ELECTROCHEMISTRY

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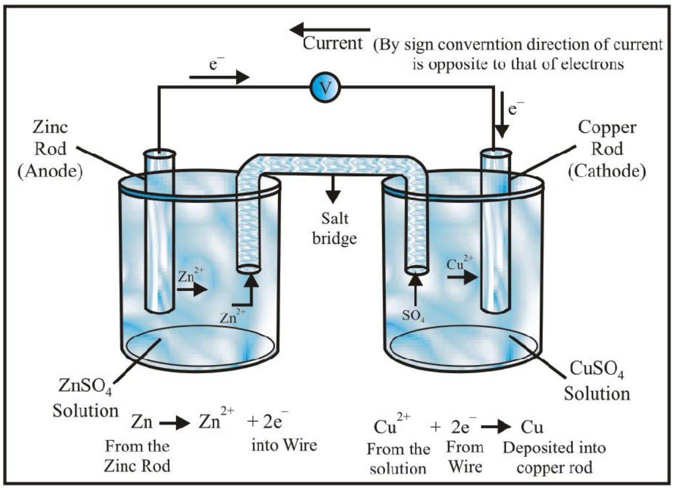


THEORY

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,

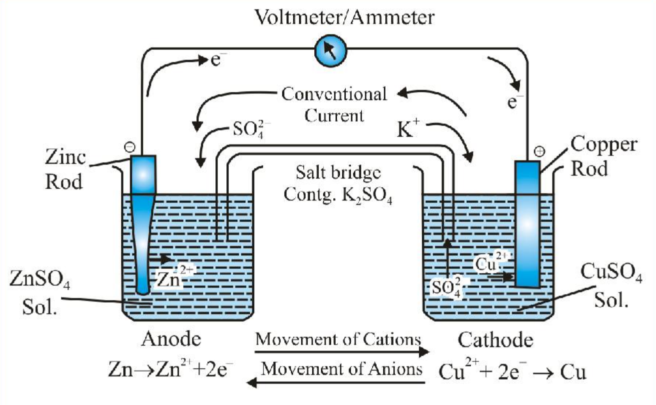
$$Zn(s)\,|\,Zn^{2+}\,(1\,M)\,||\,Cu^{2+}\,(1\,M)\,|\,Cu \quad EMF = +1.1V$$

(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

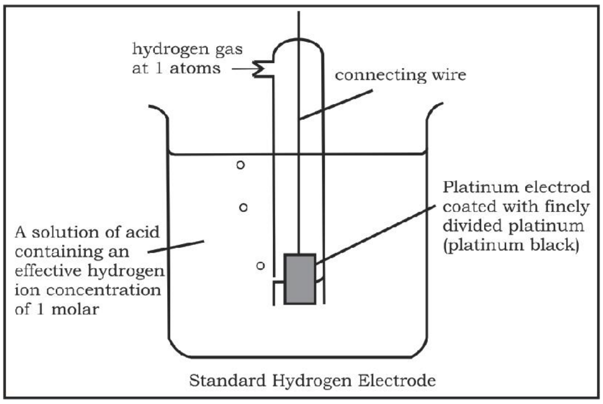
A metal rod/plate is dipped in an electrolyte solution containing metal ions. There is a potential difference between these two phases and this electrode can act as a cathode or anode both.

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.



Standard Hydrogen Electrode

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

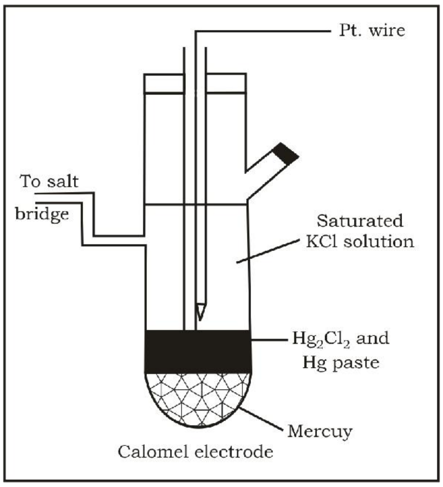
We use salts of some metals which are sparingly soluble with the metal itself as electrodes. For example, if we use AgCl with Ag there is a potential gap between these two phases which can be identified in the following reaction:

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

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.



Calomel electrode

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

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

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 :

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

At anode :

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

Overall reaction :

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

$$\text{or } 2NaCl\,(l) \xrightarrow{\text{Electrolysis}} \underset{\text{At cathode}}{2Na\,(l)} + \underset{\text{At anode}}{Cl_2\,(g)}$$

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

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

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

$\mathbf{PbSO_4(s) + 2H_2O(l)}$

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

$\mathbf{2PbSO_4(s) + 2H_2O(l)}$

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 : $\mathbf{2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) +}$

$\mathbf{PbO_2(s) + 2H_2SO_4(aq)}$

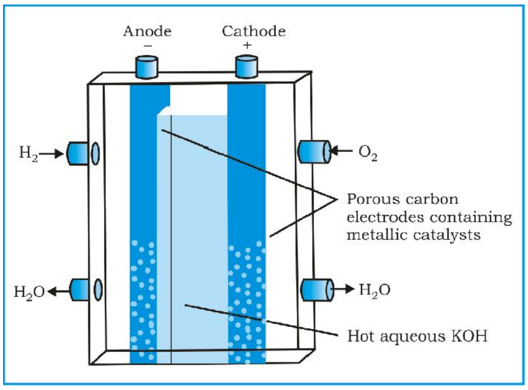
19. FUEL CELLS

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.

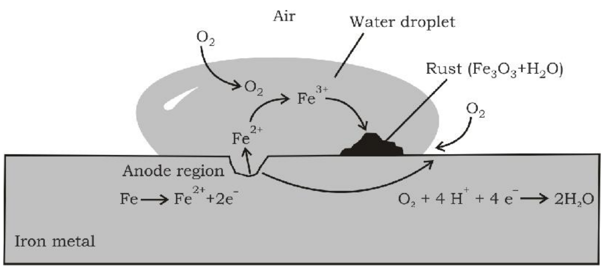
At one location oxidation of iron takes place (anode) and at another location reduction of oxygen to form water takes place (cathode). First Fe gets oxidised to Fe^{2+} and then in the presence of oxygen it forms Fe^{3+} which then reacts with water to form rust which is represented by $Fe_2O_3.xH_2O$.

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

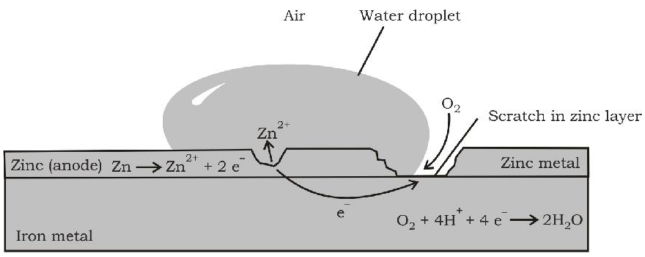
Cathode : $O_2\,(g) + 4H^+ + 4e^- \rightarrow 2H_2O\,(l)\ E^o = 1.23\ V$

Overall R × N :

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



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 ℓ = 1 cm and A = 1 cm², then κ = 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 cm².

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.

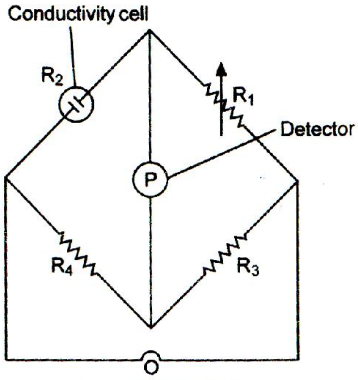
(ii) **Solvation of Ions :** Larger the magnitude of solute-solvent interactions, greater is the extent of solvation and lower will be the electrical conductance.

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

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

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 :

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

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

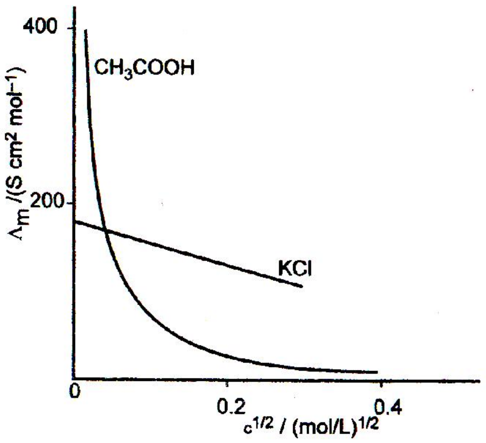
27. VARIATION OF CONDUCTIVITY AND MOLAR CONDUCTIVITY WITH DILUTION

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

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

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:

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

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

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

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

where, R = Resistance

A = Area of cross-section of the electrodes.

ρ = Resistivity

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

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. $\Lambda_m^\infty(A_xB_y) = x\Lambda_m^\infty(A^{y+}) + y\Lambda_m^\infty(B^{x-})$

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

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

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

7. Nernst equation for a general electrochemical reaction

$$aA + bB \xrightarrow{n\bar{e}} cC + dD$$

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

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

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

8. $\log K_c = \frac{n}{0.0591}E^o_{cell}$

where, K_c = Equilibrium constant.

9. $\Delta_rG^o = -nFE^o_{cell}$ (Creterion of spontaneity)

$\Delta_rG^o = -2.303RT \log K_c$

where, Δ_rG^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

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

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, $\Delta G = -$ 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:** $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-, \quad E^o_{Fe^{2+}/Fe} = -0.44 \text{ V}$

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

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

Overall reaction

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

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

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

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.

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

The E° electrode values are

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

$Ag^+/Ag = 0.81$ V

For this cell calculate/write

(a) (i) E° 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) $E^o_{Ag^+/Ag} = 0.81 \text{ V}$

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

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

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

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

$$= 3.17 - 0.0295\log 10^7$$

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

$$E_{cell} = 2.96\,V$$

(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.

$$\Lambda^o_{m(CH_3COON_a)} = \lambda^o_{CH_3COO^-} + \lambda^o_{Na^+}$$

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

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

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

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

$$R = \frac{\rho\ell}{A} \quad \text{or} \quad \rho = \frac{RA}{\ell} = \frac{5.55\times10^{3}\,\Omega\times0.785}{50\text{ cm}} =$$

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

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

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa\times1000}{c}$$

$$= \frac{0.01148\text{ S cm}^{-1}\times1000\text{ cm}^{3}\text{ L}^{-1}}{0.05\text{ mol L}^{-1}} = 229.6\text{ S cm}^{2}\text{ mol}^{-1}$$

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

$$= \frac{1}{1005\,\Omega}\times1.25\text{ cm}^{-1} = 0.001244\,\Omega^{-1}\text{ cm}^{-1}$$

$$\text{Molar conductance } (\Lambda_m) = \frac{\kappa\times1000}{\text{Molarity}}$$

$$= \frac{0.001244\,\Omega^{-1}\text{ cm}^{-1}\times1000\text{ cm}^{3}\text{ L}^{-1}}{7.5\times10^{-3}\text{ mol L}^{-1}}$$

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

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^0_m for HAc.

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

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

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

$= 390.5$ S cm^2 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. $$\Lambda_m = \frac{\kappa}{c} = \frac{4.95\times10^{-5}\text{ S cm}^{-1}}{0.001028\text{ mol L}^{-1}}\times\frac{1000\text{ cm}^{3}}{\text{L}}$$

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

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

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

$$= 1.65\times10^{-5}\text{ mol L}^{-1}$$

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

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

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

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 | 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 $Mg \mid Mg^{2+} (0.130\ M) \parallel Ag^+ (0.0001\ M) \mid Ag$

$$E_{(cell)} = E^o_{(cell)} - \frac{RT}{nF} \text{In} \frac{[Mg^{2+}]}{[Ag^+]^2} = E^o_{(cell)} - \frac{2.303RT}{2F} \log \frac{[Mg^{2+}]}{[Ag^+]}$$

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

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

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

$$E_{Zn^{2+}/Zn} = E^o_{Zn^{2+}/Zn} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$$

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

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

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

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

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

$$= -0.76 - 0.03021$$

$$= -0.79021\ V$$

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° 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,

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

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

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

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).

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

$[\text{Given } E^o_{Zn^{2+}/Zn} = -0.76\ V, E^o_{Cu^{2+}/Cu} = +0.34\ V,\ F = 96,500\ C\ mol^{-1}]$

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

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

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

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

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

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

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 × 96, 500 coulomb deposit Cr = 1 mole = 52 g

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

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

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

$\therefore$ 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:

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

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

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

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

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

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

(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 cm²/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

$$= \frac{4 \times 10^{-5}\ S/cm \times 1000}{0.001} = 40\,S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^o_m} = \frac{40}{390.5} = 0.103$$

$$K_c = \frac{C\alpha^2}{1-\alpha} = \frac{0.001 \times (0.103)^2}{1-0.103} = 1.19 \times 10^{-5}$$

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

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

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

Nernst equation

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

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

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

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

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

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

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 ?

