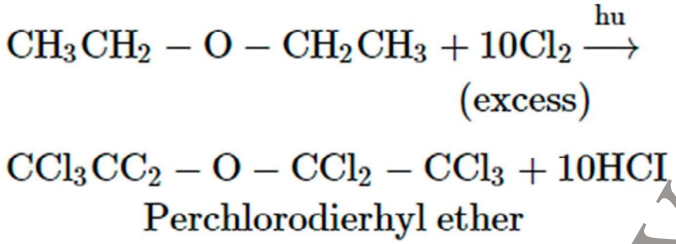
(v) (c) Perchlorodiethyl ether.

Explanation:

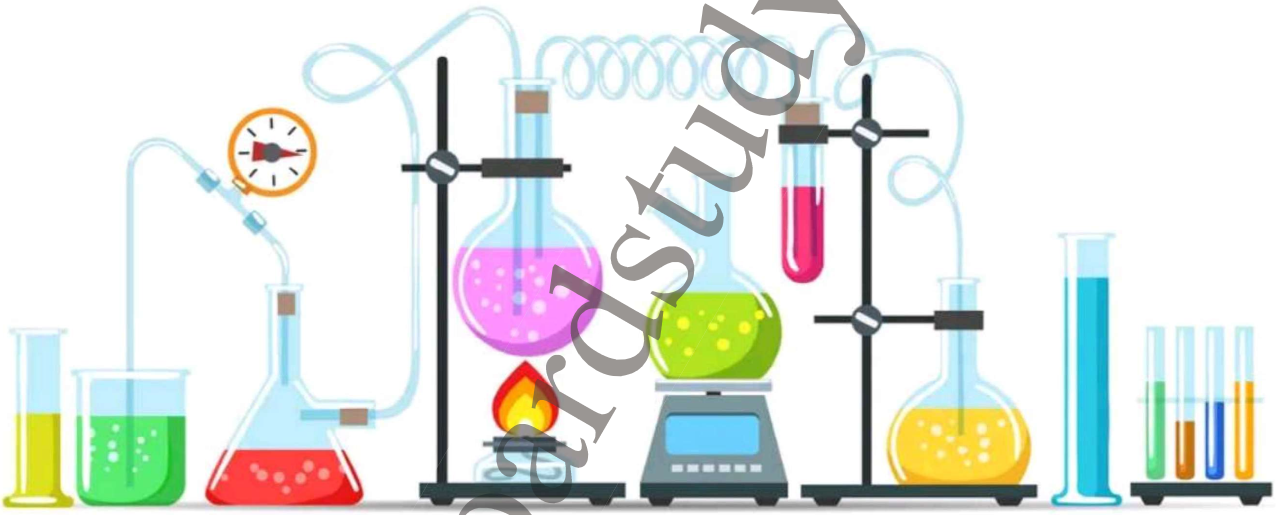
In the presence of light and excess of chlorine, all the hydrogen atoms of diethyl ether are substituted to give perchlorodiethyl ether.



$$CH_3CH_2 - O - CH_2CH_3 + \underset{\text{(excess)}}{10Cl_2} \xrightarrow{hu}$$

$$\underset{\text{Perchlorodierhyl ether}}{CCl_3CC_2 - O - CCl_2 - CCl_3} + 10HCI$$

CHEMISTRY



ELECTROCHEMISTRY

Conductivity of Solutions

What is Conductivity?

- Electrical resistance is represented by the symbol ‘R’, and it is measured in ohm (Ω).
- The electrical resistance of any object is directly proportional to its length (l) and inversely proportional to its area of cross-section (A), i.e.

$$R \propto \frac{l}{A} \qquad \text{OR} \qquad R = \rho \frac{l}{A}$$

  where the constant of proportionality ρ is called resistivity (specific resistance).
- The inverse of resistance, R, is called conductance, G, and we have the relation

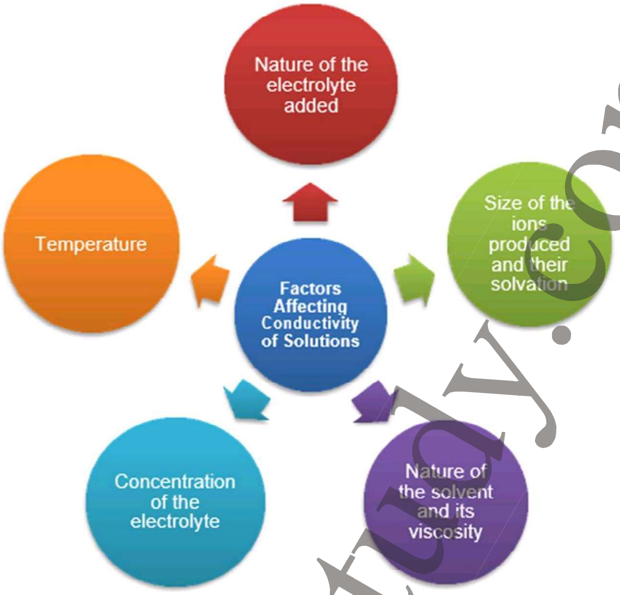
$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$$

  where the constant is called conductivity (specific conductance).
- The SI unit of conductance is Siemens, represented by the symbol ‘S’, and it is equal to ohm^{-1} (also known as mho) or Ω^{-1}. The SI unit of conductivity ( ) is S m^{-1}.

Conductivity of Electrolytic (Ionic) Solutions

- Very pure water has small amounts of hydrogen and hydroxyl ions (~10^{-7}M) which lend it very lowconductivity (3.5×10^{-5} S m^{-1}).
- When electrolytes are dissolved in water, they dissociate to give their own ions in the solution; hence, its conductivity also increases.

