Chapter

17

Electrochemistry

Electrochemistry is that branch of chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions i.e., how chemical energy produced in a redox reaction can be converted into electrical energy or how electrical energy can be used to bring about a redox reaction which is otherwise non-spontaneous.

Under electrochemistry, we study two types of cells: electro chemical and electrolytic cell.

Difference Between Electrochemical and Electrolytic Cell:

Electrochemical cell	Electrolytic cell
1. It converts chemical energy into electrical energy	1. It converts electrical energy into chemical energy.
2. It is based upon redox reaction which is spontaneous.	2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied.
3. The electrode on which oxidation takes place is called Anode (negative pole) and electrode on which reduction takes place is called cathode (positive pole).	3. The electrode which is connected to negative terminal of the battery is called cathode; the cations migrate to it, gain electrons and hence reduction takes place. The other electrode is called anode.
4. A salt bridge is used to set up the cell.	4. No salt bridge is used in this case.
5. Two electrolytes are used.	5. Only one electrolyte is taken.

GALVANIC CELL

It is also called voltaic cell. It converts chemical energy liberated during redox reaction to electrical energy.

For example reaction between Zn and $CuSO_4$.

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

The chemical reaction responsible for production of electricity takes place in two separate compartments called half cells which consists of a electrolyte solution and a electrode.

Anode: $Zn \rightarrow Zn^{2+} + 2e^-$
(Ist half cell reaction)

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$
(IInd half cell reaction)

Two half cells are connected by salt bridge.

Note:

(i) Electrode on which oxidation occurs is called anode (negative pole) while the electrode on which reduction occurs is called cathode (positive pole)

(ii) Electrons flow from anode to cathode in the external circuit.

(iii) Inner circuit is completed by flow of ions through the salt bridge.

(iv) Representation of electrochemical cell is like:

$$\text{Left electrode} \xrightarrow{\text{Electrons flow}} \text{Right electrode}$$

$$\text{Metal} \,|\, \text{Metal ion (conc)} \,||\, \text{Metal ion (conc)} \,|\, \text{Metal}$$

Oxidation occurs
Anode
negative pole

Salt
bridge

Reduction occurs
cathode
positive pole

Characteristics of Salt Bridge

(i) It allows the flow of current by completing the circuit.

(ii) It maintains electrical neutrality of electrolytes in two half cells.

ELECTROMOTIVE FORCE (EMF)

The difference in the electrode potentials of two electrodes of the cell is termed as electromotive force (EMF).

Cell potential or EMF of the cell is given by:

$$E_{cell} = E_{right} - E_{left} = E_R - E_L$$
$$= E_{cathode} - E_{anode} = E_{red} - E_{ox}$$

Conventionally, all electrode potentials are expressed at top as reduction potentials, and

Reduction potential = – Oxidation potential

For a redox reaction to be spontaneous , EMF of the cell must be positive.

Reduction occurs at the electrode having higher reduction potential and oxidation occurs at the electrode having lower reduction potential.

Electrode potential is a fixed quantity and is not multiplied by 'n' i.e. number of e^{-1}s involved in a reaction.

Standard electrode potential for fluorine is the highest indicating that fluorine gas (F_2) has the maximum tendency to get reduced to F^- ions and thus, F_2 gas is the strongest oxidising agent. Lithium has lowest electrode potential indicating that Li^+ ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution.

Note : Galvanic cell has an external voltage < 1.1.V when $E_{ext} = 1.1V$, the reaction stops and no current flows. And, if $\mathbf{E_{ext} > 1.1V}$, the reaction occurs in opposite direction and the cell functions as an **electrolytic cell** where the electrons flow from Cu to Zn and current flows from Zn to Cu.

NERNST EQUATION

The relationship between the concentration of ions and electrode potential is given by Nernst equation.

(i) For electrode potential, the reaction is,

$$M^{n+} + ne^- \longrightarrow M$$

Then Nernst equation, is applied as

$$E = E° - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

for pure solids liquids or gases at 1 atm pressure [M] = 1

$$E = E° - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

putting $R = 8.314\ Jk^{-1}\ mol^{-1}$

$F = 96500C$

$T = 298\ K$

$$E_{Red} = E°_{Red} - \frac{0.0591}{n}\log\frac{1}{\left[M^{n+}\right]}$$

(ii) For EMF of the cell, the cell reaction is:

$$aA + bB \rightleftharpoons xX + yY$$

Then by Nernst equation at 298 K,

$$E_{cell} = E°_{cell} - \frac{0.0591}{n}\log\frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

Where n is the number of electrons involved in the cell reaction.

(iii) For a cell reaction in equilibrium,

$E_{cell} = 0$

$$K_C = \frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

$$E°_{cell} = \frac{0.0591}{n}\log K_c \text{ at } 298\ K$$

where n = no. of electrons involved in the cell reaction

K_C = equilibrium constant for the cell reaction.

Gibb's Free Energy and Cell Potential

$$\Delta G° = -nFE°_{cell}$$

as $E°_{cell} = \frac{RT}{nF}\ln K_C$

$$\Delta G° = -2.303\ RT\log K_C$$

where $\Delta G°$ = standard free energy change of the reaction

F = Faraday's constant = 96500 C

$R = 8.314\ JK^{-1}mol^{-1}$

ELECTROLYSIS

It is a process of decomposition of an electrolyte by the passage of electricity through its aqueous solution of molten state.

On passing electric current, positively charged ions move towards cathode and negatively charged ions move towards anode; where they loose their charge and become neutral species. **Oxidation occurs at anode while reduction takes place at cathode.**

Faraday's Laws

The **quantitative aspects** of electrolysis were studied by Faraday. He put forward two laws as follows:

(i) **Faraday's First law of Electrolysis**:

According to this law, the amount of chemical reaction and hence the mass of any substance deposited at any electrode during electrolysis by a current is directly proportional to the quantity of electricity passed through the electrolyte i.e.,

$m \propto Q$

$m = ZQ$

as, $Q = It$

$\therefore m = ZIt$

where m → amount of subs. deposited

Q → quantity of electricity in 'C'

Z → Constant called Electrochemical equivalent

I → Current in ampere

t → time in seconds

Electrochemical equivalent can be defined as the mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second.

$$\text{Electro-chemical equivalent (Z)} = \frac{\text{equivalent wt. of element}}{96500}$$

(ii) **Faraday's second law of electrolysis**

When same amount of electricity is passed through solutions of different electrolytes connected in series, the weight of the substances produced at the electrodes are directly proportional to their equivalent weights.

Ex: for $AgNO_3$ and $CuSO_4$ solutions connected in series, if same quantity of electricity is passed, then

$$\frac{\text{wt. of Ag deposited}}{\text{Wt. of Cu deposited}} = \frac{\text{Eq. wt. of Ag}}{\text{Eq. wt. of Cu}}$$

Note:

(i) If n electrons are involved in the electrode reaction, the passage of n faradays (i.e., nF = n × 96500 C) of electricity will liberate one mole of the substance.

(ii) Equivalent weight of a substance can be calculated as:

$$\text{Eq. wt.} = \frac{m}{Q}\times 96500\begin{bmatrix}m \rightarrow \text{amount of substance deposited}\\ Q \rightarrow \text{Quantity of electricity}\end{bmatrix}$$

CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

Conductance (G)

The amount of electric current that can be passed through the solution is called conductance. Conductance is inverse of resistance.

$$\text{Conductance} = \frac{1}{\text{Resistance}} \quad \text{or} \quad G = \frac{1}{R}$$

Unit of conductance is inverse of ohm. It is represented as mho or ohm^{-1} or siemens (s).

(i) Resistance of a conductor is given as follows:

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

R = resistance; ρ = resistivity; l = length,
A = area of cross-section.

(ii) The reciprocal of resistivity is called conductivity

$$\kappa = \frac{1}{\rho} = \frac{1}{R}\frac{l}{A} \qquad \kappa \rightarrow \text{specific conductivity or conductivity.}$$

$$\text{or } \kappa = G \times \frac{l}{A} = \text{observed conductance} \times \text{cell constant}$$

$$= G \times G^* \quad (\text{where cell constant} = l/A)$$

$$\therefore \text{ Cell constant } (G^*) = \frac{\kappa}{G} = \frac{\text{Conductivity}}{\text{Conductance}}$$

Equivalent Conductivity

If one equivalent of an electrolyte is dissolved in a solution, then the conductivity of two parallel electrodes situated 1 cm apart is called equivalent conductivity. It is denoted by Λ_{eq}.

$\Lambda_{eq} = \kappa \times V$ (where V = volume)

In terms of concentration,

$$\Lambda_{eq} = \frac{\kappa \times 1000}{C_{eq}} = \frac{\kappa \times 1000}{\text{Normality}}$$

Where C_{eq} = Concentration

Unit of $\Lambda_{eq} = \text{cm}^2\ \text{ohm}^{-1}\ \text{gm eq}^{-1}$

Molar Conductivity

If one mole of an electrolyte is dissolved in a solution, then the conductivity of that solution between two parallel electrodes situated 1 cm apart, is called molar conductivity. It is represented by λ_m.

$$\lambda_m = \kappa \times V_m$$

where V_m = Volume of the solution in which 1 mole solute is dissolved. $\left(V_m = \frac{1}{C}\right)$

κ = specific conductivity

$$\lambda_m = \frac{1000\ \text{cm}^3}{M} \times \kappa$$

or Unit = $\text{cm}^2\ \text{mol}^{-1}\ \text{ohm}^{-1} = \text{S cm}^2\ \text{mol}^{-1}$

Unit of Different Quantities

Physical Quantity	Commonly used units	SI units
1. Resistance(R)	ohm(Ω)	ohm(Ω)
2. Resistivity(ρ)	ohm cm(Ω cm)	ohm m(Ω m)
3. Conductance(G)	Ω^{-1}	siemen(S)
4. Conductivity(κ)	$\Omega^{-1}\text{cm}^{-1}$	S m^{-1}
5. Equivalent Conductivity(Λ_{eq})	$\Omega^{-1}\text{cm}^2\text{eq}^{-1}$	$\text{S m}^2\text{eq}^{-1}$
6. Molar Conductivity(Λ_m)	$\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	$\text{S cm}^2\text{mol}^{-1}$
7. Cell constant(G^*)	cm^{-1}	m^{-1}

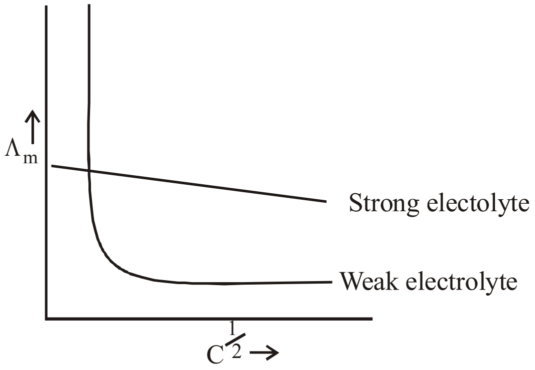
Effect of Dilution on Conductance, Specific Conductivity and Λ_m

(i) Conductance increases with increase in dilution due to increase in number of ions in solution.

