metals A, B and C whose standards reduction potentials are given below.

metal	A	B	C	iron
E°_{Value}	– 0.46 V	–0.66V	–0.20V	–0.44V

Identify in which case rusting will take place faster when coating is damaged.

Sol. As iron (–0.44V) has lower standard reduction potential than C (– 0.20V) only therefore when coating is broken, rusting will take place faster.

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

Basics of electrochemical Cell

1. Which of the following has been universally accepted as a reference electrode at all temperatures and has been assigned a value of zero volt ?

(a) platinum electrode (b) copper electrode

(c) graphite electrode (d) standard hydrogen electrode

2. The reaction $1/2H_2(g) + AgCl(s) = H^+(aq) + Cl^-(aq) + Ag(s)$ occurs in the galvanic cell :

(a) $Ag \mid AgCl(s) \mid KCl(sol.) \mid\mid AgNO_3)$ (sol.) $\mid Ag$

(b) $Pt \mid H_2(g) \mid HCl(sol. \mid\mid AgNO_3$ (sol) $\mid Ag$

(c) $Pt \mid H_2(g) \mid HCl$ (sol.) $\mid\mid AgCl(s) \mid Ag$

(d) $Pt \mid H_2$ (g) $\mid KCl$ (sol.) $\mid\mid AgCl(s) \mid Ag$

3. 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) $Zn^{2+}(aq.) + 2e^- \longrightarrow Zn(s)$

4. Which of the following statement is wrong about galvanic cell ?

(a) cathode is positive charged

(b) anode is negatively charged

(c) reduction takes place at the anode

(d) reduction takes place at the cathode

5. Which are used as secondary reference electrodes ?

(a) Calomel electrode (b) Ag/AgCl electrode

(c) $Hg/Hg_2Cl_2 - KCl$ electrode

(d) All of the above

Applications of Electrochemical Series

6. The standard electrode potentials (reduction) of Pt/Fe^{3+}, Fe^{2+} and Pt/Sn^{4+}, Sn^{2+} are + 0.77 V and 0.15 V respectively at 25°C. The standard EMF of the reaction $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$ is

(a) – 0.62 V (b) – 0.92 V

(c) + 0.31 V (d) + 0.85 V

7. Adding powdered Pb and Fe to a solution containing 1.0 M is each of Pb^{2+} and Fe^{2+} ions would result into the formation of ($E^o\ Pb^{+2}/Pb = -0.13V$, $E^o\ Fe^{+2}/Fe = -0.44V$)

(a) More of Pb and Fe^{2+} ions

(b) More of Fe and Pb^{2+} ions

(c) More of Fe and Pb (d) More of Fe^{2+} and Pb^{2+} ions

8. Strongest reducing agent is :

(a) K (b) Mg

(c) Al (d) I

9. Zn can not displace following ions from their aqueous solution :

(a) Ag^+ (b) Cu^{2+}

(c) Fe^{2+} (d) Na^+

10. Which of the following displacement does not occur :

(a) $Zn + 2H^+ \rightarrow Zn^{2+} + H_2\uparrow$

(b) $Fe + 2Ag^+ \rightarrow Fe^{2+} + Ag\downarrow$

(c) $Cu + Fe^{2+} \rightarrow Cu^{2+} + Fe\downarrow$

(d) $Zn + Pb^{2+} \rightarrow Zn^{2+} + Pb\downarrow$

11. The oxidation potential of Zn, Cu, Ag, H_2 and Ni are 0.76, –0.34, – 0.80, 0, 0.55 volt respectively. Which of the following reaction will provide maximum voltage ?

(a) $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$

(b) $Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$

(c) $H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu$

(d) $H_2 + Ni^{2+} \longrightarrow 2H^+ + Ni$

12. 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 copper and aluminium is formed

(c) The solution becomes blue

(d) There is no reaction

13. The standard reduction electrode potential values of the element A, B and C are + 0.68, –2.50, and –0.50 V respectively. The order of their reducing power is :

(a) A > B > C (b) A > C > B

(c) C > B > A (d) B > C > A

14. A metal having negative reduction potential when dipped in the solution of its own ions, has a tendency :

(a) to pass into the solution

(b) to be deposited from the solution

(c) to become electrically positive

(d) to remain neutral

15. E° for the half cell reactions are as,

(a) $Zn = Zn^{2+} + 2e$; $E° = +0.76$ V

(b) $Fe = Fe^{2+} + 2e$; $E° = +0.41$ V

The E° for half cell reaction,

$Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$ is :

(a) – 0.35 V (b) + 0.35 V

(c) + 1.17 V (d) – 0.17 V

16. An aqueous solution containing 1 M each of Au^{3+}, Cu^{2+}, Ag^{+}, Li^{+} is being electrolysed by using inert electrodes. The value of standard potentials are :

$E°_{Ag^+/Ag} = 0.80$ V, $E°_{Cu^+/Cu} = 0.34$ V and $E°_{Au^{3+}/Au} = 1.50$ V,

$E°_{Li^+/Li} = -3.03$ V

with increasing voltage, the sequence of deposition of metals on the cathode will be :

(a) Li, Cu, Ag, Au (b) Cu, Ag, Au

(c) Au, Ag, Cu (d) Au, Ag, Cu, Li

17. The standard electrode potential for the reaction

$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$

$Sn^{2+}(aq) + 2e^{-} \longrightarrow Sn(s)$

at 25°C are 0.80 volt and – 0.14 volt, respectively. The emf of the cell.

$Sn \mid Sn^{2+}(1\ M) \mid\mid Ag^{+}(1M) \mid Ag$ is

(a) 0.66 volt (b) 0.80 volt

(c) 1.08 volt (d) 0.94 volt

Relationship between emf and gibb's free energy change

18. The standard free energy change for the following reaction is – 210 kJ. What is the standard cell potential ?

$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

(a) + 0.752 (b) + 1.09

(c) + 0.420 (d) + 0.640

19. Calculate the standard free energy change for the reaction, $2\,Ag + 2H^{+} \rightarrow H_2 + 2\,Ag^{+}$,

E° for $Ag^{+} + e^{-} \rightarrow Ag$ is 0.80 V

(a) + 154.4 kJ (b) + 308.8 kJ

(c) –154.4 kJ (d) –308.8 kJ

20. The standard EMF of Daniell cell is 1.10 volt. The maximum electrical work obtained from the Daniell cell is

(a) 212.3 kJ (b) 175.4 kJ

(c) 106.15 kJ (d) 53.07 kJ

21. What is the free energy change for the half reaction $Li^{+} + e^{-} \rightarrow Li$?

Given $E°_{Li^+/Li} = -3.0V$, $F = 96500\ C\ mol^{-1}$ and $T = 298$ K.

(a) 289.5 kJ mol^{-1} (b) –298.5 kJ mol^{-1}

(c) 32.166 CV^{-1} mol^{-1} (d) –289500 CV mol^{-1}

22. The emf of Daniell cell is 1.1 volt. If the value of Faraday is 96500 coulombs per mole, the change in free energy in kJ is

(a) 212.30 (b) –212.30

(c) 106.15 (d) –106.15

Nernst Equation

23. Which of the following represents the potential of silver wire dipped in to 0.1 M $AgNO_3$ solution at 25°C ?

(a) $E°_{red}$ (b) $(E°_{red} + 0.059)$

(c) $(E°_{ox} - 0.059)$ (d) $(E°_{red} - 0.059)$

24. Consider the cell $\begin{matrix} H_2(Pt) \\ 1\,atm \end{matrix} \left| \begin{matrix} H_3O^{+}(aq) \\ pH = 5.5 \end{matrix} \right|\left| \begin{matrix} Ag^{+} \\ x\ M \end{matrix} \right| Ag$. The measured EMF of the cell is 1.023 V. What is the value of x ?

