विघ्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक, 'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

रचितः मानव धर्म प्रणेता
सद्गुरु श्री रणछोड़दासजी महाराज

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KEY CONCEPTS

ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).
An electrode and its electrolyte comprise an **Electrode Compartment.**

Electrochemical Cells can be classified as:

(i) **Electrolytic Cells** in which a non–spontaneous reaction is driven by an external source of current.

(ii) **Galvanic Cells** which produce electricity as a result of a spontaneous cell reaction

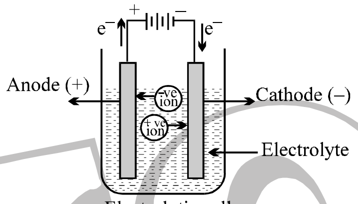
Note: In a **galvanic cell**, cathode is positive with respect to anode.
In a **electrolytic cell**, anode is made positive with respect to cathode.

ELECTROLYSIS

The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.

ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell



Electrolytic cell

ELECTRODES

The metal strip at which positive current enters is called ***anode***; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathodes are negatively charged.

Anode	Positive	Loss of electron or oxidation takes place	Positive current enters
Cathode	Negative	Gain of electron or reduction takes place	Current leaves

ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE

$NaCl(molten) \longrightarrow Na^+ + Cl^-$

Reactions at anode (oxidation) : cathode (reduction)

$2Cl^- \longrightarrow Cl_2(g) + 2e^-$: $2Na^+ + 2e^- \longrightarrow 2Na(l)$

There are two types of electrodes used in the electroytic cell, namely attackable and non - attackable. The attackable elecrodes participitate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anodes get dissolved and their mass decreases. On the other hand, non-attackable electrodes do not participiate in the electrode reaction as they made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remain same.

FARADAY'S LAWS OF ELECTROLYSIS:

(i) *First law of electrolysis :*

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$$w \propto Q$$

W = weight liberated, Q = charge in coulomb

$$w = ZQ$$

Z = electrochemical equivalent

when Q = 1 coulomb, then w = Z

Thus, weight deposited by 1 coulomb charge is called electrochemical equivalent.

Let 1 ampere current is passed till 't' seconds .

Then, $Q = It \qquad \therefore\ w = ZIt$

1 Faraday = 96500 coulomb = Charge of one mole electrons

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.

Let 'E' is equivalent weight then 'E' gm will be liberated by 96500 coulomb.

$\therefore$ 1 Coulomb will liberate $\frac{E}{96500}$ gm ; By definition, $Z = \frac{E}{96500}$

$$\therefore\ W = \frac{ItE}{96500}$$

When a gas is evolved at an electrode, then above formula changes as,

$$V = \frac{ItV_e}{96500}$$

where V = volume of liberated gas, V_e = equivalent volume of gas.

Equivalent volume may be defined as:

The volume of gas liberated by 96500 coulomb at STP.

(ii) *Second law of electrolysis :*

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. i.e. $w_1/w_2 = E_1/E_2$

QUALITATIVE ASPECTS OF ELECTROLYSIS

In the electrolysis process we have discussed above, we have taken molten salt as electrolyte, which contains only one cation and anion. Now, if the electrolyte taken contains more than one cation and anion (for example, aqueous solution of the ionic electrolyte), then the cation and anion that will get discharged depends on the ability of cation to get reduced and the ability of anion to get oxidised.

The ability of an ion to get oxidised or reduced depends upon the size, mass, positive charge, negative charge etc. Thus, it is not possible to predict qualitatively that which ion would be discharged first, as one factor might enhance the ability to discharge while the other factor may hamper it. This can only be predicted on the basis of quantitative value assigned based on the cumulative effect of all the factors reponsible for an ion's ability to discharge. The value is referred as standard potential, which is determined by keeping the concentration of ion as 1 M, pressure of gas at 1 atm, and the measurement done at 25°C. For a cation, the standard reduction potential (SRP) values are compared. The cation having higher standard reduction potential value is discharged in preference to cation with lower SRP value provided the ions are at 1 M concentration. For an anion, the standard oxidation potential (SOP) values are compared and anion having higher SOP is preferentially discharged, if the concentration is 1 M for each of the ion. The SRP values at 25°C for some of the reduction half reactions are given in the table below.

S.NO.	Reduction half cell reaction	E° in volts at 25°C
1.	$F_2 + 2e^- \rightleftharpoons 2F^-$	+ 2.65
2.	$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+ 2.01
3.	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+ 1.82
4.	$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$	+ 1.65
5.	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+ 1.52
6.	$Au^{3+} + 3e^- \rightleftharpoons Au$	+ 1.50
7.	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+ 1.36
8.	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+ 1.33
9.	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+ 1.229
10.	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+ 1.07
11.	$NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O$	+ 0.96
12.	$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	+ 0.92
13.	$Cu^{2+} + I^- + e^- \rightleftharpoons CuI$	+ 0.86
14.	$Ag^+ + e^- \rightleftharpoons Ag$	+ 0.799
15.	$Hg_2^{2+} + 2e^- \rightleftharpoons 2\,Hg$	+ 0.79
16.	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+ 0.77
17.	$I_2 + 2e^- \rightleftharpoons 2I^-$	+ 0.535
18.	$Cu^+ + e^- \rightleftharpoons Cu$	+ 0.53
19.	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+ 0.34
20.	$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$	+ 0.27
21.	$AgCl + e^- \rightleftharpoons Ag + Cl^-$	+ 0.222
22.	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+ 0.15
23.	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+ 0.13
24.	$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
25.	$Fe^{3+} + 3e^- \rightleftharpoons Fe$	– 0.036
26.	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	– 0.126
27.	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	– 0.14
28.	$AgI + e^- \rightleftharpoons Ag + I^-$	– 0.151
29.	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	– 0.25
30.	$Co^{2+} + 2e^- \rightleftharpoons Co$	– 0.28
31.	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	– 0.403
32.	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	– 0.41
33.	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	– 0.44
34.	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	– 0.74
35.	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	– 0.762
36.	$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	– 0.828
37.	$Mn^{2+} + 2e^- \rightleftharpoons Mn$	– 1.18
38.	$Al^{3+} + 3e^- \rightleftharpoons Al$	– 1.66
39.	$H_2 + 2e^- \rightleftharpoons 2H^-$	– 2.25
40.	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	– 2.37
41.	$Na^+ + e^- \rightleftharpoons Na$	– 2.71
42.	$Ca^{2+} + e^- \rightleftharpoons Ca$	– 2.87
43.	$Ba^{2+} + 2e^- \rightleftharpoons Ba$	– 2.90
44.	$Cs^+ + e^- \rightleftharpoons Cs$	– 2.92
45.	$K^+ + e^- \rightleftharpoons K$	– 2.93
46.	$Li^+ + e^- \rightleftharpoons Li$	– 3.03

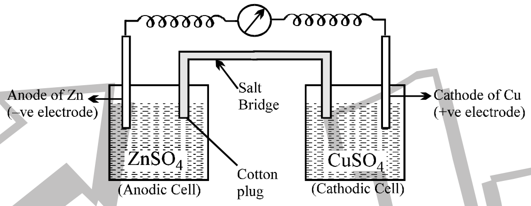
When solution of an electroyte contains more than one type of cations and anions at concentrations different than 1 M, the discharge of an ion does not depend solely on standard potentials but also depends on the concentration of ion in the solution. This value is refered as potential, called as reduction potential for cation and oxidation potential for anion. The relation between reduction potential and standard reduction potential is given by Nernst equation, as

$$E_{RP} = E^{\circ}_{RP} - \frac{RT}{nF}\ln\frac{[\text{concentration of product}]}{[\text{concentration of reactant}]}$$

where E_{RP} = Reduction potential of cation and E°_{RP} = Standard reduction potential of cation.
Thus, it is possible that a cation (A^+) with lower standard reduction potential getting discharged in preference to cation (B^+) having higher standard reduction potential because their concentration might be such that the reduction potential of A^+ is higher than that of B^+.
When two metal ions in the solution have identical values of their reduction potentials, the simultaneous deposition of both the metals will occur in the form of an alloy.

GALVANIC CELL

This cell converts chemical energy into electrical energy.



Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It is also known as ***voltaic cell***. It may be represented as shown in Fig. Zinc rod immersed in $ZnSO_4$ behaves as anode and copper rod immersed in $CuSO_4$ behaves as cathode.

Oxidation takes place at anode:

$Zn \rightleftharpoons Zn^{2+} + 2e^-$ (loss of electron : oxidation)

Reduction takes place at cathode:

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ (gain of electron ; reduction)

Over all process:

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

In galvanic cell like Daniell cell; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit; zinc dissolves as Zn^{2+} ; Cu^{2+} ion in the cathode cell picks up two electron and become deposited at cathode.

SALT BRIDGE

Two electrolyte solutions in galvanic cells are seperated using salt bridge as represented in the Fig. salt bridge is a device to minimize or eliminate the liquid junction potential. Saturated solution of salt like KCl, KNO_3, NH_4Cl and NH_4NO_3 etc. in agar-agar gel is used in salt bridge. Salt bridge contains high concentration of ions viz. K^+ and NO_3^- at the junction with electrolyte solution. Thus, salt bridge carries whole of the current across the boundary ; more over the $K^+$and NO_3^- ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions minimize the liquid junction potential & completes the electrical circuit & permits the ions to migrate.

Representation of a cell (IUPAC conventions): Let us illustrate the convention taking the example of Daniel cell.

(i) Anodic half cell is written on left and cathodic half cell on right hand side.

$Zn(s) \mid ZnSO_4\,(sol) \parallel CuSO_4\,(sol) \mid Cu(s)$

(ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.

(iii) EMF (electromotive force) may be written on the right hand side of the cell.

(iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.

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

(Illustration of Phase boundary)

(v) Inert electrodes are reprsented in the bracket

$Zn \mid ZnSO_4 \parallel H^+ \mid H_2, Pt$

CONCEPT OF ELECTROMOTIVE FORCE (EMF) OF A CELL

Electron flows from anode to cathode in external circuit due to a pushing effect called or electromotic force (e.m.f.). E.m.f. is some times called as *cell potential*. Unit of e.m.f. of cell is volt.

EMF of cell may be calculated as :

E_{cell} = reduction potential of cathode – Reduction potential of anode

Similarly, standard e.m.f. of the cell (E°) may be calculated as

$E°_{cell}$ = Standard reduction potential of cathode – Standard reduction potential of anode

SIGN CONVENTION OF EMF

EMF of cell should be positive other wise it will not be feasible in the given direction .

