CHAPTER 6

Electrochemistry

Chapter Contents

Electrochemical cells and cell reactions; Standard electrode potentials; Nernst equation and its relation of ΔG; Electrochemical series, emf of galvanic cells; Faraday's laws of electrolysis; Electrolytic conductance, specific, equivalent and molar conductivity, Kohlrausch's laws Concentration cells and Various levels of multiple-choice questions.

ELECTROCHEMISTRY

Electrochemistry is the branch of the science that deals with the transformation of chemical energy into electrical energy and vice versa or it deals with the relationship between electrical and chemical energy produced in a redox reaction.

ELECTROLYSIS

Here direct current is used to cause a non-spontaneous chemical reaction due to it chemical decomposition of electrolytes takes place or It is the flow of electrons across the boundary followed by a chemical reaction that is, redox reaction. It occurs in electrolytic cell and it takes place at electrodes.

- The electrode which is connected to the positive pole of the battery is known as anode or positive electrode.
- At anode, de-electronation of anions or oxidation takes place.

$$A- \rightarrow A + e^-$$

- The electrode which is connected to the negative pole of the battery is known as cathode or negative electrode.
- At cathode, electronation of cation or reduction takes place.

$$B^+ + e^- \rightarrow B$$

- It is interesting to note that the current enters the electrolyte through cathode while leaves through anode.
- The electrolyte as a whole remains neutral during the process of electrolysis as equal number of charges are neutralized at the electrodes.
- Electrodes are two types: (i) Inert and (ii) Active
- If inert electrode is used, the products formed at cathode and anode depends upon nature of electrolytes.
- If active electrode is used at cathode metal deposits and at anode metal is dissolved.

Example, If Ni deposits at cathode, it is called electroplating.

- When fused salts are electrolyzed by using inert electrodes they ionize into their constituent elements.

  Example, $NaCl \rightarrow Na + ½\ Cl_2$

  $NiCl_2 \rightarrow Ni + Cl_2$

- When fused salts are electrolyzed by using active electrodes anode get dissolved due to formation of ions while cathode increases due to deposition of metal on it.
- During electrolysis of aq. solution of $AgNO_3$ the concentration of $AgNO_3$ is found to be same before and after electrolysis.
- During the electrolysis of aqueous solution of salts having NO_3^- , SO_4^{2-} (oxo anions) only water molecule undergo oxidation to liberate O_2 at anode.
- During electrolysis of aqueous solution of alkali or alkaline earth metals, only water molecules undergo reduction to liberate hydrogen at cathode.

Feature	Cathode	Anode
Sign	Negative as attached to negative end of external battery	Positive as attached to positive end of external battery
Direction of movement of electrons	Into the cell	Out of the cell
Direction of movement of ions	Cations	Anions
Half-reaction	Reduction	Oxidation

Examples of Electrolysis

(i) Electrolysis of Molten or Fused NaCl:

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

Cathode: $2Na^+ + 2e^- \rightarrow Na\ (s)$

Net reaction:

$2Na^+ + 2Cl^- \rightarrow Cl_2\ (g) + 2Na\ (s)$

(ii) Electrolysis of Aqueous NaCl Solution

$NaCl \rightarrow Na^+ + Cl$

$2Cl^- \rightarrow Cl_2 + 2e^-$ at +ve electrode

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

$2H^+ + 2e^- \rightarrow H_2$ at –ve electrode

As NaOH is in solution so pH increases.

At anode, Cl^- donate e^- as $E_{O.P.}$ or $Cl^- > E_{O.P.}$ of OH^-

At cathode, H^+ accept e^- as $E_{R.P.}$ of $H^+ > E_{R.P.}$ of Na^+

O_2 is not formed at anode here as over voltage is very high for it.

(iii) Electrolysis of H_2SO_4:

For pure H_2SO_4 electrolysis is not possible due to absence of ions.

$H_2SO_4 \leftrightarrow 2H^+ + SO_4^{-2}$

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

H_2 at –ve O_2 at +ve

Solution becomes colourless and pH decreases as H_2SO_4 is formed.

If further electrolysis is done O_2 is released at anode and H_2 is released at cathode.

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ E = –1.23 V

'g' 'aq'

Electrolysis of some electrolytes

S. No	Electrolytes	Electrodes		Products		Electrode reactions	
		Anode	cathode	At anode	At cathode	At anode	At cathode
1	NaCl (fused)	Pt	Pt	Cl_2	Na	$2Cl^- \rightarrow Cl_2 + 2e^-$	$Na^+ + e^- \rightarrow Na$
2	$MgCl_2$ (fused)	Graphite	Steel	Cl_2	Mg	$2Cl^- \rightarrow Cl_2 + 2e^-$	$Mg^{2+} + 2e^- \rightarrow Mg$

3	Al_2O_3 (fused) + cryolite	Graphite	Graphite	F_2	Al	$2F- \rightarrow F_2 + 2e^-$	$Al^{3+} + 3e^- \rightarrow Al$
4	$NiCl_2$ (fused)	Pt	Pt	Cl_2	Ni	$2Cl^- \rightarrow Cl_2 + 2e-$	$Ni^{2+} + 2e^- \rightarrow Ni$
5	NaCl (aq)	Pt	Pt	O_2, Cl_2	H_2	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $2Cl^- \rightarrow Cl_2 + 2e^-$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
6	$AgNO_3$ (aq)	Pt Ag	Pt Pt	O_2 O_2, Ag+	Ag Ag	$2H_2O \rightarrow O_2 + 4H+ + 4e^-$ $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $Ag \rightarrow Ag^+ + e^-$	$Ag^+ + e^- \rightarrow Ag$ $Ag^+ + e^- \rightarrow Ag$
7	$CuSO_4$ (aq)	Pt	Pt	O_2	Cu	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$Cu^{2+} + 2e^- \rightarrow Cu$
8	50% H_2SO_4 (aq)	Pt	Pt	$H_2S_2O_8$	H_2	$2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$	$2H^+ + 2e^- \rightarrow H_2$
9	K_2SO_4 (aq)	Pt	Pt	O_2	H_2	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
10	$CuCl_2$ (molten)	Pt Cu	Pt Pt	Cl_2 Cu^{2+}	Cu Cu	$2Cl^- \rightarrow Cl_2 + 2e^-$ $Cu \rightarrow Cu^{2+} + 2e^-$	$Cu^{2+} + 2e^- \rightarrow Cu$ $Cu^{2+} + 2e^- \rightarrow Cu$

REMEMBER

- The apparatus used for measurement of quantity of electricity is called Coulomefer.
- The amount of ion discharged doing electrolysis is independent of resistance of solution and temprature of bath.
- The art of electroplating was given by Faraday.

Product of Electrolysis

According to preferential discharge theory the ion will discharge first which required less energy. The potential at which ion get discharged is called deposition potential or discharge potential.

Discharge potential = Electrode potential + Over voltage

FARADAY'S LAWS OF ELECTROLYSIS

Faraday's First Law of Electrolytes

According to the first law, "The amount of substance or quantity of chemical reaction at electrode is directly proportional to the quantity of electricity passed into the cell".

W or $m \propto q$

or $W \propto It$

$W = Zit$

$$Z = \frac{M}{nf}$$

Z = Electrochemical equivalence

M = molar mass

F = 96500

n = Number of electrons transfer

q = amount of charge utilized

Electrochemical equivalent is the amount of the substance deposited or liberated by one ampere current passing for one second (that is, one coulomb, $I \times t = Q$) or one coulomb of charge.

One gm equivalent of any substance is liberated by one faraday.

Eq. Wt. = $Z \times 96500$

$$\frac{W}{E} = \frac{q}{96500}$$

$$w = \frac{E.\,q.}{96500}$$

$$w = \frac{E\,i\,t}{96500}$$

As $w = a \times l \times d$ that is, area × length × density

Here a = area of the object to be electroplated

d = density of metal to be deposited

l = thickness of layer deposited

Hence from here we can predict charge, current strength time, thickness of deposited layer etc.

REMEMBER

One Faraday: One faraday is the quantity of charge carried by one mole of electrons.

$E \propto Z$

$E = FZ$

$I\,F = 1.6023 \times 10^{-19} \times 6.023 \times 10^{23}$

= 96500 Coulombs

Faraday's Second Law of Electrolytes

According to the second law, "When the same quantity of electricity is passed through different electrolytes, the amounts of the products obtained at the electrodes are directly proportional to their chemical equivalents or equivalent weights".

As $\frac{W}{E} = \frac{q}{96500}$ = No. of equivalents constant

So

$$\frac{E_1}{E_2} = \frac{M_1}{M_2} \text{ or } \frac{W_1}{W_2} = \frac{Z_1 It}{Z_2 It} = \frac{Z_1}{Z_2}$$

E_1 = equivalent weight mass

E_2 = equivalent weight mass

W or M = mass deposited

From this law, it is clear that 96500 coulomb of electricity gives one equivalent of any substance

Example, 1F = 1 gm eq

Application of Faraday's Laws

- It is used in electroplating of metals.
- In is used in the extraction of several metals in pure form.
- It is used in the separation of metals form non-metals.
- It is used in the preparation of compounds

REMEMBER

Current Efficiency

It is the ratio of the mass of the products actually liberated at the electrode to the theoretical mass that could be obtained

$$\text{C.E.} = \frac{\text{desired extent}}{\text{Theoretical extent of reaction}} \times 100\%$$

Illustrations

1. A solution of a salt of a metal of atomic weight 112 was electrolysed for 150 minutes with a current of 0.15 amperes. The weight of metal deposited was 0.783 mg. Find the equivalent weight and valency of the metal in the salt.

Solution Given: I = 0.15 ampere

$t = 150 \times 60$ seconds

$Q = I \times t$

$Q = 0.15 \times 150 \times 60$ coulombs

= 1350 coulombs

1350 coulombs of electricity deposit = 0.783 gm of metal

96540 coulombs of electricity

$$= \frac{0.783 \times 96540}{1350} \text{ gm} = 55.97 \text{ gm of metal}$$

Equivalent weight of metal = 55.97

$$\text{Valency of metal} = \frac{\text{Atomic weight}}{\text{Equivalent weight}}.$$

$$= \frac{112}{55.97} = 2$$

2. A current of 3.7 amperes is passed for 360 minutes between nickel electrodes of a 2 M solution of $Ni(NO_3)_2$. What will be the molarity of the solution at the end of the electrolysis? (At. wt. of Ni = 58.70)

Solution $Ni^{2+} + 2e^- \rightarrow Ni$ (s)

$$w = \frac{E.\ i.\ t}{F}$$

$$= \frac{58.70 \times 3.7 \times 360 \times 60}{96500 \times 2} = 24.307 \text{ g}$$

Number of moles of Ni deposited

$$= \frac{24.307}{58.70} = 0.414 \text{ mole}$$

Molarity of remaining solution = 2.0 – 0.414

= 1.586 M

3. How many grams of silver could be plated out on a serving tray be 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.

Solution $Ag^+ + 1e^- \rightarrow Ag$ (s)

$$\text{Wt. of Ag} = \frac{E.\ i.\ t}{F}$$

$$= \frac{107.9 \times 8.46 \times 8 \times 60 \times 60}{96500} = 272.43 \text{ g}$$

$$\text{Volume of Ag} = \frac{\text{Wt. of Ag}}{\text{density}} = \frac{272.43}{10.5} = 25.94 \text{ ml}$$

$$\text{Area of tray} = \frac{\text{Volume}}{\text{Thickness}} = \frac{25.94}{0.00254}.$$

= 10212.6 cm^2

4. A copper coulometer and a silver coulometer were connected in series. The copper coulometer contained a 5% solution of $CuSO_4.5H_2O$ while the silver coulometer contained a 2% solution of $AgNO_3$. A current of 0.01 ampere was passed through the coulometers for 30 minutes. What was the ratio of the masses of Cu and Ag deposited at the cathode of the two coulometers respectively?

