7

Electrochemistry

QUICK LOOK

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 dominates on the concentration of undissociated molecule.

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

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

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

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.

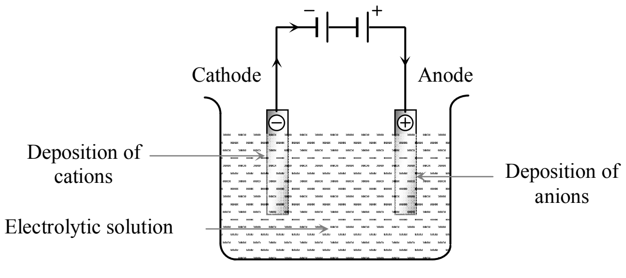


Figure: 7.1

Electrolyte $= C^+ + A^-$

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

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

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

Reaction occurring at anode ⟶

Oxidation reaction (Loss of e^-)

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

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

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:

  $$NaCl \rightleftharpoons Na^+ + Cl^- \quad H_2O \rightleftharpoons H^+ + OH^-$$

  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:

  $$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--} \quad H_2O \rightleftharpoons H^+ + OH^-$$

  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:

  $$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{--} \quad H_2O_4 \rightleftharpoons H^+ + OH^-$$

  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 : $CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$

  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.

  $$Cu \longrightarrow Cu^{++} + 2e^- \quad Cu + SO_4^{--} \rightleftharpoons CuSO_4 + 2e^-$$

  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 = 1sec

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.

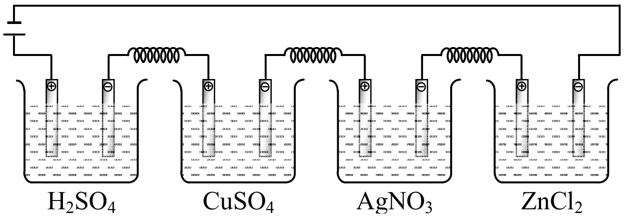


Figure: 7.2

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

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

- **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.

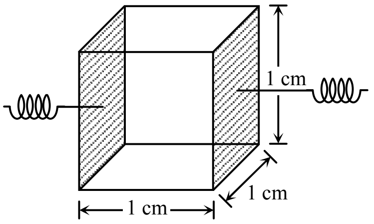


Figure: 7.3

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

Where ℓ = length of conductor,

a = cross sectional area of conductor

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

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

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 $(\Lambda) = \text{specific conductance} \times V(\text{ml})$

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

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 $\Lambda = \text{S cm}^{-1} \times \frac{\text{cm}^3}{\text{mol}} = \text{S cm}^2\ \text{mol}^{-1} = \text{S cm}^2\text{mol}^{-1}$

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

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

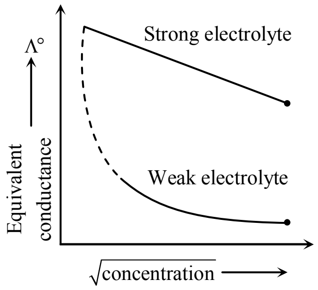


Figure: 7.4

  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

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

  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: $K_w = C^2$

Electrochemical or Galvanic Cell

Electrochemical cell or Galvanic cell is a device in which a spontaneous redox reaction is used to convert chemical energy into electrical energy *i.e.,* electricity can be obtained with the help of oxidation and reduction reaction. Electrochemical cell consists of two vessels, two electrodes, two electrolytic solutions and a salt bridge.

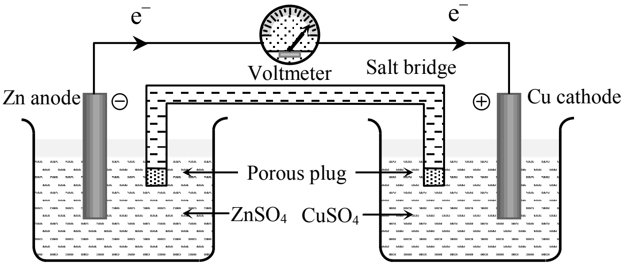


Figure 7.5: Galvanic Cell

- The two electrodes taken are made of different materials and usually set up in two separate vessels. The net reaction is the sum of two half –cell reactions.

  Oxidation half reaction $M_1(s) \longrightarrow M_1^{++}(aq) + 2e^-$

  Reduction half reaction $M_2^{++}(aq) + 2e^- \longrightarrow M_2(s)$

  $M_1(s) + M_2^{++}(aq) \longrightarrow M_1^{++}(aq) + M_2(s)$
- In electrochemical cell, ions are discharged only on the cathode. Like electrolytic cell, in electrochemical cell, from outside the electrolytes electrons flow from anode to cathode and current flow from cathode to anode.

  For electrochemical cell, $E_{cell} = +ve,\ \Delta G = -ve.$

  In a electrochemical cell, cell reaction is exothermic.
- Salt bridge prevents transference or diffusion of the solutions from one half–cell to the other. It also helps to maintain the electrical neutrality of half cells. Salt bridge is represented by a broken line or two parallel vertical lines in a cell reaction.

  $M/M_1^{++}(aq)\ ||\ M_2^{++}(aq)/M_2$

Table 7.1: Main Features of Different Cell

Name of the cell/ Battery		**Anode**	**Cathode**	**Electrolyte**
A.	Dry cell	Zinc	Graphite	MnO_2 + C (Touching cathode) NH_4Cl + $ZnCl_2$ (Touching anode)
B.	Mercury cell	Zinc	Graphite	$HgO + KOH$ (moist)
C.	Lead storage battery	Lead	Lead dioxide	H_2SO_4 (38%)
D.	Ni-Cd cell	Cadmium	Nickel diosxide	KOH solution.
E.	$H_2 — O_2$ fuel cell	Porous carbon contg catalysts (H_2 passed)	Porous carbon contg catalysis (O_2 passed	Conc. aq. KOH solution

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

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

Gibbs–Helmholtz equation from thermodynamics may be given as

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

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 $JK^{-1}\ mol^{-1}$

  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,

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

  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 daniells cell:** Daniell's cell consists of zinc and copper electrodes. The electrode reactions in Daniell's cell are,

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

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

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

  Therefore, the Nernst equation for the Daniell's 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's 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 Daniells cell, $E^{0}_{cell} = 1.1\,V$

- **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.*,

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

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

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

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

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

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

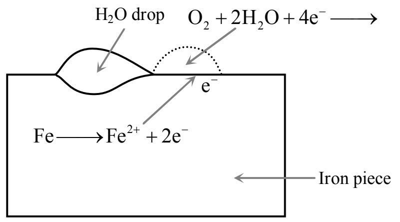


Figure: 7.6: Corrosion

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?

$$Fe_2O_3 + nH_2O \longrightarrow Fe_2O_3.nH_2O(\text{rust})$$

MULTIPLE CHOICE QUESTIONS

Electrolysis and Electrolytes

1. During the electrolysis of an electrolyte, the number of ions produced, is directly proportional to the:

a. Time consumed
b. Electro chemical equivalent of electrolysis
c. Quantity of electricity passed
d. Mass of electrons

2. When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are?

	Cathode	Anode
a.	Pure zinc	Pure copper
b.	Impure sample	Pure copper
c.	Impure zinc	Impure sample
d.	Pure copper	Impure sample

3. In the electrolytic cell, flow of electrons is from:

a. Cathode to anode in solution
b. Cathode to anode through external supply
c. Cathode to anode through internal supply
d. Anode to cathode through internal supply

4. An electric current is passed through an aqueous solution of the following. Which one shall decompose?

a. Urea
b. Glucose
c. $AgNO_3$
d. Ethyl alcohol

5. Which of the following is non-electrolytes?

a. NaCl
b. $CaCl_2$
c. $C_{12}H_{22}O_{11}$
d. CH_3COOH

6. When a molten ionic hydride is electrolysed?

a. Hydrogen is liberated at the cathode
b. Hydrogen is liberated at the anode
c. There is no reaction
d. H^- ions produced migrate to the cathode

7. Use of electrolysis is:

a. Electroplating
b. Electro-refining
c. a. and b. both
d. None of these

8. During the electrolysis of fused NaCl, which reaction occurs at anode?

a. Chloride ions are oxidized
b. Chloride ions are reduced
c. Sodium ions are oxidised
d. Sodium ions are reduced

