Electrochemistry

Electrolytes: Chemical substances which dissolve in water and furnish ions are called electrolytes. The phenomenon of the production of ions in solution is called dissociation or ionisation.

- **Strong:** Concentration of dissociated ions largely dominate on the concentration of undissociated molecule.

  $\underset{\text{Neglibilbel concentration}}{NaCl} \qquad \underset{\text{Very large concentration}}{Na^+ + Cl^-}$

- **Weak:** Lesser concentration of dissociated ions

  $\underset{\text{Large concentration}}{CH_3COOH} \qquad \underset{\text{Small concentration}}{CH_3COO^- + H^+}$

Degree of Dissociation (α)

$$\frac{\text{Moles of dissociated molecules / ions}}{\text{Total moles of molecules / ions}}$$

Range of $\alpha \Rightarrow \; 0 < \alpha < 1$

Factors Affecting of Degree of Dissociation

- Nature of electrolytes
- Nature of solvent
- Presence of other solute (common ion effect)
- Dilution
- Temperature

Electrolysis: Process in which electrolyte is decomposed into its constituents by passing electricity through its aqueous solution or fused (molten) state.

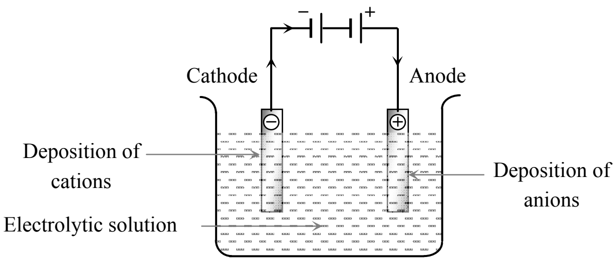


Figure: 7.1

$\text{Electrolyte} = C^+ + A^-$

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

Reaction occurring at cathode → Reduction reaction (Gain of e^-)

$Na^+ + e^-$ (from cathode) $\longrightarrow Na$

Reaction occurring at anode $\longrightarrow$

Oxidation reaction (Loss of e^-)

$Cl^- \longrightarrow Cl + e^-$ (Go to anode) (Primary reaction)

$Cl + Cl \longrightarrow \underset{\text{Molecule}}{Cl_2(g)}$ (Primary reaction)

Preferential Discharging Theory: If more than one type of ions are available during electrolysis, then that ion is discharged first at respective electrodes which requires least energy i.e. discharging potential.

- Electrolysis of sodium chloride solution: Ions produced during electrolysis:

  $NaCl \qquad Na^+ + Cl^- \;\; H_2O \qquad H^+ + OH^-$

  At cathode, H^+ ions are discharged in preference to Na^+ ions as the discharge potential of H^+ ions is lower than Na^+ ions. Similarly at anode, Cl^- ions are discharged in preference to OH^- ions.

  At cathode: $2H^+ + 2e^- \longrightarrow H_2$

  At anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$

  Thus Na^+ and OH^- remain in solution.

- Electrolysis of copper sulphate solution using platinum electrodes:

  $CuSO_4 \qquad Cu^{++} + SO_4^{--} \;\; H_2O \qquad H^+ + OH^-$

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

  At anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

- Electrolysis of sodium sulphate solution using inert electrodes:

  $Na_2SO_4 \qquad 2Na^+ + SO_4^{--} \;\; H_2O_4 \qquad H^+ + OH^-$

  At cathode: $2H^+ + 2e^- \longrightarrow H_2$

  At anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

- Electrolysis of copper sulphate solution using copper electrodes : $CuSO_4 \qquad Cu^{++} + SO_4^{--}$

  At cathode, copper is deposited. $Cu^{++} + 2e^- \longrightarrow Cu$

  At anode, Cu – electrode oxidised to Cu^{++} ions which dissolve equivalent amount of copper at the anode.

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

During electrolysis, copper is transferred from anode to cathode.

Faraday’s Law of Electrolysis

- **Faraday’s first law:** The amount of substance deposited on respective electrodes is directly proportional to the quantity of electricity passed.

  i.e. $w \propto Q$

  Or, $w = Z \times i \times t$

  Where, w = weight of deposited substance,

  i = amp

  t = time in seconds

  If $i = 1$ amp and $t = 1$ sec

  w = z,

  Where, z is electrochemical equivalent. It is the mass of substance deposited by one coulomb of charge.

- **Faraday’s second law:** When same amount of electricity passed through different electrolytes, then deposited mass of respective electrodes will be in the ratio of their equivalent masses.