$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$ $\quad E = +1.10$ volt (Feasible)

$Cu \mid CuSO_4 \parallel ZnSO_4 \mid Zn$ $\quad E = -1.10$ volt (Not Feasible)

NERNST EQUATION

Walter Nernst derived a relation between cell potential and concentration or Reaction quotient.

$$\Delta G = \Delta G° + RT \ln Q \qquad ..(1)$$

where ΔG and $\Delta G°$ are free energy and standard free energy change; 'Q' is reaction quotient.

Let n, Faraday charge is taken out from a cell of e.m.f. (E) then electrical work done by the cell may be calculated as,

Work done = Charge x Potential = nFE

From thermodynamics we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system if there is no work due to volume expansion

$\therefore\ -\Delta G = nFE \qquad \text{and } -\Delta G° = nFE°$

Thus from Eq. (i),we get $-nFE = -nFE° + RT \ln Q$

At 25°C, above equation may be written as $\mathbf{E = E^0 - \dfrac{0.0591}{n}\log Q}$

Where 'n' represents number of moles of electrons involved in process.

E, E° are e.m.f. and standard e.m.f. of the cell respectively.

In general , for a redox cell reaction involving the transference of n electrons

$aA + bB \longrightarrow cC + dD$, the EMF can be calculated as:

$$E_{Cell} = E^\circ_{Cell} - \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Prediction and feasibility of spontaniety of a cell reaction.

Work done by the cell = nFE;

It is equivalent to decrease in free energy $\Delta G = -nFE$

Under standard state $\Delta G^0 = -nFE^0$ (i)

(i) From thermodynamics we know, ΔG = negative for spontaneous process. Thus from eq.(i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.

(ii) When ΔG = positive, E = negative and the cell process will be non spontaneous.

(iii) When G = 0 , E = 0 and the cell will attain the equilibrium.

Reactions	**ΔG**	**E**
Spontaneous	(–)	(+)
Non- spontaneous	(+)	(–)
Equilibrium	0	0

Standard free energy change of a cell may be calculated by electrode potential data.

Substituting the value of E^0 (i.e., standard reduction potentialof cathode- standard reduction potential of anode) in eq. (i) we may get ΔG^0.

Let us see whether the cell (Daniell) is feasible or not: i.e. whether Zinc will displace copper or not.

$Zn \mid (s) \mid ZnSO_4\,(sol) \parallel CuSO_4\,(sol) \mid Cu(s)$

$$E^0_{Zn^{2+}/Zn} = -0.76\text{volt} \; ; \; E^0_{Cu^{2+}/Cu} = +0.34\text{volt}$$

$$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{zn^{2+}/Zn}$$

$$= 0.34 - (-0.76) = +1.10 \text{ volt}$$

Since E^0 = +ve , hence the cell will be feasible and zinc will displace copper from its salt solution. In the other words zinc will reduce copper.

THERMODYNAMIC TREATMENT OF NERNST EQUATION

Determination of equilibrium constant : We know, that

$$E = E^0 - \frac{0.0591}{n}\log Q \qquad ..(i)$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. E = 0

$\therefore$ From Eq. (i), we have

$$0 = E^0 - \frac{0.0591}{n}\log K_{eq} \quad \text{or} \quad K_{eq} = \text{anti}\log\left[\frac{nE^0}{0.0591}\right]$$

Heat of Reaction inside the cell: Let n Faraday charge flows out of a cell of e.m.f. E, then

$$-\Delta G = nFE \qquad (i)$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_p \qquad (ii)$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_p = \Delta H - nFT\left[\frac{\partial E}{\partial T}\right]_p$$

$$\therefore \qquad \Delta H=-\,nFE+nFT\left[\frac{\partial E}{\partial T}\right]_p$$

Entropy change inside the cell : We know that G = H - TS or $\Delta G = \Delta H - T\Delta S$ ...(i)

where ΔG = Free energy change ; ΔH = Enthalpy change and ΔS = entropy change.

According to Gibbs Helmoholtz equation,

$$\Delta G=\Delta H+T\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

$$\Delta G=\Delta H=T\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

From Eqs. (i) and (ii), we have

$$-T\Delta S=T\left[\frac{\partial \Delta G}{\partial T}\right]_p \qquad \text{or} \qquad \Delta S=-\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

or $$\Delta S=nF\left[\frac{\partial E}{\partial T}\right]_p$$

where $\left[\frac{\partial E}{\partial T}\right]_p$ is called temperature coefficient of cell e.m.f.

DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIAL

(1) Gas-Ion Half Cell:

In such a half cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half cell is the hydrogen-gas-hydrogen ion half cell. In this half cell, purified H_2gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.

$$H^+(aq) + e^- \rightleftharpoons 1/2\ H_2$$

$$E_{H^+/H_2}=E^0_{H^+/H_2}-\frac{0.0591}{1}\log\frac{(pH_2)^{1/2}}{\left[H^+\right]}$$

(2) Metal-Metal Ion Half Cell:

This type of cell consist of a metal M in contact with a solution containing M^{n+} ions.

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

$$E_{M^{n+}/M}=E^0_{M^{n+}/M}-\frac{0.0591}{n}\log\frac{1}{\left[M^{n+}\right]}$$

(3) Metal-Insoluble Salt - Anion Half Cell:

In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell:

This half cell is represented as $Cl^-/AgCl/Ag$. The equilibrium reaction that occurs at the electrode is

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

$$E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag} - \frac{0.0591}{1}\log\left[Cl^-\right]$$

potential of such cells depends upon the concentration of anions. Such cells can be used as **Reference Electrode**.

(4) Oxidation-reduction Half Cell:

This type of half cell is made by using an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation. eg. Fe^{2+} - Fe^{3+} half cell.

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

$$E_{Fe^{3+}/Fe^{2+}} = E^0_{Fe^{3+}/Fe^{2+}} - \frac{0.0591}{1}\log\frac{\left[Fe^{2+}\right]}{\left[Fe^{3+}\right]}$$

CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell .

(i) Electrode concentration cell

(ii) Electrolyte concentration cell

Electrode Gas concentration cell :

$Pt, H_2(P_1) \mid H^+(C) \mid H_2(P_2), Pt$

Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell process : $1/2H_2(p_1) \to H^+(c)+e^-$ (Anode process)

$$\begin{array}{c} H^+(c)+e^- \to 1/2H_2(p_2) \\ \hline 1/2H_2(p_1) \Leftrightarrow 1/2H_2(p_2) \end{array}$$

$$\therefore \quad E = -\frac{2.303RT}{F}\log\left[\frac{p_2}{p_1}\right]^{1/2}$$

or $\quad E = \left[\frac{2.303RT}{2F}\right]\log\left[\frac{p_2}{p_1}\right]$, At 25^0C , $E = \frac{0.059}{2F}\log\left[\frac{p_1}{p_2}\right]$

For spontanity of such cell reaction, $p_1 > p_2$

Electrolyte concentration cells:

$Zn(s) \mid ZnSO_4\,(C_1) \parallel ZnSO_4\,(C_2) \mid Zn(s)$

In such cells, concentration gradient arise in electrolyte solutions. Cell process may be givewn as,

$Zn(s) \to Zn^{2+}(C_1) + 2e$ (Anodic process)

$$\begin{array}{c} Zn^{2+}(C_2) + 2e \longrightarrow Zn(s) \\ \hline Zn^{2+}(C_2) \bullet Zn^{2+}(C_1) \end{array}$$ (Over all process)

$\therefore$ From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F}\log\left[\frac{C_1}{C_2}\right] \quad \text{or} \quad E = \frac{2.303RT}{2F}\log\left[\frac{C_2}{C_1}\right]$$

For spontanity of such cell reaction, $C_2 > C_1$

CONDUCTANCE

Introduction:

Both metallic and electrolytic conductors obey Ohm's law

i.e. $V = IR$

where V = Potential difference in volt; I = Current in ampere ; R = resistance in Ohm

We know, resistance is directly proportional to length of conductor and inversely proportional to cross sectional area of the conductor.

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho\frac{l}{A} \qquad (\ \rho = \text{Specific resistance}\ )$$

Specific resistance is the resistance of a conductor having lengths of 1 cm and corss sectional area of 1 cm^2.

Unit of R is ohm and unit of specific resistance is ohm cm

Reciprocal of resistance is called as *conductance* and reciprocal of specific resistance is called as *specific conductance*.

$$\frac{1}{R} = \frac{1}{\rho}\frac{A}{l} \quad \text{or} \quad C = K\frac{A}{l}$$

where C = conductance ohm^{-1} ; K = specific conductance $ohm^{-1}cm^{-1}$.

Mho and siemens are other units of conductance

$$K = \frac{l}{A}C$$

Specific conductance= Cell constant x Conductance

SPECIFIC CONDUCTANCE IS CONDUCTANCE OF 1 CM^3 OF AN ELECTROLYTE SOLUTION.

In case of electrolytic solution, the specific conductance is defined as the conductance of a solsution of definite concentration enclosed in a cell having two electrodes sof unit area separated by 1 cm apart.

1. Equivalent Conductance

Equivalent conductance is the conductance of an electrolyte solution containing 1 gm equivalent of electrolyte. It is densoted by $\wedge$.

$$\wedge = K \times V$$

$$(\wedge = ohm^{-1}\ cm^{-1} \times cm^3 = ohm^{-1}\ cm^2)$$

Usually concen ration of electrolyte solution is expressed as C gm equivalent per litre.

Thus, $V = \frac{1000}{C}$

{Volume having 1 gm equivalent electrolyte in the solution} Thus, $\wedge = K \times \frac{1000}{C}$

2. Molar Conductance

Molar conductance may be defined as conductance of an electrolyte solution having 1 gm mole electrolyte in a litre. It is denoted by $\wedge_m$.

$$\wedge_m = K \times V$$

Usually concentration of electrolyte solution is expressed as 'M' gm mole elecrtrolyte per litre.

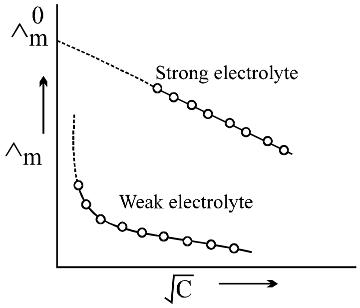
Thus, $V = \frac{1000}{M}$

Hence, $\wedge_m = K \times \frac{1000}{M}$

Relation between $\wedge$ and $\wedge_m$: $\wedge_m = n \times \wedge$

DETERMINATION OF $\wedge_m^0$ OR $\wedge^0$

A plot of $\wedge_m$ vs $\sqrt{C}$ as found experimentally is as shown below graphically.



The $\wedge_m$ vs $\sqrt{C}$ plot of strong electrolyte being linear it can be extrapolated to zero concentration. Thus, $\wedge_m$ values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

$\wedge_m$ values are then plotted against $\sqrt{C}$ when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects $\wedge_m$ axis is $\wedge_m^0$ of the strong electrolyte.
However, the plot in the case weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to $\wedge_m$ axis. Hence extrapolation in this case is not possible. Thus, $\wedge_0$ of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law to be discussed later.