(ii) **Conductivity** decreases with the decrease in concentration. This is because conductivity is the conductance of one unit volume of solution. As the number of ions per unit volume decrease on dilution, hence conductivity decreases with decrease in concentration.

(iii) **Molar conductivity** and equivalent conductivity increases with decrease in concentration. This is because $\Lambda_m = \kappa V$ and $\Lambda_{eq} = \kappa V$. Though 'κ' decreases with decrease in concentration but it is compensated by increase in volume and hence Λ_m and Λ_{eq} increase with dilution.

The variation of Λ_m for strong and weak electrolytes with concentration is as follows:



The increase in Λ_m for strong electrolyte with dilution is not very sharp. This is because strong electrolyte is already completely dissociated into ions. On dilution, ions get separated and their movement becomes easier and hence, Λ_m increases but not sharply.

On the other hand, weak electrolyte has lower degree of dissociation at higher concentrations. On dilution, the degree of dissociation increases and number of ions in the solution increases. Thus, Λ_m increases sharply.

KOHLRAUSCH'S LAW

According to this law, limiting molar conductivity of an electrolyte is the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of the electrolyte.

Mathematically, Λ°_m for $A_xB_y = x\lambda^{\circ y+}_{(A)} + y\lambda^{\circ x-}_{(B)}$

where,

Λ°_m = Limiting molar conductivity of the electrolyte

$\lambda^{\circ y+}_{(A)}$ and $\lambda^{\circ x-}_{(B)}$ = Limiting molar conductivities of cation and anion respectively.

Applications of Kohlrausch's Law

(i) **Calculation of Λ_m° for weak electrolytes.**

$$\lambda^\circ(CH_3COOH) = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+} \qquad ....(1)$$

for strong electrolytes :

$$\lambda^\circ(CH_3COOK) = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{K^+} \qquad .....(2)$$

$$\lambda^\circ(HCl) = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} \qquad .....(3)$$

$$\lambda^\circ(KCl) = \lambda^\circ_{K^+} + \lambda^\circ_{Cl^-} \qquad .....(4)$$

$\therefore$ eq^n (2) + eq^n (3) – eq^n (4) = eq^n (1)

i.e., $\lambda^\infty_{(CH_3COOK)} + \lambda^\infty_{(HCl)} - \lambda^\infty_{(KCl)} = \lambda^\infty_{(CH_3COOH)}$

(ii) **Calculation of degree of dissociation (α):**

It Λ_m^c is the molar conductivity of solution at any concentration C and Λ_m° is the molar conductivity at infinite dilution the degree of dissociation will be:

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$

(iii) Calculation of dissociation constant of a weak electrolyte

i.e., $K_c = \dfrac{C\alpha^2}{1-\alpha}$

where C is concentration and α is degree of dissociation of weak electrolyte.

(iv) **Calculation of solubility of a sparingly soluble salt:** Salts which dissolve to a very small extent in water are called sparingly soluble salts. Their solutions are considered as infinite dilute solutions as they dissolve in very little amount. Their solubility is given as:

$$\text{Solubility} = \frac{\kappa \times 1000}{\Lambda_m^\circ}$$

PREDICTING THE PRODUCTS OF ELECTROLYSIS

In electrolysis, the conversion of ions into neutral species at their respective electrodes is called primary change. The product formed as a result of primary change may be collected as such or it may undergo secondary change to form final products.

When electrolysis is carried out in molten state, the products are actually the substances obtained from the ions of the electrolyte. However, in aqueous solution, the situation is different. At each electrode, two different ions can be discharged which ion gets discharged depends:

(i) On their relative discharge potentials

(ii) Sometimes on the material of the electrode used.

Usually, the ions with **lower discharge potential** are discharged in preference to those which have high discharge potentials.

SOME COMMERCIAL CELLS (Batteries)

They are mainly of two types:

Primary Batteries or Cells

Primary cells are those in which redox reaction occurs only once and the cell becomes dead after some time and cannot be used again. Examples:

Dry cell or Leclanche cell : Particulars are:

Anode - Zinc Container

Cathode - graphite rod surrounded by MnO_2 powder

Electrolyte - paste of $NH_4Cl + ZnCl_2$

Cathode Reaction : $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

Anode Reaction : $Zn - 2e^- \longrightarrow Zn^{++}$

$$Zn^{2+} + 2NH_3 \longrightarrow [Zn(NH_3)_2]^{2+}$$

Cell potential 1.25V to 1.5V

Mercury Cell

Anode - Zn-Hg amalgam

Cathode - paste of (HgO + C)

Electrolyte - moist paste of KOH-ZnO

Cathode Reaction :

$$HgO(s) + H_2O(\ell) + 2e^- \longrightarrow Hg(\ell) + 2OH^-$$

Anode Reaction : $Zn + 2OH^- \longrightarrow ZnO + H_2O(\ell) + 2e^-$

Net Reaction : $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(\ell)$

cell potential = 1.30 volt

Secondary Batteries or Cells

These can be recharged by passing current in opposite direction so that they can be used again.

Examples: (i) Lead storage battery and Nickel cadmium storage cell.

Lead storage battery :

Anode - Spongy lead

Cathode - grid of lead packed with PbO_2

Electrolyte - 38% H_2SO_4 by mass

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

Cathode Reaction :

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

Net Reaction :

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

When recharged the cell reactions are reversed.

Nickel-cadmium storage cell

Anode - Cadmium

Cathode - metal grid containing NiO_2

Electrolyte - KOH solution

Anode Reaction $Cd(s) + 2OH^- \rightarrow Cd(OH)_2(s) + 2e^-$

Cathode Reaction :

$$NiO_2(s) + 2H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$$

Net Reaction :

$$Cd(s) + NiO_2(s) + 2H_2O(\ell) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Cell potential = 1.4V.

Fuel Cells

Galvanic cells which are designed to convert energy of combustion of fuels like H_2, CH_4, CH_3OH, etc. directly into electrical energy are called fuel cells. Ex: $H_2 - O_2$ fuel cell.

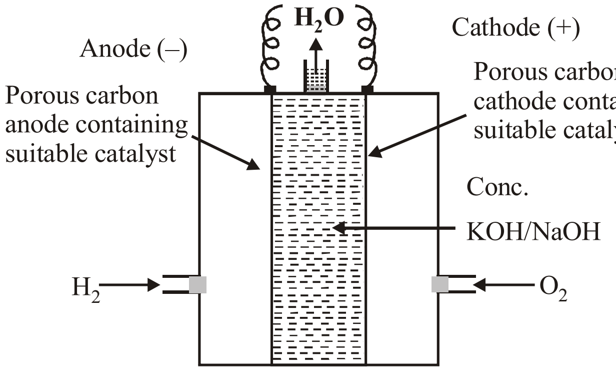


Fig : $H_2 - O_2$ fuel cell

The electrode reactions are:

cathode: $O_2\,(g) + 2H_2O\,(l) + 4e^- \rightarrow 4OH^-\,(aq)$

anode: $2H_2(g) + 4OH^-\,(aq) \rightarrow 4H_2O(l) + 4e^-$

Overall reaction:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O\,(l)$$

Advantages of fuel cells

(i) The cell runs continuously as long as the reactants are supplied.

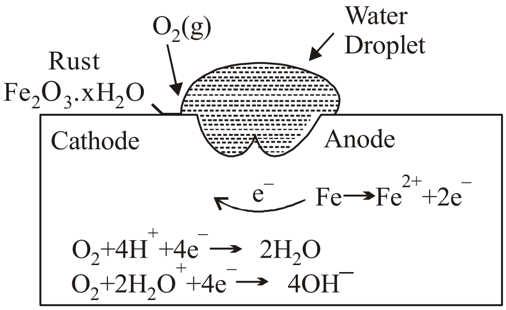
(ii) Their efficiency is about 70% compared to thermal plants whose efficiency is 40%.

(iii) They are pollution free.

CORROSION

It is the slow eating away of the metal due to attack of the atmospheric gases on the surface of the metal resulting into the formation of compounds such as oxides, sulphides, carbonates, sulphates etc.

Examples: rusting of iron, tarnishing of silver, green coating on silver and bronze, etc.



The reactions involved in the rusting of iron are:

Cathode: $O_2(g) + 4H^+\,(aq) + 4e^- \rightarrow 2H_2O\,(l)$

$$E^{\circ}_{H^+/O_2/H_2O} = 1.23V$$

Anode: $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$ $\quad E^{\circ}_{Fe^{2+}/Fe} = -0.44V$

Overall reaction: $2Fe(s) + O_2(g) + 4H^+\,(aq) \rightarrow 2Fe^{2+}\,(aq) + 2H_2O\,(l)$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in form of hydrated ferric oxide ($Fe_2O_3.xH_2O$).

$$2Fe^{2+} + \tfrac{1}{2}O_2 + H_2O \rightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \rightarrow \underset{\text{Rust}}{Fe_2O_3\,.xH_2O}$$

Factors Which Promote Corrosion

(i) More active metals are readily corroded.

(ii) Presence of impurities enhance corrosion. Pure metals do not corrode.

(iii) Air and moisture accelerate corrosion. In vacuum, there is no corrosion.

(iv) Corrosion occurs rapidly at bands, scratches, nicks and cuts in the metal.

(v) Electrolytes also increase the rate of corrosion.

Prevention of Corrosion

(i) Painting, oiling, greasing (i.e., barrier protection) prevent corrosion

(ii) Covering with a layer of more reactive metal (called sacrificial protection). For ex: iron is coated with more active zinc. The process is called Galvanisation.