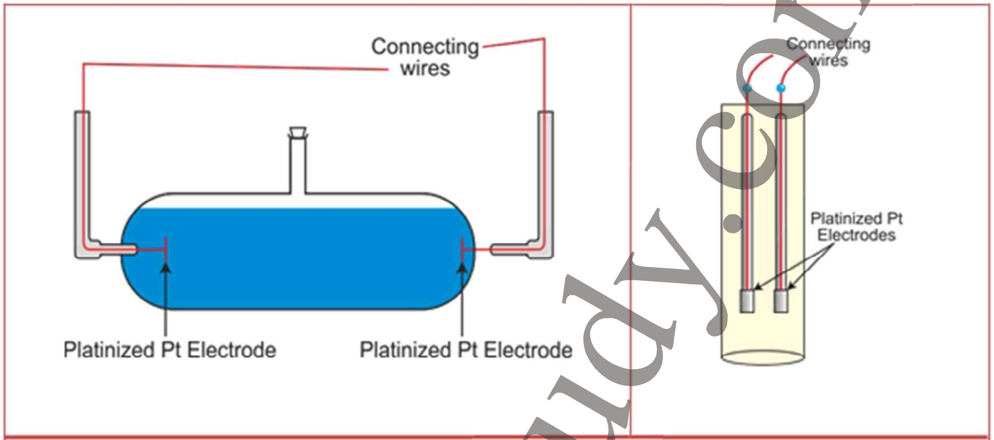
Electrolytic or ionic conductance:
Conductance of electricity by ions present in solutions



Measurement of Conductivity of Ionic Solutions

- We first need to find the resistance of an ionic solution to measure conductivity.
- We face two problems when measuring the resistance of an ionic solution:
    1. Passing direct current (DC) changes the composition of the solution
    2. A solution cannot be connected to the bridge like a metallic wire or other solid conductor
- The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called **conductivity cell**.

➢ Conditivity Cell:



Two different types of conductivity cells

- It consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically).
- These have area of cross-section equal to 'A' and are separated by distance 'l'. The resistance of such a column of solution is then given by the equation:

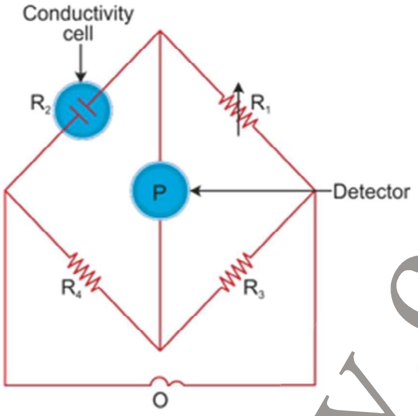
$$R = \rho \frac{l}{A} = \frac{l}{\kappa A}$$

- The quantity 'l/A' is called cell constant and is denoted by the symbol G*. It depends on the distance between the electrodes and their area of cross-section and has the dimension $[L^{-1}]$.
- Hence, the cell constant G* is given by the equation:

$$G^* = \frac{l}{A} = R\kappa$$

- When the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution.

- The set up for the measurement of the resistance is nothing but the well-known Wheatstone bridge.



Arrangement for measurement of resistance of a solution of an electrolyte

- It consists of two resistances R_3 and R_4, a variable resistance R_1 and the conductivity cell having the unknown resistance R_2.
- The Wheatstone bridge is fed by an oscillator O (a source of AC power in the audio frequency range 550–5000 cycles per second).
- P is a suitable detector (a headphone or other electronic device).
- The bridge is balanced when no current passes through the detector.
- Under these conditions,

$$\text{Unknown Resistance, } R_2 = \frac{R_1 R_4}{R_3}$$

- When the cell constant and the resistance of the solution in the cell are determined, the conductivity of the solution is given by the equation:

$$\kappa = \frac{\text{Cell Constant}}{R} = \frac{G^*}{R}$$

Molar Conductivity

- Conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to
    1. Charge and size of ions in which they dissociate
    2. Concentration of ions or ease with which the ions move under a potential

gradient

- Therefore, it becomes necessary to define a quantity called molar conductivity denoted by the symbol (λ_m). It is related to the conductivity of the solution by the equation:

$$\text{Molar Conductivity} = \lambda_m = \frac{\kappa}{c}$$

- Unit of λm is in S m^2 mol^{-1}.
- Hence, molar conductivity can be given by the formula

$$\lambda_m\left(\text{S}\,\text{m}^2\text{mol}^{-1}\right) = \frac{\kappa\left(\text{S}\,\text{m}^{-1}\right)}{1000\,\text{L}\,\text{m}^{-3} \times \text{Molarity}\left(\text{mol}\,\text{L}^{-1}\right)}$$

Variation of Conductivity and Molar Conductivity with Concentration

- Both conductivity and molar conductivity change with the concentration of the electrolyte.
- Conductivity always decreases with a decrease in concentration for both weak and strong electrolytes. It is because the number of ions per unit volume which carry the current in a solution decreases on dilution.
- Molar conductivity increases with a decrease in concentration. This is because the total volume (V) of solution containing one mole of electrolyte also increases.
- The decrease in κ on dilution of a solution is more than compensated by an increase in itsvolume.

Molar conductivity (λ_m): Conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution which contains one mole of the electrolyte.

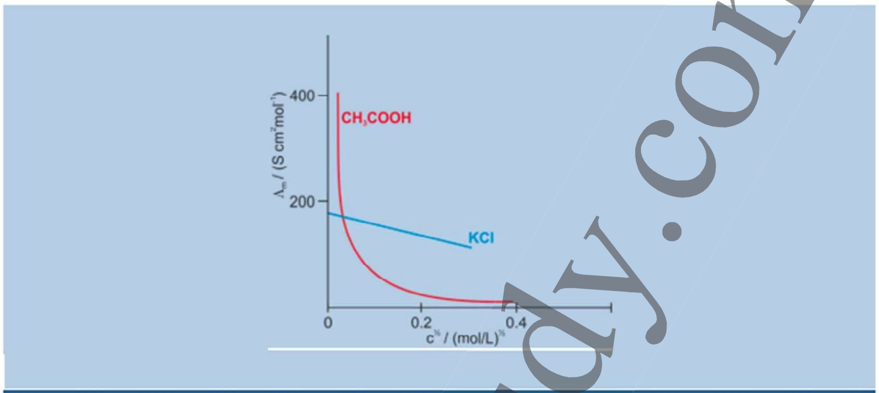
- When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol λ_m^o.
- The variation in λ_m with concentration is different for strong and weak electrolytes.

➢ Strong Electrolytes:

- λ increases slowly with dilution and can be represented by the equation:

$$\lambda_m = \lambda_m^o - A c^{1/2}$$

- It can be seen that if we plot λm against $c^{1/2}$, we obtain a straight line with intercept equal to λ^o_m and slope equal to '−A'.



