Electrochemistry

Chapter at a Glance

1. **Electrochemistry:** Electrical decomposition of a compound into its constituents is called **electrolysis** and the branch of chemistry is called **electrochemistry**.
2. **Laws of Electrolysis:**

   Faraday's Laws of Electrolysis: The decomposition of electrolytes by an electric current is obeyed by the laws of electrolysis, firstly proposed by Faraday.

   (a) **First law:** First law of electrolysis states that the amount of any substance that is deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.

   $$m \ \alpha\ Q$$

   $$m = ZIt$$

   where
   m = mass of the deposited substance,
   Q = amount of electricity passed in coulombs
   Z = electrochemical constant
   I = current strength
   t = time

   (b) **Second law:** The second law of electrolysis states that when the same quantity of electricity flows through different electrolytes, the amount of different substances produced at the electrodes are directly proportional to their equivalent masses.

   $\frac{m_1}{m_2} = \frac{E_1}{E_2}$ where E_1 and E_2 are equivalent masses

   Relation between Faraday (F), Avogadro's Number (N_A) and charge on an electron (e):

   $$F = N_A e$$

   where F = 96,500 coulombs, $N_A = 6{\cdot}02 \times 10^{23}$, $e = 1{\cdot}602 \times 10^{-19}$ coulombs.
3. **Galvanic Cells:** A galvanic cell is a device in which the free energy of a physical or chemical process is converted into electrical energy.
4. **Electrode Potential:** The potential difference between a metal and a solution containing its own ions (in equilibrium) is called electrode potential of that metal or electrode.

   $$\begin{array}{ccc} \text{Metal — Electrons} & \rightleftharpoons & \text{Positively charged metal ions} \\ \downarrow & & \downarrow \\ \text{Are let on the metal} & & \text{Go into the solution} \\ \text{to make the metal} & & \text{to make the solution} \\ \text{negatively charged} & & \text{positively charged} \end{array}$$

   $$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxd.}$$

   or

   $$E^\circ_{cell} = E^\circ_{R} - E^\circ_{L}$$
5. **Factors Affecting the Magnitude of Electrode Potential:** The magnitude of electrode potential depends on the following factors:

   (a) Nature of metal or electrode: Extremely active metal has high electrode potential, while less active has lower electrode potential.

(b) Concentration of metal ions in solution.

(c) Temperature

6. **Electrochemical Series and Standard electrode potential:** The potential of an electrode at a given temperature depends upon the concentration of the ions in the surrounding solution.

   If the concentration of the ions is unity and the temperature is 25°C, the electrode potential is termed as standard electrode potential. Its value arranged in the decreasing order is called the electrochemical series. Thus the list of elements or ions arranged in the decreasing order of their standard reduction potential values is called electrochemical or e.m.f. series.

7. **Nernst Equation:** According to electromotive force and equilibrium constant of a cell reaction, the thermodynamic equation is:

$$-\Delta G = nFE$$

$$\boxed{nFE = -\Delta G^\circ - RT/nJ}$$

where

E = EMF of the cell in volts.

nF = Faradays *i.e.*, coulombs

nFE = electrical work done by the cell in volt coulombs or joules

$= nFE^\circ = RT/nJ$

The Nernst equation which is usually written in the form

$$\boxed{E = E^\circ - \frac{0{\cdot}0591}{n} \log \frac{[\text{Red}]}{[\text{Ox}]} \text{ at } 25^\circ\text{C}}$$

or

$$E_{el} = E^\circ_{el} + \frac{RT}{nF} \ln \frac{[\text{Oxidized state}]}{[\text{Reduced state}]}$$

8. **Electrolytic Conductance:**

   (a) Specific resistance or resistivity (S): The resistance (R) of any conductor is directly proportional to its length (l) and inversely proportional to its cross-sectional area (A), *i.e.*,

$$R \propto \frac{l}{A}$$

or

$$R = S\frac{l}{A}$$

   Here S is a constant which depends on the nature of the material of the conductor and is called specific resistance or resistivity of the material.

   (b) Specific Conductance (A_{sp}): The reciprocal of specific resistance is called specific conductance.

$$A_{sp} = \frac{l}{S}$$

$$A_{sp} = \frac{l}{RA}$$

$$\because \quad R = s = \frac{l}{A}$$

9. **Corrosion:** It may be defined as the process of slow conversion of metals into their desirable compounds (usually oxides) by reaction with moisture and other gases present in the atmosphere.

   E.g., Silver gets tarnished, iron rusts, lead loses its lusture etc.

   Factors which affect corrosion:

   (a) Reactivity of the metal

   (b) Presence of impurities

   (c) Air and moisture

   (d) Strains in metals

   (e) Presence of electrolytes.

10. **Batteries:** The term battery is used to represent the arrangement of two or more galvanic cells connected in series. The galvanic cell can be broadly divided into two categories:

    (a) Primary cells: These cells cannot be recharged or used again *e.g.*, dry cell, mercury cell etc.

(b) **Secondary cells:** This type of cell can be recharged by passing direct current through them and can be used again. E.*g*., lead storage battery, nickel-cadmium storage cell etc.

11. Fuel Cells: These cells convert chemical energy of a fuel directly into electrical energy. These are voltaic cells in which the fuel such as H_2, CO, CH_4, C_3H_8 etc. are used to generate electricity. Examples. Bacon cell (also known as $H_2—O_2$ fuel cell, propane-oxygen, fuel cell, methanol oxygen fuel cell etc.

Advantages of fuel cells:

(a) Pollution free working (b) Higher efficiency

(c) Continuous source of energy.

Multiple choice questions

1. Electrolysis involves oxidation and reduction respectively at :

(a) Anode and cathode

(b) Cathode and anode

(c) At both the electrode

(d) None of these

2. All galvanic cell do not contain:

(a) A cathode (b) An anode

(c) Ions (d) A porous plate

3. The unit of equivalent conductance is :

(a) $ohm^{-1}\ cm^2\ equiv^{-1}$

(b) $ohm^{-1}\ cm^2\ gm^{-1}$

(c) $ohm\ cm^2\ equiv^{-1}$

(d) $ohm^{-1}\ mole^{-1}$

4. Conductivity of a solution is directly proportional to :

(a) Dilution (b) Number of ions

(c) Current density

(d) Volume of the solution

5. A current liberates 0·50 g of hydrogen in 2 hours. The weight of copper (at. wt. = 63·5) deposited at the same time by the same current through copper sulphate solution is:

(a) 63·5 g (b) 31·8 g

(c) 15·9 g (d) 15·5 g

6. Electrochemical equivalent is the amount of substance which gets deposited from its solution on passing electrical charge equal to:

(a) 96,500 coulomb (b) 1 coulomb

(c) 60 coulomb (d) 965 coulomb

7. Which of the following cells can convert chemical energy of H_2 and O_2 directly into electrical energy?

(a) Mercury cell (b) Daniel cell

(c) Fuel cell (d) Lead storage cell

8. When lead storage battery discharges?

(a) SO_2 is evolved

(b) $PbSO_4$ is consumed

(c) Lead is formed

(d) Sulphuric acid is consumed

9. When zinc granule is dipped into copper sulphate solution, copper is precipitated because:

(a) Both, copper and zinc have a positive reduction potential

(b) Reduction potential of copper is higher than that of zinc

(c) Reduction potential of zinc is higher than that of copper

(d) Both, zinc and copper have a negative reduction potential

10. The reaction is spontaneous if the cell potential is :

(a) Positive (b) Negative

(c) Zero (d) Infinite

11. The quantity of electricity required to deposit 1·15 g of sodium from molten NaCl (Na = 23, Cl = 35·5) is :

(a) 1 F (b) 0·5 F

(c) 0.05 F (d) 1·5 F

12. 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) Velocity of both K^+ and NO_3^- are nearly the same

(d) KNO_3 is highly soluble in water

13. The number of Faradays required to reduce one mol of Cu^{2+} to metallic copper is :

(a) One (b) Two

(c) Three (d) Four

14. On electrolysis of dilute sulphuric acid using platinum electrodes, the product obtained at the anode will be

(a) Hydrogen (b) Oxygen
(c) Hydrogen sulphide
(d) Sulphur dioxide

15. When heating one end of a metal plate, the other end gets hot because of
(a) The resistance of the metal
(b) Mobility of atoms in the metal
(c) Energised electrons moving to the other end
(d) Minor perturbation in the energy of atoms.