$E^{0}_{Ag^+, Ag} = +0.799$ V [T = 25°C]

(a) 2×10^{-2} M (b) 2×10^{-3} M

(c) 1.5×10^{-3} M (d) 1.5×10^{-2} M

25. The emf of the cell

$Ti/Ti^{+}(0.0001\ M)\,||\,Cu^{2+}(0.01\ M)/Cu$ is 0.83 V

The emf of this cell will be increased by :

(a) Increase the concentration of Cu^{++} ions

(b) Decreasing the concentration of Ti^{+}

(c) Increasing the concentration of both

(d) (a) and (b) both

26. $Co\,|\,Co^{2+}(C_2)\,||\,Co^{2+}(C_1)\,|\,Co$ for this cell, ΔG is negative if :

(a) $C_2 > C_1$ (b) $C_1 > C_2$

(c) $C_1 = C_2$ (d) unpredictable

27. What will be the emf for the given cell ?

$Pt\,|\,H_2(g, P_1)\,|\,H^{+}(aq)\,||\,H_2(g, P_2)\,|\,Pt$

(a) $\frac{RT}{F}\ln\frac{P_1}{P_2}$ (b) $\frac{RT}{2F}\ln\frac{P_1}{P_2}$

(c) $\frac{RT}{2F}\ln\frac{P_2}{P_1}$ (d) None of these

28. If the pressure of hydrogen gas is increased from 1 atm. to 100 atm., keeping the hydrogen ion concentration constant at 1 M, the voltage of the hydrogen half-cell is at 25°C will be

(a) 0.059 V (b) –0.059 V

(c) 0.295 V (d) 0.118 V.

29. The EMF of the cell

$Mg\,|\,Mg^{2+}(0.01\ M)\,||\,Sn^{2+}(0.1M)|\,Sn$ at 298 K is (Given $E^{\circ}_{Mg^{2+},Mg} = -2.34\,V,\ E^{\circ}_{Sn^{2+},\,Sn} = -0.14\,V$)

(a) 2.17 V (b) 2.23 V

(c) 2.51 V (d) 2.45 V

30. The potential of the cell containing two hydrogen electrodes as represented below

$Pt, H_2(g)\,|\,H^{+}(10^{-6}\ M)\,||\,H^{+}(10^{-4}M)|\,H_2(g), Pt$ at 298 K is

(a) –0.118 V (b) –0.0591 V

(c) 0.118 V (d) 0.0591 V

31. The emf of the cell H_2(1 atm) $Pt\,|\,H^{+}(a = x)\,||\,H^{+}(a = 1)\,|\,H_2$(1 atm) Pt at 25°C is 0.59 V. The pH of the solution is

(a) 1 (b) 4

(c) 7 (d) 10

32. The hydrogen electrode is dipped in a solution of pH = 3 at 25°C. The potential of the cell would be (the value of 2.303 RT/F is 0.059 V)

(a) 0.177 V (b) 0.087 V

(c) –0.177 V (d) 0.059 V

Relating half cell potential using dG

33. When two half-cells of electrode potential of E_1 and E_2 are combined to form a cell of electrode potential E_3, then (when n_1, n_2 and n_3 are no. of electrons exchanged in first, second and combined half-cells) :

(a) $E_3 = E_2 - E_1$ (b) $E_3 = \frac{E_1 n_1 + E_2 n_2}{n_3}$

(c) $E_3 = \frac{E_1 n_1 - E_2 n_2}{n_3^2}$ (d) $E_3 = E_1 + E_2$

34. If $E^{\circ}_{Au^{+}/Au}$ is 1.69 V and $E^{\circ}_{Au^{3+}/Au}$ is 1.40 V, then $E^{\circ}_{Au^{+}/Au^{3+}}$

(a) 0.19 V (b) 2.945 V

(c) 1.255 V (d) None of these

Electroytic cell

35. Which reaction occur at cathode during electrolysis is fused lead bromide ?

(a) $Pb \longrightarrow Pb^{2+} + 2e^{-}$ (b) $Br + e^{-} \longrightarrow Br^{-}$

(c) $Br^{-} \longrightarrow Br + e^{-}$ (d) $Pb^{2+} + 2e^{-} \longrightarrow Pb$

36. By the electrolysis of aqueous solution of $CuSO_4$, the products obtained at both the electrodes are

(a) O_2 at anode and H_2 at cathode

(b) H_2 at anode and Cu at cathode

(c) O_2 at anode and Cu at cathode

(d) $H_2S_2O_8$ at anode and O_2 at cathode

37. During the electrolysis of fused NaCl, the reaction that occurs at the anode is :

(a) Chloride ions are oxidized

(b) Chloride ions are reduced

(c) Sodium ions are oxidized

(d) Sodium ions are reduced

38. In electroplating the article to be electroplated is made :

(a) cathode (b) anode

(c) either cathode or anode

(d) simply suspended in the electrolytic bath.

39. On electrolysing a solution of dilute H_2SO_4 between platinum electrodes, the gas evolved at the anode is

(a) SO_2 (b) SO_3

(c) O_2 (d) H_2.

40. A spoon to be electroplated with gold should be :

(a) cathode (b) anode

(c) electrolyte (d) none of these

Faraday's Laws

41. 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 -

(a) 56 g (b) 84 g

(c) 112 g (d) 168 g

42. The electric charge for electrode deposition of one gram equivalent of a substance is :

(a) one amp/sec (b) 96,500 C/sec

(c) one amp/hour (d) 96,500 C

43. Number of electrons involved in the electrodeposition of 63.5 g of Cu from a solution of $CuSO_4$ is :

(a) 6.022×10^{23} (b) 3.011×10^{23}

(c) 12.044×10^{23} (d) 6.022×10^{22}

44. 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

45. W g of copper 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

46. When the same electric current is passed through the solution of different elecrolytes in series the amounts of elements deposited on the electrodes are in the ratio of their:

(a) atomic number (b) atomic masses

(c) specific gravities (d) equivalent masses

47. 13.5 g of Al get deposited when electricity is passed through the solution of $AlCl_3$. The number of faradays used are :

(a) 0.50 (b) 1.00

(c) 1.50 (d) 2.00

48. The ratio of weights of hydrogen and magnesium deposited by the same amount of electricity from aqueous H_2SO_4 and fused $MgSO_4$ are :

(a) 1 : 8 (b) 1 : 12

(c) 1 : 16 (d) None of these

49. A current of 2 ampere was passed through solutions of $CuSO_4$ and $AgNO_3$ in series. 0.635 g of copper was deposited. Then the weight of silver deposited will be :

(a) 0.59 g (b) 3.24 g

(c) 1.08 g (d) 2.16 g

50. An ion is reduced to the element when it absorbs 6×10^{20} electrons. The number of equivalents of the ion is :

(a) 0.10 (b) 0.01

(c) 0.001 (d) 0.0001

51. Electrolysis can be used to determine atomic masses. A current of 0.550 A deposits 0.55 g of a certain metal in 100 minutes. Calculate the atomic mass of the metal if n = 3 :

(a) 100 (b) 45.0

(c) 48.25 (d) 144.75

52. How many minutes will it take to plate out 0.50 g of Cr from a $Cr_2(SO_4)_3$ solution using a current of 1.50 A ? (Atomic weight : Cr = 52.0)

(a) 254 (b) 30

(c) 152 (d) 103

53. An electrolysis of a oxytungsten complex ion using 1.10 A for 40 min produces 0.838 g of tungsten. What is the charge of tungsten in the material ? (Atomic weight : W = 184)

(a) 6 (b) 2

(c) 4 (d) 1

54. When molten lithium chloride (LiCl) is electrolyzed, lithium metal is formed at the cathode. If current efficiency is 75% then how many grams of lithium are liberated when 1930 C of charge pass through the cell : (Atomic weight : Li = 7)

(a) 0.105 (b) 0.120

(c) 0.28 (d) 0.240

55. The weight ratio of Al and Ag deposited using the same quantity of current is :

(a) 9 : 108 (b) 2 : 12

(c) 108 : 9 (d) 3 : 8

56. The weight of silver (eq. wt. = 108) displaced by that quantity of current which displaced 5600 mL of hydrogen at STP is :

(a) 54 g (b) 108 g

(c) 5.4 g (d) None of these

57. A current of 9.65 ampere is passed through the aqueous solution NaCl using suitable electrodes for 1000 s. The amount of NaOH formed during electrolysis is

(a) 2.0 g (b) 4.0 g

(c) 6.0 g (d) 8.0 g

58. How many electrons are delivered at the cathode during electrolysis by a current of 1A in 60 seconds ?

(a) 3.74×10^{20} (b) 6.0×10^{23}

(c) 7.48×10^{21} (d) 6.0×10^{20}

59. The moles of electrons required to deposit 1 gm equivalent aluminium (at. wt. = 27) from a solution of aluminium chloride will be

(a) 3 (b) 1

(c) 4 (d) 2

60. Time required to deposit one millimole of aluminium metal by the passage of 9.65 amperes through aqueous solution of aluminium ion is :

(a) 30 s (b) 10 s

(c) 30,000 s (d) 10,000 s

61. How many coulomb of electricity are consumed when 100 mA current is passed through a solution of $AgNO_3$ for 30 minute during an electrolysis experiment.