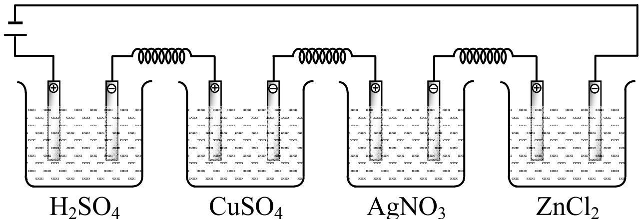


Figure: 7.2

$$\frac{\text{Mass of hydrogen}}{\text{Mass of copper}} = \frac{E_H}{E_{Cu}} \qquad \frac{\text{Mass of Copper}}{\text{Mass of Silver}} = \frac{E_{Cu}}{E_{Ag}}$$

$$\frac{\text{Mass of silver}}{\text{Mass of zinc}} = \frac{E_{Ag}}{E_{Zn}} \qquad \frac{\text{Mass of zinc}}{\text{Mass of hydrogen}} = \frac{E_{Zn}}{E_H}$$

- **Faraday's Law for Gaseous Electrolytic Product** for the gases, we use

  $V = \frac{It\, V_e}{96500}$ where, V = Volume of gas evolved at S.T.P. at an electrode

  V_e = Equivalent volume = Volume of gas evolved at an electrode at S.T.P. by 1 Faraday charge

Quantitative Aspects of Electrolysis: We know that, one Faraday (1F) of electricity is equal to the charge carried by one mole (6.023×10^{23}) of electrons. So, in any reaction, if one mole of electrons are involved, then that reaction would consume or produce 1F of electricity. Since 1F is equal to 96,500 Coulombs, hence 96,500 Coulombs of electricity would cause a reaction involving one mole of electrons. If in any reaction, n moles of electrons are involved, then the total electricity (Q) involved in the reaction is given by, Q = nF = n × 96,500C.

Electrolytic Conductance: Property of electrolytic conductor which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance *i.e.* conductance $(c) = \frac{1}{R}$

Specific Conductance (k): It is the reciprocal of specific resistance or it is the conductance produced by one centimetre cube of an electrolytic conductor.

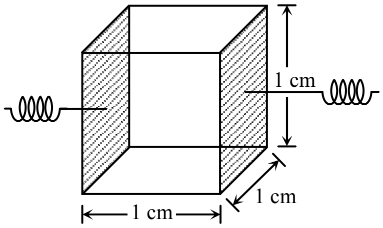


Figure: 7.3

If $R \propto \frac{}{a}$

Where, = length of conductor,

a = cross sectional area of conductor

$\therefore\ R = \rho \cdot \frac{}{a}$

or, $\frac{1}{\rho} = \frac{1}{R} \times \frac{}{a}$

or, $k = C \times \text{cell constant}$

Representation of specific conductance: $k = \frac{1}{\rho} = \text{conductance cm}^{-1}$

Unit at specific conductance: $\text{ohm}^{-1}\text{cm}^{-1} \text{or}\, \Omega^{-1}\text{cm}^{-1} \text{or}\, \text{S cm}^{-1}$ (C.G.S)

Equivalent Conductance (Λ_{eq}): Conductance of all ions which are produced by the ionisation of one equivalent of an electrolyte in a given solution.

i.e. Equivalent conductance

(Λ) = specific conductance $\times V(ml)$

or, $\Lambda = k \times V(ml)$

or, $\Lambda = \frac{K \times 1000}{N}$

Unit of equivalent conductance is $\text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$.

Molar Conductance: The units of molar conductance can be derived from the formula, $\Lambda = \frac{\kappa \times 1000}{M}$.

The units of κ are $S\,cm^{-1}$ and

Units of $\Lambda = S\,cm^{-1} \times \frac{cm^3}{mol} = S\,cm^2\,mol^{-1} = S\,cm^2 mol^{-1}$.

According to SI system, molar conductance is expressed as Sm^2mol^{-1}, if concentration is expressed as $mol\,m^{-3}$.

Effect of Dilution on Conductance

- When we increase the dilution of electrolyte, magnitude of specific conductance decreases, because number of ions in 1 cm^3 volume of electrolyte decreases.
- When dilution of electrolyte increases, magnitude of molar conductance and equivalent conductance increases, because number of ions increases after dilution.
- The molar conductivity of strong electrolytes is found to vary with concentration according to the equation.