9. Which of the following liberate hydrogen on reaction with dilute H_2SO_4 ?

a. Fe
b. Cu
c. Al
d. Hg

10. Electrolysis of molten anhydrous calcium chloride produces:

a. Calcium
b. Phosphorus
c. Sulphur
d. Sodium

11. The passage of current liberates H_2 at cathode and Cl_2 at anode. The solution is:

a. Copper chloride in water
b. NaCl in water
c. H_2SO_4
d. Water

12. In electrolysis of aqueous copper sulphate, the gas at anode and cathode is:

a. O_2 and H_2
b. SO_2 and H_2
c. H_2 and O_2
d. SO_3 and O_2

Faraday's Law of Electrolysis

13. 5 amperes is passed through a solution of zinc sulphate for 40 minutes. Find the amount of zinc deposited at the cathode:

a. 40.65 gm
b. 4.065 gm
c. 0.4065 gm
d. 65.04 gm

14. In an electroplating experiment mg of silver is deposited, when 4 amperes of current flows for 2 minutes. The amount (in mgs) of silver deposited by 6 amperes of current flowing for 40 seconds will be?

a. 4m
b. m/2
c. m/4
d. 2m

15. On passing 3 ampere of electricity for 50 minutes, 1.8 gram metal deposits. The equivalent mass of metal is:

a. 20.5
b. 25.8
c. 19.3
d. 30.7

16. How many atoms of calcium will be deposited from a solution of $CaCl_2$ by a current of 25 mill amperes flowing for 60 seconds?

a. 4.68×10^{18}
b. 4.68×10^{15}
c. 4.68×10^{12}
d. 4.68×10^{9}

17. On passing 0.5 faraday of electricity through NaCl, the amount of Cl deposited on cathode is:

a. 35.5 gm
b. 17.75 gm
c. 71 gm
d. 142 gm

18. What is the amount of chlorine evolved when 2 amperes of current is passed for 30 minutes in an aqueous solution of NaCl:

a. 66 g **b.** 1.32 g
c. 33 g **d.** 99 *g*

19. Three faradays of electricity are passed through molten Al_2O_3, aqueous solution of $CuSO_4$ and molten NaCl taken in different electrolytic cells. The amount of Al, Cu and Na deposited at the cathodes will be in the ratio of:

a. 1 mole : 2 mole : 3 mole
b. 3 mole : 2 mole : 1mole
c. 1 mole : 1.5 mole : 3 mole
d. 1.5 mole : 2 mole : 3 mole

20. An electrolytic cell contains a solution of Ag_2SO_4 and have platinum electrodes. A current is passed until 1.6 gm of O_2 has been liberated at anode. The amount of silver deposited at cathode would be :

a. 107.88 gm **b.** 1.6 gm
c. 0.8 gm **d.** 21.60 gm

21. The atomic weight of Al is 27. When a current of 5 Faradays is passed through a solution of Al^{+++} ions, the weight of Al deposited is:

a. 27 gm **b.** 36 gm
c. 45 gm **d.** 39 gm

22. Amount of electricity that can deposit 108 *gm* of silver from $AgNO_3$ solution is:

a. 1 ampere **b.** 1 coulomb
c. 1 faraday **d.** None of the above

Conductor and Conductance

23. The conductivity of strong electrolyte is:

a. Increase on dilution slightly
b. Decrease on dilution
c. Does not change with dilution
d. Depend upon density of electrolytes itself

24. If X is the specific resistance of the solution and M is the molarity of the solution, the molar conductivity of the solution is given by:

a. $\frac{1000X}{M}$ **b.** $\frac{1000}{MX}$
c. $\frac{1000M}{X}$ **d.** $\frac{MX}{1000}$

25. Conductivity (unit Siemen's) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is:

a. $Sm\ mol^{-1}$ **b.** $Sm^2\ mol^{-1}$
c. $S^{-2}m^2\ mol$ **d.** $S^2m^2\ mol^{-2}$

26. The molar conductivity is maximum for the solution of concentration:

a. 0.001 M **b.** 0.005 M
c. 0.002 M **d.** 0.004 M

27. The unit of molar conductivity is:

a. $\Omega^{-1}cm^{-2}mol^{-1}$ **b.** $\Omega\ cm^{-2}mol^{-1}$
c. $\Omega^{-1}cm^2mol^{-1}$ **d.** $\Omega\ cm^2mol$

28. If equivalent conductance of 1M benzoic acid is $12.8 ohm^{-1}cm^2$ and if the conductance of benzoate ion and H^+ ion are 42 and $288.42\ ohm^{-1}cm^2$ respectively. Its degree of dissociation is:

a. 39% **b.** 3.9%
c. 0.35% **d.** 0.039%

The unit ohm^{-1} is used for

29. In infinite dilutions, the equivalent conductance's of Ba^{2+} and Cl^- are 127 and $76\ ohm^{-1}cm^{-1}\ eqvt^{-1}$. The equivalent conductivity of $BaCl_2$ at indefinite dilution is:

a. 101.5 **b.** 139.5
c. 203.5 **d.** 279.5

30. Which of the following conducts electricity?

a. Fused NaCl **b.** CO_2
c. Br_2 **d.** Si

31. The unit ohm^{-1} is used for:

a. Molar conductivity
b. Equivalent conductivity
c. Specific conductivity
d. Conductivity

Cell Constant and Electrochemical Cell

32. If the Zn^{2+}/Zn electrode is diluted to 100 times then the change in e.m.f.:

a. Increase of 59 mV
b. Decrease of 59 mV
c. Increase of 29.5 mV
d. Decrease of 29.5 mV

33. The tendency of an electrode to lose electrons is known as:

a. Electrode potential

b. Reduction potential

c. Oxidation potential

d. e.m.f.

34. When electric current is passed through a cell having an electrolyte, the positive ions move towards the cathode and the negative ions towards the anode. If the cathode is pulled out of the solution?

a. The positive and negative ions will move towards the anode

b. The positive ions will start moving towards the anode, the negative ions will stop moving

c. The negative ions will continue to move towards the anode and the positive ions will stop moving

d. The positive and negative ions will start moving randomly

35. The specific conductance of a 0.1 *N* KCl solution at $23^\circ C$ is $0.012\,\text{ohm}^{-1}\text{cm}^{-1}$. The resistance of cell containing the solution at the same temperature was found to be 55 *ohm*. The cell constant will be:

a. $0.142\,\text{cm}^{-1}$

b. $0.66\,\text{cm}^{-1}$

c. $0.918\,\text{cm}^{-1}$

d. $1.12\,\text{cm}^{-1}$

36. When lead storage battery is charged?

a. Lead dioxide dissolves

b. Sulphuric acid is regenerated

c. The lead electrode becomes coated with lead sulphate

d. The amount of sulphuric acid decreases

37. In the cell $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$, the negative electrode is:

a. Cu

b. Cu^{2+}

c. Zn

d. Zn^{2+}

38. If a strip of Cu metal is placed in a solution of ferrous sulphate:

a. Copper will precipitate out

b. Iron will precipitate out

c. Copper will dissolve

d. No reaction will take place

39. In a hydrogen– oxygen fuel cell, combustion of hydrogen occurs to:

a. Produce high purity water

b. Create potential difference between the two electrodes

c. Generate heat

d. Remove adsorbed oxygen from electrode surfaces

40. At 25°*C* specific conductivity of a normal solution of KCl is 0.002765 mho. The resistance of cell is 400 *ohms*. The cell constant is:

a. 0.815

b. 1.016

c. 1.106

d. 2.016

41. If hydrogen electrode dipped in 2 solution of pH = 3 and pH = 6 and salt bridge is connected the e.m.f. of resulting cell is:

a. 0.177 V

b. 0.3 V

c. 0.052 V

d. 0.104 V

42. In electrolysis of dilute H_2SO_4 using platinum electrodes:

a. H_2 is evolved at cathode

b. NH_3 is produced at anode

c. Cl_2 is obtained at cathode

d. O_2 is produced

43. $\underset{\text{(anode)}}{Zn_{(s)} \mid Zn^{2+}_{(aq)}} \parallel \underset{\text{(cathode)}}{Cu^{2+}_{(aq)} \mid Cu_{(s)}}$ is:

a. Weston cell

b. Daniel cell

c. Calomel cell

d. Faraday cell

44. Saturated solution of KNO_3 is used to make 'salt-bridge' because:

a. Velocity of K^+ is greater than that of NO_3^-

b. Velocity of NO_3^- is greater than that of K^+

c. Velocities of both K^+ and NO_3^- are nearly the same

d. KNO_3 is highly soluble in water

45. The position of some metals in the electrochemical series in decreasing electropositive character is given as $Mg > Al > Zn > Cu > Ag$.