(a) 108 (b) 18000

(c) 180 (d) 3000

62. A current of 9.65 amp. flowing for 10 minute deposits 3.0 g of a metal. The equivalent wt. of the metal is :

(a) 10 (b) 30

(c) 50 (d) 96.5

63. 108 g fairly concentrate solution of $AgNO_3$ is electrolyzed using 0.1 F of electricity. The weight or resulting solution is:

(a) 94 g (b) 11.6 g

(c) 96.4 g (d) None

Batteries, Fuel Cells and Corrosion

64. When a lead storage battery is discharged

(a) $PbSO_4$ is formed (b) Pb is formed

(c) SO_2 is consumed (d) H_2SO_4 is formed

65. A fuel cell is :

(a) The voltaic cells in which continuous supply of fuels are send at anode to give oxidation

(b) The votalic cell in which fuels such as : CH_4, H_2, CO are used up at anode

(c) It involves the reactions of $H_2 - O_2$ fuel cell such as :

$$\text{Anode} : 2H_2 + 4OH^- \longrightarrow 4H_2O(l) + 4e$$

$$\text{Cathode} : O_2 + 2H_2O(l) + 4e \longrightarrow 4OH^-$$

(d) All of the above

66. Reaction that takes place at anode in dry cell is

(a) $Zn^{2+} + 2e^- \rightarrow Zn(s)$ (b) $Zn(s) \rightarrow Zn^{2+} + 2e^-$

(c) $Mn^{2+} + 2e^- \rightarrow Mn(s)$

(d) $Mn(s) \rightarrow Mn^+ + e^- + 1.5$ V.

67. As lead storage battery is charged

(a) lead dioxide dissolves

(b) sulphuric acid is regenerated

(c) lead electrode becomes coated with lead sulphate

(d) the concentration of sulphuric acid decreases.

Conductance of Solutions

68. The specific conductance of a N/10 KCl at 25°C is 0.0112 $ohm^{-1}\ cm^{-1}$. The resistance of cell containing solution at the same temperature was found to be 55 ohms. The cell constant will be

(a) $6.16\ cm^{-1}$ (b) $0.616\ cm^{-1}$

(c) $0.0616\ cm^{-1}$ (d) $616\ cm^{-1}$

69. The specific conductance of a salt of 0.01 M concentration is 1.061×10^{-4}, molar conductance of the same solution will be :

(a) 1.061×10^{-4} (b) 1.061

(c) 10.61 (d) 106.1

70. 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

71. The molar conductance at infinite dilution of $AgNO_3$, AgCl and NaCl are 116.5, 121.6 and 110.3 respectively. The molar conductances of $NaNO_3$ is :

(a) 111.4 (b) 105.2

(c) 130.6 (d) 150.2

72. If x specific resistance (in S^{-1} cm) of the electrolyte solution and y is the molarity of the solution, then $\wedge_m$ (in S cm^2 mol^{-1}) is given by :

(a) $\frac{1000x}{y}$ (b) $1000\frac{x}{y}$

(c) $\frac{1000}{xy}$ (d) $\frac{xy}{1000}$

73. Resistance of 0.1 M KCl solution in a conductance cell is 300 ohm and conductivity is 0.013 Scm^{-1}. The value of cell constant is :

(a) 3.9 cm^{-1} (b) 39 m^{-1}

(c) 3.9 m^{-1} (d) None of these

74. The specific conductance of a saturated solution of silver bromide is k S cm^{-1}. The limiting ionic conductivity of Ag^+ and Br^{-1} ions are x and y, respectively. The solubility of silver bromide in gL^{-1} is : (molar mass of AgBr = 188)

(a) $\frac{k\times1000}{x-y}$ (b) $\frac{k}{x+y}\times188$

(c) $\frac{k\times1000\times188}{x+y}$ (d) $\frac{x+y}{k}\times\frac{1000}{188}$

75. The conductivity of 0.1 N NaOH solution is 0.022 S cm^{-1}. When equal volume of 0.1 N HCl solution is added, the conductivity of resultant solution is decreases to 0.0055 S-cm^{-1}. The equivalent conductivity in S cm^2 $equivalent^{-1}$ of NaCl solution is

(a) 0.0055 (b) 0.11

(c) 110 (d) none

76. The specific conductivity of a saturated solution of AgCl is 3.40×10^{-6} ohm^{-1} cm^{-1} at 25 °C. If $\lambda_{Ag^+} = 62.3$ ohm^{-1} cm^2 mol^{-1} & $\lambda_{Cl} = 67.7$ ohm^{-1} cm^2 mol^{-1}, the solubility of AgCl at 25°C is :

(a) 2.6×10^{-5} M (b) 4.5×10^{-3} M

(c) 3.6×10^{-5} M (d) 3.6×10^{-3} M

77. Molar conductance of 0.1 M acetic acid is 7 ohm^{-1} cm^2 mol^{-1}. If the molar cond. of acetic acid at infinite dilution is 380.8 ohm^{-1} cm^2 mol^{-1}, the value of dissociation constant will be

(a) 226×10^{-5} mol dm^{-3} (b) 1.66×10^{-3} mol dm^{-1}

(c) 1.66×10^{-2} mol dm^{-3} (d) 3.442×10^{-5} mol dm^{-3}

78. At infinite dilution, the eq. conductances of CH_3COONa, HCl and CH_3COOH are 91, 426 and 391 mho cm^2 respectively at 25°C, The eq. conductance of NaCl at infinite dilution will be :

(a) 126 (b) 209

(c) 391 (d) 908

79. The equivalent conductivity of 0.1 N CH_3COOH at 25°C is 80 and at infinite dilution 400. The degree of dissociation of CH_3COOH is

(a) 1 (b) 0.2

(c) 0.1 (d) 0.5

EXERCISE - 2 : PREVIOUS YEAR COMPETITION QUESTIONS

(TOPIC-1)

ELECTROLYTES AND ELECTROLYTIC CONDUCTANCE

2011

1. A current is passed through two cells connected in series. The first cell contains $X(NO_3)_3$ (aq) and the second cell contains Y $(NO_3)_2$(aq). The relative atomic mases of X and Y are in the ratio 1:2. What is the ratio of liberated mass of X to that of Y? **[Kerala CEE]**

(a) 3:2 (b) 1:2

(c) 1:3 (d) 3:1

2. Two different electrolytic cells filled with molten $Cu(NO_3)_2$ and molten $Al(NO_3)_3$ respectively are connected in series. When electricity is passed 2.7 g Al is deposited on electrode. Calculate the weight of Cu deposited on cathode. [Cu = 63.5; Al = 27.0 g mol^{-1}] **[Guj. CET]**

(a) 190.5 g (b) 9.525 g

(c) 63.5 g (d) 31.75 g

2010

3. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to **[CBSE AIPMT]**

(a) increase in number of ions.

(b) increase in ionic mobility of ions.

(c) 100% ionisation of electrolyte at normal dilution.

(d) increase in both i.e., number of ions and ionic mobility of ions.