Molar conductivity λ_m versus $c^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions

- The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte.

➢ <u>Weak Electrolytes:</u>

- Weak electrolytes such as acetic acid have a lower degree of dissociation at higher concentrations. Hence, for such electrolytes, the change in λ_m with dilution is due to
  1. Increase in the degree of dissociation
  2. The number of ions in total volume of solution which contains 1 mol of electrolyte
- In such cases, λ^o_m increases steeply on dilution, especially near lower concentrations. Therefore, it cannot be obtained by extrapolating λ_m to zero concentration.
- At infinite dilution, electrolyte dissociates completely (α = 1), but at such low concentration, the conductivity of the solution is so low that it cannot be measured accurately. Therefore, λ^o_m for weak electrolytes is obtained by using Kohlrausch's law of independent migration of ions.
- Thus, at any concentration c, if α is the degree of dissociation, then it can be

approximated to the ratio of molar conductivity, λ_m, at the concentration c to limiting molar conductivity λ_m^o.

$$\therefore \alpha = \frac{\lambda_m}{\lambda_m^0}{}_m$$

- But we know that for a weak electrolyte,

$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

- By putting the value of α in the above equation, we get the equation:

$$K_a = \frac{c\lambda_m^2}{\lambda_m^0\left(1-\frac{\lambda_m}{\lambda_m^0}\right)} = \frac{c\lambda_m^2}{\lambda_m^0\left(\lambda_m^0-\lambda_m\right)}$$

Numerical

1) The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298K is 0.146×10^{-3} Scm^{-1}?

Answer :

Given Data:

R =1500Ω

$\kappa = 0.146 \times 10^{-3}\ Scm^{-1}$

$G^* = ?$

Solution :

The cell cons tant is givenby the equation,

$$\text{Cell constant} = G^* = R\kappa$$

$$= 1500 \times 0.146 \times 10^{-3}$$

$$= 0.219\ m^{-1}$$

Hence, cell constant of given conductivity cell is $0.219\ m^{-1}$.

2) Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} Scm^{-1}. Calculate its molar conductivity and if λ_m^o for acetic acid is 390.5 Scm^2 mol^{-1}, what is its dissociation constant?

Answer:

Given Data:

$\kappa = 7.896 \times 10^{-5}\ Scm^{-1}$

$c = 0.00241\ M$

$\lambda_m^o = 390.5\ Scm^2 mol^{-1}$

$\lambda_m = ?$

$K_a =$

Solution :

The molar conductivity can be calculated by formula,

$$\lambda_m = \frac{\kappa}{c}$$

$$= \frac{7.896 \times 10^{-5}}{0.00241}$$

$$\therefore \lambda_m = 327.63 \times 10^{-4}\ Sm^2 mol^{-1}$$

The dissociation constant of acetic acid can be given by,

$$K_a = \frac{c\lambda_m^2}{\lambda_m^0 \left(\lambda_m^0 - \lambda_m\right)}$$

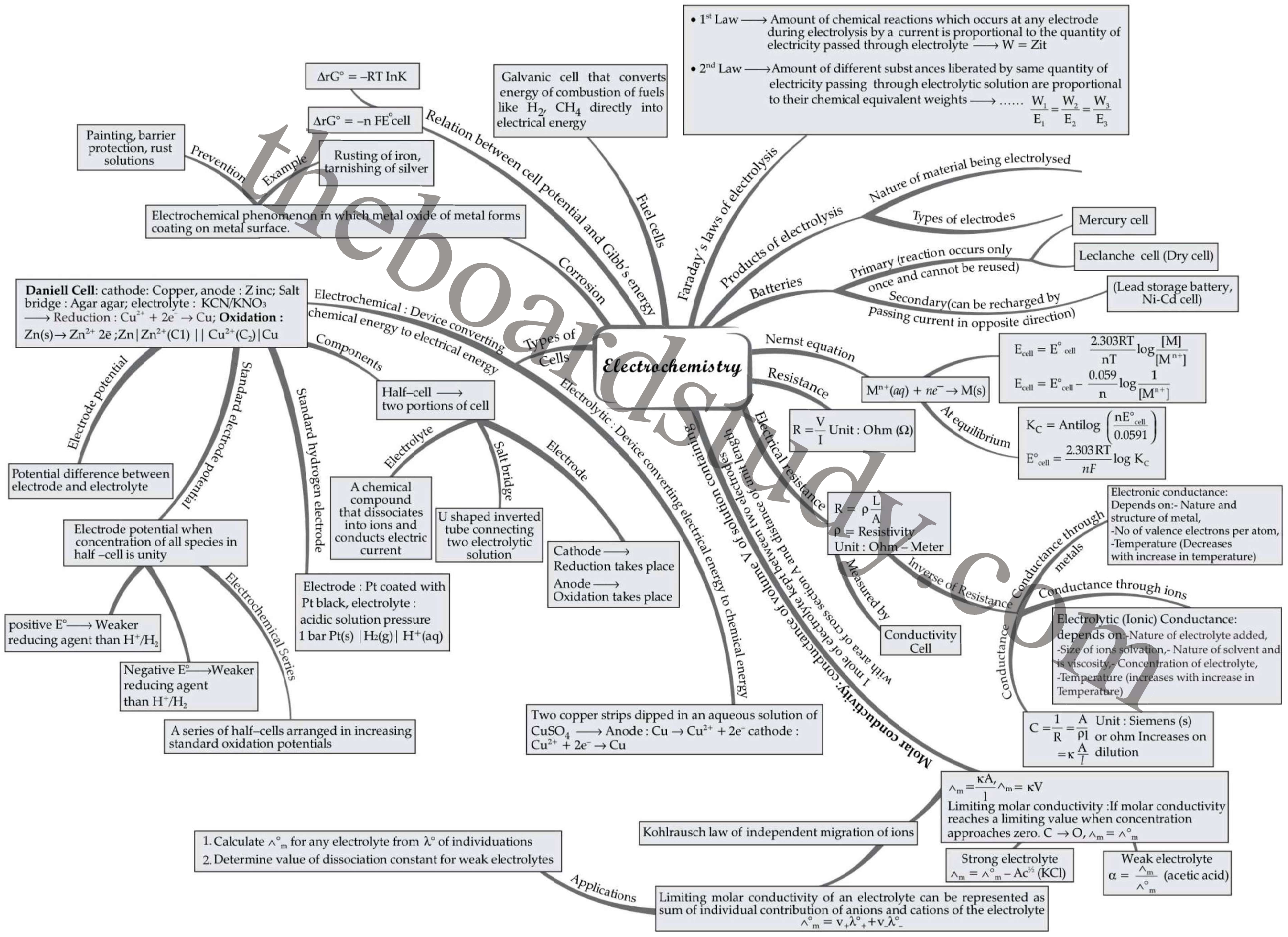
$$= \frac{0.00241 \times \left(327.63 \times 10^{-4}\right)^2}{390.5\left(390.5 - 327.63 \times 10^{-4}\right)}$$