What will happen, if a copper spoon is used to stir a solution of aluminium nitrate?

a. The spoon will get coated with Al

b. An alloy of Cu and Al is formed

c. The solution becomes blue

d. There is no reaction

46. Which of the following statement is true for an electrochemical cell?

a. H_2 is cathode and Cu is anode

b. H_2 is anode and *Cu* is cathode

c. Reduction occurs at H_2 electrode

d. Oxidation occurs at Cu electrode

47. $\lambda_{ClCH_2COONa} = 224\,ohm^{-1}cm^2gmeq^{-1}$,

$\lambda_{NaCl} = 38.2\,ohm^{-1}cm^2gmeq^{-1}$,

$\lambda_{HCl} = 203\,ohm^{-1}cm^2gmeq^{-1}$,

What is the value of λ_{ClCH_2COOH}?

a. $288.5\ ohm^{-1}cm^2gmeq^{-1}$

b. $289.5\ ohm^{-1}cm^2gmeq^{-1}$

c. $388.5\ ohm^{-1}cm^2gmeq^{-1}$

d. $59.5\ ohm^{-1}cm^2gmeq^{-1}$

Nernst's Equation

48. A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$, is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are $Ag/Ag^+ = +0.80$,

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

$Cu/Cu^{2+} = +0.34$,

$Mg/Mg^{2+} = -2.37$

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

a. Ag, Hg, Cu, Mg

b. Mg, Cu, Hg, Ag

c. Ag, Hg, Cu

d. Cu, Hg, Ag

49. Beryllium is placed above magnesium in the second group. Beryllium dust, therefore when added to $MgCl_2$ solution will

a. Have no effect

b. Precipitate Mg metal

c. Precipitate MgO

d. Lead to dissolution of be metal

50. A cell constructed by coupling a standard copper electrode and a standard magnesium electrode has emf of 2.7 volts. If the standard reduction potential of copper electrode is + 0.34 volt that of magnesium electrode is:

a. + 3.04 volts

b. – 3.04 volts

c. + 2.36 volts

d. – 2.36 volts

51. When $E^o_{Ag^+/Ag} = 0.8$ volt and $E^o_{Zn^{2+}/Zn} = -0.76$ volt, which of the following is correct?

a. Ag^+ can be reduced by H_2

b. Ag can oxidise H_2 into H^+

c. Zn^{2+} can be reduced by H_2

d. Ag can reduce Zn^{2+} ion

52. For the redox reaction

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

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

a. 2.14 volt

b. 1.80 volt

c. 1.07 volt

d. 0.82 volt

53. The emf of a Daniel cell at 298K is E_1 $Zn\,|\,\underset{(0.01\ M)}{ZnSO_4}\,||\,\underset{(1.0\ M)}{CuSO_4}\,|\,Cu$ when the concentration of $ZnSO_4$ is 1.0M and that of $CuSO_4$ is 0.01M, the *emf* changed to E_2. What is the relationship between E_1 and E_2?

a. $E_2 = 0 \neq E_1$

b. $E_1 > E_2$

c. $E_1 < E_2$

d. $E_1 = E_2$

Corrosion

54. Corrosion of iron is essentially an electrochemical phenomenon where the cell reactions are?

a. Fe is oxidised to Fe^{2+} and dissolved oxygen in water is reduced to $\overset{n}{OH}$

b. Fe is oxidised to Fe^{3+} and H_2O is reduced to O_2^{2-}

c. s is oxidised to Fe^{2+} and H_2O is reduced to O_2^-

d. Fe is oxidised to Fe^{2+} and H_2O is reduced to O_2

55. Which of the following is a highly corrosive salt?

a. $FeCl_2$

b. $PbCl_2$

c. Hg_2Cl_2

d. $HgCl_2$

NCERT EXEMPLAR PROBLEMS

More than One Answer

56. Two half cells have potential –0.76 V and –0.13 V respectively. A galvanic cell is made from these two half cells. Which of the following statements is correct?

a. Electrode of half-cell potential –0.76 V serves as cathode

b. Electrode of half-cell potential – 0.76 V serves as anode

c. Electrode of half-cell potential –0.13 V serves as cathode

d. Electrode of half-cell potential –0.76 V serves as positive electrode and 0.13 V as negative electrode

57. In which case $E_{cell} - E^o_{cell}$ is zero?

a. $Cu|Cu^{2+}(0.01M)||Ag^{+}(0.1M)|Ag$

b. $Pt(H_2)|pH = 1|| Zn^{2+}(0.01M)| Zn$

c. $Pt(H_2)|pH = 1|| Zn^{2+}(1M)| Zn$

d. $Pt(H_2)|H^{+} = (0.01M)|| Zn^{2+}(0.01M)| Zn$

58. During the purification of copper by electrolysis:

a. The anode used is made of copper ore

b. Pure copper is deposited on the cathode

c. The impurities such as Ag, Au are present in solutions as ions

d. Concentrations of $CuSO_4$, solution remains constant during dissolution of Cu

59. For the cell at 298 K $Ag(s)|AgCl(s)|KClaq||AgNO_3|Ag(s)$ Which of the following wrong?

a. The EMF of the cell is zero when $[Ag^{+}]_{anodic} = [Ag^{+}]_{cathodic}$

b. The amount of AgCl(s) precipitate in anodic compartment will decrease with the working of the cell

c. The concentration of $[Ag^{+}]$ is constant in anodic compartment with the working of cell

d. $E_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Cl^-/AgCl/Ag} - \frac{0.059}{1}\log\frac{1}{[Cl^-]}$ anodic

60. When a galvanic cell starts, working with the passage of time

a. Spontaneity of the cell reaction decreases, E_{cell} decreases

b. Reaction quotient Q decreases E_{cell}increases

c. Reaction quotient Q increases E_{cell} increases

d. At equilibrium $Q = K_c$ and $E_{cell} = 0$

61. Some statements are given below. The correct statements are:

a. The electrolysis of aqueous NaCl produces hydrogen gas at the cathode and chlorine gas at the anode

b. The electrolysis of a dilute solution of sodium fluoride produces oxygen gas at the anode and hydrogen gas at the cathode

c. The electrolysis of concentrated sulphuric acid produces SO_2 gas at the anode and O_2 gas at the cathode

d. After the electrolysis of aqueous sodium sulphate, the solution becomes acidic

62. Consider the cell: Ag(s)| AgCl (standard solution) $||AgNO_3$ (aq) (1.0M)|Ag(s) EMF of the above cell is given by $(K_{sp}$ of $AgCl = 1.0\times10^{-10} M^2)$

a. $E_{cell} = E^\circ_{As^+/Ag} + 0.0592 \log [K_{sp}(AgCl)]^{1/2}$

b. $E_{cell} = 0.0592 \log\frac{1}{[K_{sp}(AgCl)]^{1/2}}$

c. $E_{cell} = 0.0592 \times 5V$

d. $E_{cell} = 296\text{ mV}$

63. The emf of the following cell is 0.22 V.

$Ag(s)AgCl(s)\,|\,KCl(1M)\,|\,H^{+}(1M)\,|\,H_2(g)\ (1\ atm);\ Pt(s)$

Which of the following will decreases the EMF of cell?

a. Increasing pressure of $H_2(g)$ from 1 atm to 2 atm

b. Increasing Cl^{-}concentration in anodic compartment

c. Increasing H^{+} concentration in cathodic compartment

d. Increasing KCl concentration in anodic compartment

64. Which of the following statement(s) is/are correct?

a. F_2 is the strongest oxidizing agent

b. Li is the strongest reducing agent

c. Li^{+} is the weakest oxidizing agent

d. F_2 is highest reduction potential

65. The values of E° of some reactions are given:

$I_2 + 2e^- \longrightarrow 2I^-$ $E^\circ = 0.54$ volts

$Sn^{+4} + 2e^- \longrightarrow Sn^{2+}$ $E^\circ = 0.152$ volts

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ $E^\circ = 1.36$ volts

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $E^\circ = 0.76$ volts

$Ce^{+4} + e^- \longrightarrow Ce^{+3}$ $E^\circ = 1.6$ volts

Hence,

a. Fe^{3+} oxidizes Ce^{+3}

b. $Ce4^{+}$ can oxidize Fe^{2+}

c. Sn^{2+} will reduce Fe^{3+} to Fe^{2+}

d. Cl_2 will be liberated from KCl by passing I_2

66. Which one of the following metals could not be obtained on electrolysis of aqueous solution of its salts?

a. Ag **b.** Mg

c. Cu **d.** Cr

67. On the electrolysis of aqueous solution of sodium sulphate, on cathode we get:

a. Na **b.** H_2

c. SO_2 **d.** SO_3

68. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively:

a. H_2, O_2 **b.** O_2, H_2

c. O_2, Na **d.** O_2, SO_2

69. During electrolysis of NaCl solution, part of the reaction is $Na^{+} + e^{-} \longrightarrow Na$. This is termed as:

a. Oxidation **b.** Reduction

c. Deposition **d.** Cathode reaction

70. Degree of ionisation of a solution depends upon:

a. Temperature
b. Nature of the electrolyte
c. Nature of the solvent
d. None of these

71. Which of the following is not a non electrolyte?

a. Acetic acid　　**b.** Glucose
c. Ethanol　　**d.** Urea

72. A certain current liberated 0.504 *gm* of hydrogen in 2 hours. How many grams of copper can be liberated by the same current flowing for the same time in a copper sulphate solution?