Solution W = Z. i. t

For copper

$$W = \frac{31.75}{96500} \times 0.01 \times 30 \times 60$$

= 0.0059 g

For silver

$$W = \frac{108}{96500} \times 0.01 \times 30 \times 60$$

= 0.0201 g

Thus ratio of the masses of Cu and Ag deposited at the cathode is

0.0059 : 0.0201 = 1 : 3.407

5. When an aqueous solution of copper (II) sulphate, CuSO4 is electrolyzed copper metal is deposited

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

If a constant current was passed for 5.0 hour, 404 mg of copper metal was deposited, what must have been the current?

Solution According to Faraday's first law of electrolysis,

m = Z. i. t

$$404 \times 10^{-3} \text{ g} = \frac{63 \text{ g C}^{-1}}{2 \times 96500} \times i \times 5 \times 60 \times 60$$

$$i = \frac{0.404 \times 2 \times 96500}{63 \times 5 \times 60 \times 60}$$

= 0.0682 ampere

6. How long will it take 5 amperes of current to deposit 2 g of copper from a solution of copper sulphate? (Equivalent wt. of Cu = 32, F = 96500 C)

Solution W = Z . i. t

$$2 \text{ g} = \frac{32 \text{ g}}{96500 \text{ C}} \times 5 \text{ amp} \times t$$

$$t = \frac{2 \times 96500}{32 \times 5}$$

= 1206.25 s.

7. During the electrolysis of an aqueous solution of NaCl 10.3 g of chlorine was liberated. Calculate the volume of hydrogen that would be liberated at 20°C and 740 mm of Hg pressure from acidulated water, when the same quantity of current as that used in the electrolysis of NaCl was passed.

Solution

According to Faraday's law of electrolysis, as the current passed will be the same

$$\frac{\text{Weight of } H_2 \text{ liberated}}{\text{Eq. weight of } H_2} = \frac{\text{Weight of } Cl_2 \text{ liberated}}{\text{Eq. weight of } Cl_2}$$

$$\frac{\text{Weight of } H_2 \text{ liberated}}{1} = \frac{10.3}{35.5}.$$

$$\text{Weight of } H_2 \text{ liberated} = \frac{10.3}{35.5} \text{ g}$$

As 2 g of H_2 occupies 22400 cc at NTP

So $\frac{10.3}{35.5}$ g occupies $\frac{22400 \times 10.3}{2 \times 35.5} = 3249$ cc

The volume of H_2 at 20°C and 740 mm of Hg pressure will be from

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V = \frac{3249 \times 760 \times 293}{273 \times 740} = 3582 \text{ cc}$$

ELECTRICAL CONDUCTANCE

Here, conductance is due to movement of ions through electrodes. It involves transfer of matter and ions. It occurs in small magnitude. Besides nature of material, the magnitude of conductivity also depends upon temperature and pressure at which the measurements are made.

- The conductivity of electrolytic solutions depends upon
  - (a) Nature of electrolyte
  - (b) Size of ions produced and their solvation (hydration)
  - (c) Nature of solvent and its viscosity
  - (d) Concentration of the electrolytes
  - (e) Temperature (direct relation)
- Electronic conductance through metals is known as metallic or electronic conductance and it is due to the moment of electrons the conductivity of metals depends upon:
  - (a) Nature of structure of metal
  - (b) Number of valence electrons per atom
  - (c) Density of metal
  - (d) Temperature (inverse relation)
- As the electrons enter at one end go out at the other end, the composition of the metallic conductor remains unchanged. In contrast to electrolytic conductance, electronic conductance decreases with increase in temperature.

Ohm's Law

According to Ohm's law,

$$\frac{E}{I} = \text{constant (R)}$$

or

$$I = \frac{E}{R}$$

E = potential, R = resistance

Unit : Ω ohms

Resistance (R)

It offers obstruction to the passage of electric current. It is directly proportional to the length (l) and inversely proportional to the area of cross section (a) of the conductor.

$$R \propto 1/a \text{ or } R = \frac{\varrho l}{a}$$

Specific Resistance (ϱ)

The resistance offered by one cm^3 of the conductor is known as specific resistance.

If $l = 1$ cm

If $a = 1$ cm^2

$R = \varrho$

$\varrho = R. \frac{a}{l}$ ohm. cm.

Conductance (C)

It is ease of flow of electric current through the conductor and it is reciprocal of resistance.

$$C = \frac{1}{R} \ \Omega^{-} \text{ (mho)}$$

$1S = 1\ \Omega^{-}$

siemens

Specific Conductance (k, kappa)

It is the reciprocal of specific conductance.

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

$\frac{l}{a}$ = cell constant

Unit: $\Omega^{-} cm^{-1}$

■ If 'l' and 'a' are unity then conductance of one c.c. is called specific conductance or conductivity

Cell Constant

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Measured conductance}}$$

Conductance is measured by using wheat stone bridge method (for R) and 1N or .01 N KCl solution for [l/a]

Effect of Dilution on specific Conductance

The number of current carrying particles or ions per ml decrease on dilution and specific conductivity, being the conductance of one centimeter cube of solution, decreases with dilution.

Equivalent Conductivity

The conductivity of all the ions produced when one gram equivalent of an electrolyte is dissolved in V ml of solution is called equivalent conductivity. It is denoted by λv or Λv.

λ or $\Lambda = k \times V$.

Unit: $\Omega^{-1} c. m^2$

As $\frac{W}{E} = \frac{NV}{1000}$

So $\lambda = \frac{k \times 1000}{N}$

■ The equivalent conductivity increases with increase of dilution.

Molar Conductivity

The conductivity of all the ions produced when one mole of an electrolyte is dissolved in V ml of solution is known as molar conductivity.

$$\lambda m \text{ or } \Lambda m = \frac{1000 \times k \times V}{M \text{ (molarity)}}$$

Factors Affecting the Molar Conductivity (Λm)

■ **Nature of Electrolyte**: Strong electrolytes like HCl, H_2SO_4, NaOH, KOH, KNO_3, KCl, NH_4NO_3 etc., are completely ionized in aqueous solution so have high value of molar conductivity.

As weak electrolytes like H_2CO_3, CH_2COOH, NH_4OH etc., are ionized to lesser extent in aqueous solution so have lower value of molar conductivity.

■ **Temperature**

$\Lambda m \propto$ Temperature

As the increase of temperature decreases inter ionic attractions, solvation of ions, viscosity and increases kinetic energy of ions and their speed so Λm increases with the increase of temperature.

■ **Dielectric Constant of Solvent**: Higher the value of dielectric constant of a solvent, the more is the value of molar conductivity as it decreases inter ionic attractions.

■ $K = \frac{C. (\Lambda^o/\Lambda_M)_2}{1 - \Lambda^o/\Lambda_M}$.

■ **Viscosity of Solvent**

$\Lambda m \ \alpha \ 1/\eta$

that is, higher the value of viscosity lower is the value of molar conductivity.

Effect of Dilution on Molar Conductivity

Molar conductivity increases with dilution as degree of dissociation of electrolyte increase with dilution. At ∞ Dilution Λ is maximum i.e., Λ_∞ is maximum.

$$\alpha = \frac{\Lambda v}{\Lambda_\infty}$$

■ **Concentration of the Solution**

As the concentrated solutions of strong electrolytes have significant inter ionic attractions, which reduces the speed of ions so lowers the value of molar conductivity. As the dilution decreases such attractions so increases the value of molar conductivity.

The limiting value of Λm (Λm^∞ the molar conductivity at zero concentration or at infinite dilution) can be obtained by extrapolating the graph shown below.

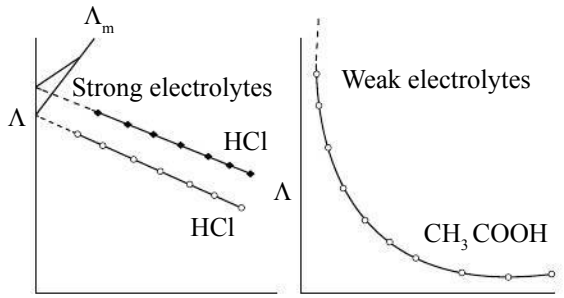


Fig (a) Fig (b)

Variation of molar conductance (Λ) with square root of concentration $\sqrt{C}$ (a) Strong electrolytes and (b) Weak electrolytes

The variation in molar conductance with concentration is different for strong and weak electrolytes.

Debye–Huckel–Onsagar Equation

It shows a relation between molar conductivity at a particular concentration and molar concentration at infinite dilution as follows:

$\Lambda m = \Lambda m^{\infty} - b\sqrt{C}$

or

$\mu = \mu_{\infty} - b\sqrt{C}$

Here, b = Constant,

C = Concentration;

Λm^{∞} or μ_{∞} = Molar conductance at infinity.

Λm or μ = Molar conductance at other dilutions The value of b for a given solvent and temperature depends upon the nature of electrolyte that is, the charges on cation and anion produced after dissociation (thus NaCl, $CaCl_2$, $MgSO_4$ are known as 1–1, 2–1 and 2–2 electro lies respectively). All electrolytes of a particular type have same value of b. The value of b is obtained from the slope value.

Kohlrausch Law

Kohlrausch examined Λ^o or Λ^{∞} values for a number of strong electrolytes and observed certain regularities. He noted that the difference in Λ^o of the electrolytes NaX and KX for any X in nearly constant.

On the basis of these observations he introduced **Kohlrausch law of Independent Migration of ions.** The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. that is, at infinite dilution, the contribution of any ion towards equivalent conductance is constant; it does not depend upon presence of any ion.

For any electrolyte:

$P_X Q_Y \rightleftharpoons XP^{+y} + YQ^{-X}$

$\Lambda^o = X\lambda^o_{+} + Y\lambda^o_{-}$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$\Lambda^{\infty}_m (CH_3COOH) = (\Lambda^{\infty}_H + \Lambda^{\infty}_{Cl^-}) + (\Lambda^{\infty}_{CH_3COO^-} + \Lambda^{\infty}_{Na^+})$

$- (\Lambda^{\infty}_{Na^+} - \Lambda^{\infty}_{Cl^-})$

$= \Lambda^{\infty}_{HCl} + \Lambda^{\infty}_{CH_3COONa} - \Lambda^{\infty}_{Nacl}$

Application of Kohlrausch's Law

1. Determination of Λ^oB of a weak electrolyte:

In case of weak electrolytes, the degree of ionization increases which increases the value of Λm. However, it cannot be obtained by extrapolating the graph. The limiting value, Λm^{∞}, for weak electrolytes can be obtained by Kohlrausch law.

for example in case of NH_4OH

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$\Lambda^{\infty}_m (NH_4OH) = (\Lambda^{\infty}_{NH_4} + \Lambda^{\infty}_{Cl^-}) + (\Lambda^{\infty}_{Na^+} + \Lambda^{\infty}_{OH^-})$

$- (\Lambda^{\infty}_{Na^+} - \Lambda^{\infty}_{Cl^-})$

$= \Lambda^{\infty}_{NH_4Cl} + \Lambda_{NaoH} - \Lambda^{\infty}_{Nacl}$

2. To determine degree of dissociation and equilibrium constant of weak electrolyte:

CH_3COOH	$\rightleftharpoons$	CH_3COO^-	+	H^+
C		0		0
C – Cα		Cα		Cα

Here C = Initial concentration

α = Degree of dissociation

$$\alpha = \frac{\Lambda^o}{\Lambda_M}.$$

Here Λ^o or Λ^{∞} = Molar conductance at infinite dilution or zero concentration.