16. The weight of silver displaced by a quantity of electricity which displaces 5600ml of O_2 at STP will be:
(a) 5.4g (b) 10.8g
(c) 54.9g (d) 108.0g

17. Which of the following statements regarding fuel cells is false?
(a) Because of continuous supply, fuel cells never become dead
(b) They do not cause pollution
(c) Fuel cells have 100% efficiency practically
(d) The cost of catalysts needed for the electrode reactions is high

18. The standard electrode potentials of four elements A, B, C and D are – 3·05, 1·66, – 0·40 and 0.80 volts respectively. The highest chemical activity will be shown by :
(a) A (b) B
(c) C (d) D

19. Galvanised iron sheets are coated with:
(a) Carbon (b) Copper
(c) Zinc (d) Nickel

20. Which of the following element act as inert electrode
(a) Cu (b) Ag
(c) Pt (d) None

21. On dilution, the specific conductance of a solution:
(a) Remains unchanged
(b) Increases
(c) Decreases
(d) First increases then decreases

22. The standard reduction potential values of three metallic cations X, Y and Z are 0.52 V, – 3.03 V and – 1.18 V respectively. The order of reducing power of the corresponding metals is:
(a) Y > Z > X (b) X > Y > Z
(c) Z > Y > X (d) Z > X > Y

23. When zinc granule is dipped into copper sulphate solution, copper is precipitated because:
(a) Both copper and zinc have a positive reduction potential.
(b) Both copper and zinc have a negative reduction potential.
(c) Reduction potential of zinc is higher than that of copper.
(d) Reduction potential of copper is higher than that of zinc.

Fill in the blanks

24. The unit of conductance is .... and that of specific conductance is ………… A galvanic cell stops after some time because ....
(a) ohm^{-1}, ohm^{-1} cm^{-1}, potential difference becomes zero
(b) ohm, ohm^{-1} $cm^{-1}eq^{-1}$, battery discharges
(c) $ohm^{-1}cm^{-1}$, $ohm^{-1}eq^{-1}$, potential difference becomes zero
(d) ohm^{-1}, $ohm^{-1}eq^{-1}$, battery discharges

25. Equivalent conductivity is the conducting power of all the ions furnished by one .... of an electrolyte present in a definite .... of the solution. In a Daniel cell the copper vessel serves as ....
(a) Equivalent weight, concentration, anode
(b) Gram equivalent, volume, cathode
(c) Mole, volume, anode
(d) Gram equivalent, Concentration, Pt electrode

26. In a galvanic cell, electrons flow from .... to .... through the connecting wires. A device in which chemical energy of a fuel is directly converted into electrical energy is called ....
(a) Anode, Pt electrode, galvanic cells
(b) Pt electrode, cathode, fuel cells
(c) Cathode, anode, Daniel cells
(d) Anode, cathode, fuel cells

27. The molar conductance of a solution .... with dilution, while its specific conductance .... with dilution. The electrode at which there is acceptance of electrons is called ....
(a) Decreases, increases, anode
(b) Remains same, decreases, Pt electrode
(c) Increases, decreases, cathode
(d) Decreases, remains same, anode

28. The more .... is standard reduction potential of a metal, the .... is its ability to displace hydrogen from acids. In representation of an electrochemical cell, the cathode is written on ....

(a) Positive, less, right hand side

(b) Negative, greater, right hand side

(c) Greater, less, left hand side

(d) Positive, more, right hand side

29. Zinc can displace .... from $CuSO_4$ solution, but cannot displace .... from $MgSO_4$ solution. The conductance of a solution placed between two opposite faces of a cm^3 is called ....

(a) Copper, magnesium, specific conductance

(b) Magnesium, zinc, conductance

(c) Magnesium, copper, molar conductance

(d) Copper, sulphate, molar conductance

30. .... the reduction potential .... is the oxidizing agent. The molar conductance (Λ_m) of a solution is related to specific conductance (k) by the relation ....

(a) Lower, higher, $R = \rho \frac{L}{A}$

(b) Stronger, lower, $\mu = kV$

(c) Stronger , lower, $\mu = kV$

(d) Higher, stronger, $\wedge_m = \frac{\kappa \times 10^3}{M}$

31. The equivalent conductance of a solution .... with decrease in concentration of the electrolyte in the solution. Specific conductance of an electrolyte solution .... with increase in dilution. The resistance of a solution is measured with the help of ....

(a) Increases, remains same, multimeter

(b) Decreases, Increases, ammeter

(c) Increases, decreases, multimeter

(d) Decreases, Increases, Ammeter

32. Strong electrolytes give almost linear plot of Λ_m versus .... The E° value of a NHE is ....

(a) $\sqrt{C}$, Zero

(b) Concentration, one

(c) Time, two

(d) Concentration, Three

33. The solution of sugar in water is .... conductor of electricity. In a galvanised iron, the iron is coated with a layer of .... metal

(a) Bad, zinc

(b) Good, copper

(c) Bad, less, chromium

(d) Good, Silver

Match the following

34. Match the columns:

Column I	Column II
1 Molar conductivity	(p) Siemen cm^{-1}
2 Dry cell	(q) Nernst equation
3 Zn/Zn^{2+} (0·1M) || Zn^{2+} (0·5M)/Zn	(r) Maximum work obtainable from cell
4 Specific conductivity	(s) Electrochemical cells
5 $E = E° + \frac{0 \cdot 59}{n} \log \frac{[M^{n+}]}{[M]}$	(t) ohm^{-1} cm^2 mol^{-1}
6 Nernst Equation	(u) Primary cell
7 E° cell	(v) Concentration cell
8 96500 C mol^{-1}	(w) Faraday's constant

(a) 1-(w), 2-(u), 3-(s), 4-(q), 5-(p), 6-(v), 7-(r), 8-(t)

(b) 1-(u), 2-(t), 3-(q), 4-(p), 5-(v), 6-(s), 7-(w), 8-(r)

(c) 1-(s), 2-(w), 3-(r), 4-(p), 5-(q), 6-(t), 7-(v), 8-(u)

(d) 1-(t), 2-(u), 3-(v), 4-(p), 5-(q), 6-(s), 7-(r), 8-(w)

35. Match the columns:

Column I	Column II
1 Dry cell	(p) Potassium hydroxide
2 Nickel-cadmium cell	(q) Aqueous H_2SO_4
3 Lead storage cell	(r) Zinc chloride

(a) 1-(r), 2-(p), 3-(q)

(b) 1-(q), 2-(r), 3-(p)

(c) 1-(p), 2-(r), 3-(q)

(d) 1-(p), 2-(q), 3-(r)

Numerical based questions

36. The standard electrode potentials of $Pb|Pb^{+2}$ and $Pt|I^-|I_2$ are $-0 \cdot 126$ and $0 \cdot 536$ volt respectively. When a galvanic cell is constructed using 0·1 molar concentrations of the respective ions Pt is found to be cathode. What is the voltage generated in the cell ?

(a) 0.6505 V (b) 0.4505 V

(c) 0.7505 V (d) 0.5505 V

37. Calculate the standard cell potential of galvanic cell in which the following reaction takes place :

$$2\,\mathrm{Cr\,(s)} + 3\mathrm{Cd}^{2+}_{(aq)} \longrightarrow 2\mathrm{Cr}^{3+}_{(aq)} + 3\mathrm{Cd}_{(s)}$$

Given : $E^\circ_{Cr^{3+}/Cr} = -\,0{\cdot}74$ V, $E^\circ_{Cd^{2+}/Cd} = -\,0{\cdot}4$V.

Also, calculate Δ_rG° and Equilibrium constant of the reaction.

(a) Antilog 24·5014 (b) Antilog 34·5014

(c) Antilog 54·5014 (d) Antilog 36·5014

38. A cell is constructed by dipping a zinc rod in 0·1 M zinc nitrate solution and a lead rod in 0·2 M lead nitrate solution.

$$E^{\circ}_{Pb^{2+}/Pb} = -\,0{\cdot}13 \text{ V and } E^{\circ}_{Zn^{2+}/Zn} = -\,0{\cdot}76 \text{ V.}$$

(i) Write the spontaneous cell reaction.

(ii) Calculate standard emf and emf of the cell.