Kohlrausch's Law of Independent Migration of Ions

Kohlrausch determined $\wedge_0$ values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in $\wedge_0$ values in each case remains the same:

$$\wedge_m^0 (KCl) - \wedge_m^0 (KF) = \wedge_m^0 (NaCl) - \wedge_m^0 (NaF)$$

He also detemined $\wedge_0$ values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc.and found that the difference in $\wedge_0$ values in each case remains the same.

$$\wedge_m^0 (KF) - \wedge_m^0 (NaF) = \wedge_m^0 (KCl) - \wedge_m^0 (NaCl)$$

This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.
At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Thus,

$$\wedge_m^0 = \lambda_+^0 + \lambda_-^0$$

Where λ_+^0 is the contribution of the cation and λ_-^0 is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus, λ_+^0 is the molar ionic conductance of cation and λ_-^0 is the molar ionic conductnace of anion, at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl, $MgSO_4$ etc.

Application of Kohlrausch's law :

(1) Determination of $\wedge_m^0$ of a weak electrolyte:

In order to calculate $\wedge_m^0$ of a weak electrolyte say CH_3COOH, we determine experimentally $\wedge_m^0$ values of the following three strong electrolytes:

(a) A strong electrolyte containing same cation as in the test electrolyte, say HCl

(b) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa

(c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

$\wedge_m^0$ of CH_3COOH is then given as:

$$\wedge_m^0\,(CH_3COOH) = \wedge_m^0\,(HCl) + \wedge_m^0\,(CH_3COONa) - \wedge_m^0\,(NaCl)$$

Proof:

$$\wedge_m^0\,(HCl) = \lambda_H^0 + \lambda_{Cl^-} \qquad \text{......................(i)}$$

$$\wedge_m^0\,(CH_3COONa) = \lambda^0_{CH_3COO^-} + \lambda_{Na^+} \qquad \text{......................(ii)}$$

$$\wedge_m^0\,(NaCl) = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \qquad \text{......................(iii)}$$

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$$\wedge_m^0\,(HCl) + \wedge^0_{(CH_3COONa)} - \wedge^0_{(NaCl)} = \lambda^0_{(H^+)} + \lambda^0_{(CH_3COO^0)} = \wedge_{0(CH_3COOH)}$$

(2) Determination of degree of dissociation (α) :

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\wedge_m}{\wedge_m^0}$$

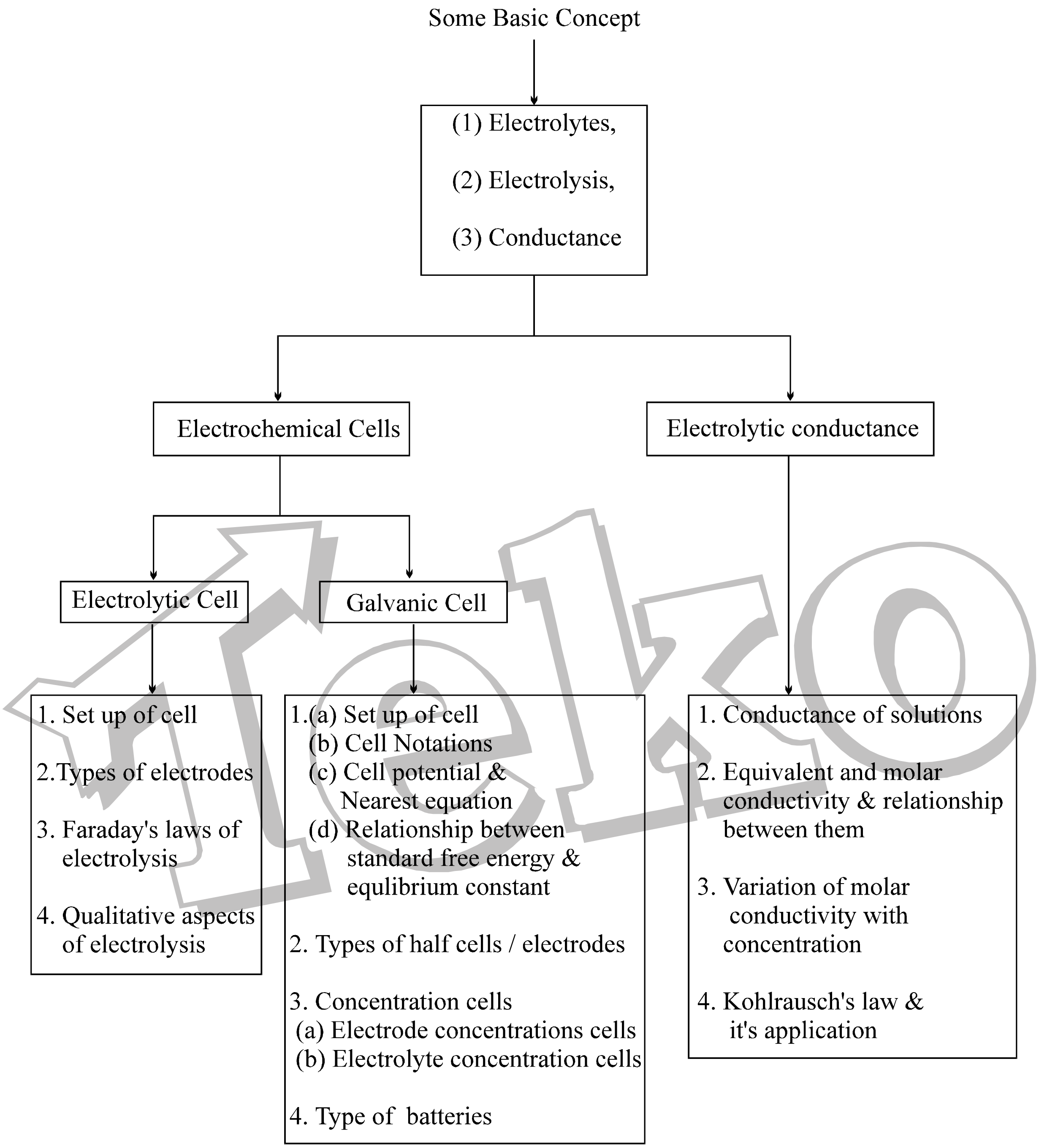
(3) Determination of solubility of sparingly soluble salt

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to $\wedge_m^0$ as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\wedge_m^0 = \frac{1000\kappa}{C},$$

where C is the molarity of solution and hence the solubility.

ATLAS



Some Basic Concept

(1) Electrolytes,

(2) Electrolysis,

(3) Conductance

Electrochemical Cells

Electrolytic conductance

Electrolytic Cell

Galvanic Cell

1. Set up of cell
2. Types of electrodes
3. Faraday's laws of electrolysis
4. Qualitative aspects of electrolysis

1. (a) Set up of cell
   (b) Cell Notations
   (c) Cell potential & Nearest equation
   (d) Relationship between standard free energy & equlibrium constant
2. Types of half cells / electrodes
3. Concentration cells
   (a) Electrode concentrations cells
   (b) Electrolyte concentration cells
4. Type of batteries

1. Conductance of solutions
2. Equivalent and molar conductivity & relationship between them
3. Variation of molar conductivity with concentration
4. Kohlrausch's law & it's application

EASY RIDE

ELECTROLYTIC CELL :

Q.1 Calculate the no. of electrons lost or gained during electrolysis of
(a) 3.55 gm of Cl^- ions (b) 1 gm Cu^{2+} ions (c) 2.7 gm of Al^{3+} ions

Q.2 How many faradays of electricity are involved in each of the case
(a) 0.25 mole Al^{3+} is converted to Al.
(b) 27.6 gm of SO_3 is convered to SO_3^{2-}
(c) The Cu^{2+} in 1100 ml of 0.5 M Cu^{2+} is converted to Cu.

Q.3 0.5 mole of electron is passed through two electrolytic cells in series. One contains silver ions, and the other zinc ions. Assume that only cathode reaction in each cell is the reduction of the ion to the metal. How many gm of each metals will be deposited.

Q.4 The electrosynthesis of MnO_2 is carried out from a solution of $MnSO_4$ in H_2SO_4 (aq). If a current of 25.5 ampere is used with a current efficiency of 85%, how long would it take to produce 1 kg of MnO_2?

Q.5 A constant current of 30 A is passed through an aqueous solution of NaCl for a time of 1.0 hr. How many grams of NaOH are produced? What is volume of Cl_2 gas at S.T.P. produced?

Q.6 If 0.224 litre of H_2 gas is formed at the cathode, how much O_2 gas is formed at the anode under identical conditions?

Q.7 If 0.224 litre of H_2 gas is formed at the cathode of one cell at S.T.P., how much of Mg is formed at the cathode of the other electrolytic cell.

Q.8 Assume 96500 C as one unit of electricity. If cost of electricity of producing x gm Al is Rs x, what is the cost of electricity of producing x gm Mg?

Q.9 Chromium metal can be plated out from an acidic solution containing CrO_3 according to 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 24000 coulombs and
(ii) How long will it take to plate out 1.5 gm of chromium by using 12.5 ampere current

Q.10 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 percent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed?

Q.11 How long a current of 2A has to be passed through a solution of $AgNO_3$ to coat a metal surface of $80 cm^2$ with 5μm thick layer? Density of silver = $10.8 g/cm^3$.

Q.12 3A current was passed through an aqueous solution of an unknown salt of Pd for 1Hr. 2.977g of Pd^{+n} was deposited at cathode. Find n.

Q.13 50mL of 0.1M $CuSO_4$ solution is electrolyzed with a current of 0.965 A for a period of 200 sec. The reactions at electrodes are:
Cathode : $Cu^{2+} + 2e^- \rightarrow Cu(s)$ Anode : $2H_2O \rightarrow O_2 + 4H^+ + 4e$.
Assuming no change in volume during electrolysis, calculate the molar concentration of Cu^{2+}, H^+ and SO_4^{2-} at the end of electrolysis.

Q.14 A metal is known to form fluoride MF_2. When 10A of electricity is passed through a molten salt for 330 sec., 1.95g of metal is deposited. Find the atomic weight of M. What will be the quantity of electricity required to deposit the same mass of Cu from $CuSO_4$?

Q.15 10g fairly concentrated solution of $CuSO_4$ is electrolyzed using 0.01F of electricity. Calculate:
(a)The weight of resulting solution (b)Equivalents of acid or alkali in the solution.

Q.16 An electric current is passed through electrolytic cells in series one containing $Ag(NO_3)$(aq.) and other H_2SO_4(aq). What volume of O_2 measured at 25^0C and 750mm Hg pressure would be liberated from H_2SO_4 if
(a) one mole of Ag^+ is deposited from $AgNO_3$ solution
(b) 8 x 10^{22} ions of Ag^+ are deposited from $AgNO_3$ solution.

