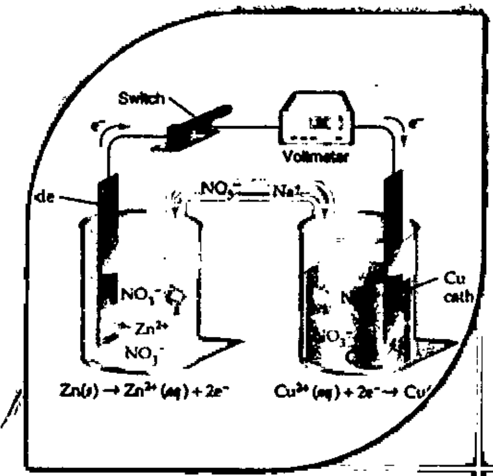
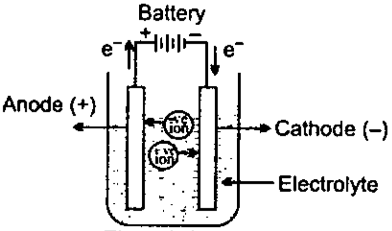


8

ELECTROCHEMISTRY

Electrolytic Cell

- **Electrolysis :** Chemical changes in electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis.
- **Electrolytic Cell :** This cell converts electrical energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell.



Electrolytic cell

Quantitative Aspect of Electrolysis

Faraday's laws of electrolysis :

- **First law of electrolysis :** Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$$W \propto Q$$

$$W = ZQ = Z \times i \times t$$

$$\text{Current efficiency} = \frac{\text{Actual charge utilised in process}}{\text{Charge passed through battery}} \times 100$$

W = weight liberated/deposited, Q = charge in coulomb, i = current, t = time

Z = electrochemical equivalent, 1 Faraday = 96500 coulomb

- **Second law of electrolysis :** When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. *i.e.*, $W_1/W_2 = E_1/E_2$

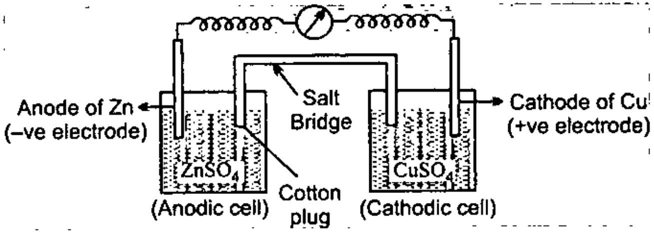
$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

Product of Electrolysis

S.No.	Electrolyte	Anode Product	Cathode Product
1.	NaCl (Molten) with Pt electrode	$Cl_2(g)$	$Na(l)$
2.	NaCl (aq) with Pt electrode	$Cl_2(g)$	$H_2(g)$
3.	$Na_2SO_4(aq)$ with Pt electrode	$O_2(g)$	$H_2(g)$
4.	$NaNO_3(aq)$ with Pt electrode	$O_2(g)$	$H_2(g)$
5.	$AgNO_3(aq)$ with Pt electrode	$O_2(g)$	$Ag(s)$
6.	$CuSO_4(aq)$ with inert electrode	$O_2(g)$	$Cu(s)$
7.	$CuSO_4(aq)$ with copper electrode	Cu dissolve	$Cu(s)$

Galvanic Cell

This cell converts chemical energy into electrical energy.



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

- **Anode half cell reaction :**

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \text{ (oxidation)}$$

- **Cathode half cell reaction :**

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \text{ (reduction)}$$

- **Over all process :**

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

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

Salt Bridge

It is U-shaped tube contains saturated solution of inert electrolyte like KCl, KNO_3, NH_4Cl and NH_4NO_3 etc. in agar-agar gel.

- Cation and anion of inert electrolyte have same mobility.
- Ions of inert electrolyte do not mix with electrolytic solution present in the half cell.
- Ions of inert electrolyte do not participate in electrochemical change.

Function of Salt Bridge

- It complete the electrical circuit.
- It maintained the two half cell electrically neutral by the flow of ions.

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

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

$$\mathrm{Zn}(s)|\mathrm{ZnSO_4}(aq)||\mathrm{CuSO_4}(aq)|\mathrm{Cu}(s)$$

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

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

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

$$\mathrm{Zn}(s) \underset{\substack{(-)\\ \text{Anode}}}{|} \mathrm{Zn}^{+2}(aq)||\mathrm{Cu}^{+2}(aq) \underset{\substack{(+)\\ \text{Catode}}}{|} \mathrm{Cu}(s)$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{OP(LHS)}} + E^{\circ}_{\text{RP(RHS)}}\ ;\quad E_{\text{cell}} = E_{\text{OP(LHS)}} + E_{\text{RP(RHS)}}\ ;\ E_{\text{cell}} = E_{\text{RP(RHS)}} - E_{\text{RP(LHS)}}$$

Nernst's Equation

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF}\cdot\log Q$$

At 298 K temp. $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log Q$; where Q is reaction quotient.

Cell Thermodynamics

(i) $\Delta G = -nFE_{\text{cell}}$

(ii) $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$

(iii) Equilibrium constant (K), $\log K = \frac{n \times E^{\circ}_{\text{cell}}}{0.0591}$

(iv) Temp. coefficient of cell $= \left(\frac{\partial E}{\partial T}\right)_P$

(v) Enthalpy of reaction inside the cell, $\Delta H = nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$

(vi) Entropy change inside the cell, $\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$

Concentration Cell

Anode and cathode both are formed by same substance so $E^{\circ}_{\text{cell}} = 0$, such type of cell is known as concentration cell. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

- **Electrode gas conc. cell :**

$$\mathrm{Pt},\ \underset{P_1\ \text{atm}}{\mathrm{H_2}(g)}|\mathrm{H}^{+}(C)|\underset{P_2\ \text{atm}}{\mathrm{H_2}(g)},\ \mathrm{Pt}$$

$$E_{\text{cell}} = \frac{0.0591}{2}\log\frac{P_1}{P_2}$$

- **Electrolyte conc. cell :**

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

$$E_{cell} = \frac{0.0591}{2}\log\frac{C_2}{C_1}$$

Different Type of Electrode

S.No.	Name of Electrode	Anode	Cathode
1.	Hydrogen electrode	$Pt(s)\|H_2(g)\|H^+(aq)$ $E_{OP} = E^\circ_{OP} - \frac{0.0591}{2}\log\frac{[H^+]^2}{P_{H_2}}$	$H^+(aq)\|H_2(g)\|Pt(s)$ $E_{RP} = E^\circ_{RP} - \frac{0.0591}{2}\log\frac{P_{H_2}}{[H^+]^2}$
2.	Metal-metal ion electrode	$M(s)\|M^{+n}(aq)$ $E_{OP} = E^\circ_{OP} - \frac{0.0591}{n}\log[M^{+n}]$	$M^{+n}(aq)\|M(s)$ $E_{RP} = E^\circ_{RP} - \frac{0.0591}{n}\log\frac{1}{[M^{+n}]}$
3.	Calomel electrode	$Hg(l), Hg_2Cl_2(s)\|Cl^-(aq)$ $E_{OP} = E^\circ_{OP} - \frac{0.0591}{2}\log\frac{1}{[Cl^-]^2}$	$Cl^-(aq)\|Hg_2Cl_2(s), Hg(l)$ $E_{RP} = E^\circ_{RP} - \frac{0.0591}{2}\log[Cl^-]^2$
4.	Redox electrode	$Pt(s)\|Fe^{+2}(aq), Fe^{+3}(aq)$ $E_{OP} = E^\circ_{OP} - \frac{0.0591}{1}\log\frac{[Fe^{+3}]}{[Fe^{+2}]}$	$Fe^{+3}(aq), Fe^{+2}(aq)\|Fe(s)$ $E_{RP} = E^\circ_{RP} - \frac{0.0591}{1}\log\frac{[Fe^{+2}]}{[Fe^{+2}]}$
5.	Metal insoluble salt anion electrode	$Ag(s)\|AgCl(s)\|Cl^-(aq)$ $E_{OP} = E^\circ_{OP} - \frac{0.0591}{1}\log\frac{1}{[Cl^-]}$	$Cl^-(aq)\|AgCl(s)\|Ag(s)$ $E_{RP} = E^\circ_{RP} - \frac{0.0591}{1}\log[Cl^-]$

Batteries

Electrochemical cells can be used as **batteries.** Batteries are of two kinds :

- **Primary battery :** Where the reaction occurs only once and can not be reused once it becomes dead over the course of time. For examples, dry cell (Leclanche cell), Mercury cell.
- **Secondary battery :** Which can be recharged by passing current through it in the opposite direction so that it can be used again. For example, lead-acid battery, Nickel-cadmium cell.

Fuel Cells

Fuel cells are the galvanic cells that convert the energy of combustion of fuels (*e.g.*, hydrogen, methane, methanol, etc.) directly into electrical energy.

Fuel cells are more efficient thermodynamically, and more of the energy of the reaction can be made available for useful work provided that the supply of reactants is maintained.

Methanol, ethanol, hydrazine, formaldehyde, carbon monoxide can be used as fuels in fuel cells apart from hydrogen.

Corrosion

When the metal exposed to some environment it gets converted to its oxides. The oxidative deterioration of metal is known as corrosion.

Example : Rusting of iron, tarnishing of silver, development of green coating on copper and bronze etc.

Oxidation $\quad Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

Reduction $\quad O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

Atmospheric oxygen oxidised Fe^{2+}

$$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$$

Hydrated feric oxide ($Fe_2O_3 \cdot xH_2O(s)$) is known as rust.

- **Factors which enhance corrosion :**
  - (i) Presence of impurities in the metal.
  - (ii) Presence of moisture.
  - (iii) Presence of electrolyte.
- **Prevention of corrosion :**
  - (i) Barrier protection by oil/grease layer, paints or electroplating.
  - (ii) Sacrificial protection by coating the metal with more electropositive metal.

Conductance

- **Conductance (*G*):** It is defined as the reciprocal of the electrical resistance *i.e.*, $G = 1/R$. It measures the ease with which the current flows through a conductor.

  Unit : Siemen, S or Ω^{-1}.

- **Specific resistance or resistivity (ρ) :** The resistivity or specific resistance is defined as the resistance in ohm of a conductor having length equal to 1 cm and area of cross-section equal to 1 cm^2.

  $R \propto \frac{l}{A}$ or $R = \rho\frac{l}{A}$ where ρ = specific resistance, l = length of conductor

  A = area of cross-section of the conductor.

  Unit : ohm cm.

- **Specific conductance or conductivity (*k*):** It is define as the reciprocal of specific resistance.

  i.e., $\quad k = \frac{1}{\rho} \quad \therefore\ R = \rho\frac{l}{A} \quad k = G \times \frac{l}{A}$

  $$k = G \times G^*$$

  $$G^* = \frac{l}{A}, \qquad \text{where } G^* = \text{cell constant}$$

  When $l = 1$ cm and $A = 1$ cm^2; $k = G$

  Thus conductivity is the conductance of one centimeter cube or conductance of one cm cube of the solution of an electrolyte.

  Unit : Ω^{-1}cm^{-1}, Scm^{-1}.

- **Molar conductivity (Λ_M):** The conducting power of all the ions produced by dissolving 1 mole of an electrolyte in solution.

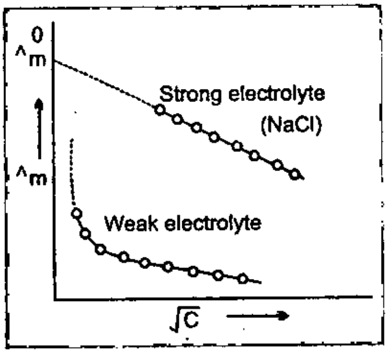
Mathematically, $\Lambda_M = k \times V$

$$\Lambda_M (\text{S cm}^2\,\text{mol}^{-1}) = k \times \frac{1000}{M} \qquad (M = \text{molarity})$$

Variation of conductivity and molar conductivity with concentration :

For weak and strong electrolytes

- Conductivity decreases with concentration.
- Molar conductivity increases with decrease in concentration.



Kohlrausch's Law

According to this law, at infinite dilution, when the dissociation is complete, each ion makes a definite contribution towards molar conductivity of the electrolyte irrespective of the nature of the other ions present.

The molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and the anions each multiplied by the number of ions present in one formula unit of the electrolyte *e.g.*, A_xB_y.

The equivalent conductivity of an electrolyte at infinite dilution is the sum of the equivalent conductivities of the cations and anions.

$$\Lambda_M^0 (A_xB_y) = x\lambda_M^0 (A^{y+}) + y\lambda_M^0 (B^{x-})$$

$$\Lambda_{eq.}^0 (A_xB_y) = \lambda_{eq.}^0 (A^{y+}) + \lambda_{eq.}^0 (B^{x-})$$

Application

(a) Determination of equivalent/molar conductivities of weak electrolytes at infinite dilution

$$\Lambda_M^0 (\text{CH}_3\text{COOH}) = \Lambda_M^0 (\text{CH}_3\text{COONa}) + \Lambda_M^0 (\text{HCl}) - \Lambda_M^0 (\text{NaCl}) - \Lambda_M^0 (\text{NaCl})$$

(b) Determination of degree of dissociation (α) and equilibrium constant (*K*) of an electrolyte at a given dilution

$$\alpha = \frac{\text{Molar conductance at concentration } C}{\text{Molar conductance at infinite dilution}} = \frac{\Lambda_M}{\Lambda_M^0}$$

$$\begin{array}{lccccc} & \text{HA} & \rightleftharpoons & \text{H}^+ & + & A^- \\ \text{Initial conc.} & C & & 0 & & 0 \\ \text{Conc. at equilibrium} & C - C\alpha & & C\alpha & & C\alpha \end{array}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{C\left(\frac{\Lambda_M}{\Lambda_M^0}\right)^2}{1-\frac{\Lambda_M}{\Lambda_M^0}}$$

(c) Determination of the solubility of a sparingly soluble salt

Since the solution is saturated at infinite dilution $\Lambda_0 = \Lambda_M^0$ and molarity = solubility.

$$\therefore \quad \Lambda_M^0 = \frac{k \times 1000}{\text{molarity}}$$

$$\therefore \quad \text{Solubility } (S) = \frac{k \times 1000}{\Lambda_M^0}$$

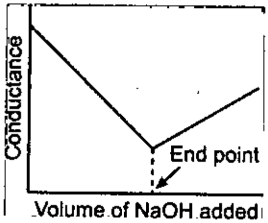
For sparingly soluble salt A_xB_y : Solubility product $K_{sp} = x^x y^y \cdot S^{x+y}$

Conductometric Titration

Titration in which end point can be determined by measuring conductance at each addition of the titre solution (for burette) is called conductometric titration.

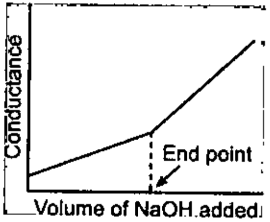
Titration of HCl(*aq*) with NaOH(*aq*) (Strong base Vs Strong acid)

$$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + H_2O(l)$$



Titration of CH_3COOH(*aq*) with NaOH(*aq*) (Weak acid *Vs* Strong base)

$$CH_3COOH(aq) + \text{NaOH}(aq) \longrightarrow CH_3COONa + H_2O(l)$$



Level 1

1. A cell reaction would be spontaneous if the cell potential and $\Delta_r G$ are respectively :
(a) positive and negative (b) negative, negative
(c) zero, zero (d) positive, zero

2. Which of the following statement is correct?
(a) Cathode is –ve terminal in both, galvanic and electrolytic cells
(b) Anode is +ve terminal in both, galvanic and electrolytic cells
(c) Cathode and anode are –ve terminal in electrolytic and galvanic cell.
(d) Cathode and anode are +ve terminal in electrolytic and galvanic cell.

3. Electrolytes when dissolved in water dissociate into ions because :
(a) They are unstable.
(b) The water dissolves it.
(c) The force of repulsion increases.
(d) The force of electrostatic attraction is broken down by water.