$$\therefore K_a = 1.696 \times 10^{-11}\ molL^{-1}$$

Hence, the molar conductivity of given solution is $327.63 \times 10^{-4}\ Sm^2 mol^{-1}$ and dissociation cons tant is $1.696 \times 10^{-11}\ molL^{-1}$.

MIND MAP : LEARNING MADE SIMPLE

CHAPTER - 3



Electrochemistry

Faraday's laws of electrolysis

- 1st Law ⟶ Amount of chemical reactions which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through electrolyte ⟶ $W = Zit$
- 2nd Law ⟶ Amount of different substances liberated by same quantity of electricity passing through electrolytic solution are proportional to their chemical equivalent weights ⟶ …… $\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}$

Products of electrolysis

- Nature of material being electrolysed
- Types of electrodes

Batteries

- Primary (reaction occurs only once and cannot be reused)
  - Mercury cell
  - Leclanche cell (Dry cell)
- Secondary(can be recharged by passing current in opposite direction)
  - (Lead storage battery, Ni-Cd cell)

Nernst equation

$M^{n+}(aq) + ne^- \rightarrow M(s)$

$$E_{cell} = E^\circ_{cell} \quad \frac{2.303RT}{nT} \log \frac{[M]}{[M^{n+}]}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

At equilibrium

$$K_C = \text{Antilog}\left(\frac{nE^\circ_{cell}}{0.0591}\right)$$

$$E^\circ_{cell} = \frac{2.303\,RT}{nF} \log K_c$$

Resistance

$R = \frac{V}{I}$ Unit : Ohm (Ω)

Electrical resistance

$R = \rho \frac{L}{A}$

ρ = Resistivity

Unit : Ohm – Meter

Measured by

Conductivity Cell

Inverse of Resistance

Conductance

$C = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$ Unit : Siemens (s) or ohm Increases on dilution

Conductance through metals

Electronic conductance: Depends on:- Nature and structure of metal, -No of valence electrons per atom, -Temperature (Decreases with increase in temperature)

Conductance through ions

Electrolytic (Ionic) Conductance: depends on:-Nature of electrolyte added, -Size of ions solvation,- Nature of solvent and is viscosity,- Concentration of electrolyte, -Temperature (increases with increase in Temperature)

Molar conductivity: conductance of volume V of solution containing 1 mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length

$\wedge_m = \frac{\kappa A}{l}$, $\wedge_m = \kappa V$

Limiting molar conductivity :If molar conductivity reaches a limiting value when concentration approaches zero. $C \rightarrow O$, $\wedge_m = \wedge^\circ_m$

Strong electrolyte

$\wedge_m = \wedge^\circ_m - Ac^{1/2}$ (KCl)

Weak electrolyte

$\alpha = \frac{\wedge_m}{\wedge^\circ_m}$ (acetic acid)

Kohlrausch law of independent migration of ions

Limiting molar conductivity of an electrolyte can be represented as sum of individual contribution of anions and cations of the electrolyte

$\wedge^\circ_m = v_+\lambda^\circ_+ + v_-\lambda^\circ_-$

Applications

1. Calculate $\wedge^\circ_m$ for any electrolyte from λ° of individuations
2. Determine value of dissociation constant for weak electrolytes

Types of Cells

Electrolytic : Device converting electrical energy to chemical energy

Two copper strips dipped in an aqueous solution of $CuSO_4$ ⟶ Anode : $Cu \rightarrow Cu^{2+} + 2e^-$ cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

Electrochemical : Device converting chemical energy to electrical energy

Daniell Cell: cathode: Copper, anode : Zinc; Salt bridge : Agar agar; electrolyte : KCN/KNO_3 ⟶ Reduction : $Cu^{2+} + 2e^- \rightarrow Cu$; **Oxidation :** $Zn(s) \rightarrow Zn^{2+}\ 2\bar{e}$;$Zn|Zn^{2+}(C1) || Cu^{2+}(C_2)|Cu$

Components

Half–cell ⟶ two portions of cell

- Electrolyte
  - A chemical compound that dissociates into ions and conducts electric current
- Salt bridge
  - U shaped inverted tube connecting two electrolytic solution
- Electrode
  - Cathode ⟶ Reduction takes place
  - Anode ⟶ Oxidation takes place

Standard hydrogen electrode

Electrode : Pt coated with Pt black, electrolyte : acidic solution pressure 1 bar $Pt(s) \mid H_2(g) \mid H^+(aq)$

Standard electrode potential

Electrode potential when concentration of all species in half –cell is unity

- positive E° ⟶ Weaker reducing agent than H^+/H_2
- Negative E° ⟶ Weaker reducing agent than H^+/H_2

Electrochemical Series

A series of half–cells arranged in increasing standard oxidation potentials

Electrode potential

Potential difference between electrode and electrolyte

Corrosion

Electrochemical phenomenon in which metal oxide of metal forms coating on metal surface.