  $\Lambda_m^c = \Lambda_m^o - b\sqrt{c}$

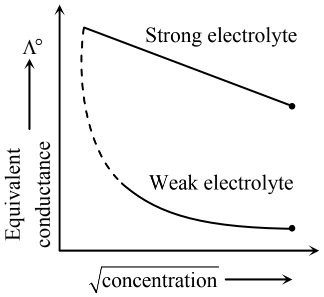


Figure: 7.4

Where, Å = equivalent conductivity at fixed concentration
Å = equivalent conductivity of infinite dilution

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

Kohlrausch's Law of Independent Migration of Ions: At infinite dilution, conductance of any electrolyte is the sum of contribution of its constituents ions *i.e.* anions and cations.

For an electrolyte of the type of A_xB_y,

We have $\Lambda_m^o = x\lambda_+^o + y\lambda_-^o$

Application of Kohlrausch's Law

- Determination of Λ_m^o of a weak electrolyte: In order to calculate Λ_m^o of a weak electrolyte say CH_3COOH, we determine experimentally Λ_m^o values of the following three strong electrolytes:
  - A strong electrolyte containing same cation as in the test electrolyte, say HCl
  - A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa
  - A strong electrolyte containing same anion of (a) and cation of (b) *i.e.* NaCl.

  Λ_m^o of CH_3COOH is then given as:

  $\Lambda_m^o(CH_3COOH) = \Lambda_m^o(HCl) + \Lambda_m^o(CH_3COONa) -$

  $\Lambda_m^o(NaCl)$

  Proof: $\Lambda_m^o(HCl) = \lambda_H^o + \lambda_{Cl^-}$ . . .(*i*)

  $\Lambda_m^o(CHCOONa) = \lambda_{CH_3COO^-}^o + \lambda_{Na^+}$ . . .(*ii*)

  $\Lambda_m^o(NaCl) = \lambda_{Na^+}^o + \lambda_{Cl^-}^o$ . . .(*iii*)

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

  $$\Lambda_{(HCl)}^o + \Lambda_{(CH_3COONa)}^o - \Lambda_{(NaCl)}^o = \lambda_{(H^+)}^o + \lambda_{(CH_3COO^o)}^o = \Lambda_{0(CH_3COOH)}$$

- **Determination of degree of dissociation (α)**

  $$\alpha = \frac{\text{Number of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^o}$$

- **Determination of ionic product of water:** From Kohlrausch's law, we determine Λ_m^o of H_2O where Λ_m^o is the molar conductance of water at infinite dilution when one mole of water is completely ionised to give one mole of H^+ and one mole of OH^- ions i.e., $\Lambda_m^o(H_2O) = \lambda_{H^+}^0 + \lambda_{OH^-}^0$

  Again using the following equation,

  $\Lambda_m = \frac{\kappa \times 1000}{C}$, where $C =$ molar concentration i.e. mol L^{-1} or mol dm^{-3}

  $\Rightarrow \Lambda_m = \frac{\kappa}{C}$, where, $C =$ concentration in mol m^{-3}

  Assuming that Λ_m differs very little from Λ_m^o

  $$\Lambda_m^o = \frac{\kappa}{C}$$

  $$\Rightarrow C = \frac{\kappa}{\Lambda_m^o}$$

  Specific conductance (κ) of pure water is determined experimentally. Thereafter, molar concentration of dissociated water is determined using the above equation.

  K_w is then calculated as: $K_w = C^2$

Heat of Reaction in an Electrochemical Cell: Let *n* Faraday charge flows out of a cell of emf E, then

$-\Delta G = nFE$ . . .(*i*)

Gibbs–Helmholtz equation from thermodynamics may be given as

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

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

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

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

Where, $\left(\frac{\partial E}{\partial T}\right)_P$ = Temperature coefficient of cell

Case (i): When $\left(\frac{\partial E}{\partial T}\right)_P = 0$, then $\Delta H = -nFE$

Case (ii): When $\left(\frac{\partial E}{\partial T}\right) > 0$, then $nFE > \Delta H$, i.e. process inside the cell is endothermic.

Case (iii): When $\left(\frac{\partial E}{\partial T}\right) < 0$, then $nFE < \Delta H$, *i.e.*, process inside the cell is exothermic.