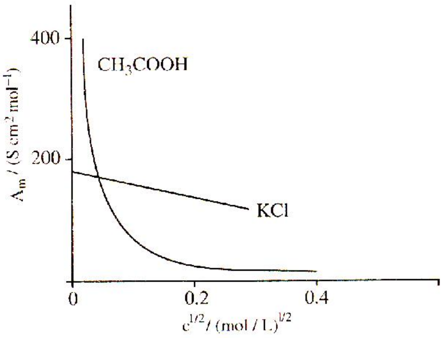
(b) A voltaic cell is set up at 25 °C with the following half cells:

$Ag^+ (0.001 \text{ M}) | Ag$ 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, $E^o_{cell} = 0.46 \text{ V}, n = 2$

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

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

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

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

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

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

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

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

where, $\kappa =$ Conductivity

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

R = Resistance

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

where, Λ_m = Molar conductivity

κ = Conductivity

M = Molarity of Solution

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

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

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

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

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

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

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

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

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

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

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

$$= 1.41 + 0.0502 = 1.4602\text{V}$$

$E_{cell} = 1.46$ 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 : $E^o_{Ni^{2+}|Ni} = -0.25\text{ V}$, $E^o_{Al^{3+}|Al} = -1.66\text{V}$).

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

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

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

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

$\mathrm{\longrightarrow PbSO_4(s) + 2H_2O(\ell)}$

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

$\mathrm{PbSO_4(s) + 2H_2O(\ell)}$

(b) $\mathrm{2A\mathit{l}\,(s) + 3Ni^{+2}(aq) \rightarrow 3Ni(s) + 2Al^{+3}(aq)}$

$E^o_{cell} = 1.41$ 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.

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

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

Sol. (a) Conductivity $(\kappa) = \dfrac{1}{\text{Resistance }(R)} \times$ 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 : $Ag^+(aq) + e^- \longrightarrow Ag(s)] \times 2$

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

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

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

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

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

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

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

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

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

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

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

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

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

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.

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

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

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

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

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

$E^o_{cell} = 0.04V$

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

$\log k_c = 1.3536$

$k_c = \text{Antilog } 1.3536$

$k_c = 22.57$

Example – 31

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

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

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

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

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

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

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

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

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

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

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

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

$$\Rightarrow \text{cell constant} = \kappa \times R$$

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

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

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.

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

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

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

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

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

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

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

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

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

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

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^o_{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) $Ag \,|\, AgCl(s) \,|\, KCl(sol.) \,||\, AgNO_3)\ (sol.) \,|\, Ag$

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

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

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

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

(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. 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?

(a) Co (b) Mn

(c) Fe (d) Cr

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

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

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

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

17. 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 :

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

$E^\circ_{Li^+/Li} = -3.03\ V$

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

18. 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.

$Sn\,|\,Sn^{2+}(1\ M)\,||\,Ag^+(1M)\,|\,Ag$ 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

19. 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

20. 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

21. 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

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

Given $E^\circ_{Li^+/Li} = -3.0V$, $F = 96500\ C\ mol^{-1}$ 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}

23. 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

24. 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) $(E^\circ_{red} + 0.059)$

(c) $(E^\circ_{ox} - 0.059)$ (d) $(E^\circ_{red} - 0.059)$

25. The reduction electrode potential E, of 0.1 M solution of M^+ ions ($E^\circ_{RP} = -2.36\ V$) is :

(a) – 2.41 (b) + 2.41

(c) – 4.82 (d) None

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

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

(a) 2×10^{-2} M (b) 2×10^{-3} M

(c) 1.5×10^{-3} M (d) 1.5×10^{-2} M

27. The emf of the cell

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

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

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

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

29. 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

30. 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.

31. The EMF of the cell

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

(a) 2.17 V (b) 2.23 V

(c) 2.51 V (d) 2.45 V

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

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

(a) –0.118 V (b) –0.0591 V

(c) 0.118 V (d) 0.0591 V

33. 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

34. 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

35. 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) $E_3 = \frac{E_1n_1 + E_2n_2}{n_3}$

(c) $E_3 = \frac{E_1n_1 - E_2n_2}{n_3^2}$ (d) $E_3 = E_1 + E_2$

36. If $E°_{Au^+/Au}$ is 1.69 V and $E°_{Au^{3+}/Au}$ is 1.40 V, then $E°_{Au^+/Au^{3+}}$

(a) 0.19 V (b) 2.945 V

(c) 1.255 V (d) None of these

Electroytic cell

37. 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) $Pb^{2+} + 2e^- \longrightarrow Pb$

38. 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

39. 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

40. 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.

41. 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.

42. During the electrolysis of fused NaCl, Which reaction occures at anode?

(a) Chloride ions are oxidised

(b) Chloride ions are reduced

(c) Sodium ions are oxidised

(d) Soldium ions are reduced.

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

(a) cathode (b) anode

(c) electrolyte (d) none of these

Faraday's Laws

44. 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

45. 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

46. 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}

47. 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

48. 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

49. 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

50. 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

51. 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

52. 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

53. 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

54. 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

55. 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

56. 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

57. 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

58. 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

59. 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

60. 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

61. 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}

62. 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

63. 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

64. 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

65. 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

66. 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

67. 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

68. 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 :

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

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

(d) All of the above

69. Reaction that takes place at graphite 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.

70. 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

71. 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}

72. 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

73. 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

74. 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

75. 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) $\frac{xy}{1000}$

76. 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

77. 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) $\frac{k \times 1000}{x - y}$ (b) $\frac{k}{x + y} \times 188$

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

78. 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

79. 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

80. 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}

81. 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

82. 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 JEE MAINS QUESTION

1. Consider the following reaction at 1100°C

(I) $2C + O_2 \longrightarrow 2CO,\ \Delta G^o = -460\ \text{kJ mol}^{-1}$

(II) $2Zn + O_2 \longrightarrow 2ZnO,\ \Delta G^o = -360\ \text{kJ mol}^{-1}$

Based on these, select correct alternate. **(2002)**

(a) zinc can be oxidised by CO

(b) zinc oxide can be reduced by carbon

(c) Both (a) and (b)

(d) None of the above

2. For the following cell with hydrogen electrodes at two different pressure p_1 and p_2

$$\underset{p_1}{Pt\,(H_2)}\,|\,\underset{1M}{H^+\,(aq)}\,|\,\underset{p_2}{Pt\,(H_2)}$$

emf is given by **(2002)**

(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) $\frac{RT}{2F}\log_e\frac{p_2}{p_1}$

3. For a cell given below :

$\underset{-}{Ag\,|}\ Ag^+\,\|\,Cu^{2+}\underset{+}{|\,Cu}$

$Ag^+ + e^- \longrightarrow Ag;$ $E^o = x$

$Cu^{2+} + 2e^- \longrightarrow Cu;$ $E^o = y$

E^o cell is

(a) x + 2y (b) 2x + y

(c) y – x (d) y – 2x

4. Which of the following reaction is possible at anode ? **(2002)**

(a) $F_2 + 2e^- \rightarrow 2F^-$

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

(c) $2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$

(d) None of these

5. Conductivity (Seimen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then constant of proportionality is expressed in **(2002)**

(a) $S\ m\ mol^{-1}$ (b) $S^2\ m^2\ mol^{-2}$

(c) $S\ m^2\ mol^{-1}$ (d) $S^2\ m^2\ mol$

6. Which of the following is a redox reaction ? **(2002)**

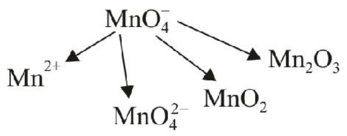
(a) $NaCl + KNO_3 \rightarrow NaNO_3 + KCl$

(b) $CaC_2O_4 + 2HCl \rightarrow CaCl_2 + H_2C_2O_4$

(c) $Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + 2H_2O$

(d) $2K[Ag(CN)_2] + Zn \rightarrow 2Ag + K_2[Zn(CN)_4]$

7. MnO_4^- is a good oxidising agent in different medium changing to



Changes in oxidation number respectively, are **(2002)**

(a) 1, 3, 4, 5 (b) 5, 4, 3, 2

(c) 5, 1, 3, 4 (d) 2, 6, 4, 3

8. Oxidation number of Cl in $CaOCl_2$ (bleaching powder) is **(2002)**

(a) zero, since it contains Cl_2

(b) –1, since it contains Cl^-

(c) +1, since it contains ClO^-

(d) +1 and –1, since it contains ClO^- and Cl^-

9. For a cell reaction involving a two electron change, the standard emf of the cell is found to be 0.295V at 25°C. The equilibrium constant of the reaction at 25°C will be **(2003)**

(a) 1×10^{-10} (b) 29.5×10^{-2}

(c) 10 (d) 1×10^{10}

10. For the redox reaction

$Zn(s) + Cu^{2+}$ (0.1 M) $\rightarrow Zn^{2+}$ (1 M) + Cu (s)

taking place in a cell, E^o_{cell} is 1.10V. E^o_{cell} for the cell will be $\left(2.303\frac{RT}{F} = 0.0591\right)$ **(2003)**

(a) 2.14 V (b) 1.80 V

(c) 1.07 V (d) 0.82 V

11. Standard reduction electrode potentials of three metals A, B and C are + 0.5V, –3.0V and –1.2V respectively. The reducing power of these metals are **(2003)**

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

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

12. When during electrolysis of a solution of $AgNO_3$, 9650 C of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be **(2003)**

(a) 1.08 g (b) 10.8 g

(c) 21.6 g (d) 108g

13. Several blocks of magnesium are fixed to the bottom of a ship to **(2003)**

(a) keep away the sharks (b) make the ship lighter

(c) prevent action of water and salt

(d) prevent puncturing by under sea rocks

14. The standard emf of a cell, involving one electron change is found to be 0.591 V at 25ºC. The equilibrium constant of the reaction is (F = 96,500 C mol^{-1}) **(2004)**

(a) 1.0×10^1 (b) 1.0×10^5

(c) 1.0×10^{10} (d) 1.0×10^{30}

15. In a cell that utilises the reaction

$Zn\ (s) + 2H^+\ (aq) \rightarrow Zn^{2+}\ (aq) + H_2(g)$

addition of H_2SO_4 to cathode compartment will **(2004)**

(a) lower the E and shift equilibrium to the left

(b) lower the E and shift the equilibrium to the right

(c) increase the E and shift the equilibrium to the right

(d) increase the E and shift the equilibrium to the left

16. Consider the following E^o values :

$E^o_{Fe^{3+}/Fe^{2+}} = +0.77V$

$E^o_{Sn^{2+}/Sn} = -0.14\ V$

Under standard conditions the potential for the reaction $Sn(s) + 2Fe^{3+}\ (aq) \rightarrow 2Fe^{2+}\ (aq) + Sn^{2+}\ (aq)$ is **(2004)**

(a) 1.68 V (b) 1.40 V

(c) 0.91 V (d) 0.63 V

17. In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to **(2004)**

(a) generate heat

(b) create potential difference between the two electrodes

(c) produce high purity water

(d) remove adsorbed oxygen from electrode surfaces.

18. The limiting molar conductivities Λ^o for NaCl, KBr and KCl are 126, 152 and 150 S $cm^2\ mol^{-1}$ respectively, The Λ^o for NaBr is **(2004)**

(a) 128 S $cm^2\ mol^{-1}$ (b) 176 S $cm^2\ mol^{-1}$

(c) 278 S $cm^2\ mol^{-1}$ (d) 302 S $cm^2\ mol^{-1}$

19. Among the properties (A) reducing, (B) oxidising (C) complexing, the set of properties shown by CN^- ion towards metal species is **(2004)**

(a) A, B (b) B, C

(c) C, A (d) A, B, C

20. The $E^o_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are – 0.41, + 1.57, + 0.77 and + 1.97V respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest ? **(2004)**

(a) Fe (b) Mn

(c) Cr (d) Co

21.

Electrolyte :	KCl	KNO_3	HCl	NaOAc	NaCl
Λ^∞(S $cm^2\ mol^{-1}$) :	149.9	145	426.2	91	126.5

Calculate Λ^∞_{HOAc} using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25ºC **(2005)**

(a) 217.5 (b) 390.7

(c) 552.7 (d) 517.2

22. During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are **(2005)**

(a) Fe and Ni (b) Ag and Au

(c) Pb and Zn (d) Sn and Ag

23. Aluminium oxide may be electrolysed at 1000ºC to furnish aluminium metal (At. Mass = 27 amu; 1 Faraday = 96,500 Coulombs). The cathode reaction is–

$Al^{3+} + 3e^- \longrightarrow Al^o$

To prepare 5.12 kg of aluminium metal by this method we require **(2005)**

(a) 5.49×10^1 C of electricity

(b) 5.49×10^4 C of electricity

(c) 1.83×10^7 C of electricity

(d) 5.49×10^7 C of electricity

24. The highest electrical conductivity of the following aqueous solutions is of **(2005)**

(a) 0.1 M difluoroacetic acid

(b) 0.1 M fluoroacetic acid

(c) 0.1 M chloroacetic acid

(d) 0.1 M acetic acid

25. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is **(2005)**

(a) +3 (b) +2

(c) +6 (d) +4

26. The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is **(2005)**

(a) 0 (b) +1

(c) +2 (d) +3

27. Given the data at 25ºC,

$Ag + I^- \rightarrow AgI + e^-;\ E^o = 0.152$ V

$Ag \rightarrow Ag^+ + e^-;\ E^o = -0.800$ V

What is the value of log K_{sp} for AgI ?