(iii) Coating of iron surface with phosphate or other chemicals which forms a protective, tough, adherent in soluble film.

Note:

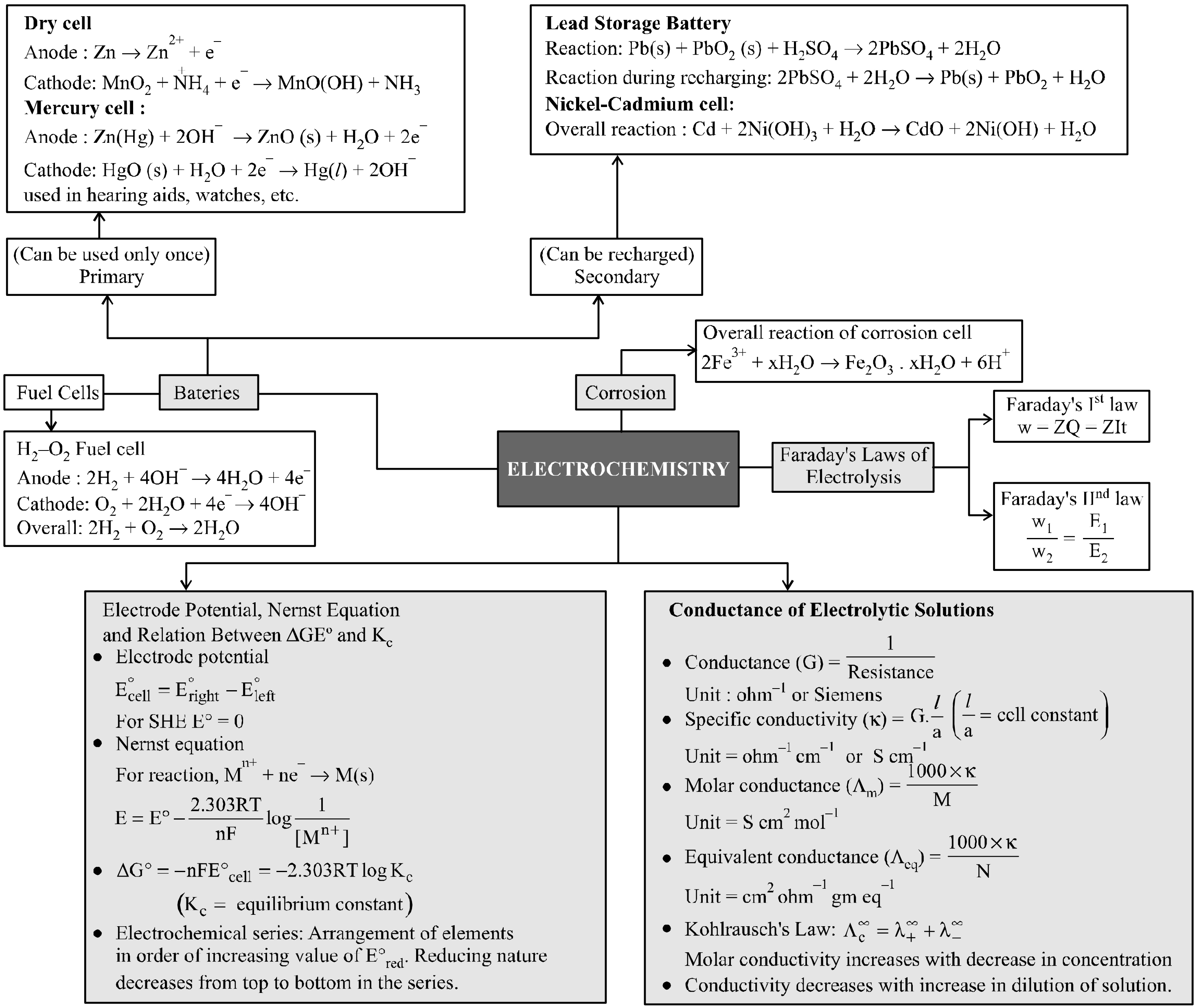
(i) Iron in contact with a solution whose pH is above 9-10 does not corrode. This is because H^+ ions are involved in the reduction of O_2. As concentration of H^+ decreases, i.e., pH is increased, the reduction of O_2 becomes less favourable.

(ii) If water is saline, it helps in the flow of current in the miniature cell and hence enhances the process of corrosion.

(iii) Rust is formed at a site other than the site where pitting has occurred.

(iv) Iron corrodes more rapidly then it does in the absence of copper and tin. This is because when iron is coated with copper or tin; if the coating is broken, iron is exposed and it being more reactive than both copper and tin, gets corroded.

CONCEPT MAP



ELECTROCHEMISTRY

Bateries

Fuel Cells

(Can be used only once)
Primary

Dry cell
Anode : $Zn \rightarrow Zn^{2+} + e^-$
Cathode: $MnO_2 + \overset{+}{N}H_4 + e^- \rightarrow MnO(OH) + NH_3$
Mercury cell :
Anode : $Zn(Hg) + 2OH^- \rightarrow ZnO\ (s) + H_2O + 2e^-$
Cathode: $HgO\ (s) + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$
used in hearing aids, watches, etc.

(Can be recharged)
Secondary

Lead Storage Battery
Reaction: $Pb(s) + PbO_2\ (s) + H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$
Reaction during recharging: $2PbSO_4 + 2H_2O \rightarrow Pb(s) + PbO_2 + H_2O$
Nickel-Cadmium cell:
Overall reaction : $Cd + 2Ni(OH)_3 + H_2O \rightarrow CdO + 2Ni(OH) + H_2O$

H_2–O_2 Fuel cell
Anode : $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Overall: $2H_2 + O_2 \rightarrow 2H_2O$

Corrosion

Overall reaction of corrosion cell
$2Fe^{3+} + xH_2O \rightarrow Fe_2O_3\ .\ xH_2O + 6H^+$

Faraday's Laws of Electrolysis

Faraday's Ist law
$w = ZQ = ZIt$

Faraday's IInd law
$$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$

Electrode Potential, Nernst Equation and Relation Between ΔGE° and K_c

- Electrode potential

  $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$

  For SHE E° = 0
- Nernst equation

  For reaction, $M^{n+} + ne^- \rightarrow M(s)$

  $$E = E^\circ - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}]}$$
- $\Delta G^\circ = -nFE^\circ_{cell} = -2.303RT\log K_c$

  $(K_c =$ equilibrium constant$)$
- Electrochemical series: Arrangement of elements in order of increasing value of E°_{red}. Reducing nature decreases from top to bottom in the series.

Conductance of Electrolytic Solutions

- Conductance $(G) = \dfrac{1}{\text{Resistance}}$

  Unit : ohm^{-1} or Siemens
- Specific conductivity $(\kappa) = G.\dfrac{l}{a}\left(\dfrac{l}{a} = \text{cell constant}\right)$

  Unit = $ohm^{-1}\ cm^{-1}$ or $S\ cm^{-1}$
- Molar conductance $(\Lambda_m) = \dfrac{1000 \times \kappa}{M}$

  Unit = $S\ cm^2\ mol^{-1}$
- Equivalent conductance $(\Lambda_{eq}) = \dfrac{1000 \times \kappa}{N}$

  Unit = $cm^2\ ohm^{-1}\ gm\ eq^{-1}$
- Kohlrausch's Law: $\Lambda^\infty_c = \lambda^\infty_+ + \lambda^\infty_-$

  Molar conductivity increases with decrease in concentration
- Conductivity decreases with increase in dilution of solution.

EXERCISE - 1

Conceptual Questions

1. The amount of chlorine evolved by passing 2A of current in aq. solution of NaCl for 30 minutes is :
(a) 0.84 gm (b) 1.32 gm
(c) 3.34 gm (d) 5.47 gm

2. The conjugate acid of NH_3 is :
(a) NH_4^+ (b) NH_2OH
(c) NH_3 (d) N_2H_4

3. If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of 0.4 cm^{-1}, then its molar conductance in $ohm^{-1}\ cm^2\ mol^{-1}$ is
(a) 10^2 (b) 10^4
(c) 10 (d) 10^3

4. Specific conductance of a 0.1 N KCl solution at 23ºC is 0.012 $ohm^{-1}\ cm^{-1}$. Resistance of cell containing the solution at same temperature was found to be 55 ohm. The cell constant is
(a) 0.0616 cm^{-1} (b) 0.66 cm^{-1}
(c) 6.60 cm^{-1} (d) 660 cm^{-1}

5. The highest electrical conductivity of the following aqueous solutions is of
(a) 0.1 M difluoroacetic acid (b) 0.1 M fluoroacetic acid
(c) 0.1 M chloroacetic acid (d) 0.1 M acetic acid

6. When an electric current of 0.5 ampere is passed through acidulated water for two hours, then volume of hydrogen (H_2) at NTP produced will be (1 Coulomb of electricity deposits 0.00001 gm of hydrogen)
(a) 0.1 litre (b) 0.6 litre
(c) 0.4 litre (d) 0.8 litre

7.