Nernst's Equation

- **Nernst's equation for electrode potential:** The potential of the electrode at which the reaction, $M^{n+}(aq) + ne^- \longrightarrow M(s)$ takes place is described by the equation, $E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{[M(s)]}{[M^{n+}(aq.)]}$

Or $E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303\ RT}{nF}\log\frac{[M(s)]}{[M^{n+}(aq)]}$

Above eq. is called the **Nernst equation**.

Where, $E_{M^{n+}/M}$ = the potential of the electrode at a given concentration,

$E^o_{M^{n+}/M}$ = the standard electrode potential

R = the universal gas constant, $8.31\ J\ K^{-1}\ mol^{-1}$

T = the temperature on the absolute scale,

n = the number of electrons involved in the electrode reaction,

F = the Faraday constant: (96500 *C*),

$[M(s)]$ = the concentration of the deposited metal,

$[M^{n+}(aq)]$ = the molar concentration of the metal ion in the solution,

The concentration of pure metal M(s) is taken as unity. So, the Nernst equation for the M^{n+}/M electrode is written as,

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303\ RT}{nF}\log\frac{1}{[M^{n+}(aq)]}$$

At 298 *K,* the Nernst equation for the M^{n+}/M electrode can be written as,

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}(aq)]}$$

For an electrode (half - cell) corresponding to the electrode reaction,

Oxidised form $+ ne^- \longrightarrow$ Reduced form

The Nernst equation for the electrode is written as,

$$E_{half-cell} = E^o_{half-cell} - \frac{2.303\,RT}{nF}\log\frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

At 298 *K,* the Nernst equation can be written as,

$$E_{half-cell} = E^o_{half-cell} - \frac{0.0591}{n}\log\frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

- **Nernst's equation for cell EMF:** For a cell in which the net cell reaction involving *n* electrons is,

$aA + bB \longrightarrow cC + dD$

The Nernst equation is written as,

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

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

The E^o_{cell} is called the standard cell potential.

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

At 298 *K,* above eq. can be written as,

or $E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$

It may be noted here, that the concentrations of A, B, C and D referred in the eqs. are the concentrations at the time the cell emf is measured.

- **Nernst's Equation for Daniell Cell:** Daniell cell consists of zinc and copper electrodes. The electrode reactions in Daniell cell are,

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

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

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

Therefore, the Nernst equation for the Daniell cell is,

$$E_{cdll} = E^o_{cell} - \frac{2.303\,RT}{2F}\log\frac{[Cu(s)][Zn^{2+}(aq)]}{[Zn(s)][Cu^{2+}(aq)]}$$

Since, the activities of pure copper and zinc metals are taken as unity, hence the Nernst equation for the Daniell cell is, $E_{cdll} = E^o_{cell} - \frac{2.303\,RT}{2F}\log\frac{[Zn^{2+}(aq]}{[Cu^{2+}(aq)]}$

The above *eq*. at 298 *K* is,

$$E_{cdll} = E^{o}_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}(aq]}{[Cu^{2+}(aq)]}V$$

For Daniell cell, $E^{0}_{cell} = 1.1V$

- **Nernst's equation and equilibrium constant:** For a cell, in which the net cell reaction involving *n* electrons is, $aA + bB \longrightarrow cC + dD$

  The Nernst equation is $E_{cell} = E^{o}_{cell} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$ . . .(*i*)

  At equilibrium, the cell cannot perform any useful work. So at equilibrium, E_{Cell} is zero. Also at equilibrium, the ratio

  $$\frac{[C]^c[D]^d}{[A]^a[B]^b} = \left[\frac{[C]^c[D]^d}{[A]^a[B]^b}\right]_{equilibrium} = K_c$$

Relation Among Potential, Gibbs Energy and Equilibrium Constant: The electrical work (electrical energy) is equal to the product of the *EMF* of the cell and electrical charge that flows through the external circuit *i.e.*,

$W_{max} = nFE_{cell}$ . . .(*i*)

According to thermodynamics the free energy change (ΔG) is equal to the maximum work. In the cell work is done on the surroundings by which electrical energy flows through the external circuit, So $-W_{max,} = \Delta G$ . . .(*ii*)

From eq. (*i*) and (*ii*) $\Delta G = -nFE_{cell}$

In standard conditions $\Delta G^{o} = -nFE^{o}_{cell}$

Where ΔG^{o} = standard free energy change

But $E^{o}_{cell} = \frac{2.303}{nF}RT\log K_c$

$\therefore \quad \Delta G^{o} = -nF \times \frac{2.303}{nF}RT\log K_c$

$\Delta G^{o} = -\,2.303\ RT\ \log K_c$ or $\Delta G = \Delta G^{\circ} + 2.303RT\log Q$

$\Delta G^{o} = -RT\ln K_c \quad (2.303\log X = \ln X)$

Corrosion: The conversion of a metal into undesirable compounds by the action of air, moisture is called corrosion; In case of iron corrosion it is called rusting. Corrosion is a redox reaction by which metal gets oxidised by air in presence of moisture. Small cathode and anodic cells are set up on metal. The area of metal in contact with water acts as anode. Metal loses electrons to form cations.