$\left(2.303\dfrac{RT}{F} = 0.059V\right)$ **(2006)**

(a) – 8.12 (b) + 8.612

(c) – 37.83 (d) –16.13

28. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100Ω. The conductivity of this solution is 1.29S m^{-1}. Resistance of the same cell when filled with 0.02 M of the same solution is 520Ω. The molar conductivity of 0.02 M solution of electrolyte will be **(2006)**

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

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

29. The molar conductivities Λ^o_{NaOAc}, and Λ^o_{HCl} at infinite dilution in water at 25ºC are 91.0 and 426.2S cm^2/mol respectively. To calculate Λ^o_{HOAc}, the additional value required is **(2006)**

(a) Λ^o_{NaOH} (b) Λ^o_{NaCl}

(c) $\Lambda^o_{H_2O}$ (d) Λ^o_{KCl}

30. Which of the following chemical reactions depicts the oxidising behaviour of H_2SO_4 ? **(2006)**

(a) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

(b) $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$

(c) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

(d) $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

31. What products are expected from the disproportionation reaction of hypochlorous acid ? **(2006)**

(a) $HClO_3$ and Cl_2O (b) $HClO_2$ and $HClO_4$

(c) HCl and Cl_2O (d) HCl and $HClO_3$

32. The cell, Zn | Zn^{2+} (1M) || Cu^{2+} (1M) | Cu (E^o_{cell} = 1.10v) was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\dfrac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is **(2007)**

(a) 9.65×10^4 (b) antilog (24.08)

(c) 37.3 (d) $10^{37.3}$

33. The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25ºC are given below :

$$\Lambda^o_{CH_3COONa} = 91.0 \text{ S cm}^2\text{/equiv.}$$

$$\Lambda^o_{HCl} = 426.2 \text{ S cm}^2\text{/equiv.}$$

What additional information/quantity one needs to calculate Λ^o of an aqueous solution of acetic acid ? **(2007)**

(a) Λ^o of chloroacetic acid ($ClCH_2COOH$)

(b) Λ^o of NaCl
(c) Λ^o of CH_3COOK

(d) The limiting equivalent conductance of $H^+ (\lambda^o_{H^+})$.

34. Given $E^0_{Cr^{3+}/Cr} = -0.72$ V, $E^o_{Fe^{2+}/Fe} = -0.42$ V.

The potential for the cell

$Cr \mid Cr^{3+}$ (0.1M) $\|$ Fe^{2+} (0.01M) $\mid$ Fe is **(2008)**

(a) – 0.26 V
(b) 0.26 V
(c) – 0.339 V
(d) 0.336 V

35. Given,

$$E^o_{Fe^{3+}/Fe} = 0.036 \text{ V}, \; E^o_{Fe^{2+}/Fe} = -0.439 \text{ V}$$

The value of standard electrode potentail for the charge, $Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ will be **(2009)**

(a) –0.072 V
(b) 0.385 V
(c) 0.770 V
(d) –0.270 V

36. The Gibbs energy for the decomposition of Al_2O_3 at 500ºC is as follows **(2010)**

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3} Al + O_2, \; \Delta_rG = +\,966 \text{ kJ mol}^{-1}$$

The potential difference needed for electrolytic reduction of Al_2O_3 at 500ºC is at least

(a) 4.5 V
(b) 3.0 V
(c) 2.5 V
(d) 5.0 V

37. Resistance of 0.2 M solution of an electrolyte is 50Ω. The specific conductance of the solution is 1.3 S m^{-1}. If resistance of the 0.4M solution of the same electrolyte is 260Ω, its molar conductivity is **(2011)**

(a) 6250 S m^2 mol^{-1}
(b) 6.25×10^{-4}S m^2 mol^{-1}
(c) 625×10^{-4}S m^2 mol^{-1}
(d) 62.5 S m^2 mol^{-1}

38. The reduction potential of hydrogen half-cell will be negative if **(2011)**

(a) $p(H_2) = 1$ atm and $[H^+] = 2.0$ M

(b) $p(H_2) = 1$ atm and $[H^+] = 1.0$ M

(c) $p(H_2) = 2$ atm and $[H^+] = 1.0$ M

(d) $p(H_2) = 2$ atm and $[H^+] = 2.0$ M

39. The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are – 0.76, –0.23 and – 0.44 V respectively. The reaction $X + Y^2 \longrightarrow X^2 + Y$ will be spontaneous when **(2012)**

(a) X = Ni, Y = Fe
(b) X = Ni, Y = Zn
(c) X = Fe, Y = Zn
(d) X = Zn, Y = Ni

40. Four successive members of the first row transition elements listed below with atomic numbers. Which one of them is expected to have the highest $E^o_{M^{3+}/M^{2+}}$ value ? **(2013)**

(a) Cr (Z = 24)
(b) Mn (Z = 25)
(c) Fe (Z = 26)
(d) Co (Z = 27)

41. Resistance of 0.2M solution of an electrolyte is $50\ \Omega$. The specific conductance of the solution is 1.4S m^{-1}. The resistance of 0.5M solution of the same electrolyte is $280\ \Omega$. The molar conductivity of 0.5 M solution of the electrolyte in S m^2 mol^{-1} is : **(2014)**

(a) 5×10^{-3}
(b) 5×10^{3}
(c) 5×10^{2}
(d) 5×10^{-4}

42. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is : **(2014)**

(a) Ca
(b) Cu
(c) Cr
(d) Ag

43. Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is :

(*at. mass of Cu =63.5 amu*) **(2015)**

(a) 2g
(b) 127g
(c) 0 g
(d) 63.5 g

44. Galvanization is applying a coating of : **(2016)**

(a) Cr (b) Cu

(c) Zn (d) Pb

45. Given, $E^{o}_{Cl_2/Cl^-} = 1.36\ V, E^{o}_{Cr^{3+}/Cr} = -0.74\ V$

$E^{o}_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\ V, E^{o}_{MnO_4^-/Mn^{2+}} = 1.51\ V$

Among the following, the strongest reducing agent is **(2017)**

(a) Cr (b) Mn^{2+}

(c) Cr^{3+} (d) Cl^-

46. How long (apporoximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane ? (Atomic weight of B = 10.8u) **(2018)**

(a) 3.2 hours (b) 1.6 hours

(c) 6.4 hours (d) 0.8 hours

JEE MAINS ONLINE QUESTION

1. The standard electrode potentials $\left(E^{o}_{M^+/M}\right)$ four metals A, B, C and D are – 1.2 V, 0.6 V, 0.85 V and –0.76 V, respectively. The sequence of deposition of metals on applying potential is: **Online 2014 SET (1)**

(a) A, C, B, D (b) B, D, C, A

(c) C, B, D, A (d) D, A, B, C

2. A current of 10.0 A flows for 2.00 h through an electrolytic cell containing a molten salt of metal X. This result in the decomposition of 0.250 mol of metal X at the cathode. The oxidation state of X in the molten salt is: (F = 96, 500 C)

Online 2014 SET (1)

(a) + 1 (b) + 2

(c) + 3 (d) + 4

3. Given

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq); E^0 = +0.77\ V$

$Al^{3+}(aq) + 3e^- \rightarrow Al(s); E^0 = -1.66V$

$Br_2(aq) + 2e^- \rightarrow 2Br^-; E^0 = +1.09\ V$

Considering the electrode potentials, which of the following represents the correct order of reducing power?

Online 2014 SET (2)

(a) $Al < Br^- < Fe^{2}+$ (b) $Al < Fe^{2+} < Br^-$

(c) $Br^- < Fe^{2+} < Al$ (d) $Fe^{2+} < Al < Br^-$

4. How many electrons would be required to deposit 6.35 g of copper at the cathode during the electrolysis of an aqueous solution of copper sulphate? (Atomic mass of copper = 63.5 u, N_A = Avogadro's constant):

Online 2014 SET (3)

(a) $\frac{N_A}{2}$ (b) $\frac{N_A}{5}$

(c) $\frac{N_A}{10}$ (d) $\frac{N_A}{20}$

5. At 298 K, the standard reduction potentials are 1.51 V for $MnO_4^-|Mn^{2+}$, 1.36 V for $Cl_2|Cl^-$, 1.07 V for $Br_2|Br$, and 0.54 V for $I_2|I^-$. At pH = 3, permanganate is expected to oxidize : $\left(\frac{RT}{F} = 0.059\ V\right)$ **Online 2015 SET (1)**

(a) Cl^-, Br^- and I^- (b) Br^- and I^-

(c) Cl^- and Br^- (d) I^- only

6. What will happen if a block of copper metal is dropped into a beaker containing a solution of 1M $ZnSO_4$?

Online 2016 SET (1)

(a) The copper metal will dissolve and zinc metal will be deposited.

(b) The copper metal will dissolve with evolution of hydrogen gas.

(c) The copper metal will dissolve with evolution of oxygen gas.

(d) No reaction will occur.

7. Oxidation of succinate ion produces ethylene and carbon dioxide gases. On passing 0.2 Faraday electricity through an aqueous solution of potassium succinate, the total volume of gases (at both cathode and anode) at STP (1 atm and 273 K) is : **Online 2016 SET (2)**

(a) 2.24 L (b) 4.48 L

(c) 6.72 L (d) 8.96 L

8. Identify the correct statement :

Online 2016 SET (2)

(a) Iron corrodes in oxygen-free water.

(b) Iron corrodes more rapidly in salt water because its electrochemical potential is higher.

(c) Corrosion of iron can be minimized by forming a contact with another metal with a higher reduction potential.

(d) Corrosion of iron can be minimized by forming an impermeable barrier at its surface.

9. What is the standard reduction potential (E°) for

$Fe^{3+} \to Fe$?

Given that **Online 2017 SET (1)**

$Fe^{2+} + 2e^- \to Fe;\quad E^o_{Fe^{2+}/Fe} = -0.47\,V$

$Fe^{3+} + e^- \to Fe^{2+};\quad E^o_{Fe^{3+}/Fe^{2+}} = +0.77\,V$

(a) –0.057 V (b) + 0.057 V

(c) +0.030 V (d) –0.30 V

10. To find the standard potential of M^{3+}/M electrode, the following cell is constituted :

$Pt/M/M^{3+}\,(0.001\ mol\ L^{-1})/Ag^+\,(0.01\ mol\ L^{-1})/Ag$

The emf of the cell is found to be 0.421 volt at 298 K. The standard potential of half reaction $M^{3+} + 3e^- \to M$ at 298 K will be : **Online 2017 SET (2)**

(Given $E^-_{Ag^+/Ag}$ at 298 K = 0.80 Volt)

(a) 0.38 Volt (b) 0.32 Volt

(c) 1.28 Volt (d) 0.66 Volt

11. When an electric current is passed through acidified water, 112 mL of hydrogen gas at N.T.P. was collected at the cathode in 965 seconds. The current passed, in ampere, is: **Online 2018 SET (1)**

(a) 1.0 (b) 0.5

(c) 0.1 (d) 2.0

12. When 9.65 ampere current was passed for 1.0 hour into nitrobenzene in acidic medium, the amount of p-aminophenol produced is : **Online 2018 SET (3)**

(a) 9.81 g (b) 10.9 g

(c) 98.1 g (d) 109.0 g

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. All questions marked **"S"** are single choice questions
2. All questions marked **"M"** are multiple choice questions
3. All questions marked **"C"** are comprehension based questions
4. All questions marked **"A"** are assertion–reason type questions

   (A) If both assertion and reason are correct and reason is the correct explanation of assertion.

   (B) If both assertion and reason are true but reason is not the correct explanation of assertion.

   (C) If assertion is true but reason is false.

   (D) If reason is true but assertion is false.
5. All questions marked **"X"** are matrix–match type questions
6. All questions marked **"I"** are integer type questions

Basics of electrochemical Cell

1. (S) In the cell, $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$, the negative terminal is

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

(c) Zn (d) Zn^{2+}

2. (S) Which one of the following reaction occurs at the cathode ?

(a) $2OH^- \longrightarrow H_2O + O + 2e^-$

(b) $Ag \longrightarrow Ag^+ + e^-$

(c) $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

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

3. (S) Reaction taking place at anode is

(a) ionisation (b) reduction

(c) oxidation (d) hydrolysis

4. (S) Which of the following reaction is possible at anode ?

(a) $2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^+$

(b) $F_2 \longrightarrow 2F^-$

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

(d) None of these

5. (S) In the reaction :

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

the reduction half cell reaction is

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

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

(c) $Ag^+ + e \longrightarrow Ag$

(d) $Ag - e \longrightarrow Ag^+$

6. (S) The electrochemical cell stops working after some time because

(a) Electrode potentials of both the electrodes become zero

(b) Electrode potentials of both the electrodes become equal

(c) One of the electrode is eaten way

(d) The reaction starts proceeding in opposite direction

7. (M) Which one of the following statements is incorrect regarding an electrochemical cell ?

(a) The electrode on which oxidation takes place is called anode.

(b) Anode is a negative pole

(c) The direction of current is same as that of flow of electrons

(d) The flow of current is partly due to flow of electrons and partly due to flow of ions.

8. (S) Cell reaction for the cell

$Zn \mid Zn^{2+}$ (1.0 M) $\parallel Cd^{2+}$ (1.0 M) $\mid Cd$ is given by

(a) $Cd \rightarrow Cd^{2+} + 2e^-$

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

(c) $Cd + Zn^{2+} \rightarrow Zn + Cd^{2+}$

(d) $Zn + Cd^{2+} \rightarrow Zn^{2+} + Cd$.

9. (S) Which one of the following is not a function of a salt bridge ?

(a) To allow the flow of cations from one solution to the other

(b) To allow the flow of anions from one solution to the other

(c) To allow the electrons to flow from one solution to the other

(d) To maintain electrical neutrality of the two solutions.

10. (S) If the salt bridge is removed suddenly from a working cell, the voltage

(a) increases (b) decreases

(c) drops to zero

(d) may increases or decrease depending upon cell reaction.

11. (S) Which one of the following represents a standard hydrogen electrode correctly ?