a. 12.7 *gm*　　**b.** 15.9 *gm*
c. 31.8 *gm*　　**d.** 63.5 *gm*

73. On passing one faraday of electricity through the electrolytic cells containing Ag^+, Ni^{+2} and Cr^{+3} ions solution, the deposited $Ag\,(At.\ wt. = 108)$, $Ni\,(At.wt. = 59)$ and $Cr\,(At.wt. = 52)$ is:

	Ag	Ni	Cr
a.	108 gm	29.5 gm	17.3 gm
b.	108 gm	59.0 gm	52.0 gm
c.	108.0 gm	108.0 gm	108.0 gm
d.	108 gm	117.5 gm	166.0 gm

74. Given $1/a = 0.5 cm^{-1}, R = 50 ohm, N = 1.0$. The equivalent conductance of the electrolytic cell is:

a. $10\,ohm^{-1}cm^2 gm\,eq^{-1}$
b. $20\,ohm^{-1}cm^2 gm\,eq^{-1}$
c. $300\,ohm^{-1}cm^2 gmeq^{-1}$
d. $100 ohm^{-1}cm^2\ gmeq^{-1}$

75. Which one is not a conductor of electricity?

a. NaCl (aqueous)　　**b.** NaCl (solid)
c. NaCl (molten)　　**d.** Ag metal

Assertion and Reason

Note: Read the Assertion (A) and Reason (R) carefully to mark the correct option out of the options given below:

a. If both assertion and reason are true and the reason is the correct explanation of the assertion.
b. If both assertion and reason are true but reason is not the correct explanation of the assertion.
c. If assertion is true but reason is false.
d. If the assertion and reason both are false.
e. If assertion is false but reason is true.

76. **Assertion:** A large dry cell has high e.m.f.
Reason: The e.m.f. of a dry cell is proportional to its size.

77. **Assertion:** The resistivity for a substance is its resistance when its one meter long and its area of cross section is one square meter.
Reason: The *SI* uints of resistivity are ohm metre (Ωm) and ohm centimeter (Ωcm).

78. **Assertion:** If $\lambda^o_{Na^+} + \lambda^o_{Cl^-}$ are molar limiting conductivity of the sodium and chloride ions respectively, then the limiting molar conducting for sodium chloride is given by the equation: $\Lambda^o_{NaCl} = \lambda^o_{Na^+} + \lambda^o_{Cl^-}$.
Reason: This is according to Kohlrausch law of independent migration of ions.

79. **Assertion:** For a cell reaction $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(aq)$; at the equilibrium, voltmeter gives zero reading.
Reason: At the equilibrium, there is no change in the concentration of Cu^{2+} and Zn^{2+} ions.

80. **Assertion:** A negative value of standard reduction potential means that reduction take place on this electrode with reference to standard hydrogen electrode.
Reason: The standard electrode potential of a half cell has a fixed value.

81. **Assertion:** Weston is a standard cell.
Reason: Its *e.m.f.* does not change with temperature.

82. **Assertion:** Galvanised iron does not rust.
Reason: Zinc has a more negative electrode potential than iron.

83. **Assertion:** $Ni/Ni^{2+}(1.0\ M)\,||\,Au^{3+}(1.0\ M)\,|\,Au$, for this cell emf is 1.75V f $E^o_{Au^{3+}/Au} = 1.50$ and $E^o_{Ni^{2+}/Ni} = 0.25$ V.
Reason: Emf of the cell $= E^o_{cathode} - E^o_{anode}$.

84. **Assertion:** Sodium ions are discharged in preference to hydrogen ions at a mercury cathode.
Reason: The nature of the cathode can effect the order of discharge of ions.

85. **Assertion:** In electrolysis, the quantity of electricity needed for depositing 1 mole of silver is different from that required for 1 mole of copper.
Reason: The molecular weights of silver and copper are different

Comprehension Based

Paragraph-I

A student prepare 2 L buffer solution of 0.3 M NaH_2PO_4 and 0.3 M Na_2HPO_4. The solution is divided in half between the two compartments (each containing 1 L buffer) of an electrolysis cell, using Pt electrodes. Assume that the only reaction is the electrolysis of water and the electrolysis is carried out for 200 min with a constant current of 0.965 A. [Assume that $pK_{a(H_2PO_4^-)} = 7.2$]

86. pH at cathode is:

a. 7.2 **b.** 6.83
c. 7.57 **d.** 7.0

87. pH at anode is:

a. 7.2 **b.** 6.83
c. 7.57 **d.** 7.0

Paragraph –II

Fuel cells: Fuel cells are galvanic cells in which the chemical energy of fuel is directly converted into electrical energy. A type of fuel cell is a hydrogen-oxygen fuel cell. It consists of two electrodes made up of two porous graphite impregnated with a catalyst (platinum, silver or metal oxide). The electrodes are placed in aqueous solution of NaOH. Oxygen and hydrogen are continuously fed into the cell. Hydrogen gets oxidized to H^+ which is neutralized by OH^-, *i.e.,* anodic reaction.

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

$$2H^+ + 2OH^- \rightleftharpoons 2H_2O$$

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

At cathode, O_2 gets reduced to OH^-

Hence, the net reaction is $2H_2 + O_2 \rightleftharpoons 2H_2O$

The overall reaction has $\Delta H = -285.6$ kJ Mol^{-1} and $\Delta G = -237.4$ kJ mol^{-1} at 25°C

88. If the cell voltage is 1.23 V for the H_2–O_2 full cell and for the half cell $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ has $E^- = 0.40V$ then E^- for $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ will be:

a. 0.41 V **b.** 0.83 V
c. – 0.41 V **d.** – 0.83 V

89. What is the value of ΔS^- for the fuel cell at 25ºC?

a. $-1600\ J\ K^{-1}$ **b.** $-160\ J\ K^{-1}$
c. $160\ J\ K^{-1}$ **d.** $1600\ J\ K^{-1}$

90. Suppose the concentration of hydroxide ion in the cell is doubled, then the cell voltage will be:

a. Reduced by half
b. Increased by a factor of 2
c. Increased by a factor of 4
d. Unchanged

91. A fuel cell is:

I. A voltaic cell in which continuous supply of fuels are sent at anode to perform oxidation

II. A voltaic cell in which fuels such as CH_4,H_2 and CO are used up at anode

III One which involves the reaction of H_2 — O_2 fuel cell such as:

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

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

IV. The efficiency of H_2 — O_2 fuel cell is 70 to 75%

a. I, III **b.** I, III, IV
c. I, II, III, IV **d.** I, II, III

Match the Column

92. Match the statement of Column with those in Column II:

Given: $E^-_{Cu^{2+}|Cu} = 0.34V$,

$E^-_{Cl_2|Cu^-} = 1.36V$,

$E^-_{Br_2|Br^-} = 1.08V$,

$E^-_{I_2|I^-} = 0.54V$

Column I	Column II
(A) $Cu^{+2} + 2Cl^- \rightarrow Cu + Cl_2$	**1.** Can produce electricity in the galvanic cell
(B) $Cu_2 + Cu \rightarrow Cu^{+2} + 2Cl^-$	**2.** Can be made to occur in electrolysis cell
(C) $2I^-$ + Starch solution + Chlorine water	**3.** Appearance of brown colour
(D) $2Br^- + CCl_4 +$ Chlorine water	**4.** Appearance of violet colour

a. A→3, B→1, C→4, D→2
b. A→2, B→1, C→4, D→3
c. A-1, B→3, C→2, D→4
d. A→4, B-1, C→3, D→2

93. Match the statement of Column with those in Column II:

Column I EMF of given cell at 30°C (Take 2.303 RT/F = 0.06)	Column II pH
(A) $Pt \mid H_2(g)(1atm) \mid H^- = (x\,m) \mid$ $\mid H^+(10^{-4}M) \mid H_2(g)(1atm) \mid Pt$ $(E_{cell} = 0.06\,V)$	**1.** 10

(B) $Pt \mid H_2(g)(1\,atm) \mid H_2O \mid$ $\mid HCl(x\,M) \mid H_2(g)(1\,atm) \mid Pt$ $(E_{cell} = 0.18\,V)$	**2.** 5
(C) $Pt, \underset{1\,atm}{H_2(g)} \left\| \begin{matrix} NH_4ClO_4(0.2\,M) \\ pK_b(NH_4OH) = 4.74 \end{matrix} \right\| \left| \begin{matrix} CH_3COOK(x\,M) \\ pK_a(CH_3COOH) = 4.74 \end{matrix} \right| \underset{1\,atm}{H_2(g)}, Pt$ $(E_{cell} = -0.24\,V)$	**3.** 4
(D) $Pt \mid H_2(g)(1atm) \mid H_2SO_4(0.05M) \mid$ $\mid CsOH(x\,M) \parallel H_2(g)(1\,atm) \mid Pt$ $(E_{cell} = -0.54\,V)$	**4.** 8.98

a. A→2, B→3, C→4, D→1
b. A→2, B→4, C→3, D→1
c. A→1, B→3, C→2, D→4
d. A→4, B→1, C→3, D→2