Q.17 Cadmium amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. How long should a current of 5A be passed in order to prepare 12% Cd–Hg amalgam on a cathode of 2gm Hg (Cd=112.4)

Q.18 After electrolysis of NaCl solution with inert electrodes for a certain period of time. 600 mL of the solution was left. Which was found to be 1N in NaOH. During the same time, 31.75 g of Cu was deposited in the copper voltameter in series with the electrolytic cell. Calculate the percentage yield of NaOH obtained.

Q.19 Three electrolytic cells A, B, C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 2 ampere was passed through them until 1.08 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and of zinc were deposited?

Q.20 Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the concentration of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the original solution.

Q.21 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 ampere for 20 mintue. What mass of Ni is deposited at the cathode?

Q.22 A current of 3.7A is passed for 6hrs. between Ni electrodes in 0.5L of 2M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?

GALVANIC CELL :

Representation of Cell diagrams, complete and half cell reactions :

Q.23 Make complete cell diagrams of the following cell reactions :
(a) $Cd^{2+}\,(aq) + Zn\,(s) \rightleftharpoons Zn^{2+}\,(aq) + Cd\,(s)$
(b) $2Ag^+\,(aq) + H_2\,(g) \rightleftharpoons 2H^+\,(aq) + 2Ag\,(s)$
(c) $Hg_2Cl_2\,(s) + Cu\,(s) \rightleftharpoons Cu^{2+}\,(aq) + 2Cl^-\,(aq) + 2Hg\,(l)$
(d) $Cr_2O_7^{2-}\,(aq.) + 14H^+\,(aq) + 6Fe^{2+}\,(aq) \rightleftharpoons 6Fe^{3+}\,(aq) + 2Cr^{3+}\,(aq) + 7H_2O\,(l)$

Q.24 Write cell reaction of the following cells :
(a) $Ag \mid Ag^+\,(aq) \mid\mid Cu^{2+}\,(aq) \mid Cu$
(b) $Pt \mid Fe^{2+}, Fe^{3+} \mid\mid MnO_4^-, Mn^{2+}, H^+ \mid Pt$
(c) $Pt, Cl_2 \mid Cl^-\,(aq) \mid\mid Ag^+\,(aq) \mid Ag$
(d) $Pt, H_2 \mid H^+\,(aq) \mid\mid Cd^{2+}\,(aq) \mid Cd$

Q.25 Write half cells of each cell with following cell reactions :

(a) $Zn\,(s) + 2H^+\,(aq) \rightleftharpoons Zn^{2+}\,(aq) + H_2\,(g)$

(b) $2Fe^{3+}\,(aq) + Sn^{2+}\,(aq) \rightleftharpoons 2Fe^{2+}\,(aq) + Sn^{4+}\,(aq)$

(c) $MnO_4^-\,(aq) + 8H^+\,(aq) + 5Fe^{2+}\,(aq) \rightleftharpoons 2Fe^{3+}\,(aq) + Mn^{2+}\,(aq) + 4H_2O\,(l)$

(d) $Pb\,(s) + Br_2\,(l) \rightleftharpoons Pb^{2+}\,(aq) + 2Br^-\,(aq)$

Electrode potential and standard electrode potential :

Q.26 For the cell reaction $2Ce^{4+} + Co \rightleftharpoons 2Ce^{3+} + Co^{2+}$

E^o_{cell} is 1.89 V. If $E^o_{Co^{2+}|Co}$ is – 0.28 V, what is the value of $E^o_{Ce^{4+}|Ce^{3+}}$?

Q.27 Determine the standard reduction potential for the half reaction :

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$$

Given $Pt^{2+} + 2Cl^- \rightleftharpoons Pt + Cl_2$, $E^o_{Cell} = -\,0.15\text{ V}$

$Pt^{2+} + 2e^- \rightleftharpoons Pt$ $E° = 1.20\text{ V}$

Q.28 What is E^o_{Cell} if

$$2Cr + 3H_2O + 3OCl^- \rightleftharpoons 2Cr^{3+} + 3Cl^- + 6OH^-$$

$2Cr^{3+} + 3e^- \rightleftharpoons Cr,$ $E° = -\,0.74\text{ V}$

$OCl^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-,$ $E° = 0.94\text{ V}$

$\Delta G°$, E^o_{Cell} and K_{eq} :

Q.29 Is 1.0 M H^+ solution under H_2SO_4 at 1.0 atm capable of oxidising silver metal in the presence of 1.0 M Ag^+ ion?

$$E^o_{Ag^+|Ag} = 0.80\text{ V},\quad E^o_{H^+|H_2(Pt)} = 0.0\text{ V}$$

Q.30 If for the half cell reactions $Cu^{2+} + e^- \rightleftharpoons Cu^+$ $E° = 0.15\text{ V}$

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E° = 0.34\text{ V}$

Calculate E° of the half cell reaction

$$Cu^+ + e^- \rightleftharpoons Cu$$

also predict whether Cu^+ undergoes disproportionation or not.

Q.31 If $E^o_{Fe^{2+}|Fe} = -\,0.44\text{ V}$, $E^o_{Fe^{3+}|Fe^{2+}} = 0.77\text{ V}$. Calculate $E^o_{Fe^{3+}|Fe}$.

Q.32 If $E^o_{Cu^+|Cu} = 0.52\text{ V}$, $E^o_{Cu^{2+}|Cu} = 0.34\text{ V}$, what is E^o_{Cell} of the cell reaction

$$Cu + Cu^{2+} \rightleftharpoons 2Cu^+?$$

is cell reaction spontaneous?

Q.33 Calculate the EMF of a Daniel cell when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001 M and 0.1M respectively. The standard potential of the cell is 1.1V.

Q.34 Calculate the equilibrium constant for the reaction $Fe + CuSO_4 \rightleftharpoons FeSO_4 + Cu$ at 25^0C.
Given $E^0\,(Fe/Fe^{2+}) = 0.44V$, $E^0\,(Cu/Cu^{2+}) = -0.337V$.

Q.35 For a cell Mg(s) | Mg^{2+}(aq) || Ag^+ (aq) | Ag, Calculate the equilibrium constant at 25^0C. Also find the maximum work that can be obtained by operating the cell.
E^0 (Mg^{2+}/Mg) = –2.37V, E^0 (Ag^+/Ag) = 0.8 V.

Q.36 The standard reduction potential at 25^0C for the reduction of water
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ is –0.8277 volt. Calculate the equilibrium constant for the reaction
$2H_2O \rightleftharpoons H_3O^+ + OH^-$ at 25^0C.

Q.37 At 25^0C the value of K for the equilibrium $Fe^{3+} + Ag \rightleftharpoons Fe^{2+} + Ag^+$ is 0.531mol/litre. The standard electrode potential for $Ag^+ + e^- \rightleftharpoons Ag$ is 0.799V. What is the standard potential for $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$?

Q.38 The EMF of the cell M | M^{n+} (0.02M) || H^+ (1M) | H_2(g) (1 atm), Pt at 25^0C is 0.81V. Calculate the valency of the metal if the standard oxidation of the metal is 0.76V.

Q.39 Equinormal Solutions of two weak acids, HA ($pK_a = 3$) and HB ($pK_a = 5$) are each placed in contact with standard hydrogen electrode at 25^0C. When a cell is constructed by interconnecting them through a salt bridge, find the emf of the cell.

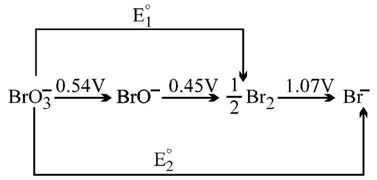
Q.40 In two vessels each containing 500ml water, 0.5m mol of aniline ($K_b = 10^{-9}$) and 25mmol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.

Q.41 Calculate E^0 and E for the cell Sn | Sn^{2+} (1M) || Pb^{2+} | Pb(10^{-3}M), E^0 (Sn^{2+}| Sn) = –0.14V, E^0 (Pb^{2+}| Pb) = –0.13V. Is cell representation is correct?

Q.42 At what concentration of Cu^{2+} in a solution of $CuSO_4$ will the electrode potential be zero at 25^0C?
Given : E^0 (Cu | Cu^{2+}) = –0.34 V.

Q.43 A zinc electrode is placed in a 0.1M solution at 25^0C. Assuming that the salt is 20% dissociated at this dilutions calculate the electrode potential. E^0 (Zn^{2+}| Zn) = –0.76V.

Q.44 From the standard potentials shown in the following diagram, calculate the potentials E_1° and E_2°.



Q.45 For the reaction, $4Al(s) + 3O_2(g) + 6H_2O + 4OH^- \rightleftharpoons 4\,[Al(OH)_4^-]$; $E^\circ_{cell} = 2.73$ V. If $\Delta G_f^\circ(OH^-) = -157$ kJ mol^{-1} and $\Delta G_f^\circ(H_2O) = -237.2$ kJ mol^{-1}, determine $\Delta G_f^\circ\,[Al(OH)_4^-]$.

Concentration cells :

Q.46 Calculate the EMF of the following cell

$Zn \mid Zn^{2+}\ (0.01M) \parallel Zn^{2+}\ (0.1\ M) \mid Zn$

at 298 K.

Q.47 Calculate the EMF of the cell,

$Zn - Hg(c_1M) \mid Zn^{2+}\ (aq) \mid Hg - Zn(c_2M)$

at 25°C, if the concentrations of the zinc amalgam are: c_1 = 10g per 100g of mercury and c_2 = 1g per100 g of mercury.

Q.48 Calculate pH using the following cell :

$Pt\ (H_2) \mid H^+\ (x\ M) \mid\mid H^+\ (1\ M) \mid Pt\ (H_2)$ if $E_{cell} = 0.2364$ V.

1 atm 1 atm

Q.49 Calculate the EMF of following cells at 25^0C.

(i) $Fe \mid Fe^{2+}\ (a_1 = 0.3) \parallel Sn^{2+}\ (a_2 = 0.1) \mid Sn$ $E^0\ (Fe^{2+}/Fe) = -0.44$ V

(ii) Pt, H_2 (2atm) | HCl |H_2 (10 atm), Pt. $E^0\ (Sn^{2+}/Sn) = -0.14$ V

Q.50 EMF of the cell $Zn \mid ZnSO_4\ (a_1 = 0.2) \parallel ZnSO_4(a_2) \mid Zn$ is –0.0088V at 25^0C. Calculate the value of a_2.

CONDUCTANCE

Conductivities and cell constant:

Q.51 The resistance of a conductivity cell filled with 0.01N solution of NaCl is 210 ohm at 18 °C. Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is 0.88 cm^{-1}.