(a) Pt, H_2 (1 atm) | H^+ (1 M), 298 K

(b) Pt, H_2 (1 atm) | H^+ (0.1 M), 298 K

(c) Pt, H_2 (0.1 atm) | H^+ (1 M), 273 K

(d) Pt, H_2 (0.1 atm) | H^+ (0.1 M), 273 K.

12. (S) The reference electrode is made by using

(a) $ZnCl_2$ (b) $CuSO_4$

(c) $HgCl_2$ (d) Hg_2Cl_2

13. (S) The standard hydrogen electrode potential is zero, because

(a) there is no potential difference between the electrode and the solution

(b) hydrogen ions acquire electrons from a platinum electrode

(c) it has been measured accurately

(d) it has been defined that way

14. (M) A calomel electrode is represented as Hg, Hg_2Cl_2,KCl. If in such a half cell

(a) reduction takes place then Cl^- ion concentration increases

(b) oxidation takes place then Cl^- ion concentration decreases

(c) the electrode reaction may be represented as

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

(d) the electrode reaction taking place is

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-\,(aq)$$

15. (M) During the working of the cell, with the passage of time

(a) spontaniety of the cell reaction decreases, E_{cell} decreases

(b) Q decreases, E_{cell} increases

(c) W_{useful} increases

(d) At equilibrium $Q = K_c$, $E_{cell} = 0$

Applications of electrochemical series

16. (S) The reduction potential of the two half cell reactions (occuring in an electrochemical cell) are

$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ ($E^o = -0.31$ V)

$Ag^+\,(aq) + e^- \rightarrow Ag\,(s)$ ($E^o = 0.80$ V)

The feasible reaction will be

(a) $Pb + SO_4^{2-} + 2\,Ag^+\,(aq) \rightarrow 2\,Ag\,(s) + PbSO_4$

(b) $PbSO_4 + 2\,Ag^+\,(aq) \rightarrow Pb + SO_4^{2-} + 2\,Ag\,(s)$

(c) $Pb + SO_4^{2-} + Ag\,(s) \rightarrow Ag^+\,(aq) + PbSO_4$

(d) $PbSO_4 + Ag\,(s) \rightarrow Ag^+\,(aq) + Pb + SO_4^{2-}$.

17. (S) The standard potentials at 25°C for the following half reactions are given against them

$Zn^{2+} + 2e^- \longrightarrow Zn$, $E^o = -0.762$ V

$Mg^{2+} + 2e^- \longrightarrow Mg$, $E^o = -2.37$ V

When zinc dust is added to a solution of magnesium chloride

(a) No reaction will take place

(b) Zinc chloride is formed

(c) Zinc dissolves in the solution

(d) Magnesium is precipitated.

18. (S) If a strip of copper metal is placed in a solution of ferrous sulphate

(a) Copper will precipitate out

(b) Iron will precipitate out

(c) Copper and iron both will be dissolved

(d) No reaction will take place.

19. (S) To a mixture containing pieces of zinc, copper and silver, 1 M H_2SO_4 was added. H_2 gas was found to be evolved. Which of the metal/metals do you think has/have reacted ?

Given $E^o_{Zn/Zn^{2+}} = +0.76V$, $E^o_{Cu^{2+}/Cu} = +0.34V$,

$E^o_{Ag^+/Ag} = +0.80$ V.

(a) All the metals (b) Only Zn

(c) Both Zn and Cu (d) Only Ag.

20. (S) In a simple electrochemical cell, which is in standard state, half cell reactions with their appropriate oxidation potentials are

$Pb\ (s) - 2e^- \longrightarrow Pb^{2+}\ (aq)\quad E^0 = +0.13$ volt

$Ag\ (s) - e^- \longrightarrow Ag^+\ (aq)\ E^0 = -0.80$ volt

Which of the following reaction takes place ?

(a) Pb^{2+} (aq.) + 2 Ag (s) → 2 Ag^+ (aq.) + Pb (s)

(b) Pb^{2+} (aq.) + Ag (s) → Ag^+ (aq.) + Pb (s)

(c) Ag^+ (aq.) + Pb (s) → Ag (s) + Pb^{2+} (aq.)

(d) 2 Ag^+ (aq.) + Pb (s) → 2Ag (s) + Pb^{2+} (aq.)

21. (S) When the cell reaction attains a state of equilibrium, the EMF of the cell is

(a) zero (b) positive

(c) negative (d) not definite.

22. (S) I_2 and Br_2 are added to a solution containing 1 M each of I^- and Br^- ions. Which of the following reaction will take place ? (Given : standard reduction potentials of I_2 and Br_2 are 0.53 and 1.09 volts respectively)

(a) Iodine will reduce bromide ions

(b) Bromine will reduce iodide ions

(c) Iodide ions will reduce bromine

(d) Bromide ions will reduce iodine.

23. (S) The standard reduction potential values of the three metallic cations X, Y and Z are 0.52, – 3.03 and – 1.18V respectively. The order of reducing power of the corresponding metals is

(a) Y > Z > X (b) X > Y > Z

(c) Z > Y > X (d) Z > X > Y

24. (S) Electrode potential data are given below :

$Fe^{+3}_{(aq)} + e^- \longrightarrow Fe^{+2}_{(aq)};\qquad E^o = +0.77V$

$Al^{3+}_{(aq)} + 3e^- \longrightarrow Al_{(s)};\qquad E^o = -1.66\ V$

$Br_{2\ (aq)} + 2e^- \longrightarrow 2Br^-_{(aq)};\qquad E^o = +1.08\ V$

Based on the data, the reducing power of Fe^{2+}, Al and Br^- will increase in the order

(a) $Br^- < Fe^{2+} < Al$ (b) $Fe^{2+} < Al < Br^-$

(c) $Al < Br^- < Fe^{2+}$ (d) $Al < Fe^{2+} < Br^-$

25. (S) The standard reduction potentials at 298K for the following half reactions are given against each

$Zn^{2+}_{(aq)} + 2e \rightleftharpoons Zn_{(s)};\ -0.762\ V$

$Cr^{3+}_{(aq)} + 3e \rightleftharpoons Cr_{(s)};\ -0.740\ V$

$2H^+_{(aq)} + 2e \rightleftharpoons H_{2\ (g)};\ 0.00V$

$Fe^{3+}_{(aq)} + e \rightleftharpoons Fe^{2+}_{(aq)};\ 0.770\ V$

Which is the strongest reducing agent ?

(a) $Zn_{(s)}$ (b) $Cs_{(s)}$

(c) H_2 (g) (d) $Fe^{3+}_{(aq)}$

26. (S) Standard potentials (E°) for some half-reactions are given below :

(I) $Sn^{4+} + 2e \longrightarrow Sn^{2+}$; $E^o = +0.15$ V

(II) $2Hg^{2+} + 2e \longrightarrow Hg_2^{2+}$; $E^o = 0.92$ V

(III) $PbO_2 + 4H^+ + 2e \longrightarrow Pb^{2+} + 2H_2O; E^o = +1.45$ V

based on the above, which one of the following statements is correct ?

(a) Sn^{4+} is a stronger oxidising agent than Pb^{4+}

(b) Sn^{2+} is a stronger reducing agent than Hg_2^{2+}

(c) Pb^{2+} is a stronger oxidising agent than Pb^{4+}

(d) Pb^{2+} is a stronger reducing agent than Sn^{2+}

27. (S) The standard reduction potentials E° for the half reactions are as

$Zn \longrightarrow Zn^{2+} + 2e^-$; E° = 0.76V

$Fe \longrightarrow Fe^{2+} + 2e^-$; E° = 0.41V

The EMF for the cell reaction will be

(a) – 0.3V (b) 0.35V

(c) 1.17V (d) –1.17V

28. (S) The standard reduction potential for Fe^{2+}/Fe and Sn^{2+}/Sn electrodes are – 0.44 and – 0.14 volt respectively. For the cell reaction

$Fe^{2+} + Sn \longrightarrow Fe + Sn^{2+}$

the standard emf will be

(a) + 0.30 V (b) – 0.58 V

(c) + 0.58 V (d) – 0.30 V

29. (S) The emf of the cell

Ni/Ni^{2+} (1.0M) || Au^{3+} (1.0M)/Au is [E° for $Ni^{2+}/Ni = -0.25V$; E° for $Au^{3+}/Au = 1.5$ V]

(a) + 1.25 V (b) +1.75V

(c) – 1.25V (d) – 1.75 V

30. (S) Electrode potentials (E^{o}_{red}) of four elements, A, B, C, D are –1.36, –0.32, 0, –1.26V respectively. The decreasing reactivity order of these elements is

(a) A, D, B and C (b) C, B, D and A

(c) B, D, C and A (d) C, A, D and B

31. (S) An unknown metal M displaces nickel from nickel (II) sulphate solution but does not displace manganese from manganese sulphate solution. Which order represents the correct order of reducing power ?

(a) Mn > Ni > M (b) Ni > Mn > M

(c) Mn > M > Ni (d) M > Ni > Mn

32. (S) The standard reduction potentials of four elements are given below. Which of the following will be the most suitable reducing agent ?

I = – 3.04 V II = – 1.90V

III = 0 V IV = 1.90 V

(a) III (b) II

(c) I (d) IV

33. (S) 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 is Z > Y > X, then

(a) Y will oxidise X and not Z

(b) Y will oxidise X and not X

(c) Y will oxidise both X and Z

(d) Y will reduce both X and Z

34. (S) Standard reduction electrode potentials three metals A, B and C are respectively – 0.5, – 3.0 V and – 1.2 V. The reducing powers these metals are

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

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

35. (M) Given that

$$E^{o}_{Ni^{2+}/Ni} = -0.25\text{ V},\quad E^{o}_{Cu^{2+}/Cu} = 0.34\text{ V},$$

$$E^{o}_{Ag^{+}/Ag} = 0.80\text{ V},\quad E^{o}_{Zn^{2+}/Zn} = -0.76\text{ V}$$

Which of the following reactions under standard conditions will not take place in the specified directions ?

(a) $Ni^{2+}(aq) + Cu(s) \rightarrow Ni(s) + Cu^{2+}(aq)$

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

(c) $Cu(s) + 2H^{+}(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$

(d) $Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

36. (S) For the cell :-

$2Ag + Pt^{2+} \longrightarrow 2Ag^{+} + Pt$ E° = 0.4 volt

$2Ag + F_2 \longrightarrow 2Ag^{+} + 2F^{-}$ E° = 2.07 volt

If the potential for the reaction $Pt \longrightarrow Pt^{2+} + 2e^{-}$ is assigned zero. Then

(a) $E^{o}_{Ag/Ag^{+}} = -0.4V$ (b) $E^{o}_{Ag^{+}/Ag} = 0.4V$

(c) $E^{o}_{F_2/F^{-}} = 1.67V$ (d) $E^{o}_{F_2/F^{-}} = 2.74V$

37. (A) **Assertion (A) :** We cannot add the electrode potentials in order to get the cell potential if number of moles of electrons exchanged are not same.

Reason (R) : Because the potentials are non thermodynamic properties.

(a) A (b) B

(c) C (d) D

Comprehension

Electrochemical series is a series of elements arranged in increasing order of their reduction potential. $E^{o}_{H^{+}/H_2} = 0.$ The metals above H have –ve reduction potential, they are more reactive than hydrogen whereas metals below hydrogen are less reactive than H. Reduction potential of metal depends upon (i) sublimation energy (ii) ionisation energy and (iii) hydration energy of ions.

38. (C) Which of the following is best oxidising agent ?

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

(c) Ag^{+} (d) Al^{3+}

39. (C) Which of the following is weakest reducing agent among alkali metals in aqueous ?

(a) Na (b) K

(c) Rb (d) Cs

40. (C) Which of the following cannot evolve H_2 from dil acid ?

(a) Pt (b) Zn

(c) Mg (d) Pb

Nernst Equation

41. (S) The e.m.f. of a Daniell cell at 298K is E_1

$$\mathrm{Zn}\left|\begin{matrix}\mathrm{ZnSO_4}\\(0.01\mathrm{M})\end{matrix}\right|\left|\begin{matrix}\mathrm{CuSO_4}\\(1.0\mathrm{M})\end{matrix}\right|\mathrm{Cu}$$

When the concentration of $ZnSO_4$ is 1.0 M and that of $CuSO_4$ is 0.01 M, the e.m.f. changed to E_2. What is the relationship between E_1 and E_2 ?

(a) $E_1 < E_2$ (b) $E_1 = E_2$

(c) $E_2 = 0 \neq E_1$ (d) $E_1 > E_2$

42. (S) E° of a cell $aA + bB \longrightarrow cC + dD$ is

(a) $E + RT \ln \dfrac{[a]^A[b]^B}{[c]^C[d]^D}$ (b) $E + \dfrac{RT}{nF} \ln \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

(c) $E + \dfrac{RT}{nF} \ln \dfrac{[C]^C[D]^D}{[A]^A[B]^B}$ (d) $E + \dfrac{RT}{nF} \ln \dfrac{[a]^A[B]^B}{[C]^C[d]^D}$

43. (S) The standard EMF for the cell reaction,

$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$ is 1.1 volt at 25°C.