4. The compound exhibiting maximum value of equivalent conductance in a fused state is` **[AMU]**

(a) $SrCl_2$ (b) $CaCl_2$

(c) $MgCl_2$ (d) $BeCl_2$

5. At 18°C, the conductance of H^+ and CH_3COO^- at infinite dilution are 315 and 35 mho cm^2 eq^{-1} respectively. The equivalent conductivity of CH_3COOH at infinite dilution is ..... mho cm^2 eq^{-1}. **[AFMC]**

(a) 350 (b) 280

(c) 30 (d) 315

6. How many coulombs are required to deposit 50g of aluminium when the electrode reaction is **[RPMT]**

$$Al^{3+} + 3e^- \rightarrow Al$$

(a) 536111 C (b) 536.111C

(c) 96500 C (d) 38600 C

7. The resistance of 1 N solution of acetic acid is 250 Ω, when measured in a cell having a cell constant of 1.15 cm^{-1}. The equivalent conductance (in ohm^{-1} cm^2 $equiv^{-1}$) of 1 N acetic acid is **[Guj. CET]**

(a) 2.3 (b) 4.6

(c) 9.2 (d) 18.4

8. The conductivity of 0.20 M KCl solution at 298 K is 0.0248 S cm^{-1}. What will be its molar conductivity? **[Haryana PMT]**

(a) 124 S cm^2 (b) 124 cm^{-1}

(c) 124 $ohm^{-1}cm^2$ $equiv^{-1}$ (d) 124 S cm^2 mol^{-1}

9. When same quantity of electricity is passed for half an hour, an amount of Cu and Cr deposited are respectively 0.375 g and 0.30 g . Ratio of electrochemical equivalent of Cu and Cr is **[OJEE]**

(a) 0.8 (b) 1.25

(c) 2.5 (d) 1.62

10. In electrolysis of dil. H_2SO_4 using platinum electrodes **[BVP]**

(a) H_2 is evolved at cathode.

(b) SO_2 is produced at anode.

(c) O_2 is obtained at cathode.

(d) SO_2 is produced at cathode.

2009

11. Al_2O_3 is reduced by electrolysis at low potentials and high current. If 4.0×10^4 amperes of current is passed through molten Al_2O_3 for 6 h, what mass of aluminium is produced? (Assume 100% current efficiency, at. wt. of Al=27) **[CBSE AIPMT]**

(a) 9.0×10^3 g (b) 8.1×10^4 g

(c) 2.4×10^3 g (d) 1.3×10^4 g

12. The equivalent conductance of $\frac{M}{32}$ solution of a weak monobasic acid is 8.0 mho cm^2 and at infinite dilution is 400 mho cm^2.The dissolution constant of this acid is **[CBSE AIPMT]**

(a) 1.25×10^{-5} (b) 1.25×10^{-6}

(c) 6.25×10^{-4} (d) 1.25×10^{-4}

13. **Assertion** On dilution, the equivalent as well as molar conductivity of solution increases.

Reason With dilution, the number of current carrying particles per cm^3 increases. **[AIIMS]**

(a) Both Assertion and Reason are true and Reason is correct explanation of the Assertion.

(b) Both Assertion and Reason are true and Reason is not the correct explanation of the Assertion.

(c) Assertion is true but Reason is false.

(d) Both Assertion and Reason are false.

14. An aqueous solution containing 6.5 g of NaCl of 90% purity was subjected to electrolysis. After the complete electrolys is, the solution was evaporated to get solid NaOH. The volume of 1 M acetic acid required to neutralise NaOH obtained above is **[KCET]**

(a) 2000 cm^3 (b) 100 cm^3

(c) 200 cm^3 (d) 1000 cm^3

15. In the electrolysis of acidulated water, it is desired to obtained 1.12 cc of hydrogen per second under STP condition. The current to be passed is **[KCET]**

(a) 9.65 A (b) 19.3 A

(c) 0.965 A (d) 1.93 A

16. The one which decreases with dilution is **[KCET]**

(a) conductance

(b) specific conductance

(c) equivalent conductance

(d) molar conductance

17. 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} $S.m^2.mol^{-1}$ respectively $\lambda^0_m Ba(OH)_2$ in $S.m^2.mol^{-1}$ **[EAMCET]**

(a) 52.4×10^{-4} (b) 524×10^{-4}

(c) 402×10^{-4} (d) 262×10^{-4}

18. 4.5 g of aluminium (at. mass 27 u) is deposited at cathode from a molten electrolyte containing Al^{3+} ions by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in a solution by the same quantity of electric charge will be **[Manipal]**

(a) 44.8 L (b) 11.2 L

(c) 22.4 L (d) 5.6 L

19. How many coulombs of electricity are required for the reduction of 1 mole of MnO_4^- to Mn^{2+}? **[Manipal]**

(a) 96500 C (b) 9.65×10^6 C

(c) 4.83×10^5 C (d) 1.93×10^5 C

20. The correct expression in SI system relating the equivalent conductance (Λ_C), specific conductance (κ) and equivalent concentration (C) is

(where, C is the number of gram equivalents in one litre of the solution). **[J&K CET]**

(a) $\Lambda_C = \frac{\kappa}{C}$ (b) $\Lambda_C = \frac{\kappa\times1000}{C}$

(c) $\Lambda_C = \frac{\kappa\times10^{-3}}{C}$ (d) $\Lambda_C = \frac{\kappa\times10^{-6}}{C}$

2008

21. Kohlraush's law states that at **[CBSE AIPMT]**

(a) 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.

(b) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte.

(c) infinite dilution, each ion makes definite contribution to 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, whatever be the nature of the other ion of the electrolyte.

22. What is the time (in sec) required for depositing all the silver present in 125 mL of 1M $AgNO_3$ solution by passing a current of 241.25 A? (1 F=96500 C) **[AFMC]**

(a) 10 (b) 50

(c) 1000 (d) 100

23. Which of the following does not conduct electricity? **[AFMC]**

(a) Fused NaCl (b) Solid NaCl

(c) Brine solution (d) Copper

24. Which of the following electrolytic solutions has the least specific conductance? **[KCET]**

(a) 0.02 N (b) 0.2 N

(c) 2 N (d) 0.002 N

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

(a) 4.5 g (b) 5.4 g

(c) 54 g (d) 2.7 g

26. What will be the proportion of moles of metal (Cu:Ni:Ag) at cathode according to the second law of Faraday? **[Guj. CET]**

(a) 1 : 2 : 1 (b) 2 : 2 : 1

(c) 1 : 2 : 2 (d) 1 : 1: 2

2007

27. Which of the following is not a non-electrolyte ? **[AFMC]**

(a) Acetic acid (b) Glucose

(c) Ethanol (d) Urea

28. A current of 96.5 A is passed for 18 min between nickel electrodes in 500 mL solution of 2M $Ni(NO_3)_2$. The molarity of solution after electrolysis would be **[AIIMS]**

(a) 0.46 M (b) 0.92 M

(c) 0.625 M (d) 1.25 M

29. **Assertion** According to Kohlrausch's law the molar conductivity of a strong electrolyte at infinite dilution is sum of molar conductivities of its ions.

Reason The current carried by cation and anion is always equal. **[AIIMS]**

(a) Both Assertion and Reason are true and Reason is correct explanation of the Assertion.

(b) Both Assertion and Reason are true and Reason is not the correct explanation of the Assertion.

(c) Assertion is true but Reason is false.

(d) Both Assertion and Reason are false.

30. The resistance of N/10 solution is found to be $2.5 \times 10^3\ \Omega$. The equivalent conductance of the solution is (cell constant=1.25 cm^{-1}) **[Kerala CEE]**

(a) 2.5 $\Omega^{-1}\ cm^{-2}\ equiv^{-1}$ (b) 5.0 $\Omega^{-1}\ cm^{-2}\ equiv^{-1}$

(c) 2.5 $\Omega^{-1}\ cm^{-2}\ equiv^{-1}$ (d) 50 $\Omega^{-1}\ cm^{-2}\ equiv^{-1}$

31. When 3.86 A current is passed through an electrolyte for 50 min, 2.4 g of a divalent metal is deposited. The gram atomic weight of the metal (in gram) is **[EAMCET]**

(a) 24 (b) 12

(c) 64 (d) 40

32. How many atoms of calcium will be deposited from a solution of $CaCl_2$ by a current of 25 mA flowing for 60 s ? **[MP PMT]**

(a) 4.68×10^{18} (b) 4.68×10^{15}

(c) 4.68×10^{12} (d) 4.68×10^{9}

33. The specific conductance (κ) of an electrolyte of 0.1 N concentration is related to equivalent conductance (Λ) by the following formula **[J&K CET]**