- Example
  - Rusting of iron, tarnishing of silver
- Prevention
  - Painting, barrier protection, rust solutions

Relation between cell potential and Gibb's energy

$\Delta rG^\circ = -n FE^\circ cell$

$\Delta rG^\circ = -RT\ lnK$

Fuel cells

Galvanic cell that converts energy of combustion of fuels like H_2, CH_4 directly into electrical energy

Important Questions

Multiple Choice questions-

Question 1. If the conductivity and conductance of a solution is same then its cell constant is equal to:

(a) 1

(b) 0

(c) 10

(d) 1000

Question 2.The units of conductivity are:

(a) ohm^{-1}

(b) ohm^{-1} cm^{-1}

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

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

Question 3.The resistance of 0.1 N solution of acetic acid is 250 ohm, when measured in a cell of cell constant 1.15 cm^{-1}. The equivalent conductance (in ohm^{-1} cm^2 $equivalent^{-1}$) of 0.1 N acetic acid is

(a) 18.4

(b) 0.023

(c) 46

(d) 9.2

Question 4.In infinite dilution of aqueous solution of BaCl2, molar conductivity of Ba^{2+} and Cl^- ions are = 127.32 S cm^2/mol and 76.34 S cm^2/mol respectively. What is A°m for BaCl2 at same dilution?

(a) 280 S cm^2 mol^{-1}

(b) 330.98 S cm^2 mol^{-1}

(c) 90.98 S cm² mol^{-1}

(d) 203.6 S cm² mol^{-1}

Question 5.The specific conductance of 0.1 M NaCl solution is 1.06×10^{-2} ohm^{-1} cm^{-1}. Its molar conductance in ohm^{-1} cm² mol^{-1} is

(a) 1.06×10^2

(b)1.06×10^3

(c) 1.06×10^4

(d) 53

Question 6.The limiting molar conductivities A° for NaCl, KBr and KCl are 126, 152 and 150 S cm² mol^{-1} respectively. The A° for NaBr is

(a) 278 S cm² mol^{-1}

(b) 976 S cm² mol^{-1}

(c) 128 S cm² mol^{-1}

(d) 302 S cm² mol^{-1}

Question 7. λ(ClCH2COONa) = 224 ohm^{-1} cm² gm eq^{-1}, λ(NaCl) = 38.2 ohm^{-1} cm² gm eq^{-1}. λ(HCl) = 203 ohm^{-1} cm² gm eq^{-1}, what is the value of λ(ClCH2COOH)?

(a) 288.5 ohm^{-1} cm² gm eq^{-1}

(b) 289.5 ohm^{-1} cm² gm eq^{-1}

(c) 388.8 ohm^{-1} cm² gm eq^{-1}

(d) 59.5 ohm^{-1} cm² gm eq^{-1}

Question 8. The limiting molar conductivities of HCl, CH_3COONa and NaCl are respectively 425, 90 and 125 mho cm² mol^{-1} at 25 °C. The molar conductivity of 0.1 M CH3COOH solution is 7.8 mho cm² mol^{-1} at the same temperature. The degree of dissociation of 0.1 M acetic acid solution at the same temperature is

(a) 0.10

(b) 0.02

(c) 0.15

(d) 0.03

Question 9.The values of limiting ionic conductance of H and HCOO– ions are respectively 347 and 53 S cm² mol^{-1} at 298 K. If the molar conductance of 0.025 M methanoic acid at 298 K is 40 S cm² mol^{-1}, the dissociation constant of methanoic acid at 298 K is

(a) 1×10^{-5}

(b) 2×10^{-5}

(c) $1.5 \times 10\text{-}^{4}$

(d) 2.5×10^{-4}

Question 10.The ionisation constant of a weak electrolyte is 2.5×10^{-5} and molar conductance of its 0.01 M solution is 19.6 S cm² mol^{-1}. The molar conductance at infinite dilution (S cm² mol^{-1}) is

(a) 402

(b) 392

(c) 306

(d) 39.2

Very Short Question:

Question 1. Can you store AgCl solution in Zinc pot?

Question 2. Define the term – standard electrode potential?

Question 3. What is electromotive force of a cell?

Question 4. Can an electrochemical cell act as electrolytic cell? How?

Question 5. Single electrode potential cannot be determined. Why?

Question 6. What is SHE? What is its electrode potential?

Question 7. What does the positive value of standard electrode potential indicate?

Question 8. What is an electrochemical series? How does it predict the feasibility of a certain redox reaction?

Question 9. Give some uses of electrochemical cells?

Question 10. State the factors that affect the value of electrode potential?

Short Questions:

Question 1. What is the cell potential for the cell at 25^0C $Cr/Cr^{3+}10.1\,m]//Fe^{2+}(0.01m)/Fe$

$E^0{}_{cr+/cr} = -0.74V$. $E^0Fe^{2+}/Fe = -0.44V$

Question 2. Calculate ΔG^0 for the reaction

25^0C $Zn(s)1Zn^2+[0.0004m]11cd^2+(0.2m)1cd(s)$ $E^0{}_{Zn}{}^{2+}{}_{/Zn} = -0.763V$

$E^0{}_{cd}{}^{2+}/cd = -0.403v,$ $F = 96500\ CMol^{-1}$ R = 8.314 J/K

Question 3. Calculate Equilibrium constant K for the reaction

$298K\ Zn(s)+Cu^{2+}(aq) \rightleftharpoons Zn^{2+}/aq)+Cu\ E^0{}_{Zn}{}^{2+}1Zn = -0.076v; E^0Cu^2+/Cu$ +0.34v.

Question 4. For what concentration of $Ag+(aq)$ will the emf of the given cell be zero at 25^0C if the concentration of $CU^{2+}(aq)$ is 0.1 M? $Cu(s)/Cu^{2+}(0.1M)//Ag^+(aq)/Ag(s)$ $E^0Ag^+/Ag = +0.80V;\ E^0{}_{Cu}{}^{2+/Cu} = 0.34\ V$

Question 5. Calculate the standard free energy change for the cell- reaction.

$Fe^{2+}(aq)+Ag^+(s)\grave{a}\rightarrow Fe^3+(aq)+Ag(s)$ How is it related to the equilibrium

constant of the reaction? $E^0{}_{Fe}{}^{3+}/Fe^{2+} = +0.77V$, $E^0{}_{Ag}{}^{+1/Ag} = +0.08V$ $F = 96500\ C/mol.$

Question 6. How much charge is required for the following reductions:

(i) 1 mol of to Al.
(ii) 1 mol of to Cu.
(iii) 1 mol of to .