(a) Zn/Zn^{2+} || Pb^{2+}/Pb, 0·638 V

(b) Cr| Cr^{3+} || Fe^{2+} | Fe , 0.611 V

(c) Zn/Zn^{2+} || Pb^{2+}/Pb, 0.452 V

(d) Cr| Cr^{3+} || Fe^{2+} | Fe , 0.821 V

39. (i) Calculate the e.m.f., of the cell

Cr(s) | Cr^{3+} (0·1 M) || Fe^{2+} (0·01 M) | Fe (s)

$E^\circ_{Cr^{+3}/Cr} = -\,0{\cdot}75$, $E^\circ_{Fe^{2+}/Fe} = -\,0{\cdot}45$ V

(ii) Calculate the emf :

Al/Al^{3+} (0·01 M) // Fe^{2+} (0·02M) /Fe

Given :

$E^\circ_{Al^{3+}/Al} = -\,1{\cdot}66$ V

$E^\circ_{Fe^{2+}/Fe} = -\,0{\cdot}44$ V

(iii) Calculate the e.m.f., of the following cell.

$Mg_{(s)}$ | Mg^{2+} (0·001 M) || Cu^{2+} (0·0001 M) | $Cu_{(s)}$

$E^\circ_{Cu^{2+}/Cu} = 0{\cdot}337$ V, $E^\circ_{Mg^{2+}/Mg} = -2{\cdot}37$ V

(a) 0·1607 V, 1·309 V, 2·5775 V

(b) 0·6607 V, 1·309 V, 2·4775 V

(c) 0·2607 V, 1·209 V, 2·6775 V

(d) 0·2637 V, 1·249 V, 2·7875 V

40. Consider the following cell reaction at 298 K :

$$2Ag^+ + Cd \rightarrow 2\,Ag + Cd^{2+}$$

The standard reduction potential (E°) for Ag^+/Ag and Cd^{2+}/Cd are 0·80 V and – 0·40 V respectively:

(i) Write the cell representation.

(ii) What will be the emf of the cell if the concentration of Cd^{2+} is 0·1 M and that of Ag^+ is 0·2 M ?

(iii) Will the cell work spontaneously for the condition given in (ii) above ?

(a) Cd | $Cd^{2+}_{(0.1M)}$ | 2Ag, 1·1882177 V, –229.32kJ

(b) Cd | $Cd^{2+}_{(0.1M)}$ || $2Ag^{2+}_{(0.1M)}$ | 2Ag, 2·188 V, –329.32kJ

(c) Cd | $Cd^{2+}_{(0.1M)}$ || $2Ag^{2+}_{(0.2M)}$ | 2Ag, 3.214 V, –536.32kJ

(d) Cd | $Cd^{2+}_{(0.1M)}$ || $2Ag^{2+}_{(0.2M)}$ | 2Ag, 5·188 V, –389.32kJ

41. Chromium metal can be plated out from an acidic solution containing CrO_3, according to the following equation :

$$CrO_3(aq.) + 6H^+(aq.) + 6e^- \longrightarrow Cr(s) + 3H_2O$$

(i) Calculate, how many gram of Cr (At. wt. 52) will be plated out by passing 24000 C of electricity?

(ii) If a current of 24 amp is being used, how long will it take to plate out the amount of Cr calculated in part (i).

(a) 3.64 g of Cr, 100 sec

(b) 5·15 g of Cr, 1000 sec

(c) 2·155 g of Cr, 1000 sec

(d) 6·155 g of Cr, 100 sec

42. (i) Calculate the mass of silver deposited at cathode when a current of 2 amperes is passed through a solution of $AgNO_3$ for 15 minutes.(At. wt. of Ag = 108, 1 F = 96,500 C)*

(ii) Calculate the e.m.f. and ΔG for the cell reaction at 298 K:*

$Mg_{(s)}$ /$Mg^{2+}_{(0{\cdot}1\,M)}$//$Cu^{2+}_{(0{\cdot}01M)}$/$Cu_{(s)}$

Given $E^0_{cell} = 2{\cdot}71$ V

1 F = 96,500 C

(a) 6.14 g of Ag, – 417·36 kJ mol^{-1}

(b) 3·214 g of Ag, – 417·226 kJ mol^{-1}

(c) 3.14 g of Ag, – 317·26 kJ mol^{-1}

(d) 2·014 g of Ag, – 517·326 kJ mol^{-1}

43. (i) If a current of 0·5 ampere flows through metallic wire for two hours, then how many electrons flow through the wires ?

(ii) Consider the reaction:

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

What is the quantity of electricity in Coulomb's needed to reduce 1 mol of $Cr_2O_7^{2-}$?

(iii) The conductivity of 0·20 M solution of KCl at 298 K is 0·0248 S cm^{-1}. Calculate its molar conductivity.

(a) 5.464×10^{22} electrons, 248000 C, 224 S cm^2 mol^{-1}

(b) $4{\cdot}466 \times 10^{22}$ electrons, 478000 C, 324 S cm^2 mol^{-1}

(c) $2{\cdot}246 \times 10^{22}$ electrons, 579000 C, 124 S cm^2 mol^{-1}

(d) $3{\cdot}426 \times 10^{22}$ electrons, 679000 C, 134 S cm^2 mol^{-1}

44. A 0·05 M NH_4OH solution offers the resistance of 50 ohm to a conductivity cell at 298 K. If the cell constant is 0·50 cm^{-1} and molar conductance of NH_4OH at infinite dilution is 471·4 ohm^{-1} cm^2 mol^{-1}, calculate :

(i) Specific conductance

(ii) Molar conductance

(iii) Degree of dissociation

(a) 0·21 ohm^{-1} cm^{-1}, 400 mol^{-1} ohm^{-1} cm^{-1}, 0·524

(b) 0·01 ohm^{-1} cm^{-1}, 200 mol^{-1} ohm^{-1} cm^{-1}, 0·424

(c) 0·02 ohm^{-1} cm^{-1}, 220 mol^{-1} ohm^{-1} cm^{-1}, 0·224

(d) 0·201 ohm^{-1} cm^{-1}, 230 mol^{-1} ohm^{-1} cm^{-1}, 0·334

45. The specific conductance of a 0·01 M solution of acetic acid at 298K is $1{\cdot}65 \times 10^{-4}$ ohm^{-1} cm^{-1}. The molar conductance at infinite dilution for H^+ ion and CH_3COO^- ion are 349·1 ohm^{-1} cm^2 mol^{-1} and 40·9 ohm^{-1} cm^2 mol^{-1} respectively. Calculate :

(i) Molar conductance of the solution.

(ii) Degree of dissociation of CH_3COOH.

(iii) Dissociation constant for acetic acid.

(a) 16·5 ohm^{-1} cm^2 mol^{-1}, 0·0423, $1{\cdot}86 \times 10^{-5}$

(b) 26·5 ohm^{-1} cm^2 mol^{-1}, 0·0223, $1{\cdot}76 \times 10^{-5}$

(c) 15.5 ohm^{-1} cm^2 mol^{-1}, 0·0323, $2{\cdot}86 \times 10^{-5}$

(d) 26·5 ohm^{-1} cm^2 mol^{-1}, 0·0523, $3{\cdot}86 \times 10^{-5}$

46. When two Faradays of electricity is passed through an aqueous solution of $CuSO_4$ and an aqueous solution of $AgNO_3$. (Atomic weight of Cu = 63.5 g mol^{-1}, Ag = 108 g mol^{-1})

(i) The mass of copper deposited at the anode is :

(a) 127.02 g (b) 63.50 g

(c) 31.75 g (d) 15.87 g

(ii) The mass of silver deposited at the cathode is :

(a) 54 g (b) 108 g

(c) 216 g (d) 270 g

47. The limiting molar conductivities (Λ^{∞}_{m}) for NaCl, KBr and KCl are 126, 152 and 150 ohm^{-1} cm^2 mol^{-1} respectively.

(i) The molar conductivity at infinite dilution for NaBr is :

(a) 128 ohm^{-1} cm^2 mol^{-1}

(b) 176 ohm^{-1} cm^2 mol^{-1}

(c) 278 ohm^{-1} cm^2 mol^{-1}

(d) 302 ohm^{-1} cm^2 mol^{-1}

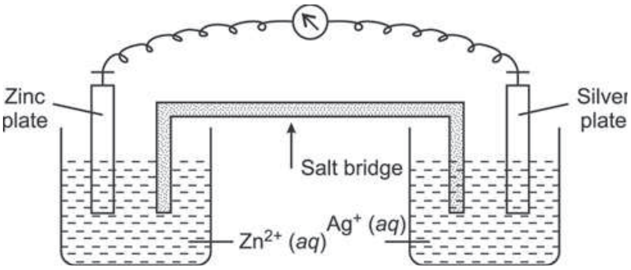
(ii) The law applied to determine the molar conductivity of infinite dilution is known as :

(a) Faraday's Law (b) Avogadro's Law

(c) Kohlrausch's Law (d) Ohm's Law

Structure based questions

48. Consider the figure given below and the answer the question (i) to (v).



(i) Write the direction of electron flow.