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

The electrons flow along the metal into the cathode area. Where, O_2 is reduced to hydroxyl ions in presence of H_2O.

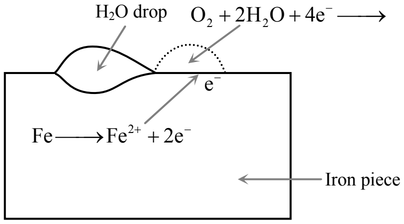


Figure: 7.5

Cathode reaction $O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-}$

The overall reaction is $2Fe + O_2 + 2H_2O \longrightarrow 2Fe(OH)_2$

$Fe(OH)_2$ may dehydrate to form its oxide FeO, which than further gets oxidised to Fe_2O_3. Which is further hydrated to form rust?

$$Fe_2O_3 + nH_2O \longrightarrow Fe_2O_3.nH_2O(rust)$$

Corrosion of a metal weakness the metal and hence is undesirable. The following methods are used to protect a metal from corrosion.

- Applying a protective film such as metal oxide.
- Plating the metal with a more electropositive metal, which loses electrons in preference to the less electropositive metal *e.g.* Zn is coated on steel. (Galvanisation)

By connecting the metal with more electropositive metal (Electrical protection)

Multiple Choice Questions

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

   (a) 9.65×10^{4}sec

   (b) 19.3×10^{4}sec

   (c) 28.95×10^{4}sec

   (d) 38.6×10^{4}sec

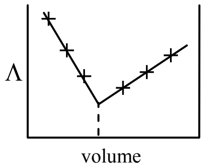
2. **Among the electrolytes Na_2SO_4, $CaCl_2$, Al_2, $(SO_4)_3$ and NH_4Cl, the most effective coagulating agent for Sb_2S_3 sol is:**

   (a) Na_2SO_4 (b) $CaCl_2$

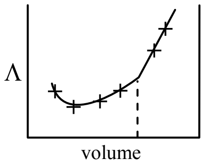
   (c) $Al_2(SO_4)_3$ (d) NH_4Cl

3. **$AgNO_3$(aq.) was added to an aqueous KCI solution gradually and the conductivity of the solution was measured. The plot of conductance (^) versus the volume of $AgNO_3$ is:**

(a)



(b)



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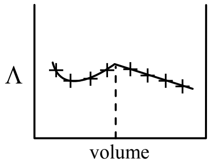
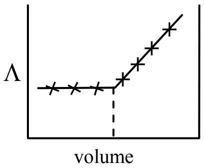


(d)



4. **Consider the following cell reaction:**

$\mathbf{2Fe_{(S)} + O_{2(g)} + 4H^{0}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + 2H_2O_{(1)} E^\circ = 1.67V}$

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

(a) 1.47 V (b) 1.77 V (c) 1.87 V (d) 1.57 V

5. **Given: $E^\circ_{Cr^{3+}/Cr} = -0.74V; E^\circ_{MnO_4^-/Mn^{2+}} = 1.51V\ E^\circ_{CrO_7^{2-}/Cr^{3+}} = 1.33V;\ E^\circ_{Cl/Cl^-} = 1.36$ V. Based on the data given above, strongest oxidizing agent will be:**

(a) Cl^- (b) Cr^{3+}

(c) Mn^{2+} (d) MnO_4^-

6. **In a galvanic cell, the salt bridge**

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

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

(c) is necessary for the occurrence of the cell reaction

(d) ensures mixing of the two electrolytic solutions

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

(a) 0 g (b) 63.5 g

(c) 2 g (d) 127 g

8. **For the following electrochemical cell at 298 K,**

$Pt(S)|H_2$ (g, 1bar) H^+ (aq, 1M) $||M^{4+}$ (aq), M^{2+}(aq)|Pt(S)