Question 7. How much electricity in terms of Faraday is required to produce

(i) 20.0 g of Ca from molten .
(ii) 40.0 g of Al from molten

Question 8. How much electricity is required in coulomb for the oxidation of

(i) 1 mol of to .
(ii) 1 mol of FeO to

Question 9. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Question 10. Depict the galvanic cell in which the reaction takes place. Further show:

(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
(iii) Individual reaction at each electrode.

Long Questions:

Question 1. Explain construction and working of standard Hydrogen electrode? (b) Write any two differences between amorphous solids and crystalline solids.

Question 2.

The molar conductivity of 0.025 mol L-1 methanoic acid is 46.1 S $cm^2 \, mol^{-1}$. Calculate its degree of dissociation and dissociation constant. Given $\lambda^{\circ}H^{+}$ = 349.6 S $cm^2 \, mol^{-1}$ and $\lambda^{\circ}(HCOO-) = 54.6 S \, cm^2 \, mol$

Question 3.Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

Question 4 Calculate the standard cell potentials of galvanic cells in which the following reactions take place:

Question 4. Write the Nernst equation and emf of the following cells at 298 K:

Question 5. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Assertion and Reason Questions:

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: At the end of electrolysis using platinum electrodes, an aqueous solution of copper sulphate tums colourless.

Reason: Copper in $CuSO_4$ is converted to $Cu(OH)_2$ during the electrolysis.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Zinc displaces copper from copper sulphate solution.

Reason: Eº of zinc is -0.vV and that of copper is +0.34V.

Case Study Questions:

1. The concentration of potassium ions inside a biological cell is at least twenty times higher than t outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is,

$M_{(s)}$ | M^+(aq.; 0.05 molar) || M^+(aq; 1 molar) | $M_{(s)}$

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) For the above cell,

a) $E_{cell} < 0; \Delta G > 0$
b) $E_{cell} > 0; \Delta G < 0$
c) $E_{cell} < 0; \Delta G^\circ > 0$
d) $E_{cell} > 0; \Delta G^\circ < 0$

(ii) If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitu of the cell potential would be:

a) 130mV
b) 185mV
c) 154mV
d) 600mV

(iii) The value of equilibrium constant for a feasible cell reaction is:

a) < 1
b) $= 1$
c) > 1
d) Zero

(iv) What is the emf of the cell when the cell reaction attains equilibrium?

a) 1
b) 0
c) > 1
d) < 1

(v) The potential of an electrode change with change in:

a) Concentration ofions in solution.
b) Position of electrodes.
c) Voltage of the cell.
d) All of these.

2. All chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules are present in a few gram of any chemical compound varying with their atomic/ molecular masses. To handle such large number conveniently, the mole concept was introduced. All electrochemical cell reactions are also based on mole concept. For example, a 4.0 molar aqueous solution of NaCl is prepared and 500mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrode. The amount of products formed can be calculated by using mole concept.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The total number of moles of chlorine gas evolved is:

a) 0.5
b) 1.0
c) 1.5
d) 1.9

(ii) If cathode is a Hg electrode, then the maximum weight of amalgam formed from this solution is:

a) 300g
b) 446g
c) 396g
d) 296g

(iii)The total charge (coulomb) required for complete electrolysis is:

a) 186000
b) 24125
c) 48296
d) 193000

(iv)In the electrolysis, the number of moles of electrons involved are:

a) 2
b) 1
c) 3
d) 4

(v) In electrolysis of aqueous NaCl solution when Pt electrode is taken, then which gas is liberated at cathode?

a) H_2gas
b) Cl_2gas
c) O_2gas
d) None of these.

Answers key

MCQ answers:

1. Answer: (a) 1
2. Answer: (b) ohm^{-1} cm^{-1}
3. Answer: (c) 46
4. Answer: (a) 280 S cm^2 mol^{-1}
5. Answer: (a) 1.06×10^2
6. Answer: (c) 128 S cm^2 mol^{-1}
7. Answer: (c) 388.8 ohm^{-1} cm^2 gm eq^{-1}
8. Answer: (b) 0.02
9. Answer: (d) 2.5×10^{-4}
10. Answer: (b) 392

Very Short Answers:

1. No. We can't store AgCl solution in Zinc pot because standard electrode potential of Zinc is less than silver..
2. When the concentration of all the species involved in a half-cell is unity, then the electrode potential is called standard electrode potential.
3. Answer: Electromotive force of a cell is also called the cell potential. It is the difference between the electrode potentials of the cathode and anode.

$$E_{cell} = E_{cathode} - E_{anode}$$

4. Answer: Yes, An electrochemical cell can be converted into electrolytic cell by applying an external opposite potential greater than its own electrical potential.
5. Answer: A single half cell does not exist independently as reduction and oxidation occur simultaneously therefore single electrode potential cannot be measured.
6. Answer: SHE stands for standard Hydrogen electrode. By convention, its electrode potential is taken as 0 (zero).
7. Answer: The positive value of standard electrode potential indicates that the element gets reduced more easily than ions and its reduced form is more stable than Hydrogen gas.
8. The arrangement of metals and ions in increasing order of their electrode potential values is known as electrochemical series.The reduction half reaction for which the reduction potential i lower than the other will act as anode and one with greater value will act as cathode. Reverse reaction will not occur.
9. Electrochemical cells are used for determining the
    - pH of solutions
    - solubility product and equilibrium constant
    - in potentiometric titrations
10. Factors affecting electrode potential values are –
    - Concentration of electrolyte
    - Temperature.