Λ_M = Molar conductance at given conc. C

$$K = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

$$K = \frac{C\alpha \,.\, C\alpha}{C(1-\alpha)}$$

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

$$K = \frac{C.(\Lambda^o/\Lambda_M)^2}{(1-\Lambda^o/\Lambda_M)}.$$

$$= \frac{C(\Lambda^o)^2}{\Lambda^o(\Lambda^o - \Lambda_m)}$$

These are Ostwald's relations.

3. To determine solubility of salt and K_{sp}:

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

$$\Lambda^o = \frac{1000\,K}{M}$$

$\Lambda^o = \lambda^o Ag^+ + \lambda^o Cl^-$

$$M = \frac{1000\,K}{\Lambda^o}$$

Here M = Solubility of AgCl

Solubility product:

$Ksp = [Ag^+][Cl^-]$

As $[Ag^+] = [Cl^-]$

$$Ksp = \frac{1000\,K}{\Lambda^o} \times \frac{1000\,K}{\Lambda^o}$$

$Ksp = (1000\,K/\Lambda^o)^2$

Illustrations

8. Calculate the equivalent conductivity of 1M H_2SO_4 solution, if its conductivity is 26×10^{-2} $ohm^{-1}\,cm^{-1}$. (Atomic weight of sulphur = 32)

Solution $N = nM = 2 \times 1\,M = 2N$

As H_2SO_4 is a diprotic acid so n = 2

k = Specific conductivity = 26×10^{-2} $ohm^{-1}\,cm^{-1}$

$$\Lambda eq = \frac{1000\,k}{N} = ohm^{-1}\,cm^2\,equiv^{-1}$$

$$= \frac{1000 \times 26 \times 10^{-2}}{2N}$$

$= 1.3 \times 10^2$ $ohm^{-1}\,cm^2\,equiv^{-1}$

9. If Λ^∞_m of HCl, NaCl and CH_3COONa are 425, 128 and 96 $\Omega^{-1}\,cm^2\,mol^{-1}$ respectively, calculate the value of Λ^∞_m for acetic acid.

Solution $\Lambda^\infty_{m\,CH3COOH} = \Lambda^\infty_{m\,CH3COOH} + \Lambda^\infty_{m\,HCl} - \Lambda^\infty_{mNaCl}$

$= 96.0 + 425.0 - 128.0$

$= 393.0\ \Omega^{-1}\,cm^2\,mol^{-1}$

10. A salt solution of 0.30 N placed in a cell whose electrodes are 1.9 cm apart and 3.6 cm^2 in area offers a resistance pf 20 Ω. Calculate equivalent conductivity of solution.

Solution R = 20 Ω, l = 1.9 cm

a = 3.6 cm^2 , N = 0.30 N

$$\text{Cell constant} = \frac{l}{a} = \frac{1.9}{3.6} = 0.528\ cm^{-1}$$

Specific conductance (k) = conductance × cell constant = (1/R) × cell constant

$= (1/20) \times 0.528$

$= 0.0264\ s\,cm^{-1}$

$$\Lambda_{eq} = \frac{k \times 1000}{N} = \frac{0.0264 \times 1000}{0.30}$$

$= 88\ s\,cm^2\,eq^{-1}$.

11. 0.05 M NaOH solution offered a resistance of 31.16 Ω in a conductivity cell at 298 K. If cell constant is 0.367 cm^{-1}. Find out the molar conductivity of NaOH solution.

Solution $\text{Conductivity (k)} = \frac{\text{Cell constant}}{R}$

$$= \frac{0.367}{31.16} = 0.0118\ s\,cm^{-1}$$

$$\Lambda_m = \frac{k \times 1000}{M} = \frac{0.0118 \times 1000}{0.05}$$

$= 236\ s\,cm^2\,mol^{-1}$

12. The molar conductivities of CH_3COOH at 25°C at the concentration of 0.1 M and 0.001 M are 5.20 and 49.2 $s\,cm^2\,mol^{-1}$ respectively. Calculate the degree of dissociation of CH_3COOH at these concentrations. (Λ^∞_m (CH_3COOH) = 390.7 s $cm^2\,mol^{-1}$)

Solution $\text{Degree of dissociation } (\alpha) = \frac{\Lambda^c_m}{\Lambda^\infty_m}$

$= \frac{5.20}{390.7} = 0.013 = 1.3\%$

$0.001\ M = \frac{49.2}{390.7} = 0.125 = 12.5\%$

Electrochemical Cell or Galvanic Cell or Voltaic Cell

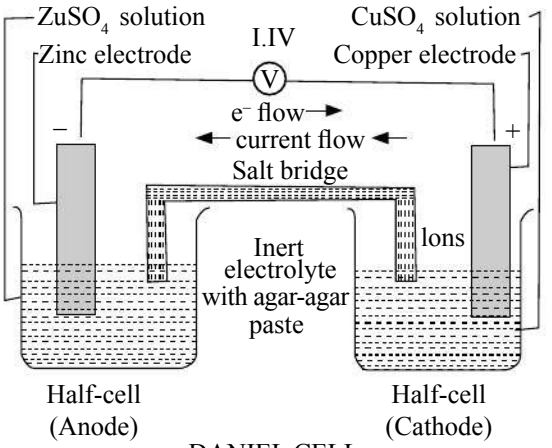
It is the device in which the decrease of free energy during the indirect redox reaction is made to convert chemical energy into electrical energy.

Galvanic and Voltaic developed such devices therefore these cells are also known as Galvanic cells or Voltaic cell or Redox cells.

Feature	Cathode	Anode
Sign	Positive due to consumption of electrons	Negative due to release of electrons
Reaction	Reduction	Oxidation
Movement of electrons	Into the cell	Out of cell

Electrochemical Cell	Electrolytic Cell
It is a combination of two half cells, containing the same or different electrodes in the same or different electrolytes.	It is a single cell containing the same electrodes present in the same electrolyte.
Anode is negative, cathode is positive	Anode is positive, cathode is negative
Electrons move from anode to cathode in external circuit	Electrons enter through cathode and leave through anode.
It converts chemical energy into electrical energy, produced as a result of redox reaction.	It converts electrical energy into chemical energy. Energy is supplied to the electrolytic solution to bring about the redox reaction.
Cell reaction is spontaneous.	Cell reaction is non spontaneous.
Salt bridge is required.	No salt bridge is required.

Galvanic or Daniel cell



DANIEL CELL

- The Daniel cell is a typical galvanic cell. It is designed to make use of the spontaneous redox reaction between zinc and cupric ion to produce an electric current.
- The Daniel cell can be conventionally represented as

$$Zn\ (s)\ |\ ZnSO_4\ (aq)\ ||\ CuSO_4\ (aq)\ |\ Cu(s)$$

Saltbridge

- The Daniel cell reaction is represented as

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

- In Daniel cell, electrons flow from zinc electrode to copper electrode through external circuit while metal ions flow form one half cell to the other through salt bridge.
- Here current flows from copper electrode to zinc electrode that is, cathode to anode in external circuit.
- Daniel cell is a reversible cell while a voltaic cell may be reversible or irreversible.

A voltaic cell is reversible only when it satisfies following conditions:

- The emf of external source is more than that of voltaic cell so that current may flow from external source into the voltaic cell and cell reaction can be reversed.
- If emf of voltaic cell is more than that of external source current flows from voltaic cell into external source.

Saltbridge

It maintains electrical neutrality in two compartments by allowing movement of anions towards anodic compartment and cations towards cathodic compartment.

- It is a glass tube having KCl, KNO_3, ammonium nitrate in a gelatin gel or agar–agar past.
- The gelatin gel allows ionic movement through it but prevents any kind of mixing.
- In case of KCl or ammonium nitrate, the ionic mobility of cation and anion are same.

Function of a Saltbridge

- A salt bridge acts as an electrical contact between the two half-cells.
- It prevents mechanical flow of solution but it provides free path for the migration of ions to maintain an electric current through the electrolyte solution. It prevents the accumulation of charges.
- A salt bridge helps in maintaining the charge balance in the two half cells.
- A salt bridge minimizes/eliminates the liquid junction potential.

Liquid Junction Potential: The unequal rates of migration of the cations and anions across a liquid-liquid junction give rise to a potential difference across the junction. This potential difference across the liquid-liquid junction is called liquid junction potential.

REMEMBER

- If salt bridge is removed the emf of the cell drops to zero.

Electrodes or Half Cells

- An electrode and the solution in which it is dipped is called a half-cell.
- Half cells are called anodic half cells and cathodic half cells.
- The electrode at which oxidation takes place is called anode.
- The electrode at which reduction takes place is called cathode.
- Anode is positively charged and cathode is negatively charged in electrolytic cell.
- In voltaic cell anode has negative charge as the electron will flow from it.
- In voltaic cell cathode has positive charge as the electrons are drawn from it.
- At anode deelectronation or oxidation occurs as the elements goes into the solution due to loss of electrons by ions.
- At cathode electronation or reduction process occurs as ions gain electron and get discharged here.

Types of Electrodes or Half Cells

The various types of electrodes which are frequently used in the electrochemical cells are as follows:

1. **Metal-Metal Ion Electrode**: It includes a metal strip dipped in the solution of its own cations.

   Example, Zn/Zn^{2+}, Cu/Cu^{2+}, Ag/Ag^{+} etc.

2. **Amalgam Electrode:** It is similar to metal-metal ion type electrode, but here, metal is replaced by its amalgam with Hg. This is done to improve the activity of metal.

   Example, $Zn - Hg/Zn^{2+}$

3. **Gas Electrode**: It involves the inert metal foil like Pt immersed in the solution capable of furnishing ions of gas.

   Example, Pt, H_2/H^{+} and Pt, Cl_2/Cl^{-}

4. **Metal-Metal Insoluble Salt-Salt Anion**: This type of electrode includes metal in contact with its sparingly soluble salt and aqueous solution of solution salt containing same anion.

   Example, Hg– Hg_2Cl_2 (s) – KCl (aq) Calomel electrode

   Pb– $PbSO_4$ (s) – K_2SO_4 (aq)

5. **Redox Electrode**: This electrode includes a platinum wire dipped in a solution of mixture of the two salts of the same metal but with different oxidation states.

   Example, Pt, Fe^{2+}/Fe^{3+}.

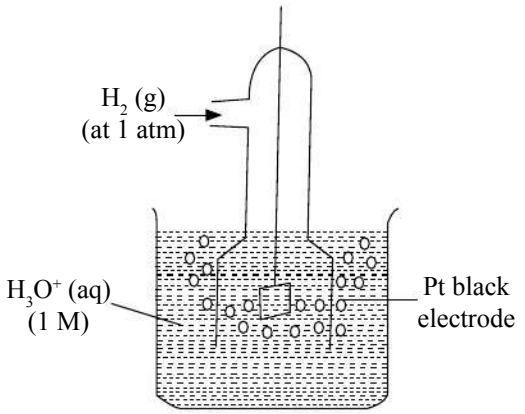
6. **Glass Electrode**:
   It consists of a thin walled glass bulb made out of special types of low melting glass.

Glass electrodes are not affected by oxidizing and reducing agents and are not easily poisoned so

they are finding great applications, in industry, in analytical chemical and biological laboratories in the measurement of pH.

Glass electrode gives very good results for pH value ranging between 0 and 6. For solutions of high alkalinity, high accuracy is not obtained.

7. Standard Hydrogen Electrode (SHE):



Hydrogen electrode

A hydrogen electrode in which pressure of hydrogen gas is maintained at 1 atm and the concentration of H^+ ions in the solution is 1 M, is called a standard hydrogen electrode (SHE).