(a) $\Lambda = \kappa$ (b) $\Lambda = 10\kappa$

(c) $\Lambda = 100\kappa$ (d) $\Lambda = 10000\kappa$

34. Pure water does not conduct electricity because it is **[J&K CET]**

(a) basic (b) almost not ionised

(c) decomposed easily (d) acidic

2006

35. In the electrolysis of water, one faraday of electrical energy would evolve **[AMU]**

(a) one mole of oxygen

(b) one gram atom of oxygen

(c) 8 g of oxygen

(d) 22.4 L of oxygen

36. If the aqueous solution of the following salts are electrolysed for 1 h with 10 A current, which solution will deposit the maximum mass of the metal at the cathode? The atomic weights are Fe^{2+}=56, Zn^{2+}=65, Ag^{+}=108, Hf^{3+}=178 and W^{3+}=184 **[Kerala CEE]**

(a) $ZnSO_4$ (b) $FeCl_3$

(c) $HfCl_4$ (d) $AgNO_3$

37. The ionic conductance of Ba^{2+} and Cl^{-} are respectively 127 and 76Ω^{-1} cm^2 eq^{-1} at infinite dilution. The equivalent conductance (in Ω^{-1} cm^2) of $BaCl_2$ at infinite dilution will be **[MHT CET]**

(a) 139.5 (b) 203

(c) 279 (d) 101.5

38. The charge required to liberate one gram equivalent of an element is **[BCECE]**

(a) 96500 F (b) 1F

(c) 1C (d) None of these

2005

39. A current of strength 2.5 A was passed through $CuSO_4$ solution for 6 min 26 s. The amount of copper deposited is (Atomic weight of Cu=63.5, 1F= 96500 C) **[Punjab PMET]**

(a) 0.3175 g (b) 3.175 g

(c) 0.635 g (d) 6.35 g

40. What is the electrochemical equivalent (in g-C^{-1}) of silver? (Ag=108, F=Faraday) **[EAMCET]**

(a) 108 F (b) $\frac{108}{F}$

(c) $\frac{F}{108}$ (d) $\frac{1}{108F}$

2004

41. At 25°C the specific conductivity of a normal solution of KCl is 0.002765 mho. The resistance of cell is 400Ω. The cell constant is **[Punjab PMET]**

(a) 0.815 (b) 1.016

(c) 1.106 (d) 2.016

2003

42. On passing electric current of one ampere for 16 min and 5 s through one litre solution of $CuCl_2$, all copper of solution was deposited at cathode. The strength of $CuCl_2$ slolution was (molar mass of Cu=63.5, Faraday constant =96500 C/mol) **[AMU]**

(a) 0.2 N (b) 0.01N

(c) 0.1 N (d) 0.02 N

43. An electric current is passed through silver voltameter connected to a water voltameter. The cathode of the silver voltameter weighed 0.108g more at the end of the electrolysis. The volume of oxygen evolved at STP is **[Kerala CEE]**

(a) 56 cm^3 (b) 550 cm^3

(c) 5.6 cm^3 (d) 11.2 cm^3

TOPIC 2

ELECTROCHEMICAL SERIES, ELECTRODE POTENTIAL AND EMF

2011

44. If the E^{o}_{cell} for a given reaction has a negative value, then which of the following gives the correct relationships for the values of ΔG^{o} and K_{eq}? **[CBSE AIPMT]**

(a) $\Delta G^{o}>0$; $K_{eq}<1$ (b) $\Delta G^{o}>0$; $K_{eq}>1$

(c) $\Delta G^{o}<0$; $K_{eq}>1$ (d) $\Delta G^{o}<0$; $K_{eq}<1$

45. The electrode potentials for

$Cu^{2+}(aq)+e^{-}\rightarrow Cu^{+}(aq)$ and $Cu^{+}(aq)+e^{-}\rightarrow Cu(s)$

are +0.15 V and + 0.50 V respectively. The value of $E^{o}_{Cu^{2+}/Cu}$ will be **[CBSE AIPMT]**

(a) 0.150 V (b) 0.500 V

(c) 0.325 V (d) 0.650 V

46. Standard electrode potential of three metals X, Y and Z are –1.2 V, +0.5 V and –3.0 V respectively. The reducing power of these metals will be **[CBSE AIPMT]**

(a) X>Y>Z (b) Y>Z>X

(c) Y>X>Z (d) Z>X>Y

47. Standard electrode potential for Sn^{4+}/Sn^{2+} couple is +0.15 V and that for the Cr^{3+}/Cr couple is –0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be **[CBSE AIPMT]**

(a) +1.83 V (b) +1.19 V

(c) +0.89 V (d) +0.18 V

48. Given the following reactions involving, A, B, C and D

(i) $C + B^+ \rightarrow C^+ + B$

(ii) $A^+ + D \rightarrow$ No reaction

(iii) $C^+ + A \rightarrow$ No reaction

(iv) $D + B^+ \rightarrow D^+ + B$

The correct arrangement of A, B, C, D in order of their decreasing ability as reducing agent **[DPMT]**

(a) D > B > C > A (b) A > C > D > B

(c) C > A > B > D (d) C > A > D > B

49. The standard emf of a galvanic cell involving 2 moles of electrons in its redox reaction is 0.59 V. The equilibrium constant for the redox reaction of the cell is **[KCET]**

(a) 10^{20} (b) 10^5

(c) 10 (d) 10^{10}

50. E_1, E_2 and E_3 are the emfs of the following three galvanic cells respectively

(i) $Zn(s) \mid Zn^{2+}(0.1M) \parallel Cu^{2+}(1M) \mid Cu(s)$

(ii) $Zn(s) \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu(s)$

(iii) $Zn(s) \mid Zn^{2+}(1M) \parallel Cu^{2+}(0.1M) \mid Cu(s)$

Which one of the following is true? **[KCET]**

(a) $E_2 > E_1 > E_3$ (b) $E_1 > E_2 > E_3$

(c) $E_3 > E_1 > E_2$ (d) $E_3 > E_2 > E_1$

2010

51. For the reduction of silver ions with copper metals, 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}) **[CBSE AIPMT]**

(a) –98.0kJ (b) –89.0 kJ

(c) –89.0 J (d) –44.5 kJ

52. The logarithm of the equilibrium constant of the cell reaction corresponding to the cell $X(s) \mid X^{2+}(aq) \parallel Y^+(aq) \mid Y(s)$ with standard cell potential, E°_{Cell} =1.12 V is given by **[AMU]**

(a) 12.5 (b) 21.5

(c) 37.9 (d) 47.2

53. If the half cell reactions are given as

(i) $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$; $E^\circ = -0.44V$

(ii) $2H^+(aq) + \frac{1}{2}O_2(g) + 2e^- \rightarrow H_2O(\ell)$ $E^\circ = +1.23V$

The E° for the reaction

$$Fe(s) + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+}(aq) + H_2O(\ell)$$ **[AMU]**

(a) +1.67 V (b) –1.67 V

(c) +0.79 V (d) –0.79 V

54. Given for Sn^{4+}/Sn^{2+}, standard reduction potential is 0.15 V and for Au^{3+}/Au, standard reduction potential is 1.5 V. For the reaction,

$$3Sn^{2+} + 2Au^{3+} \rightarrow 3Sn^{4+} + 2Au$$

the value of E°_{cell} is **[MHT CET]**

(a) +1.35 (b) +2.55

(c) –1.35 (d) –2.55

55. The $E^\circ_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are –0.41, +1.57, +0.77, and +1.97 V respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest? **[Manipal]**

(a) Cr (b) Mn

(c) Fe (d) Co

56. At 25°C temperature, the cell potential of a given electrochemical cell is 1.92 V. Find the value of x.

$Mg(s) \mid Mg^{2+}(aq)\ x\ M \parallel Fe^{2+}(aq)\ 0.01M \mid Fe(s)$

$E^\circ Mg/Mg^{2+}(aq) = 2.37V; E^\circ Fe/Fe^{2+}(aq) = 0.45$ V

[Guj. CET]

(a) x=0.01M (b) x<0.01 M

(c) x>0.01M (d) x cannot be predicted

57. The potential of a hydrogen electrode at pH=10 is **[WB JEE]**

(a) 0.59 V (b) 0.00V

(c) –0.59V (d) –0.059 V

2009

58. Given : (i) $Cu^{2+} + 2e^- \rightarrow Cu$; E^o=0.337 V

(ii) $Cu^{2+} + e^- \rightarrow Cu^+$; E^o=0.153V

Electrode potential, E^o for the reaction, $Cu^+ + e^- \rightarrow Cu$, will be **[CBSE AIPMT, AMU]**

(a) 0.52 V (b) 0.90 V

(c) 0.30 V (d) 0.38 V

59. Given , Pb^{2+}/Pb=–0.126 V; Zn^{2+}/Zn=–0.763 V Find the emf of the following cell $Zn \mid Zn^{2+}(0.1\ M) \| Pb^{2+}(1M) \mid Pb$. **[AFMC]**

(a) –0.637 (b) +0.637

(c) >0.637 (d) +0.889

60. The reduction potential at pH=14 for the Cu^{2+}/Cu couples is

[Given, $E^o_{Cu^{2+}/Cu}$ =0.34V; $K_{sp}[Cu(OH)_2]=1\times10^{-19}$] **[AIIMS]**

(a) 0.34 V (b) –0.34V

(c) 0.22 V (d) –0.22V

61. A gas X at 1 atm is bubbled through a solution containing a mixture of 1M Y^- and 1 M Z^- at 25°C. If the reduction potential of Z > Y > X, then **[AIIMS]**

(a) Y will oxidise X but not Z.