$E_{cell} = 0.092$ V when $\frac{[M^{2+}(aq)]}{[M^{4+}(aq)]} = 10^{x}$. Given: $E^0_{M^{4+}/M^{2+}} = -0.151V;\ 2.303\frac{RT}{F} = 0.059V$. The value of *x* is:

(a) –2 (b) –1 (c) 1 (d) 2

9. **Given $E^\circ_{Cl_2/Cl^-} = 1.36V,\ E^\circ_{Cr^{3+}/Cr} = -0.74V,\ E^\circ_{Cr_2O_7^{2-}} = 1.33V,\ E^0_{MnO_4^-/Mn^{2+}} = 1.51$ V. Among the following, the strongest reducing agent is:**

(a) Cl^- (b) Cr (c) Mn^{2+} (d) Cr^{3+}

10. **For the following cell, Zn(s) | $ZnSO_4$(aq) || $CuSO_4$(aq) | Cu(s) when the concentration of Zn^{2+} is 10 times the concentration of Cu^{2+}, the expression for ΔG (in J mol^{-1}) is [F is Faraday constant; R is gas constant; T is temperature; E°(cell) = 1 .1 V]**

(a) 2.303 RT–2.2 F (b) 1.1 F

(c) – 2.2 F (d) 2.303 RT+1.1 F

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

(a) 1.6 hours (b) 6.4 hours

(c) 0.8 hours (d) 3.2 hours

12. **Given that:**

$E^\circ_{O_2/H_2O} = +1.23V$

$E^\circ_{S_2O_8^{2}/SO_4^{2}} = 2.05V$

$E^\circ_{Br_2/Br} = +1.09V$

$E^\circ_{Au^{3+}/Au} = +1.4V$

The strongest oxidising agent is

(a) O_2 (b) Br_2 (c) $S_2O^{2}_{8-}$ (d) Au^{3+}

13. **Calculate the standard cell potential in (V) of the cell in which following reaction takes place:**

Fe^{2+} (aq) + Ag+(aq) Fe^{3+} (aq) + Ag(s)

Given that

$E^\circ_{Ag^+/Ag} = xV$

$E^\circ_{Fe^{2+}/Fe} = yV$

$E^\circ_{Fe^{3+}/Fe} = zV$

(a) x + 2y – 3z (b) x – z

(c) x – y (d) x + y – z

14. **The anodic half cell of lead acid battery is recharged using electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolysed in g during the process in: (Molar mass of $PbSO_4$ = 303 g mol^{-1})**

(a) 22.8 (b) 15.2 (c) 7.6 (d) 11.4

15. **If the standard electrode potential for a cell is 2 V at 300 K, the equilibrium constant (K) for the reaction Zn(S) + Cu^{2+}(aq) → Zn^{2+}(aq) + Cu(S) at 300 K is approximately.**

(R = 8 JK^{-1} mol^{-1}, F = 96000 C mol^{-1})

(a) e^{160} (b) e^{320} (c) e^{320} (d) e^{-80}

16. **Consider the following reduction processes:**

$\mathbf{Zn^{2+} + 2e^- \longrightarrow Zn(S);\ E^\circ = -0.76V}$

$\mathbf{Ca^{2+} + 2e^- \longrightarrow Ca(S);\ E^\circ = -2.87V}$

$\mathbf{Mg^{2+} + 2e^- \longrightarrow Mg(S);\ E^\circ = -2.36V}$

$\mathbf{Ni^{2+} + 2e^- \longrightarrow Ni(S);\ E^\circ = -0.25V}$

The reducing power of the metals increases in the order:

(a) Ca < Zn < Mg < Ni (b) Ni < Zn < Mg < Ca

(c) Zn < Mg < Ni < Ca (d) Ca < Mg < Zn < Ni

17. **In the cell Pt(s)|H_2(g,1bar|HCl(aq)|Ag(s)|Pt(s) the cell potential is 0.92 when a 10^{-6} molal HCl solution is used. The standard electrode potential of (AgCl/Ag,Cl^-) electrode is: {given, $\frac{2.303RT}{F}$ = 0.06Vat 298K}**

(a) 0.20 V (b) 0.76 V

(c) 0.40 V (d) 0.94 V

18. **The electrolytes usually used in the electroplating of gold and silver, respectively, are:**

(a) $[Au(OH)_4]^-$ and $[Ag(OH)_2]^-$

(b) $[Au(CN)_2]^-$ and $[Ag\ Cl_2]^-$

(c) $[Au(NH3)_2]^+$ and $[Ag(CN)_2]^-$

(d) $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$

19. **For the cell Zn(s) | Zn^{2+}(aq) || Mx^+ (aq) | M(s), different half cells and their standard electrode potentials are given below:**

M^{x+}(aq /M(s)	Au^{3+}(aq)/ Au(s)	Au^+(aq) /Au(s)	Fe^{3+} (aq)/ Fe (aq)	Fe^{2+}(aq) / Fe (aq)
$E^\circ_{M^{x+}/M^{(v)}}$	**1.40**	**0.80**	**0.77**	**–0.44**

If $E^\circ_{zn^2/Zn}$ = –0.76V, which cathode will give a maximum value of E°_{cell} per electron transferred?