Short Answers:

1. **Answer**

The cell reaction is

$$2Cr+3Fe^{2+}6e^{-}\rightarrow 2Cr^{3+}+3Fe$$

Nernst Equation –

$$E_{cell}=\left(E^{0}{}_{Fe}{}^{2}+{}/{}_{Fe}-E^{0}{}_{cr}{}^{3+}{}_{/cr}\right)-\frac{0.059}{6}\log\frac{\left[Cr^{3+}\right]^{2}}{\left[Fe^{2+}\right]^{3}}$$

$$= (-0.44v-(-0.74v)-\frac{0.059}{6}\log\frac{(0.10)^{2}}{(0.01)^{3}}$$

$$= 0.3V-\frac{0.059}{6}\log 10^{4}$$

$$= 0.3V - 0.0394V$$

$$= +0.2606\ V$$

2. **Answer:**

The half-cell reactions are

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

Cathode: $Cd^{2}+(aq)+2e^{-}\rightarrow Cd(s)$

Nernst Equation

$$E_{cell}=\left(E^{0}{}_{Cathode}-E^{0}{}_{anode}\right)-\frac{0.059}{n}\log\frac{\left[Zn^{2+}\right]}{\left[Cd^{2+}\right]}$$

$= (- 0.403 – (-0.763) –$

$= 0.36V – 0.0798V = 0.4398V$

$$\Delta G^{0} = -n\,F\,E^{0}{}_{cell}$$

$$=\frac{-2mol\times 96500\ C}{mol\times 0.4398V}$$

$= - 8488\ J\ mol^{-1}$

3. **Answer:**

From the reaction, n =2

$E^0_{cell} = E^0 cu^2 + / cu - E^0 Zn^2 + / Zn$

= + 0.34v – (-0.76v) = 1.10V

$E^0_{cell} = \frac{2.303RT}{nF} \log k_c$

At 298k, $E^0_{cell} \times \frac{n}{0.059} \log k_c$

Log k_c = $E^0_{cell} \times \frac{n}{0.059}$

$1.10 \times \frac{2}{0.059} = 37.29$

$K_c = Antilog\ 37.29$

$= 1.95 \times 10^{37}$

4. **Answer:**

$[Ag^+] = 5.3 \times 10^{-9} M$

5. Answer :

$E^0_{cell} = 0.03V$

6. Answer

(i)

Therefore, Required charge = 3 F

= 289461 C

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

Therefore, Required charge = 2 F

$= 2 \times 96487$ C

= 192974 C

(iii) $MnO_4^- \rightarrow Mn^{2+}$

i.e., $Mn^{7+} + 5e^- \rightarrow Mn^{2+}$

Therefore, Required charge = 5 F

$= 5 \times 96487$ C

= 482435 C

7. Answer:

.(i) According to the question,

Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium =

= 1 F

(ii) According to the question,

$Al^{3+} + 3e^{-1} \rightarrow \underset{27g}{Al}$

Electricity required to produce 27 g of Al = 3 F

Therefore, electricity required to produce 40 g of Al = $\frac{3\times40}{27}F$

= 4.44 F

8. Answer:

(i) According to the question,

Now, we can write:

$O^{2} \rightarrow \frac{1}{2}O_2 + 2e^-$

Electricity required for the oxidation of 1 mol of H_2O to O_2 = 2 F

= 2×96487 C

= 192974 C

(ii) According to the question

$Fe^{2+} \rightarrow Fe^{3+} + e^{-1}$

Electricity required for the oxidation of 1 mol of FeO to Fe_2O_3 = 1 F

= 96487 C

9. Answer :

Given,

Current = 5A

Time = 20×60 = 1200 s

Therefore, Charge = current × time

= 5×1200

= 6000 C

According to the reaction,

$Ni^{2+}_{(aq)} + 2e^- \rightarrow \underset{58.7g}{Ni_{(s)}}$

Nickel deposited by 2×96487 C = 58.71 g

Therefore, nickel deposited by 6000 C $= \frac{58.71\times6000}{2\times96487}$ g

= 1.825 g

Hence, 1.825 g of nickel will be deposited at the cathode.

10.Answer :

The galvanic cell in which the given reaction takes place is depicted as:

$Zn_{(s)} | Zn^{2+}_{(aq)} || Ag^{+}_{(aq)} | Ag_{(s)}$

(i) Zn electrode (anode) is negatively charged.

(ii) Ions are carriers of current in the cell and in the external circuit, current will flow from silver to zinc.

(iii) The reaction taking place at the anode is given by,

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

The reaction taking place at the cathode is given by,

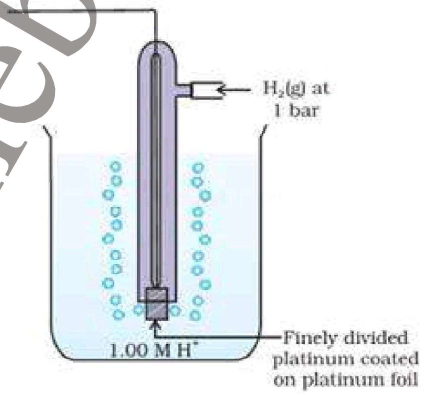
$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$

Long Answers:

1. **Answer:**

Construction: SHE consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure Hydrogen gas is bubbled through it. The concentration of both the reduced and oxidized. Forms of Hydrogen is maintained at unity i.e) pressure of gas is 1 bar and concentration of Hydrogen ions in the solution is 1 molar.

Working – The reaction taking place in SHE is At 298 K , the emf of the cell constructed by taking SHE as anode and other half-cell as cathode, gives the reduction potential of the other half cell whereas for a cell constructed by taking SHE as anode gives the oxidation potential of other half cell as conventionally the electrode potential of SHE is zero.



2. Answer:

$\Lambda_m = 46.1 \, S\,cm^2\,mol^{-1}$

$\lambda^\circ(H^+) = 349.6 \, S\,cm^2\,mol^{-1}$

$\lambda^\circ(HCOO^-) = 54.6 \, S\,cm^2\,mol^{-1}$

$\Lambda_m^0(HCOOH) = \lambda^\circ(H^+) + \lambda^\circ(HCOO^-)$

= 349.6 + 54.6 = $404.2 \, S\,cm^2\,mol^{-1}$

Now, degree of dissociation:

$$\alpha = \frac{\Lambda_m(HCOOH)}{\Lambda_m^0(HCOOH)}$$

$= \frac{46.1}{404.2}$ = 0.114 (approximately)

Thus, dissociation constant:

$$K = \frac{c\alpha^2}{(1-\alpha)}$$

$$= \frac{(0.025\,mol\,L^{-1})(0.114)^2}{(1-0.114)}$$

$$= 3.67 \times 10^{-4}\,mol\,L^{-1}$$

3. **Answer:**

In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,

Electrons released at the anodic spot move through the metallic object and go to another spot of the object.

There, in the presence of ions, the electrons reduce oxygen. This spot behaves as the cathode. These H+ ions come either from , which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water.

The reaction corresponding at the cathode is given

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

The overall reaction is: $2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)}$

Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide $(Fe_2O_3.xH_2O$ i.e., rust.