Electrolyte:	KCl	KNO_3	HCl	NaOAc	NaCl
Λ^{∞} ($S\ cm^2\ mol^{-1}$) :	149.9	145	426.2	91	126.5

Calculate Λ^{∞}_{HOAc} using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25ºC
(a) 217.5 (b) 390.7
(c) 552.7 (d) 517.2

8. The unit of equivalent conductivity is
(a) ohm cm
(b) $ohm^{-1}\ cm^2$ (g equivalent)$^{-1}$
(c) ohm cm^2 (g equivalent)
(d) S cm^{-2}

9. The resistance of 0.01 N solution of an electrolyte was found to be 220 ohm at 298 K using a conductivity cell with a cell constant of 0.88cm^{-1}. The value of equivalent conductance of solution is –
(a) 400 mho cm^2 g eq^{-1} (b) 295 mho cm^2 g eq^{-1}
(c) 419 mho cm^2 g eq^{-1} (d) 425 mho cm^2 g eq^{-1}

10. How much chlorine will be liberated on passing one ampere current for 30 min. through NaCl solution?
(a) 0.66 mole (b) 0.33 mole
(c) 0.66 g (d) 0.33 g

11. A 0.5 M NaOH solution offers a resistance of 31.6 ohm in a conductivity cell at room temperature. What shall be the approximate molar conductance of this NaOH solution if cell constant of the cell is 0.367 cm^{-1}.
(a) 234 S cm^2 $mole^{-1}$ (b) 23.2 S cm^2 $mole^{-1}$
(c) 4645 S cm^2 $mole^{-1}$ (d) 5464 S cm^2 $mole^{-1}$

12. For the electrochemical cell,
$M \mid [M^+ \parallel X^- \mid X$, $E°(M^+/M) = 0.44$ V and $E°\ (X/X^-) = 0.33$ V. From this data one can deduce that:
(a) $M + X \longrightarrow M^+ + X^-$ is spontaneous reaction
(b) $M^+ + X^- \longrightarrow M + X$ is spontaneous reaction
(c) $E_{cell} = 0.77V$
(d) $E_{cell} = -0.77V$

13. If 0.5 amp current is passed through acidified silver nitrate solution for 100 minutes. The mass of silver deposited on cathode, is (eq.wt.of silver nitrate = 108)
(a) 2.3523 g (b) 3.3575 g
(c) 5.3578 g (d) 6.3575 g

14. Using same quantity of current, which among Na, Mg, and Al is deposited to the highest extent during electrolysis.
(a) Mg (b) Al
(c) Na (d) All in same amount

15. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (At. Mass = 27 amu; 1 Faraday = 96,500 Coulombs). The cathode reaction is– $Al^{3+} + 3e^- \rightarrow Al$
To prepare 5.12 kg of aluminium metal by this method we require electricity of
(a) 5.49×10^1 C (b) 5.49×10^4 C
(c) 1.83×10^7 C (d) 5.49×10^7 C

16. When electric current is passed through acidified water, 112 ml of hydrogen gas at STP collected at the cathode in 965 seconds. The current passed in amperes is
(a) 1.0 (b) 0.5
(c) 0.1 (d) 2.0

17. An electrolytic cell contains a solution of Ag_2SO_4 and has platinum electrodes. A current is passed until 1.6 gm of O_2 has been liberated at anode. The amount of silver deposited at cathode would be
(a) 107.88 gm (b) 1.6 gm
(c) 0.8 gm (d) 21.60 gm

18. Which of the following will form a cell with the highest voltage?
(a) 0.1 M Ag^+, 2 MCo^{2+} (b) 2 M Ag^+, 0.1 MCo^{2+}
(c) 1 M Ag^+, 1 M Co^{2+} (d) 2 M Ag^+, 2 M Co^{2+}

19. When 9650 coulombs of electricity is passed through a solution of copper sulphate, the amount of copper deposited is (given at. wt. of Cu = 63.6)
(a) 0318g (b) 3.18 g
(c) 31.8g (d) 63.6g

20. Find the charge in coulombs required to convert 0.2 mole VO_3^{-2} into VO_4^{-3} –

(a) 1.93×10^4 (b) 9.65×10^4

(c) 1.93×10^5 (d) 9.65×10^5

21. Iron pipes, lying in acidic soil, are often attached to the blocks of magnesium for their protection from rusting, because magnesium :

(a) is lighter than iron

(b) is readily converted into positive ion

(c) forms a corrosion-resistant alloy with iron

(d) prevents air from reaching the surface of iron

22. A silver cup is plated with silver by passing 965 coulombs of electricity. The amount of Ag deposited is :

(a) 107.89 g (b) 9.89 g

(c) 1.0002 g (d) 1.08 g

23. Total charge on 1 mole of a monovalent metal ion is equal to

(a) 9.65×10^4 coulombs (b) 1.6×10^{-19} coulombs

(c) 6.2×10^{18} coulombs (d) None of these

24. On passing current through two cells, connected in series containing solution of $AgNO_3$ and $CuSO_4$, 0.18 g of Ag is deposited. The amount of the Cu deposited is:

(a) 0.529 g (b) 10.623 g

(c) 0.0529 g (d) 1.2708 g

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

(a) 4.68×10^{18} (b) 4.68×10^{15}

(c) 4.68×10^{12} (d) 4.68×10^9

26. To deposit one equivalent weight of silver at cathode, the charge required will be

(a) 9.65×10^4 C (b) 9.65×10^3 C

(c) 9.65×10^5 C (d) 9.65×10^7 C

27. In the electrolysis of water, one faraday of electrical energy would liberate

(a) one mole of oxygen

(b) one gram atom of oxygen

(c) 8 g oxygen

(d) 22.4 lit. of oxygen

28. When an acid cell is charged, then :

(a) voltage of cell increases

(b) electrolyte of cell dilutes

(c) resistance of cell increases

(d) none of the above

29. The volume of oxygen gas liberated at NTP by passing a current of 9650 coulombs through acidified water is :

(a) 1.12 litre (b) 2.24 litre

(c) 11.2 litre (d) 22.4 litre

30. Three faradays electricity was passed through an aqueous solution of iron (II) bromide. The weight of iron metal (at. wt = 65) deposited at the cathode (in gm) is

(a) 56 (b) 84

(c) 112 (d) 168

31. On passing C ampere of electricity through a electrolyte solution for t second. m gram metal deposits on cathode. The equivalent weight E of the metal is

(a) $E = \dfrac{C \times t}{m \times 96500}$ (b) $E = \dfrac{C \times m}{t \times 96500}$

(c) $E = \dfrac{96500 \times m}{C \times t}$ (d) $E = \dfrac{C \times t \times 96500}{m}$

32. What is the time (in sec) required for depositing all the silver present in 125 mL of 1 M $AgNO_3$ solution by passing a current of 241.25 A? (1 F = 96500 C)

(a) 10 (b) 50

(c) 1000 (d) 100

33. The number of electrons passing per second through a cross-section of copper wire carrying 10^{-6} amperes of current per second is found to be

(a) 1.6×10^{-19} (b) 6×10^{-35}

(c) 6×10^{-16} (d) 6×10^{12}

34. What is the E°_{cell} for the reaction

$$Cu^{2+}(aq) + Sn^{2+}(aq) + \rightleftharpoons Cu(s) + Sn^{4+}(aq)$$

at 25ºC if the equilibrium constant for the reaction is 1×10^6?

(a) 0.5328 V (b) 0.3552 V

(c) 0.1773 V (d) 0.7104 V

35. Which of the following reaction is possible at anode?

(a) $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$

(b) $F_2 \rightarrow 2F^-$

(c) $(1/2)\ O_2 + 2H^+ \rightarrow H_2O$

(d) None of these.

36. In electrolysis of dilute H_2SO_4, what is liberated at anode?

(a) H_2 (b) SO_4^{2-}

(c) SO_2 (d) O_2

37. The reference electrode is made by using

(a) $ZnCl_2$ (b) $CuSO_4$

(c) $HgCl_2$ (d) Hg_2Cl_2

38. The standard hydrogen electrode potential is zero, because

(a) hydrogen oxidized easily

(b) electrode potential is considered as zero

(c) hydrogen atom has only one electron

(d) hydrogen is a very light element

39. The element that is easiest to be reduced:

(a) Ag (b) Fe

(c) Cu (d) Sn

40. Which one is not called a anode reaction from the following

(a) $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ (b) $Cu \rightarrow Cu^{++} + 2e^-$

(c) $Hg^+ \rightarrow Hg^{++} + e^-$ (d) $Zn^{2+} + 2e^- \rightarrow Zn$

41. The chemical reaction,

$$2AgCl_{(s)} + H_{2(g)} \longrightarrow 2HCl_{(aq)} + 2Ag(s)$$

taking place in a galvanic cell is represented by the notation

(a) $Pt_{(s)} \mid H_{2(g)}, 1\ bar \mid 1M\ KCl_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)}$

(b) $Pt_{(s)} \mid H_{2(g)}, 1\ bar \mid 1M\ HCl_{(aq)} \mid 1M\ Ag^+_{(aq)} \mid Ag_{(s)}$

(c) $Pt_{(s)} \mid H_{2(g)}, 1\ bar \mid 1M\ HCl_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)}$

(d) $Pt_{(s)} \mid H_{2(g)}, 1\ bar \mid 1M\ HCl_{(aq)} \mid Ag_{(s)} \mid AgCl_{(s)}$

42. The cell reaction $Cu + 2Ag^+ \rightarrow Cu^{+2} + Ag$ is best represented by

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

(b) $Pt | Cu^{+2} || Ag^+(aq) | Ag(s)$

(c) $Cu^{+2} | Cu || Pt | Ag$

(d) None of the above representations

43. The resistance of 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 $ohm^{-1}\ cm^2\ equiv^{-1}$) of 1 N acetic acid will be

(a) 4.6 (b) 9.2

(c) 18.4 (d) 0.023

44. Specific conductance of 0.1 M HNO_3 is 6.3×10^{-2}. The molar conductance of the solution is

(a) 100 $ohm^{-1}\ cm^2$ (b) 515 $ohm^{-1}\ cm^2$

(c) 630 $ohm^{-1}\ cm^2$ (d) 6300 $ohm^{-1}\ cm^2$

45. Which of the following statements about galvanic cell is incorrect

(a) anode is positive

(b) oxidation occurs at the electrode with lower reduction potential

(c) cathode is positive

(d) reduction occurs at cathode

46. Which of the following reactions occurs at the cathode?

(a) $Sn^{2+} \longrightarrow Sn^{4+} + 2\,e^-$

(b) $Ag^+ + e^- \longrightarrow Ag$

(c) $Zn \longrightarrow Zn^{2+} + 2\,e^-$

(d) $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

47. At 298K the standard free energy of formation of $H_2O\,(\ell)$ is –237.20 kJ/mole while that of its ionisation into H^+ ion and hydroxyl ions is 80 kJ/mole, then the emf of the following cell at 298 K will be [Take Faraday constant F = 96500C]

$H_2\,(g, 1\ bar) | H^+\,(1M) || OH^-\,(1M) | O_2(g, 1\ bar)$

(a) 0.40V (b) 0.81V

(c) 1.23 V (d) –0.40 V

48. If the following half cells have E° values as

$A^{3+} + e^- \longrightarrow A^{2+},\ E^\circ = y_2 V$

$A^{2+} + 2e^- \longrightarrow A,\ E^\circ = -y_1 V$

The E° of the half cell $A^{3+} + 3e \longrightarrow A$ will be

(a) $\frac{2y_1 - y_2}{3}$ (b) $\frac{y_2 - 2y_1}{3}$

(c) $2y_1 - 3y_2$ (d) $y_2 - 2y_1$

49. To deposit 0.634 g of copper by electrolysis of aqueous cupric sulphate solution, the amount of electricity required (in coulombs) is