94. Match the statement of Column with those in Column II:

Column I (Concentration of cell at 30°C (Take 2.303 RT/F = 0.06))	**Column II** (E_{cell})
(A) $Pt \mid H_2(g)(1\ atm)\ \mid CH_3COOK\ (10^{-1}M) + CH_3COOH(10^{-2}M)\ pK_{a(CH3COOH)} = 4.74\ \mid (NH_4)_2SO_4\ (0.2M) \mid + NH_4OH(0.24)\ pK_{b(NH4OH)} = 4.74 \mid H_2(g)(1amt)Pt$	**1.** 0.03V
(B) $Cu(s) \mid Cu^{2+}(1M) \mid\ Cu^{2+}(0.1M) \mid Cu(s)$	**2.** 0.2178 V
(C) $Pt \mid Cl_2(g)(1\ atm) \mid Cl^-(10^{-2}M) \mid Cl^-(10^{-3}M) \mid Cl_2(g)(2atm)Pt$	**3.** – 0.1932 V
(D) $Pt \mid H_2(g)(1\ atm)\ \mid NH_4OH(10^{-2}M)$ pK_b □ $4.74 \parallel CH_3COONH_4 pK_a CH_3COOH = 4.74 pK_b NH_4OH = 4.74 \mid H_2(g)\ (1\ atm) \mid Pt$	**4.** 0.1 V
(E) Glass electrode ‖ Buffer solution pH = 6 | Standard calomel electrode Given: $E_{SCE} = 0.24\,V; E^{-}_{glass} = 0.5\,V$	**5.** 0.069 V

a. A→3, B→1, C→5, D→2, E→4
b. A→2, B-5, C→3, D→1, E→4
c. A→1, B-3, C→2, D→4, E→5
d. A→4, B-1, C→3, D→5, E→2

95. Match the statement of Column with those in Column II:

Column I (Electrolysis)	**Column II** (pH and products at anode and cathode)
(A) Electrolysis of 100 L aqueous solution of CH_3COOK by passing 2 F of electricity.	**1.** pH = 12.3 Anode=Ethane(g) +CO_2(g) Cathode =H_2(g)
(B) Electrolysis of 10 L aqueous solution of HCOOK by passing 1 F of electricity.	**2.** pH = 13.0 Anode = H_2 (g) + CO_2(g) Cathode = H_2(g)
(C) Electrolysis of 10 L aqueous solution of K_2SO_4 by passing 1 F of electricity.	**3.** pH = 7.0 Anode = O_2 (g) Cathode = H_2 (g)
(D) Electrolysis of 10 L aqueous solution of CuF_2 by passing 1 F of electricity.	**4.** pH = 1.0 Anode = O_2 (g) Cathode = Cu (g)

a. A→3, B→1, C→4, D→2
b. A→2, B→4, C→3, D→1
c. A→1, B→2, C→3, D→4
d. A→4, B→1, C→3, D→2

Integer

96. How many Faradays are required to reduce 1 mol of BrO_3^- to Br^- in basic medium?

97. The total number of faradays required to oxidize the following separately:

a. 1 mol of $S_2O_3^{2-}$ in acid medium

b. 1 Equivalent of $S_2O_3^{2-}$ in neutral medium

c. 1 mol of $S_2O_3^{2-}$ in basic medium.

98. For the oxidation of ferric oxalate to CO_2, 18 F of electricity is required. How many moles of ferric oxalate is oxidized?

99. During the discharge of a lead storage battery, the density of 40% H_2SO_4 by weight fell from 1.225 to 0.98 (which is 20% by weight). What is the change in molarities of H_2SO_4?

100. ΔG for the reaction: $\frac{4}{3}Al + O_2 \longrightarrow \frac{2}{3}Al_2O_3$ is $-772kJ\ mol^{-1}$ of O_2. Calculate the minimum EMF in volts required to carry out an electrolysis of Al_2O_3.

ANSWER

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
c	d	d	c	c	b	c	a	c	a
11.	**12.**	**13.**	**14.**	**15.**	**16.**	**17.**	**18.**	**19.**	**20.**
b	a	b	b	c	a	b	b	c	d
21.	**22.**	**23.**	**24.**	**25.**	**26.**	**27.**	**28.**	**29.**	**30.**
c	c	a	b	b	a	c	b	b	a
31.	**32.**	**33.**	**34.**	**35.**	**36.**	**37.**	**38.**	**39.**	**40.**
d	a	c	d	b	b	c	d	b	c
41.	**42.**	**43.**	**44.**	**45.**	**46.**	**47.**	**48.**	**49.**	**50.**
a	a	b	c	d	b	c	c	a	d
51.	**52.**	**53.**	**54.**	**55.**	**56.**	**57.**	**58.**	**59.**	**60.**
a	c	b	a	d	b,c	a,b	a,b,d	b,c,d	a,d
61.	**62.**	**63.**	**64.**	**65.**	**66.**	**67.**	**68.**	**69.**	**70.**
a,b	b,c,d	a,d	all	b,c	b	b	a	b	d
71.	**72.**	**73.**	**74.**	**75.**	**76.**	**77.**	**78.**	**79.**	**80.**
a	b	a	a	b	a	b	a	a	e
81.	**82.**	**83.**	**84.**	**85.**	**86.**	**87.**	**88.**	**89.**	**90.**
a	a	a	a	b	c	b	d	b	d
91.	**92.**	**93.**	**94.**	**95.**	**96.**	**97.**	**98.**	**99.**	**100.**
c	b	a	a	c	6	10	3	3	2

SOLUTION

Multiple Choice Questions

1. **(c)** According to Faraday's law.

2. **(d)** Impure metal made anode while pure metal made cathode.

3. **(d)** In electrolytic cell, cathode acts as source of electrons.

4. **(c)** $AgNO_3$ is an electrolyte.

5. **(c)** $C_{12}H_{22}O_{11}$ is an non-electrolyte.

6. **(b)** On electrolysis molten ionic hydride liberate H_2 at the anode.

7. **(c)** Electrolysis use for electroplating and electro-refining.

8. **(a)** In fused NaCl chloride ions are oxidized at anode and it is called oxidation.

9. **(c)** $2Al + dil.H_2SO_4 \longrightarrow Al_2SO_4 + H_2 \uparrow$.

10. **(a)** Calcium is produces when molten anhydrous calcium chloride is electrolysed.

11. **(b)** Since discharge potential of water is greater than that of sodium so water is reduced at cathode instead of Na^+

Cathode: $H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH^-$

Anode: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$.

12. **(a)** Cathode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Anode: $H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$.

13. **(b)** $W = zit;\ W = \frac{32.69 \times 5 \times 60 \times 40}{96500} = 4.065\,gm$.

14. **(b)** $m = Z \times 4 \times 120;\ M = Z \times 6 \times 40$

$$\frac{M}{m} = \frac{6 \times 40}{4 \times 120} = \frac{1}{2};\quad M = m/2.$$

15. **(c)** $W_{metal} = \frac{E \times I \times t}{96500} = \frac{E \times 3 \times 50 \times 60}{96500}$

$$E = \frac{96500 \times w}{3 \times 50 \times 60} = \frac{96500 \times 1.8}{3 \times 50 \times 60} = 19.3.$$

16. **(a)** Quantity of electricity passed

$$= \frac{25}{1000} \times 60 = 1.5$$

$2F = 2 \times 96500\,C$ deposit $Ca = 1mole$

$\therefore$ $1.5\ C$ will deposit $Ca = \frac{1}{2 \times 96500} \times 1.5\,mole$

$$= \frac{1}{2 \times 96500} \times 1.5 \times 6.023 \times 10^{23}\ atom = 4.68 \times 10^{18}.$$

17. **(b)** Equivalent of Cl deposited

= No. of Faraday passed = 0.5

Wt. of $Cl = 0.5 \times Eq.wt.$

$= 0.5 \times 35.5 = 17.75\ gm$.

18. **(b)** At Andoe $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

$$E_{Cl_2} = \frac{35.5 \times 2}{2} = 35.5$$

$$W_{Cl_2} = \frac{E_{Cl_2} \times I \times t}{96500}$$

$$= \frac{35.5 \times 2 \times 30 \times 60}{96500} = 1.32\ gm.$$

19. **(c)** At cathode: $Al^{3+} + 3e^- \longrightarrow Al$

$$E_{Al} = \frac{\text{Atomic mass}}{3}$$

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

$$E_{Cu} = \frac{\text{Atomic mass}}{2}$$

At cathode: $Na^+ + e^- \longrightarrow Na$

$$E_{Na} = \frac{\text{Atomic mass}}{1}$$

For the passage of 3 faraday;

Mole atoms of Al deposited = 1

Mole atoms of Cu deposited $= \frac{1\times 3}{2} = 1.5$

Mole atoms of Na deposited $= 1\times 3 = 3$.