(ii) Is silver plate anode or cathode ?

(iii) What will happen if salt bridge is removed ?

(iv) When will the cell stop functioning ?

(v) How will concentration of Zn^{2+} ion and Ag^+ ions be affected when the cell functions ?

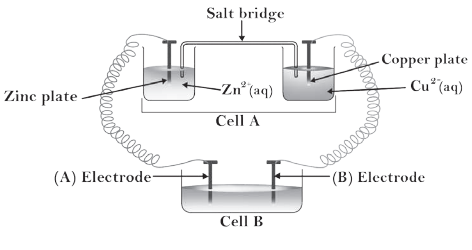
(a) Zn to Ag, cathode, stop functioning, $E_{cell} = 0$, Conc. of Zn^{2+} and Ag^+ ions will increase and decrease respectively.

(b) Ag to Zn, Anode, electrons will move at faster rate, $E_{cell} > 0$, Conc of Zn^{2+} and Ag^+ ions will decrease and increase respectively.

(c) Anode to Cathode, Cathode, electrons will move at slower rate, $E_{cell} \neq 0$, Conc of Zn^{2+} and Ag+ will decrease remain same.

(d) Zn to Ag, Cathode, electrons will move at faster rate, $E_{cell} > 0$, Conc. of Zn^{2+} will increase and Ag+ will remains same.

49. Consider the Fig. and answer the following questions.



(i) Cell 'A' has E_{Cell} = 2V and Cell 'B' has E_{Cell} =

1.1V which of the two cells 'A' or 'B' will act as an electrolytic cell. Which electrode reactions will occur in this cell?

(ii) If cell 'A' has $E_{Cell} = 0.5V$ and cell 'B' has $E_{Cell} = 1.1V$ then what will be the reactions at anode and cathode?

(a) (i) At Cathode, $Zn^{2+} + 2e^- \longrightarrow Zn(s)$
At Anode $Cu(s) \longrightarrow Cu^{2+} + 2e$
(ii) At Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$
At Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

(b) (i) At Anode, $Zn^{2+} + 2e^- \longrightarrow Zn(s)$
At Cathode $Cu(s) \longrightarrow Cu^{2+} + 2e$
(ii) At Cathode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$
At Anode: $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

Assertion and Reason based questions

Directions: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

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

50. **Assertion:** In cell, current stops flowing when $E_{cell} = 0$.

Reason: Equilibrium of the cell reaction is attained.

51. **Assertion:** The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion.

Reason: It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron.

52. **Assertion:** Molar conductivity increases with decrease in concentration of solution.

Reason: Conductivity always decreases with decrease in concentration of solution.

53. **Assertion:** Zinc can be used while copper cannot be used in the recovery of Ag from the complex $[Ag(CN)_2]^-$.

Reason: Zinc is a powerful reducing agent than copper.

54. **Assertion:** The resistivity for a substance is its resistance when it is one meter long and its area of cross section is one square meter.

Reason: The SI units of resistivity is ohm metre (Ωm).

55. **Assertion:** On increasing dilution, the specific conductance keep on increasing.

Reason: On increasing dilution, degree of ionisation of weak electrolyte increases and molality of ions also increases.

56. **Assertion:** The conductivity of electrolytic solutions increases with increase of temperature.

Reason: Electronic conductance of metals decreases with increase of temperature.

57. **Assertion:** During electrolysis of $CuSO_4(aq)$ using copper electrodes, copper is dissolved at anode and deposited at cathode.

Reason: Oxidation takes place at anode and reduction at cathode.

58. **Assertion:** To obtain maximum work from a galvanic cell charge has to be passed reversibly.

Reason: The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy.

59. **Assertion:** Conductivity of an electrolyte increases with decrease in concentration.

Reason: Number of ions per unit volume decreases on dilution.

Answers

Multiple choice questions

1. (a) Anode and cathode

Explanation: An electrochemical cell consist of two conductive electrodes, *i.e.*, anode and cathode. In the process of electrolysis, oxidation and reduction occurs at anode and cathode respectively.

2. (d) A porous plate

Explanation: A galvanic cell is an electrochemical cell that converts the chemical energy of spontaneous oxidation-reduction reactions into electrical energy. Majority of the galvanic cells contain following components:

- Anode – Where oxidation occurs
- Cathode – Where reduction occurs.

- Salt bridge – Electrolytes to complete the circuit in a galvanic cell and provide ions.
- Half-cells – Where oxidation and reduction reactions are separated into compartments.
- External circuit – Required to conducts the flow of electrons between electrodes

Therefore, all galvanic cells do not contain a porous plate.

3. (a) $\text{ohm}^{-1}\ \text{cm}^{2}\ \text{equiv}^{-1}$

Explanation: Equivalent conductance is defined as the conductance of an electrolyte solution containing one gram equivalent of the electrolyte. It is equal to the product of specific conductance (*k*) of the solution and the volume (V) of the solution that contains one gram equivalent of the electrolyte.

$$\lambda = k \times V$$

Let us consider the V cm^2 of solution containing one equivalent of an electrolyte. Its conductance is equal to equivalent conductance, Λ.

Also we know that the conductance shown by 1 cm^3 solution (between two electrodes of cross sectional area 1 cm^2 and separated by a distance of 1 cm) containing this electrolyte is called specific conductance, *k*.

i.e., the conductance of V cm^3 .... Λ

the conductance of 1 cm^3 .... κ

Therefore :

$\lambda = \kappa, V$ .... equation (3)

We know that the normally (N) of a solution is given by the equation:

$$N = \frac{n_e}{V(\text{in } cc)} \times 1000$$

For above electrolytic solution, no. of equivalent $n_e = 1$.

Hence :

$$V\ (\text{in cc}) = \frac{1000}{N}$$

By substituting the above value in the equation (3), we can now write :

$$\lambda = \kappa \frac{1000}{N}$$

Units of A :

$$= \frac{\text{Ohm}^{-1}\ \text{cm}^{-1}}{\text{equivalents cm}^{-3}}$$

$= \text{cm}^2, \text{ohm}^{-1}, \text{equiv}^{-1} = \text{cm}^2, \text{ohm}, \text{equiv}^{-1}$

Hence, the required equivalent conductance unit is $\text{ohm}^{-1}\ \text{cm}^2\ \text{equi}^1$.

4. (b) Number of ions

Explanation: Conductivity is defined as the ability of an aqueous solution to transfer an electrical current. The current is carried by ions present in the solution, and therefore the conductivity increases with the increase in the concentration of ions present in solution, their mobility, and temperature. Hence, conductivity of a solution is directly proportional to the number of ions.

5. (c) 15·9 g

Explanation: Hydrogen ion will accept an electron and get neutralised as follows:

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

Now, the formula to calculate the mole ratio of hydrogen can be given as,

Mole ratio of hydrogen

$$= \frac{\text{moles of hydrogen produced in the half reaction}}{\text{moles of electrons required in the half reaction}}$$

$$\text{Mole ratio of hydrogen} = \frac{1}{2}$$

Similarly, copper ion will accept electron and get neutralised as follows:

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

Now, the formula to calculate the mole ratio of copper can be given as,

$$\text{moler ratio of Cu} = \frac{\text{moles of Cu produced in the half reaction}}{\text{Moles of electrons required in the half reaction}}$$

$$\text{Mole ratio of Cu} = \frac{1}{2}$$

Now,

$$\frac{\text{Moles of hydrogen produced}}{\text{moles of copper produced}} = \frac{\text{mole ratio of hydrogen half reaction}}{\text{mole ratio of copper half reaction}}$$

$$\frac{0.50/2}{\text{moles of copper produced}} = \frac{1/2}{1/2}$$

moles of copper produced = 0.25

On multiplying the moles of copper produced with its atomic weight (63.5 g), we will get the deposited weight of copper,

Mass of copper deposited = 0.25 × 63.5 = 15.9 g.