Q.52 The molar conductivity of 0.1 M CH_3COOH solution is 4.6 S cm^2 $mole^{-1}$. What is the specific conductivity and resistivity of the solution ?

Q.53 The conductivity of pure water in a conductivity cell with electrodes of cross sectional area 4 cm^2 and 2 cm apart is 8×10^{-7} S cm^{-1}.

(i) What is resistance of conductivity cell ?

(ii) What current would flow through the cell under an applied potential difference of 1 volt?

Q.54 Resistivity of 0.1M KCl solution is 213 ohm cm in a conductivity cell. Calculate the cell constant if its resistance is 330 ohm.

Q.55 Resistance of a 0.1M KCl solution in a conductance cell is 300 ohm and specific conductance of 0.1M KCl is 1.29×10^{-2} ohm^{-1} cm^{-1}. The resistance of 0.1M NaCl solution in the same cell is 380 ohm. Calculate the equivalent conductance of the 0.1M NaCl solution.

Q.56 For 0.01N KCl, the resistivity 709.22 mho cm. Calculate the conductivity and equivalent conductance.

Q.57 A solution containing 2.08 g of anhydrous barium chloride is 400 CC of water has a specific conductivity 0.0058 $ohm^{-1}cm^{-1}$. What are molar and equivalent conductivities of this solution.

Application of Kohlrausch's law:

Q.58 Equivalent conductance of 0.01 N Na_2SO_4 solution is 112.4 ohm^{-1} cm^2 eq^{-1}. The equivalent conductance at infinite dilution is 129.9 ohm^{-1} cm^2. What is the degree of dissociation in 0.01 N Na_2SO_4 solution?

Q.59 Specific conductance of a saturated solution of AgBr is 8.486×10^{-7} $ohm^{-1}cm^{-1}$ at 25^0C. Specific conductance of pure water at 25^0C is 0.75×10^{-6} ohm^{-1} cm^{-2}. Λ_m^∞ for KBr , $AgNO_3$ and KNO_3 are 137.4 , 133 , 131 (S cm^2 mol^{-1}) respectively. Calculate the solubility of AgBr in gm/litre.

Q.60 Saturated solution of AgCl at 25^0C has specific conductance of 1.12×10^{-6} ohm^{-1} cm^{-1}. The $\lambda_\infty Ag^+$ and $\lambda_\infty Cl^-$ are 54.3 and 65.5 ohm^{-1} cm^2 / equi. respectively. Calculate the solubility product of AgCl at 25^0C.

Q.61 Hydrofluoric acid is weak acid. At 25^0C, the molar conductivity of 0.002M HF is 176.2 ohm^{-1} cm^2 $mole^{-1}$. If its $\Lambda_m^\infty = 405.2$ ohm^{-1} cm^2 $mole^{-1}$, calculate its degree of dissociation and equilibrium constant at the given concentration.

Q.62 The value of Λ_m^∞ for HCl, NaCl and CH_3CO_2Na are 426.1, 126.5 and 91 S cm^2 mol^{-1} respectively. Calculate the value of Λ_m^∞ for acetic acid. If the equivalent conductivity of the given acetic acid is 48.15 at 25° C, calculate its degree of dissociation.

Q.63 Calculate the specific conductance of a 0.1 M aqueous solution of NaCl at room temperature, given that the mobilities of Na^+ and Cl^- ions at this temperature are 4.26×10^{-8} and 6.80×10^{-8} m^2 v^{-1} s^{-1}, respectively.

Q.64 For the strong electroytes NaOH, NaCl and $BaCl_2$ the molar ionic conductivities at infinite dilution are 248.1×10^{-4}, 126.5×10^{-4} and 280.0×10^{-4} mho cm^2 mol^{-1} respectively. Calculate the molar conductivity of $Ba(OH)_2$ at infinite dilution.

Q.65 At 25°C, $\lambda_\infty(H^+) = 3.4982\times10^{-2}$ S m^2 mol^{-1} and $\lambda_\infty(OH^-) = 1.98\times10^{-2}$ S m^2mol^{-1}.
Given: Sp. conductnace = 5.1×10^{-6} S m^{-1} for H_2O, determine pH and K_w.

PROFICIENCY TEST

1. In highly alkaline medium, the anodic process during the electrolytic process is
$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$.

2. Compounds of active metals (Zn, Na, Mg) are reducible by H_2 whereas those of noble metals (Cu, Ag, Au) are not reducible.

3. The mass of a substance deposited on the cathode or anode during electrolysis is given by $w = \frac{EIt}{F}$.

4. Faraday's second law of electrolysis is related to the equivalent, mass of the electrolyte.

5. Equivalent conductance at infinite dilution of salt AB is equal to the sum of equivalent conductances of ions, A^+ and B^- at infinite dilution.

6. The standard reduction potential of $Cl^- | AgCl | Ag$ half-cell is related to that of $Ag^+ | Ag$ half-cell through the expression $E^\circ_{Ag^+|Ag} = E^\circ_{Cl^-|AgCl|Ag} + \frac{RT}{F} \ln K_{SP}(AgCl)$.

7. The cell potential is given by $E_{cell} = E_{RP(cathode)} - E_{RP(anode)}$.

8. A half-cell reaction is $A^{(x+n)} + ne^- \longrightarrow A^{x+}$. It is possible to determine the value of n from the measurements of cell potential.

9. In a galvanic cell, the half-cell with higher reduction potential acts as a reducing agent.

10. In an electrode concentration cell, the cel reaction $Zn(c_1) \longrightarrow Zn(c_2)$ will be spontaneous if $c_1 > c_2$.

11. The absolute value of electrode potential cannot be determined.

12. All chemical reactions used in galvanic cells are redox reactions.

13. The amount of the product formed by the passage of 1 coulomb of electricity through electrolyte is called electrochemical equivalent of the substance.

14. The redox reaction involved in galvanic cell is a non- spontaneous process.

15. In galvanic cell, the cathode is a – ve terminal of the cell.

16. The specific conductance of a 0.1 N KCl solution at 23°C is 0.012 $ohm^{-1}\ cm^{-1}$. The resistance of the cell containing the solution at the same temperature was found to be 55 ohms. The cell constant is ____.

17. Dilute sulphuric acid on electrolysis liberates___________ at the anode.

18. The electrical conductivity of a solution of acetic acid will _______ if a solution of sodium hydroxide is added.

19. A cation having a ________reduction potential is preferentially reduced at the cathode.

20. When an aqueous solution of sodium sulphate is electrolysed, the gases liberated at the anode & cathode are ________ and __________, respectively.

21. A cell in which two electrodes of the same metal are dipped in solutions of metal ion of different concentrations in called___________.

22. The half-cell involving the reaction,

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

is represented as _____________.

23. During discharge of lead storage battery, the overall reaction is___________.

24. In the calomel half-cell, the reduction reaction is ___________.

25. Temperature coefficient and change in enthalpy are related by the expression__________.

26. In salt bridge, the electrolyte used should be _________.

27. In electrochemical cell, the electrical neutrality in two half cells is maintained by _________.

28. The E° value for $H_2 \longrightarrow 2H^+ + 2e^-$ is ____________.

29. E°_{cell} of $E^\circ_{oxi.}$(anode) + __________.

30. Coulomb refers to _______ of electricity while ampere refers to ________ at which it flows.

31. The cathodic reactions always involve__________.

32. During electrolysis of aqueous solution of $CuSO_4$ using Pt electrodes the product at anode is ______.

33. The quantity of electricity required for complete reduction of 0.5 mole MnO_4^- to Mn^{2+} is ______C.

34. During electrolysis process ________energy is converted into _______.

35. $\wedge_{eq} \times$ normality = _________.

MIDDLE GAME

Q.1 Same quantity of electricity is being used to liberate iodine (at anode) and a metal x (at cathode). The mass of x deposited is 0.617g and the iodine is completely reduced by 46.3 cc of 0.124M sodium thiosulphate. Find the equivalent mass of x.

Q.2 The standard reduction potential values, $E^0(Bi^{3+}|Bi)$ and $E^0(Cu^{2+}|Cu)$ are 0.226V and 0.344V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolysed at 25^0C. to what value can $[Cu^{2+}]$ be brought down before bismuth starts to deposit, in electrolysis.

Q.3 In a fuel cell, H_2 & O_2 react to produce electricity. In the process, H_2 gas is oxidized at the anode & O_2 at the cathode . If 67.2 litre of H_2 at STP react in 15 minutes, what is the average current produced ? If the entire current is used for electrode deposition of Cu from Cu (II) solution, how many grams of Cu will be deposited?
Anode : $H_2 + 2OH^- \longrightarrow 2H_2O + 2\,e^-$ Cathode : $O_2 + 2\,H_2O + 4e^- \longrightarrow 4\,OH^-$

Q.4 One of the methods of preparation of per disulphuric acid, $H_2S_2O_8$, involve electrolytic oxidation of H_2SO_4 at anode ($2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$) with oxygen and hydrogen as by–products. In such an electrolysis, 9.722 L of H_2 and 2.35 L of O_2 were generated at STP. What is the weight of $H_2S_2O_8$ formed?

Q.5 During the discharge of a lead storage battery the density of sulphuric acid fell from 1.294 to 1.139 g.ml^{-1}. H_2SO_4 of density 1.294 g mL^{-1} is 39% and that of density 1.39 g mL^{-1} is 20% by weight. The battery holds 3.5L of acid and the volume practically remains constant during the discharge. Calculate the number of ampere hours for which the battery must have been used. The discharging reactions are:
$Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^-$ (anode)
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$ (cathode)

Q.6 The emf of the cells obtained by combining Zn and Cu electrode of a Daniel cell with N calomel electrode in two different arrangements are 1.083V and 0.018V respectively at 25^0C. If the standard reduction potential of N calomel electrode is –0.28V and that of Zn is –0.76 V, find the emf of Daniel cell.

Q.7 Given the standard reduction potentials $TI^+ + e^- \rightleftharpoons TI$, $E^0 = -0.34V$ and $TI^{3+} + 2e^- \rightleftharpoons TI^+$, $E^0 = 1.25V$. Examine the spontaneity of the reaction, $3TI^+ \rightleftharpoons 2TI + TI^{3+}$. Also find E^0 for this disproportionation.

Q.8 The emf of the cell Ag|AgI|KI(0.05M) || $AgNO_3$(0.05M) |Ag is 0.788V. Calculate the solubility product of AgI.

Q.9 The cell Pt, H_2(1 atm) | H^+(pH=x) || Normal calomel Electrode has an EMF of 0.67V at 25^0C. Calculate the pH of the solution. The oxidation potential of the calomel electrode on hydrogen scale is –0.28 V.