20. **(d)** At cathode: $Ag^+ + e^- \longrightarrow Ag$

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

$$E_{Ag} = \frac{108}{1} = 108;$$

$$E_{O_2} = \frac{\frac{1}{2}\times 32}{2} = 8$$

$$\frac{W_{Ag}}{E_{Ag}} = \frac{W_{O_2}}{E_{O_2}};$$

$$W_{Ag} = \frac{1.6\times 108}{8} = 21.6 \text{ gm}.$$

21. **(c)** $Al^{3+} + 3e^- \longrightarrow Al$

$$E_{Al} = \frac{27}{3} = 9$$

$$W_{Al} = E_{Al} \times \text{No. of faradays} = 9\times 5 = 45 \text{ gm}.$$

22. **(c)** $Ag^+ + e^- \longrightarrow Ag$;

$$E_{Ag} = \frac{\text{Atomic Mass}}{1} = 108$$

Number of faraday $= \frac{W_{Ag}}{E_{Ag}} = \frac{108}{108} = 1$.

23. **(a)** Generally strong electrolyte on dilution shows conductivity characters.

24. **(b)** Molar conductivity $= \frac{1000}{MX}$.

25. **(b)** $C = \frac{K[A]A}{l}$, $K = \frac{C\times l}{[A]A}$

$$= \frac{Sm}{mol\,m^{-3}\,m^2} = Sm^2mol^{-1}.$$

26. **(a)** Since molar conductance $\propto \frac{1}{\text{Molarity}}$.

27. **(c)** Molar conductivity $= \frac{1}{\rho M}$

So its unit will be $\Omega^{-1}cm^2mol^{-1}$.

28. **(b)** $\Lambda^o_{m(C_6H_5COOH)} = \Lambda^o_{(C_6H_5COO^-)} + \Lambda^o_{(H^+)}$

$$= 42 + 288.42 = 330.42$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{12.8}{330.42} = 3.9\%$$

29. **(b)** $\lambda^\infty BaCl_2 = \frac{1}{2}\lambda^\infty Ba^{2+} + \lambda^\infty Cl^-$

$$= \frac{127}{2} + 76 = 139.5 \text{ ohm}^{-1}\text{ cm}^{-1}\text{ eq}^{-1}.$$

30. **(a)** $NaCl \rightleftharpoons Na^+ + Cl^-$

So it conducts electricity.

31. **(d)** Conductance $= \frac{1}{\text{resistance}}$

$$= \frac{1}{\text{ohm}} = \text{ohm}^{-1} \text{ or mho}$$

32. **(a)** $E_{cell} = \frac{0.059}{n}\log\frac{1}{C}$

$$= -\frac{0.059}{2}\log\frac{1}{100}$$

$$= -\frac{0.059}{2}(-2) = 0.059V = 59mV. \text{ (increase)}$$

33. **(c)** The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons. *i.e.,* it is a measure of the relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons).

$M \longrightarrow M^{n+} + ne^-$ (oxidation potential)

$M^{n+} + ne^- \longrightarrow M$ (reduction potential)

34. **(d)** In the absence of electric field the ions in the solution move randomly due to thermal energy.

35. **(b)** $K = \frac{1}{R}\times \text{Cell constant}$

Cell constant $= K\times R$; $0.012\times 55 = 0.66\ cm^{-1}$.

36. **(b)** During charging of a lead storage battery, the reaction at the anode and cathode are

Anode: $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$

Cathode: $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

In both the reactions H_2SO_4 is regenerated.

37. **(c)** In the cell $Zn\,|\,Zn^{2+}\,||\,Cu^{2+}\,|\,Cu$ the negative electrode (anode) is *Zn*. In electrochemical cell representation anode is always written on left side while cathode on right side.

38. **(d)** $Cu + FeSO_4 \longrightarrow$ No reaction.

Because Cu has $E^\circ = 0.34\,volt$

And Fe has $E^\circ = -0.44$ volt.

39. **(b)** In hydrogen–oxygen fuel cell following reactions take place to create potential difference between two electrodes.

$$2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(l)} + 4e^-$$

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$$

Overall reaction $= 2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$

The net reaction is the same as burning (Combustion) of hydrogen to form water.

40. **(c)** Cell constant $= \dfrac{\text{Specific conductivity}}{\text{Observed conductance}}$

$$= \frac{0.002765}{1/R} = 0.002765 \times 400 = 1.106.$$

41. **(a)** $E_{cell} = -0.059 \log \dfrac{10^{-6}}{10^{-3}} = -0.059 \log 10^{-3}$

$$= -0.059 \times (-3) = 0.177V.$$

42. **(a)** When platinum electrodes are dipped in dilute solution H_2SO_4 than H_2 is evolved at cathode.

43. **(b)** The cell in which Cu and Zn roads are dipped in its solutions called Daniel cell.

44. **(c)** Velocities of both K^+ and NO_3^- are nearly the same in KNO_3 so it is used to make salt-bridge.

45. **(d)** The metal placed below in electrochemical series does not react with that metal salt solution which metal is placed above in series.

46. **(b)** Elements with lower reduction potential act as anode. His placed above Cu in electrochemical series so it has lesser reduction potential and thus act as anode and Cu act as cathode.

47. **(c)** $ClCH_2COONa + HCl \longrightarrow ClCH_2COOH + NaCl$

$$\lambda_{ClCH_2COONa} + \lambda_{HCl} = \lambda_{ClCH_2COOH} + \lambda_{NaCl}$$

$$224 + 203 = \lambda_{ClCH_2COOH} + 38.2$$

$$\lambda_{ClCH_2COOH} = 427 - 38.2 = 388.8\ ohm^{-1}cm^2gmeq^{-1}.$$

48. **(c)** A cation having highest reduction potential will be reduced first and so on. However, Mg^{2+} in aqueous solution will not be reduced $\left(E^0_{Mg^{2+}/Mg} < E_{H_2O/\frac{1}{2}H_2 + OH^-}\right)$. Instead water would be reduced in preference.

49. **(a)** No doubt Be is placed above Mg in the second group of periodic table but it is below Mg in electrochemical series.

50. **(d)** Mg lies above Cu in electrochemical series and hence *Cu* electrode acts as cathode

$$E^o_{cell} = E^o_{Cu^{++}/Cu} - E^o_{Mg^{++}/Mg}$$

$$2.70\ V = 0.34 - E^o_{Mg^{++}/Mg};$$

$$E^o_{Mg^{++}/Mg} = -2.36\ V$$

51. **(a)** Because H_2 has greater reduction potential so it reduced the Ag^+.

52. **(c)** $E = E^\circ - \dfrac{0.059}{n} \log \dfrac{[Zn^{++}]}{[Cu^{++}]}$

$$= 1.10 - \frac{0.059}{2} \log \frac{1}{0.1}$$

$$= 1.10 - 0.0295 \log 10 = 1.07\ volt.$$

53. **(b)** $E_1 = E_o - \dfrac{0.0591}{2} \log \dfrac{0.01}{1}$

$$= E_o + \frac{0.0591}{2} \times 2$$

$$E_2 = E_o - \frac{0.0591}{2} \log \frac{100}{0.01}$$

$$= E_o - \frac{0.0591}{2} \times 4$$

$\therefore$ $E_1 > E_2$.

54. **(a)** $Fe \longrightarrow Fe^{2+} + 2e$ (anode reaction)

$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$ (cathode reaction)

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

$Fe(OH)_2$ may be dehydrated to iron oxide FeO, or further oxidised to $Fe(OH)_3$ and then dehydrated to iron rust, Fe_2O_3

55. **(d)** $HgCl_2$ has corrosive action. It is highly poisonous. It sublimes on heating. It is, therefore, known as corrosive sublimate.