Hence, the mass of copper deposited is 15.9 g

6. (a) 96,500 coulomb

Explanation: Electrochemical equivalent is the amount of substance which gets deposited from its solution on passing electrical charge equal to 96,500 coulomb. It is important to note that

96500 coulomb corresponds to the charge on one mole of electrons. It is called as electrochemical equivalent.

7. (c) Fuel cell

Explanation: Fuel cells can convert chemical energy of H_2 and O_2 directly into electrical energy. In $H_2 - O_2$ fuel cell, hydrogen acts as a fuel and oxygen acts as an oxidising agent. In fuel cell, the energy of the combustion of hydrogen is converted into electrical energy.

8. (d) Sulphuric acid is consumed

Explanation: In a lead storage battery, the electrodes of the cells consist of lead grids and dilute sulphuric acid H_2SO_4 acts as the electrolyte. During the discharging of the battery or delivering a current, the lead at the anode is oxidized and sulphuric acid is consumed and water is produced. The overall reaction during discharging is the reaction between lead, lead dioxide and sulphuric acid to produce water and lead sulphate. The overall reaction can be represented as:

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

9. (b) Reduction potential of copper is higher than that of zinc

Explanation: When zinc granule is dipped into copper sulphate solution, copper is precipitated because both copper and zinc have a positive reduction potential and reduction potential of copper is higher than that of zinc.

10. (a) Positive

Explanation: The reaction is spontaneous if the cell potential is positive. This can be explained as follows:

The change in Gibb's free energy is related to the emf of a redox reaction given by the equation:

$$\Delta G = -nFE_{cell}$$

where ΔG = change in Gibbs free energy

n = number of electrons transferred

F = Faraday's constant = 96,485 J/V mol

E = emf under nonstandard conditions

Now, for a spontaneous reaction we know that change in Gibb's free energy is,

$$\Delta G = -ve$$

$$\therefore \quad E_{cell} = +ve \qquad (\because n, \text{F are constant})$$

Hence, when the potential of the cell is positive the reaction will be spontaneous.

11. (c) 0.05 F

Explanation: Na^+ ion will accept an electron and get neutralised as follows

$$Na^+ + e^- \rightarrow Na$$

Number of moles of sodium can be obtained by dividing the mass of deposited sodium, i.e., 1.15 g to its atomic mass which is 23

$$\text{Number of moles of Na} = \frac{1.15}{23} = 0.05 \text{ moles.}$$

Thus, deposition of 1 mole Na will require 1 mole of electrons which is equal to 1 faraday of electricity. Hence, the deposition of 1.15 moles of Na will require 0.05 moles of electrons which is equal to 0.05 faraday of electricity.

12. (c) Velocity of both K^+ and NO_3^- are nearly the same

Explanation: If the velocities of ions are not same then the ions would not be able to neutralize the charge equally in both half cells. Therefore, for a good salt bridge the velocities of ions should be same. Saturated solution of KNO_3 is used to make salt bridge because velocity of both K^+ and NO_3^- are nearly the same. Therefore, saturated solution of KNO_3 makes a good salt bridge.

13. (b) Two

Explanation: Faraday's First Law of Electrolysis states that the chemical deposition due to the flow of current through an electrolyte is directly proportional to the quantity of electricity (coulombs) passed through it.

The reduction of one mole of Cu^{2+} to Cu can be represented as:

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

Since in the reduction of one mole of Cu^{2+}, two moles of electrons are required thus the amount of charge required is 2F.

14. (b) Oxygen

Explanation: The dissociation of water and sulphuric acid can be represented as:

Dissociation of water,

$H_2O \rightarrow H^+ (aq) + OH^- (aq)$

Dissociation of sulphuric acid,

$H_2SO_4 \rightarrow 2H+ (aq) + SO_4^{-2} (aq)$

The redox reaction showing oxidation and reduction at anode and cathode can be represented as:

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

At Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Thus, on electrolysis of dilute sulphuric acid using platinum electrodes, the product obtained at the anode will be oxygen.

15. (c) Energised electrons moving to the other end

Explanation: On heating one end of a piece of metal plate, the other end becomes hot because of energised electrons moving to the other hand. These molecules during vibration collide with the neighbouring molecules and transfer part of their energy to the neighbouring molecules.

16. (d) 108.0g

Explanation:

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

or $$\frac{W_{Ag}}{108} = \frac{\frac{5600}{22400} \times 32}{8}$$

or $$\frac{W_{Ag}}{108} = \frac{8}{8}$$

$\Rightarrow$ $$W_{Ag} = 108 \text{ g}$$

17. (c) Fuel cells have 100% efficiency practically

Explanation: Theoretically, the fuel cells are expected to have an efficiency of 100% but practically they give efficiency of 60-70%. Still, they are much superior to the thermal power plants because they do not cause pollution, they never become dead and the cost of catalysts needed for the electrode reactions is high.

18. (a) A

Explanation: The highest chemical activity will be shown by A because lower the reduction potential better will be the chemical reactivity. Among A, B, C and D, A is having least reduction potential -3.05 therefore, it will have highest chemical reactivity.

19. (c) Zinc

Explanation: Galvanization is the process of applying a protective zinc coating to steel or iron, to prevent it from rusting. Zinc decomposes at a really slow rate, therefore the coating of zinc protects the inner surface of the metal and protects it from getting rusted and increases its life.

20. (c) Platinum (Pt)

Explanation: Inert electrode is a metal that does not take part or interfere in any chemical reaction. It is a metal submerged in an aqueous solution that transfers electrons rather than exchanging ions with the aqueous solution. They are generally made up of noble metals like platinum. Therefore Pt acts as inert electrode.

21. (c) Decreases

Explanation: On dilution, the specific conductance of a solution decreases. Conductivity changes with the concentration of the electrolyte. On dilution as volume of solution increases. Thus, the number of ions per ml decreases and hence conductivity decreases. Thus, the specific conductivity decreases on dilution.

22. (a) Y > Z > X

Explanation: As the reduction potential drops, the reducing power of the electrode increases

Y (– 3.03 V) > Z (– 1.18 V) > X (0.52 V)

23. (d) Reduction potential of copper is higher than that of zinc.

Explanation: When zinc granule is dipped into copper sulphate solution, copper is precipitated because reduction potential of copper is higher than that of zinc. Therefore, copper get reduced more easily as compared to zinc.

For a spontaneous reaction ΔG^o and E^o_{cell} will be respectively:

(a) –ve and –ve	(b) +ve and +ve
(c) +ve and –ve	(d) –ve and +ve

(d) –ve and +ve

Explanation: For a spontaneous reaction, the standard change in Gibbs free energy ΔG_0 and the standard cell potential E^0_{cell} will be negative and positive respectively.

Fill in the blanks

24. (a) ohm^{-1}, ohm^{-1} cm^{-1}, potential difference becomes zero

Explanation: The unit of conductance is ohm^{-1} and that of specific conductance is ohm^{-1} cm^{-1} A galvanic cell stops after some time because potential difference becomes zero.

25. (b) Gram equivalent, volume, cathode

Explanation: Equivalent conductivity is the conducting power of all the ions furnished by one Gram equivalent of an electrolyte present in a definite volume of the solution. In a Daniel cell the copper vessel serves as cathode.

26. (d) Anode, cathode, fuel cells

Explanation: In a galvanic cell, electrons flow from anode to cathode through the connecting wires. A device in which chemical energy of a fuel is directly converted into electrical energy is called fuel cells.

27. (c) Increases, decreases, cathode

Explanation: The molar conductance of a solution increases with dilution, while its specific conductance decreases with dilution. The electrode at which there is acceptance of electrons is called cathode.

28. (b) Negative, greater, right hand side

Explanation: The more negative is standard reduction potential of a metal, the greater is its ability to displace hydrogen from acids. In representation of an electrochemical cell, the cathode is written on right hand side.

29. (a) Copper, magnesium, specific conductance

Explanation: Zinc can displace copper from $CuSO_4$ solution, but cannot displace magnesium from $MgSO_4$ solution. The conductance of a solution placed between two opposite faces of a cm^3 is called specific conductance.

30. (d) Higher, stronger, $\wedge_m = \dfrac{\kappa \times 10^3}{M}$

Explanation: Higher the reduction potential stronger is the oxidizing agent. The molar conductance (*lm*) of a solution is related to specific conductance (*k*) by the relation $\wedge_m = \dfrac{\kappa \times 10^3}{M}$

31. (c) Increases, decreases, multimeter

Explanation: The equivalent conductance of a solution increases with decrease in concentration of the electrolyte in the solution. Specific conductance of an electrolyte solution decreases with increase in dilution. The resistance of a solution is measured with the help of multimeter.