(b) Y will oxidise both X and Z.

(c) Y will oxidise Z but not X.

(d) Y will reduce both X and Z.

62. The potential of standard hydrogen electrode is zero. This implies that **[AMU]**

(a) $\Delta G^o_f(H^+, aq)=0$ (b) $\Delta H^o_f(H^+, aq)=0$

(c) $\Delta G^o_f(H^+, aq)<0$ (d) $\Delta G^o_f(H^+, aq)>0$

63. E^o for Mg^{2+}/Mg = –2.37 V, Zn^{2+}/Zn = –0.76 V, and Fe^{2+}/Fe = –0.44 V. Which statement is correct? **[CPMT]**

(a) Zn reduces Fe^{2+} (b) Zn reduces Mg^{2+}

(c) Mg oxidises Fe (d) Zn oxidises Fe

64. The standard elecrode potential for the half cell reactions are

$Zn^{2+} + 2e^- \rightarrow Zn$; $E^o = -0.76V$

$Fe^{2+} + 2e^- \rightarrow Fe$; $E^o = -0.44V$

The emf of the cell reaction

$Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ **[KCET]**

(a) –1.20 V (b) +1.20 V

(c) +0.32 V (d) –0.32 V

65. A solution of nickel sulphate in which nickel rod is dipped is diluted 10 times. The reduction potential of Ni at 298 K **[Kerala CEE]**

(a) decreases by 60mV (b) decrease by 30 mV

(c) decreases by 30 V (d) increases by 30 mV

66. The standard reduction potentials for Cu^{2+}/Cu; Zn^{2+}/Zn; Li^+/Li; Ag^+/Ag and H^+/H_2 are +0.34 V, –0.762 V, –3.05 V, +0.80 V and 0.00 V respectively. Choose the strongest reducing agent among the following. **[Kerala CEE]**

(a) Zn (b) H_2

(c) Ag (d) Li

67. The standard emf of a cell involving one electron charge is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is (1F=96500 C mol^{-1}, R=8.314 $JK^{-1}mol^{-1}$) **[Manipal]**

(a) 1.0×10^1 (b) 1.0×10^{30}

(c) 1.0×10^{10} (d) 1.0×10^5

2008

68. On the basis of the following E^o values, the strongest oxidising agent is

$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-; E^o = -0.35V$

$Fe^{2+} \rightarrow Fe^{3+} + e^-; E^o = -0.77V$ **[CBSE AIPMT]**

(a) $[Fe(CN)_6]^{4-}$ (b) Fe^{2+}

(c) Fe^{3+} (d) $[Fe(CN)_6]^{3-}$

69. What is the electrode potential (in volt) of the following electrode at 25°C?

$Ni^{2+}(0.1\,M)\,|\,Ni(s)$

(Standard reduction potential of Ni^{2+}/Ni is –0.25 V, $\frac{2.303RT}{F} = 0.06$) **[Punjab PMET]**

(a) –0.28V (b) –0.34 V

(c) –0.82 V (d) –0.22V

70. Hydrogen gas is not liberated when the following metal is added to dil HCl **[KCET]**

(a) Ag (b) Zn

(c) Mg (d) Sn

71. The equilibrium constant for the following redox reaction at 298 K of 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+}? **[Kerala CEE]**

(a) +1.006 V (b) –1.006 V

(c) +0.77 V (d) –0.77V

72. The cell potential of the following cell at 25°C (in volts) is

$$\underset{(1\,atm)}{(pt)}\,H_2\,|\,\underset{(0.01M)}{H^+}\,||\underset{(0.1\,M)}{Cu^{2+}}\,|Cu(E^{o}_{Cu^{2+}/Cu} = 0.337V)$$ **[EAMCET]**

(a) 0.308 (b) 0.427

(c) –0.308 (d) 0.337

73. $Cu^{+}(aq)$ is unstable in solution and undergoes simultaneous oxidation and reduction, according to the reaction

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

choose the correct E^{o} for the above reaction if

$E^{o}_{Cu^{2+}|Cu} = 0.34\,V$ and $E^{o}_{Cu^{2+}|Cu^{+}} = 0.15\,V$ **[MHTCET]**

(a) –0.38 V (b) +0.49V

(c) +0.38V (d) –0.19 V

2007

74. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 **[Punjab PMET]**

(a) Zn act as oxidising agent when react 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.

75. EMF of hydrogen electrode in terms of pH is (at 1 atm pressure) **[MHTCET]**

(a) $E_{H_2} = \frac{RT}{F}pH$ (b) $E_{H_2} = \frac{RT}{F}\frac{1}{pH}$

(c) $E_{H_2} = \frac{2.303RT}{F}pH$ (d) $E_{H_2} = -0.0591pH$

76. The standard electrode potential of hydrogen electrode at 1 M concentration and hydrogen gas at 1 atm pressure is **[J&K CET]**

(a) 1 V (b) 6 V

(c) 8 V (d) 0 V

2006

77. A hypothetical electrochemical cell is shown below

$A\,|\,A^{+}(xM)\,||B^{+}(yM)\,|\,B$

The emf measured is +0.20V. The cell reaction is **[CBSE AIPMT]**

(a) $A^{+} + B \rightarrow A + B^{+}$

(b) $A^{+} + e^{-} \rightarrow A; B^{+} + e^{-} \rightarrow B$

(c) the cell reaction cannot be predicted

(d) $A + B^{+} \rightarrow A^{+} + B$

78. **Assertion** E^{o} for Mn^{3+}/Mn^{2+} is more positive than Cr^{3+}/Cr^{2+}.

Reason The third ionisation energy of Mn is larger than that of Cr. **[AIIMS]**

(a) Both Assertion and Reason are true and Reason is correct explanation of the Assertion.

(b) Both Assertion and Reason are true and Reason is not the correct explanation of the Assertion.

(c) Assertion is true but Reason is false.

(d) Both Assertion and Reason are false.

79. For the electrochemical cell, $M \mid M^+ \parallel X^- \mid X$, $E^o(M^+/M) = 0.44V$ and $E^o(X/X^-) = 0.33V$, From this data one can deduce that **[BHU]**

(a) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction

(b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction

(c) $E_{cell} = 0.77V$

(d) $E_{cell} = -0.77V$

80. The reduction electrode potential, E of 0.1 M solution of M^+ ions ($E^o_{RP} = -2.36V$) is **[MHTCET]**

(a) –4.82V (b) –2.41 V

(c) +2.41V (d) None of these

81. $E^o = \frac{RT}{nF} \ln K_{eq}$

This equation is called **[MPPMT]**

(a) Gibbs equation (b) Nernst equation

(c) Gibbs-Helmholtz equation

(d) van der Waals' equation

82. During electrochemical process **[Guj. CET]**

(a) Gibbs free energy increases.

(b) Gibbs free energy remains constant.

(c) no prediction can be about Gibbs free energy.

(d) Gibbs free energy decreases.