Q.10 Estimate the cell potential of a Daniel cell having 1 M Zn^{++} & originally having 1 M Cu^{++} after sufficient NH_3 has been added to the cathode compartment to make NH_3 concentration 2 M.
K_f for $[Cu(NH_3)_4]^{2+} = 1 \times 10^{12}$, E^0 for the reaction,
$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$ is 1.1 V.

Q.11 Consider the cell Ag|AgBr(s)|Br^-||AgCl(s), Ag | Cl^- at 25° C . The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10} . For what ratio of the concentrations of Br^- & Cl^- ions would the emf of the cell be zero ?

Q.12 The pK_{sp} of AgI is 16.07 . If the E° value for Ag^+| Ag is 0.7991 V . Find the E° for the half cell reaction $AgI\,(s) + e^- \rightleftharpoons Ag + I^-$.

Q.13 Voltage of the cell Pt, H_2 (1 atm)|HOCN (1.3×10^{-3} M)||Ag^+ (0.8 M)|Ag(s) is 0.982 V . Calculate the K_a for HOCN . Neglect $[H^+]$ because of oxidation of $H_2(g)$.
$Ag^+ + e \rightleftharpoons Ag(s) = 0.8$ V.

Q.14 The normal potential of Zn referred to SHE is 0.76V and that of Cu is –0.34V at 25^0C. When excess of Zn is added to $CuSO_4$, Zn displaces Cu^{2+} till equilibrium is reached. What is the ratio of Zn^{2+} to Cu^{2+} ions at equilibrium?

Q.15 Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained 0.1M MnO_4^- and 0.8M H^+ and which was treated with 90% of the Fe^{2+} necessary to reduce all the MnO_4^- to Mn^{+2}.
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O, E^0 = 1.51V$

Q.16 K_d for complete dissociation of $[Ag(NH_3)_2]^+$ into Ag^+ and $2NH_3$ is 6×10^{-8}. Calculate E^0 for the following half reaction; $Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag + 2NH_3$
$Ag^+ + e^- \rightleftharpoons Ag, \quad E^0 = 0.799$ V

Q.17 The overall formation constant for the reaction of 6 mol of CN^- with cobalt (II) is
1×10^{19}. The standard reduction potential for the reaction
$[Co(CN)_6]^{3-} + e^- \rightleftharpoons Co(CN)_6^{4-}$ is –0.83 V. Calculate the formation constant of $[Co(CN)_6]^{3-}$
Given $Co^{3+} + e^- \rightleftharpoons Co^{2+}$; $E^0 = 1.82$ V

Q.18 Calculate the emf of the cell
Pt, H_2(1.0 atm) | CH_3COOH (0.1M) || NH_3(aq, 0.01M) | H_2 (1.0 atm),
Pt $K_a(CH_3COOH) = 1.8 \times 10^{-5}$, $K_b(NH_3) = 1.8 \times 10^{-5}$.

Q.19 A current of 3 amp was passed for 2 hour through a solution of $CuSO_4$,3 g of Cu^{2+} ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.

Q.20 The Edison storage cell is represented as Fe(s) | FeO(s) | KOH(aq) | Ni_2O_3 (s) | Ni(s) The half–cell reaction are
$Ni_2O_3(s) + H_2O(i) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-, \quad E^0 = +0.40V$
$FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-, \quad E^0 = -0.87V$
(i) What is the cell reaction?
(ii) What is the cell e.m.f.? 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?

Q.21 For the galvanic cell : Ag|AgCl(s)| KCl (0.2M) || K Br (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 25^0C.
$[K_{sp(AgCl)} = 2.8 \times 10^{-10}; K_{sp(AgBr)} = 3.3 \times 10^{-13}]$

Q.22 An aqueous solution of NaCl on electrolysis gives $H_{2(g)}$, $Cl_{2(g)}$ and NaOH according to the reaction:

$$2Cl^-_{(aq)} + 2H_2O \rightleftharpoons 2OH^-_{(aq)} + H_{2(g)} + Cl_{2(g)}$$

A direct current of 25 amperes with a current efficiency of 62% is passed through 20 liters of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the 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).

Q.23 An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolyzed 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 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis.

Q.24 In the refining of silver by electrolytic method what will be the weight of 100 gm Ag anode if 5 ampere current is passed for 2 hours? Purity of silver is 95% by weight.

Q.25 Hydrogen peroxide can be prepared by successive reactions:
$2NH_4HSO_4 \rightarrow H_2 + (NH_4)_2S_2O_8$
$(NH_4)_2S_2O_8 + 2H_2O \rightarrow 2NH_4HSO_4 + H_2O_2$
The first reaction is an electrolytic reaction the second is steam distillation. What amount of current would have to be used in first reaction to produce enough intermediate to yield 100 gm pure H_2O_2 per hour? Assume 50% anode current efficiency.

Q.26 Dal lake has water 8.2×10^{12} litre approximately. A power reactor produces electricity at the rate of 1.5×10^{6}coulomb per second at an appropriate voltage.How many years would it take to electrolyse the lake?

Q.27 Calculate the potential at 25°C for the cell
$$\text{Cd} \mid \text{Cd}^{2+}\ (2.00\ \text{M}) \parallel \text{Pb}^{2}\ (0.0010\ \text{M}) \mid \text{Pb}$$
Given $E^\circ_{cell} = 0.277$ V.

Q.28 Calculate E° for the following reactions at 298 K,
$$\text{Ag(NH}_3)_2^+ + e^- \rightleftharpoons \text{Ag} + 2\text{NH}_3$$
$$\text{Ag(CN)}_2^- + e^- \rightleftharpoons \text{Ag} + 2\text{CN}^-$$
Given: $E^\circ_{Ag^+|Ag} = 0.7991\text{V}, K_{Ins}[\text{Ag(NH}_3)_2^+] = 6.02\times10^{-8}$ and $K_{Ins}[\text{Ag(CN)}_2^-] = 1.995\times10^{-19}$

Q.29 Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride in M/32 solution of salt at 298 K from the following cell data at 298 K.
$\text{Pt} \mid H_2\ (1\ \text{atm}) \mid H^+(1\text{M}) \parallel \text{M/32}\ C_6H_5NH_3Cl \mid H_2\ (1\ \text{atm}) \mid \text{Pt}\ ;\ E_{cell} = -0.188$ V.

Q.30 The emf of the cell, $\text{Pt} \mid H_2\ (1\ \text{atm}), \mid H^+\ (0.1\ \text{M}, 30\ \text{ml}) \parallel Ag^+\ (0.8\ \text{M}) \mid Ag$ is 0.9 V. Calculate the emf when 40 ml of 0.05 M NaOH is added.

Q.31 Given, $E^\circ = -0.268$ V for the $Cl^- \mid PbCl_2 \mid Pb$ couple and -0.126 V for the $Pb^{2+} \mid Pb$ couple, determine K_{sp} for $PbCl_2$ at 25°C?

Q.32 The equivalent conductance of 0.10 N solution of $MgCl_2$ is 97.1 mho cm^2 $equi^{-1}$ at 25^0C. a cell with electrode that are 1.5 cm^2 in surface area and 0.5 cm apart is filled with 0.1 N $MgCl_2$ solution. How much current will flow when potential difference between the electrodes is 5 volt.

Q.33 A dilute aqueous solution of KCl was placed between two electrodes 10 cm apart, across which a potential of 6 volt was applied. How far would the K^+ ion move in 2 hours at 25^0C? Ionic conductance of K^+ ion at infinite dilution at 25^0C is 73.52 ohm^{-1} cm^2 $mole^{-1}$?

Q.34 When a solution of specific conductance 1.342 ohm^{-1} $metre^{-1}$ was placed in a conductivity cell with parallel electrodes, the resistance was found to be 170.5 ohm. Area of electrodes is 1.86×10^{-4} m^2. Calculate separation of electrodes.

Q.35 The specific conductance at 25^0C of a saturated solution of $SrSO_4$ is 1.482×10^{-4} ohm^{-1} cm^{-1}while that of water used is 1.5×10^{-6} mho cm^{-1}. Determine at 25^0C the solubility in gm per litre of $SrSO_4$ in water. Molar ionic conductance of Sr^{2+} and SO_4^{2-} ions at infinite dilution are 59.46 and 79.8 ohm^{-1} cm^2 $mole^{-1}$ respectively. [Sr = 87.6 , S = 32 , O = 16]

ZENITH

Q.1 A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6 % by weight (density 1.261g ml^{-1} at 25°C) to 27 % by weight. The original volume of electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as H_2SO_4 is used up. Over all reaction is

$$Pb(s) + PbO_2(s) + 2H_2SO_4(l) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

Q.2 Assume that impure copper contains only iron, silver and a gold as impurities. After passage of 140 A, for 482.5s of the mass of the anode decreased by 22.260g and the cathode increased in mass by 22.011 g. Estimate the % iron and % copper originally present.

Q.3 100ml $CuSO_4$(aq) was electrolyzed using inert electrodes by passing 0.965 A till the pH of the resulting solution was 1. The solution after electrolysis was neutralized, treated with excess KI and titrated with 0.04M $Na_2S_2O_3$. Volume of $Na_2S_2O_3$ required was 35 ml. Assuming no volume change during electrolysis, calculate:
(a) duration of electrolysis if current efficiency is 80% (b) initial concentration (M) of $CuSO_4$.

Q.4 Calculate the equilibrium constant for the reaction:

$$3Sn(s) + 2Cr_2O_7^{2-} + 28H^+ \longrightarrow 3Sn^{4+} + 4Cr^{3+} + 14H_2O$$

E^0 for Sn/Sn^{2+} =0.136 V E^0 for Sn^{2+}/Sn^{4+} = – 0.154 V
E^0 for $Cr_2O_7^{2-}/Cr^{3+}$ = 1.33 V

Q.5 Calculate the equlibrium concentrations of all ions in an ideal solution prepared by mixing 25.00 mL of 0.100M Tl^+ with 25.00mL of 0.200M Co^{3+}.
E^0 (Tl^+/Tl^{3+})= –1.25 V ; E^0 (Co^{3+}/Co^{2+}) = 1.84 V

Q.6 Calculate the voltage, E, of the cell at 25^0 C

$$Mn(s) \mid Mn(OH)_2(s) \mid Mn^{2+}(x\ M),\ OH^-(1.00 \times 10^{-4} M) \parallel Cu^{2+}(0.675M) \mid Cu(s)$$

given that $K_{sp} = 1.9 \times 10^{-13}$ for $Mn(OH)_2$(s) E^0 (Mn^{2+}/Mn) = –1.18 V

Q.7 Calculate the voltage, E, of the cell

$$Ag(s) \mid AgIO_3(s) \mid Ag^+(x\ M),\ HIO_3\ (0.300M) \parallel Zn^{2+}\ (0.175M) \mid Zn(s)$$

if K_{sp} = 3.02 x 10^{-8} for $AgIO_3$(s) and K_a = 0.162 for HIO_3.