32. (a) $\sqrt{C}$, Zero

Explanation: Strong electrolytes give almost linear plot of Λ_m versus $\sqrt{C}$ The E° value of a NHE is Zero .

33. (a) Bad, zinc

Explanation: The solution of sugar in water is bad conductor of electricity. In a galvanised iron, the iron is coated with a layer of zinc metal

Match the following

34. (d) 1-(t), 2-(u), 3-(v), 4-(p), 5-(q), 6-(s), 7-(r), 8-(w)

Explanation: The unit of molar conductivity is $Ohm^{-1}cm^2mol^{-1}$. Dry cell is a primary cell. The equation Zn/Zn^{2+} (0.1 M) || Zn^{2+} (0.5M)/Zn represents concentration cell. The unit of specific conductivity is siemen cm^{-1}. The equation $E = E° + \dfrac{0.59}{n} \log \dfrac{[M^{n+}]}{[M]}$ represents Nernst equation. The $E°_{cell}$ is the maximum work obtainable from cell. The value 96500 $Cmol^{-1}$ is Faraday constant.

35. (a) 1-(r), 2-(p), 3-(q)

Explanation: The electrolyte used in dry cell, nickel-cadmium cell and leads storage cell is zinc chloride, potassium hydroxide and aqueous H_2SO_4 respectively.

Numerical based questions

36. (c) 0.7505 V

Explanation: Pt works as cathode, therefore, the cell reduction reaction will take place on it thus, the cell reaction will be :

$$Pb + I_2 \longrightarrow Pb^{+2} + 2I^-$$

$$\begin{aligned} E°_{Cell} &= E°_{Cathode} - E°_{Anode} \\ &= 0{\cdot}536 - (-0{\cdot}126) = 0{\cdot}662 \text{ V} \end{aligned}$$

Voltage generated *i.e.*, E_{cell} of the 0·1 M concentration of respective ions can be calculated by

$$\begin{aligned} E_{cell} &= E°_{cell} + \frac{0{\cdot}059}{n} \log \frac{1}{[Pb^{2+}][I^-]^2} \\ E_{cell} &= 0{\cdot}662 + \frac{0{\cdot}059}{n} \log \frac{1}{[0{\cdot}1][0{\cdot}1]^2} \\ &= 0{\cdot}662 + \frac{0{\cdot}059}{2} \log 10^3 \\ &= 0{\cdot}7505 \text{ V.} \end{aligned}$$

37. (b) Antilog 34·5014

Explanation:

$$\begin{aligned} E°_{Cell} &= E°_{cathode} - E°_{anode} \\ &= -0{\cdot}40 \text{ V} - (-0{\cdot}74 \text{ V}) \\ &= +0{\cdot}34\text{V} \\ \Delta_r G° &= -nFE°_{Cell} \\ &= -6 \times 96500 \text{ C mol}^{-1} \times 0{\cdot}34\text{V} \\ &= -196860 \text{ C V mol}^{-1} \\ &= -196860 \text{ J mol}^{-1} \\ &= -196{\cdot}86 \text{ kJ mol}^{-1} \\ \Delta_r G° &= -2{\cdot}303 \text{ RT} \log K_C \\ -196860 &= -2{\cdot}303 \times 8{\cdot}314 \times 298 \log K_C \end{aligned}$$

or $$K_C = \text{Antilog } 34{\cdot}5014$$

38. (a) $Zn/Zn^{2+} \,||\, Pb^{2+}/Pb$, 0·638 V

Explanation:

(i) Spontaneous cell reaction

At anode $Zn - 2e^- \longrightarrow Zn^{2+}$; E = + 0·76 volt.

At cathode $Pb^{2+} + 2e^- \longrightarrow Pb$; E = – 0·13 volt

Cell reaction : $Zn + Pb^{2+} \longrightarrow Zn^{2+} + Pb$

As cell representation $Zn/Zn^{2+} \,||\, Pb^{2+}/Pb$

(ii)
$$E^\circ_{cell} = E_{anode} + E_{cathode}$$
$$= 0{\cdot}76 + (-0{\cdot}13) = 0{\cdot}76 - 0{\cdot}13$$
$$E^\circ_{cell} = +0{\cdot}63 \text{ volt}$$
$$\Rightarrow \quad E_{cell} = E^\circ_{cell} - \frac{0{\cdot}059}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$
$$= 0{\cdot}63 - \frac{0{\cdot}059}{2}\log\frac{[Zn^{2+}]}{[Pb^{2+}]}$$
$$= 0{\cdot}63 - 0{\cdot}0295\log\frac{[0{\cdot}1]}{[0{\cdot}2]}$$
$$E_{cell} = 0{\cdot}63 - 0{\cdot}0295\log\left(\frac{1}{2}\right) \text{ volt.}$$
$$= 0{\cdot}63 - 0{\cdot}0295\log({\cdot}5) \text{ volt.}$$
$$= 0{\cdot}638 \text{ V}$$

39. (c) 0·2607 V, 1·209 V, 2·6775 V

Explanation:

(i)
$$E^\circ_{Cell} = E^\circ_{Right} - E^\circ_{Left}$$
$$= -0{\cdot}45 - (-0{\cdot}75)$$
$$= +0{\cdot}30 \text{ V}$$
$$2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe$$
$$E_{Cell} = E^\circ_{Cell} - \frac{0{\cdot}059}{n}\log\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$
$$= +0{\cdot}30 - \frac{0{\cdot}059}{6}\log\frac{[0{\cdot}1]^2}{[0{\cdot}01]^3}$$
$$= 0{\cdot}30 - \frac{0{\cdot}059}{6}\log\frac{[10^{-2}]}{[10^{-6}]}$$
$$= 0{\cdot}30 - \frac{0{\cdot}059}{6}\log 10^4$$
$$= 0{\cdot}30 - \frac{0{\cdot}059}{6} \times 4$$
$$= 0{\cdot}30 - 0{\cdot}0393 \text{ V}$$
$$= 0{\cdot}2607 \text{ V.}$$

(ii) For the cell

$Al \mid Al^{3+}$ (0·01 M) $||$ Fe^{2+} (0·02M) $\mid Fe$

Anode Cathode

$$E^\circ_{Al^{3+}/Al} = -1{\cdot}66 \text{ V}$$
$$E^\circ_{Fe^{2+}/Fe} = -0{\cdot}44 \text{ V}$$
$$E^\circ_{cell} = E^\circ_{Fe} - E^\circ_{Al} = -0{\cdot}44 - (-1{\cdot}66)$$
$$= +1{\cdot}22 \text{ V}$$

Nernst equation for the cell reaction:
$$2Al + 3Fe^{2+} \longrightarrow 2Al^{3+} + 3Fe$$
$$E_{cell} = E^\circ_{cell} + \frac{0{\cdot}0591}{6}\log\frac{[Fe^{2+}]^3}{[Al^{3+}]^2}$$
$$= 1{\cdot}22 + \frac{0{\cdot}0591}{6}\log\frac{(0{\cdot}02)^3}{(0{\cdot}01)^2}$$
$$= 1{\cdot}22 + \frac{0{\cdot}0591}{6}\log 8 \times 10^{-2}$$
$$= 1{\cdot}22 + 0{\cdot}00985\,[\log 8 - 2\log 10]$$
$$= 1{\cdot}22 + 0{\cdot}00985\,[0{\cdot}8451 - 2 \times 1]$$
$$= 1{\cdot}22 + 0{\cdot}00985\,[-1{\cdot}1549]$$
$$= 1{\cdot}220 - 0{\cdot}011 = 1{\cdot}209 \text{ V}$$

(iii) The cell reaction is:
$$Mg + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu$$
$$E^\circ_{Cell} = E^\circ_{Right} - E^\circ_{Left}$$
$$= +0{\cdot}337 - (-2{\cdot}37)$$
$$= 2{\cdot}707 \text{ V}$$
$$E_{Cell} = E^\circ_{Cell} - \frac{0{\cdot}0591}{n}\log\frac{[Mg^{+2}]}{[Cu^{+2}]}$$
$$= 2{\cdot}707 - \frac{0{\cdot}0591}{2}\log\frac{10^{-3}}{10^{-4}}$$
$$= 2{\cdot}707 - {\cdot}0{\cdot}0295\log 10$$
$$= 2{\cdot}707 - 0{\cdot}0295$$
$$= 2{\cdot}6775 \text{ V}$$

40. (a) $Cd \mid Cd^{2+}_{(0.1M)} \mid 2Ag$, 1·1882177 V, –229.32kJ

Explanation:

(i) Cell representation
$$Cd \,\big|\, Cd^{2+}_{(0{\cdot}1M)} \,\big|\,\big|\, 2Ag^{2+}_{(0{\cdot}2M)} \,\big|\, 2\,Ag$$

(ii) E°(red) cell = E°(red) cathode – E°(red) anode = 0·80 – (– 0·40)

= 1·2 V

[n = 2]
$$E_{cell} = E^\circ_{(red)cell} - \frac{0{\cdot}059}{n}\log\left[\frac{M}{M^{n+}}\right]$$

$$= 1{\cdot}2 - \frac{0{\cdot}059}{2}\log\left[\frac{0{\cdot}1}{0{\cdot}04}\right]$$

$E_{cell} = 1{\cdot}1882177$ volt.