4. The electric charge required for electrode deposition of one gram-equivalent of a substnace is :
(a) one ampere per second (b) 96500 coulombs per second
(c) one ampere for one hour (d) charge on one mole of electrons

5. The amount of an ion liberated on an electrode during electrolysis does not depend upon :
(a) Conductance of the solution (b) Current strength
(c) Time (d) Electrochemical equivalent of the element

6. How many electrons are there in one coulomb of electricity?
(a) 6.023×10^{23} (b) 1.64×10^{-24} (c) 6.24×10^{18} (d) 6.24×10^{-24}

7. How many coulombs are provided by a current of 0.010 mA in the calculator battery that can operate for 1000 hours?
(a) 1.0 (b) 10 (c) 0.010 (d) 36

8. How many minutes are required to deliver 3.21×10^6 coulombs using a current of 500 A used in the commercial production of chlorine?
(a) 8.3 (b) 5.3×10^4 (c) 6420 (d) 107

9. Passage of a current for 548 seconds through a silver coulometer results in the deposition of 0.746 g of silver. What is the current (in A)?
(a) 1.22 (b) 1.16 (c) 1.07 (d) 1.00

10. Electrolysis can be used to determine atomic masses. A current of 0.550 A deposits 0.55 g of a certain metal in 100 minutes. Calculate the atomic mass of the metal if eq. wt. = mole. wt./3
(a) 100 (b) 45.0 (c) 48.25 (d) 144.75

11. Beryllium occurs naturally in the form of beryl. The metal is produced from its ore by electrolysis after the ore has been converted to the oxide and then to the chloride. How many grams of Be(*s*) is deposited from a $BeCl_2$ solution by a current of 5.0 A that flows for 1.0 h? (Atomic weight : Be = 9)
(a) 0.840 (b) 1.68 (c) 1.42 (d) 1.08

12. How many minutes will it take to plate out 5.0 g of Cr from a $Cr_2(SO_4)_3$ solution using a current of 1.50 A? (Atomic weight : Cr = 52.0)

(a) 254 (b) 30 g (c) 152 (d) 103

13. Calculate the current (in mA) required to deposit 0.195 g of platinum metal in 5.0 hours from a solution of $PtCl_6^{2-}$: (Atomic weight : Pt = 195)

(a) 310 (b) 31 (c) 21.44 (d) 5.36

14. How many Faradays are required to reduce 0.25 g of Nb (V) to the metal? (Atomic weight : Nb = 93g)

(a) 2.7×10^{-3} (b) 1.3×10^{-2} (c) 2.7×10^{-2} (d) 7.8×10^{-3}

15. One gm metal M^{3+} was discharged by the passage of 1.81×10^{23} electrons. What is the atomic weight of metal?

(a) 33.35 (b) 133.4 (c) 66.7 (d) None of these

16. Total charge required for the oxidation of two moles Mn_3O_4 into MnO_4^{2-} in presence of alkaline medium is :

(a) 5 F (b) 10 F (c) 20 F (d) None of these

17. The electrolytic decomposition of dilute sulphuric acid with platinum electrode, cathodic reaction is :

(a) Reduction of H^+ (b) Oxidation of SO_4^{2-} (c) Reduction SO_3^{2-} (d) Oxidation of H_2O

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

(a) Mg (b) Ag (c) Cu (d) Cr

19. A solution of potassium 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) None of these

20. The passage of current through a solution of certain electrolyte results in the evolution of $H_2(g)$ at cathode and $Cl_2(g)$ at anode. The electrolytic solution is :

(a) Water (b) *aq*. H_2SO_4 (c) *aq*. NaCl (d) *aq*. $CuCl_2$

21. When an aqueous solution of H_2SO_4 is electrolysed, the product at anode is :

(a) H^- (b) OH^- (c) SO_4^{2-} (d) O_2

22. An aqueous solution of Na_2SO_4 in water is electrolysed using Pt electrodes.The products at the cathode and anode are respectively :

(a) H_2, SO_2 (b) O_2, NaOH (c) H_2, O_2 (d) O_2, SO_2

23. The electrolysis of a solution resulted in the formation of $H_2(g)$ at the cathode and $O_2(g)$ at the anode. The solution is :

(a) $AgCl(aq)$ (b) $H_2SO_4(aq)$

(c) highly concentrated $NaCl(aq)$ solution (d) $CuCl_2(aq)$

24. If mercury is used as cathode in the electrolysis of aqueous NaCl solution, the ion discharged at cathode is :

(a) H^+ (b) Na^+ (c) OH^- (d) Cl^-

25. A dilute aqueous solution of $CuSO_4$ is electrolyzed using platinum electrodes.The products at the anode and cathode are :

(a) O_2, H_2 (b) H_2, O_2 (c) O_2, Cu (d) $S_2O_8^{2-}, H_2$

26. What products are formed during the electolysis of concentrated aqueous solution of sodium chloride?
(I) $Cl_2(g)$ at anode (II) NaOH as electrolyte (III) $H_2(g)$ at cathode
(a) I only (b) I and II only (c) I and III only (d) I, II and III

27. Which of the following aqueous solution produces metal after electrolysis ?
(a) $K_2Cr_2O_7$ (b) $KMnO_4$ (c) CH_3COONa (d) $CuCl_2$

28. How much time is required for complete decomposition of 4 moles of water using 4 ampere?
(a) 3.86×10^5 sec (b) 1.93×10^5 sec (c) 96500 sec (d) 48250 sec

29. An aqueous solution containing 1 M each of Au^{3+}, Cu^{2+}, Ag^+, Li^+ is being electrolysed by using inert electrodes. The value of standard potentials are :
$E^\circ_{Ag^+/Ag} = 0.80$ V, $E^\circ_{Cu^+/Cu} = 0.34$ V, and $E^\circ_{Au^{3+}/Au} = 1.50$ V, $E^\circ_{Li^+/Li} = -3.03$ V,
With increasing voltage, the sequence of deposition of metals on the cathode will be :
(a) Li, Cu, Ag, Au (b) Cu, Ag, Au (c) Au, Ag, Cu (d) Au, Ag, Cu, Li

30. If 0.50 L of a 0.60 M $SnSO_4$ solution is electrolyzed for a period of 30.0 min using a current of 4.60 A. If inert electrodes are used, what is the final concentration of Sn^{2+} remaining in the solution? [at. wt. of Sn = 119]
(a) 0.342 M (b) 0.544 M (c) 0.389 M (d) 0.514 M

31. A 100.0 mL dilute solution of Ag^+ is electrolyzed for 15.0 minutes with a current of 1.25 mA and the silver is removed completely. What was the initial $[Ag^+]$?
(a) 2.32×10^{-1} (b) 2.32×10^{-4} (c) 2.32×10^{-3} (d) 1.16×10^{-4}

32. A 250.0 mL sample of a 0.20 M Cr^{3+} is electrolyzed with a current of 96.5 A. If the remaining $[Cr^{3+}]$ is 0.1 M the duration of process is :
(a) 25 sec (b) 225 sec (c) 150 sec (d) 75 sec

33. The element indium is to be obtained by electrolysis of a molten halide of the element. Passage of a current of 3.20 A for a period of 40.0 min results in formation of 3.05 g of In. What is the oxidation state of indium in the halide melt? (Atomic weight : In = 114.8)
(a) 3 (b) 2 (c) 5 (d) 1

34. An electrolysis of a oxytungsten complex ion using 1.10 A for 40 min produces 0.838 g of tungsten. What is the charge on tungsten in the material? (Atomic weight : $W = 184$)
(a) 6 (b) 2 (c) 4 (d) 1

35. In the electrolysis of aqueous NaCl, what volume of $Cl_2(g)$ is produced in the time that it takes to liberate 5.0 liter of $H_2(g)$? Assume that both gases are measured at STP.
(a) 5.0 (b) 2.50 (c) 7.50 (d) 10.0

36. How many grams of Cr are deposited in the electrolysis of solution of $Cr(NO_3)_3$ in the same time that it takes to deposit 0.54 g of Ag in a silver coulometer arranged in series with the $Cr(NO_3)_3$ cell? (Atomic weight : Cr = 52.0; Ag = 108)
(a) 0.0866 (b) 0.0288 (c) 0.173 (d) 0.220

37. In the electrolysis of a $CuSO_4$ solution, how many grams of Cu are plated out on the cathode in the time that it takes to liberate 5.6 litre of $O_2(g)$, measured at STP, at the anode?
(a) 31.75 (b) 14.2 (c) 4.32 (d) None of these

38. Ammonium perchlorate, NH_4ClO_4, used in the solid fuel in the booster rockets on the space shuttle, is prepared from sodium perchlorate, $NaClO_4$, which is produced commercially by the electrolysis of a hot, stirred solution of sodium chloride. How many faradays are required to produce 1.0 kg of sodium perchlorate?

$$NaCl + 4H_2O \longrightarrow NaClO_4 + 4H_2$$

(a) 40.3 (b) 18.3 (c) 31.6 (d) 65.3

39. In the commercial preparation of aluminum, aluminum oxide (Al_2O_3) is electrolyzed at 1000°C. How many coulombs of electricity are required to give 54 kg of aluminum? Assume following reaction takes place at cathode :

$$Al^{3+} + 3e^- \longrightarrow Al$$

(a) 17.3×10^8 (b) 3.21×10^7 (c) 1.82×10^4 (d) 57.9×10^7

40. When molten lithium chloride (LiCl) is electrolyzed, lithium metal is formed at the cathode. If current efficiency is 75% then how many grams of lithium are liberated when 1930 C of charge pass through the cell ? (Atomic weight : Li = 7)

(a) 0.105 (b) 0.120 (c) 0.28 (d) 0.240

41. Sodium metal is produced commercially by the electrolysis of molten sodium chloride and chlorine is produced as a by product. How many litres of chlorine at 1.8 atm and 27°C will be produced if a current of 1.0×10^3 A is passed through NaCl (*l*) for 9.65 h?

(a) 2463 (b) 460 (c) 1800 (d) 1231.6

42. $H_2(g)$ and $O_2(g)$, can be produced by the electrolysis of water. What total volume (in L) of O_2 and H_2 are produced at STP when a current of 30 A is passed through a K_2SO_4 (*aq*) solution for 193 min.?

(a) 20.16 (b) 40.32 (c) 60.48 (d) 80.64

43. The cost of 2 Rs/kWh of operating an electric motor for 10 hours takes 10 amp at 110 V is :

(a) 79200 Rs (b) 22000 Rs (c) 220 Rs (d) 22 Rs

44. A 1 *M* solution of H_2SO_4 is electrolyzed. Select right statement with products at anode and cathode respectively :

Given : $2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-;\ E° = -2.01$ V

$H_2O(l) \longrightarrow 2H^+(aq) + 1/2O_2(g) + 2e^-;\ E° = -1.23$ V

(a) concentration of H_2SO_4 remain constant; H_2, O_2
(b) concentration of H_2SO_4 increases; O_2, H_2
(c) concentration of H_2SO_4 decreases; O_2, H_2
(d) concentration of H_2SO_4 remains constant; $S_2O_8^{2-}$, H_2

45. Cadmium amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. How long should a current of 4 A be passed in order to prepare 10% by wt. Cd in Cd—Hg amalgam on cathode of 4.5 g Hg? (atomic wt. of Cd = 112)

(a) 400 sec (b) 215.40 sec (c) 861.6 sec (d) 430.8 sec

46. Use of electrolysis is in :

(a) Electrorefining (b) Electroplating
(c) Both (a) and (b) (d) None of these

47. When a solution of $AgNO_3$ (1 *M*) is electrolyzed using platinum anode and copper cathode. What are the products obtained at two electrodes?

Given : $E^\circ_{Cu^{2+}|Cu} = +0.34$ volt; $E^\circ_{O_2, H^+|H_2O} = +1.23$ volt; $E^\circ_{H^+|H_2} = +0.0$ volt;

$E^\circ_{Ag^+|Ag} = +0.8$ volt

(a) $Cu \longrightarrow Cu^{2+}$ at anode; $Ag^+ \longrightarrow Ag$ at cathode
(b) $H_2O \longrightarrow O_2$ at anode; $Cu^{2+} \longrightarrow Cu$ at cathode
(c) $H_2O \longrightarrow O_2$ at anode; $Ag^+ \longrightarrow Ag$ at cathode
(d) $NO_3^- \longrightarrow NO_2$ at anode; $Ag^+ \longrightarrow Ag$ at cathode

48. Which of the following statements is correct about Galvanic cell ?
(a) It converts chemical energy into electrical energy.
(b) It converts electrical energy into chemical energy.
(c) It converts metal from its free state to the combined state.
(d) It converts electrolyte into individual ions.

49. E° for $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$ is 1.36 V; E° for $Cl^-(g) \longrightarrow 1/2Cl_2(g) + e^-$ is :
(a) 1.36 V (b) −1.36 V (c) −0.68 V (d) 0.68 V

50. When two half-cells of electrode potential of E_1 and E_2 are combined to form a cell of electrode potential E_3, then
(when n_1, n_2 and n_3 are no. of electrons exchanged in first, second and combined half-cells) :
(a) $E_3 = E_2 - E_1$ (b) $E_3 = \frac{E_1n_1 + E_2n_2}{n_3}$
(c) $E_3 = \frac{E_1n_1 - E_2n_2}{n_3^2}$ (d) $E_3 = E_1 + E_2$

51. The function of a salt bridge is to :
(a) maintain electrical neutrality of both half cells
(b) increase the cell potential at the positive electrode
(c) decrease the cell potential at the negative electrode
(d) eliminate the impurities present in the electrolyte

52. Saturated solution of KNO_3 with agar-agar is used to make 'salt bridge' because :
(a) size of K^+ is greater than that of NO_3^-
(b) velocity of NO_3^- is greater than that of K^+
(c) velocities of K^+ and NO_3^- are nearly the same
(d) both velocity and sizes of K^+ and NO_3^- ions are same

53. A salt bridge contains :
(a) A saturated solution of KCl and agar-agar
(b) A saturated solution of KNO_3 and agar-agar
(c) A saturated solution of NH_4NO_3 and agar-agar
(d) All of these

54. The nature of curve of E°_{cell} *vs.* $\log K_c$ is :
(a) straight line (b) parabola (c) hyperbola (d) elliptical curve

55. Consider the following equations for a cell reaction

$$A + B \rightleftharpoons C + D; \quad E^\circ = x \text{ volt}, \ K_{eq} = K_1$$

$$2A + 2B \rightleftharpoons 2C + 2D; \quad E^\circ = y \text{ volt}, \ K_{eq} = K_2$$

then :

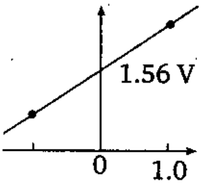
(a) $x = y, K_1 = K_2$ (b) $x = 2y, K_1 = 2K_2$

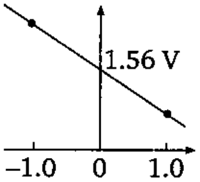
(c) $x = y, K_1^2 = K_2$ (d) $x^2 = y, K_1^2 = K_2$

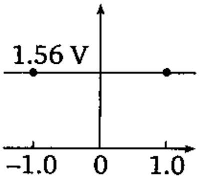
56. Which graph correctly correlates E_{cell} as a function of concentrations for the cell

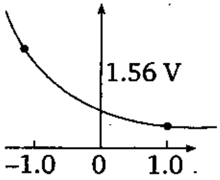
$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s), \quad E^\circ_{cell} = 1.56\text{ V}$$

Y-axis : E_{cell}, X-axis : $\log_{10} \frac{[Zn^{2+}]}{[Ag^+]}$

(a)


(b)


(c)


(d)


57. The Nernst equation $E = E^\circ - RT/nF \ln Q$ indicates that the Q will be equal to equilibrium constant K_c when :

(a) $E = E^\circ$ (b) $RT/nF = 1$ (c) $E = \text{zero}$ (d) $E^\circ = 1$

58. The cell reaction $2Ag^+(aq) + H_2(g) \longrightarrow 2H^+(aq) + 2Ag(s)$, is best represented by :

(a) $Ag(s) \mid Ag^+(aq) \parallel H^+(aq) \mid H_2(g) \mid Pt(s)$ (b) $Pt(s) \mid H_2(g) \mid H^+(aq) \parallel Ag^+(aq) \mid Ag(s)$

(c) $Ag(s) \mid Ag^+(aq) \parallel H_2(g) \mid H^+(aq) \mid Pt(s)$ (d) $Ag^+(aq) \mid Ag(s) \parallel H_2(g) \mid H^+(aq)$