Q.8 The voltage of the cell

$$Pb(s) \mid PbSO_4(s) \mid NaHSO_4(0.600M) \parallel Pb^{2+}(2.50 \times 10^{-5}M) \mid Pb(s)$$

is E = +0.061 V. Calculate $K_2 = [H^+]\ [SO_4^{2-}]\ /\ [HSO_4^-]$, the dissociation constant for HSO_4^-.
Given : Pb (s) + SO_4^{2-}(aq) $\rightleftharpoons$ $PbSO_4$ (s) + $2e^-$ (E^0 = 0.356) E^0(Pb^{2+}/Pb) = –0.126 V

Q.9 The voltage of the cell

$$Zn(s) \mid Zn(CN)_4^{2-}(0.450M),\ CN^-(2.65 \times 10^{-3}M) \parallel Zn^{2+}(3.84 \times 10^{-4}M) \mid Zn(s)$$

is E = +0.099 V. Calculate the constant K_f for $Zn^{2+} + 4CN^- \rightleftharpoons Zn(CN)_4^{2-}$, the only $Zn^{2+} + CN^-$ complexation reaction of importance.

Q.10 An external current source giving a current of 5.0 A was joined with Daniel cell and removed after 10 hrs. Before passing the current the LHE and RHE contained 1L each of 1M Zn^{2+} and Cu^{2+} respectively. Find the EMF supplied by the Daniel cell after removal of the external current source. E^0 of Zn^{2+}/Zn and Cu^{2+}/Cu at 25°C is –0.76 and +0.34V respectively.

Q.11 Determine at 298 for cell

Pt | Q, QH_2, H^+ || 1M KCl | $Hg_2Cl_2(s)$ | Hg(l) | Pt

(a) it's emf when pH = 5.0

(b) the pH when $E_{cell} = 0$

(c) the positive electrode when pH = 7.5

given $E^0_{RP(RHS)} = 0.28$, $E^0_{RP(LHS)} = 0.699$

Q.12 At 25°C, $\Delta H_f(H_2O,l) = -56700$ cal / mol and energy of ionization of H_2O (l) = 19050 cal/mol. What will be the reversible EMF at 25°C of the cell,

Pt | $H_2(g)$ (1 atm) | H^+ || OH^- | $O_2(g)$ (1 atm) | Pt, if at 26°C the emf increas by 0.001158 V.

Q.13 Calculate the cell potential of a cell having reaction: $Ag_2S + 2e^- \rightleftharpoons 2Ag + S^{2-}$ in a solution buffered at pH = 3 and which is also saturated with 0.1 M H_2S.

For H_2S : $K_1 = 10^{-8}$ and $K_2 = 1.1 \times 10^{-13}$, $K_{sp}(Ag_2S) = 2 \times 10^{-49}$, $E^{\circ}_{Ag^+/Ag} = 0.8$.

Q.14 Calculate the solubility and solubility product of $Co_2[Fe(CN)_6]$ in water at 25^0C from the following data:

Conductivity of a saturated solution of $Co_2[Fe(CN)_6]$ is $2.06 \times 10^{-6}\Omega^{-1}\ cm^{-1}$ and that of water used $4.1 \times 10^{-7}\Omega^{-1}\ cm^{-1}$. The ionic molar conductivities of Co^{2+} and $Fe(CN)_6^{4-}$ are 86.0 $\Omega^{-1}\ cm^2\ mol^{-1}$ and 444.0 $\Omega^{-1}\ cm^{-1} mol^{-1}$.

Q.15 A sample of water from a large swimming pool has a resistance of 9200 Ω at 25°C when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of 85 Ω at 25°C. 500 gm of NaCl were dissolved in the pool, which was throughly stirred. A sample of this solution gave a resistance of 7600 Ω. Calculate the volume of water in the pool.

Given : Molar conductance of NaCl at that concentration is 126.5 $\Omega^{-1}\ cm^2\ mol^{-1}$ and molar conductivity of KCl at 0.02 M is 138 $\Omega^{-1}\ cm^2\ mol^{-1}$.

SUHANA SAFAR

OBJECTIVE

Q.1 A dilute aqueous solution at Na_2SO_4 is electrolysed using platinum electrodes.The products at the anode and cathode are

(A) O_2, H_2 (B) $S_2O_8^{2-}$, Na (C) O_2, Na (D) $S_2O_8^{2-}$, H_2 **[JEE 1996]**

Q.2 The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^{+} are 0.337 and 0.153 V respectively. The standard electrode potential of Cu^{+}/Cu half cell is

(A) 0.184 V (B) 0.827 V (C) 0.521 V (D) 0.490 V **[JEE 1997]**

Q.3 A standard hydrogen electrons has zero electrode potential because

(A) hydrogen is easier to oxidise
(B) this electrode potential is assumed to be zero
(C) hydrogen atom has only one electron
(D) hydrogen is the lighest element. **[JEE 1997]**

Q.4 The standard reduction potential values of the three metallic cations X, Y, Z are 0.52, –3.03, and –1.18 V respectively. The order of reducing power of the corresponding metals is

(A) $Y > Z > X$ (B) $X > Y > Z$ (C) $Z > Y > X$ (D) $Z > X > Y$ **[JEE 1998]**

Q.5 A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential of $Z > Y > X$, then

(A) Y will oxidise X and not Z (B) Y will oxidise Z and X
(C) Y will oxidise both X and Z (D) Y will reduce both X and Z. **[JEE 1999]**

Q.6 For the electrochemical cell, $M \mid M^+ \parallel X^- \mid X$, $E^\circ(M^+/M) = 0.44$ V and $E^\circ(X/X^-) = 0.33$V. From this data , 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 **[JEE 2000]**

Q.7 The reaction,

$3ClO^-(aq) \longrightarrow ClO_3^-(aq) + 2Cl^-(aq)$

is an example of

(A) Oxidation reaction (B) Reduction reaction
(C) Disproportionation reaction (D) Decomposition reaction **[JEE 2001]**

Q.8 The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is

(A) LiCl > NaCl > KCl (B) KCl > NaCl > LiCl
(C) NaCl > KCl > LiCl (D) LiCl > KCl > NaCl **[JEE 2001]**

Q.9 Saturated solution of KNO_3 is used to make salt bridge because

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

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

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

(D) KNO_3 is highly soluble in water **[JEE 2001]**

Q.10 Standard electrode potential data are useful for understanding the suitablilty of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:

$$MnO_4^-\,(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}\,(aq) + 4H_2O\,(l);\ E° = 1.51\ V$$

$$Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) + 6e^- \rightleftharpoons 2Cr^{3+}\,(aq) + 7H_2O\,(l);\ E° = 1.38\ V$$

$$Fe^{3+}\,(aq) + e^- \rightleftharpoons Fe^{2+}\,(aq);\ E° = 0.77\ V$$

$$Cl_2\,(g) + 2e^- \rightleftharpoons 2Cl^-\,(aq);\ E° = 1.40\ V$$

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

(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 **[JEE 2002]**

Q.11 In the electrolytic cell, flow of electrons is from:
(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.
[JEE 2003]

Q.12 Zn | Zn^{2+} (a = 0.1M) || Fe^{2+} (a = 0.01M)|Fe. The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is
(A) $10^{0.32/0.0591}$
(B) $10^{0.32/0.0295}$
(C) $10^{0.26/0.0295}$
(D) $e^{0.32/0.295}$ **[JEE 2004]**

Q.13 The half cell reactions for rusting of iron are: **[JEE 2005]**

$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightleftharpoons H_2O;\ E^0 = +\,1.23\ V,\ Fe^{2+} + 2e^- \rightleftharpoons Fe;\ E^0 = -0.44\ V$$

ΔG^0 (in kJ) for the reaction is:
(A) –76
(B) –322
(C) –122
(D) –176

SUBJECTIVE

Q.14 The standard reduction potential for Cu^{2+} / Cu is 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1×10^{-19}. **[JEE 1996]**

Q.15 Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the reaction, $Mn^{2+}_{aq} + 2H_2O \rightarrow MnO_2(s) + 2H^+_{aq} + H_2(g)$
Passing a current of 27A for 24 hours gives one kg of MnO_2. What is the value of current efficiency? Write the reaction taking place at the cathode and at the anode. **[JEE 1997]**

Q.16 How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 Amperes? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3.**[JEE 1997]**

Q.17 Calculate the equilibrium constant for the reaction

$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$, [given : $E^0_{Ce^{4+}/Ce^{3+}} = 1.44V; E^0_{Fe^{3+}/Fe^{2+}} = 0.68V$] **[JEE 1997]**

Q.18 Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for Fe^{3+} / Fe^{2+} and I_3^- / I^- couples. **[JEE 1998]**

Q.19 Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $Ag|Ag^+$ (satd. Ag_2CrO_4 soln.) || Ag^+(0.1 M) | Ag is 0.164 V at 298K. **[JEE 1998]**

Q.20 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 mintue. It was founf that agfter 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. **[JEE 2000]**

Q.21 The following electrochemical cell has been set up

$$Pt_{(I)} \mid Fe^{3+}, Fe^{2+}(a=1) \parallel Ce^{4+}, Ce^{3+}(a=1) \mid Pt_{(II)}$$

$$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\text{ V and } E^\circ_{Ce^{4+}/Ce^{3+}} = 1.61\text{ V}$$

If an ammetter is connected between the two platinum electrodes. predict the direction of flow of current. Will the current increase or decrease with time? **[JEE 2000]**

Q.22 The standard potential of the following cell is 0.23 V at 15^0 C & 0.21 V at 35^0 C

Pt | H_2(g) | HCl (aq) | AgCl(s) | Ag(s)

(i) Write the cell reaction.

(ii) Calculate ΔH^0, ΔS^0 for the cell reaction by assuming that these quantities remain unchanged in the range 15^0C to 35^0C.