(iii) Since E_{cell} is +ve therefore, cell reaction will be spontaneous.

$$\Delta G^\circ = -nFE_{cell} = -229{\cdot}32 \text{ kJ}$$

Since ΔG^{o} is (–ve) it will also favour spontaneous reaction.

41. (c) 2·155 g of Cr, 1000 sec

Explanation:

(i) According to the equation one mol of Cr is plated out by 6 mol of electrons.

$$Cr^{6+}_{(aq.)} + 6e^- \longrightarrow Cr_{(s)}$$

6 mol 1 mol

or 6 F 52 g

or 6 × 96500 C

∵ 6 × 96500 C are used to plate out = 52 g Cr

∴ 24000 C is used to plate out = $\frac{52\times24000}{6\times96500}$ g Cr

= 2·155 g Cr.

(ii) Where, Q = Quantity of electricity = 24000 C (given)

I = 24 A (given)

t = Time in sec = ?

We know that Q = I × t

Hence, $t = \frac{24000}{24}$ = 1000 sec.

Hence, to plate out 2·155 g of Cr, 24 A current should be passed for 1000 sec. through CrO3 solution.

42. (d) 2·014 g of Ag, – 517·326 kJ mol^{-1}

Explanation:

(i) Time, t = 15 × 60 = 900 sec;

Charge = Current × Time

= 2A × 900s = 1800 C

According to the reaction,

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

So, we need 1F or 96500 C to deposit one mole or 108 g of silver, so, by 1800 C, the mass of silver deposited would be:

$$= 108 \text{ g mol}^{-1} \times \frac{1800\,C}{96500\,C\,mol^{-1}}$$

= 2·014 g

So, 2·014 g of silver is deposited in 15 minutes.

(ii) Considering the cell reaction as:

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

The $E_{(cell)}$ would be given by:

$$E_{(cell)} = E^{\Theta}_{(cell)} - \frac{RT\log}{nF}\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

So, $E_{(cell)}$ will be:

$$E_{(cell)} = 2{\cdot}71\text{ V} - \left(\frac{0.059\text{V}}{2}\right)\log_{10}\left(\frac{0.1}{0.01}\right)$$

= 2·68045 V

Now, ΔG of the reaction is given by:

$\Delta Gr = -nFE_{cell}$

$= -2 \times 96500 \text{ C mol}^{-1} \times 2{\cdot}68045 \text{ V}$

$= -517{\cdot}326 \text{ kJ mol}^{-1}$

43. (c) $2{\cdot}246 \times 10^{22}$ electrons, 579000 C, 124 S cm^2 mol^{-1}

Explanation:

(i) Q (coulomb) = 1 (ampere) × t (s)

= 0·5 × 2 × 60 × 60

= 3600 C

A flow of 96500 C is equivalent to the flow of 1 mole of electrons

= $6{\cdot}02 \times 10^{23}$ electrons

∴ 3600 C is equivalent to flow of electrons

$$= \frac{6{\cdot}02\times10^{23}}{96500}\times3600$$

= $2{\cdot}246 \times 10^{22}$ electrons.

(ii) From the given reaction 1 mole of $Cr_2O_7^{2-}$ ion require 6F = 6 × 96500 C = 579000 C of electricity for reduction of Cr^{3+}

(iii) $$\Lambda_m = \frac{K\times1000}{\text{Molarity}} = \frac{0{\cdot}0248 \text{ S cm}^{-1}\times1000 \text{ cm}^3\text{ L}^{-1}}{0{\cdot}20 \text{ mol L}^{-1}}$$

[M = mol L^{-1}]

= 124 S cm^2 mol^{-1}

44. (b) 0·01 ohm^{-1} cm^{-1}, 200 mol^{-1} ohm^{-1} cm^{-1}, 0·424

Explanation:

(i) Specific conductance :

$$\frac{\text{Cell constant}}{\text{Resistance}} = \frac{0{\cdot}50 \text{ cm}^{-1}}{50 \text{ ohm}}$$

$$\Lambda_{sp} = 0{\cdot}01 \text{ ohm}^{-1}\text{ cm}^{-1}$$

(ii) Molar conductance :

$$\frac{1000\Lambda_{sp}}{c} = \frac{1000\times0{\cdot}01 \text{ ohm}^{-1}\text{ cm}^{-1}}{0{\cdot}05 \text{ mol}}$$

$$= \frac{1000\times 0{\cdot}01}{0{\cdot}05}$$

$$\Lambda_m = 200\ \text{mol}^{-1}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

(iii) Degree of dissociation (α)

$$\alpha = \frac{\Lambda^{c}{}_{m}}{\Lambda^{\infty}{}_{m}}$$

$$= \frac{200\ \text{mol}^{-1}\ \text{ohm}^{-1}\ \text{cm}^{-1}}{471{\cdot}4\ \text{ohm}^{-1}\ \text{cm}^{2}\ \text{mol}^{-1}}$$

$$\alpha = 0{\cdot}424$$

45. (a) $16{\cdot}5\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$, 0·0423, $1{\cdot}86 \times 10^{-5}$

Explanation:

(i) Molar conductance

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

$$= \frac{1{\cdot}65\times 10^{-4}\times 1000}{0{\cdot}01}$$

$$= 16{\cdot}5\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

(ii) Degree of dissociation

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\infty}}$$

$$\Lambda_m = 16{\cdot}5\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

$$\Lambda_m^{\infty}\,(CH_3COOH) = \lambda^{\infty}[H^+] + \lambda^{\infty}[CH_3COO^-]$$

$$= 349{\cdot}1 + 40{\cdot}9$$

$$= 390\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

$$\alpha = \frac{16{\cdot}5}{390} = 0{\cdot}0423$$

(iii)

$$\begin{array}{llll} & CH_3COOH & \rightleftharpoons CH_3COO^- & + \ H^+ \\ \text{Initial} & 0{\cdot}01\ \text{M} & 0 & 0 \\ \text{At equilibrium} & 0{\cdot}01\,(1-\alpha) & 0{\cdot}01\,\alpha & 0{\cdot}01\,\alpha \end{array}$$

Dissociation constant,

$$K_d = \frac{[CH_3COO^-][H^+]}{[CH_3COO^-]} = \frac{0{\cdot}01\,\alpha\times 0{\cdot}01\,\alpha}{0{\cdot}01\,(1-\alpha)}$$

$$= \frac{0{\cdot}01\,\alpha^2}{1-\alpha} = 0{\cdot}01\alpha^2$$

[Taking 1 – α = 1, as α is negligible as compared to 1]

$$= 0{\cdot}01 \times (0{\cdot}0423)^2$$

$$K_d = 1{\cdot}86 \times 10^{-5}$$

Hence, the dissociation constant (K_d) for acetic acid is $1{\cdot}86 \times 10^{-5}$.