(a) 1930 (b) 3960

(c) 4825 (d) 9650

50. Without losing its concentration $ZnCl_2$ solution cannot be kept in contact with

(a) Au (b) Al

(c) Pb (d) Ag

51. $Cu^+(aq)$ is unstable in solution and undergoes simultaneous oxidation and reduction according to the reaction :

$2Cu^+(aq) \rightleftharpoons Cu^{2+}(aq) + Cu(s)$ choose correct E° for given reaction if $E^\circ\ Cu^{2+}/Cu = 0.34$ V and $E^\circ\ Cu^{2+}/Cu^+ = 0.15$ V

(a) –0.38 V (b) +0.49 V

(c) +0.38 V (d) –0.19 V

52. In the silver plating of copper, $K[Ag(CN)_2]$ is used instead of $AgNO_3$. The reason is

(a) a thin layer of Ag is formed on Cu

(b) more voltage is required

(c) Ag^+ ions are completely removed from solution

(d) less availability of Ag^+ ions, as Cu cannot displace Ag from $[Ag(CN)_2]^-$ ion

53. On passing electric current of one ampere for 16 min and 5 sec through one litre solution of $CuCl_2$, all copper of solution was deposited at cathode. The strength of $CuCl_2$ solution was (molar mass of Cu = 63.5, Faraday constant = 96500 C/mol):

(a) 0.2 N (b) 0.01 N

(c) 0.1 N (d) 0.02 N

54. The standard e.m.f. of a galvanic cell involving cell reaction with n = 2 is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be (Given F = 96500 C mol^{-1}; R = 8.314 $JK^{-1}mol^{-1}$)

(a) 2.0×10^{11} (b) 4.0×10^{12}

(c) 1.0×10^{2} (d) 1.0×10^{10}

55. What will be the emf for the given cell

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

(a) $\frac{RT}{F}\log_e \frac{P_1}{P_2}$ (b) $\frac{RT}{2F}\log_e \frac{P_1}{P_2}$

(c) $\frac{RT}{F}\log_e \frac{P_2}{P_1}$ (d) None of these.

56. In a cell that utilises the reaction

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$ addition of H_2SO_4 to cathode compartment, will

(a) increase the E and shift equilibrium to the right

(b) lower the E and shift equilibrium to the right

(c) lower the E and shift equlibrium to the left

(d) increase the E and shift equilibrium to the left

57. The same amount of electricity was passed through two cells containing molten Al_2O_3 and molten NaCl. If 1.8 g of Al were liberated in one cell, the amount of Na liberated in other cell is:

(a) 2.8 g (b) 3.2 g

(c) 4.6 g (d) 6.8 g

58. According to Nernst equation, which is not correct if $Q = K_c$:

(a) $E_{cell} = 0$ (b) $\frac{RT}{nF}\ln Q = E^\circ_{cell}$

(c) $K_c = e^{\frac{nFE^\circ_{cell}}{RT}}$ (d) $E_{cell} = E^\circ_{cell}$

59. The volume of oxygen gas liberated at NTP by passing a current of 9650 coulombs through acidified water is :
(a) 1.12 litre (b) 2.24 litre
(c) 11.2 litre (d) 22.4 litre

60. The emf of the cell
$Ni \mid Ni^{2+}$ (1.0 M) || Au^{3+} (1.0M) | Au is
[Given $E^\circ Ni^{2+}/Ni = -0.25$ V and $E^\circ Au^{3+}/Au = +1.5$ V]
(a) 2.00 V (b) 1.25 V
(c) – 1.25 V (d) 1.75 V

61. What is the e.m.f for the given cell ?
$Cr \mid Cr^{3+}$(1.0M) || Co^{2+}(1.0M) | Co
(E° for $Cr^{3+}/Cr = -0.74$ volt and E° for $Co^{2+}/Co = -0.28$ volt)
(a) – 0.46 volt (b) – 1.02 volt
(c) + 0.46 volt (d) 1.66 volt

62. If a salt bridge is removed between the two half cells, the voltage
(a) Drops to zero (b) Does not change
(c) Increase gradually (d) Increases rapidly

63. The standard emf of a cell, involving one electron change is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is ($F = 96500$ C mol^{-1})
(a) 1.0×10^{1} (b) 1.0×10^{5}
(c) 1.0×10^{10} (d) 1.0×10^{30}

64. Given the electrode potentials
$Fe^{3+} + e^- \longrightarrow Fe^{2+}, E^\circ = 0.771$ volts
$I_2 + 2e^- \longrightarrow 2I^-, E^\circ = 0.536$ volts
E°_{cell} for the cell reaction
$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$, is
(a) 1.006 V (b) 0.503 V
(c) 0.235 V (d) –0.235 V

65. For the galvanic cell
$Zn \mid Zn^{2+}$ (0.1M) || Cu^{2+} (1.0M)|Cu the cell potential increase if:
(a) $[Zn^{2+}]$ is increased
(b) $[Cu^{2+}]$ is increased
(c) $[Cu^{2+}]$ is decreased
(d) surface area of anode is increased

66. Adding powered lead and iron to a solution that is 1.0 M in both Pb^{2+} and Fe^{2+} ions, would result in a reaction, in which:
(a) More iron and Pb^{2+} ions are formed
(b) More lead and Fe^{2+} ions are formed
(c) Concentration of both Pb^{2+} and Fe^{2+} ion increases
(d) There is no net change

67. The standard cell potential of $Zn \mid Zn^{2+}(aq) \mid\mid Cu^{2+}(aq) \mid Cu$ cell is 1.10 V. The maximum work obtained by this cell will be
(a) 106.15 kJ (b) –212.30 kJ
(c) –318.45 kJ (d) – 424.60 kJ

68. A hydrogen electrode is immersed in a solution with pH = 0 (HCl). By how much will the potential (reduction) change if an equivalent amount of NaOH is added to the solution. (Take $p_{H_2} = 1$ atm), T = 298 K.
(a) increase by 0.41 V (b) increase by 59 mV
(c) decrease by 0.41 V (d) decrease by 59 mV

69. Following cell has EMF 0.7995V.
$Pt \mid H_2$ (1 atm) | HNO_3 (1M) || $AgNO_3$ (1M) | Ag
If we add enough KCl to the Ag cell so that the final Cl^- is 1M. Now the measured emf of the cell is 0.222V. The K_{sp} of AgCl would be –
(a) $1 \times 10^{-9.8}$ (b) $1 \times 10^{-19.6}$
(c) 2×10^{-10} (d) 2.64×10^{-14}

70. $E^\circ = \frac{RT}{nF} \text{In}\, K_{eq}$
The above equation is called :
(a) Gibb's equation
(b) Gibb's–Helmholtz equation
(c) Nernst equation
(d) Van der Waal's equation

71. Standard cell voltage for the cell $Pb \mid Pb^{2+} \mid\mid Sn^{2+} \mid Sn$ is – 0.01 V. If the cell is to exhibit $E_{cell} = 0$, the value of $[Sn^{2+}] / [Pb^{2+}]$ should be antilog of –
(a) +0.3 (b) 0.5
(c) 1.5 (d) – 0.5

72. An electrochemical cell is set up as: Pt; H_2 (1atm)|HCl(0.1 M) || CH_3COOH (0.1 M)| H_2 (1atm); Pt. The e.m.f of this cell will not be zero, because
(a) the temperature is constant
(b) e.m.f depends on molarities of acids used
(c) acids used in two compartments are different
(d) pH of 0.1 M HCl and 0.1 M CH_3COOH is not same

73. The quantity of electricity needed to liberate 0.5 gram equivalent of an element is
(a) 48250 faraday (b) 48250 coulomb
(c) 19300 faraday (d) 19300 coulomb

74. For the cell reaction,
Cu^{2+} (C_1, *aq*) + Zn(*s*) → Zn^{2+} (C_2, *aq*) + Cu(*s*) of an electrochemical cell, the change in free energy, ΔG, at a given temperature is a function of
(a) $ln(C_1)$ (b) $ln(C_2/C_1)$
(c) $ln(C_2)$ (d) $ln(C_1 + C_2)$

75. The most durable metal plating on iron to protect against corrosion is
(a) nickel plating (b) copper plating
(c) tin plating (d) zinc plating

76. A certain current liberated 0.504 gm of hydrogen in 2 hrs. How many grams of copper can be liberated by the same current flowing for the same time in a copper sulphate solution ?
(a) 12.7 gms (b) 15.9 gms
(c) 31.8 gms (d) 63.5 gms

77. Several blocks of magnesium are fixed to the bottom of a ship to
(a) make the ship lighter
(b) prevent action of water and salt
(c) prevent puncturing by under-sea rocks
(d) keep away the sharks

78. In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to
(a) produce high purity water
(b) create potential difference between two electrodes
(c) generate heat
(d) remove adsorbed oxygen from elctrode surfaces

79. During the charging of lead storage battery, the reaction at anode is represented by :

(a) $Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

(b) $PbSO_4 + 2H_2O \longrightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$

(c) $Pb \longrightarrow Pb^{2+} + 2e^-$

(d) $Pb^{2+} + 2e^- \longrightarrow Pb$

80. Two electrolytic cells, one containing acidified ferrous chloride and another acidified ferric chloride, are connected in series. The ratio of iron deposited at cathodes in the two cells will be :

(a) 3 : 1 (b) 2 : 1

(c) 1 : 1 (d) 3 : 2

81. Which colourless gas evolves, when NH_4Cl reacts with zinc in a dry cell battery

(a) NH_4 (b) N_2

(c) H_2 (d) Cl_2

82. When a lead storage battery is discharged

(a) SO_2 is evolved

(b) Lead sulphate is consumed

(c) Lead is formed

(d) Sulphuric acid is consumed

83. $Zn^{2+} \rightarrow Zn_{(s)}$; $E^0 = -0.76$ V

$Cu^{2+} \rightarrow Cu_{(s)}$; $E^0 = -0.34$ V

Which of the following is spontaneous?