59. The cell reaction $Hg_2Cl_2(s) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Cl^-(aq) + 2Hg(l)$, is best represented by :

(a) $Cu(s) \mid Cu^{+2}(aq) \parallel Hg_2Cl_2(s) \mid Hg(l)$

(b) $Cu(s) \mid Cu^{+2}(aq) \parallel Hg(l) \mid HgCl_2(s)$

(c) $Cu(s) \mid Cu^{+2}(aq) \parallel Cl^-(aq) \mid Hg_2Cl_2(s) \mid Hg(l) \mid Pt(s)$

(d) $Hg_2Cl_2(s) \mid Cl^-(aq) \parallel Cu^{+2}(aq) \mid Cu(s)$

60. The cell reaction $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \longrightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$, is best represented by :

(a) $Pt(s) \mid Fe^{+2}(aq), Fe^{3+}(aq) \parallel Cr_2O_7^{2-}(aq), Cr^{3+}(aq) \mid Pt(s)$

(b) $Pt(s) \mid Cr_2O_7^{2-}(aq), Cr^{+3}(aq) \parallel Fe^{3+}(aq), Fe^{+2}(aq) \mid Pt(s)$

(c) $Fe^{2+}(aq) \mid Fe^{3+}(aq) \parallel Cr_2O_7^{2-}(aq) \mid Cr^{3+}(aq)$

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

61. Select the correct cell reaction of the cell $Ag(s) \mid Ag^+(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$:

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

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

(c) $2Ag(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + 2Ag^+(aq)$
(d) $Cu^{2+}(aq) + 2Ag^+(aq) \longrightarrow 2Ag(s) + Cu(s)$

62. Select the correct cell reaction of the cell $Pt(s) \mid Cl_2(g) \mid Cl^-(aq) \parallel Ag^+(aq) \mid Ag(s)$:
(a) $Cl_2(g) + Ag^+(aq) \longrightarrow Ag(s) + 2Cl^-(aq)$
(b) $Cl_2(g) + Ag(s) \longrightarrow 2Cl^-(aq) + Ag^+(aq)$
(c) $2Cl^-(aq) + 2Ag^+(aq) \longrightarrow 2Ag(s) + Cl_2(g)$
(d) $AgCl(s) \longrightarrow Ag^+(aq) + Cl^-(aq)$

63. Standard electrode potential of SHE at 298 K is :
(a) 0.05 V (b) 0.10 V (c) 0.50 V (d) 0.00 V

64. The e.m.f. of the following galvanic cells :
(a) $Zn|Zn^{2+}(1\,M)||Cu^{2+}(1M)|Cu$ (b) $Zn|Zn^{2+}(0.1\,M)||Cu^{2+}(1\,M)|Cu$
(c) $Zn|Zn^{2+}(1\,M)||Cu^{2+}(0.1\,M)|Cu$ (d) $Zn|Zn^{2+}(0.1\,M)||Cu^{2+}(0.1\,M)|Cu$
are represented by E_1, E_2, E_3 and E_4 respectively. Which of the following statement is true?
(a) $E_1 > E_2 > E_3 > E_4$ (b) $E_3 > E_2 > E_1 > E_4$
(c) $E_3 > E_1 = E_4 > E_2$ (d) $E_2 > E_1 = E_4 > E_3$

65. Based on the cell notation for a spontaneous reaction, at the anode :

$$Ag(s) \mid AgCl(s) \mid Cl^-(aq) \parallel Br^-(aq) \mid Br_2(l) \mid C(s)$$

(a) AgCl becomes reduced (b) Ag becomes oxidized
(c) Br^- becomes oxidized (d) Br_2 becomes reduced

66. Given the listed standard electrode potentials, what is $E°$ for the cell :
$4BiO^+(aq) + 3N_2H_5^+(aq) \longrightarrow 4Bi(s) + 3N_2(g) + 4H_2O(l) + 7H^+(aq)$

$$N_2(g) + 5H^+(aq) + 4e^- \longrightarrow N_2H_5^+(aq),\ E° = -0.23\ V$$
$$BiO^+(aq) + 2H^+(aq) + 3e^- \longrightarrow Bi(s) + H_2O(l),\quad E° = +0.32\ V$$

(a) +0.55 (b) +0.34 (c) +1.88 (d) +0.09

67. What is the standard electrode potential for the reduction of HClO?

$$HClO(aq) + H^+(aq) + 2e^- \longrightarrow Cl^-(aq) + H_2O(l)$$

Given : $Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq) + e^-,\quad E° = 0.41\ V$

$$HClO(aq) + H^+(aq) + 2Cr^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + Cl^-(aq) + H_2O(l),\ E° = 1.80$$

(a) 1.39 (b) 1.54 (c) 1.22 (d) 0.90

68. The $E°$ for the following cell is +0.34 V. $In(s) \mid In(OH)_3(aq) \parallel SbO_2^-(aq) \mid Sb(s)$.
Using $E° = -1.0V$ for the $In(OH)_3 \mid In$ couple, calculate $E°$ for the $SbO_2^- \mid Sb$ half-reaction :
(a) −1.34 (b) + 0.66
(c) +0.82 (d) −0.66

69. From the following half-cell reactions and their potentials, what is the smallest possible standard e.m.f. for spontaneous reactions?

$$PO_4^{3-}(aq) + 2H_2O(l) + 2e^- \longrightarrow HPO_3^{2} + 3OH^-(aq);\quad E° = -1.05\ V$$
$$PbO_2(s) + H_2O(l) + 2e^- \longrightarrow PbO(s) + 2OH^-(aq);\quad E° = +0.28\ V$$

$$IO_3^-(aq) + 2H_2O(l) + 4e^- \longrightarrow IO^-(aq) + 4OH^-(aq); \quad E° = +0.56\text{ V}$$

(a) +0.00 (b) +0.74 (c) +0.56 (d) +0.28

70. Determine which substance is the best reducing agent in Q. no. 47 :
(a) HPO_3^{2-} (b) PO_4^{3-} (c) IO^- (d) IO_3^-

71. Which substance is the best oxidizing agent in Q. no. 47?
(a) IO_3^- (b) IO^- (c) PbO (d) PO_4^{3-}

72. Consider the following half-cell reactions and associated standard half-cell potentials and determine the maximum voltage that can be obtained by combination resulting in spontaneous processes :

$$AuBr_4^-(aq) + 3e^- \longrightarrow Au(s) + 4Br^-(aq); \quad E° = -0.86\text{ V}$$
$$Eu^{3+}(aq) + e^- \longrightarrow Eu^{2+}(aq); \quad E° = -0.43\text{V}$$
$$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s); \quad E° = -0.14\text{ V}$$
$$IO^-(aq) + H_2O(l) + 2e^- \longrightarrow I^-(aq) + 2OH^-(aq); \quad E° = +0.49\text{ V}$$

(a) +0.72 (b) +1.54 (c) +1.00 (d) +1.35

73. The position of some metals in the electrochemical series in decreasing electropositive character is Mg > Al > Zn > Cu > Ag. What will happened if copper spoon is used to stirred a solution of aluminium nitrate ?
(a) The spoon gets coated with aluminium.
(b) An alloy of aluminium and copper is formed.
(c) No reaction occurs
(d) The solution starts turning blue

74. Zn can displace :
(a) Mg from its aqueous solution (b) Cu from its aqueous solution
(c) Na from its aqueous solution (d) Al from its aqueous solution

75. Based on the following information arrange four metals *A*, *B*, *C* and *D* in order of decreasing ability to act as reducing agents :
(I) Only *A*, *B* and *C* react with 1 *M*HCl to give $H_2(g)$
(II) When *C* is added to solutions of the other metal ions, metallic *B* and *D* are formed
(III) Metal *C* does not reduce A^{n+}.
(a) $C > A > B > D$ (b) $C > A > D > B$ (c) $A > C > D > B$ (d) $A > C > B > D$

76. When an aqueous solution of $CuSO_4$ is stirred with a silver spoon then :
(a) Cu^+ will be formed (b) Ag^+ will be formed
(c) Cu^{2+} will be deposited (d) None of these

77. Based on the following information arrange four metals, *A*, *B*, *C* and *D* in order of increasing ability to act as reducing agents :
(I) Only *C* react with 1 *M* HCl to give $H_2(g)$
(II) When *A* is added to solution of the other metal ions, metallic *D* is formed but not *B* or *C*
(a) $D < A < C < B$ (b) $A < D < C < B$ (c) $B < D < A < C$ (d) $D < A < B < C$

78. In the reaction :

$$4Fe(s) + 3O_2(g) \longrightarrow 4Fe^{3+}(aq) + 6O^{2-}(aq)$$

which of the following statement is incorrect ?
(a) A redox reaction (b) Fe is reducing agent
(c) O_2 is an oxidizing agent (d) Fe is reduced to Fe^{3+}

79. Which of the following is displaced by Fe ?
(a) Ag (b) Zn (c) Na (d) All of these

80. The standard potential at 25°C for the following half reactions is given :

$$Zn^{2+} + 2e^- \longrightarrow Zn\ ;\ E^\circ = -0.762\ V$$

$$Mg^{2+} + 2e^- \longrightarrow Mg\ ;\ E^\circ = -2.37\ V$$

When Zinc dust is added to the solution of $MgCl_2$.
(a) $ZnCl_2$ is formed (b) Mg is precipitated
(c) Zn dissolved in the solution (d) No reaction takes place

81. The element which can displace three other halogens from their compound is :
(a) F (b) Cl (c) Br (d) I

82. Using the standard half-cell potential listed, calculate the equilibrium constant for the reaction :

$$Co(s) + 2H^+(aq) \longrightarrow Co^{2+}(aq) + H_2(g) \text{ at 298 K}$$

$$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)\quad E^\circ = -0.277\ V$$

(a) 2.3×10^9 (b) 4.8×10^4 (c) 4.8×10^7 (d) 4.8×10^{11}

83. The E° at 25°C for the following reaction is 0.22 V calculate the equilibrium constant at 25°C :

$$H_2(g) + 2AgCl(s) \longrightarrow 2Ag(s) + 2HCl(aq)$$

(a) 2.8×10^7 (b) 5.2×10^8 (c) 5.2×10^6 (d) 5.2×10^3

84. Electrode potential of the half cell $Pt(s) \mid Hg(l) \mid Hg_2Cl_2(s) \mid Cl^-(aq)$ can be increased by :
(a) Increasing $[Cl^-]$ (b) Decreasing $[Cl^-]$
(c) Increasing $Hg_2Cl_2(s)$ (d) Decreasing $Hg(l)$

85. The equilibrium constant for the following general reaction is 10^{30}. Calculate E° for the cell at 298 K.

$$2X_2(s) + 3Y^{2+}(aq) \longrightarrow 2X_2^{3+}(aq) + 3Y(s)$$

(a) +0.105 V (b) +0.2955 V (c) 0.0985 V (d) −0.2955 V

86. A solution containing H^+ and D^+ ions is in equilibrium with a mixture of H_2 and D_2 gases at 25°C. If the partial pressures of both gases are 1.0 atm, find the ratio of $[D^+]/[H^+]$:

(Given : $E^\circ_{D^+/D_2} = -0.003\ V$)

(a) 1.23 (b) 1.12 (c) 0.11 (d) 1.0

87. The E° at 25C° for the following reaction is 0.55 V. Calculate the ΔG° in kJ :

$$4BiO^+(aq) + 3N_2H_5^+ \longrightarrow 4Bi(s) + 3N_2(g) + 4H_2O(l) + 7H^+$$

(a) −637 (b) −424 (c) −106 (d) − 318.5

88. Use the following E° for the electrode potentials, calculate ΔG° in kJ for the indicated reaction :

$$5Ce^{4+}(aq) + Mn^{2+}(aq) + 4H_2O(l) \longrightarrow 5\,Ce^{3+}(aq);\quad + MnO_4^-(aq) + 8H^+(aq)$$

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

$$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq) \qquad E^\circ = +1.61\ V$$

(a) −9.65 (b) −24.3 (c) −48.25 (d) −35.2

89. Consider an electrochemical cell in which the following reaction occurs and predict which changes will decrease the cell voltage :

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

(I) decrease the $[Ag^+]$ (II) increase in $[Fe^{3+}]$ (III) increase the amount of Ag

(a) I (b) II and III (c) II (d) I and II

90. Consider the following equation for an electrochemical cell reaction. Which of the following changes in condition will increase the cell voltage?

$$H_2(g) + PbCl_2(s) \longrightarrow Pb(s) + 2HCl(aq)$$

(I) dissolve concentrated $HClO_4$ in the cell solution

(II) increase the pressure of $H_2(g)$ (III) increase the amount of $Pb(s)$

(a) III (b) I and II (c) II and III (d) II

91. The standared electrode potential for the following reaction is +1.33 V. What is the potential at pH = 2.0?

$$Cr_2O_7^{2-}(aq, 1M) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq, 1M) + 7H_2O(l)$$

(a) +1.820 V (b) +1.990 V (c) +1.608 V (d) +1.0542 V

92. The standard electrode potential for the following reaction is −0.57 V. What is potential at pH = 12.0?

$$TeO_3^{2-}(aq, 1M) + 3\,H_2O(l) + 4e^- \longrightarrow Te(s) + 6OH^-(aq)$$

(a) −0.17 V (b) +0.21 V (c) −0.39 V (d) +1.95 V

93. $Co|Co^{2+}(C_2)||Co^{2+}(C_1)|Co$; for this cell, ΔG is negative if :

(a) $C_2 > C_1$ (b) $C_1 > C_2$ (c) $C_1 = C_2$ (d) unpredictable

94. What will be the emf for the given cell?

$$Pt|H_2(g, P_1)|H^+(aq)||H_2(g, P_2)|Pt$$

(a) $\frac{RT}{F}\ln\frac{P_1}{P_2}$ (b) $\frac{RT}{2F}\ln\frac{P_1}{P_2}$ (c) $\frac{RT}{F}\ln\frac{P_2}{P_1}$ (d) None of these

95. For the electrochemical cell $Pt(s)|\underset{1\ atm}{H_2(g)}|H^+(1M)||Cu^{2+}(1M)|Cu(s)$, which one of the following statements is true ?

(a) H_2 liberated at anode and Cu is deposite at cathode.

(b) H_2 liberated at cathode and Cu is deposite at anode.

(c) Oxidation occurs at cathode.

(d) Reduction occurs at anode.

96. In a concentration cell the same reactants are present in both the anode and the cathode compartments, but at different concentrations. Calculate the emf of a cell containing 0.040 M. Cr^{3+} in one compartment and 1.0M Cr^{3+} in the other if Cr electrodes are used in both.

(a) 0.028 V (b) 0.249 V (c) 0.083 V (d) 0.125 V

97. A 1.0 M solution of Cd^{2+} is added to excess iron and the system is allowed to reach equilibrium. What is the concentration of Cd^{2+}?

$$Cd^{2+}(aq) + Fe(s) \longrightarrow Cd(s) + Fe^{2+}(aq); \quad E^\circ = 0.037$$

(a) 0.195 (b) 0.097 (c) 0.053 (d) 0.145

98. The measured voltage for the reaction with the indicated concentrations is 1.50 V. Calculate E°.

$$Cr(s) + 3Ag^+(aq,\ 0.10\ M) \longrightarrow Ag(s) + Cr^{3+}(aq,\ 0.30\ M)$$

(a) 1.35 (b) 1.40 (c) 1.65 (d) 1.55

99. Calculate the standard voltage that can be obtained from an ethane oxygen fuel cell at 25°C.

$$C_2H_6(g) + 7/2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);\quad \Delta G^\circ = -1467\ \text{kJ}$$

(a) +0.91 (b) +0.54 (c) +0.72 (d) +1.08

100. $I_2(s)\,|\,I^-(0.1M)$ half cell is connected to a $H^+(aq)\,|\,H_2$ (1 bar)$\,|\,$Pt half cell and e.m.f. is found to be 0.7714 V. If $E^\circ_{I_2|I^-} = 0.535$ V, find the pH of $H^+|H_2$ half-cell.