(a) Fe^{3+} / Fe^{2+} (b) Ag^+ / Ag

(c) Au^{3+} / Au (d) Fe^{2+} / Fe

20. **Given the equilibrium constant:**
KC of the reaction:

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

10 × 10^{15}, calculate the E°_{cell} of this reaction at 298 K

[2.303 $\frac{RT}{F}$ at 298 K = 0.059V]

(a) 0.04736 V

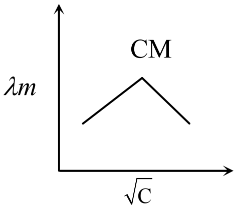
(b) 0.4736 V

(c) 0.4736 mV

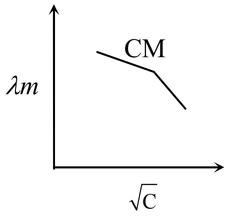
(d) 0.04736 mV

21. **Which of the following plot is correct regarding its conductance?**

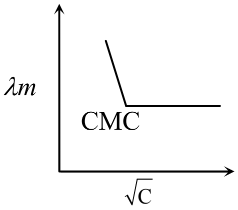
(a)



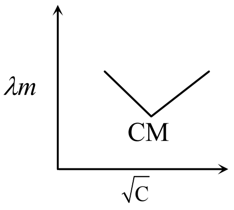
(b)



(c)



(d)



ANSWERS and SOLUTIONS

1. (b) $Q = i \times t \quad Q = 10 \times 10^{-3} \times t$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

To liberate 0.01 mole of H_2 0.02 Faraday charge is required $Q = 0.02 \times 96500$ C

$\therefore \quad 0.02 \times 96500 = 10^{-2} \times t$

$t = 19.30 \times 10^4$ sec

2. (c) As Sb_2S_3 is a negative solution. So, $Al_2(SO_4)_3$ will be the most effective coagulant due to higher charge density on Al^{3+} in accordance with Hardy-Schulze rule. Order of effectiveness of cations:

$$Al^{3+} > Ca^{++} > Na^+ > NH_4^+$$

3. (d)

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

N = 4 (no. of moles of electron involved)

From Nernst's equation,

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

$$= 1.67 - \frac{0.0597}{4}\log\frac{(10^{-3})^2}{0.1 \times (10^{-3})^4} \quad \{\ [H^+] = 10^{-pH}\}$$

$$= 1.67 - 0.106 = 1.57\ V$$

5. (d) MnO_4^- is strongest oxidising agent.

6. (a)

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

2 mol 1 mol = 63.5

8. (d) $E_{cell} = E^o_{cell} - \frac{0.059}{2}\log_{10}\frac{[M^{2+}][H^+]^2}{[M^{4+}]pH_2}$

$$0.092 = 0.151 = \frac{0.059}{2}\log_{10} 10^x$$

$\therefore \quad x = 2$

9. (a) $E^{o}_{MnO_4^-/Mn^{+2}} = 1.51\,V$ . . .(*i*)

$E^{o}_{Cl_2/Cl^-} = 1.36\,V$ . . .(*ii*)

$E^{o}_{Cr_2O_7^{-2}/Cr^{+3}} = 1.33\,V$ . . .(*iii*)

$E^{o}_{Cr^{+3}/Cr} = -0.74$ . . .(*iv*)

Since, Cr^{+3} is having least reducing potential, so Cr is the best reducing agent.