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

- The emf of a standard hydrogen electrode is taken as 0.00 V at all temperature.
- It is a reversible electrode.
- It is used as a reference electrode.
- A saturated calomel electrode is also used as a secondary reference electrode. It has a potential of –0.24 volt.

8. Electrode Potential or Single Electrode Potential:

It is the tendency of an electrode to accept or to lose electrons.

When a metal strip M is placed in contact with the solution of its own ions M^{n+}, an electrical potential difference is set up between the metal strip and the solution due to either of the two tendencies.

Oxidation: $(M \leftrightarrow M^{n+} + ne^-)$

Reduction: $(M^{n+} + ne^- \leftrightarrow M)$

- The electrical potential difference between metal strip and solution is known as half cell electrode potential (E).
- Single electrode potential cannot be measured experimentally.
- The potential difference between two single electrodes can be measured by using Potentiometer.
- The tendency of oxidation can be represented by oxidation potential (E_{oxi}).
- The tendency of reduction can be represented by reduction potential (E_{red}).
- Oxidation potential of element is same in magnitude but opposite in sign to the reduction potential, that is, ($E_{red} = -E_{oxi}$). Therefore, by conventions, the electrode potentials (E) are represented by their reduction potentials E_{red}.
- E_{red} values vary with the concentration of the ions in solution at particular temperature. The reduction potential of the electrode at standard state conditions (1 molar conc. of the ions, 298 K and 1 atm pressure) is called Standard reduction potential (E^o).
- The absolute values of E^o for any electrode can not be determined because it is impossible to work with single half cell hence the E^o values are determined with respect to standard hydrogen electrode (SHE) whose standard electrode potential (E^o) is taken to be zero by conventions.
- E^o is an intensive property like temperature or molar volume. This means that E^o is same for half cell reaction whether it is represented as

  $2X^+ + 2e^- \rightarrow X_2$

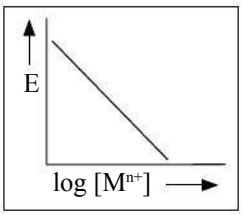
  $X^+ + e^- \rightarrow \frac{1}{2} X_2$.
- E^o values are not thermodynamic functions and may not be added directly. However, they can be calculated from free energy which is extensive property.

The value of electrode potential developed on an electrode depends upon

- Temperature of the system.
- Concentration of ions in solutions.
- Chemical nature of the metal or non metal
- Number of electrons transferred in the half cell reaction
- It does not depend upon length of electron.

Types Of Electrode Potential

(i) Oxidation Potential: When electrode is negatively charged with respect to solution then it acts as anode and oxidation takes place here.



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

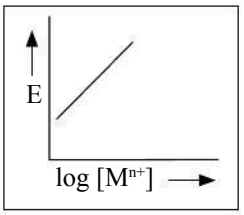
$$E_{OX} = E^o_{OX} - \frac{2.303\ RT}{nF} \cdot \log_{10}[M^{n+}]$$

Here

Intercept = E^o_{OX}

$$\text{Slope} = \frac{-2.303\ RT}{nF}$$

(ii) Reduction potential: When electrode is positively charged with respect to solution then it acts as cathode and reduction takes place here.



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

$$E_{red} = E^o_{red} \frac{-2.303\ RT}{nF} \log_{10} \frac{1}{[M^{n+}]} \cdot$$

$$E_{red} = E^o_{red} + \frac{2.303\ RT}{nF} \log_{10}[M^{n+}]$$

Here

Intercept = E^o_{red}

$$\text{Slope} = \frac{2.303\ RT}{nF}$$

EMF of the Cell or Cell Voltage

It is the potential difference between the two terminals of the cell when no current is drawn from it. It is measured with the help of potentiometer or vacuum tube voltmeter.

Calculation of the EMF of the Cell

Mathematically, it may be expressed as

$$E_{cell} \text{ or EMF} = [E_{red}\ (\text{cathode}) - E_{red}\ (\text{anode})]$$

$$E^o_{cell} \text{ or EMF}^o$$

$$= [E^o_{red}\ (\text{cathode}) - E^o_{red}\ (\text{anode})]$$

- For cell reaction to occur the E_{cell} should be positive. This can happen only if E_{red} (cathode) > E_{red} (anode).
- E^ocell must be positive for a spontaneous reaction.
- Rate of reaction is directly proportional to the emf of the cell.
- The emf of the cell depends on the intensity of the reaction in the cell.
- It measures free energy change for maximum convertibility of heat into useful work.
- It causes flow of current from higher value of E^o electrode to lower E^o value electrode.

Difference between EMF and Cell Potential

EMF	Cell potential
It is measured by potentiometer.	It is measured by voltmeter.
It is potential difference between two electrodes when no current is flowing in the circuit	It is potential difference between two electrodes when current is flowing through the circuit
It is maximum voltage obtained from cell	It is less than maximum voltage
It corresponds to maximum useful work obtained from galvanic cell.	It does not correspond.

Nernst Equation

This equation gives the relationship between electrode potential and concentration of ions in the solution.

Or

It shows the dependency of electrode potential on the concentration of the ions with which the electrode is reversible.

For a single electrode involving the reduction process,

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

The Nernst equation is

$$E = E^o + \frac{2.303\ RT}{nF} \log_{10} \frac{[M^{n+}]}{[M]}$$

or

$$E = E^o \frac{-2.303\ RT}{nF} \log_{10} \frac{[M]}{[M^{n+}]}.$$

At 25°C or 298 K

$$E = E^o + \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log_{10} \frac{[M^{n+}]}{[M]}$$

$$E = E^o + \frac{0.059}{n} \log_{10} \frac{[M^{n+}]}{[M]}$$

or

$$E = E^o - \frac{0.059}{n} \log_{10} \frac{[M]}{[M^{n+}]}.$$

Here R = Gas constant

T = Absolute temperature

E^o = emf of the cell

E = Electrode potential of cell

F = Faraday number

n = number of electrons transferred

- If electrode is solid its active mass is taken as one.
- For an electrochemical cell having net reaction

$$xA + yB \xrightarrow{ne^-} mC + nD,$$

The emf can be calculated as

$$Ecell = E^o cell + \frac{0.059}{n} \log \frac{[A]^x\ [B]^y}{[C]^m\ [D]^n}$$

In using the above equation, the following facts should be kept in mind.

- Concentration or activity of gases is expressed in terms of their partial pressures.
- n, the number of electrons transferred should be calculated from the balanced net cell reaction
- Concentration or activity of solids in taken to be unity.

Equilibrium Constant and Cell Potential

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

At equilibrium

$$E_{cell} = 0,\ Q = K$$

$$0 = E^o_{cell} - \frac{0.0591}{n} \log_{10} K$$

$$\log_{10} K = \frac{E^o_{cell} \cdot n}{0.0591}.$$

- **Relationship between free energy change (ΔG) and cell potential (E)**: Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic call then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf (it is the potential of the cell when no current is drawn) of the cell is E and nF is the amount of charge passed and ΔG is the Gibbs energy of the reaction then

$$\Delta G = -nF\ Ecell$$

for standard state conditions,

$$\Delta G^o = -nF\ E^o cell$$

Thermodynamics Relationship of Cell

(i) **Gibbs-Helmholtz equation:**

$$\Delta G = \Delta H + T \left(\frac{\partial}{\partial T} \Delta G\right)_P$$

Here ΔH = Change in enthalpy

T = Temperature

(ii) Temperature Coefficient:

$$\Delta G = \Delta H + T \left(\frac{\partial}{\partial T} \Delta G\right)_P$$

$$-n\ FE_{cell} = \Delta H + T \left[\frac{\partial}{\partial T} (-nF\ E_{cell})\right]_P$$

$$\Delta H = -nF\ E_{cell} + nFT \left(\frac{\partial}{\partial T} E_{cell}\right)_P$$

$$\left(\frac{\partial}{\partial T} E_{cell}\right)_P = \text{Temperature coefficient}$$

(iii) Change in Entropy:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G - \Delta H = -T\Delta S \qquad \ldots\ldots. (i)$$

$$\Delta G = \Delta H + T \left(\frac{\partial}{\partial T} \Delta G\right)_P$$

$$\Delta G - \Delta H = T \left(\frac{\partial}{\partial T} \Delta G\right)_P \qquad \ldots\ldots (ii)$$

From equation (i) and (ii), we get

$$-T\Delta S = T\left(\frac{\partial}{\partial T}\Delta G\right)_P$$

$$\Delta S = -\left(\frac{\partial}{\partial T}\Delta G\right)_P$$

$$\Delta S = +nF\left(\frac{\partial}{\partial T}E_{cell}\right)_P.$$

Concentration Cells

Concentration cell is one in which emf arises as a result of different concentrations of the same electrolyte in the component half-cells.

- The two solutions are connected by a salt bridge and the electrodes are joined by a piece of metallic wire.
- The reduction occurs in the more concentrated compartment while oxidation occurs in the diluted compartment.

$$E = E^o - \frac{2.303\ RT}{nF}\log\frac{[C_2]}{[C_1]}$$

or

$$E = E^o + \frac{2.303\ RT}{nF}\log\frac{[C_1]}{[C_2]}$$

Concentration cells are of following two types:

(i) Electrode concentration cell

(ii) Electrolyte concentration cell

(i) Electrode Concentration Cell: When emf is produced between two similar electrodes at different concentrations dipped in the same solution of electrolyte.

$Pt, H_2\ (p_1) \mid H^+ \mid H_2\ (p_2), Pt$

Anode Cathode

At anode: $\frac{1}{2}\ H_2\ (p_1) \rightarrow H^+ + 1e^-$

At cathode: $H^+ + 1e^- \rightarrow \frac{1}{2}\ H_2\ (p_2)$

Cell reaction: $\frac{1}{2}\ H_2\ (p_1) \rightarrow \frac{1}{2}\ H_2\ (p_2)$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{1}\log_{10}(p_2/p_1)^{1/2}$$

$$E_{cell} = \frac{0.0591}{2}\cdot\log_{10}\frac{p_1}{p_2}.$$

(ii) Electrolyte Concentration Cell: When identical electrodes are dipped into the solutions of same electrolyte of different concentration, emf produced due to the difference in concentration is called liquid-junction potential. This type of cell is called electrolyte concentration cell.

$Cu \mid Cu^{2+}\ (C_1) \parallel Cu^{2+}\ (C_2) \mid Cu$

(–) Salt (+)

Anode bridge Cathode

At anode: $Cu \rightarrow Cu^{2+}\ (C_1) + 2e^-$

At Cathode: $Cu^{2+}\ (C_2) + 2e^- \rightarrow Cu$

Cell Reaction: $Cu^{2+}\ (C_2) \rightarrow Cu^{2+}\ (C_1)$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2}\cdot\log_{10}\frac{C_2}{C_1}.$$

$$E_{cell} = \frac{0.0591}{2}\log_{10}\frac{C_2}{C_1}.$$

Illustrations

13. If $E^oFe^{2+}/Fe = -0.441$ V and $E^o Fe^{3+}/Fe^{2+} = 0.771$ V, the standard EMF of the reaction will be

$Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$

Solution $E^oFe^{2+}/Fe = -0.441$ V

$E^o Fe^{3+}/Fe^{2+} = 0.771$ V

If $E^ocell = E^oOPFe/Fe^{2+} + E^oRPFe^{3+}/Fe^{2+}$

$= +0.441 + 0.771 = 1.212$ V

Illustrations

14. For a Ag-Zn button cell, net reaction is

$Zn(s) + Ag_2O\ (s) \rightarrow ZnO\ (s) + 2Ag\ (s)$

$\Delta G^o_f\ (Ag_2O) = -11.21$ kJ mol^{-1}

$\Delta G^o_f\ (ZnO) = -318.3$ kJ mol^{-1}

Find the E^ocell of the button cell here.