NCERT Exemplar Problems

More than One Answer

56. **(b, c)** Electrode of half-cell potential – 0.76 V serves as anode, Electrode of half-cell potential – 0.13 V serves as cathode

57. **(a, b)** $Cu|Cu^{2+}(0.01M)||Ag^+(0.1M)|Ag$, $Pt(H_2)|pH = 1||Zn^{2+}(0.01M)|Zn$

58. **(a, b, d)** The anode used is made of copper ore, Pure copper is deposited on the cathode, Concentrations of $CuSO_4$, solution remains constant during dissolution of Cu

59. **(b, c, d)** The amount of AgCl(s) precipitate in anodic compartment will decrease with the working of the cell, The concentration of $[Ag^+]$ is constant in anodic compartment with the working of cell,

$$E_{cell} = E°_{Ag^+/Ag} - E°_{Cl^-/AgCl/Ag} - \frac{0.059}{1}\log\frac{1}{[Cl^-]} \text{ anodic}$$

60. **(a, d)** Spontaneity of the cell reaction decreases, E_{cell} decreases, At equilibrium $Q = K_c$ and $E_{cell} = 0$

61. **(a, b)** The electrolysis of aqueous NaCl produces hydrogen gas at the cathode and chlorine gas at the anode, The electrolysis of a dilute solution of sodium fluoride produces oxygen gas at the anode and hydrogen gas at the cathode

62. **(b, c, d)** $E_{cell} = 0.0592 \log\frac{1}{[K_{sp}(AgCl)]^{½}}$

$E_{cell} = 0.0592 \times 5V'$, $E_{cell} = 296mV$

63. **(a, d)** Increasing pressure of $H_2(g)$ from 1 atm to 2 atm, Increasing KCl concentration in anodic compartment

64. **(a, b, c, d)** F_2 is the strongest oxidizing agent, Li is the strongest reducing agent, Li^+ is the weakest oxidizing agent, F_2 is highest reduction potential

65. **(b, c)** $Ce4^+$ can oxidize Fe^{2+}, Sn^{2+} will reduce Fe^{3+} to Fe^{2+}

66. **(b)** The reduction potential of Mg is less than that of water ($E° = -0.83V$). Hence their ions in the aqueous solution cannot be reduced instead water will be reduced

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

67. **(b)** Water is reduced at the cathode and oxidized at the anode instead of Na^+ and SO_4^{2-}.

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

Anode: $H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$.

68. **(a)** At cathode: $2H^+ + 2e \longrightarrow H_2$,

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

69. **(b)** $\underset{+1}{Na^+} + e^- \longrightarrow \underset{0}{Na}$, means oxidation number is decreased so the reaction is reduction.

70. **(d)** The degree of ionization depend upon the nature of the solute the size of the solute molecules and the concentration of the solution.

71. **(a)** The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed electrolytes. Electrolytic substances are classified as strong or weak according to how readily they dissociate into conducting ions. Acetic acid is a weak electrolyte. Glucose, ethanol and urea are non-electrolytes.

72. **(b)** $\frac{\text{Weight of Cu}}{\text{Weight of } H_2} = \frac{\text{Eq. weight of Cu}}{\text{Eq. weight. of H}}$

$\frac{\text{Weight of Cu}}{0.50} = \frac{63.6/2}{1}$

Weight of Cu = 15.9 gm.

73. **(a)** Wt. of Ag deposited = Eq. wt of Ag = 108 gm

Wt. of Ni deposited = Eq. wt. of Ni = 29.5 gm

Wt. of Cr deposited = Eq. wt. of Cr = 17.3 gm.

74. **(a)** $1/a = 0.5\,cm^{-1}, R = 50\,ohm$

$p = \frac{Ra}{1} = \frac{50}{0.5} = 100$

$\Lambda = k \times \frac{1000}{N} = \frac{1}{p} \times \frac{1000}{N} = \frac{1}{100} \times \frac{1000}{1}$

$10\,ohm^{-1}cm^2\,gm\,eq^{-1}$

75. **(b)** In solid state NaCl does not dissociate into ions so it does not conduct electricity.

Assertion and Reason

76. **(a)** K and Cs emit electrons on exposure to light hence, both are used in photoelectric cells. Here, assertion and reason are true and reason is a correct explanation.

77. **(b)** We know, $R \propto \frac{l}{A}$ or $R = \rho\left(\frac{l}{A}\right)$, where proportionality constant ρ is called resistivity. If l = 1m and A = $1m^2$, then R= ρ *i.e.* Resistance = Resistivity.

78. **(a)** According to Kohlrausch law, "Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte".

79. **(a)** $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

As the time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing. At the same time voltage of the cell keeps on decreasing. When there is no change in concentration of Cu^{2+} and Zn^{2+} ions, voltmeter gives zero reading and this state is known as equilibrium.

80. **(e)** A negative value of standard reduction potential means that oxidation takes place on this electrode with reference to SHE.

81. **(a)** A standard cell is one whose *e.m.f.* almost does not change with temperature.

82. **(a)** Zinc metal which has a more negative electrode potential than iron will provide electrons in preference of the iron, and therefore corrode first. Only when all the zinc has been oxidised does the iron start to rust.

83. **(a)** Both assertion and reason are true and reason is the correct explanation of assertion.

$$E^{o}_{Au^{3+}/Au} - E^{o}_{Ni/Ni^{2+}} = 1.50 - (-0.25) = 1.75\ V$$

84. **(a)** The nature of the cathode can affect the order of discharge of ions.

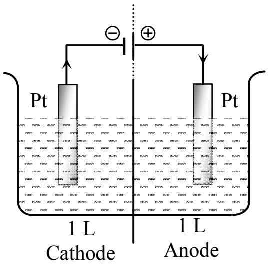
85. **(b)** 1 mole of silver =1g equivalent of silver

1 mole of copper = 2g equivalent of copper

We know from Faraday's law of electrolysis that "The weight of ion deposited on an electrode is directly proportional to the quantity of electricity passed".

Comprehension Based

86. **(c)**



Number of faradays passed during electrolysis

$$= \frac{It}{96500} = \frac{0.965 \times 200 \times 60}{96500} = 0.12$$

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

1 F electricity $\equiv$ 1mole H^{+} consumed

0.12 F electricity $\equiv$ 0.12 mole H^{+} consumed $\equiv$ 0.12 mole OH^{-} left in excess

After 200 min, $[OH^{-}] = \frac{0.12}{1} = 0.12\ M$

Now, these OH^{-} ions will react with $H_2PO_4^{-}$ ions ($\equiv$ acid).

$$\begin{array}{llll} H_2PO_4^{-} \quad + & OH^{-} \longrightarrow & HPO_4^{2-} & + \quad H_2O \\ 0.3\ M & 0.12\ M & 0.3\ M & \\ 0.18\ M\ (acid) & - & - & 0.42\ M\ (salt) \end{array}$$

It forms acidic buffer.

$$pH_{sol} = pK_a + \log\frac{[Salt]}{[Acid]} = 7.2 + \log\frac{0.42}{0.18} = 7.57$$

87. **(b)** At anode: $4OH^{-} \longrightarrow O_2 + 2H_2O + 4e^{-}$

1 F electricity $\equiv$ 1 mole OH^{-} consumed

0.12 F electricity $\equiv$ 1mole OH^{-} consumed $\equiv$ 0.12 mole H^{+} left in excess

After 200 min, $[H^{+}] = \frac{0.12}{1} = 0.12\ M$

Now, these H^{+} ions will react with $H_2PO_4^{-}$ ions ($\equiv$ Salt).

$$\begin{array}{lll} H_2PO_4^{2-} \quad + & H^{+} \longrightarrow & HPO_4^{-} \\ 0.3\ M & 0.12\ M & 0.3\ M \\ 0.18\ M\ (salt) & -- & 0.42\ M\ (acid) \end{array}$$

It also forms acidic buffer.

$$pH_{sol} = pK_a + \log\frac{[Salt]}{[Acid]} = 7.2 + \log\frac{0.18}{0.42} = 6.83$$

Note: In a buffer solution of $H_2PO_4^{-} | HPO_4^{2-}$, $H_2PO_4^{-}$ will act as an acid and HPO_4^{2-} will act as a salt and this will behave as an acidic buffer.

88. **(d)** Cathode $O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-}$

Cathode: $H_2 + 2OH^{-} \longrightarrow 2H_2O + 2e^{-}$

Cell reaction: $O_2 + 2H_2 \rightleftharpoons 2H_2O$

$$E^{-}_{cell} = 1.23 = 0.4 - (E^{-}_{red})_a = -0.83\ V$$

89. **(b)** $\Delta G^{-} = \Delta H^{-} - T\Delta S^{-}$ $-237.4 = -285.6 - 298\ \Delta S^{-}$

$\therefore$ $\Delta S^{-} = -160\ J\ K^{-1}$

90. **(d)** E_{cell} is independent of $[OH^{-}]$ in this case

91. **(c)** All are facts.

Match the Column

92. **(b)** A→2, B→1, C→4, D→3

(A) $E^{-}_{red\ of\ Cl_2|Cl^{-}} > E^{-}_{red\ of\ Cu^{2+}|Cu}$

So reduction of Cl_2 to Cl^{-} will occur at cathode and oxidation of Cu to Cu^{2+} will occur at anode.

So reverse reaction is possible. It means such reverse reaction can be made to occur in an electrolysis cell.

(B) As mentioned in (a), the reaction is feasible and hence can produce electricity in the galvanic cell.

(C) $2I^{-} + Cl_2 \longrightarrow I_2(violet) + 2Cl^{-}$

Since $E^{-}_{red\ of\ Cl_2|Cl^{-}} > E^{-}_{red\ of\ I_2|I^{-}}$

(D) $2Br^{-} + Cl_2 \longrightarrow Br_2(brown) + 2Cl^{-}$

Since $E^{-}_{red\ of\ Cl_2|Cl^{-}} > E^{-}_{red\ of\ Br_2|Br^{-}}$

93. **(a)** A→2, B→3, C→4, D→1

Refer Illustration 3.36.