Hence, the rusting of iron is envisaged as the setting up of an electrochemical cell.

4. **Answer (i)** $E^{\circ}_{Cr^{3+}/Cr} = 0.74V$

$E^{\circ}_{Cd^{2+}/Cd} = 0.40V$

The galvanic cell of the given reaction is depicted as: $Cr_{(s)} \mid Cr^{3+}_{(aq)} \parallel Cd^{2+}_{(aq)} \mid Cd_{(s)}$

Now, the standard cell potential is $E^{\circ}_{cell} = E^{\circ}_{R} - E^{\circ}_{L}$

= 0.40 – (–0.74)

= +0.34 V

$\Delta_r G^{\circ} = -nFE^{\circ}_{cell}$

In the given equation,

n = 6

F = 96487 C mol – 1

E°_{cell} = +0.34 V

Then, $\Delta_r G^{\circ} = -\ 6 \times 96487\ C\ mol^{-1} \times 0.34\ V$

= –196833.48 CV mol^{-1}

= –196833.48 J mol^{-1}

= –196.83 kJ v

Again, $\Delta_r G^{\circ} = -RT\ In\ K$

$\Delta_r G^{\circ} = -2.303\ RT\ In\ K$

$$\log K = -\frac{\Delta_r G}{2.303\ RT}$$

$$= \frac{196.83 \times 10^3}{2.303 \times 8.314 \times 298}$$

= 34.496

Therefore, K = antilog (34.496)

$= 3.13 \times 1034$

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

$E^{\circ}_{Ag^{+}/Ag} = 0.80V$

The galvanic cell of the given reaction is depicted as: $Fe^{2+}_{(aq)} \mid Fe^{3+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$

Now, the standard cell potential is $E^{\circ}_{cell} = E^{\circ}_{R} - E^{\circ}_{L}$

= 0.80 – 0.77

= 0.03 V

Here, n = 1.

Then, $\Delta_r G^{\circ} = -nFE^{\circ}_{cell}$

$= -1 \times 96487\ C\ mol^{-1} \times 0.03\ V$

= –2894.61 J mol^{-1}

= –2.89 kJ mol^{-1}

Again, $\Delta_r G^{\circ} = 2.303\ RT\ In\ K$

$$\log K = -\frac{\Delta_r G}{2.303\ RT}$$

$= \frac{-2894.61}{2.303 \times 8.314 \times 298}$

= 0.5073

Therefore, K = antilog (0.5073)

= 3.2 (approximately)

5. Answer (i) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0591}{n} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$= \{0.34 - (-236)\} - \frac{0.0591}{2} \log \frac{.001}{.0001}$$

$$= 2.7 - \frac{0.0591}{2} \log 10$$

= 2.7 – 0.02955

= 2.67 V (approximately)

(ii) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0591}{n} \log \frac{[Fe^{2+}]}{[H^+]^2}$$

$$= \{0 - (-0.44)\} - \frac{0.0591}{2} \log \frac{0.001}{1^2}$$

= 0.44−0.02955(−3)

= 0.52865 V

= 0.53 V (approximately)

(iii) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0591}{n} \log \frac{[Sn^{2+}]}{[H^+]^2}$$

$$= \{0 - (-0.14)\} - \frac{0.0591}{2} \log \frac{0.050}{(0.020)^2}$$

$= 0.14 - 0.0295 \times \log 125$

= 0.14−0.062

= 0.078 V

= 0.08 V (approximately)

(iv) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0591}{n} \log \frac{1}{[Br^-]^2 [H^+]^2}$$

$$= (0 - 1.09) - \frac{0.0591}{2} \log \frac{1}{(0.010)^2 (0.030)^2}$$

$$= -1.09 - 0.02955 \times \log \frac{1}{0.00000009}$$

$$= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}}$$

$$= -1.09 - 0.02955 \times \log \left(1.11 \times 10^{7}\right)$$

$= -1.09 - 0.02955(0.0453+7)$
$= -1.09 - 0.208$
$= -1.298$ V

Assertion and Reason Answers:

1. (c) Assertion is correct statement but reason is wrong statement.

Explanation:

Cu^{2+} ions are deposited as Cu.

2. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Case Study Answers:

1. Answer :

i. (b) $E_{cell} > 0; \Delta G < 0$

Explanation:

$$\underset{(1M)}{M} \longrightarrow \underset{(0.05M)}{M^+} + e^-$$

For concentration cell, $E_{cell} = \frac{0.059}{1} \log \frac{0.05}{1}$

$$E_{cell} = \frac{0.059}{1} \log(5 \times 10^{-2})$$

$$E_{cell} = \frac{0.059}{1} [(-2) + \log 5] - 0.059(-2 + 0.698)$$

$$= -0.059(-1.302) = 0.0768$$

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

If E_{cell} is positive, ΔG is negative.

ii. (c) 154mV

Explanation:

$$\frac{E_1}{E_2} = \frac{\log 0.05}{\log 0.0025}$$

$$\frac{E_1}{E_2} = \frac{\log 5\times10^{-2}}{\log 25\times10^{-4}}$$

$$E_1 = 0.0768$$

$$\frac{0.0168}{E_2} = \frac{-1.3}{-2.6} = \frac{1}{2} \text{ or } E_2 = 154\text{mV}$$

iii. (c) > 1

Explanation:

$$K = \text{antilog}\left(\frac{nE^\circ}{0.0591}\right)$$

For feasible cell, E^o is positive,
hence from the above equation,
K > 1 for a feasible cell reaction.

iv. (b) 0

v. (a) Concentration ofions in solution.

2. Answer :

i. (b) 1.0

Explanation:

$$n_{NaCl} = \frac{4\times500}{1000} = 2\text{mol}$$

$$\therefore n_{Cl_2} = 1\text{mol}$$

ii. (b) 446g

Explanation:

n_{Na} deposited = 2mol

$\therefore n_{Na-Hg}$ formed = 2 mol

∴ Mass of amalgam formed = 2 × 223 = 446g

iii. (d) 193000

Explanation:

$$\underset{}{2Na^+} + \underset{(2F)}{2e^-} \rightarrow 2Na$$

Total charge required = 2F = 2 × 96500 = 193000C

iv. (a) 2

v. (a) H_2gas