(iii) Calculate the solubility of AgCl in water at 25^0C. Given standard reduction potential of the Ag^+/Ag couple is 0.80 V at 25^0C. **[JEE 2001]**

Q.23 Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The e.m.f of one cell is 0.3 V higher than the other. The conc. of $CuSO_4$ in the cell with higher e.m.f value is 0.5 M. Find out the conc. of $CuSO_4$ in the other cell $\left(\frac{2.303RT}{F} = 0.06\right)$. **[JEE 2003]**

Q.24 Find the equilibrium constant at 298 K for the reaction,

$$Cu^{2+}(aq) + In^{2+}(aq) \rightleftharpoons Cu^+(aq) + In^{3+}(aq)$$

Given that $E^\circ_{Cu^{2+}|Cu^+} = 0.15V$, $E^\circ_{In^{3+}|In^+} = -0.42V$, $E^\circ_{In^{2+}|In^+} = -0.40V$ **[JEE 2004]**

Q.25(a) Calculate ΔG_f^0 of the following reaction

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Given: ΔG_f^0 (AgCl) = –109 kJ/mole, ΔG_f^0 (Cl^-) = –129 kJ/mole, ΔG_f^0 (Ag^+) = 77 kJ/mole

Represent the above reaction in form of a cell

Calculate E^0 of the cell. Find $\log_{10}K_{SP}$ of AgCl

(b) 6.593×10^{-2} g of metallic Zn (amu = 65.39) was added to 100 ml of saturated solution of AgCl. Calculate $\log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2}$, given that

$Ag^+ + e^- \rightleftharpoons Ag$ $E^0 = 0.80$ V

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^0 = -0.76$V

Also find how many moles of Ag will be formed? **[JEE 2005]**

ANSWER KEY

EASY RIDE

Q.1 (a) 6.02×10^{22} electrons lost, (b) 1.89×10^{22} electrons gained, (c) (b) 1.80×10^{23} electrons gained

Q.2 (a) 0.75 F, (b) 0.69 F, (c)1.1 F

Q.3 (i) 54 gm, (ii) 16.35 gm

Q.4 1.023×10^{5} sec

Q.5 1.12 mol, 12.535 litre

Q.6 0.112 litre

Q.7 0.24 gms

Q.8 Rs. 0.75x

Q.9 (i) 2.1554 gm ; (ii) 1336. 15 sec

Q.10 115800C, 347.4 kJ

Q.11 t = 193 sec

Q.12 n = 4

Q.13 $Cu^{2+} = 0.08M$, $H^{+} = 0.04M$, $SO^{2-}_{4} = 0.1M$

Q.14 A = 114, Q = 5926.8C

Q.15 Final weight = 9.6g,0.01Eq of acid

Q.16 (a) $V(O_2)$=6.2L, (b)$V(O_2)$ = 0.824L

Q.17 t = 93.65 sec.

Q.18 60 %

Q.19 (i) 482.5 sec (ii) 0.3175 gm (iii) 0.327 gm

Q.20 7.958×10^{-5}M

Q.21 1.825 g

Q.22 2M

Q.23 (a) $Zn \mid Zn^{2+} \mid\mid Cd^{2+} \mid Cd$, (b) $Pt, H_2 \mid H^{+} \mid\mid Ag^{+} \mid Ag$, (c) $Cu \mid Cu^{2+} \mid\mid Cl^{-} \mid Hg_2Cl_2 \mid Hg$

(d) $Pt \mid Fe^{2+}, Fe^{3+} \mid\mid Cr_2O_7^{2-}, Cr^{3+} \mid Pt$

Q.24 (a) $2Ag + Cu^{2+} \longrightarrow 2Ag^{+} + Cu$, (b) $MnO_4^{-} + 5Fe^{2+} + 8H^{+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(c) $2Cl^{-} + 2Ag^{+} \longrightarrow 2Ag + Cl_2$, (d) $H_2 + Cd^{2+} \longrightarrow Cd + 2H^{+}$

Q.25

Anode	Cathode
(a) $Zn \mid Zn^{2+}$	$H^{+}, H_2 \mid Pt$
(b) $Pt \mid Sn^{2+}, Sn^{4+}$	$Fe^{3+}, Fe^{2+} \mid Pt$
(c) $Pt \mid Fe^{2+}, Fe^{3+}$	$MnO_4^{-}, Mn^{2+} \mid Pt$
(d) $Pb \mid Pb^{2+}$	$Br_2, Br^{-} \mid Pt$]

Q.26 1.61 V

Q.27 1.35 V

Q.28 1.68 V

Q.29 – 0.80 V, NO

Q.30 0.53 V, disproportionation

Q.31 – 0.0367 V

Q.32 $E^{o}_{Cell} = -0.36$ V, not spontaneous

Q.33 E =1.159V

Q.34 $K_c = 2.18 \times 10^{26}$

Q.35 $K_c = 1.864 \times 10^{107}$, $\Delta G^0 = -611.8$ kJ

Q.36 $K_w \approx 10^{-14}$

Q.37 $E^0 = 0.7826$ V

Q.38 n = 2

Q.39 E = 0.059

Q.40 E = 0.395 V

Q.41 $E^0_{cell} = +0.01V$, $E_{cell} = -0.0785V$, correct representation is $Pb|Pb^{2+} (10^{-3}M)||Sn^{2+}(1M)|Sn$

Q.42 $[Cu^{2+}] = 2.97 \times 10^{-12}$M for E =0

Q.43 E = –0.81eV

Q.44 0.52 V, 0.61 V

Q.45 -1.30×10^{3} kJ mol^{-1}

Q.46 0.0295 V

Q.47 0.0295 V

Q.48 pH = 4

Q.49 (i) E = 0.286V; (ii) E = –0.0206V

Q.50 $a_2 = 0.1006$ M

Q.51 419 S cm^2 $equivalent^{-1}$

Q.52 0.00046 S cm^{-1} ; 2174 ohm cm

Q.53 (i) 6.25×10^{5} ohm, (ii) 1.6×10^{-6} amp

Q.54 1.549 cm^{-1}

Q.55 101.8 ohm^{-1} cm^2 / gm equivalent

Q.56 0.0141 mho g $equiv^{-1}$ m^2, 0.141 mho m^{-1}

Q.57 (i) 232 Mho cm^2 mol^{-1} , (ii) 116 Mho cm^2 $equivalent^{-1}$

Q.58 0.865

Q.59 1.33×10^{-4} gm/litre

Q.60 8.74×10^{-11} $mole^2$ /$litre^2$

Q.61 $\alpha = 0.435$, $k = 6.7 \times 10^{-4}$

Q.62 (i) 390.6 S cm^2 mol^{-1} (ii) 12.32%

Q.63 1.067 S m^{-1}

Q.64 523.2×10^{-4} mho cm^2 mol^{-1}

Q.65 (i) 6.98 (ii) 1.08×10^{-14}

PROFICIENCY TEST

1.	T	2.	F	3.	T	4.	T	5.	T
6.	F	7.	T	8.	T	9.	F	10.	T
11.	T	12.	T	13.	T	14.	F	15.	F
16.	0.66 cm^{-1}	17.	O_2	18.	increase	19.	higher		
20.	O_2 & H_2	21.	Electrolyte concentration cell						

22. $Cr_2O_7^{2-}$ (aq.), Cr^{3+}(aq.), H^+ | Pt

23. $Pb(s) + PbO_2(s) + 2H_2SO_4 \rightarrow 2PbSO_4(s) + 2H_2O\ (l)$

24. $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq.)$

25.	$\Delta H = nF\left[T\left(\frac{dE}{dT}\right) - E\right]$	26.	inert, i.e., should not interfere with net cell reaction		
27.	Salt bridge or porous partition	28.	zero	29.	E°_{red} cathode
30.	Amount, rate	31.	reduction process	32.	Oxygen
33.	2.5 × 96500 C				

MIDDLE GAME

Q.1	Eq. wt. = 107.3	Q.2	$[Cu^{2+}] = 10^{-4}M$	Q.3	643.33amp,190.5g
Q.4	43.456g	Q.5	265 Amp. hr.	Q.6	E = 1.1 V
Q.7	E° = –1.59V, non-spontaneous			Q.8	$K_{sp} = 1.1 \times 10^{-16}$
Q.9	pH = 6.61	Q.10	$E^0 = 0.71V$	Q.11	$[Br^-] : [Cl^-] = 1 : 200$
Q.12	$E^0 = {}^-0.1511V$	Q.13	$K_a = 6.74 \times 10^{-4}$	Q.14	$[Zn^{2+}]/[Cu^{2+}] = 1.941 \times 10^{37}$
Q.15	1.39V	Q.16	0.373V	Q.17	$K_f = 8.227 \times 10^{63}$
Q.18	–0.46 V	Q.19	42.2 %	Q.20	(ii). 1.2V, (iii) 245.1 kJ
Q.21	–0.037 V	Q.22	A48.71 hour, $[OH^-] = 1.41$ M		
Q.23	$V(O_2) = 99.68$ mL, $V(H_2) = 58.46$ mL, Total vol. = 158.1 mL				
Q.24	57.5894 gm	Q.25	315.36 A	Q.26	1.9 million year
Q.27	0.179 V				
Q.28	0.372 V , – 0.307 V	Q.29	$h = 2.12 \times 10^{-2}$, $K_h = 1.43 \times 10^{-5}$ M		
Q.30	0.95 V	Q.31	$1.536 \times 10^{-5}\ M^3$	Q.32	0.1456 ampere
Q.33	3.29 cm	Q.34	4.25×10^{-2} metre	Q.35	0.1934 gm/litre

ZENITH

Q.1	1.21×10^5 coulomb	Q.2	Cu = 98.88%, Fe = 0.85%	Q.3	1250 s, 0.064 M
Q.4	$K = 10^{268}$	Q.5	$Tl^+ = 10^{-8}$; $Co^{3+} = 2 \times 10^{-8}$	Q.6	1.66V
Q.7	–1.188V	Q.8	10^{-2}	Q.9	5.24×10^{16}
Q.10	1.143V	Q.11	(a) –0.124 V, (b) 7.1, (c) calomel electrode		
Q.12	0.4414 V	Q.13	– 0.167 V	Q.14	$K_{SP} = 7.682 \times 10^{-17}$
Q.15	$2 \times 10^5\ dm^3$				

SUHANA SAFAR

OBJECTIVE

Q.1	A	Q.2	C	Q.3	B	Q.4	A	Q.5	A
Q.6	B	Q.7	C	Q.8	B	Q.9	C	Q.10	A
Q.11	C	Q12	B	Q.13	B				

SUBJECTIVE

Q.14 $E^0 = -0.22N$

Q.15 $\eta = 94.8\%$; Cathode : $2H^+ + 2e^- \rightarrow H_2$, Anode : $Mn^{2+} \rightarrow Mn^{4+} + 2e^-$

Q.16 $W_{Ag} = 272.2g$, area $=1.02 \times 10^4\ cm^2$ Q.17 $K_c = 7.6 \times 10^{12}$ Q.18 $K_C = 6.26 \times 10^7$

Q.19 $K_{sp} = 2.287 \times 10^{-12}\ M^{-3}$ Q.20 $7.95 \times 10^{-5} M$

Q.21 decrease with time

Q.22 $\Delta H^0 = -49987\ Jmol^{-1}$, $\Delta S^0 = -96.5\ J\ mol^{-1}\ K^{-1}$, $s = 1.47 \times 10^{-5}\ M$

Q.23 0.05 M Q.24 $K_C = 10^{10}$

Q.25 (a) $E^0 = 0.59\ V$, $\log_{10} K_{SP} = -10$
(b) 52.8, 10^{-6} moles