46. (i) (b) 63.50 g

Explanation: Given

$$2F \xrightarrow{Cu\,SO_4} \text{mass} = ?$$

At mass Cu = 63.5

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

2 mol of *e*– required to deposit 1 mole Cu

or 2 F of electricity are 11 deport 1 mole cu

$$\text{moles} = \frac{gm}{\text{M.N}}$$

$$1 = \frac{x}{63.5} \text{ or } x = 63.5\ \text{g}$$

(ii) (c) 216 g

Explanation: According Faraday's law :

$$m = z \times Q = \frac{E \times Q}{96500}$$

$$m = \frac{108}{96500} \times 2 \times 96500 = 216g$$

47. (i) (a) $128\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

Explanation: The limiting molar conductivities of NaCl, KBr and KCl are 126 , 152 and 150 $\text{Scm}^2\ \text{mol}^{-1}$ respectively

The limiting molar conductivity λ^{∞} for NaBr is calculated by the following expression.

$$\lambda^{\infty}_{NaBr} = \lambda^{\infty}_{NaCl} + \lambda^{\infty}_{KBr} - \lambda^{\infty}_{KCl}$$

$$\lambda^{\infty}_{NaBr} = 126 + 152 - 150 = 128\ \text{ohm}^{-1}\text{cm}^2\ \text{mol}^{-1}$$

(ii) Kohlraush's Law

Explanation: Kohlrausch law states that, "At time infinite dilution, the molar conductivity of an electrolyte can be expressed as the sum of the contributions from its individual ions."

Structure based questions

48. (a) Zn to Ag, cathode, stop functioning, Ecell = 0, Conc of Zn^{2+} and Ag^+ ions will increase and decrease respectively.

Explanation:

(i) Electrons move from Zn to Ag.

(ii) Ag is the cathode.

(iii) Cell will stop functioning.

(iv) When $E_{cell} = 0$.

(v) Concentration of Zn^{2+} ions will increase and concentration of Ag^+ ions will decrease.

49. (a) (i) At Cathode, $Zn^{2+} + 2e^- \longrightarrow Zn(s)$

At Anode $Cu(s) \longrightarrow Cu^{2+} + 2e$

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

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

Explanation:

(i) Cell 'B' will act as electrolytic cell because potential of 'B' is less than that of 'A'. Electrode process in the cell 'B' may be given as

$Zn^{2+} + 2e^- \longrightarrow Zn(s)$ (Cathode)

$Cu(s) \longrightarrow Cu^{2+} + 2e$ (Anode)

(ii) Cell 'B' at higher potential will act as galvanic cell. The electrode process may be given as,

Anode : $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

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

Assertion and Reason based questions

50. (a) For reaction to be spontaneous, E_{cell} should have a positive value and $\Delta_r G_{cell}$ negative. Hence, Current stops flowing when $E_{Cell} = 0$ because equilibrium of the cell reaction is attained. Thus, both assertion and reason are true and reason is the correct explanation of assertion.

51. (a) Corrosion is usually defined as the degradation of metals due to an electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper and bronze are all examples of corrosion. Rust is hydrated ferric oxide $Fe_2O_3.H_2O$. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. Thus, both assertion and reason are true and reason is the correct explanation of assertion.

52. (b) Conductivity always decreases with a decrease in concentration whereas, molar conductivity increase with dilution. This is because the conductivity of a solution is the conductance of one unit volume of the solution, but molar conductivity is the conductance of that volume of solution containing one mole of an electrolyte. Thus, both assertion and reason are correct but reason is not the correct explanation of assertion.

53. (a) Zinc is used in the recovery of Ag from the complex $[Ag(CN)_2]^-$ whereas copper is not used because zinc is more powerful reducing agent than copper. Thus, both assertion and reason are true and reason is the correct explanation of assertion.

54. (b) We know that:

$R \propto l / A$ or

$R = \rho\ (l/ A\ )$

Where, l = length of substance

A = area of cross-section

ρ = proportionality constant is called resistivity.

If $l = 1$ m and $A = 1\ m^2$

Then, $R = \rho$ *i.e.,* resistance = Resistivity.

The SI units of resistivity is ohm metre (Ωm).

Thus, both assertion and reason are true but reason is not the correct explanation of the assertion.

55. (b) On increasing dilution specific conductance increases because it is directly proportional to dilution.When more amount of solvent such as water is added to the solution, it results in dissociating the molecules into ions of a weak electrolyte. Thus, the degree of ionisation of weak electrolyte increases upon dilution. The mobility of ions will also increase because the ions will get the more free space to move. Thus, both assertion and reason are correct but reason is not the correct explanation of assertion.

56. (b) As the temperature increases the electrolytic conductivity of solutions increases because with increase in the temperature ionisation increases and the mobility of ions also increases. In metals, conductivity is due to movement of free electrons. When we increase the temperature the vibrational motion of electrons increases which causes unwanted collisions which results in the increase of resistance in metals. Therefore the mobility of electrons decreases and causes decrease in conductivity. Thus, both assertion and reason are correct but reason is not the correct explanation of assertion.

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

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

57. (a) From the above redox reactions, it is clear that during the electrolysis of $CuSO_4(aq)$ using copper electrodes, copper is dissolved at anode and deposited at cathode. Also, oxidation takes place at anode and reduction at cathode. Thus, both assertion and reason are true and reason is the correct explanation of assertion.

58. (a) To obtain maximum work from a galvanic cell charge has to be passed reversibly because electrical work done in one second is equal to the electrical potential multiplies by total charge. The reversible work done by a galvanic cell is equal to the decrease in its Gibbs energy. Therefore, if nF is the amount of charge passed and E is the emf of the cell and ΔG is the Gibbs energy of reaction then,

$\Delta G = -\,nF\ E_{cell}$

Hence, both Assertion and reason are correct and also reason is the correct explanation for Assertion.

59. (a) For both strong and weak electrolyte, conductivity always decreases with the decrease in concentration. This is because the number of ions per unit volume that carry the current in a solution decreases on dilution. Thus, both assertion and reason are true and reason is the correct explanation of assertion.

Word of Advice

1. Most of the students did not write the Nernst equation correctly and they substituted the value of E° instead of the value of E° in the formula ΔG = –*n*FE.
2. Molar conductivity at infinite dilution (λ^{∞}m) for CH_3COOH was calculated correctly by most of the students but the degree of disassociation (α) was not calculated correctly as majority of students used incorrect formulae.
3. Majority of the students made an error in the calculation of equivalent weight of silver, either by writing the mass of deposited silver as 54 instead of 108 or by substituting the value of time in minutes instead of seconds. Also, few students did not expressed the final answer with the correct unit.
4. Most of the students wrote incorrect formula of Nernst equation and instead of calculating ΔG, some of the students calculated ΔG° which was not asked in the question. Also, a few students did not expressed the final answer with the negative sign.
5. Most of the students wrote an incorrect definition of specific conductance.
6. Most of the students did not write the correct definition of Kohlrausch's law.
7. Most of the students were able to calculate the correct values of cell constant and molar conductivity but were unable to express the answer with the correct unit.
8. Most of the students wrote incorrect formula for Nernst equation and they calculated the value of E°cell with negative sign *i.e.* – 0.36 V instead of +0. 36 V. Also, some of them calculated ΔG instead of calculating ΔG°.
9. Most of the students either wrote incorrect definition of equivalent conductivity or wrote an incorrect formula and its relationship with specific conductance.
10. Some of the students wrote the definition of 'rusting' instead of explaining 'corrosion of metals.'
11. Most of the students correctly calculated the values of molar conductivity and equivalent conductivity of the solution but they did not gave the correct unit of molar conductivity and equivalent conductivity of the solution.
12. Most of the students wrote the definition of 'metal activity series' instead of 'electrochemical series'. Some students wrote that metals above hydrogen can liberate hydrogen gas from acid. They did not write the answer in terms of reduction potential value.
13. Majority of the students gave the cell reaction and value of emf of the cell correctly but some students were not able to calculate the value of free energy change (ΔG°) because they did not know the correct equation. Also, most of the students did not write negative sign before the value of (ΔG°).
14. Some of the students wrote the incorrect value of Kc because they did not substitute the correct values in the formula. Apart from this, most of the students wrote the incorrect value of Kc.
15. Majority of the students calculated the value of molar conductance correctly but the unit given was not correct.
16. Most of the students wrote wrong units for conductance and specific conductance.
17. Some of the students wrote that the electrochemical equivalent is the amount of substance which gets deposited from its solution on passing electrical charge equal '96,500 coulombs' instead of '1 coulomb'.
18. Most of the students calculated the charge in terms of Faraday whereas according to the question, the answer had to be written in Coulombs.
19. Most of the students interchanged (reversed) the answer, instead of writing that on dilution of a solution, its specific conductance 'decreases' while its equivalent conductance 'increases' they wrote 'increases' and 'decreases' which was correct.
20. Some of the students wrote that more 'positive' is the standard reduction potential of a substance instead of negative' the 'greater' is its ability to displace hydrogen from acids but instead of 'greater' a few students wrote 'more' which was not given in the list of words.