All are concentration cells.

(A) $E_{cell} = -0.06(pH_c - pH_a) + 0.06V = -0.06(4 - pH_a)$

⇒ $pH_a = 5$

(B) $E_{cell} = -0.06(pH_c - pH_a)$ (Since pH of H_2O =7)

$0.18\,V = -0.06(pH_c - 7) \Rightarrow pH_c = 4$

(C) At anode, NH_4ClO_4 is a salt of W_B / S_A.

$$\text{Thus, } pH_a = \frac{1}{2}(pK_w - pK_b - \log c)$$

$$= \frac{1}{2}(14 - 4.74 - \log 0.2)$$

$$E_{cell} = -0.06(pH_c - pH_a)$$

$$-0.24 = -0.06(pH_c - 4.98) \Rightarrow pH_c = 8.98$$

(D) Since $[H_2SO_4] = [H^+]_a = 0.05 \times 2((n\,\text{factor})$

$$= 0.1\,N = 10^{-1}\,N\,PH_a = 1.$$

$$E_{cell} = -0.06(pH_c - pH_a)$$

$$-0.54\,V = -0.06(pH_c - 1) \Rightarrow pH_c = 10$$

94. **(a)** A→3, B→1, C→5, D→2, E→4

Also refer illustration 3.33.

(A) Refer illustration 3.33(g).

At anode: Mixture of W_A (CH_3COOH) and salt of W_A/S_B (CH_3COOK). It is an acidic buffer.

$$pH_a = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.74 + \log\frac{10^{-1}M}{10^{-2}M} = 5.74$$

At cathode: Mixture of W_B(CH_4OH) and salt of $W_B / S_A[(NH_4)_2SO_4]$. It is a basic buffer.

$$[\text{Salt}] = [(NH_4)_2SO_4] = 2\overset{\oplus}{N}H_4 = 0.2 \times 2 = 0.4N$$

$$(pOH)_c = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$= 4.74 + \log\frac{0.4}{0.2} = 5.04$$

$$pH_c = 14 - 5.04 = 8.96$$

$$E_{cell} = -0.06(pH_c - pH_a) = -0.06(8.96 - 5.74)$$

$$= -0.1932V$$

(B) Refer illustration 3.34 (d) also

$$E_{cell} = E^{-}_{cell} - \frac{0.06}{n_{cell}}\log\frac{[Cu^{2+}]_a}{[Cu^{2+}]_c}$$

$$= 0 - \frac{0.06}{n_{cell}}\log\frac{1M}{0.1M}$$

(C) Refer illustration 3.34 (f) also.

Anode: $2Cl^-\ (10^{-2}\ M) \longrightarrow Cl_2(g)\ (1\ atm) + 2e^-$

Cathode: $Cl_2(g)\ (2\ atm) + 2e^- \longrightarrow 2Cl^-\ (10^{-3}\ M)$

Cell reaction:

$$2Cl^-\ (10^{-2}\ M) + Cl_2(g)\ (2\ atm) \longrightarrow$$

$$2Cl^-\ (10^{-3}\ M) + Cl_2(g)\ (1\ atm)$$

$$E_{cell} = E^{-}_{cell} = 0 - \frac{0.06}{2}\log\frac{[Cl^-]_c^2 (p_{Cl_2})_a}{[Cl^-]_a^2 (p_{Cl_2})_c}$$

$$= 0 - 0.03\log\frac{(10^{-3})^2 \times 1\,atm}{(10^{-2})^2 \times 2\,atm}$$

$$= -0.03[\log 10^{-2} - \log 2]$$

$$= -0.03[-2 - 0.3]$$

$$= -0.03 \times (-2.3) = 0.069\,V$$

(D) At anode: W_B (NH_4OH)

$$pOH = \frac{1}{2}(pK_b - \log c) = \frac{1}{2}(4.74 - \log 10^{-2}) = 3.37$$

$$pH_a = 14 - 3.37 = 10.63$$

At cathode: Salt of

$W_B / W_A (CH_3COONH_4)$

$$pH_c = \frac{1}{2}(pK_w + pK_a - pK_b)$$

$$= \frac{1}{2}(14 + 4.74 - 4.74) = 7$$

$$E_{cell} = -0.06(pH_c - pH_a) = -0.06(7 - 10.63)$$

$$= (-0.06) \times (-3.63) = 0.2178\ V$$

(e → 4) Refer illustration 3.40.

$$E_{cell} = E_{SCE} - E_{glass}$$

$$= 0.24 - (E^{-}_{glass} - 0.06\,pH)$$

$$= 0.24\,V - (0.5 - 0.06 \times 6)$$

$$= 0.24\,V - 0.14\,V = 0.1V$$

95. **(c)** A→1, B→2, C→3, D→4

(A) Refer illustration 3.70(b).

$2F = 2\,Eq$ of OH^-

$$[OH^-] = \frac{2F}{100\,L} = 2 \times 10^{-2}\ N$$

$$pOH = 1.7, pH = 14 - 1.7 = 12.3$$

At anode: Ethane (g) $+ CO_2(g)$

At cathode: $H_2(g)$

(B) Refer illustration 3.70(c) also.

$1F = 1Eq \text{ of } OH^{-}$

$[OH^{-}] = \frac{1Eq}{10\text{ L}} = 10^{-1}\text{ N}$

$pOH = 1, pH = 14 - 1 = 13$

At anode: $H_2(g) + CO_2(g)$

At cathode: $H_2(g)$

(C) Refer illustration 3.70(a) (ii)

$IF = 1EqOH^{-} = 1Eq\ H^{+}$

So solution is neutral.

$\therefore$ PH =7

At anode: $O_2(g)$

At cathode: $H_2(g)$

(D) $CuF_2 \xrightarrow{\text{Electrolysis}} Cu^{2+} + 2F^{-}$

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

At anode: $H_2O \longrightarrow \frac{1}{2}O_2(g) + 2H^{+} + 2e^{-}$

(Since $E^{-}_{\text{oxid of } H_2O} > E^{-}_{\text{oxid of } F^{-}}$)

At anode: $1F = 1Eq\ H^{+}, [H^{+}] = \frac{Eq}{V_L} = \frac{1Eq}{10\text{ L}} = 10^{-1}\text{N}$

$\Rightarrow$ $pH = 1$

Integer

96. **(6)** $6e^{-} + BrO_3^{-}(aq) + 3H_2O \longrightarrow Br^{-}(aq) + 6\overline{O}H(aq)$

1 mol of $BrO_3^{-} = 6F = 6$ mol of electrons

97. **(10)** **(a)** $S_2O_3^{2-} \longrightarrow \frac{1}{2}S_4O_6^{2-} + e^{-}[1F]$

(b) $S_2O_3^{2-} + 5H_2O \longrightarrow 2HSO_4^{-} + 8H^{+} + 8e^{-}$

[1 mole = 8 F but 1 Eq = 1 F]

(c) $S_2O_3^{2-} + 10\overline{O}H \longrightarrow 2SO_4^{2-} + 5H_2O + 8e^{-}$

[1 mol = 8 F]

Total Faradays in (i), (ii),
and (iii) =1 + 1 + 8 = 10 F

98. **(3)** Ferric oxalate $[Fe_2(C_2O_4)_3 \longrightarrow 2Fe^{3+} + 3C_2O_4^{2-}]$

$3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^{-}$ $[Fe^{3+}$ does not change]

$\therefore$ 6 F = 1 mol of $Fe_2(C_2O_4)_3$

18 F = 3 mol of $Fe_2(Fe_2(C_2O_4)_3)$

99. **(3)** Discharging reaction:

$PbO_2 + 4H^{+} + SO_4^{2-} + \rightleftharpoons PbSO_4 + 2H_2O$

$$M_1 = \frac{\%\text{ by weight} \times 10 \times d}{Mw_2} = \frac{40 \times 1.225 \times 10}{98} = 5M$$

$$M_2 = \frac{\%\text{ by weight} \times 10 \times d}{Mw_2} = \frac{20 \times 10 \times 0.98}{98} = 2M$$

Change is molarities

$= M_1 - M_2 = 5 - 2 = 3M$

100. **(2)** $Al \longrightarrow Al^{3+} + 3e^{-}$

$\frac{4}{3}$ mol of $Al = \frac{4}{3} \times 3$ mol $e^{-} = 4\text{ mol } e^{-}$

$\Rightarrow$ $n = 4$

$\Delta G = -nFE \quad -772 \times 1000\text{ J} = -4 \times 96500 \times E$

$\therefore$ $E = \frac{772 \times 1000}{4 \times 96500} = 2.0\text{ V}$

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