Solution $\Delta G^o = \Delta G_f\ (ZnO) - \Delta G_f\ (Ag_2O)$

$= -318.30 + 11.21 = -307.09$ kJ

$= -307.09 \times 10^3$ J

$\Delta G^o = -nFE^ocell$

$-307.09 \times 10^3 = -2 \times 96500 \times E^ocell$

$E^ocell = 1.591$ V

Illustrations

15. The observed emf of the cell

Pt | H_2 (1 atm) | H^+ (3×10^{-4} M) || H^+ (M_1) | H_2 (1 atm) | Pt

is 0.154 V. Calculate the value of M_1 and pH of cathodic solution.

Solution $E_{cell} = 0.0591 \log_{10} \frac{M_1}{3 \times 10^{-4}}$.

$$\log_{10} \frac{M}{3 \times 10^{-4}} = \frac{0.154}{0.0591} = 2.6058$$

$$\frac{M_1}{3 \times 10^{-4}} = 4.034 \times 10^2$$

$$M_1 = 4.034 \times 10^2 \times 3 \times 10^{-4} \text{ M}$$

$$= 0.121 \text{ M}$$

$$pH = -\log_{10} [H^+] = -\log_{10} 0.121 = 0.917$$

16. Calculate the cell potential for the cell containing 0.10 M Ag^+ and 4.0 M Cu^{2+} at 298 K.

Given $E^oAg^+/Ag = 0.80$ V

$E^oCu^{2+}/Cu = 0.34$ V

Solution Cu (s) | Cu^{2+} (4.0 M) || Ag^+ (0.1 M) | Ag (s)

Here n = 2;

$$E = E^o_{cell} + \frac{0.0591}{2} \log \frac{[Ag^+]^2}{[Cu^{2+}]}$$

$$= 0.80 - 0.34 + \frac{0.0591}{2} \log_{10} \frac{[0.1]^2}{[4.0]}$$

$$= 0.46 + 0.0295 \times \log_{10} 2.5 \times 10^{-3}$$

$$= 0.46 - 0.07676 = 0.3832 \text{ V}$$

17. Calculate the e.m.f of the following cell at 298 K.

Zn | Zn^{2+} (0.1 M) || Ag^+ (0.01 M) | Ag

Given: $E^oZn^{2+}/Zn = -0.76$ C

$E^oAg^+/Ag = +0.80$ V

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

$$= 0.80 - (-0.76) + \frac{0.0591}{2} \log_{10} \frac{[0.01]^2}{[0.1]}$$

$$= 1.56 + \frac{0.0591}{2} \log_{10} 1 \times 10^{-3}$$

$$= 1.56 - 0.08865 = 1.471 \text{ V}$$

18. Find the EMF of the following cells:

Fe | Fe^{2+} || Sn^{2+} | Sn $E^o_{Fe} = -0.44$ V

a = 0.6 a = 0.2 $E^o_{Sn} = +0.14$ V

Solution Fe | Fe^{2+} || Sn^{2+} | Sn

$$E^o_{cell} = E^o_R - E^o_L$$

$$= 0.14 - (-0.44) = 0.58 \text{ V}$$

Cell reaction

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

According to Nernst's equation,

$$E = E^o - \frac{0.059}{N} \log_{10} \frac{[Fe^{2+}]}{[Sn^{2+}]}$$

$$= 0.58 - \frac{0.059}{2} \log_{10} \frac{0.6}{0.2}$$

$$= 0.58 - 0.0295 \log_{10} 3$$

$$= 0.58 - 0.0295 \times 0.4771$$

$$= 0.58 - 0.014$$

$$= 0.566 \text{ V}$$

19. Find the pH of the following half-cell

Pt H_2/H_2SO_4.

The oxidation electrode potential = 0.3 V.

Solution $H_2 \rightarrow 2H^+ + 2e^-$

$$E = E^o - \frac{0.059}{N} \log_{10} \frac{[H^+]^2}{[H_2]}$$

$$0.3 = 0 - \frac{0.059}{2} \log_{10} [H^+]^2$$

$$-\log [H^+] = \frac{0.3}{0.059} = 5.08$$

$$pH = 5.08$$

20. Calculate the cell potential of the given cell at 25°C. (R = 8.31 J K^{-1} mol^{-1}, F = 96500 C mol^{-1}).

$Ni\ (s) \mid Ni^{2+}\ (0.01\ M) \parallel Cu^{2+}\ (0.1\ M) \mid Cu(s)$

Given: $E^oCu^{2+}/Cu = +0.34$ V

$E^oNi^{2+}/Ni = -0.25$ V

Solution $E_{cell} = E^o_{cell} + \frac{2.303\ RT}{nF} \log_{10} \frac{[Cu^{2+}]}{[Ni^{2+}]}$

$= 0.34 - (-0.25) + \frac{2.303 \times 8.31 \times 298}{2 \times 96500} \log \frac{0.1}{0.01}$

$= 0.59 + \frac{0.0591}{2} \log_{10} 10 = 0.6195$ V

21. The emf of a cell corresponding to the reaction,

$Zn + 2H^+\ (aq) \rightarrow$

$Zn^{2+}\ (0.1\ M) + H_2\ (g)\ 1\ atm$

is 0.28 volt at 25°C. Write the half cell reactions and calculate the pH of the solution at the hydrogen electrode.

$E^oZn^{2+}/Zn = -0.76$ volt

$E^oH^+/H_2 = 0$

Solution $E^o_{cell} = 0.76$ volt

According to Nernst equation,

$E_{cell} = E^o_{cell} - \frac{0.0591}{2} \log_{10} \frac{[Zn^{2+}][H_2]}{[H^+]^2}$

$0.28 = 0.76 - \frac{0.0591}{2} \log_{10} \frac{(0.1) \times 1}{[H^+]^2}$

$\log_{10} \frac{0.1}{[H^+]^2} = \frac{2 \times 0.48}{0.0591}$

$\log_{10} 0.1 - \log_{10} [H^+]^2 = 16.2436$

$[As\ -\log_{10} [H^+] = pH]$

$2\ pH = 16.2436 - \log_{10} 0.1$

$pH = \frac{17.2436}{2} = 8.6218$

22. 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 25°C. Calculate the concentration of hydrogen ions at the positive electrode.

Solution Suppose $[H^+]$ at the cathode = X mol litre^{-1}

$E_2 = E^o + 0.059 \log_{10} X$ ……. (i)

$E_1 = E^o + 0.059 \log_{10} 10^{-6}$ …… (ii)

Subtracting equation (ii) from (i),

$E_2 - E_1 = 0.059 (\log_{10} X - \log_{10} 10^{-6})$

$0.118 = 0.059 (\log_{10} X + 6)$

$X = 10^{-4}$

$[H^+] = 10^{-4}$ mole litre^{-1}

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

$Pt \mid M \mid M^{3+}(0.0018\ mol^{-1}L) \parallel Ag^+(0.01\ mol^{-1}\ L) \mid Ag$

The emf of this cell is found to be 0.42 volt. Calculate the standard potential of the half reaction.

$M^{3+} + 3e^- \rightarrow M$, $EAg^+/Ag = 0.80$ volt.

Solution The cell reaction is

$M + 3Ag^+ \rightarrow 3Ag + M^{3+}$

According to Nernst equation

$E_{cell} = E^o_{cell} - \frac{0.0591}{3} \log_{10} \frac{[M^{3+}]}{[Ag^+]^3}$.

$0.42 = E^o_{cell} - \frac{0.0591}{3} \log_{10} \frac{(0.0018)}{(0.01)^3}$

$= E^o_{cell} - 0.064$

$E^o_{cell} = (0.42 + 0.064) = 0.484$ volt

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

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

$= (0.80 - 0.484) = 0.32$ volt.

ELECTROCHEMICAL SERIES

Reaction (oxidized form)	Reduced form	ε^o/V
$Li^+ + e^-$	Li (s)	–3.05
$K^+ + e^-$	K (s)	–2.93
$Ca^{2+} + 2e^-$	Ca (s)	–2.87
$Na^+ + e^-$	Na (s)	–2.71
$Mg^{2+} + 2e^-$	Mg (s)	–2.36
$Al^{3+} + 3e^-$	Al (s)	–1.66
$Zn^{2+} + 2e^-$	Zn (s)	–0.76
$Cr^{3+} + 3e^-$	Cr (s)	–0.74
$Fe^{2+} + 2e^-$	Fe (s)	–0.44
$Ni^{2+} + 2e^-$	Ni (s)	–0.25
$Sn^{2+} + 2e^-$	Sn (s)	–0.14
$Pb^{2+} + 2e^-$	Pb (s)	–0.13
$2H^+ + 2e^-$	H_2 (g)	0.00
AgBr (s) + e^-	Ag (s) + Br^-	0.10
AgCl (s) + e^-	Ag (s) + Cl^-	0.22
$Cu^{2+} + 2e^-$	Cu (s)	0.34
$Cu^+ + e^-$	Cu (s)	0.52
$I_2 + 2e^-$	$2I^-$	0.54
O_2 (g) + $2H^+ + 2e^-$	H_2O_2	0.68
$Fe^{3+} + e^-$	Fe^{2+}	0.77
$Ag^+ + e^-$	Ag (s)	0.80
$2Hg^{2+} + 2e^-$	Hg_2^{2+}	0.92
$NO_3^- + 4H^+ + 3e^-$	NO (g) + $2H_2O$	0.97
$Br_2 + 2e^-$	$2Br^-$	1.09
MnO_2 (s) + $4H^+ + 2e^-$	$Mn^{2+} + 2H_2O$	1.23
O_2 (g) + $4H^+ + 4e^-$	$2H_2O$	1.23
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$2Cr^{3+} + 7H_2O$	1.33
Cl_2 (g) + $2e^-$	$2Cl^-$	1.36
$Au^{3+} + 3e^-$	Au (s)	1.40
$MnO_4^- + 8H^+ + 5e^-$	$Mn^{2-} + 4H_2O$	1.51
$H_2O_2 + 2H^+ + 2e^-$	$2H_2O$	1.78
$Co^{3+} + e^-$	Co^{2+}	1.81
F_2 (g) + $2e^-$	$2F^-$	2.87
Decreasing strength of oxidising agent	Decreasing strength of reducing agent	

It is the arrangement of various electrodes or elements in the increasing order of their standard reduction potential or decreasing order of their standard oxidation potential. It is called electromotive or activity series of the elements

Features of Electrochemical Series

- Metals with positive E^o_{op} or negative E^o_{rp} are strongly electro positive and have more reactivity. It means a lower placed element or metal is replaced by upper placed or higher element while higher element can be coated by lower metal.

  Example, (i) $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

  Here Cu is replaced by Zn due to more oxidation potential or reactivity of Zn, while Zn is coated by Cu.

  Zn – Cu couple is also coated by Cu. Here, solution turns from blue to colourless and rod becomes Reddish brown from Gray white.

  (ii) $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$

  Here solution becomes colourless to blue and rod becomes reddish brown to white.

- Metals above H_2 can easily replace H_2 from acid, bases etc. due to there more positive E^o_{op} or reactivity

  For example,

  $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$

$E^{o}_{O.P.}$ of Mg > $E^{o}_{O.P.}$ of H_2

$R - OH + Na \rightarrow R - ONa + H^+$

- Lower placed metals (Cu Hg Ag Pt Au) to H_2 can not do that as $E^{o}_{O.P.}$ of H_2 is more than their E^{o}_{op}

$Cu + H_2SO_4 \rightarrow$ no reaction

- Oxides of lower metals (Cu, Hg, Ag, Pt, Au) are easily reduced by H_2 or Carbon as they are unstable thermally due to positive E^{o}_{rp} they also decomposed on heating.
- More $E^{o}_{O.P.}$ means ease of tendency to oxidize that is, reducing agents while more $E^{o}_{R.P.}$ means ease to be reduce that is, oxidizing agents. It means metal above hydrogen having positive $E^{o}_{O.P.}$ are reducing agents.