(a) 1 (b) 3 (c) 5 (d) 7

101. What is the SRP for $S^{2-}|CuS|Cu$ half-cell?

Given : $K_{sp}(CuS) = 10^{-35}$ and $E^\circ_{Cu^{2+}|Cu} = 0.34$ V

(a) 1.034 V (b) 1.0 V (c) −0.694 V (d) 0.694 V

102. Given the following standard electrode potentials, the K_{sp} for $PbBr_2$ is :

$$PbBr_2(s) + 2e^- \longrightarrow Pb(s) + 2Br^-(aq);\quad E^\circ = -0.248\ \text{V}$$

$$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s);\quad E^\circ = -0.126\ \text{V}$$

(a) 7.4×10^{-5} (b) 4.9×10^{-14} (c) 5.2×10^{-6} (d) 2.3×10^{-13}

103. The standard free energy change for the following reaction is −210 kJ. What is the standard cell potential?

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

(a) +0.752 (b) +1.09 (c) +0.420 (d) +0.640

104. At equilibrium :

(a) $E^\circ_{cell} = 0,\ \Delta G^\circ = 0$ (b) $E_{cell} = 0,\ \Delta G = 0$

(c) both are correct (d) none is correct

105. The E° at 25°C for the following reaction at the indicated concentrations is 1.50 V. Calculate the ΔG in kJ at 25°C :

$$Cr(s) + 3Ag^+(aq,\ 0.1\ M) \longrightarrow Ag(s) + Cr^{3+}(aq,\ 0.1\ M)$$

(a) −140.94 (b) −295 (c) −212 (d) −422.83

106. If $E^\circ_{Au^+/Au}$ is 1.69 V and $E^\circ_{Au^{3+}/Au}$ is 1.40 V, then $E^\circ_{Au^+/Au^{3+}}$ will be :

(a) 0.19 V (b) 2.945 V (c) 1.255 V (d) None of these

107. Consider the following standard electrode potentials and calculate the equilibrium constant at 25°C for the indicated disproportionation reaction :

$$3Mn^{2+}(aq) \longrightarrow Mn(s) + 2Mn^{3+}(aq)$$

$$Mn^{3+}(aq) + e^- \longrightarrow Mn^{2+}(aq);\quad E^\circ = 1.51\ \text{V}$$

$$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s);\quad E^\circ = -1.185\ \text{V}$$

(a) 1.2×10^{-43} (b) 2.4×10^{-73} (c) 6.3×10^{-92} (d) 1.5×10^{-62}

108. A galvanic cell is composed of two hydrogen electrodes, one of which is a standard one. In which of the following solutions should the other electrode be immersed to get maximum e.m.f. :
(a) 0.1 M HCl (b) 0.1 M H_2SO_4 (c) 0.1 M NH_4OH (d) 0.01 M HCOOH

109. $Ag|AgCl|Cl^-(C_2)||Cl^-(C_1)|AgCl|Ag$ for this cell ΔG is negative if :
(a) $C_1 = C_2$ (b) $C_1 > C_2$ (c) $C_2 > C_1$ (d) Both (a) and (c)

110. By how much is the oxidizing power of $Cr_2O_7^{2-}|Cr^{3+}$ couple decreased if the H^+ concentration is decreased from 1 M to 10^{-3} M at 25°C?
(a) 0.001 V (b) 0.207 V (c) 0.441 V (d) 0.414 V

111. The temperature coefficient of a cell whose operation is based on the reaction

$$Pb(s) + HgCl_2(aq) \longrightarrow PbCl_2(aq) + Hg(l) \text{ is :}$$

$$\left(\frac{dE}{dT}\right)_p = 1.5 \times 10^{-4}\,VK^{-1} \text{ at } 298\text{ K}$$

The change in entropy (in J/K mol) during the operation is :
(a) 8627 (b) 57.9 (c) 28.95 (d) 14.475

112. Thermodynamic efficiency of a cell is given by :
(a) $\frac{\Delta H}{\Delta G}$ (b) $\frac{nFE}{\Delta G}$ (c) $\frac{-nEF}{\Delta H}$ (d) $nFE°$

113. Calculate the value of equilibrium constant (K_f) for the reaction :

$$Zn^{2+}(aq) + 4OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$$

Given :

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s); \quad E° = -0.76\text{ V}$$

$$Zn(OH)_4^{2-}(aq) + 2e^- \longrightarrow Zn(s) + 4OH^-(aq); \quad E° = -1.36\text{ V}$$

$$2.303\frac{RT}{F} = 0.06$$

(a) 10^{10} (b) 2×10^{10} (c) 10^{20} (d) none of these

114. Which of the following statement is false for fuel cells ?
(a) They are more efficient (b) They are free from pollution
(c) They run till reactants are active (d) Fuel burned with O_2

115. When a lead storage battery is charged it acts as :
(a) a fuel cell (b) an electrolytic cell
(c) a galvanic cell (d) a concentration cell

116. The metal that forms a self-protecting film of oxide to prevent corrosion is :
(a) Na (b) Al (c) Cu (d) Au

117. Rusting of iron is catalyzed by which of the following ?
(a) Fe (b) Zn (c) O_2 (d) H^+

118. Which of the following is a highly corrosive salt ?
(a) Hg_2Cl_2 (b) $HgCl_2$ (c) $FeCl_2$ (d) $PbCl_2$

119. The Zn acts as sacrificial or cathodic protection to prevent rusting of iron because :
(a) $E°_{OP}$ of Zn < $E°_{OP}$ of Fe (b) $E°_{OP}$ of Zn > $E°_{OP}$ of Fe
(c) $E°_{OP}$ of Zn = $E°_{OP}$ of Fe (d) Zn is cheaper than iron

120. In electrochemical corrosion of metals, the metal undergoing corrosion :
(a) acts as anode (b) acts as cathode
(c) undergoes reduction (d) None

121. When an acid cell is charged, then :
(a) Voltage of cell increases (b) Resistance of cell increases
(c) Electrolyte of cell dilutes (d) None of these

122. Electrolytic conduction is due to the movement of :
(a) electrons (b) ions
(c) atoms (d) electrons as well as ions

123. Molten sodium chloride conducts electricity due to the presence of :
(a) Free electron (b) Free ions
(c) Free molecules (d) Atoms of sodium and chlorine

124. Pure water does not conduct electricity because it :
(a) is neutral (b) is readily decomposed
(c) is almost totally unionized (d) has a low boiling point

125. The relation among conductance (G), specific conductance (κ) and cell constant (l/A) is :
(a) $G = \kappa\frac{l}{A}$ (b) $G = \kappa\frac{A}{l}$ (c) $G\kappa = \frac{l}{A}$ (d) $G = \kappa A l$

126. If x is specific resistance (in S^{-1}cm) of the electrolyte solution and y is the molarity of the solution, then Λ_m (in S $cm^2 mol^{-1}$) is given by :
(a) $\frac{1000x}{y}$ (b) $1000\frac{y}{x}$ (c) $\frac{1000}{xy}$ (d) $\frac{xy}{1000}$

127. Equivalent conductance can be expressed in terms of specific conductance (κ) and concentration (N) in gram equivalent per dm^{-3} as :
(a) $\kappa \times N$ (b) $\frac{\kappa \times 1000}{N}$ (c) $\frac{\kappa \times N}{1000}$ (d) $\kappa \times N \times 1000$

128. Resistance of a decimolar solution between two electrodes 0.02 meter apart and 0.0004 m^2 in area was found to be 50 ohm. Specific conductance (κ) is :
(a) 0.1 Sm^{-1} (b) 1 S m^{-1} (c) 10 S m^{-1} (d) 4×10^{-4} S m^{-1}

129. Resistance of 0.1 M KCl solution in a conductance cell is 300 ohm and conductivity is 0.013 Scm^{-1}. The value of cell constant is :
(a) 3.9 cm^{-1} (b) 39 m^{-1} (c) 3.9 m^{-1} (d) None of these

130. Ionisation constant of a weak acid (HA) in terms of Λ_m^∞ and Λ_m is :
(a) $K_a = \frac{C\Lambda_m^\infty}{(\Lambda_m - \Lambda^\infty)}$ (b) $K_a = \frac{C\Lambda_m^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m)}$
(c) $K_a = \frac{C(\Lambda_m^\infty)^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m)}$ (d) None of these

131. When a concentrated solution of an electrolyte is diluted?
(a) its specific conductance increases
(b) its equivalent conductance decreases

(c) its specific conductance decreases and equivalent conductance increases
(d) both specific and equivalent conductance increase

132. Molar conductivity of a solution of an electrolyte AB_3 is $150\,\text{Scm}^2\text{mol}^{-1}$. If it ionises as $AB_3 \longrightarrow A^{3+} + 3B^-$, its equivalent conductivity will be :

(a) 150 (in $\text{Scm}^2\text{eq}^{-1}$)
(b) 75 (in $\text{Scm}^2\text{eq}^{-1}$)
(c) 50 (in $\text{Scm}^2\text{eq}^{-1}$)
(d) 80 (in $\text{Scm}^2\text{eq}^{-1}$)

133. Equivalent conductivity of $Fe_2(SO_4)_3$ is related to molar conductivity by the expression :

(a) $\Lambda_{eq} = \Lambda_m$
(b) $\Lambda_{eq} = \Lambda_m/3$
(c) $\Lambda_{eq} = 3\Lambda_m$
(d) $\Lambda_{eq} = \Lambda_m/6$

134. The limiting equivalent conductivity of NaCl, KCl and KBr are 126.5, 150.0 and 151.5 S cm^2 eq^{-1}, respectively. The limiting equivalent ionic conductance for Br^- is 78 S $\text{cm}^2\text{eq}^{-1}$. The limiting equivalent ionic conductance for Na^+ ions would be :

(a) 128
(b) 125
(c) 49
(d) 50

135. The specific conductance of a saturated solution of silver bromide is κ Scm^{-1}. The limiting ionic conductivity of Ag^+ and Br^- ions are x and y, respectively. The solubility of silver bromide in gL^{-1} is : (molar mass of AgBr = 188)

(a) $\dfrac{\kappa \times 1000}{x - y}$
(b) $\dfrac{\kappa}{x + y} \times 188$
(c) $\dfrac{\kappa \times 1000 \times 188}{x + y}$
(d) $\dfrac{x + y}{\kappa} \times \dfrac{1000}{188}$

136. The resistance of 0.1 N solution of formic acid is 200 ohm and cell constant is 2.0 cm^{-1}. The equivalent conductivity (in $\text{Scm}^2\text{eq}^{-1}$) of 0.1 N formic acid is :

(a) 100
(b) 10
(c) 1
(d) none of these

137. A conductance cell was filled with a 0.02 M KCl solution which has a specific conductance of 2.768×10^{-3} ohm^{-1} cm^{-1}. If its resistance is 82.4 ohm at 25°C, the cell constant is :

(a) 0.2182 cm^{-1}
(b) 0.2281 cm^{-1}
(c) 0.2821 cm^{-1}
(d) 0.2381 cm^{-1}

138. The ionic conductivity of Ba^{2+} and Cl^- at infinite dilution are 127 and 76 ohm^{-1} $\text{cm}^2\text{eq}^{-1}$ respectively. The equivalent conductivity of $BaCl_2$ at infinity dilution (in $\text{ohm}^{-1}\text{cm}^2\text{eq}^{-1}$) would be :

(a) 203
(b) 279
(c) 101.5
(d) 139.5

139. Unit of ionic mobility is :

(a) $\text{m V}^{-1}\text{ s}^{-1}$
(b) $\text{m}^2\text{ V}^{-2}\text{ s}^{-1}$
(c) $\text{m}^2\text{ V}^{-1}\text{ s}^{-1}$
(d) $\text{m}^{-2}\text{ V s}^{-1}$

140. Λ^{∞}_{AgCl} can be obtained :

(a) by extraplotation of the graph Λ and $\sqrt{C}$ to zero concentration
(b) by known values of Λ^{∞} of $AgNO_3$, HCl and HNO_3
(c) both (a) and (b)
(d) None of these

141. The conductance of a salt solution (AB) measured by two parallel electrodes of area 100 cm^2 separated by 10 cm was found to be $0.0001\,\Omega^{-1}$. If volume enclosed between two electrode contain 0.1 mole of salt, what is the molar conductivity ($\text{Scm}^2\text{mol}^{-1}$) of salt at same concentration :

(a) 10
(b) 0.1
(c) 1
(d) none of these

142. The conductivity of a strong electrolyte :

(a) Increases on dilution
(b) Decreases on dilution
(c) Does not change with dilution
(d) Depends upon density of electrolytes

143. The increase in equivalent conductance of a weak electrolyte with dilution is due to :

(a) Increase in degree of dissociation and decrease in ionic mobility
(b) Decrease in degree of dissociation and decrease in ionic mobility
(c) Increase in degree of dissociation and increase in ionic mobility
(d) Decrease in degree of dissociation and increase in ionic mobility

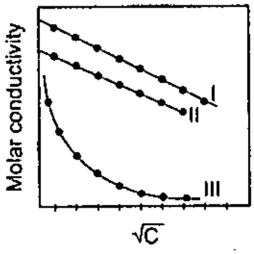
144. Strong electrolytes are those which :

(a) Conduct electricity
(b) Dissolve readily in water
(c) Dissociate into ions at high dilution
(d) Completely dissociate into ions

145. The electric conduction of a salt solution in water depends on the :

(a) Size of its molecules
(b) Shape of its molecules
(c) Size of solvent molecules
(d) Extent of its ionization

146. A graph was plotted between molar conductivity of various electrolytes (NaCl, HCl and NH_4OH) and $\sqrt{C}$ (in mol L^{-1}). Correct setting :

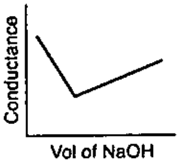


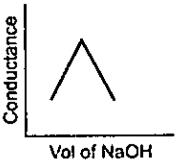
(a) I(NaCl), II(HCl), III(NH_4OH)
(b) I(HCl), II(NaCl), III(NH_4OH)
(c) I(NH_4OH), II(NaCl), III(HCl)
(d) I(NH_4OH), II(HCl), III(NaCl)

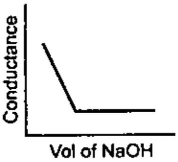
147. Which of the following is arranged in increasing order of ionic mobility ?