The EMF for the cell reaction, when 0.1M Cu^{2+} and 0.1 M Zn^{2+} solutions are used, at 25°C is

(a) 1.10 V (b) 0.10 V

(c) –1.10 V (d) – 0.110 V

44. (S) For the cell reaction,

$$Cu^{2+}[C_{1\,(aq)}] + Zn_{(s)} \longrightarrow Zn^{2+}_{(C_2)} + Cu_{(s)}$$

of an electrochemical cell, the change in free energy, ΔG at a given temperature is a function of

(a) $\ln (C_1)$ (b) $\ln \left(\dfrac{C_2}{C_1}\right)$

(c) $\ln (C_1 + C_2)$ (d) $\ln (C_2)$

45. (S) The relationship between standard reduction potential of a cell and equilibrium constant is shown by

(a) $E^o_{cell} = \dfrac{n}{0.059} \log k_c$ (b) $E^o_{cell} = \dfrac{0.059}{n} \log k_c$

(c) $E^o_{cell} = 0.059\, n \log k_c$ (d) $E^o_{cell} = \dfrac{\log k_c}{n}$

46. (S) E° for the cell,

$Zn \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu$ is 1.10 V at 25°C. The equilibrium constant for the cell reaction

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

is of the order of

(a) 10^{-37} (b) 10^{37}

(c) 10^{-17} (d) 10^{17}

47. (S) For a cell reaction involving a two-electron change, the standard e.m.f. of the cell is found to be 0.295V at 25°C. The equilibrium constant of the reaction at 25°C will be

(a) 1×10^{-10} (b) 29.5×10^{-2}

(c) 10 (d) 1×10^{10}

48. (S) For the redox reaction :

$Zn\ (s) + Cu^{2+}\ (0.1M) \longrightarrow Zn^{2+}\ (1M) + Cu\ (s)$

taking place in a cell, E^o_{cell} is 1.10 volt. E_{cell} for the cell will be $\left(2.303\dfrac{RT}{F} = 0.0591\right)$

(a) 2.14 volt (b) 1.80 volt

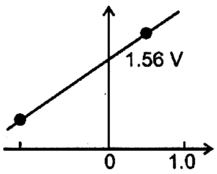
(c) 1.07 volt (d) 0.82 volt

49. (S) Which graph correctly correlates E_{cell} as a function of concentrations for the cell

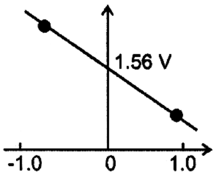
$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s),\ E^\circ_{cell} = 1.56\ V$$

$$\text{Y-axis} : E_{cell},\ \text{X-axis} : \log_{10}\frac{[Zn^{2+}]}{[Ag^+]}$$

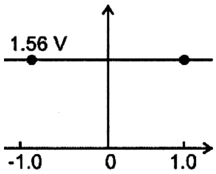
(a)



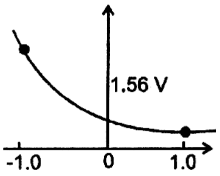
(b)



(c)



(d)



50. (M) Which of the following changes will increase the emf of cell ?

Co(s) | $CoCl_2$ (M_1) || HCl (M_2) | $H_2(g)$ (p_1)| Pt(s)

(a) Increase volume of $CoCl_2$ solution from 500 ml to 1000 ml

(b) increase M_2 from 0.1 to 0.5 M

(c) Decrease pressure of $H_2(g)$ from 0.2 to 0.1 atm

(d) increase mass of cobalt electrode

51. (A) **Assertion (A) :** If standard reduction potential for the reaction

$Ag^+ + e^- \rightarrow Ag$ is 0.80

volts then for the reaction

$3\,Ag^+ + 3\,e^- \rightarrow 3\,Ag \qquad E^\circ = 2.4V$

Reason (R) : If concentration is increased, reduction electrode potential is increased.

(a) A (b) B

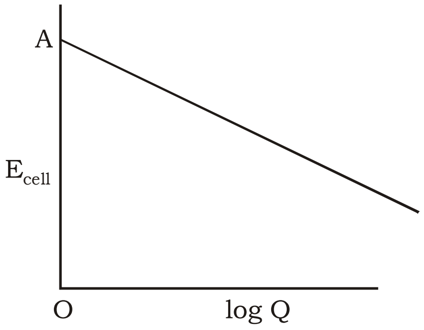
(c) C (d) D

Comprehension

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

Reaction Quotient = $\frac{[Zn^{2+}]}{[Cu^{2+}]}$, variation of E_{cell} with Q is given by

(where Q = concentration quotient)



OA = 1.10 volts, hence

52. (C) When E_{cell} is 1.1591 volts. It implies,

(a) $\frac{[Cu^{2+}]}{[Zn^{2+}]} = 0.01$ (b) $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 0.01$

(c) $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 0.1$ (d) $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 1$

53. (C) The ΔG for the process will be –ve if,

(a) $\frac{[Cu^{2+}]}{[Zn^{2+}]} = 10^2$ (b) $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^3$

(c) $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 10$ (d) $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^5$

54. (C) When E_{cell} is 1.1591 and concentration ratio is, $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{-2}$ it implies,

(a) T = 273 °C (b) T = 298 °C

(c) T = 298 K (d) T = 300 K

Electrolytic Cell

55. (S) During electrolysis of a concentrated aqueous solution of NaCl, what is the product at cathode?

(a) Na (b) Cl_2

(c) O_2 (d) H_2

56. (S) During the electrolysis of aqueous sodium chloride, the cathodic reaction is

(a) Oxidation of Cl^- ion

(b) Reduction of Na^+ ion

(c) Reduction of H_2O

(d) Oxidation of H_2O

57. (S) The electrolysis of silver nitrate solution is carried out using silver electrodes. Which of the following reaction occurs at the anode?

(a) $Ag \rightarrow Ag^+ + e^-$ (b) $Ag^+ + e^- \rightarrow Ag$

(c) $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

(d) $4\,OH^- \rightarrow 2H_2 + O_2 + 4e^-$

58. (S) Which one of the following reactions occurs at the anode when $CuSO_4$ solution is electrolysed using platinum electrodes?

(a) $Cu \rightarrow Cu^{2+} + 2e^-$

(b) $2SO_4^{2-} + 2H_2O \rightarrow 2H_2SO_4 + O_2 + 4e^-$

(c) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

(d) $SO_4^{2-} \rightarrow SO_2 + O_2 + 2e^-$

59. (S) Which one of the following reactions takes place at the anode when an aqueous solution of $CuSO_4$ is electrolysed using copper electrodes?

(a) $Cu \to Cu^{2+} + 2e^-$

(b) $SO_4^{2-} \to SO_2 + O_2 + 2e^-$

(c) $2SO_4^{2-} + 2H_2O \to 2H_2SO_4 + O_2 + 4e^-$

(d) $2H_2O \to O_2 + 4H^+ + 4e^-$

60. (S) The passage of current liberates H_2 at cathode and Cl_2 at anode. The solution is

(a) Copper chloride in water

(b) NaCl in water

(c) Ferric chloride in water

(d) $AuCl_3$ in water.

61. (M) At an anode in an electrolytic cell where electrolysis is taking place, which of the following processes must occur ?

(a) Oxidation

(b) Loss of electrons by anions

(c) Formation of cations by anode

(d) Electron density is higher

62. (M) On passing electricity through an aqueous solution of copper sulphate using copper electrodes then

(a) copper is deposited at cathode

(b) copper is dissolved at anode

(c) O_2 is liberated at anode

(d) the concentration of the solution does not change

Faraday's Laws

63. (S) The number of coulombs required for the deposition of 107.870g of silver is

(a) 96500 (b) 48250

(c) 193000 (d) 10000

64. (S) 1.08 g of pure silver was converted into silver nitrate and its solution was taken in a beaker. It was electrolysed using platinum cathode and silver anode. 0.01 Faraday of electricity was passed using 0.15 volt above the oxidation potential of silver. The silver content of the beaker after the above shall be

(a) 0 g (b) 0.108g

(c) 0.108 g (d) 1.08 g

65. (S) 96500 C of electricity liberates from $CuSO_4$ solution

(a) 63.5g of Cu (b) 31.75 g of Cu

(c) 96500 g of Cu (d) 100 g of Cu

66. (S) A current of 2.0 A passed for 5 hours through a molten metal salt deposits 22.2 g of metal (At wt. = 177). The oxidation state of the metal in the metal salt is

(a) + 1 (b) + 2

(c) + 3 (d) + 4

67. (S) A 5 ampere current is passed through a solution of zinc sulphate for 40 minutes. Find the amount of zinc deposited at the cathode

(a) 40.65 g (b) 4.065 g

(c) 0.4065 g (d) 65.04 g

68. (S) On passing a current of 1.0 ampere for 16 min and 5 sec through one litre solution of $CuCl_2$, all copper of the solution was deposited at cathode. The strength of $CuCl_2$ solution was (Molar mass of Cu = 63.5, Faraday constant = 96500 C mol^{-1}).

(a) 0.07 M (b) 0.2 N

(c) 0.005M (d) 0.02N

69. (S) In a solution of $CuSO_4$ how much time will be required to precipitate 2 g copper by 0.5 ampere current ?

(a) 12157.48 sec (b) 102 sec

(c) 510 sec (d) 642 sec

70. (S) What is the amount of chlorine evolved when 2 amperes of current is passed for 30 minutes in an aqueous solution of NaCl ?

(a) 66 g (b) 1.32 g

(c) 33 g (d) 99 g

71. (S) When 9.65 coulombs of electricity is passed through a solution of silver nitrate (atomic mass of Ag = 108 g mol^{-1}), the amount of silver deposited is

(a) 16.2 mg (b) 21.2 mg

(c) 10.8 mg (d) 6.4 mg

72. (S) The charge required to deposit 9 g of Al from Al^{3+} solution is (At. wt. of Al = 27.0)

(a) 3216.3 C (b) 96500 C

(c) 9650 C (d) 32163 C

73. (S) Silver is monovalent and has atomic mass of 108. Copper is divalent and has an atomic mass of 63.6. The same electric current is passed for the same length of time through a silver coulometer and a copper coulometer. If 27.0 g of silver is deposited, then the corresponding amount of copper deposited is

(a) 63.60 g (b) 31.80 g

(c) 15.90 g (d) 7.95 g

74. (S) The quantity of electricity needed to deposit 127.08 g of copper is

(a) 1 Faraday (b) 4 Coulombs

(c) 4 Faraday (d) 1 Ampere

75. (S) By passing 0.1 Faraday of electricity through fused sodium chloride, the amount of chlorine liberated is

(a) 35.45 g (b) 70.9 g

(c) 3.545 g (d) 17.77 g

76. (M) Faraday's law of electrolysis are not related to the

(a) atomic number of cation

(b) atomic number of anion

(c) equivalent weight of the cation as well as anion

(d) speed of cation

77. (M) If 9 g of H_2O is electrolysed completely with 50% current efficiency

(a) 1F of electricity will be needed

(b) 2F of electricity is needed

(c) 5.6 L of O_2 at STP will be formed

(d) 11.2 L of O_2 will be formed at STP.

78. (X)

Column I	Column II
(A) Electrolytic cell	(p) $\Delta G = -$ ve
(B) Galvanic cell	(q) $\Delta G = +$ ve
(C) Faraday's First Law	(r) Salt bridge
(D) Faraday's Second Law	(s) $m = Z \times I \times t$
	(t) $\frac{W_1}{E_1} = \frac{W_2}{E_2}$

79. (X)

Column I	Column II
(A) Charge on one mole of electrons	(p) 1 F
(B) 108g of silver deposited at electrode from	(q) 96500 C
(C) 22.4L of hydrogen at STP collected from	(r) 2 F
(D) 8g of oxygen collected from	(s) 5.6 L at STP

80. (I) Find the strength of current that will liberate 5.60 L of O_2 at NTP from acidulated water in 3 h.

81. (I) If a 500 mL brine is electrolyzed with a current of strength 0.5 A, how many seconds would it take for the pH of solution to rise to a value of 9 ?

82. (I) A constant current of 30 A is passed through an aqueous solution of NaCl for a time of 1.0 h. How many grams of NaOH and how many litres of $Cl_2(g)$ at STP are produced ?

83. (I) How many amperes must be passed through a Down's cell to produce Na-metal at a rate of 30 kg/hr (in 10^{-3}) ?

Batteries, Fuel Cells and Corrosion

84. (S) Which of the following reaction occurs at the anode during the charging of lead storage battery ?

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

(b) $Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

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

(d) $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

85. (S) 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

86. (S) The electroplating with chromium is undertaken because

(a) Electrolysis of chromium is easier

(b) Chromium can form alloys with other metals

(c) Chromium gives protective and decorative coating to the base metal

(d) Of the high reactivity of metallic chromium

87. (S) Prevention of corrosion of iron by Zn coating is called

(a) Galvanization (b) Cathodic protection

(c) Electrolysis (d) Photoelectrolysis

88. (S) Which of the following cell is a secondary cell ?

(a) Mercury cell (b) Ni cell

(c) Dry cell (d) Fuel cell.

89. (S) Which of the following material is not present in a dry cell ?

(a) MnO_2 (b) NH_4Cl

(c) $ZnCl_2$ (d) KCl.

90. (S) Which of the following material is not present in mercury cell ?

(a) HgO (b) KOH

(c) Zinc (d) $HgCl_2$.

91. (S) Which cell has a constant voltage throughout its life ?

(a) Leclamche cell (b) Electrolytic cell

(c) Mercury cell (d) Daniell cell

92. (S) When a lead storage battery is charged, it acts as

(a) a primary cell (b) an electrolytic cell

(c) a galvanic cell (d) a concentration cell.

93. (M) Iron tanks are protected from rusting by connecting them with magnesium wire. Which of the following statements (s) is/are correct ?