Reducing property α $E^{o}_{O.P.}$

For example, Li is the strongest reducing agent due to maximum $E^{o}_{O.P.}$

For example, If for A is $E^{o}_{O.P.}$ is –0.44 V and for B, E is –0.28 V than A is better reducing agent than B.

- Metals (Cu Hg Ag Pt Au) having high $E^{o}_{R.P.}$ are oxidizing agents. and they have tendency to be reduced

For example, Oxidizing power α $E_{R.P.}$

$F_2 > Cl_2 > Br_2 > I_2$

⟶

Oxidizing power decreases

$HI > HBr > HCl > HF$

⟶

Reducing power decreases

As $E^{o}_{O.P.}$ of $I^- > Br^- > Cl^- > F^-$

- Elements with more positive $E^{o}_{R.P.}$ will be discharged first at cathode i.e., discharging order increases from Li to F (for M^+).

Increasing order of deposition of some cation

Li^+ , K^+, Ca^{+2}, Na^+, Mg^{+2}, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}

- In case of negative ions, anion with stronger reducing nature is discharged first at anode

$$\text{Discharging order } \alpha \frac{1}{\text{Value of } E^{o}_{R.P.}}$$

Increasing order of discharge of some anion

$SO_4^{-2} < NO_3^- < OH^- < Cl^- < Br^- < Cl^-$

- Hydroxides of upper metals are strongly basic and their salts do not undergo hydrolysis while hydroxides of lower metals are weakly acidic and their salts undergo hydrolysis.

Enhance Your Knowledge

Primary Cells

- In such cells redox reaction occurs only once so cells can not be recharged again.
- The Cell become dead after some time as electrode reactions cannot be reversed.

Example, Dry cell, mercury cell

Dry Cell

- It is compact form of Lechlanche cell.
- It has anode of Zn-container and cathode of graphite rod surrounded by MnO_2 + Carbon.
- Here a paste of NH_4Cl and $ZnCl_2$ is filled in between the electrodes.

Cell Reactions

At anode

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

At cathode

$2MnO_2\ (s) + 2NH_4^+\ (aq) + 2e^- \rightarrow$

$Mn_2O_3\ (s) + 2NH_3\ (g) + H_2O$

- Zn^{+2} combines with NH_3 to form diammine Zn(II) cation.
- Dry cell has short life as NH_4Cl (acidic) corrodes the Zn-container even if the cell is not in use.
- The cell potential is 1.25 to 1.5 volt

Mercury Cell

- In commonly used mercury cell the reducing agent is zinc and the oxidizing agent is mercury (II) oxide.
- **Cell Reactions**

At anode:

$Zn\ (Hg) + 2OH^- \rightarrow ZnO\ (s) + H_2O + 2e^-$

At cathode:

$HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

The overall reaction is

$Zn(Hg) + HgO\ (s) \rightarrow ZnO\ (s) + Hg(l)$

■ The cell potential is approximately 1.35 V and remains constant throughout its life as overall reaction does not involve any ion, whose concentration can change during its life time. It is used in hearing aids, watches etc.

Secondary Cell

■ It can be recharged by passing current to use again as electrode reactions are reversible. Example, lead storage battery, Ni-Cd storage cell.

Batteries

Electrochemical cell used as battery. The voltage provided by the battery is sum of individual voltage of cells.

Types of Batteries: Batteries are of following types:

(i) Lead Storage Batteries: Six cells are connected in series each cell provided 2V so total volt provided by the battery is 12 V. The anode, a series of lead grids packed with spongy lead and cathode, a series of grids packed with lead dioxide 38% by weight H_2SO_4 act as electrolyte.

Cell reaction (When discharging takes place)

At anode:

$$Pb\ (s) + HSO_4^-\ (aq) \rightarrow PbSO_4\ (s) + 2H^+ + 2e^-$$

$$E^o = 0.296\ V$$

At cathode:

$$PbO_2\ (g) + 3H^+\ (aq) + HSO_4^-\ (aq) + 2e^- \rightarrow$$

$$2PbSO_4\ (s) + 2H_2O\ (l),\ E^o = 1.628\ V$$

Net reaction

$$Pb\ (s) + PbO_2\ (s) + 2H^+ + 2HSO_4^-\ (aq) \rightarrow$$

$$2PbSO_4\ (s) + 2H_2O\ (s),\ E^o = 1.924\ V$$

Nickel-Cadmium Cell:

■ A rechargeable nickel-cadmium cell is a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

Fuel Cell

■ The best example of fuel cell is Hydrogen–oxygen fuel cell

$$2H_2 + O_2 \rightarrow 2H_2O$$

■ Astronauts (Apollo moon flight) used H_2, O_2 fuel cell

■ It is pollution free, continuous source of energy and highly efficient.

Cell Reactions

At anode

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

At cathode

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

Net reaction is

$$2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (l)$$

■ ***Requirement:*** It should have compactness, lightness, ruggedness and not much volume drop during use.

■ The thermodynamic efficiency of fuel cells is the ratio of the electrical fee energy to the ΔH of the reaction.

$$\eta = \frac{\Delta G}{\Delta H}$$

■ **Rusting or Corrosion of Metals**

It is the destruction of metal on reaction with environment. It is reverse extraction of metals and it is a redox process.

Example, Rust of iron is $Fe_2O_3 . xH_2O$

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$$

$Fe(OH)_2$ dehydrates and oxidizes into FeO $Fe(OH)_3$, then finally into rust by dehydration.

■ An electrochemical cell known as corrosion cell is developed at the surface of iron.

Anode-Pure iron

Cathode-impure surface

Electrolyte

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

Anode reaction

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

Cathode reaction

$$2H^+ + 2e^- \rightarrow 2H$$

$$2H + \tfrac{1}{2}\ O_2 \rightarrow H_2O$$

Net reaction

$Fe + 2H^+ + ½\ O_2 \rightarrow Fe^{2+} + H_2O$

At surface

$2Fe^{2+} + ½\ O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+$

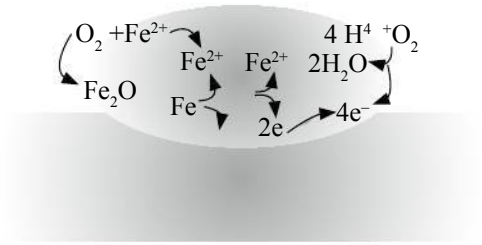
$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3\ .xH_2O$

Net reaction at surface

$2Fe^{2+} + ½\ O_2 + (x + 2)H_2O \rightarrow$

$Fe_2O_3.xH_2O + 4H^+$

Rust



Oxidation: $Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^-$
Reducation: $O^2\ (g) + 4H^+(aq) + 4e^- \rightarrow 2H_2\ O(1)$
Atomospheric Oxidation: $2Fe^{2+}\ (aq) + 2H_2\ O\ (1) + 1/2\ O \rightarrow Fe_2\ O_3(s) + 4H^+(aq)$

Factors Promoting Corrosion

Reactivity of metal, presence of impurities, presence of air and moisture, strains in metal and presence of electrolyte etc.

Prevention of Corrosion

Sacrifical protection: By covering the surface of iron with a layer of metal which is more active than iron thus prevents the iron from losing electrons (Plating metal with a thin layer of less easily oxidizable metal like Mg, Zn, Sn)

Galvanization

- By covering iron with more active metal like zinc. The layer of Zn on the iron surface when comes in contact with moisture, oxygen and CO_2 in air, a protective invisible thin layer of basic zinc carbonate $ZnCO_3$. $Zn(OH)_2$ is formed due to which the galvanized iron sheets lose their lusture and tends to protect it from further corrosion.
- Iron can be coated with Cu or by Sn. Now if the coating is broken, iron is exposed and being more reactive than iron, Cu and Sn corrode more rapidly.

Electrical Protection

Cathodic Protection More electropositive metals like Zn, Mg or Al may be connected with the iron pipes buried in the moist soil, canals, storage tanks etc.

Using Anti-rust Solutions These are alkaline phosphate and alkaline chromate solutions. The alkaline nature of solutions prevents availability of H^+ ions. On the surface of iron, a protective, insoluble thin film of iron phosphate is formed. These are used in car radiators etc., to prevent rusting.

Solved Problems from the IITs

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

[IIT 1990]

Solution The reduction reaction is as follows:

$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$

123 g 6 g

1 mole 3 mole

Hydrogen required for reduction of 12.3/123 or 0.1 mole of nitrobenzene

$= 0.1 \times 3 = 0.3$ mole

Amount of charge required for liberation of 0.3 mole of hydrogen

$= 2 \times 96500 \times 0.3 = 57900$ coulomb

Actual amount of charge required as efficiency is 50%

$= 2 \times 57900 = 115800$ coulomb

Energy consumed = 115800 × 3.0 = 347400 J

= 347.4 kJ

2. The standard reduction potential of Cu^{2+}/Cu and Ag^{+}/Ag electrodes are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of Ag^{+} will the emf of the cell at 25°C be zero if concentration of Cu^{2+} is 0.01 M?

[IIT 1990]

Solution Given $E^{o}Cu^{2+}/Cu = 0.337$ V

$E^{o}Ag^{+}/Ag = 0.799$ V.

The standard emf will be positive if Cu/Cu^{2+} is anode and Ag^{+}/Ag is cathode. The cell may be represented as follows:

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

The cell reaction is as follows:

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

E^{o}_{cell} = Oxidation Potential of anode + Reduction Potential of cathode

= –0.337 + 0.799

= 0.462 Volt

According to Nernst equation,

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{2} \log_{10} \frac{[Cu^{2+}]}{[Ag^{+}]^2}.$$

When $E_{cell} = 0$

$$E^{o}_{cell} = \frac{0.0591}{2} \log_{10} \frac{[Cu^{2+}]}{[Ag^{+}]^2}.$$

$$\log_{10} \frac{[Cu^{2+}]}{[Ag^{+}]^2} = \frac{0.462 \times 2}{0.0591} = 15.6345$$

$$\frac{[Cu^{2+}]}{[Ag^{+}]^2} = 4.3102 \times 10^{15}$$

$$[Ag^{+}]^2 = \frac{0.01}{4.3102 \times 10^{15}}.$$

$= 0.2320 \times 10^{-17}$

$= 2.320 \times 10^{-18}$

$[Ag^{+}] = 1.523 \times 10^{-9}$ M

3. A current of 1.70 ampere is passed through 300 ml of 0.160 M solution of zinc sulphate for 230 seconds with a current efficiency of 90%. Calculate the molarity of Zn^{2+} ions after the deposition of zinc. Assume the volume of the solution to remain constant during electrolysis.

[IIT 1991]

Solution Amount of charge passed = 1.70 × 230 coulomb

Amount of actual charge passed

$$= \frac{90}{100} \times 1.70 \times 230$$

= 351.9 coulomb

Number of moles of Zn deposited by passing 351.9 coulomb of charge

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

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

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

= 0.154 M.

4. Zinc granules are added in excess to 500 ml of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potentials of Zn^{2+}/Zn and Ni^{2+}/Ni are –0.75 and –0.24 volt respectively, find out the concentration of Ni^{2+} ions in solution at equilibrium.