(a) $Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}$

(b) $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$

(c) $Zn^{2+} + Cu^{2+} \rightarrow Zn + Cu$

(d) None of these

84. The efficiency of a fuel cell is given by

(a) $\frac{\Delta G}{\Delta S}$ (b) $\frac{\Delta G}{\Delta H}$

(c) $\frac{\Delta S}{\Delta G}$ (d) $\frac{\Delta H}{\Delta G}$

85. The equilibrium constant of the reaction:

$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$;
$E° = 0.46$ V at 298 K is

(a) 2.0×10^{10} (b) 4.0×10^{10}

(c) 4.0×10^{15} (d) 2.4×10^{10}

86. On the basis of the following E° values, the strongest oxidizing agent is :

$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$; $E° = -0.35$ V

$Fe^{2+} \rightarrow Fe^{3+} + e^-$; $E° = -0.77$ V

(a) $[Fe(CN)_6]^{4-}$ (b) Fe^{2+}

(c) Fe^{3+} (d) $[Fe(CN)_6]^{3-}$

87. Kohlrausch's law states that at :

(a) finite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.

(b) infinite dilution each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte.

(c) infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte.

(d) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.

88. Standard free energies of formation (in kJ/mol) at 298 K are – 237.2, – 394.4 and – 8.2 for $H_2O(l)$, $CO_2(g)$ and pentane (g), respectively. The value $E°_{cell}$ for the pentane-oxygen fuel cell is :

(a) 1.968 V (b) 2.0968 V

(c) 1.0968 V (d) 0.0968 V

89. Given:

(i) $Cu^{2+} + 2e^- \rightarrow Cu$, $E^o = 0.337$ V

(ii) $Cu^{2+} + e^- \rightarrow Cu^+$, $E^o = 0.153$ V

Electrode potential, E^o for the reaction,
$Cu^+ + e^- \rightarrow Cu$, will be :

(a) 0.90 V (b) 0.30 V

(c) 0.38 V (d) 0.52 V

90. Al_2O_3 is reduced by electrolysis at low potentials and high currents. If 4.0×10^4 amperes of current is passed through molten Al_2O_3 for 6 hours, what mass of aluminium is produced? (Assume 100% current efficiency. At. mass of Al = 27 g mol^{-1})

(a) 8.1×10^4 g (b) 2.4×10^5 g

(c) 1.3×10^4 g (d) 9.0×10^3 g

91. The equivalent conductance of $\frac{M}{32}$ solution of a weak monobasic acid is 8.0 mho cm^2 and at infinite dilution is 400 mho cm^2. The dissociation constant of this acid is:

(a) 1.25×10^{-6} (b) 6.25×10^{-4}

(c) 1.25×10^{-4} (d) 1.25×10^{-5}

92. For the reduction of silver ions with copper metal, the standard cell potential was found to be + 0.46 V at 25°C. The value of standard Gibbs energy, $\Delta G°$ will be

$(F = 96500 \text{ C mol}^{-1})$

(a) – 89.0 kJ (b) – 89.0 J

(c) – 44.5 kJ (d) – 98.0 kJ

93. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to:

(a) increase in ionic mobility of ions

(b) 100% ionisation of electrolyte at normal dilution

(c) increase in both i.e. number of ions and ionic mobility of ions

(d) increase in number of ions

94. Which of the following expressions correctly represents the equivalent conductance at infinite dilution of $Al_2(SO_4)_3$, Given that $\overset{\circ}{\Lambda}_{Al^{3+}}$ and $\overset{\circ}{\Lambda}_{SO_4^{2-}}$ are the equivalent conductances at infinite dilution of the respective ions?

(a) $\frac{1}{3}\overset{\circ}{\Lambda}_{Al^{3+}} + \frac{1}{2}\overset{\circ}{\Lambda}_{SO_4^{2-}}$ (b) $2\overset{\circ}{\Lambda}_{Al^{3+}} + 3\overset{\circ}{\Lambda}_{SO_4^{2-}}$

(c) $\overset{\circ}{\Lambda}_{Al^{3+}} + \overset{\circ}{\Lambda}_{SO_4^{2-}}$ (d) $\left(\overset{\circ}{\Lambda}_{Al^{3+}} + \overset{\circ}{\Lambda}_{SO_4^{2-}}\right) \times 6$

95. Consider the following relations for emf of a electrochemical cell:

(i) emf of cell = (Oxidation potential of anode) – (Reduction potential of cathode)

(ii) emf of cell = (Oxidation potential of anode) + (Reduction potential of cathode)

(iii) emf of cell = (Reduction potential of anode) + (Reduction potential of cathode)

(iv) emf of cell = (Oxidation potential of anode) – (Oxidation potential of cathode)

Which of the above relations are correct?

(a) (ii) and (iv) (b) (iii) and (i)
(c) (i) and (ii) (d) (iii) and (iv)

96. Standard electrode potential of three metals X, Y and Z are – 1.2 V, + 0.5 V and – 3.0 V, respectively. The reducing power of these metals will be :

(a) Y > Z > X (b) X > Y > Z
(c) Z > X > Y (d) X > Y > Z

97. The electrode potentials for

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

and $Cu^+(aq) + e^- \longrightarrow Cu(s)$

are + 0.15 V and + 0.50, respectively. The value of $E^\circ_{Cu^{2+}/Cu}$ will be :

(a) 0.500 V (b) 0.325 V
(c) 0.650 V (d) 0.150 V

98. Standard electrode potential for Sn^{4+}/Sn^{2+} couple is + 0.15 V and that for the Cr^{3+}/Cr couple is – 0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be :

(a) + 1.19 V (b) + 0.89 V
(c) + 0.18 V (d) + 1.83 V

99. If the E°_{cell} for a given reaction has a negative value, then which of the following gives the correct relationships for the values of ΔG° and K_{eq} ?

(a) $\Delta G^\circ > 0 ; K_{eq} > 1$ (b) $\Delta G^\circ < 0 ; K_{eq} > 1$
(c) $\Delta G^\circ < 0 ; K_{eq} < 1$ (d) $\Delta G^\circ > 0 ; K_{eq} < 1$

100. Limiting molar conductivity of NH_4OH $\left(\text{i.e.}, \Lambda^\circ_{m(NH_4OH}\right)$ is equal to :

(a) $\Lambda^\circ_{m(NH_4Cl)} + \Lambda^\circ_{m(NaCl)} - \Lambda^\circ_{m(NaOH)}$

(b) $\Lambda^\circ_{m(NaOH)} + \Lambda^\circ_{m(NaCl)} - \Lambda^\circ_{m(NH_4Cl)}$

(c) $\Lambda^\circ_{m(NH_4OH)} + \Lambda^\circ_{m(NH_4Cl)} - \Lambda^\circ_{m(HCl)}$

(d) $\Lambda^\circ_{m(NH_4Cl)} + \Lambda^\circ_{m(NaOH} - \Lambda^\circ_{m(NaCl)}$

EXERCISE - 2

Applied Questions

1. Molar conductances of $BaCl_2$, H_2SO_4 and HCl at infinite dilutions are x_1, x_2 and x_3 respectively. Equivalent conductance of $BaSO_4$ at infinite dilution will be :

(a) $(x_1 + x_2 - x_3)/2$ (b) $x_1 + x_2 - 2x_3$
(c) $(x_1 - x_2 - x_3)/2$ (d) $(x_1 + x_2 - 2x_3)/2$

2. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 S m^{-1}. Resistance of the same cell when filled with 0.02 M of the same solution is 520 Ω. The molar conductivity of 0.02 M solution of electrolyte will be

(a) 1.24×10^{-4} S m^2 mol^{-1} (b) 12.4×10^{-4} S m^2 mol^{-1}
(c) 124×10^{-4} S m^2 mol^{-1} (d) 1240×10^{-4} S m^2 mol^{-1}

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

(a) 66 g (b) 1.32 g
(c) 33 g (d) 99 g

4. A galvanic cell is set up from electrodes *A* and *B*

Electrode *A* : $Cr_2O_7^{2-}/Cr^{3+}$, $E^\circ_{red} = +1.33\ V$

Electrode *B* : Fe^{3+}/Fe^{2+}, $E^\circ_{red} = 0.77\ V$

Which of the following statements is false ?

(a) Standard e.m.f of the cell is 0.56 *V*
(b) Current will flow from electrode *A* to *B* in the external circuit
(c) *A* will act as cathode and have positive polarity
(d) None of these

5. The electric charge for electrode decomposition of one gram equivalent of a substance is

(a) one ampere per second
(b) 96500 coulombs per second
(c) one ampere for one hour
(d) charge on one mole of electrons

6. On passing a current of 1.0 ampere for 16 min and 5 sec through one litre solution of $CuCl_2$, all copper of the solution was deposited at cathode. The strength of $CuCl_2$ solution was (Molar mass of Cu= 63.5; Faraday constant = 96,500 Cmol^{-1})

(a) 0.01 N (b) 0.01 M
(c) 0.02 M (d) 0.2 N

7. In electrolysis of NaCl when Pt electrode is taken then H_2 is liberated at cathode while with Hg cathode it forms sodium amalgam. This is because

(a) Hg is more inert than Pt
(b) more voltage is required to reduce H^+ at Hg than at Pt
(c) Na is dissolved in Hg while it does not dissolve in Pt
(d) conc. of H^+ ions is larger when Pt electrode is taken

8. Given : $2Br^- \rightarrow Br_2 + 2e^- \quad E^\circ = -1.09\,V$;

$$I_2 + 2e^- \rightarrow 2I^- \quad E^\circ = 0.54\,V$$

$$Fe^{2+} + 2e \rightarrow Fe \quad E^\circ = -0.44\,V$$

Which of the following reactions will not be spontaneous?

(a) $Fe + Br_2 \rightarrow FeBr_2$ (b) $Fe + I_2 \rightarrow FeI_2$

(c) $I_2 + 2Br^- \rightarrow 2I^- + Br_2$ (d) $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

9. $Sn^{4+} + 2e^- \longrightarrow Sn^{2+} \quad E^\circ = 0.13\,V$

$Br_2 + 2e^- \longrightarrow 2Br^- \quad E^\circ = 1.08\,V$

Calculate K_{eq} for the cell formed by two electrodes

(a) 10^{41} (b) 10^{32}

(c) 10^{-32} (d) 10^{-42}

10. The e.m.f. of a Daniell cell at 298 K is E_1.

$$\mathrm{Zn}\left|\begin{matrix}\mathrm{ZnSO_4}\\(0.01\ \mathrm{M})\end{matrix}\right|\left|\begin{matrix}\mathrm{CuSO_4}\\(1.0\ \mathrm{M})\end{matrix}\right|\mathrm{Cu}$$

When the concentration of $ZnSO_4$ is 1.0 M and that of $CuSO_4$ is 0.01 M, the e.m.f. changed to E_2. What is the relationship between E_1 and E_2?