(a) Mg acts as anode and iron acts as cathode

(b) Moist soil acts as electrolyte

(c) Corrosion prevention is electrochemical phenomenon

(d) Corrosion prevention is spontaneous phenomenon

94. (A) **Assertion (A) :** The voltage of mercury cell remains constant for longer period of time.

Reason (R) : It is because net cell reaction does not involve any ion.

(a) A (b) B

(c) C (d) D

Conducance of solutions

95. (S) Conductance (unit Siemen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then the unit of constant of proportionality is

(a) $S\ m\ mol^{-1}$ (b) $S\ m^2 mol^{-1}$

(c) $S^{-2} m^2 mol$ (d) $S^2 m^2\ mol^{-2}$

96. (S) The unit of specific conductivity is

(a) $ohms\ cm^{-1}$ (b) $ohms\ cm^{-2}$

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

97. (S) The cell constant of a given cell is 0.47 cm^{-1}. The resistance of a solution placed in this cell is measured to be 31.6 ohm. The conductivity of the solution (in Scm^{-1} where S has usual meaning) is

(a) 0.15 (b) 1.5

(c) 0.015 (d) 150

98. (S) The specific conductivity of N/10 KCl solution at 20ºC is 0.212 $ohm^{-1}\ cm^{-1}$ and the resistance of the cell containing this solution at 20ºC is 55 ohm. The cell constant is

(a) 4.616 cm^{-1} (b) 11.66 cm^{-1}

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

99. (S) The equivalent conductance at infinite dilution of a weak acid such as HF

(a) can be determined by extrapolation of measurements on dilute solutions of HCl, HBr and HI

(b) can be determined by measurement on very dilute HF solutions

(c) can be determined from measurements on dilute solutions of NaF, NaCl and HCl

(d) is an undefined quantity

100. (S) The unit of equivalent conductivity is

(a) ohm cm

(b) $\text{ohm}^{-1}\ \text{cm}^{+2}$ (g equivalent)$^{-1}$

(c) ohm cm^2 (g equivalent)

(d) S cm^{-2}

101. (S) The resistance of 0.1 N solution of a salt is found to be 2.5×10^3 ohm. The equivalent conductance of the solution in Scm^2/eq is (cell constant = $1.15\ \text{cm}^{-1}$)

(a) 4.6 (b) 5.6

(c) 6.6 (d) 7.6

102. (S) If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of $0.4\ \text{cm}^{-1}$ then its molar conductance in $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ will be

(a) 10^4 (b) 10^3

(c) 10^2 (d) 10^{-6}

103. (S) Specific conductance of 0.1 M sodium chloride solution is $1.06 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1}$. Its molar conductance in $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ is

(a) 1.06×10^2 (b) 1.06×10^3

(c) 1.06×10^4 (d) 5.3×10^2

104. (S) Molar conductivity of a solution is $1.26 \times 10^2\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. Its molarity is 0.01. Its specific conductivity will be

(a) 1.26×10^{-5} (b) 1.26×10^{-3}

(c) 1.26×10^{-4} (d) 0.0063

105. (S) Molar ionic conductivities of a two-bivalent electrolytes x^{2+} and y^{2-} are 57 and 73 respectively. The molar conductivity of the solution formed by them will be

(a) 130 S $\text{cm}^2\ \text{mol}^{-1}$ (b) 65 S $\text{cm}^2\ \text{mol}^{-1}$

(c) 260 S $\text{cm}^2\ \text{mol}^{-1}$ (d) 187 S $\text{cm}^2\ \text{mol}^{-1}$

106. (S) Equivalent conductances of NaCl, HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and 91 $\text{ohm}^{-1}\ \text{cm}^2$ respectively. The equivalent conductance of CH_3COOH at infinite dilution would be

(a) 101.38 $\text{ohm}^{-1}\text{cm}^2$ (b) 253.62 $\text{ohm}^{-1}\text{cm}^2$

(c) 390.71 $\text{ohm}^{-1}\text{cm}^2$ (d) 678.90 $\text{ohm}^{-1}\text{cm}^2$

107. (S) The conductance of 0.1 M HCl solution is greater than that of 0.1 M NaCl. This is because

(a) HCl is more ionized than NaCl

(b) HCl is an acid whereas NaCl solution is neutral

(c) H^+ ions have greater mobility than Na^+ ions

(d) Interionic forces in HCl are weaker than those in NaCl.

108. (S) Which of the following is wrong about molar conductivity ?

(a) The solution contains Avogadro's number of molecules of the electrolyte

(b) It is the product of specific conductivity and volume of solution in cc containing 1 mole of the electrolyte

(c) Its units are $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

(d) Its value for 1 M NaCl solution is same as that of 1M glucose solution.

109. (S) $\Omega^{-1}\ \text{m}^{-1}$ is the unit of

(a) Molar conductivity

(b) Specific conductivity

(c) Equivalent conductivity

(d) Molar conductivity at inifinite dilution.

110. (S) The units of cell constant are

(a) Ω^{-1} (b) $\Omega^{-1}\ \text{cm}^{-1}$

(c) cm^{-1} (d) Ω cm.

111. (S) The value of specific conductance is equal to the conductance of the solution when

(a) The cell constant is zero

(b) The cell constant is one

(c) The electrodes are made of copper

(d) The size of the vessel is very large

112. (S) The increase in the molar conductivity of HCl with dilution is due to

(a) increase in the self ionisation of water

(b) hydrolysis of HCl

(c) decrease in the self ionisation of water

(d) decrease in the interionic forces.

113. (S) The increase in the value of molar conductivity of acetic acid with dilution is due to

(a) decrease in interionic forces

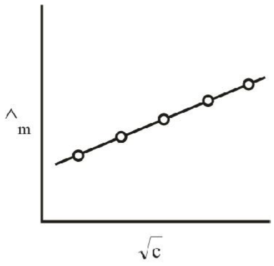
(b) increase in degree of ionisation

(c) increase in self ionisation of water

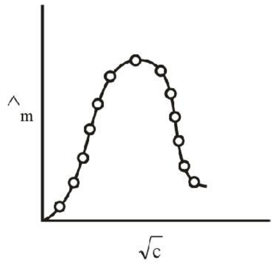
(d) none of these.

114. (S) The variation of $\wedge_m$ of acetic acid with concentration is correctly represented by

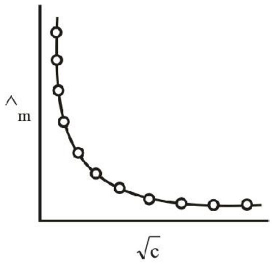
(a)



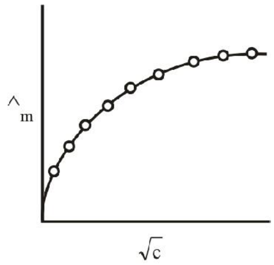
(b)



(c)



(d)



115. (S) According to Kohlrausch law, the limiting value of molar conductivity of an electrolyte, A_2B is

(a) $\lambda^{\infty}_{(A^+)} + \lambda^{\infty}_{(B^-)}$ (b) $\lambda^{\infty}_{(A^+)} - \lambda^{\infty}_{(B^-)}$

(c) $2\lambda^{\infty}_{(A^+)} + \frac{1}{2}\lambda^{\infty}_{(B^-)}$ (d) $2\lambda^{\infty}_{(A^+)} + \lambda^{\infty}_{(B^-)}$.

116. (S) The ionization constant of a weak electrolyte is 25×10^{-6} while the equivalent conductance of its 0.01 M solution is 19.6 S cm^2 eq^{-1}. The equivalent conductance of the electrolyte at infinite dilution (in S cm^2 eq^{-1}) will be

(a) 250 (b) 196

(c) 408 (d) 384

117. (S) The limiting conductivity of NaCl, KCl and KBr are 126.5, 150.0 and 151.5 S cm^2 eq^{-1}, respectively. The limiting equivalent ionic conductance for Br^- is 78 Scm^2eq^{-1}. The limiting equivalent ionic conductance for Na^+ ions would be :

(a) 128 (b) 125

(c) 49 (d) 50

118. (A) **Assertion (A) :** Increasing the concentration increases the value of conductance.

Reason (R) : Increasing the concentration increases interionic forces of attraction.

(a) A (b) B

(c) C (d) D

119. (A) **Assertion (A) :** The correct order of equivalent conductance at infinite dilution is

KCl > NaCl > LiCl

Reason (R) : KCl is stronger electrolyte than NaCl which is stronger than LiCl.

(a) A (b) B

(c) C (d) D

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTION

Objective Questions (Only one correct option)

1. For the following cell, **(2017)**

$$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$$

When the concentration of Zn^{2+} is 10 times the concentration of Cu^{2+}, the expression for ΔG (in J mol^{-1}) is

[F is Faraday constant; R is gas contant; T is temperature; E° (cell) = 1.1 V]

(a) 2.303 RT + 1.1F (b) 1.1 F

(c) 2.303 RT – 22F (d) – 2.2 F

2. For the following electrochemical cells at 298K,

$$Pt(s) \mid H_2(g, 1bar) \mid H^+ (aq, 1M) \mid \mid M^{4+}(aq), M^2(aq) \mid Pt(s)$$

$$E_{cell} = 0.092V \text{ when } \frac{[M^{2+}(aq)]}{[M^{4+}(aq)]} = 10^X.$$

$$\text{Given : } E^0_{M^{4+}/M^{2+}} = 0.151V; 2.303\frac{RT}{F} - 0.059V$$

The value of x is **(2016)**

(a) –2 (b) –1

(c) 1 (d) 2

3. Consider the following cell reaction,

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{+2}(aq) + 2H_2O(l),$$

$$E^\circ = 1.67 \text{ V}$$

At $[Fe^{2+}] = 10^{-3}$ M, $P(O_2)$ = 0.1 atm and pH =3, the cell potential at 25°C is **(2011)**

(a) 1.47 V (b) 1.77 V

(c) 1.87 V (d) 1.57 V

4. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of H_2 gas at the cathode is (1 Faraday = 96500 C mol^{-1}) **(2008)**

(a) 9.65×10^4sec (b) 19.3×10^4sec

(c) 28.95×10^4sec (d) 38.6×10^4sec

5. The half cell reactions for rusting of iron are :

$$2H^+ + 2e^- + \frac{1}{2} \longrightarrow H_2O\ (l)\ ;\ E^\circ = + 1.23V$$

$$Fe^{2+} + 2e \longrightarrow Fe\ (s), \quad E^\circ = -0.44V$$

The ΔG° (in kJ) for the reaction is **(2005)**

(a) – 76 (b) – 322

(c) – 122 (d) – 176

6. $Zn \mid Zn^{2+}$ (a = 0.1 M) $\parallel Fe^{2+}$ (a = 0.01 M) | Fe.

The emf of the above cell is 0.2905V. Equilibrium constant for the cell reaction is **(2004)**

(a) $10^{0.32/0.059}$ (b) $10^{0.32/0.0295}$

(c) $10^{0.26/0.0295}$ (d) $10^{0.32/0.295}$

7. In the electrolytic cell, flow of electrons is from **(2003)**

(a) cathode to anode in solution

(b) cathode to anode through external supply

(c) cathode to anode through internal supply

(d) anode to cathode through internal supply.

8. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half-cell reactions and their standard potentials are given below :

$$MnO_4^- (aq) + 8H^+ (aq) + 5e^- \longrightarrow Mn^{2+} (aq) + 4H_2O(l),$$

$$E^\circ = 1.51 \text{ V}$$

$$Cr_2O_7^{2-} (aq) + 14H^+ (aq) + 6e^- \longrightarrow 2Cr^{3+} (aq) + 7H_2O(l),$$

$$E^\circ = 1.38 \text{ V}$$

$$Fe^{3+} (aq) + e^- \longrightarrow Fe^{2+} (aq) \quad E^\circ = 1.77V$$

$$Cl_2 (g) + 2e^- \longrightarrow 2Cl^- (aq) \quad E^\circ = 1.40 \text{ V}$$

Identify the incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$ **(2002)**

(a) MnO_4^- can be used in aqueous HCl

(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl

(c) MnO_4^- can be used in aqueous H_2SO_4

(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

9. Saturated solution of KNO_3 is used to make 'salt-bridge' because **(2001)**

(a) velocity of K^+ is greater than that of NO_3^-

(b) velocity of NO_3^- is greater than that of K^+

(c) velocities of both K^+ and NO_3^- are nearly the same

(d) KNO_3 is highly soluble in water

10. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is **(2001)**

(a) LiCl > NaCl > KCl (b) KCl > NaCl > LiCl

(c) NaCl > KCl > LiCl (d) LiCl > KCl > NaCl

11. For the electrochemical cell, $(M \mid M^+) \parallel (X^- \mid X)$, $E^\circ (M^+ \mid M) = 0.44$ V and $E^\circ (X \mid X^-) = 0.33$V.