[IIT 1991]

Solution The reaction is

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

The cell involving this reaction would be

$Zn\ (s) \mid Zn^{2+}\ (aq) \parallel Ni^{2+}\ (aq) \mid Ni\ (s)$

$E^{o}_{cell} = -0.24 + 0.75 = 0.51$ volt

$$\log_{10} K_{eq} = \frac{nFE^{o}}{2.303\ RT} = \frac{nE^{o}}{0.0591}.$$

$$= \frac{2 \times 0.51}{0.0591} = 17.25$$

So $K_{eq} = 1.78 \times 10^{17}$

Suppose 'X' is the concentration of Ni^{2+} that have been reduced to nickel at equilibrium.

$$Zn\ (s) + Ni^{2+}\ (eq) \rightleftharpoons Zn^{2+}\ (aq) + Ni\ (s)$$
$$(1.0 - X) \qquad X$$

$$K_{eq} = \frac{[Zn^{2+}]}{[Ni^{2+}]} = \frac{X}{(1 - X)} = 1.78 \times 10^{17}$$

X = 1.0 M.

So $(1 - X) = [Ni^{2+}] = \frac{1.0}{1.78 \times 10^{17}}$.

$= 5.6 \times 10^{-18}$ M

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

$2Cl^- (aq) + 2H_2O \rightarrow$

$2OH^- (aq) + H_2 (g) + Cl_2 (g)$

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

[IIT 1992]

Solution Reactions at anode and cathode are as follows:

$2Cl^- \rightarrow Cl_2 + 2e^-$ (at anode)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (at cathode)

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

Charge to produce one mole of Cl_2

$= 2 \times 96500$ coulomb

Charge to produce 14.08 mole of Cl_2

$= 2 \times 96500 \times 14.08$ coulomb

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

Time $= \frac{\text{Charge}}{\text{Current}}$.

$= \frac{2 \times 96500 \times 14.08}{15.5}$

$= 175318.7$ second $= 48.699$ hour

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

$= 2 \times 14.08 = 28.16$ mole

Molarity $= \frac{\text{Mole}}{\text{Volume}}$.

$= \frac{28.16}{20} = 1.408$ M

6. 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 the spontaneous process after taking into account in the cell reaction at 25°C.

Given, $Ksp_{AgCl} = 2.8 \times 10^{-10}$,

$Ksp_{AgBr} = 3.3 \times 10^{-13}$

[IIT 1992]

Solution E_{cell} = E (Oxidation potential of L.H.S electrode) + E (Reduction potential of R.H.S electrode)

$= E^o$ (Oxidation potential of Ag/Ag^+) $- 0.0591 \log [Ag^+]_{L.H.S} + E^o$ (Reduction potential of Ag^+/Ag) $+ 0.0591 \log [Ag^+]_{R.H.S}$

$= 0.0591 \log_{10} \frac{[Ag^+]_{R.H.S}}{[Ag^+]_{L.H.S}}$

(As $E^oAg/Ag^+ + E^oAg^+/Ag = 0$)

$= 0.0591 \log_{10} \frac{Ksp_{AgBr}/[Br^-]}{Ksp_{AgCl}\,[Cl^-]}$

$= 0.0591 \log_{10} \frac{3.3 \times 10^{-13}}{0.001} \times \frac{0.2}{2.8 \times 10^{-10}}$.

$= -0.0371$ volt

As the cell potential is negative, so the cell reaction is non-spontaneous. For spontaneous reaction, emf should be positive.

Hence the correct cell reaction is as follows:

Ag | AgBr, KBr || KCl, AgCl | Ag
Anode Cathode

7. The standard reduction potential for the half cell having reaction,

$NO_3^- (aq) + 2H^+ (aq) + e^- \rightarrow$

$NO_2 (g) + H_2O$

is 0.78 volt.

(i) Calculate the reduction potential in 8 MH^+.

(ii) What will be the reduction potential of the half cell in a neutral solution?

Assume all other species to be at unit concentration.

[IIT 1993]

Solution $E_{red} = E^{o}_{red} + \frac{0.0591}{n} \log_{10} [H^+]^2$

$= 0.78 + \frac{0.0591}{2} \log_{10} (8)^2$

$= 0.78 + 0.0591 \times 3 \times 0.3010$

$= 0.833$ volt

(ii) $E_{red} = 0.78 + \frac{0.0591}{2} \log_{10} (10^{-7})^2$

(For neutral solution $[H^+] = 10^{-7}$ M)

$= 0.78 - 0.0591 \times 7$

$= 0.367$ volt.

8. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following reaction: $CrO_3 + 6H^+ + 6e^- \rightarrow Cr + 3H_2O$

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

[IIT 1993]

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

6×96500 C : 1 mole : 52 g

Mass of chromium plated out by 24000 coulomb charge

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

Charge required for plating out 1.5 g of chromium

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

Time $= \frac{\text{Charge}}{\text{Current}}$.

$= \frac{16701.92}{12.5} =$ 1336.15 second

$= 22.27$ minute

9. The standard reduction potential of Ag^+/Ag electrode at 298 K is 0.799 volt. Given for AgI, Ksp $= 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also find the standard reduction potential of the I^- / AgI / Ag electrode.

[IIT 1994]

Solution In the saturated solution of AgI, the half cell reactions are

$AgI + e^- \rightarrow Ag + I^-$ (Cathode-reduction)

$Ag \rightarrow Ag^+ + e^-$ (Anode-oxidation)

The cell reaction is

$AgI \rightarrow Ag^+ + I^-$

$EAg^+/Ag = E^o Ag^+/Ag + 0.0591 \log_{10} [Ag^+]$

$[Ag^+] [I^-] = Ksp (AgI) = [Ag^+]^2 = [I^-]^2$

So $[Ag^+]^2 = 8.7 \times 10^{-17}$

$[Ag^+] = \sqrt{(8.7 \times 10^{-17})} = 9.3 \times 10^{-9}$

On putting the value of E^oAg^+/Ag and $[Ag^+]$, we get

$E\ Ag^+/Ag = 0.799 - 0.0591 \log_{10} (9.3 \times 10^{-9})$

$= 0.324$ volt

$E^o_{cell} = 0.0591 \log_{10} Ksp\ (AgI)$

$= 0.0591 \log_{10} (8.7 \times 10^{-17})$

$= -0.95$ volt

E^o_{cell} = Oxidation potential of anode + Reduction potential of cathode

Reduction potential of cathode $E^o I^- / Ag^+ / Ag$

$= -0.95 - (-0.799)$

$= -0.95 + 0.799$

$= -0.151$ volt

10. The Edison storage cell is represented as

$Fe(s) \mid FeO(s) \mid KOH(aq) \mid Ni_2O_3(s) \mid Ni(s)$

The half cell reactions are:

$Ni_2O_3(s) + H_2O(l) + 2e^- \rightarrow 2NiO(s) + 2OH^-$

$E^o = +0.40$ volt

$FeO(s) + H_2O(l) + 2e^- \rightarrow Fe(s) + 2OH^-$

$E^o = -0.87$ volt

(a) What is the cell reaction?

(b) What is the emf of the cell? How does it depend on the concentration of KOH?

(c) What is the maximum amount of energy that can be obtained from one mole of Ni_2O_3?

[IIT 1994]

Solution Actual half reactions are:

$Fe + 2OH^- \rightarrow FeO + H_2O + 2e^-$ (Anode-Oxidation)

$Ni_2O_3 + H_2O + 2e^- \rightarrow 2NiO + 2OH^-$ (Cathode-Reduction)

So the cell reaction is:

(a) $Fe + Ni_2O_3 \rightarrow FeO + 2NiO$

(b) $E_{cell} = E^o_{cell} - \frac{0.0591}{2} \log_{10} \frac{[NiO]^2\,[FeO]}{[Fe]\,[Ni_2O_3]} = E^o_{cell}$

Since $\frac{[NiO]^2\,[FeO]}{[Fe]\,[Ni_2O_3]} = 1$ as all are solids

$= 0.87 + 0.40 = 1.27$ volt

The emf of the cell is independent of KOH concentration.

(c) Maximum amount of electrical energy

$= n\,f\,E^o$

$= 2 \times 96500 \times 1.27$

$= 245.11$ kJ

11. An excess of liquid mercury is added to an acidified solution of 1.0×10^{-3} M Fe^{3+}. It is found that 5% of Fe^{3+} remains at equilibrium at 25°C. Calculate $E^o\ Hg_2^{2+}/Hg$ assuming that the only reaction that occurs is

$2Hg + 2Fe^{3+} \rightarrow Hg_2^{2+} + 2Fe^{2+}$

(Given $EFe^{3+}/Fe^{2+} = 0.77$ volt)

[IIT 1995]

Solution $2Hg + 2Fe^{3+} \rightarrow Hg_2^{2+} + 2Fe^{2+}$

At eq. Excess $\frac{10^{-3} \times 5}{100}\ \ \frac{10^{-3} \times 95}{2 \times 100}\ \ \frac{10^{-3} \times 95}{100}$

At eq. $E_{cell} = 0$

$0 = E^o_{cell} - \frac{0.0591}{2} \log_{10} \frac{[Hg_2^{2+}]\,[Fe^{2+}]^2}{[Fe^{3+}]^2}$

$= (E^o\ Hg/Hg_2^{2+} + E^o\ Fe^{3+}/Fe^{2+})$

$- \frac{0.0591}{2} \log_{10} \frac{\frac{(10^{-3} \times 95)}{2 \times 100}\,(10^{-3} \times 95\ 100)^2}{(10^{-3} \times 5\ 100)^2}$

$E^o\ Hg/Hg_2^{2+} = -0.77 + \frac{0.0591}{2} \log_{10} \frac{(95)^3 \times 10^{-5}}{25 \times 2}$

$= -(0.77 + 0.0226)$

$= -0.7926$ volt

$E^o Hg_2^{2+}/Hg = +0.7926$ volt

12. The standard reduction potential for Cu^{2+}/Cu is +0.34 V. Find the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1.0×10^{-19}.

[IIT 1996]

Solution $Cu^{2+} + 2e^- \rightarrow Cu \quad E^o = +0.34$ V …(i)

For $Cu(OH)_2$

$K_{sp} = 1.0 \times 10^{-19}$

$[Cu^{2+}]\,[OH^-]^2 = 1.0 \times 10^{-19}$

As pH of the solution is 14

So $[OH^-] = 1$ M

$[Cu^{2+}] = 10^{-19}$

According to Nernst's equation for (i)

$E = E^o - \frac{0.059}{N} \log_{10} \frac{[Cu]}{[Cu^{2+}]}$

$= 0.34 - \frac{0.059}{2} \log_{10} \frac{1}{10^{-19}}$

$= 0.34 - \frac{0.059}{2} \times 19$

$= -0.22$ V

13. 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/cm³.

[IIT 1997]

Solution Mass of silver deposited (W) = Z × C × t

$W = \frac{E \times C \times t}{F}$

(As Z = E/F)

$$W = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500}$$

$$= 272.178 \text{ g}$$

$$\text{Volume of silver} = \frac{\text{Weight}}{\text{Density}}$$

$$= \frac{272.178}{10.5} = 25.92 \text{ cc}$$

$$\text{Surface area} = \frac{\text{Volume}}{\text{Thickness}}$$

$$= \frac{25.92 \text{ cc}}{0.00254} \text{ cm}$$

$$= 10205.43 = 1.02 \times 10^4 \text{ cm}^2$$

14. 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 27 A for 24 hours gives one Kg of MnO_2. What is the value of current efficiency.

[IIT 1997]

Solution $\text{Wt. of } MnO_2 \text{ (w)} = \frac{E.I.t}{F}$

$$1000 = \frac{87 \times I \times 24 \times 60 \times 60}{2 \times 96500}$$

$$I = 25.67 \text{ ampere}$$

$$\text{Current efficiency} = \frac{25.67 \times 100}{27} = 95\%$$

15. Calculate the equilibrium constant for the reaction:

$Fe^{2+} + Ce^{4+} \leftrightarrow Fe^{3+} + Ce^{3+}$.