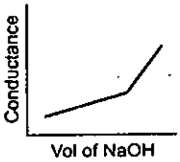
(a) $I^- < Br^- < Cl^- < F^-$
(b) $F^- < Cl^- < Br^- < I^-$
(c) $F^- < I^- < Cl^- < Br^-$
(d) $F^- < Cl^- < I^- < Br^-$

148. $HNO_3(aq)$ is titrated with NaOH(*aq*) conductometrically, graphical representation of the titration as :

(a)


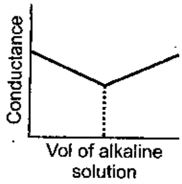
(b)


(c)


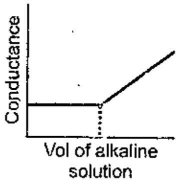
(d)


149. Which of the following plots will obtained for a conductometric titration of strong acid against a weak base?

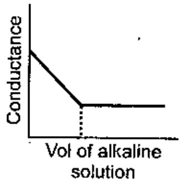
(a)



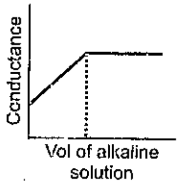
(b)



(c)

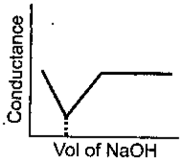


(d)

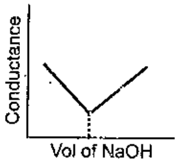


150. Conductometric titration curve of a equimolar mixture of a HCl and HCN with NaOH(*aq*) is :

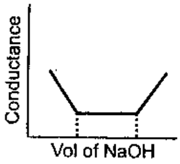
(a)



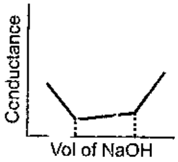
(b)



(c)



(d)



Level 2

1. In the Hall process, aluminum is produced by the electrolysis of molten Al_2O_3 by the following reactions. How many second would it take to produce enough aluminum by the Hall process to make a case of 24 cans of aluminum soft-drink, if each can uses 5.0 g of Al, a current of 9650 amp is employed, and the current efficiency of the cell is 90.0% :
(a) 203.2 (b) 148.14 (c) 333 (d) 6.17

2. 108 g fairly concentrate solution of $AgNO_3$ is electrolyzed using 0.1 F of electricity. The weight of resulting solution is :
(a) 94 g (b) 11.6 g (c) 96.4 g (d) None of these

3. The electrolysis of acetate solution produces ethane according to reaction :
$$2CH_3COO^- \longrightarrow C_2H_6(g) + 2CO_2(g) + 2e^-$$
The current efficiency of the process is 80%. What volume of gases would be produced at 27°C and 740 torr, if the current of 0.5 amp is passed through the solution for 96.45 min?
(a) 6.0 L (b) 0.60 L (c) 1.365 L (d) 0.91 L

4. A layer of chromium metal 0.25 mm thick is to be plated on an auto bumper with a total area of $0.32\ m^2$ from a solution containing CrO_4^{2-}? What current flow is required for this electroplating if the bumper is to be plated in 60 s ? The density of chromium metal is $7.20\ g/cm^3$.
(a) 4.9×10^3 A (b) 1.78×10^3 A (c) 5.3×10^4 A (d) 10.69×10^6 A

5. 100 mL of 0.05 *M* $CuSO_4(aq)$ solution was electrolyzed using inert electrodes by passing current till the pH of the resulting solution was 2. The solution after electrolysis was neutralized and then treated with excess KI and formed I_2 titrated with 0.04 *M* $Na_2S_2O_3$. Calculate the required volume (in mL) of $Na_2S_2O_3$:
(a) 112.5 mL (b) 100 mL (c) 125 mL (d) None of these

6. If the equilibrium constant for the reaction $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$ is 10^{13} at certain temperature then what is the $E°$ for the reaction, $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$
Given : $\frac{2.303RT}{F} = 0.066$
(a) 1.230 V (b) −0.858 V (c) −0.80 V (d) −0.8274 V

7. A fuel cell develops an electrical potential from the combustion of butane at 1 bar and 298 K
$$C_4H_{10}(g) + 6.5O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l); \quad \Delta_rG° = -2746\ kJ/mol$$
What is $E°$ of a cell?
(a) 4.74 V (b) 0.547 V (c) 4.37 V (d) 1.09 V

8. The cell $Pt|H_2(g, 0.1\ bar)|H^+\ (aq), pH = X||Cl^-(aq, 1\ M)|Hg_2Cl_2|Hg|Pt$,
has e.m.f. of 0.5755 V at 25°C. The SOP of calomel electrode is −0.28V, then pH of solution will be :
(a) 11 (b) 4.5 (c) 5.5 (d) None of these

9. For a cell reaction $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ $\Delta_r S^\circ_{298} = -0.32$ kJ/K. What is the value of $\Delta_f H^\circ_{298}(H_2O, l)$?

Given : $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$; $E^\circ = 1.23$ V

(a) -285.07 kJ/mol
(b) -570.14 kJ/mol
(c) 285.07 kJ/mol
(d) None of these

10. What is the potential of an electrode which originally contained 0.1 M NO_3^- and 0.4 M H^+ and which has been treated by 80% of the cadmium necessary to reduce all the NO_3^- to NO(g) at 1 bar?

Given : $NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$; $E^\circ = 0.96$ V; log 2 = 0.3

(a) 0.84 V
(b) 1.08 V
(c) 1.23 V
(d) 1.36 V

11. The standard reduction potential of normal calomel electrode and reduction potential of saturated calomel electrodes are 0.27 and 0.33 volt respectively. What is the concentration of Cl^- in saturated solution of KCl?

(a) 0.1 M
(b) 0.01 M
(c) 0.001
(d) None

12. Determine the potential of the following cell :

$Pt|H_2(g, 0.1\ \text{bar})|H^+(aq, 10^{-3}\ M)||MnO_4^-(aq, 0.1\ M),$
$Mn^{2+}(aq, 0.01\ M), H^+(aq, 0.01\ M)|Pt$

Given : $E^\circ_{MnO_4^-|Mn^{2+}} = 1.51$ V

(a) 1.54 V
(b) 1.48 V
(c) 1.84 V
(d) none of these

13. Copper reduces NO_3^- into NO and NO_2 depending upon concentration of HNO_3 in solution. Assuming $[Cu^{2+}] = 0.1\ M$, and $P_{NO} = P_{NO_2} = 10^{-3}$ bar. At which concentration of HNO_3, thermodynamic tendency for reduction of NO_3^- into NO and NO_2 by copper is same?

[Given : $E^\circ_{Cu^{2+}|Cu} = +0.34$ volt, $E^\circ_{NO_3^-|NO} = +0.96$ volt, $E^\circ_{NO_3^-|NO_2} = +0.79$ volt]

(a) $10^{1.23}$ M
(b) $10^{0.56}$ M
(c) $10^{0.66}$ M
(d) $10^{0.12}$ M

14. For the cell, $Pt|Cl_2(g, 0.4\ \text{bar})|Cl^-(aq, 0.1\ M)||Cl^-(aq, 0.01\ M)|Cl_2(g, 0.2\ \text{bar})|Pt$

The measured potential at 298 K is:

(a) 0.051 V
(b) -0.051 V
(c) 0.102 V
(d) 0.0255 V

15. The chlorate ion can disproportionate in basic solution according to reaction,

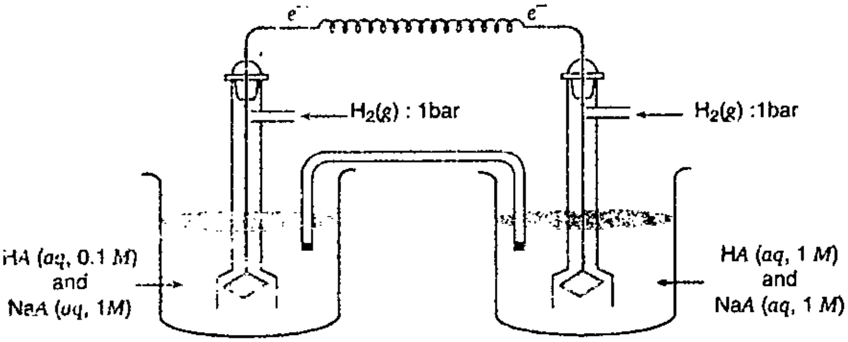
$$2ClO_3^- \rightleftharpoons ClO_2^- + ClO_4^-$$

What is the equilibrium concentration of perchlorate ions from a solution initially at 0.1 M in chlorate ions at 298 K?

Given : $E^\circ_{ClO_4^-|ClO_3^-} = 0.36$ V and $E^\circ_{ClO_3^-|ClO_2^-} = 0.33$ V at 298 K

(a) 0.019 M
(b) 0.024 M
(c) 0.1 M
(d) 0.19 M

16. A cell diagram shown below contains one litre of buffer solution of HA(pK_a = 4) and NaA in both compartment. What is the cell e.m.f.?



(a) 0.03 V (b) 0.06 V (c) −0.06 V (d) None of these

17. Given the cell : $Cd(s)|Cd(OH)_2(s)|NaOH(aq, 0.01\ M)|H_2(g, 1\ bar)|Pt(s)$

with $E_{cell} = 0.0$ V. If $E^\circ_{Cd^{2+}|Cd} = -0.39$ V, then K_{sp} of $Cd(OH_2)$ is :

(a) 0.1 (b) 10^{-13} (c) 10^{-15} (d) None of these

18. Calculate the e.m.f. (in V) of the cell :

$$\underset{}{Pt}|\underset{0.1\ bar}{H_2(g)}|\underset{1\ M}{BOH(aq)}||\underset{0.1\ M}{HA(aq)}|\underset{1\ bar}{H_2(g)}|Pt;$$

Given : $K_a(HA) = 10^{-7}$, $K_b(BOH) = 10^{-5}$

(a) 0.39 V (b) 0.36 V (c) 0.93 V (d) None of these

19. Calculate the potential of a half cell having reaction : $Ag_2S(s) + 2e^- \rightleftharpoons 2Ag(s) + S^{2-}(aq)$ in a solution buffered at pH = 3 and which is also saturated with 0.1 $M\ H_2S(aq)$:
[Given: $K_{sp}(Ag_2S) = 10^{-49}$, $K_{a_1} \cdot K_{a_2} = 10^{-21}$]

(a) 1.18 (b) 0.19 (c) −0.19 V (d) none of these

20. The conductivity of 0.1 N NaOH solution is 0.022 S cm^{-1}. When equal volume of 0.1 N HCl solution is added, the conductivity of resultant solution is decreases to 0.0055 S cm^{-1}. The equivalent conductivity in S cm^{2}equivalent^{-1} of NaCl solution is :

(a) 0.0055 (b) 0.11 (c) 110 (d) None of these

21. In above question after formation of NaCl, further 0.1 N HCl is added, the volume of which is double to that of the first portion added, the conductivity increases to 0.018 S cm^{-1}. The value of Λ_{eq}(HCl) is [assume no change in conductivity of NaCl (aq)] :

(a) 330 S cm^{2}eq^{-1} (b) 305 S cm^{2}eq^{-1}
(c) 415 S cm^{2}eq^{-1} (d) 360 S cm^{2}eq^{-1}

22. Given the following molar conductivities at 25°C :, HCl, 426 Ω^{-1} cm^{2}mol^{-1}; NaCl, 126 Ω^{-1} cm^{2}mol^{-1}; NaC (sodium crotonate), 83 Ω^{-1}cm^{2}mol^{-1}. What is the ionization constant of crotonic acid? If the conductivity of a 0.001 M crotonic acid solution is $3.83 \times 10^{-5}\ \Omega^{-1}$cm^{-1} ?

(a) 10^{-5} (b) 1.11×10^{-5} (c) 1.11×10^{-4} (d) 0.01

23. Equivalent conductivity of $BaCl_2$, H_2SO_4 and HCl, are x_1, x_2 and x_3 $S cm^{-1} eq^{-1}$ at infinite dilution. If conductivity of saturated $BaSO_4$ solution is x $S cm^{-1}$, then K_{sp} of $BaSO_4$ is :

(a) $\dfrac{500x}{(x_1 + x_2 - 2x_3)}$ (b) $\dfrac{10^6 x^2}{(x_1 + x_2 - 2x_3)^3}$

(c) $\dfrac{2.5 \times 10^5 x^2}{(x_1 + x_2 - x_3)^2}$ (d) $\dfrac{0.25x^2}{(x_1 + x_2 - x_3)^2}$

24. The conductivity of $0.001\,M$ Na_2SO_4 solution is 2.6×10^{-4} $S cm^{-1}$ and increases to 7.0×10^{-4} $S cm^{-1}$, when the solution is saturated with $CaSO_4$. The molar conductivities of Na^+ and Ca^{2+} are 50 and 120 $S cm^2 mol^{-1}$, respectively. Neglect conductivity of used water.

What is the solubility product of $CaSO_4$?

(a) 4×10^{-6} (b) 1.57×10^{-3}

(c) 4×10^{-4} (d) 2.46×10^{-6}

25. The ionization constant of a weak acid is 1.6×10^{-5} and the molar conductivity at infinite dilution is 380×10^{-4} $S\,m^2 mol^{-1}$. If the cell constant is 0.01 m^{-1} then conductance of $0.01\,M$ acid solution is :

(a) 1.52×10^{-5} S (b) 1.52 S

(c) 1.52×10^{-3} S (d) 1.52×10^{-4} S

26. Three electrolytic cells X, Y, Z containing solution of NaCl, $AgNO_3$ and $CuSO_4$ respectively are connected in series combination. During electrolysis 21.6 gm of silver deposite at cathode in cell Y. Which is incorrect statement.

(a) 6.35 gm copper deposite at cathode in cell Z

(b) 2.24 litre Cl_2 liberated at 1 atm and 273 K at cathode in cell X

(c) 2.24 litre O_2 liberated at 1 atm and 273 K at anode in cell Y

(d) 2.24 litre H_2 liberated at 1 atm and 273 K at cathode in cell X

27. During electrolysis of $H_2SO_4(aq)$ with high charge density, $H_2S_2O_8$ formed as by product. In such electrolysis 22.4 L $H_2(g)$ and 8.4 L $O_2(g)$ liberated at 1 atm and 273 K at electrode. The moles of $H_2S_2O_8$ formed is :

(a) 0.25 (b) 0.50 (c) 0.75 (d) 1.00

28. $Zn(s) \mid Zn(CN)_4^{2-}(0.5M),\ CN^-(0.01) \parallel Cu(NH_3)_4^{2+}(0.5M),\ NH_3(1M) \mid Cu(s)$

Given: K_f of $Zn(CN)_4^{-2} = 10^{16}$, K_f of $Cu(NH_3)_4^{2+} = 10^{12}$,

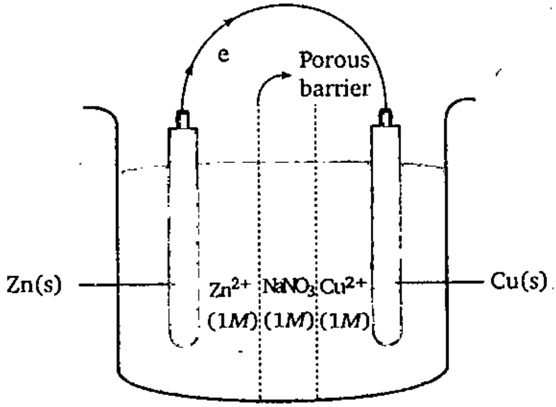
$$E^\circ_{Zn|Zn^{+2}} = 0.76V\ ;\ E^\circ_{Cu^{+2}|Cu} = 0.34V\ ,\ \frac{2.303RT}{F} = 0.06$$

The emf of above cell is :

(a) 1.22 V (b) 1.10 V (c) 0.98 V (d) None of these

Level 3

PASSAGE 1



A Galvanic cell consist of three compartment as shown in figure. The first compartment contain $ZnSO_4(1\ M)$ and III compartment contain $CuSO_4(1\ M)$. The mid compartment contain $NaNO_3(1\ M)$. Each. compartment contain 1 L solution :

$$E^\circ_{Zn^{2+}/Zn} = -0.76;\quad E^\circ_{Cu^{2+}/Cu} = +0.34$$

1. The concentration of Zn^{2+} in first compartment after passage of 0.1 F charge will be :
(a) 1 M (b) 1.05 M (c) 1.025 M (d) 0.5 M

2. The concentration of NO_3^- in mid compartment after passage of 0.1 F of charge will be :
(a) 0.95 M (b) 0.90 M (c) 0.975 M (d) 1.05 M

3. The concentration of SO_4^{2-} ion in III compartment will be :
(a) 1.05 M (b) 1.025 M (c) 0.95 M (d) 0.975 M

PASSAGE 2

The cell potential (E_{cell}) of a reaction is related as $\Delta G = -nF\,E_{cell}$, where ΔG represents max. useful electrical work

n = no. of moles of electrons exchanged during the reaction

for reversible cell reaction $d(\Delta G) = (\Delta_r V)dp - (\Delta_r S).\,dT$

at constant pressure $d(\Delta G) = -(\Delta_r S)\cdot dT$

∵ At constant pressure $\Delta G = \Delta H - T\cdot\Delta S$ ...(1)

∴ $\Delta G = \Delta H + T\left(\dfrac{d(\Delta G)}{dT}\right)_p$ ...(2)

$\left(\dfrac{dE_{cell}}{dT}\right)_p$ is known as temperature coefficient of the e.m.f of the cell

1. The temperature coefficient of the e.m.f. of cell, $\left(\frac{dE}{dT}\right)_p$ is given by :
   (a) $\frac{nF}{\Delta S}$ (b) $\frac{\Delta S}{nF}$ (c) $\frac{\Delta S}{nFT}$ (d) $-nFE$
2. At 300 K, ΔH for the reaction
   $Zn(s) + AgCl(s) \longrightarrow ZnCl_2(aq) + 2Ag(s)$ is
   -218 kJ/mol while the e.m.f. of the cell was 1.015 V. $\left(\frac{dE}{dT}\right)_p$ of the cell is :
   (a) $-4.2 \times 10^{-4}\,VK^{-1}$ (b) $-3.81 \times 10^{-4}\,VK^{-1}$
   (c) $0.11\,VK^{-1}$ (d) $7.62 \times 10^{-4}\,VK^{-1}$
3. Colculate ΔS for the given cell reaction in Q. no. 2 :
   (a) $-73.53\,J/K\,mol$ (b) $83.53\,J/K\,mol$ (c) $100\,J/K\,mol$ (d) none of these

PASSAGE 3

Molar conductivity (Λ_m) is defined as conducting power of the ions produced by 1 mole of an electrolyte in a solution. $\Lambda_m = \frac{\kappa}{C}$ where κ is conductivity (in $S cm^2 mol^{-1}$) and C is molar concentration (in mole/cm^3)

The molar conductivity of 0.04 M solution of $MgCl_2$ is 200 Scm^3mol^{-1} at 298 K. A cell with electrodes that are 2.0 cm^2 in surface area and 0.50 cm apart is filled with $MgCl_2$ solution.