From this data one can deduce that

(a) $M + X \longrightarrow M^+ + X^-$ is the spontaneous reaction

(b) $M^+ + X^- \longrightarrow M + X$ is the spontaneous reaction

(c) $E_{cell} = 0.77$ V (d) $E_{cell} = -0.77$V

12. The gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1M Z^- at 25°C. If the order of reduction potential is Z > Y > X, then **(1999)**

(a) Y will oxidise X and not Z

(b) Y will oxidise Z and not X

(c) Y will oxidise both X and Z

(d) Y will reduce both X and Z

13. The standard reduction potential values of three metallic cations, X, Y, Z are 0.52, –3.03 and –1.18V respectively. The order of reducing power of the corresponding metals is **(1998)**

(a) Y > Z > X (b) X > Y > Z

(c) Z > Y > X (d) Z > X > Y

14. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are 0.337 V and 0.153 V respectively. The standard electrode potential of Cu^+/Cu half-cell is **(1997)**

(a) 0.184 V (b) 0.827 V

(c) 0.521 V (d) 0.490 V

15. The standard oxidation potentials E°, for the half reactions are as

$Zn = Zn^{2+} + 2e^-$, $E^\circ = +0.76$ V

$Fe = Fe^{2+} + 2e^-$, $E^\circ = 0.41$ V

The emf for the cell reaction,

$Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ is **(1989)**

(a) – 0.35 V (b) + 0.35 V

(c) + 1.17 V (d) – 1.17 V

16. When a lead storage battery is discharged **(1986)**

(a) SO_2 is evolved (b) lead is formed

(c) lead sulphate is consumed

(d) sulphuric acid is consumed

17. The reaction,

$$\frac{1}{2}H_2\,(g) + AgCl\,(s) = H^+\,(aq) + Cl^-\,(aq) + Ag\,(s)$$

occurs in the galvanic cell **(1985)**

(a) Ag | AgCl (s) | KCl (soln) | $AgNO_3$ | Ag

(b) Pt | H_2 (g) | HCl (soln) | $AgNO_3$ (soln) | Ag

(c) Pt | H_2 (g) HCl (soln) | AgCl (s) | Ag

(d) Pt/H_2 (g) | KCl (soln) | AgCl (s) | Ag

18. The electric charge for electrode deposition of one gram equivalent of a substance is **(1984)**

(a) one ampere per second

(b) 96,500 coulombs per second

(c) one ampere for one hour

(d) charge on one mole of electrons

19. A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potential) are

$Ag^+/Ag = +0.80,\ Hg_2^{2+}/2Hg = +0.79$

$Cu^{2+}/Cu = +0.34,\ Mg^{2+}/Mg = -2.37$

With increasing voltage, the squence of deposition of metals on the cathode will be **(1984)**

(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag

(c) Ag, Hg, Cu (d) Cu, Hg, Ag

20. Faraday's laws of electrolysis are related to the **(1983)**

(a) atomic number of the cation

(b) atomic number of the anion

(c) equivalent weight of the electrolyte

(d) speed of the cation

21. The standard reduction potentials at 298K for the following half cells are given :

Zn^{2+} (aq) + $2e^-$ $\rightleftharpoons$ Zn (s) E° = –0.762 V

Cr^{3+} (aq) + $3e^-$ $\rightleftharpoons$ Cr(s) E° = – 0.740 V

$2H^+$ (aq) + $2e^-$ $\rightleftharpoons$ H_2(g) E° = 0.000 V

Fe^{3+} (aq) + e^- $\rightleftharpoons$ Fe^{2+} (aq) E° = 0.770 V

Which is the strongest reducing agent ? **(1981)**

(a) Zn(s) (b) Cr(s)

(c) H_2(g) (d) Fe^{2+} (aq)

Objective Questions II (One or more than one correct option)

22. In a galvanic cell, the salt bridge **(2014)**

(a) does not participate chemically in the cell reaction.

(b) Stops the diffusion of ions from one electrode to another

(c) in necessary for the occurrence of the cell reaction.

(d) ensures mixing of the two electrolytic solutions.

23. For the reduction of NO_3^- ion in an aqueous solution E° is + 0.96V. Values of E° for some metal ions are given below

V^{2+} (aq) + $2e^-$ $\longrightarrow$ V E° = – 1.19V

Fe^{3+} (aq) + $3e^-$ $\longrightarrow$ Fe E° = – 0.04 V

Au^{3+} (aq) + $3e^-$ $\longrightarrow$ Au E° = + 1.40 V

Hg^{2+} (aq) + $2e^-$ $\longrightarrow$ Hg E° = + 0.86V

The pair (s) of metals that is (are) oxidized by NO_3^- in aqueous solution is (are) **(2009)**

(a) V and Hg (b) Hg and Fe

(c) Fe and Au (d) Fe and V

Comprehension Based Questions

Passage-1 (Ques. 24 to 26)

Tollen's reagent is used for the detection of aldehydes. When a solution of $AgNO_3$ is added to glucose with NH_4OH, then gluconic acid is formed. **(2006)**

$Ag^+ + e^- \rightarrow Ag;\ E^o_{red} = 0.80$ V

$$C_6H_{12}O_6 + H_2O \rightarrow \underset{\text{gluconic acid}}{C_6H_{12}O_7} + 2H^+ + 2e^-;$$

$E^o_{oxidation} = -\,0.05$ V

$Ag(NH_3)_2^+ + e^- \longrightarrow Ag\ (s) + 2NH_3;\ E^o_{red} = 0.337V$

[Use $2.303 \times \dfrac{RT}{F} = 0.0592$ and $\dfrac{F}{RT} = 38.92$ at 298 K]

(2006)

24. $2Ag^+ + C_6H_{12}O_6 + H_2O \rightarrow 2Ag\ (s) + C_6H_{12}O_7 + 2H^+$

Find ln K of this reaction

(a) 66.13 (b) 58.38

(c) 28.30 (d) 46.29

25. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much ?

(a) E_{oxi} will increases by a factor of 0.65 from E^o_{oxi}

(b) E_{oxi} will decrease by a factor of 0.65 from E^o_{oxi}

(c) E_{red} will increase by a factor of 0.65 from E^o_{red}

(d) E_{red} will decrease by a factor of 0.65 from E^o_{red}

26. Ammonia is always added in this reaction. Which of the following must be incorrect ?

(a) NH_3 combines with Ag^+ to form a complex

(b) $Ag(NH_3)^+_2$ is a stronger oxidising reagent than Ag^+

(c) In absence of NH_3 silver salt of gluconic acid is formed

(d) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode

Passage-2 (Ques. 27 to 29)

(2007)

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/ molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 M aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass : Na = 23, Hg = 200; 1 Faraday = 96500 coulombs)

27. The total number of moles of chlorine gas evolved is

(a) 0.5 (b) 1.0

(c) 2.0 (d) 3.0

28. If the cathode is a Hg electrode, the maximum weight (in g) of amalgam formed from this solution is

(a) 200
(b) 225
(c) 400
(d) 446

29. The total charge (coulombs) required for complete electrolysis is

(a) 24125
(b) 48250
(c) 96500
(d) 193000

Passage-3 (Ques. 30 to 32)

(2007)

Redox reaction play a pivotal role in chemistry and biology. The values of standard redox potential (E°) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values.

$I_2 + 2e^- \ 2I^-$	$E^o = 0.54$
$Cl_2 + 2e^- \rightarrow 2Cl^-$	$E^o = 1.36$
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	$E^o = 1.50$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$E^o = 0.77$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$E^o = 1.23$

30. Among the following, identify the correct statement

(a) chloride ion is oxidised by O_2
(b) Fe^{2+} is oxidised by iodine
(c) iodide ion is oxidised by chlorine
(d) Mn^{2+} is oxidised by chlorine

31. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because

(a) O_2 oxidises Mn^{2+} to Mn^{3+}
(b) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(c) Fe^{3+} oxidises H_2O to O_2
(d) Mn^{3+} oxidises H_2O to O_2

32. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of

(a) $Fe_4[Fe(CN)_6]_3$
(b) $Fe_3[Fe(CN)_6]_2$
(c) $Fe_4\,[Fe(CN)_6]_2$
(d) $Fe_3[Fe(CN)_6]_3$

Passage-4 (Ques. 33 to 34)

(2010)

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is :

$$M(s)\,|\,M^+(aq;\,0.05\text{ molar})\,||\,M^+\,(aq;\,1\text{ molar})\;M\,(s)$$

For the above electrolytic cell the magnitude of the cell potential $|E_{cell}| = 70$ mV. **(2010)**

33. For the above cell

(a) $E_{cell} < 0; \Delta G > 0$
(b) $E_{cell} > 0; \Delta G < 0$
(c) $E_{cell} < 0; \Delta G^o > 0$
(d) $E_{cell} > 0; \Delta G^o < 0$

34. If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be

(a) 35 mV
(b) 70 mV
(c) 140 mV
(d) 700 mV

Passage-5 (Ques. 35 to 36)

(2012)

The electrochemical cell shown below is a concentration cell. $M|M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2) | |M^{2+} (0.001 mol dm^{-3})|M.

The emf of the cell depends on the difference in concentration of M^{2+} ions at the two electrodes. The emf of the cell at 298 is 0.059 V.

35. The solubility product (K_{sp} ; mol^3 dm^{-9}) of MX_2 at 298 based on the information available the given concentration cell is (take 2.303 × R × 298/F = 0.059 V)

(a) 1×10^{-15}
(b) 4×10^{-15}
(c) 1×10^{-12}
(d) 4×10^{-12}

36. The value of ΔG (kJ mol^{-1}) for the given cell is (take 1F = 96500 C mol^{-1})

(a) – 5.7
(b) 5.7
(c) 11.4
(d) – 11.4

Subjective Questions

37. A current of 3.7 A is passed for 6 h between nickel electrodes in 0.5 L of a 2.0 M solution of Ni $(NO_3)_2$. What will be the molarity of solution at the end of electrolysis ?

38. Consider the cell

Zn | Zn^{2+} (aq) (1.0 M) || Cu^{2+} (aq) (1.0 M) | Cu

The standard recuction potentials are 0.350 V for

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

and –0.763 V for Zn^{2+} (aq) + $2e^- \longrightarrow$ Zn

(i) Write down the cell reaction.

(ii) Calculate the emf of the cell.

(iii) Is the cell reaction spontaneous or not ? **(1982)**

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

(At. wt. of Au = 197 and At. wt. of Cu = 63.5) **(1983)**

40. How long a current of 3A has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer ? (density of Ag = 10.5g/cm^3)

41. Give reasons in one or two sentences.

" Anhydrous HCl is a bad conductor of electricity but aqueous HCl is a good conductor." **(1985)**

42. The emf of a cell corresponding to the reaction.

Zn (s) + $2H^+$ (aq) $\longrightarrow$ Zn^{2+} (0.1 M) + H_2, (g, 1atm) is 0.28 V at 25ºC.

Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.

$E^o(Zn^{2+}/Zn) = -0.76V$ $\qquad E^o_{H^+/H_2} = 0$ **(1996)**

43. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g/mL. Sulphuric acid of density 1.294 g/mL is 39% H_2SO_4 by weight and that of density 1.139 g/mL is 20% H_2SO_4 by weight. The battery holds 3.5 L of the acid and the volume remained practically constant during the discharge.

Calculate the number of ampere-hours for which the battery must have been used. The charging and discharging reactions are

$$Pb + SO_4^{2-} = PbSO_4 + 2e^- \text{ (charging)}$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- = PbSO_4 + 2H_2O \text{ (discharging)}$$

(1986)

44. A 100 watt, 110 V incandecent lamp is connected in series with an electrolyte cell containing cadmium sulphate solution. What weight of cadmium will be deposited by the current flowing for 10 h ? **(1987)**

45. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The emf of the cell is 0.118 V at 25ºC. Calculate the concentration of hydrogen ions at the positive electrode.

(1988)

46. In a fuel cell hydrogen and oxygen react to produces electricity. In the process hydrogen gas is oxidised at the anode and oxygen at the cathode. If 67.2 L of H_2 at STP react in 15 min, what is the average current produced ? If the entire current is used for electro-deposition of copper from copper (II) solution, how many grams of copper will be deposited ?

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

Cathode reaction : $O_2 + 2H_2O + 2e^- \longrightarrow 4OH^-$

(1988)

47. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 mL and the current at 1.2 A. Calculate the volume of gases evolved at NTP during the entire electrolysis. **(1989)**

48. The standard reduction potential at 25ºC of the reaction,

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$, is –0.8277V. Calculate the equilibrium constant for the reaction,

$2H_2O \rightleftharpoons H_3O^+ + OH^-$ at 25ºC. **(1989)**

49. The standard reduction potential of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.337 and 0.7999 V respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of Ag^+ will the emf of the cell, at 25ºC, be zero if the concentration of Cu^{2+} is 0.01 M. **(1990)**

50. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50%. If the potential drop across the cell is 3.0 V, how much energy will be consumed ?

(1990)

51. Zinc granules are added in excess to a 500 mL of 1.0 M nickel nitrate solution at 25ºC until the equilibrium is reached. If the standard reduction potential of Zn^{2+}/Zn and Ni^{2+}/Ni are –0.75V and –0.24 V respectively. Find out the concentration of Ni^{2+} in solution at equilibrium.

(1991)

52. A current of 1.70 A is passed through 300.0 mL of 0.160M solution of a $ZnSO_4$ for 230 s with a current efficiency of 90%. Find out the molarity of Zn^{2+} after the deposition Zn. Assume the volume of the solution to remain constant during the electrolysis. **(1991)**

53. For the galvanic cell,

Ag | AgCl (s), KCl (0.2 M) || KBr (0.001 M), AgBr (s) | Ag
Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25ºC.

$[K_{sp}\ (AgCl) = 2.8 \times 10^{-10},\ K_{sp}\ (AgBr) = 3.3 \times 10^{-13}]$

(1992)

54. An aqueous solution of NaCl on electrolysis gives $H_2(g)$, Cl_2 (g) and NaOH according to the reaction.

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

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

(1992)

55. The standard reduction-potential for the half-cell

$$NO_3^-\ (aq) + 2H^+ + e^- \longrightarrow NO_2\ (g) + H_2O \text{ is } 0.78\ V$$

(i) Calculate the reduction-potential in 8M H^+.