2005

83. If hydrogen electrode dipped in two solutions of pH=3 and pH=6 and salt bridge is connected, the emf of resulting cell is **[DUMET]**

(a) 0.177 V (b) 0.3 V

(c) 0.052 V (d) 0.104 V

84. The standard electrode potential is measured by **[KCET]**

(a) electrometer (b) voltmeter

(c) pyrometer (d) galvanometer

85. Na is used in reduction of Zn salt because **[MHTCET]**

(a) $E^o_{Zn(oxi)} > E^o_{Na(oxi)}$ (b) $E^o_{Zn(red)} < E^o_{Na(red)}$

(c) $E^o_{Zn(oxi)} < E^o_{Na(oxi)}$ (d) Both (a) and (b)

86. Reduction potentials of A, B, C and D are 0.8 V, 0.79 V, 0.34 V and –2.37 V respectively. Which element displaces all the other three elements? **[MHTCET]**

(a) B (b) A

(c) D (d) C

87. The standard emf of Daniell cell is 1.10 V. The maximum electrical work obtained from the cell is **[Haryana PMT]**

(a) 212.3 kJ (b) 175.4 kJ

(c) 106.15 kJ (d) 350.8 kJ

88. For cell reaction

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

cell representation is **[BCECE]**

(a) $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

(b) $Cu \mid Cu^{2+} \parallel Zn^{2+} \mid Zn$

(c) $Cu \mid Zn^{2+} \parallel Zn \mid Cu^{2+}$

(d) $Cu^{2+} \mid Zn \parallel Zn^{2+} \mid Cu$

89. Alkali metals have high oxidation potential and hence, they behave as **[JCECE]**

(a) oxidising agents (b) Lewis bases

(c) reducing agents (d) electrolytes

90. What is the potential of platinum wire dipped into a solution of 0.1 M in Sn^{2+} and 0.01 M in Sn^{4+}? **[JCECE]**

(a) E^o (b) $E^o + 0.059$

(c) $E^o + \frac{0.059}{2}$ (d) $E^o - \frac{0.059}{2}$

2004

91. **Assertion** Copper metal gets readily corroded in an acidic aqueous solution.

Reason Free energy change for this process is positive. **[AIIMS]**

(a) Both Assertion and Reason are true and Reason is correct explanation of the Assertion.

(b) Both Assertion and Reason are true and Reason is not the correct explanation of the Assertion.

(c) Assertion is true but Reason is false.

(d) Both Assertion and Reason are false.

92. Aluminium displaces hydrogen from dilute HCl whereas silver does not. The emf of a cell prepared by combining Al/Al^{3+} and Ag/Ag^{+} is 2.46 V. The reduction potential of silver electrode is +0.80 V. The reduction potential of aluminium electrode is **[KCET]**

(a) +1.66V (b) –3.26 V

(c) 3.26 V (d) –1.66 V

93. Standard electrode potential of cell

$H_2/H^+ \,||\, Ag^+/Ag$ is $(E^oAg^+/Ag = 0.80V)$ **[Kerala CEE]**

(a) 0.8 V (b) –0.8 V

(c) –1.2 V (d) 1.2 V

94. For the following cell with hydrogen electrode at two different pressures p_1 and p_2

$$Pt(H_2)_{p_1} \,|\, H^+(aq) \,||\, Pt(H_2)_{p_2} \,|\, H^+(aq)$$

emf is given by **[MHT CET]**

(a) $\frac{RT}{F}\log_e\frac{p_1}{p_2}$ (b) $\frac{RT}{2F}\log_e\frac{p_1}{p_2}$

(c) $\frac{RT}{F}\log_e\frac{p_2}{p_1}$ (d) $\frac{RT}{2F}\log_e\frac{p_2}{p_1}$

95. For the cell,

$Tl\,|\,Tl^+(0.001M)\,||\,Cu^{2+}(0.1)M\,|\,Cu$

E_{cell} at 25°C is 0.83 V. E_{cell} can be increased **[Haryana PMT]**

(a) by decreasing $[Cu^{2+}]$ (b) by increasing $[Cu^{2+}]$

(c) by increasing $[Tl^+]$ (d) None of these

2003

96. On the basis of information available from the reaction

$$\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3, \Delta G = -827\,kJ\,mol^{-1}$$

of O_2, the minimum emf required to carry out an electrolysis of Al_2O_3, is (F=96500 C mol^{-1}) **[CBSE AIPMT]**

(a) 6.42 V (b) 8.56 V

(c) 2.14 V (d) 4.28 V

97. If the standard electrode potential of Cu^{2+}/Cu electrode is 0.34 V, what is the electrode potential at 0.01 M concentration of Cu^{2+}? (T = 298 K) **[EAMCET]**

(a) 0.399 V (b) 0.281 V

(c) 0.222 V (d) 0.176 V

TOPIC 3

ELECTROCHEMICAL CELLS, (INCLUDING FUEL CELLS), CORROSION

2011

98. Which of the following reactions is correct for a given electrochemical cell at 25°C ? **[Guj. CET]**

$Pt/Br_2(g)/Br^-(aq)//Cl^-(aq)/Cl_2(g)/Pt.$

(a) $2Br^-(aq) + Cl_2(g) \rightarrow 2Cl^-(aq) + Br_2(g)$

(b) $Br_2(g) + 2Cl^-(aq) \rightarrow 2Br^-(aq) + Cl_2(g)$

(c) $Br_2(g) + Cl_2(g) \rightarrow 2Br^-(aq) + 2Cl^-(aq)$

(d) $2Br^-(aq) + 2Cl^-(aq) \rightarrow Br_2(g) + Cl_2(g)$

2010

99. When iron is rusted, it is **[MP PMT]**

(a) reduced (b) decomposed

(c) oxidised

(d) changed in the fine powder

100. Which of the following statements is true for the electrochemical Daniel cell? **[Manipal]**

(a) Electrons flow from copper electrode to zinc electrode

(b) Current flows from zinc electrode to copper electrode.

(c) Cations move toward copper electrode.

(d) Cations move toward zinc electrode.

101. Chemical formula of rust is **[OJEE]**

(a) $Fe_2O_3.H_2O$ (b) $Fe_2O_3.5H_2O$

(c) $Fe_2O_3.xH_2O$ (d) None of these

102. When lead storage battery discharges **[VMMC]**

(a) SO_2 is evolved (b) $PbSO_4$ is consumed

(c) Lead is formed (d) H_2SO_4 is consumed

103. E^o_{cell} and ΔG^o are related as **[VMMC]**

(a) $\Delta G^o = nFE^o_{cell}$ (b) $\Delta G = -nFE^o_{cell}$

(c) $\Delta G^o = -nFE^o_{cell}$ (d) $\Delta G^o = nFE^o_{cell} = 0$

104. The rusting of iron is catalysed by **[CG PMT, Haryana PMT]**

(a) Fe (b) O_2

(c) H^+ (d) Zn

105. Standard solution of KNO_3 is used to make salt bridge because **[CG PMT, Haryana PMT]**

(a) velocity of K^+ is greater than NO_3^-.

(b) velocity of NO_3^- is greater than K^+.

(c) velocity of K^+ and NO_3^- are same.

(d) KNO_3 is highly soluble in water.

2008

106. Standard free energies of formation (in kJ/mol) at 298 K are –237.2, –394.4 and –8.2 for $H_2O(\ell)$, $CO_2(g)$ and pentane (g), respectively. The value of E^o_{cell} for the pentane-oxygen fuel cell is **[CBSE AIPMT]**

(a) 1.968 V (b) 2.0968 V

(c) 1.0968 V (d) 0.0968 V

107. **Assertion** The cell potential of mercury cell is 1.35 V, which remains constant.

Reason In mercury cell, the electrolyte is a paste of KOH and ZnO. **[AIIMS]**

(a) Both Assertion and Reason are true and Reason is correct explanation of the Assertion.

(b) Both Assertion and Reason are true and Reason is not the correct explanation of the Assertion.

(c) Assertion is true but Reason is false.

(d) Both Assertion and Reason are false.

108. Galvanic cell is a device in which **[CBSE AIPMT]**

(a) chemical energy is converted into electrical energy.

(b) electrical energy is converted into chemical energy.

(c) chemical energy is seen in the form of heat.

(d) thermal energy from an outside source is used to drive the cell reaction.