Given: $E^oCe^{+4}/Ce^{+3} = 1.44$ V

$E^oFe^{+3}/Fe^{+2} = 0.68$ V

[IIT 1997]

Solution $\log K_C = \frac{n}{0.0591} \times E^o_{cell}$

$$= \frac{1}{0.0591} \times 0.76 = 12.8813$$

K_C = antilog of 12.8813

$K_C = 7.608 \times 10^{12}$

16. Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightarrow 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for Fe^{3+}/Fe^{2+} and I_3^-/I^- couples.

[IIT 1998]

Solution Oxidation half $3I^- \rightarrow I_3^- + 2e^-$

Reduction half $[Fe^{3+} + e^- \rightarrow Fe^{2+}] \times 2$

Cell reaction $Fe^{3+} + 3I^- \rightarrow 2Fe^{2+} + I_3^-$

Here n = 2, $E_{cell} = 0.77 - 0.54 = 0.23$ V

According to Nernst equation,

$$E = E_{cell} - \frac{0.0591}{n} \log_{10} K_C$$

At equilibrium E = 0

$$\text{So } 0 = 0.23 - \frac{0.0591}{2} \log_{10} K_C$$

On solving, we get

$K_C = 6.26 \times 10^7$

17. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell

$Ag \mid Ag^+$ (saturated Ag_2CrO_4 solution) $\parallel Ag^+$ (0.1 M) $\mid$ Ag. is 0.164 V at 298 K.

[IIT 1998]

Solution $E_{cell} = \frac{0.0591}{1} \log_{10} \frac{[Ag^+]_{R.H.S}}{[Ag^+]_{L.H.S}}$

$$0.164 = \frac{0.0591}{1} \log_{10} \frac{0.1}{[Ag^+]_{L.H.S}}$$

$[Ag^+]_{L.H.S} = 1.66 \times 10^{-4}$ M

$$[CrO_4^{2-}] = \frac{1.66 \times 10^{-4}}{2}$$

$Ksp\ (Ag_2CrO_4) = [Ag^+]\ [CrO_4^{2-}]$

$$= (1.66 \times 10^{-4})^2 \times \frac{1.66 \times 10^{-4}}{2}$$

$= 2.287 \times 10^{-12}$ mol^3 L^{-3}

18. The following electrochemical cell has been set up,

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

$E^o\ (Fe^{3+}/Fe^{2+}) = 0.77$ V

$E^o\ (Ce^{4+}/Ce^{3+}) = 1.61$ V

If an ammeter is connected between the two platinum electrodes, predict the direction of

flow of current. Will the current increase or decrease with time?

[IIT 2000]

Solution Current will flow from higher reduction potential electrode to lower reduction potential electrode, that is, from Pt (2) electrode to Pt (1) electrode.

$E^o_{cell} = 1.61 - 0.77 = 0.84$ volt

19. Copper sulphate solution (250 ml) was electrolyzed using a platinum anode and a copper cathode. A constant current of 2 Ampere was passed for 16 minutes. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.

[IIT 2000]

Solution As number of Faraday passed through the aqueous solution of $CuSO_4$

$$= \frac{I \times t}{96500} = \frac{(2 \times 10^{-3}) \times 16 \times 60}{96500}$$

$= 1.98 \times 10^{-5}$

So number of equivalents of $CuSO_4$ involved in electrolysis from 1 litre solution

$= 4 \times 1.98 \times 10^{-5} = 7.92 \times 10^{-5}$

As after electrolysis, the absorbance reduces to 50% so initial number of equivalents of $CuSO_4$ per litre

$= 2 \times 7.92 \times 10^{-5}$

$= 1.584 \times 10^{-4}$

Normality of $CuSO_4$ solution $= 1.584 \times 10^{-4}$ N

20. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 25°C

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

(i) Write cell reaction.

(ii) Calculate ΔH^o and ΔS^o for the cell reaction by assuming that these quantities remain uncharged in the range 15°C to 35°C.

(iii) Calculate the solubility of AgCl in water at 25°C. Given the standard reduction potential of the Ag^+/Ag couple is 0.80 volt at 25°C.

[IIT 2001]

Solution

(i) Electrode process

$\frac{1}{2} H_2 \rightarrow H^+ + e^-$ (Anode)

$AgCl + e^- \rightarrow Ag + Cl^-$ (Cathode)

Net reaction is:

$\frac{1}{2} H_2 + AgCl \rightleftharpoons H^+ + Ag + Cl^-$

(ii) As $\Delta G^o = \Delta H^o - T\Delta S^o$

$-22195 = \Delta H^o - 288 \times \Delta S^o$

$-20265 = \Delta H^o - 308 \times \Delta S^o$

On solving we get

$\Delta S^o = -96.5$ J

$\Delta H^o = 49.987$ kJ

(iii) $E = E^o - \frac{0.0591}{n} \log_{10} Q$

At eq. $E = 0$, $Q = K = [Ag^+][Cl^-]$

$$0 = (0.8 - 0.22) + \frac{0.0591}{1} \log_{10} Ksp$$

$$\frac{(-0.8 + 0.22)}{0.0591} = \log_{10} Ksp$$

$Ksp = 1.47 \times 10^{-10}$

Solubility (S) $= \sqrt{Ksp}$

$= \sqrt{(1.47 \times 10^{-10})}$

$= 1.21 \times 10^{-5}$ M

21. Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than that of other. The concentration of $CuSO_4$ in the cell with higher emf value is 0.5 M. Calculate the concentration of $CuSO_4$ in the other cell. ($\frac{2.303\ RT}{F} = 0.06$)

[IIT 2003]

Solution

Student I.

Zn (s) | $ZnSO_4$ (C_1) || 0.5 M $CuSO_4$ | Cu (s)

$$E_1 = E^o - \frac{0.06}{2} \log_{10} \frac{C_1}{0.5} \quad \ldots\ldots(i)$$

Student II

Zn (s) | $ZnSO_4$ (C_1) || $CuSO_4$ (C_2) | Cu (s)

$$E_2 = E^o - \frac{0.06}{2} \log_{10} \frac{C_1}{C_2} \quad \ldots\ldots(ii)$$

On subtracting equation (ii) from (i), we get

$$E_1 - E_2 = \frac{0.06}{2}\left[\log_{10}\frac{C_1}{C_2} - \log_{10}\frac{C_1}{0.5}\right]$$

$$0.03 = \frac{0.06}{2}\left[\log_{10}(0.5/C_2)\right]$$

$$1 = \log\frac{0.5}{2}$$

$$C_2 = 0.05\ M$$

22. Find the equilibrium constant for the reaction,

$In^{2+} + Cu^{2+} \rightleftharpoons In^{3+} + Cu^{+}$ at 298 K.

Given: $ECu^{2+}/Cu^{+} = 0.15$ V

$E^o\ In^{2+}/In^{+} = -0.4$ V

$E^oIn^{3+}/In^{+} = -0.42$ V

[IIT 2004]

Solution

The given reversible reaction is obtained as follows:

$Cu^{2+} + e^- \rightarrow Cu^{+}$; $\Delta G^o = -0.15$ F

$In^{2+} + e^- \rightarrow In^{+}$; $\Delta G^o = +0.40$ F

$In^{+} \rightarrow In^{3+} + 2e^-$; $\Delta G^o = -0.84$ F

The net reaction is

$Cu^{2+} + In^{2+} \rightleftharpoons In^{3+} + Cu^{+}$; $\Delta G^o = -0.59$ F

As $\Delta G^o = -nFE^o$

So $-nFE^o = -0.59$ F

$E^o = 0.59$ volt

Equilibrium constant is calculated as:

$$K = \text{antilog}\frac{nE^o}{0.059}.$$

$$= \text{antilog}\frac{1 \times 0.59}{0.059} = 10^{10}$$

23. For the reaction

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

Given:

Species	ΔG^o_f (kJ/mol)
Ag^{+} (aq)	+77
Cl^{-} (aq)	–129
AgCl (s)	–109

Write the cell representation of above reaction and calculate E^o_{cell} at 298 K.

Also find the solubility product of AgCl.

(b) If 6.539×10^{-2} g of metallic zinc is added to 100 ml saturated solution of AgCl. Find the value of $\log_{10}\frac{[Zn^{2+}]}{[Ag^{+}]^2}$.

How many moles of Ag will be precipitate in the above reaction?

Given that:

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

$Zn^{2+} + 2e^- \rightarrow Zn$; $E^o = -0.76$ V

(Atomic mass of Zn = 65.39)

[IIT 2005]

Solution

The reaction is as follows:

At anode:

$$Ag(s) + Cl^{-}(aq) \rightarrow AgCl(s) + e^-$$

At cathode:

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

The net reaction is as follows:

$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$$

Cell representation is as follows:

$$Ag(s) \mid AgCl(s) \mid Cl^{-}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$$

$\Delta G^o = \Delta G^o_f(AgCl) - [\Delta G^o_f(Ag^{+}) + \Delta G^o_f(Cl^{-})]$

$= -109 - (-129 + 77)$

$= -57$ kJ/mol $= -57000$ J/mol

$\Delta G^o = -n\ F\ E^o_{cell}$

$-57000 = -1 \times 96500 \times E^o_{cell}$

(as n = electrons transferred = 1)

$$E^o_{cell} = \frac{57000}{96500} = 0.59 \text{ volts}$$

$$E^o_{cell} = \frac{0.0591}{n}\log_{10} K_C$$

$$E^o_{cell} = \frac{0.0591}{n}\log_{10}\frac{[AgCl]}{[Ag^{+}]\,[Cl^{-}]}$$

$$E^o_{cell} = \frac{0.0591}{1}\log_{10}\frac{1}{Ksp}$$

[As [AgCl (s)] = 1 and Ksp = $[Ag^{+}]\,[Cl^{-}]$]

$0.59 = -0.059 = \log_{10} Ksp$

$\log_{10} Ksp = -10$

$Ksp = 10^{-10}$

(b) When Zn is added to 100 ml of saturated AgCl solution.

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

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

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

$E^o_{cell} = E^o\ Ag^+ \mid Ag\ (s) - E^o\ Zn^{2+} \mid Zn\ (s)$

$= 0.80 - (-0.76) = 1.56\ V$

$$E^o_{cell} = \frac{0.0591}{n} \log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$1.56 = \frac{0.0591}{2} \log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$\log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2} = 52.9$$

As the value of equilibrium constant is very high so the reaction moves in forward direction completely.

$[Ag^+] = \sqrt{(10^{-10})} = 10^{-5}$

(As $Ksp = 10^{-10} = [Ag^+]\ [Cl^-]$)

Ag^+ in 100 ml of solution

$$= \frac{10^{-5} \times 100}{1000} = 10^{-6}$$

24. We have taken a saturated solution of AgBr. Ksp of AgBr is 12×10^{14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of 10^{-7} S m^{-1} units.

Given $\lambda^o(Ag^+) = 6 \times 10^{-3}\ Sm^2\ mol^{-1}$,

$\lambda^o(Br^-) = 8 \times 10^{-3}\ S\ m^2\ mol^{-1}$,

$\lambda^o\ (NO_3^-) = 7 \times 10\ S\ m^2\ mol^{-1}$.

[IIT 2006]

The solubility of AgBr in presence of 10^{-7} molar $AgNO_3$ is 3×10^{-7} M.

Therefore $[Br^-] = 3 \times 10^{-4}\ m^3$, $[Ag^+] = 4 \times 10^{-4}\ m^3$ and $[NO_3^-] = 10^{-4}\ m^3$

Therefore $K_{total} = KBr^- + KAg^+ + KNO_3^- = 55\ Sm^{-1}$