(ii) What will be the reduction-potential of the half-cell in a neutral solution ? Assume all the other species to be at unit concentration.

(1993)

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

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

Calculate

(i) How many grams of chromium will be plated out by 24,000 C and (ii) How long will it take to plate out 1.5g of chromium by using 12.5 A current ? **(1993)**

57. The standard reduction potential of the Ag^+/Ag electrode at 298 K is 0.799 V. Given that for AgI, $K_{sp} = 8.7 \times 10^{-17}$, evalutate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of the $I^-/AgI/Ag$ electrode.

(1994)

58. The Edison storage cell is a represented as :

$$Fe\ (s)/FeO\ (s)/KOH\ (aq)/Ni_2O_3\ (s)/Ni\ (s)$$

The half-cell reactions are :

$$Ni_2O_3\ (s) + H_2O\ (l) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-$$

$E^o = + 0.40V$

$$FeO\ (s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-$$

$E^o = – 0.87\ V$

(i) What is the cell reaction ?

(ii) What is the cell emf ? How does it depend on the concentration of KOH ?

(iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ? **(1994)**

59. An excess of liquid mercury is added to an acidified solution of 1.0×10^{-3}M Fe^{3+}. It is found that 5% of Fe^{3+} remains at equilibrium at 25ºC. Calculate $E^o\ (Hg^{2+}/Hg)$ assuming that the only reaction that occurs is

$$2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+}$$

Given, $E^o\ (Fe^{3+}/Fe^{2+}) = 0.77V$ **(1995)**

60. The standard reduction potential for Cu^{2+}/Cu is +0.34V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of Cu $(OH)_2$ is 1.0×10^{-19}. **(1996)**

61. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 h at a current of 8.46 A ? What is the area of the tray, if the thickness of the silver plating is 0.00254 cm ? Density of silver is 10.5 g/cm³.

(1997)

62. Calculate the equilibrium constant for the reaction

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

Given, $E^o\ (Ce^{4+}/Ce^{3+}) = 1.44\ V$, $E^o\ (Fe^{3+}/Fe^{2+}) = 0.68\ V$

(1997)

63. Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for Fe^{3+}/Fe^{2+} and I_3^-/I^- couples. **(1998)**

64. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K, if the emf of the cell Ag | Ag^+ (sat. Ag_2CrO_4 soln.) || Ag^+ (0.1 M) | Ag is 0.164 V at 298K. **(1998)**

65. A cell, Ag | Ag^+ || Cu^{2+} | Cu, initially contains 1M Ag^+ and 1 M Cu^{2+} ions. Calculate the change in the cell potential after the passage of 9.65 A of current of 1 h. **(1999)**

66. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 min. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. **(2000)**

67. The following electrochemical cell has been set-up :

Pt (1) | Fe^{3+}, Fe^{2+} (a = 1) | Ce^{4+}, Ce^{3+} (a = 1) | Pt (2)

E° (Fe^{3+}, Fe^{2+}) = 0.77 V and E° (Ce^{4+}, Ce^{3+}) = 1.61 V

If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current, will the current increases or decreases with time ? **(2000)**

68. The standard potential of the following cell is 0.23 V at 15ºC and 0.21 V at 35ºC.

Pt | H_2(g) | HCl (aq) | AgCl (s) | Ag (s)

(i) Write the cell reaction.

(ii) Calculate ΔH° and ΔS° for the cell reaction by assuming that these quantitites remain unchanged in the range 15ºC to 35ºC.

(iii) Calculate the solubility of AgCl in water at 25ºC.

Given : The standard reduction potential of the (Ag^+ (aq)/Ag (s) is 0.80 V at 25ºC. **(2001)**

69. (a) Will pH value of water be same at temperature 25ºC and 4ºC. Justify in not more than 2 or 3 sentences.

(b) Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03V higher than the other. The conc of $CuSO_4$ in the cell with higher emf value is 0.5 M. Find out the conc of $CuSO_4$ in the other cell. Given : 2.303 RT/F = 0.06V. **(2003)**

70. Find the equilibrium constant for the reaction

$$Cu^{2+} + In^{2+} \rightleftharpoons Cu^+ + In^{3+}$$

Given

$$E^o_{Cu^{2+}/Cu^+} = 0.15V,\ E^o_{In^{2+}/In^+} = -0.4V,$$

$$E^o_{In^{3+}/In^+} = -0.42\ V$$ **(2004)**

71. (a) Calculate ΔG_r^o of the following reaction :

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

Given

ΔG_f^o (AgCl)	– 109 kJ/mol
ΔG_f^o $(Cl)^-$	– 129 kJ/mol
ΔG_f^o (Ag^+)	77 kJ/mol

Represent the above reaction in form of a cell.

Calculate E° of the cell. Find $\log_{10} K_{sp}$ of AgCl. **(2005)**

(b) 6.539×10^{-2} g of metallic Zn (u = 65.39) was added to 100 mL of saturated solution of AgCl. Calculate $\log_{10} \dfrac{[Zn^{2+}]}{[Ag^+]^2}$. Given that

$Ag^+ + e^- \longrightarrow Ag \qquad E^o = 0.80V$

$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E^o = -76V$

Also find how many moles of Ag will be formed ?

72. We have taken a saturated solution of AgBr, K_{sp} is 12×10^{-14}. If 10^{-7} M of $AgNO_3$ are added to 1L of this solution, find conductivity (specific conductance) of this solution in terms of 10^{-7} Sm^{-1} units. **(2006)**

Given $\lambda^o_{(Ag^+)} = 6 \times 10^{-3}\ Sm^2\ mol^{-1}$,

$\lambda^o_{(Br^-)} = 8 \times 10^{-3}\ Sm^2\ mol^{-1}$,

$\lambda^o_{(NO_3^-)} = 7 \times 10^{-3}\ Sm^2\ mol^{-1}$.

73. For the electrochemical cell, **(2018)**

$$\mathrm{Mg(s)\,|\,Mg^{2+}(aq, 1M)\,||\,Cu^{2+}\,(aq, 1M)\,|\,Cu(s)}$$

the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of x is ....

(given, $\frac{F}{R} = 11500\ \mathrm{K\ V^{-1}}$, where F is the Faraday constant and R is the gas constant, ln (10) = 2.30)

74. Consider an electrochemical cell : **(2018)**

$$\mathrm{A(s)\,|\,A^{n+}\,(aq, 2M)\,||\,B^{2n+}\,(aq, 1M)\,|\,B(s).}$$

The value of ΔH^{-} for the cell reaction is twice of ΔG^{-} at 300 K. If the emf of the cell is zero, the ΔS^{-} (in J K^{-1} mol^{-1}) of the cell reaction per mole of B formed at 300 K is ....

(Given : ln(2) = 0.7, R (universal gas constant) = 8.3 J K^{-1} mol^{-1}. H, S and G are enthalpy, entropy and Gibbs energy, respectively.)

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.** (d) **16.** (b) **17.** (c) **18.** (d) **19.** (b) **20.** (a)

21. (a) **22.** (a) **23.** (b) **24.** (d) **25.** (a) **26.** (a) **27.** (d) **28.** (b) **29.** (b) **30.** (b)

31. (b) **32.** (c) **33.** (d) **34.** (c) **35.** (b) **36.** (d) **37.** (d) **38.** (c) **39.** (a) **40.** (a)

41. (c) **42.** (a) **43.** (a) **44.** (b) **45.** (d) **46.** (c) **47.** (c) **48.** (a) **49.** (d) **50.** (c)

51. (b) **52.** (d) **53.** (c) **54.** (c) **55.** (b) **56.** (a) **57.** (a) **58.** (a) **59.** (a) **60.** (b)

61. (a) **62.** (a) **63.** (a) **64.** (c) **65.** (c) **66.** (c) **67.** (a) **68.** (d) **69.** (b) **70.** (b)

71. (b) **72.** (c) **73.** (d) **74.** (b) **75.** (a) **76.** (a) **77.** (c) **78.** (c) **79.** (a) **80.** (d)

81. (a) **82.** (b)

EXERCISE - 2 : (Previous Year JEE Mains Questions)

1. (b) **2.** (b) **3.** (c) **4.** (c) **5.** (c) **6.** (d) **7.** (c) **8.** (d) **9.** (d) **10.** (c)

11. (a) **12.** (b) **13.** (c) **14.** (c) **15.** (c) **16.** (c) **17.** (b) **18.** (a) **19.** (c) **20.** (c)

21. (b) **22.** (b) **23.** (d) **24.** (a) **25.** (a) **26.** (d) **27.** (d) **28.** (c) **29.** (b) **30.** (a)

31. (d) **32.** (d) **33.** (b) **34.** (b) **35.** (c) **36.** (c) **37.** (b) **38.** (c) **39.** (d) **40.** (d)

41. (d) **42.** (a) **43.** (d) **44.** (c) **45.** (a) **46.** (a)

JEE Mains Online

1. (c) **2.** (c) **3.** (c) **4.** (b) **5.** (b) **6.** (d) **7.** (d) **8.** (d) **9.** (a) **10.** (b)

11. (a) **12.** (a)

EXERCISE - 3 : (Advanced Objective Questions)

1. (c) **2.** (d) **3.** (c) **4.** (a) **5.** (c) **6.** (b) **7.** (bc) **8.** (d) **9.** (c) **10.** (c)

11. (a) **12.** (d) **13.** (d) **14.** (abc) **15.** (ad) **16.** (a) **17.** (a) **18.** (d) **19.** (b) **20.** (d)

21. (a) **22.** (c) **23.** (a) **24.** (a) **25.** (a) **26.** (b) **27.** (b) **28.** (d) **29.** (b) **30.** (a)

31. (c) **32.** (c) **33.** (a) **34.** (a) **35.** (a, c) **36.** (c) **37.** (a) **38.** (c) **39.** (a) **40.** (a)

41. (d) **42.** (b) **43.** (a) **44.** (b) **45.** (b) **46.** (b) **47.** (d) **48.** (c) **49.** (b)

50. (a, b, c) **51.** (d) **52.** (b) **53.** (a, b, c, d) **54.** (c) **55.** (d) **56.** (c) **57.** (a) **58.** (c)

59. (a) **60.** (b) **61.** (ad) **62.** (abd) **63.** (a) **64.** (a) **65.** (b) **66.** (c) **67.** (b) **68.** (c)
69. (a) **70.** (b) **71.** (c) **72.** (b) **73.** (d) **74.** (c) **75.** (c) **76.** (a, b, d) **77.** (b, d)

78. A → q; B → p,r; C → s; D → t **79.** A → p, q; B → p,q; C → r; D → p,q,s **80.** (0009) **81.** (0001)

82. (0013) **83.** (0035) **84.** (d) **85.** (b) **86.** (c) **87.** (a) **88.** (b) **89.** (d) **90.** (d) **91.** (c)

92. (b) **93.** (a, b, c, d) **94.** (a) **95.** (b) **96.** (d) **97.** (c) **98.** (b) **99.** (c) **100.** (b)

101. (a) **102.** (b) **103.** (a) **104.** (b) **105.** (a) **106.** (c) **107.** (c) **108.** (d) **109.** (b) **110.** (c)
111. (b) **112.** (d) **113.** (b) **114.** (c) **115.** (d) **116.** (c) **117.** (d) **118.** (d) **119.** (b)

EXERCISE - 4 : (Previous Year JEE Advanced Questions)

1. (a) **2.** (d) **3.** (d) **4.** (b) **5.** (b) **6.** (b) **7.** (c) **8.** (a) **9.** (c) **10.** (b)
11. (b) **12.** (a) **13.** (a) **14.** (c) **15.** (b) **16.** (d) **17.** (c) **18.** (d) **19.** (c) **20.** (c)

21. (a) **22.** (a,b,c) **23.** (abd) **24.** (b) **25.** (a) **26.** (b) **27.** (b) **28.** (d) **29.** (d) **30.** (c)

31. (d) **32.** (a) **33.** (b) **34.** (c) **35.** (b) **36.** (d) **37.** 1.172 m **38.** (ii) 1.113V

39. 4.7625g, 0.80A **40.** 125s **42.** pH = 8.6 **43.** 265 Ah **44.** 19.1g **45.** 10^{-4} M **46.** 190.50g

47. O_2 = 99.79 mL, H_2 = 58.46 mL **48.** $K = 1.04 \times 10^{-14}$ **49.** 1.57×10^{-9} M **50.** 115800C, 347.40 kJ

51. 5×10^{-18}M **52.** 0.154 M **53.** – 0.037 V **54.** 48.72 h, 1.4085 M **55.** (i) 0.887V, (ii) – 0.0488V

56. (i) 2.15 g, **(ii)** 22.27 min **57.** 0.324 V, – 0.151V **58.** (iii) 2451.1 kJ **59.** 0.7926 V

60. – 0.222 V **61.** 272.68g, 80.01g, 3000 cm^2 **62.** 6.88×10^{12} **63.** 5.89×10^{7}

64. 2.45×10^{-12} **65.** 0.01V **66.** $C = 8 \times 10^{-5}$ M

68. (ii) $\Delta H^o = -49.987$ kJ, $\Delta S^o = -96.5$ J (iii) 1.6×10^{-10}

69. 1.6×10^{-10} **70.** $K = 10^{10}$ **71.** 2×10^{-3} **72.** 55 (in terms of 10^{-7} S m^{-1})

73. 10 **74.** – 11.62

Dream on !!