2007

109. The eficiency of a fuel cell is given by **[CBSE AIPMT]**

(a) $\frac{\Delta H}{\Delta G}$ (b) $\frac{\Delta G}{\Delta S}$

(c) $\frac{\Delta G}{\Delta H}$ (d) $\frac{\Delta S}{\Delta G}$

110. When lead storage battery is charge **[AFMC]**

(a) lead dioxide dissolves.

(b) sulphuric acid is regenerated.

(c) the lead electrode becomes coated with lead sulphate.

(d) the amount of sulphuric acid decreases.

111. Anode in the galvanic cell, is **[RPMT]**

(a) negative electrode (b) positive electrode

(c) neutral electrode (d) None of these

2006

112. What is the cell reaction occuring in Daniell cell (Galvanic cell)? **[J&K CET]**

(a) $Cu(s) + ZnSO_4(aq) \rightarrow CuSO_4(aq) + Zn(s)$

(b) $Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq)$

(c) $Ni(s) + ZnSO_4(aq) \rightarrow NiSO_4(aq) + Zn(s)$

(d) $2Na(s) + CdSO_4(aq) \rightarrow Na_2SO_4(aq) + Cd(s)$

2005

113. When an acid cell is charged then **[AFMC]**

(a) voltage of cell increases

(b) electrolyte of cell dilutes

(c) resistance of cell increases

(d) None of the above

114. The chemical reaction,

$$2AgCl(s) + H_2(g) \rightarrow 2HCl(aq) + 2Ag(s)$$

taking place in a galvanic cell is represented by the notation **[AIIMS]**

(a) $Pt(s) \mid H_2(g), 1bar \mid 1M\ KCl(aq) \mid AgCl(s) \mid Ag(s)$

(b) $Pt(s) \mid H_2(g), 1bar \mid 1M\ HCl(aq) \mid 1MAg^+(aq) \mid Ag(s)$

(c) $Pt(s) \mid H_2(g), 1bar \mid 1M\ HCl(aq) \mid AgCl(s) \mid Ag(s)$

(d) $Pt(s) \mid H_2(g), 1bar \mid 1M\ HCl(aq) \mid Ag(s) \mid AgCl(s)$

115. **Assertion** Galvanised iron does not rust.

Reason Zinc has a more negative electrode potential than iron **[AIIMS]**

(a) Both Assertion and Reason are true and Reason is correct explanation of the Assertion.

(b) Both Assertion and Reason are true and Reason is not the correct explanation of the Assertion.

(c) Assertion is true but Reason is false.

(d) Both Assertion and Reason are false.

2004

116. Iron pipes, lying in acidic soil, are often attached to the blocks of magnesium for their protection from rusting because magnesium **[BHU, DUMET]**

(a) is lighter than iron

(b) is readily converted into positive ion

(c) forms a corrosion–resistant alloy with iron

(d) prevents air from reaching the surface of iron.

117. Which of the following statements is true for fuel cells? **[Punjab PMET]**

(a) They run till the reactant are active

(b) They are free from pollution.

(c) They are more efficient.

(d) All of the above.

118. In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to **[DUMET]**

(a) generate heat.

(b) create potential difference between the two electrodes.

(c) produce high purity water

(d) remove adsorbed oxygen from electrode surfaces.

2003

119. Which of the following reaction is used to make a fuel cell? **[AIIMS]**

(a) $Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(\ell)$

(b) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(\ell)$

(c) $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$

(d) $2Fe(s) + O_2(g) + 2H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(\ell)$

120. Which cell convert electrical energy into chemical energy? **[Punjab PMET]**

(a) Voltaic cell (b) Electrolytic cell

(c) Galvanic cell (d) Electrochemical cell

121. The cell reaction of the galvanic cell $Cu(s)\,|\,Cu^{2+}(aq)\,||\,Hg^{2+}(aq)\,|\,Hg(\ell)$ is **[EAMCET]**

(a) $Hg + Cu^{2+} \rightarrow Hg^{2+} + Cu$

(b) $Hg + Cu^{2+} \rightarrow Cu^{+} + Hg^{+}$

(c) $Cu + Hg \rightarrow CuHg$

(d) $Cu + Hg^{2+} \rightarrow Cu^{2+} + Hg$

122. Which one of the following metal is used in galvanisation? **[RPMT]**

(a) Cu (b) Ag

(c) Zn (d) Fe

ANSWER KEY

EXERCISE - 1 : (Basic Objective Questions)

1. (d)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (d)	**6.** (a)	**7.** (a)	**8.** (a)	**9.** (d)	**10.** (c)
11. (b)	**12.** (d)	**13.** (d)	**14.** (a)	**15.** (b)	**16.** (c)	**17.** (d)	**18.** (b)	**19.** (a)	**20.** (a)
21. (a)	**22.** (b)	**23.** (d)	**24.** (a)	**25.** (d)	**26.** (b)	**27.** (b)	**28.** (b)	**29.** (b)	**30.** (c)
31. (d)	**32.** (c)	**33.** (b)	**34.** (d)	**35.** (d)	**36.** (c)	**37.** (a)	**38.** (a)	**39.** (c)	**40.** (a)
41. (b)	**42.** (d)	**43.** (c)	**44.** (c)	**45.** (a)	**46.** (d)	**47.** (c)	**48.** (b)	**49.** (d)	**50.** (c)
51. (c)	**52.** (b)	**53.** (a)	**54.** (a)	**55.** (a)	**56.** (a)	**57.** (b)	**58.** (a)	**59.** (b)	**60.** (a)
61. (c)	**62.** (c)	**63.** (d)	**64.** (a)	**65.** (d)	**66.** (b)	**67.** (b)	**68.** (b)	**69.** (c)	**70.** (d)
71. (b)	**72.** (c)	**73.** (a)	**74.** (c)	**75.** (c)	**76.** (a)	**77.** (d)	**78.** (a)	**79.** (b)	

EXERCISE - 2 : (Previous Year Competition Questions)

1 . (c)	**2 .** (b)	**3.** (b)	**4.** (a)	**5.** (a)	**6.** (a)	**7.** (b)	**8.** (d)	**9.** (b)	**10.** (a)
11. (b)	**12.** (a)	**13.** (c)	**14.** (b)	**15.** (a)	**16.** (b)	**17.** (b)	**18.** (d)	**19.** (c)	**20.** (c)
21. (d)	**22.** (b)	**23.** (b)	**24.** (d)	**25.** (a)	**26.** (d)	**27.** (a)	**28.** (b)	**29.** (c)	**30.** (b)
31. (d)	**32.** (a)	**33.** (d)	**34.** (b)	**35.** (c)	**36.** (d)	**37.** (b)	**38.** (b)	**39.** (a)	**40.** (b)
41. (c)	**42.** (b)	**43.** (c)	**44.** (a)	**45.** (c)	**46.** (d)	**47.** (c)	**48.** (d)	**49.** (a)	**50.** (b)
51. (b)	**52.** (c)	**53.** (a)	**54.** (a)	**55.** (a)	**56.** (a)	**57.** (c)	**58.** (a)	**59.** (c)	**60.** (d)
61. (a)	**62.** (a)	**63.** (a)	**64.** (c)	**65.** (b)	**66.** (d)	**67.** (c)	**68.** (c)	**69.** (a)	**70.** (a)
71. (c)	**72.** (b)	**73.** (c)	**74.** (d)	**75.** (d)	**76.** (d)	**77.** (d)	**78.** (b)	**79.** (b)	**80.** (b)
81. (b)	**82.** (d)	**83.** (a)	**84.** (b)	**85.** (c)	**86.** (c)	**87.** (a)	**88.** (a)	**89.** (c)	**90.** (d)
91. (c)	**92.** (d)	**93.** (a)	**94.** (b)	**95.** (b)	**96.** (c)	**97.** (b)	**98.** (a)	**99.** (c)	**100.** (c)
101. (c)	**102.** (d)	**103.** (c)	**104.** (c)	**105.** (c)	**106.** (c)	**107.** (b)	**108.** (a)	**109.** (c)	**110.** (b)
111. (a)	**112.** (b)	**113.** (a)	**114.** (c)	**115.** (a)	**116.** (b)	**117.** (d)	**118.** (b)	**119.** (c)	**120.** (b)
121. (d)	**122.** (c)								