1. Conductance of $MgCl_2$ solution is :
   (a) 8×10^{-3}S (b) 32 S (c) 0.032 S (d) None of these
2. How much current will flow when the potential difference between the two electrodes is 5.0 V?
   (a) 156.25 A (b) 0.16 A (c) 160 A (d) None of these

PASSAGE 4

In a hydrogen oxygen fuel cell, electricity produced. In this process $H_2(g)$ is oxidised at anode and $O_2(g)$ reduced at cathode.

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

Anode $H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$

4.48 litre H_2 at 1 atm and 273 K oxidised in 9650 sec.

1. The current produced is (in amp) :
   (a) 1 amp (b) 2 amp (c) 4 amp (d) 8 amp
2. The mass of water produced is :
   (a) 7.2 gm (b) 3.6 gm (c) 1.8 gm (d) 0.9 gm
3. If current produced in fuel cell, use for the deposition of Cu^{+2} in 1 L, 2M $CuSO_4(aq)$ solution for 241.25 sec using Pt electrode. The pH of solution after electrolysis is :
   (a) 1 (b) 2 (c) 3 (d) 4

PASSAGE 5

A saturated solution in $AgX(K_{sp} = 3\times10^{-12})$ and $AgY(K_{sp} = 10^{-12})$ has conductivity $0.4\times10^{-6}\,\Omega^{-1}cm^{-1}$.

Given : Limiting molar conductivity of $Ag^+ = 60\,\Omega^{-1}cm^2mol^{-1}$

Limiting molar conductivity of $X^- = 90\,\Omega^{-1}cm^2mol^{-1}$

1. The conductivity of Y^- is (in $\Omega^{-1}\,cm^{-1}$) :

(a) 1.45×10^{-7} (b) 1.45×10^{-5}
(c) 1.45×10^{-9} (d) None of these

2. The limiting molar conductivity of Y^- is (in $\Omega^{-1}\,cm^2\,mol^{-1}$) :

(a) 290 (b) 2900 (c) 2.90 (d) None of these

ONE OR MORE ANSWERS IS/ARE CORRECT

1. If the e.m.f of a galvanic cell is negative, it implies that :
(a) the cell reaction is spontaneous
(b) the cell reaction is non-spontaneous
(c) the cell reaction is exothermic
(d) the cell is working in reverse direction

2. Select right statement(s) about electrolysis :
(a) Electric current is used to drive a non-spontaneous reaction
(b) ΔG is positive for chemical process during electrolysis
(c) Cations and anions are moved toward the anode and cathode respectively
(d) Over voltage is generally associated with evolution of O_2 gas

3. If the half-cell reaction $A + e^- \longrightarrow A^-$ has a large negative reduction potentials, it follows that :
(a) A is readily reduced (b) A is readily oxidised
(c) A^- is readily reduced (d) A^- is readily oxidised

4. Which of the following statement is correct?
If $E^\circ_{Cu^{2+}|Cu} = 0.34\,V$ and $E^\circ_{Sn^{2+}|Sn} = -0.136\,V$, $E^\circ_{H^+|H_2} = -0.0\,V$
(a) Cu^{2+} ions can be reduced by $H_2(g)$ (b) Cu can be oxidized by H^+
(c) Sn^{2+} ions can be reduced by H_2 (d) Sn can be oxidized by Cu^{2+}

5. The oxidation potential of hydrogen half-cell will be negative if :
(a) $p(H_2) = 1$ atm and $[H^+] = 1\,M$ (b) $p(H_2) = 1$ atm and $[H^+] = 2\,M$
(c) $p(H_2) = 0.2$ atm and $[H^+] = 1\,M$ (d) $p(H_2) = 0.2$ atm and $[H^+] = 0.2\,M$

6. Which of the following arrangement will produce oxygen at anode during electrolysis?
(a) Dilute H_2SO_4 with Pt electrodes
(b) Fused NaOH with inert electrodes

(c) Dilute H_2SO_4 with Cu electrodes
(d) Concentrate aq. NaCl with Pt electrodes

7. When an aqueous concentrate solution of lithium chloride is electrolysed using inert electrodes :
(a) Cl_2 is liberated at the anode
(b) Li is deposited at the cathode
(c) as the current flows, pH of the solution around the cathode remains constant
(d) as the current flows, pH of the solution around the cathode increases

8. Oxygen and hydrogen gas are produced at the anode and cathode during the electrolysis of fairly concentrate aqueous solution of :
(a) K_2SO_4 (b) $AgNO_3$ (c) H_2SO_4 (d) NaOH

9. 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 present in solution as ions
(d) concentration of $CuSO_4$ solution remains constant during dissolution of Cu

10. When a lead storage battery is discharged :
(a) SO_2 is evolved
(b) lead sulphate is produced at both electrodes
(c) sulphuric acid is consumed
(d) water is formed

11. Which of the following is characteristic of the cathode in a voltaic cell?
(a) It may gain weight during reaction
(b) Electrons flow to it through the external circuit
(c) It is where oxidation occurs
(d) It received electrons from ions in solution

12. In an electrochemical process, a salt bridge is used :
(a) to maintain electrical neutrality in each solution
(b) to complete the external circuit so that current can flow for long time
(c) to mix the solution of anodic and cathodic compartment
(d) to supply voltage

13. For a reaction in a galvanic cell the value of $-\Delta G^\circ$ at certain temperature is not necessarily equal to :
(a) nFE° (b) $RT \ln K$ (c) $T \cdot \Delta S^\circ - \Delta H^\circ$ (d) zero

14. Standard electrode potential of two half-reactions are given below :

$$Fe^{2+} \rightleftharpoons Fe \qquad E^\circ = -0.44 \text{ V}$$

$$Fe^{3+} \rightleftharpoons Fe^{2+} \qquad E^\circ = +0.77 \text{ V}$$

If Fe^{2+}, Fe^{3+} and Fe are kept together :
(a) the concentration of Fe^{3+} increases
(b) the concentration of Fe^{3+} decreases
(c) the mass of Fe increases
(d) the concentration of Fe^{2+} decreases

15. Which of the following statements are correct regarding to galvanic cell?
(a) A reaction is spontaneous from left to right if $E_{\text{cell}} > 0$
(b) A reaction occurs from right to left if $E_{\text{cell}} < 0$
(c) If the system is at equilibrium no net reaction occurs
(d) E_{cell} is temperature-independent

16. Which of the following are concentration cells?
(a) $\text{Pt}|\underset{P_1}{\text{H}_2(g)}|\text{HCl}|\underset{P_2}{\text{H}_2(g)}|\text{Pt}$
(b) $\underset{a_1}{\text{Cd, (Hg)}}|\underset{(c)}{\text{Cd}^{2+}}|\underset{a_2}{\text{(Hg), Cd}}$
(c) $\text{Zn}(s)|\underset{c_1}{\text{Zn}^{2+}}||\underset{c_2}{\text{Cu}^{2+}}|\text{Cu}$
(d) $\text{Ag}|\text{AgCl}|\underset{c_1}{\text{Cl}^-}(aq)||\underset{c_2}{\text{Br}^-}(aq)|\text{AgBr}|\text{Ag}$

17. In electrolyte concentration cell :
(a) the electrode material and the solution in both half-cells are composed of the same substances
(b) only the concentrations of solutions of the same substances is different
(c) $E^\circ_{\text{cell}} = 0$
(d) the Nernst equation reduces to $E_{\text{cell}} = -\left(\frac{0.0591}{n}\right)\log Q$ at 25°C

18. The standard electrode potential of a metal-metal ion ($\text{Ag}|\text{Ag}^+$) and metal-sparingly soluble salt anion ($\text{Ag}|\text{AgCl}|\text{Cl}^-$) are related as :
(a) $E^\circ_{\text{Ag}^+|\text{Ag}} = E^\circ_{\text{Cl}^-|\text{AgCl}|\text{Ag}} + \frac{RT}{F}\ln K_{sp}$
(b) $E^\circ_{\text{Cl}^-|\text{AgCl}|\text{Ag}} = E^\circ_{\text{Ag}^+|\text{Ag}} + \frac{RT}{F}\ln K_{sp}$
(c) $E^\circ_{\text{Cl}^-|\text{AgCl}|\text{Ag}} = E^\circ_{\text{Ag}^+|\text{Ag}} - \frac{RT}{F}\ln\frac{[\text{Cl}^-]}{K_{sp}}$
(d) $E^\circ_{\text{Cl}^-|\text{AgCl}|\text{Ag}} = E^\circ_{\text{Ag}^+|\text{Ag}} - \frac{RT}{F}\ln\frac{K_{sp}}{[\text{Cl}^-]}$

19. Which of the following units is correctly matched?
(a) SI units of conductivity is S m^{-1}
(b) SI units of molar conductivity is $\text{S cm}^2\text{mol}^{-1}$
(c) SI unit of conductance is S^{-1}
(d) All of these

20. Which of the following statements is/are correct?
(a) The conductance of one cm^3 (or 1 unit^3) of a solution is called specific conductance
(b) Specific conductance increases while molar conductivity decreases on progressive dilution
(c) The limiting equivalent conductivity of weak electrolyte cannot be determine exactly by extraplotation of the plot of Λ_{eq} against $\sqrt{c}$
(d) The conductance of metals is due to the movement of free electrons

21. Which is/are correct statement ?
(a) No corrosion takes place in vacuum
(b) corrosion protecting by electroplating
(c) During rusting $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ formed
(d) In presence of electrolyte, corrosion takes place with greater rate

22. A dilute solution of KCl was placed between two Pt electrode 10 cm apart across which a potential difference of 10 volt was applied. Which is/are correct statement (Given : molar conductivity of K^+ at infinite dilution is 96.5 $\text{Scm}^2\ \text{mol}^{-1}$.)

Which is/are correct statement ?

(a) Ionic mobility of K^+ is 10^{-3} $cm^2\ sec^{-1}\ volt^{-1}$.

(b) The speed of K^+ is 10^{-3} cm sec^{-1}.

(c) Distance travelled by K^+ is 5×10^3 sec is 5 cm.

(d) The potential gradient is 1.0 volt cm^{-1}.

23. Given : $Pt(s)\ |\ \underset{1\,bar}{H_2(g)}\ |\ 0.1M\ NH_4OH(aq)\ ||\ 0.1M\ CH_3COOH(aq)\ |\ \underset{1\,bar}{H_2(g)}\ |\ Pt(s)$

$pK_b(NH_4OH) = 5;\ pK_a(CH_3COOH) = 5;\ \frac{2.303RT}{F} = 0.06$

Volume of $0.1M$ NH_4OH in anode half cell = 100 mL,

Volume of $0.1M$ CH_3COOH in cathode half cell = 100 mL

Which is/are correct statement ?

(a) The emf of given cell is 0.48 V.

(b) The emf of given cell is 0.36 V when 50 mL, 0.1 M NaOH added to cathode compartment

(c) The emf of given cell is 0.36 V when 50 mL 0.1 M HCl added to anode compartment

(d) The emf of given cell is 0.192 V when 100 mL 0.1 M NaOH added to anode compartment

24. Given : $Pt(s)\ |\ \underset{P_1\,atm}{Cl_2(g)}\ |\ Cl^-(C_1)\ ||\ Cl^-(C_2)\ |\ \underset{P_2\,atm}{Cl_2(g)}\ |\ Pt(s)$

Identify in which of following condition working of cell takes place :

(a) $C_1 > C_2$ and $P_1 = P_2$ (b) $P_2 > P_1$ and $C_1 = C_2$

(c) $C_1 < C_2$ and $P_1 = P_2$ (d) $P_2 < P_1$ and $C_1 = C_2$

25. 1000 mL $1M$ $CuSO_4(aq)$ is electrolysed by 9.65 amp current for 100 sec using Pt-electrode. Which is/are correct statement ?

(a) Blue colour intensity decreases during electrolysis.

(b) Blue colour intensity remains constant if Cu-electrode used.

(c) pH of solution is 8 after electrolysis.

(d) 28 mL of CH_4 at 1 atm and 273 K required to its combustion by O_2, liberated during electrolysis.

MATCH THE COLUMN

Column–I and **Column–II** contains four entries each. Entries of Column-I are to be matched with some entries of Column-II. One or more than one entries of Column-I may have the matching with the same entries of Column-II

1.

Column–I	Column–II
(A) Dilute solution of HCl	(P) O_2 evolved at anode
(B) Dilute solution of NaCl	(Q) H_2 evolved at cathode
(C) Concentrate solution of NaCl	(R) Cl_2 evolved at anode
(D) Fairly concentrate solution of $AgNO_3$	(S) Ag deposition at cathode

2.

Column–I	Column–II
(A) If SOP of substance is exist between −1.23 to −0.81 V	(P) Oxidation of substance is not possible
(B) If SOP of substance is exist between −0.81 V to −0.40 V	(Q) Oxidation possible only in acidic medium
(C) If SOP is less than −1.23 V	(R) Oxidation possible in any medium
(D) If SOP is greater than −0.40 V	(S) Oxidation easily takes place

3.

Column–I	Column–II (SRP)
(A) $F_2 + 2e^- \rightleftharpoons 2F^-$	(P) 0.54
(B) $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	(Q) 1.09
(C) $Br_2 + 2e^- \rightleftharpoons Br^-$	(R) 1.36
(D) $I_2 + 2e^- \rightleftharpoons 2BI^-$	(S) 2.87

4.

Column–I	Column–II
(A) $Pt\|Fe^{3+}, Fe^{2+}$	(P) Metal-metal ion half-cell
(B) $Pt\|H_2\|H^+$	(Q) Gas-gas ion half-cell
(C) $Pt\|Hg\|Hg_2^{2+}$	(R) Oxidation-reduction half-cell
(D) $Pb\|PbSO_4\|SO_4^{2-}$	(S) Metal sparing soluble salt half-cell

5.

Column–I (Property)	Column–II (Unit)
(A) Conductance	(P) Sm^{-1}
(B) Conductivity	(Q) $S^{-1}m$
(C) Molar conductivity	(R) Sm^2mol^{-1}
(D) Resistivity	(S) S

6.

Column–I (Ion)	Column–II (Molar Conductivity)
(A) H^+	(P) 350
(B) Na^+	(Q) 50
(C) Li^+	(R) 39
(D) Cs^+	(S) 77

7.