(a) $E_2 = 0 \neq E_1$ (b) $E_1 > E_2$

(c) $E_1 < E_2$ (d) $E_1 = E_2$

11. Sodium is made by the electrolysis of a molten mixture of about 40% NaCl and 60% $CaCl_2$ because

(a) $CaCl_2$ helps in conduction of electricity

(b) this mixture has a lower melting point than NaCl

(c) Ca^{++} can displace Na from NaCl

(d) Ca^{++} can reduce NaCl to Na

12. In anodising :

(a) The metal ion present in electrodyte gets reduced and a film of metal gets coated on the surface of metal cathode

(b) The anode metal gets oxidised to form a metal oxide coat

(c) both the above are correct

(d) none of the above is correct

13. At 25°C, the molar conductance at infinite dilution for the strong electrolytes NaOH, NaCl and $BaCl_2$ are 248×10^{-4}, 126×10^{-4} and 280×10^{-4} Sm^2mol^{-1} respectively.

Λ_m^0 $Ba(OH)_2$ in $S\,m^2\,mol^{-1}$ is

(a) 52.4×10^{-4} (b) 524×10^{-4}

(c) 402×10^{-4} (d) 262×10^{-4}

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

(a) $0.142\ cm^{-1}$ (b) $0.66\ cm^{-1}$

(c) $0.918\ cm^{-1}$ (d) $1.12\ cm^{-1}$

15. A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$, is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are $Ag^+ / Ag = +0.80$, $Hg_2^{2+} / 2Hg = +0.79$, $Cu^{2+} / Cu = +0.34$, $Mg^{2+} / Mg = -2.37$ with increasing voltage, the sequence of deposition of metals on the cathode will be

(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag

(c) Ag, Hg, Cu (d) Cu, Hg, Ag

16. The e.m.f. of the cell $Zn \mid Zn^{2+}\ (0.01M) \mid\mid Fe^{2+}\ (0.001M) \mid Fe$ at 298 K is 0.2905 then the value of equilibrium for the cell reaction is

(a) $e^{\frac{0.32}{0.0295}}$ (b) $10^{\frac{0.32}{0.0295}}$

(c) $10^{\frac{0.26}{0.0295}}$ (d) $10^{\frac{0.32}{0.0591}}$

17. Aluminium displaces hydrogen from acids but copper does not. A galvanic cell prepared by combining Cu / Cu^{2+} and Al / Al^{3+} has an e.m.f. of 2.0 V at 298 K. If the potential of copper electrode is + 0.34 V, that of aluminium is

(a) + 1.66 V (b) – 1.66 V

(c) + 2.34 V (d) – 2.3 V

18. 1. 0 L each of a buffer containing 1 mole NH_3 and 1 mol of NH_4^+ were placed in the cathodic and anodic half-cells and 965 C of electricity was passed. If anodic and cathodic half cells reactions involve oxidation and reduction of water only as

$$2H_2O \longrightarrow 4H^+ + O_2 - 4e^-;$$

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

Then pH of

(a) cathodic solution will increase

(b) anodic solution will decrease

(c) both the solutions will remain practically constant

(d) both the solutions will increase

19. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential of Z > Y > X, then

(a) Y will oxidize X and not Z

(b) Y will oxidize Z and not X

(c) Y will oxidize both X and Z

(d) Y will reduce both X and Z

20. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (At. Mass = 27 amu; 1 Faraday = 96,500 Coulombs). The cathode reaction is

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

To prepare 5.12kg of aluminium metal by this method would require

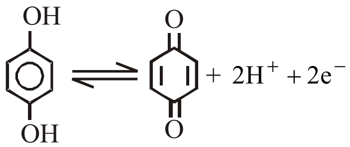
(a) 5.49×10^7 C of electricity

(b) 1.83×10^7 C of electricity

(c) 5.49×10^4 C of electricity

(d) 5.49×10^1 C of electricity

21. At pH = 2, E° (quinhydron) = 1.30 V, E(quinhydron) will be



(a) 1.20 V (b) 1.42 V

(c) 1.36 V (d) 1.30 V

22. The cell,

$Zn \mid Zn^{2+}(1\ M) \parallel Cu^{2+}(1\ M) \mid Cu\ (E°_{cell} = 1.10\ v)$

was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is

(a) 9.65×10^4 (b) antilog (24.08)
(c) 37.3 (d) $10^{37.3}$.

23. Given $E°_{Cr^{3+}/Cr} = -0.72$ V, $E°_{Fe^{2+}/Fe} = -0.42$ V. The potential for the cell

$Cr|Cr^{3+}(0.1M)\|Fe^{2+}(0.01\ M)|$ Fe is

(a) 0.26V (b) 0.336V
(c) −0.339 (d) 0.26V

24. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$CH_3OH(l) + 3/2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

At 298 K standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and and $CO_2(g)$ are –166.2 –237.2 and –394.4 $kJ\ mol^{-1}$ respectively. If standard enthalpy of combustion of methonal is – 726 kJ mol^{-1}, efficiency of the fuel cell will be:

(a) 87% (b) 90%
(c) 97% (d) 80%

25. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows :

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2, \Delta_r G = +966\ kJ\ mol^{-1}$$

The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least

(a) 4.5V (b) 3.0V
(c) 2.5V (d) 5.0V

26. The correct order of $E°_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is

(a) Mn > Cr > Fe > Co (b) Cr < Fe > Mn > Co
(c) Fe > Mn > Cr > Co (d) Cr > Mn > Fe > Co

27. The reduction potential of hydrogen half-cell will be negative if:

(a) $p(H_2) = 1$ atm and $[H^+] = 2.0$ M
(b) $p(H_2) = 1$ atm and $[H^+] = 1.0$ M
(c) $p(H_2) = 2$ atm and $[H^+] = 1.0$ M
(d) $p(H_2) = 2$ atm and $[H^+] = 2.0$ M

28. Consider the following cell reaction:

$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l); E° = 1.67V$

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

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

29. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.3 S m^{-1}. If resistance of the 0.4 M solution of the same electrolyte is 260 Ω, its molar conductivity is :

(a) 6.25×10^{-4} S m^2 mol^{-1} (b) 625×10^{-4} S m^2 mol^{-1}
(c) 62.5 S m^2 mol^{-1} (d) 6250 S m^2 mol^{-1}

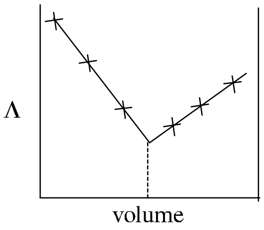
30. The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are –0.76,–0.23 and –0.44 V respectively. The reaction $X + Y^{2+} \longrightarrow X^{2+} + Y$ will be spontaneous when :

(a) X = Ni, Y = Fe (b) X = Ni, Y = Zn
(c) X= Fe, Y = Zn (d) X= Zn, Y = Ni

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

(a) 9.65×10^4 sec (b) 19.3×10^4 sec
(c) 28.95×10^4 sec (d) 38.6×10^4 sec

32. $AgNO_3(aq.)$ was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) versus the volume of $AgNO_3$ is



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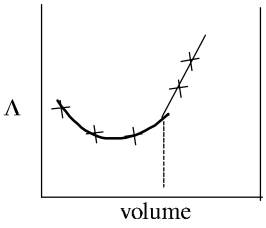

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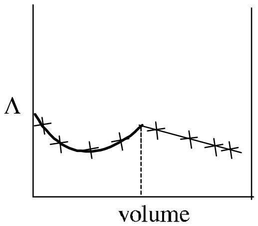
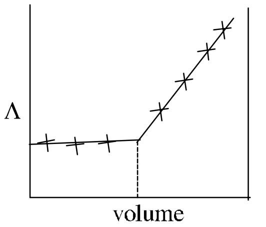


(R)



(S)

(a) (P) (b) (Q)
(c) (R) (d) (S)

33. Given : $E°_{Cr^{3+}/Cr} = -0.74$ V; $E°_{MnO_4^-/Mn^{2+}} = 1.51$ V

$E°_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V; $E°_{Cl/Cl^-} = 1.36$ V

Based on the data given above, strongest oxidising agent will be :

(a) Cl (b) Cr^{3+}
(c) Mn^{2+} (d) MnO_4^-

34. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E°_{M^{3+}/M^{2+}}$ value ?

(a) Cr(Z = 24) (b) Mn(Z = 25)
(c) Fe(Z = 26) (d) Co(Z = 27)

35. A solution contains Fe^{2+}, Fe^{3+} and I^- ions. This solution was treated with iodine at 35°C. $E°$ for Fe^{3+}/Fe^{2+} is + 0.77 V and E° for $I_2/2I^- = 0.536$ V. The favourable redox reaction is :

(a) I_2 will be reduced to I^-
(b) There will be no redox reaction
(c) I^- will be oxidised to I_2
(d) Fe^{2+} will be oxidised to Fe^{3+}

36. Standard reduction potentials of the half reactions are given below :

$F_2(g) + 2e^- \rightarrow 2F^-(aq);\ E° = +2.85$ V

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq);\ E° = +1.36$ V

$Br_2(l) + 2e^- \rightarrow 2Br^-(aq);\ E° = +1.06$ V

$I_2(s) + 2e^- \rightarrow 2I^-(aq);\ E° = +0.53$ V

The strongest oxidising and reducing agents respectively are :

(a) F_2 and I^- (b) Br_2 and Cl^-

(c) Cl_2 and Br^- (d) Cl_2 and I_2

37. Molar conductivities ($\Lambda°_m$) at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. $\Lambda°_m$ for CH_3COOH will be :

(a) 425.5 S cm^2 mol^{-1} (b) 180.5 S cm^2 mol^{-1}

(c) 290.8 S cm^2 mol^{-1} (d) 390.5 S cm^2 mol^{-1}

38. The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25°C are given below :

$$\Lambda°_{CH_3COONa} = 91.0 \text{ S cm}^2/\text{equiv.}$$

$$\Lambda°_{HCl} = 426.2 \text{ S cm}^2/\text{equiv.}$$

What additional information/ quantity one needs to calculate $\Lambda°$ of an aqueous solution of acetic acid?