10. (a) $Zn \,|\, \underset{(aq)}{ZnSO_4} \,||\, \underset{(aq)}{CuSO_4} \,|\, Cu$

$$\Delta G = \Delta G^\circ + RT\ln Q$$

$$\Delta G = \Delta G^\circ + 2.303RT\log Q \left(Q = \frac{[Zn^{+2}]}{[Cu^{+2}]} = \frac{10}{1} \right)$$

$$\Delta G^\circ = -nFE^\circ_{Cell} = -2F \times 1.1 = -2.2F$$

11. (d) $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$

27.66 of B_2H_6 = 1 mole of B_2H_6 which requires three moles of oxygen (O_2) for complete burning

$6H_2O \longrightarrow 6H_2 + 3O_2$ (On electrolysis)

Number of faraday

=12 = Amount of charge

12 × 96500 = i × t

12 × 96500 = 100 × t

$$t = \frac{12 \times 96500}{100}\text{ seconds}$$

$$t = \frac{12 \times 96500}{100 \times 3600}\text{ hours} \Rightarrow t = 3.2\text{ hours}$$

12. (c) For strongest oxidising agent, standard reduction potential should be highest.

13. (a) $Fe^{2+}(aq) + Ag+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

Cell reaction

Anode: $Fe^{+2}(aq) \longrightarrow Fe^{+3}(aq) + e^{\ominus}$; $E^{o}_{Fe^{+2}/Fe^{+3}} = mV$

Cathode: $Ag^{+}(aq) + e^{\ominus} \longrightarrow Ag(s)$; $E^{o}_{Ag^{+}/Ag} = xV$

$\Rightarrow$ cell standard potential = (m + x)V

$\therefore$ to find 'm';

$Fe^{+2} + 2e^{\ominus} \longrightarrow Fe$; $E^{o}_{1} = yV \Rightarrow \Delta^{o}_{1}G = -(2Fy)$

$Fe^{+3} + 3e^{\ominus} \longrightarrow Fe$; $E^{o}_{2} = zV \Rightarrow \Delta^{o}_{2}G = -(3Fz)$

$Fe^{+2}(aq) \longrightarrow Fe^{+3}(aq) + e^{\ominus}$;

$E^{o}_{3} = mV \Rightarrow \Delta^{o}_{3}G = -(1Fm)$

$\Delta^{o}_{3}G = \Delta^{o}_{1}G - \Delta^{o}_{2}G = (-2Fy + 3Fz) = -Fm$

$\Rightarrow$ m = (2y – 3z)

$\Rightarrow$ $E^{o}_{cell} = (x + 2y - 3z)V$

14. (b) (i) $\underset{0.05/2mole}{PbSO_4(s)} + 2OH^- \longrightarrow PbO_2 + H_2SO_4 + \underset{0.05F}{2e^-}$

(ii) $\underset{0.05/2mole}{PbSO_4} + \underset{0.05F}{2e^-} + 2H^+ \longrightarrow Pb(s) + H_2SO_4$

$n_T(PbSO_4) = 0.05mole$

$m_{PbSO_4} = 0.05 \times 303 = 15.2gm$

15. (a) $\Delta G^o = -RT\ln k = -nFE^{\circ}_{cell}$

$$\ln k = \frac{n \times F \times E^o}{R \times T} = \frac{2 \times 96000 \times 2}{8 \times 300}$$

$\ln k = 160$ $k = e^{160}$

16. (b) Higher the oxidation potential better will be reducing power.

17. (a) Pt(s) H_2(g, 1bar) HCl(aq) AgCl(s) Ag(s) |Pt(s)

For 10^{-6}mol HCl

Anode: $H_2 \longrightarrow 2H^+ + 2e \times 1$

Cathode: $e^- + AgCl(s) \longrightarrow Ag(s) + Cl^-(aq) \times 2$

$H_2(g)l + AgCl(s) \longrightarrow 2H^+ + 2Ag(s) + 2Cl^-(aq)$

$$E_{cell} = E^0_{cell} - \frac{0.06}{2}\log_{10}((H^+)^2 \cdot (Cl^-)^2)$$

$$.925 = \left(E^0_{H_2/H^+} + E^0_{Agcl/Ag,Cl^-}\right) - \frac{0.06}{2}\log 10\left((10^{-6})^2(10^{-6})^2\right)$$

$$.92 = 0 + E^0_{Agcl/Ag,Cl^-} - 0.03\log_{10}(10^{-6})^4$$

$$E^0_{AgCl}/Ag,Cl^- = .92 + .03 \times -24 = 0.2V$$

18. (d)

19. (b)

20. (b) $E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n}\log Q$

At equilibrium

$$= E^{\circ}_{cell} - \frac{0.059}{n}\log 10^{16} = 0.059 \times 8 = 0.472V$$

21. (b)

❑❑❑