Column–I	Column–II
(A) Galvanic cell	(P) Used in space craft
(B) Electrolytic cell	(Q) No transformation of electrical energy into chemical energy

(C) Dead battery	(R) Cell reaction is spontaneous
(D) Fuel cell	(S) Cell reaction is non-spontaneous

C ASSERTION-REASON TYPE QUESTIONS

Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Examine the statements carefully and mark the correct answer according to the instructions given below :

(A) If both the statements are TRUE and STATEMENT-2 is the correct explanation of STATEMENT-1

(B) If both the statements are TRUE but STATEMENT-2 is NOT the correct explanation of STATEMENT-1

(C) If STATEMENT-1 is TRUE and STATEMENT-2 is FALSE

(D) If STATEMENT-1 is FALSE and STATEMENT-2 is TRUE

1. **STATEMENT-1 :** E°_{cell} is negative for electrolytic cell.
   STATEMENT-2 : ΔG° is +ve for electrolytic cell.
2. **STATEMENT-1 :** When 2 faraday of electricity is passed through 0.1 M $H_2SO_4(aq)$, 11.2 litre O_2 evolved at STP.
   STATEMENT-2 : Molecular weight of oxygen is 32.
3. **STATEMENT-1 :** Copper is dissolved at anode and deposited at cathode when Cu electrodes are used and electrolyte is 1 M $CuSO_4(aq)$ solution.
   STATEMENT-2 : SOP of Cu is less than SOP of water and SRP of Cu is greater than SRP of water.
4. **STATEMENT-1 :** 1 coulomb electricity deposits 1 g-equivalent of a substance.
   STATEMENT-2 : 1 faraday is charge on 1 mole of electricity.
5. **STATEMENT-1 :** If SRP of substance is – 0.3 V, it's reduction is possible at cathode.
   STATEMENT-2 : Reduction potential of water exist between 0 to –0.8274 V at 25°C.
6. **STATEMENT-1 :** If SRP of substance is –0.5 V then reduction of substance is possible only in basic medium.
   STATEMENT-2 : SRP of water is –0.8274 V and at reduction potential is zero at pH = 7
7. **STATEMENT-1 :** The voltage of mercury cell remains constant for longer period of time.
   STATEMENT-2 : It is because net cell reaction does not involve ions.
8. **STATEMENT-1 :** Lead storage battery is a galvanic cell without salt bridge.
   STATEMENT-2 : A secondary cell is rechargeable cell.
9. **STATEMENT-1 :** The SRP of three metallic ions A, B, C are $-0.3, -0.5, 0.8$ volt respectively, so oxidizing power of ions is $C > A > B$.
   STATEMENT-2 : Higher the SRP, higher the oxidizing power.
10. **STATEMENT-1 :** If SOP of substance is less than –1.23 V and over voltage = 0 V, then it's oxidation in it's aqueous solution is not possible at 298 K.
    STATEMENT-2 : Standard reduction potential (SRP) of water is + 1.23 V.
11. **STATEMENT-1 :** We cannot add the electrode potential in order to get electrode potential of third electrode if no. of moles of electrons exchanged are not same.

STATEMENT-2 : Electrode potential is an extensive property.

12. STATEMENT-1 : $E^\circ_{cell} = 0$ for a chloride ion concentration cell.

STATEMENT-2 : For this concentration cell where $E_{cell} = \frac{RT}{nF} \ln \frac{[Cl^-]_{LHS}}{[Cl^-]_{RHS}}$

13. STATEMENT-1 : If $\left(\frac{dE_{cell}}{dT}\right)_p > 0$ for a cell reaction then ΔS is positive.

STATEMENT-2 : $\Delta S = nFT\left(\frac{dE}{dT}\right)_p$

14. STATEMENT-1 : Molar conductivity increases with decrease in concentration for weak electrolytes.

STATEMENT-2 : No. of ions increases and no. of ions per unit volume decreases due to dilution.

15. STATEMENT-1 : Conductivity decreases with the decreases in concentration both the weak and strong electrolytes.

STATEMENT-2 : No. of ions per unit volume linearly decreases in both electrolytes.

SUBJECTIVE PROBLEMS

1. How many faradays are required for reduction of 1 mol $C_6H_5NO_2$ into $C_6H_5NH_2$?
2. What is the equivalent weight of O_2 in the following reaction, $H_2O + \frac{1}{2}O_2 + 2e^- \longrightarrow 2OH^-$?
3. The amount of electricity which releases 2.0g of gold from a gold salt is same as that which dissolves 0.967 g of copper anode during the electrolysis of copper sulphate solution. What is the oxidation number of gold in the gold state ? (At. wt. of Cu = 63.5; Au = 197)
4. When a molten salt was electrolysed for 5 min with 9.65 A current, 0.72g of the metal was deposited.
   Calculate the Eq. wt. of metal.
5. During the electrolysis of a concentrated brine solution. Calculate the moles of chlorine gas produced by the passage of 4F electricity.
6. Calculate the cell potential (in V) if $\Delta G = -96.5$ kJ/mol and $n = 1$.
7. If K_c for the reaction
   $Cu^{2+}(aq) + Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + Cu(s)$
   at 25°C is represented as $y \times 10^9$ then find the value of y.
   (Given : $E^\circ_{Cu^{2+}|Cu} = 0.34\,V$; $E^\circ_{Sn^{4+}|Sn^{2+}} = 0.15\,V$)
8. If ΔG° for the half cell $MnO_4^-|MnO_2$ in an acid solution is xF then find the value of x.
   (Given : $E^\circ_{MnO_4^-|Mn^{2+}} = 1.5\,V$; $E^\circ_{MnO_2|Mn^{2+}} = 1.25\,V$)
9. If the equilibrium constant for the reaction $Cd^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cd(NH_3)_4^{2+}(aq)$ is 10^x then find the value of x.
   (Given : $E^\circ_{Cd^{2+}|Cd} = -0.04\,V$; $E^\circ_{Cd(NH_3)_4^{2+}|Cd} = -0.61\,V$)

Level 3

Passage-1: 1. (c) 2. (a) 3. (d)

Passage-2: 1. (b) 2. (b) 3. (a)

Passage-3: 1. (c) 2. (b)

Passage-4: 1. (c) 2. (b) 3. (b)

Passage-5: 1. (a) 2. (a)

One or More Answers is/are correct

1. (b,d) **2.** (a,b,d) **3.** (d) **4.** (a,d) **5.** (b,c) **6.** (a,b) **7.** (a,d) **8.** (a, c, d)

9. (a,b,d) **10.** (b,c,d) **11.** (a,b) **12.** (a) **13.** (b,d) **14.** (b) **15.** (a,b,c) **16.** (a,b,d)

17. (a,b,c,d) **18.** (b) **19.** (a) **20.** (a,c,d) **21.** (a,b,c,d) **22.** (a,b,c,d) **23.** (a,b,c) **24.** (a,b)

25. (a,b,d)

Match the Column

1. A → P, Q; B → P, Q; C → Q, R; D → P, S
2. A → Q; B → R; C → P; D → S, R
3. A → S; B → R; C → Q; D → P
4. A → R; B → Q; C → P; D → S
5. A → S; B → P; C → R; D → Q
6. A → P; B → Q; C → R; D → S
7. A → Q, R; B → S; C → Q; D → P, Q, R

Assertion-Reason Type Questions

1. (A) **2.** (B) **3.** (C) **4.** (D) **5.** (A) **6.** (C) **7.** (A) **8.** (B) **9.** (A) **10.** (C)

11. (C) **12.** (B) **13.** (C) **14.** (A) **15.** (C)

Subjective Problems

1. 6 **2.** 8 **3.** 3 **4.** 6 **5.** 2 **6.** 1 **7.** 6 **8.** 5 **9.** 7 **10.** 7

11. 3 **12.** 8 **13.** 4 **14.** 4 **15.** 7

Hints and Solutions

Level 1

6. (c) 1 F = 96500 C,

$$1\,C = \frac{6.023\times10^{23}}{96500} = 6.24\times10^{18}$$

10. (c) $\frac{0.55}{M}\times3 = \frac{0.55\times100\times60}{96500}$

$\Rightarrow \quad M = 48.25\,g/mol$

13. (c) $\frac{W}{E} = \frac{I\times t}{96500}$; $\frac{0.195}{195}\times4 = \frac{5\times60\times60\times I}{96500}$,

$I = 21.44$

15. (d) When 1 mole of e^- passed, wt. of substance deposited

$$= \frac{1\times6.023\times10^{23}}{1.81\times10^{23}} \Rightarrow 3.34\,g = \text{eq. wt}$$

$\therefore$ atomic wt. of metal $= 3.34\times3 = 10.03\,g$

16. (c) 1 mole Mn_3O_4 lose $\left(6-\frac{8}{3}\right)\times3 = 10$ mole e^-; so total charge required $= 2\times10 \Rightarrow 20$ F

28. (b) Let t sec be used; No. of faradays $= \frac{4\times t}{96500}$

No. of moles of H_2O = 4, no. of equivalents of $H_2O = 4\times2$

$\therefore \quad \frac{4\times t}{96500} = 4\times2$

$\Rightarrow \quad t = 1.93\times10^5$

29. (c) only Au^{3+}, Ag^+ and Cu^{2+} will deposit at cathode.

Li will not deposit at cathode because SRP of water is -0.8274 V so after Cu^{2+}; H_2 will evolve at cathode.

30. (d) $\frac{W}{M}\times2 = \frac{4.6\times30\times60}{96500}$

moles of Sn^{2+} reduced = 0.043

Initial moles of $Sn^{2+} = 0.5\times0.6 \Rightarrow 0.30$;

remaining moles of $Sn^{2+} = 0.30 - 0.043$

$\therefore \quad [Sn^{2+}] = \frac{0.257}{0.5} = 0.514\,M$

32. (d) Initial moles of $Cr^{3+} = 0.25\times0.2 \Rightarrow 0.05$;

final moles of $Cr^{3+} = 0.25\times0.1 \Rightarrow 0.025$

moles of Cr^{3+} reduced,

$0.05 - 0.025 \Rightarrow 0.025$;

$\therefore$ eq. of Cr^{3+} reduced, $0.025\times3 = \frac{t\times96.5}{96500}$;

$t = 75$ sec

34. (a) $\frac{W}{M}\times n = \frac{I\times t}{96500}$; $\frac{0.838}{184}\times n$

$= \frac{40\times60\times1.0}{96500}$

$\Rightarrow n = 6$

38. (d) no. of eq = no. of $F = \frac{1000}{122.5}\times8 \Rightarrow 65.3$

40. (a) $\frac{W}{7} = \frac{1930\times0.75}{96500}$; $W = 0.105$ gm

41. (a) equivalents of Cl_2 produced

$= \frac{1000\times9.65\times3600}{96500} = 360$

moles of $Cl_2 = 180$

so $V = \frac{nRT}{P} \Rightarrow \frac{180\times0.0821\times300}{1.8}$

$= 2463$ L

42. (c) No. of equivalent of H_2 produced = Eq. of O_2

$= \frac{I\times t}{96500} = \frac{30\times193\times60}{96500}$

$= 3.6$

vol. of O_2 and H_2 produced are

$= 3.6\times5.6 + 3.6\times11.2$

$= 60.48$ litre

43. (d) 1 watt = 1 J/sec; 1 kWh $= \frac{V\times I\times t}{1000}$ (in hr)

Total kWh $= 10^{-3}\times110\times10\times10 \Rightarrow 11$

Total cost $= 11\times2 \Rightarrow 22$ Rs.

45. (b) 10 g Cd should present with 90 g Hg.

wt. of Cd required with 4.5 g of Hg at cathode

$= \frac{10}{90}\times4.5 \Rightarrow 0.5$; $(Cd^2 + 2e^- \rightarrow Cd)$

146. (b) Ionic molar conductivity of H^+ is very high and NH_4OH is a weak electrolyte.

150. (d) Molar conductivity of H^+ and OH^- are very high as compare to other ions.

Initially conductance of solution sharply decreases due to consumption of free H^+ then increases due to formation of salt (NaCN) and After complete neutralization further sharply increases due to presence of OH^-

Level 2

1. (b) No. of equivalent of aluminum, $\frac{W}{E} = \frac{I \times \eta \times t}{96500}$

$$\frac{24 \times 5}{27} \times 3 = \frac{9650 \times 0.9 \times t}{96500}$$

$$t = 148.14 \text{ sec}$$

2. (c) At Anode:

$$2H_2O(l) \longrightarrow 4H^+(aq) + O_2(g) + 4e^-$$

At Cathode : $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Eq. of O_2 evolved = Eq. of Ag formed $\Rightarrow$ 0.1

Total loss in wt. $= \frac{0.1 \times 32}{4} + 0.1 \times 108$

$$\Rightarrow \quad 0.8 + 10.8 \Rightarrow 11.6$$

wt. of final solution $= 108 - 11.6 \Rightarrow 96.4$ g

3. (d) Equivalents of CO_2 produced $= \frac{(I \times \eta) \times t}{96500}$

$$= \frac{0.5 \times 0.8 \times 96.5 \times 60}{96500} = 0.024$$

moles of CO_2 $(n = 1)$ produced = 0.024

moles of C_2H_6 $(n = 2)$ produced

$$= \frac{0.024}{2} = 0.012$$

Total moles of gases produced $\Rightarrow$ 0.036

$$V_{\text{gases}} = \frac{nRT}{P} = \frac{0.036 \times 0.0821 \times 300}{\left(\frac{740}{760}\right)}$$

$$= 0.91 \text{ litre}$$

4. (d) Total volume of metal layer

$$= 0.25 \times 0.32 \times 10^{-3}$$

$$\Rightarrow 0.08 \times 10^{-3} \text{ m}^3$$

Total wt. of chromium layer

$$= 0.08 \times 7.20 \times 10^6 \times 10^{-3} = 576 \text{ g}$$

$$\frac{576}{52} \times 6 = \frac{I \times 60}{96500}$$

$$I = 10.69 \times 10^4 \text{ A}$$

5. (a) Initial *m* moles of $Cu^{2+} = 5$;

m-eq. or *m*-moles of H^+ produced

$$= 100 \times 10^{-2} = 1$$

$\Rightarrow$ *m*-moles of Cu^{2+} converted into

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

m-moles of Cu^{2+} remaining in solution

$$= 5 - 0.5 = 4.5$$

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$$

and $I_2 + 2NaS_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

m-moles of Cu^{2+} remaining = *m*-moles of $Na_2S_2O_3$

$$4.5 = 0.04 \times V \qquad \Rightarrow V = 112.5 \text{ mL}$$

6. (b)
$$\begin{array}{ll} 2H_2O(l) \rightleftharpoons 2H^+(aq) + 2OH^-(aq); & \Delta G_1^\circ \\ \underline{2H^+(aq) + 2e^- \rightleftharpoons H_2(g);} & \underline{\Delta G_2^\circ} \\ 2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq); & \Delta_r G_3^\circ \end{array}$$

$$\Delta_r G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$-2 \times F \times E^\circ = -RT \ln (10^{-26}) - 2 \times F \times 0$$

$$E^\circ = \frac{0.066}{2} \log (10^{-26})$$

$$= -0.858 \text{ V}$$

7. (d) To find *n* we break the cell reaction into two half cell reduction

Anode :

$$13H_2O(l) \longrightarrow 6.5O_2(g) + 26H^+(aq.) + 26e^-$$

Cathode :

$$4CO_2(g) + 26H^+(aq.) + 26e^- \longrightarrow C_4H_{10}(g) + 8H_2O(l)$$

$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{(-2746) \times 1000}{26 \times 96500} = 1.09 \text{ V}$$

8. (c) For normal calomel electrode $E_{RP} = E_{RP}^\circ$;

$$\therefore \; E_{\text{cell}} = (0.28 - 0) - \frac{0.0591}{2} \log \frac{[H^+]^2}{P_{H_2}}$$

$$0.5755 = 0.28 + 0.0591 \text{ pH} + \frac{0.0591}{2} \log (0.1)$$

pH = 5.5

9. (a) We know

$$\begin{array}{ll} 2H_2(g) \longrightarrow 4H^+ + 4e^-; & E = 0.0 \text{ V} \\ \underline{O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)\;;} & \underline{E = 1.23 \text{ V}} \\ 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)\;; & E^\circ_{\text{cell}} = 1.23 \text{ V} \end{array}$$

$$\Delta G^\circ_{298} = -nFE^\circ = -4 \times 96500 \times 1.23$$

$$= -474.78 \text{ kJ}$$

$$\Delta_f H^\circ_{298} = \Delta_r G^\circ_{298} + T.\Delta_r S^\circ_{298}$$
$$= (-474.78) + 298 \times (-0.32)$$
$$= -570.14 \text{ kJ/mol}$$
$$\therefore \qquad \Delta_f H^\circ_{298} = -285.07 \text{ kJ/mol}$$

10. (a) After addition of Cd and it's oxidation into Cd^{2+}.

$$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$$
$$0.1 - x \qquad 0.4 - 4x;$$

where $x = 0.08$

$[NO_3^-]$ remaining $= 0.02\,M$; $[H^+]$ remaining $= 0.08\,M$

$$E_{NO_3^-|NO} = E^\circ_{NO_3^-|NO} - \frac{0.0591}{3}\log\frac{1}{[NO_3^-][H^+]^4}$$
$$= 0.96 - \frac{0.0591}{3}\log\frac{1}{(0.02)(0.08)^4}$$
$$= 0.84\text{ V}$$

11. (a) E° for normal calomel electrode $= E^\circ$ for saturated calomel electrode

$$0.33 = 0.27 - \frac{0.06}{2}\log[Cl^-]^2; \quad [Cl^-] = 0.1\,M$$

12. (b) Anode : $H_2(g) \longrightarrow 2H^+(aq) + 2e^-;\quad E^\circ = 0.0\text{ V}$

Cathode : $MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l);\quad E^\circ = 1.51\text{ V}$

$E_{cell} = E_{RP(RHS)} - E_{RP(LHS)}$

$$\Rightarrow \left(1.51 - \frac{0.06}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}\right) - \left(0 - \frac{0.06}{2}\log\frac{P_{H_2}}{[H^+]^2}\right)$$
$$= 1.51 - \left(\frac{0.06}{5}\log\frac{0.01}{0.1\times(10^{-2})^8}\right) + \frac{0.06}{2}\log\left(\frac{0.1}{(10^{-3})^2}\right)$$
$$= 1.48\text{ V}$$

13. (c) $3Cu(s) + 8H^+ + 2NO_3^- \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$

$Cu(s) + 4H^+ + 2NO_3^- \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$

Let concentration of HNO_3 is X so $[H^+] = X$

and $[NO_3^-] = X$

$$E_{NO_3^-|NO} - E_{Cu^{2+}|Cu} = E_{NO_3^-|NO_2} - E_{Cu^{2+}|Cu}$$

or $\quad \therefore \quad E_{NO_3^-|NO} = E_{NO_3^-|NO_2}$

$$0.96 - \frac{0.0591}{3}\log\frac{10^{-3}}{x^5} = 0.79 - \frac{0.0591}{1}\log\left(\frac{10^{-3}}{x^3}\right)$$
$$\Rightarrow \quad 0.62 = \frac{0.0591}{6}\log\frac{10^{-9}}{x^{10}} = 0.45 - \frac{0.0591}{2}\log\frac{10^{-9}}{x^6}$$
$$\log x = 0.657 \simeq 0.66 \text{ or } x = 10^{+0.66}$$

14. (a) Anode : $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

Cathode : $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$

Cell reaction : $2Cl^-(aq) + Cl_2(g) \longrightarrow 2Cl^-(aq) + Cl_2(g)$

$$E_{cell} = -\frac{0.06}{2}\log\frac{[Cl^-]^2_{RHS}\cdot(P_{Cl_2})_{LHS}}{[Cl^-]^2_{LHS}\cdot(P_{Cl_2})_{RHS}} \qquad (\because E^\circ_{cell} = 0)$$

$$= -\frac{0.06}{2}\log\frac{(0.01)^2}{(0.1)^2}\times\left(\frac{0.4}{0.2}\right) \Rightarrow 0.051\text{ V}$$

15. (a)

$$\begin{array}{r}
H_2O(l) + ClO_3^-(aq) \longrightarrow ClO_4^-(aq) + 2H^+(aq) + 2e^- \\
\underline{2H^+(aq) + ClO_3^-(aq) + 2e^- \longrightarrow 2ClO_2^-(aq) + H_2O(l)} \\
2ClO_3^-(aq) \longrightarrow ClO_2^-(aq) + ClO_4^-(aq)
\end{array}$$

$$E^\circ_{cell} = 0.33 - 0.36 = -0.03; \qquad E^\circ_{cell} = \frac{RT}{2F}\ln K$$

$$-0.03 = \frac{0.06}{2}\log K \quad \text{or} \quad K = 0.1$$

$$\begin{array}{ccc}
2ClO_3^- & \rightleftharpoons ClO_4^- + & ClO_2^- \\
0.1 - 2x & x & x
\end{array}$$

$$\frac{x^2}{(0.1-2x)^2} = \frac{1}{10}; \; 3.16x = 0.1 - 2x$$

$$5.16x = 0.1$$

⇒ $$x = 0.1/5.16 = 0.0193 \cong 1.9\times 10^{-2}$$

16. (b) $$E_{cell} = \frac{0.06}{1}\log\frac{[H^+]_{RHS}}{[H^+]_{LHS}}$$

or $$E_{cell} = 0.06\,[(pH)_{LHS} - (pH)_{RHS}]$$

$$(pH)_{LHS} = pK_a + \log\frac{[A^-]}{[HA]}$$

$$= 4 + \log\left(\frac{1}{0.1}\right) = 5; \quad (pH)_{RHS} = 4$$

$$E_{cell} = 0.06\,(5-4) = +\,0.06\text{ V}$$

17. (c) $$E_{cell} = E_{H^+|H_2} - E_{OH^-|Cd(OH)_2|Cd}$$

$$= E_{H^+|H_2} - E_{Cd^{2+}|Cd}$$

or $$E_{cell} = E^\circ - \frac{0.06}{2}\log\frac{[Cd^{2+}]}{[H^+]^2}$$

∵ $$E_{cell} = 0,$$

∴ $$E^\circ_{cell} = 0.03\log\times\frac{[Cd^{2+}][OH^-]^2}{K_w^2}$$

$$\log\frac{K_{sp}}{K_w^2} = \frac{0.39}{0.03} = 13$$

$$K_{sp} = 10^{13}\times(10^{-14})^2 = 10^{-15}$$

18. (a) $$E_{cell} = \frac{0.06}{2}\log\frac{[H^+]^2_{RHS}[P_{H_2}]_{LHS}}{[H^+]^2_{LHS}[P_{H_2}]_{RHS}}; \qquad \because \quad \alpha << 1$$

∴ $$[OH^-] = \sqrt{K_b\times C}; \; [OH^-] = 10^{-3}$$

or $$[H^+]_{LHS} = 10^{-11}$$

$$[H^+]_{RHS} = \sqrt{K_a\times C} \Rightarrow 10^{-4}$$

∴ $$E_{cell} = \frac{0.06}{2}\log\frac{(10^{-4})^2\times 0.1}{(10^{-11})^2}\times 1 = 0.39\text{ V}$$

19. (c) $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$$K_{a_1} . K_{a_2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$= 10^{-21} \times 0.1 = (10^{-3})^2[S^{-2}]$$

$$[S^{-2}] = 10^{-16}$$

$$E_{S^{-2}|Ag_2S|Ag} = E^\circ_{Ag^+|Ag} - \frac{0.06}{2} \log \frac{[S^{2-}]}{K_{sp}}$$

$$= 0.80 - \frac{0.06}{2} \log \frac{10^{-16}}{10^{-49}}$$

$$= 0.80 - \frac{0.06}{2} \times 33 \Rightarrow -0.19 \text{ V}$$

20. (c) Normality of resultant solution

$$= \frac{0.1 \times V}{V \times V} = 0.05\,N$$

$$\Lambda_{eq} = 1 \times \frac{0.0055}{0.05} = 110 \text{ S cm}^2\text{eq}^{-1}$$

21. (b) Resultant conc. of NaCl $= \frac{0.1 \times V}{4V} = 0.025\,N$

and HCl $= \frac{0.1 \times 2V}{4V} = 0.05\,N$

$$\therefore \quad \kappa_{total} = \kappa_{NaCl} + \kappa_{HCl}$$

$$\kappa_{solution} = \frac{N(\text{NaCl}).\,\Lambda_{eq}(\text{NaCl})}{1000} + \frac{N(\text{HCl}).\,\Lambda_{eq}(\text{HCl})}{1000}$$

$$0.018 = \frac{0.025 \times 110}{1000} + \frac{0.05.\,\Lambda_{eq}(\text{HCl})}{1000}$$

$$\Lambda_{eq}(\text{HCl}) = \frac{18 - 2.75}{0.05} = 305 \text{ S cm}^2 \text{ mol}^{-1}$$

22. (b) The molar conductivity of the dissociated form of crotonic acid is

$$\Lambda_m(\text{HC}) = \Lambda_m(\text{HCl}) + \Lambda_m(\text{NaC}) - \Lambda_m(\text{NaCl})$$

$$= (426 + 83 - 126)\ \Omega^{-1} \text{ cm}^2\text{mol}^{-1}$$

$$= 383\ \Omega^{-1} \text{ cm}^2\text{mol}^{-1}$$

The molar conductivity of HC,

$$\Lambda_m(\text{HC}) = \frac{\kappa}{C} = \frac{3.83 \times 10^{-5}\Omega^{-1}\text{cm}^{-1}}{0.001} \times 1000$$

$$= 38.3\Omega^{-1} \text{ cm}^2\text{mol}^{-1}$$

The degree of dissociation,

$$\alpha = \frac{\Lambda_m(\text{HC})}{\Lambda_m^\infty(\text{HC})} = \frac{(38.3\Omega^{-1} \text{ cm}^2\text{mol}^{-1})}{(383\Omega^{-1} \text{ cm}^2\text{mol}^{-1})} = 0.1$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{(10^{-3})(0.1)^2}{1 - 0.1} = 1.11 \times 10^{-5}$$

23. (c) $\Lambda_m^\infty(\text{BaSO}_4) = 2\Lambda_{eq}^\infty(\text{BaSO}_4)$

$$\Lambda_{eq}^\infty(\text{BaSO}_4) = \Lambda_{eq}^\infty(\text{Ba}^{2+}) + \Lambda_{eq}^\infty(\text{SO}_4^{2-})$$

$$= \Lambda_{eq}^\infty(\text{BaCl}_2) + \Lambda_{eq}^\infty(\text{H}_2\text{SO}_4) - \Lambda_{eq}^\infty(\text{HCl})$$

$$\Lambda_{eq}^\infty(\text{BaSO}_4) = x_1 + x_2 - x_3$$

$$\Lambda_m^\infty = 2(x_1 + x_2 - x_3)$$

for sparingly soluble salt

$$\Lambda_m^\infty = \frac{\kappa}{M} \times 1000$$

$$\text{or } M = \frac{x}{2(x_1 + x_2 - x_3)} \times 1000$$

$$\Rightarrow \quad \frac{500x}{(x_1 + x_2 - x_3)}$$

$$K_{sp} = M^2 \quad \Rightarrow \quad \frac{2.5 \times 10^5 x^2}{(x_1 + x_2 - x_3)^2}$$

24. (a) Conductivity of $\text{Na}_2\text{SO}_4 = 2.6 \times 10^{-4}$

$$\Lambda_m(\text{Na}_2\text{SO}_4) = \frac{1000 \times 2.6 \times 10^{-4}}{0.001}$$

$$= 260 \text{ S cm}^2\text{mol}^{-1}$$

$$\lambda_m(\text{SO}_4^{2-}) = \Lambda_m(\text{Na}_2\text{SO}_4) - 2\lambda_m(\text{Na}^+)$$

$$= 260 - 2 \times 50$$

$$= 160 \text{ S cm}^2\text{mol}^{-1}$$

Conductivity of CaSO_4 solution

$$= 7 \times 10^{-4} - 2.6 \times 10^{-4}$$

$$= 4.4 \times 10^{-4} \text{ S cm}^{-1}$$

$$\Lambda_m(\text{CaSO}_4) = \lambda_m(\text{Ca}^{2+}) + \lambda_m(\text{SO}_4^{2-})$$

$$= 120 + 160$$

$$= 280 \text{ S cm}^2\text{mol}^{-1}$$

$$\text{Solubility } C = \frac{1000 \times \kappa}{\Lambda_m} = \frac{1000 \times 4.4 \times 10^{-4}}{280}$$

$$= 1.57 \times 10^{-3}\ M$$

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]_{\text{total}}$$

$$= (0.00157)(0.00157 + 0.001)$$

$$= 4.0 \times 10^{-6}\ M^2$$

25. (b) $K_a = \frac{c\alpha^2}{1-\alpha} \Rightarrow 1.6 \times 10^{-5} = \frac{0.01 \times \alpha^2}{1-\alpha}$

$$\alpha = \sqrt{\frac{1.6 \times 10^{-5}}{0.01}} \Rightarrow 0.04$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty};\ \Lambda_m = 0.04 \times 380 \times 10^{-4}$$

$$= 15.2 \times 10^{-4} \text{ S m}^2\text{mol}^{-1}$$

$$\kappa = \Lambda_m \times C = 15.2 \times 10^{-4} \times 10^3 \times 10^{-2}$$

$$(\because 1 \text{ m}^3 = 1000 \text{ litre})$$

$$k = G.G^* \text{ and } G^* = 0.01 \text{ m}^{-1},$$

where $G^* = \frac{l}{A}$

$$\therefore G = \frac{1.52 \times 10^{-2}}{0.01} \Rightarrow 1.52\,\text{S}$$

27. (a) $x_{H_2} = x_{O_2} + x_{H_2S_2O_8}$

$$2 \times \frac{22.4}{22.4} = \frac{4 \times 8.4}{22.4} + 2 \times n$$

$$2 = 1.5 + 2n \Rightarrow n = 0.25$$

Level 3

Passage–1

1. (c), **2.** (a), **3.** (d)

Equivalent of Zn^{2+} produced = 0.1 or

moles of $Zn^{2+} = \frac{0.1}{2} \Rightarrow 0.05$

+ve charge increases in first compartment so due to interaction and maintain electrical neutrality Zn^{2+} move toward II compartment and NO_3^- move towards first compartment. Solution is always electrically neutral so charge of 1 Zn^{2+} is neutralized by 2 NO_3^-.

$\therefore [Zn^{2+}]$ in first compartment

$$= 1 + \frac{0.05}{2} = 1.025\,M$$

Concentration of NO_3^- in second compartment

$$= 1 - 0.05 = 0.95\,M$$

In third compartment moles of Cu^{2+} reduced

$$= \frac{0.05}{2} = 0.025$$

Relatively –ve charge increased so SO_4^{2-} and Na^+ move toward opposite direction to maintain electrical neutrality

$$[SO_4^{2-}]_{\text{remaining}} = 1 - \frac{0.025}{2} \Rightarrow 0.975\,M$$

Passage–2

1. (b) From equation 1 and 2, $\Delta S = \frac{d(\Delta G)}{dT}$

$$\Delta S = \frac{d(-nFE)}{dT} \Rightarrow nF\frac{dE}{dT} \text{ or } \left(\frac{dE}{dT}\right)_p = \frac{\Delta S}{nF}$$

2. (b) From equation 2;

$$\Delta H = nF\left(\frac{dE}{dT}\right)_p T - nFE_{\text{cell}}$$

$$-218 \times 1000 = 2 \times 96500 \times 300 \left(\frac{dE}{dT}\right)_p - 2 \times 96500 \times 1.015$$

$$\left(\frac{dE}{dT}\right)_p = -3.81 \times 10^{-4}\,\text{VK}^{-1}$$

3. (a) $\Delta S = nF\left(\frac{dE}{dT}\right)_p = 2 \times 96500 \times -3.81 \times 10^{-4}$

$$= -75.53\,\text{J/mol-K}$$

Passage–3

2. (b) $\kappa = \Lambda_m \cdot C \Rightarrow \frac{\Lambda_m \cdot M}{1000}$

$$\kappa = \frac{200 \times 0.04}{1000} \Rightarrow 8 \times 10^3\,\text{Scm}^{-1}$$

$$\kappa = G\left(\frac{l}{A}\right) \Rightarrow 8 \times 10^{-3} = G\left(\frac{0.50}{2}\right)$$

or $G = 0.032\,\text{S}; \quad V = IR \Rightarrow \frac{I}{G}$

$$I = 5 \times 0.032 \Rightarrow 0.16\,\text{A}$$

Subjective Problems

14. $\Lambda_M^\infty(HA) = \Lambda_M^\infty(HCl) + \Lambda_M^\infty(NaA) - \Lambda_M^\infty(NaCl)$

$$= 425 + 100 - 125 = 400\,\text{S cm}^2\,\text{mol}^{-1}$$

$pH = 4$, $[H^+] = 10^{-4} = \alpha C$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{200}{400} = 0.5;$$

$$K_a = \frac{(C\alpha)\cdot\alpha}{(1-\alpha)} = \frac{10^{-4}(0.5)}{(1-\alpha)} = 10^{-4};\ pK_a = 4$$

15. $E^\circ_{Cl^-}/AgCl/Ag = E^\circ_{Ag/Ag} + \frac{0.0591}{1}\log K_{sp}$

$$0.209 = 0.80 + \frac{0.0591}{1}\log K_{sp}$$

$K_{sp} = 10^{-10}$; Let solubility of AgCl in 0.01 M solution is x

$$10^{-10} = x(x + 0.01)$$

$$x = 10^{-8}$$

$\therefore$ Moles of AgCl dissolved in

$$10\,\text{L} = 10^{-8} \times 10 = 10^{-7}$$