(a) $\Lambda°$ of chloroacetic acid ($ClCH_2COOH$)

(b) $\Lambda°$ of NaCl

(c) $\Lambda°$ of CH_3COOK

(d) the limiting equivalent coductance of $H^+ (\lambda°_{H^+})$.

39. Given: $E°_{Fe^{3+}/Fe} = -0.036V,\ E°_{Fe^{2+}/Fe} = -0.439V$

The value of standard electrode potential for the change,

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ will be:

(a) 0.385 V (b) 0.770 V

(c) –0.270 V (d) –0.072 V

40. Consider the following four electrodes:

$P = Cu^{2+}$ (0.0001 M)/$Cu_{(s)}$

$Q = Cu^{2+}$ (0.1 M)/$Cu_{(s)}$

$R = Cu^{2+}$ (0.01 M)/$Cu_{(s)}$

$S = Cu^{2+}$ (0.001 M)/$Cu_{(s)}$

If the standard reduction potential of Cu^{2+}/Cu is +0.34 V, the reduction potentials in volts of the above electrodes follow the order.

(a) P > S > R > Q (b) S > R > Q > P

(c) R > S > Q > P (d) Q > R > S > P

41. Which pair of electrolytes could not be distinguished by the products of electrolysis using inert electrodes?

(a) 1 M $CuSO_4$ solution, 1 M $CuCl_2$ solution

(b) 1 M KCl solution, 1 M KI solution

(c) 1 M $AgNO_3$ solution, 1 M $Cu(NO_3)_2$ solution

(d) 1 M KCl solution, 1 M NaCl solution

42. A current is passed through two cells connected in series. The first cell contains $X(NO_3)_{3(aq)}$ and the second cell contains $Y(NO_3)_{2(aq)}$. The relative atomic masses of X and Y are in the ratio 1 : 2. What is the ratio of liberated mass of X to that of Y?

(a) 3 : 2 (b) 1 : 2

(c) 1 : 3 (d) 3 : 1

43. The electrode potential $E_{(Zn^{2+}/Zn)}$ of a zinc electrode at 25°C with an aqueous solution of 0.1 M $ZnSO_4$ is

$[E°_{(Zn^{2+}/Zn)} = -0.76$ V. Assume $\dfrac{2.303RT}{F} = 0.06$ at 298 K].

(a) +0.73 (b) –0.79

(c) –0.82 (d) –0.70

44. The electrical properties and their respective SI units are given below. Identify the wrongly matched pair.

	Electrical property	**SI unit**
(a)	Specific conductance	S m^{-1}
(b)	Conductance	S
(c)	Equivalent conductance	S m^2 $gequiv^{-1}$
(d)	Cell constant	m

45. The ion of least limiting molar conductivity among the following is

(a) SO_4^{2-} (b) H^+

(c) Ca^{2+} (d) CH_3COO^-

46. The reduction potential (in volt) of a hydrogen electrode set up with a 2×10^{-2} M aqueous solution of a weak mono basic acid ($K_a = 5 \times 10^{-5}$) at one atmosphere and 25°C is

(a) +0.09 (b) +0.18

(c) –0.09 (d) –0.18

47. A current strength of 3.86 amp was passed through molten calcium oxide for 41 minutes and 40 seconds. The mass of calcium in grams deposited at the cathode is (Atomic mass of Ca is 40 g/mol, 1 F = 96500 C)

(a) 4 (b) 2

(c) 6 (d) 8

DIRECTIONS for Qs. 48 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

(a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement-1

(b) Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True

48. **Statement-1 :** The resistivity for a substance is its resistance when it is one meter long and its area of cross section is one square meter.

Statement-2 : The SI units of resistivity is ohm metre (Ωm).

49. **Statement-1 :** On increasing dilution, the specific conductance keep on increasing.

Statement-2 : On increasing dilution, degree of ionisation of weak electrolyte increases and molality of ions also increases.

50. **Statement-1 :** Galvanised iron does not rust.

Statement-2 : Zinc has a more negative electrode potential than iron.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Which cell measure standard electrode potential of copper electrode?

(a) $Pt(s)|H_2(g, 0.1\ bar)||H^+(aq, 1\ M)||Cu^{2+}(aq, 1\ M)|\ Cu$

(b) $Pt(s)|H_2(g, 1\ bar)||H^+(aq, 1\ M)||Cu^{2+}(aq, 2\ M)|\ Cu$

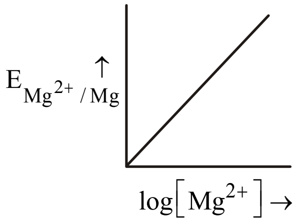
(c) $Pt(s)|H_2(g, 1\ bar)||H^+(aq, 1\ M)||Cu^{2+}(aq, 1\ M)|\ Cu$

(d) $Pt(s)|H_2(g, 0.1\ bar)||H^+(aq, 0.1\ M)||Cu^{2+}(aq, 1\ M)|\ Cu$

2. Electrode potential for Mg electrode varies according to the equation

$E_{Mg^{2+}/Mg} = E^{\ominus}_{Mg^{2+}/Mg} - \frac{0.059}{2}\log\frac{1}{[Mg^{2+}]}$. The graph of $E_{Mg^{2+}/Mg}$ vs log $[Mg^{2+}]$ is

(a)



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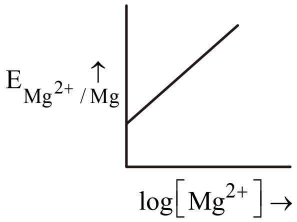

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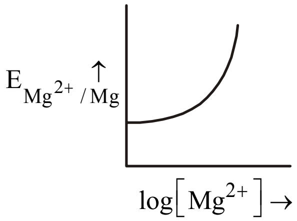

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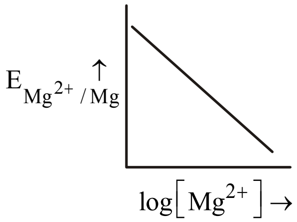


3. Which of the following statement is correct?

(a) E_{cell} and Δ_rG of cell reaction both are extensive properties.

(b) E_{cell} and Δ_rG of cell reaction both are intensive properties.

(c) E_{cell} is an intensive property while Δ_rG of cell reaction is an extensive property.

(d) E_{cell} is an extensive property while Δ_rG of cell reaction is an intensive property.

4. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called......

(a) cell potential (b) cell emf

(c) potential difference (d) cell voltage

5. Which of the following statement is not correct about an inert electrode in a cell?

(a) It does not participate in the cell reaction

(b) It provides surface either for oxidation or for reduction reaction

(c) It provides surface for conduction of electrons

(d) It provides surface for redox reaction

6. An electrochemical cell can behave like an electrolytic cell when ......

(a) $E_{cell} = 0$ (b) $E_{cell} > E_{ext}$

(c) $E_{ext} > E_{cell}$ (d) $E_{cell} = E_{ext}$

7. Which of the statements about solutions of electrolytes is not correct?

(a) Conductivity of solution depends upon size of ions

(b) Conductivity depends upon viscosity of solution

(c) Conductivity does not depend upon solvation of ions present in solution

(d) Conductivity of solution increases with temperature

8. Using the data given below find out the strongest reducing agent.

$E^{\ominus}_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33V;\quad E^{\ominus}_{Cl_2/Cl^-} = 1.36V$

$E^{\ominus}_{MnO_4^-/Mn^{2+}} = 1.51V;\quad E^{\ominus}_{Cr^{3+}/Cr^-} = -0.74V$

(a) Cl^- (b) Cr

(c) Cr^{3+} (d) Mn^{2+}

9. Use the data given in Q. 8 and find out which of the following is the strongest oxidising agent?

(a) Cl^- (b) Mn^{2+}

(c) MnO_4^- (d) Cr^{3+}

10. Using the data given in Q. 8 find out in which option the order of reducing power is correct.

(a) $Cr^{3+} < Cl^- > Mn^{2+} < Cr$

(b) $Mn^{2+} < Cl^- > Cr^{3+} < Cr$

(c) $Cr^{3+} < Cl^- < Cr_2O_7^{2-} < Mn^{2+}$

(d) $Mn^{2+} < Cr^{3+} < Cl^- < Cr$

11. Use the data given in Q.8 and find out the most stable ion in its reduced form.

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

(c) Cr (d) Mn^{2+}

12. Use the data of Q. 8 and find out the most stable oxidised species.

(a) Cr^{3+} (b) MnO_4^-

(c) $Cr_2O_7^{2-}$ (d) Mn^{2+}

13. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is ....
(a) 1 F (b) 6 F
(c) 3 F (d) 2 F

14. The cell constant of a conductivity cell ....
(a) changes with change of electrolyte
(b) changes with change of concentration of electrolyte
(c) changes with temperature of electrolyte
(d) remains constant for a cell

15. While charging the lead storage battery ....
(a) $PbSO_4$ anode is reduced to Pb
(b) $PbSO_4$ cathode is reduced to Pb
(c) $PbSO_4$ cathode is oxidised to Pb
(d) $PbSO_4$ anode is oxidised to PbO_2

16. $\overset{\circ}{\Lambda}_{m(NH_4OH)}$ is equal to ....
(a) $\overset{\circ}{\Lambda}_{m(NH_4OH)} + \overset{\circ}{\Lambda}_{(NH_4Cl)} - \overset{\circ}{\Lambda}_{m(HCl)}$
(b) $\overset{\circ}{\Lambda}_{m(NH_4Cl)} + \overset{\circ}{\Lambda}_{m(NaOH)} - \overset{\circ}{\Lambda}_{m(NCl)}$
(c) $\overset{\circ}{\Lambda}_{m(NH_4Cl)} + \overset{\circ}{\Lambda}_{m(NaCl)} - \overset{\circ}{\Lambda}_{m(NaOH)}$
(d) $\overset{\circ}{\Lambda}_{m(NaOH)} + \overset{\circ}{\Lambda}_{m(NaCl)} - \overset{\circ}{\Lambda}_{m(NH_4Cl)}$

17. In the electrolysis of aqueous sodium chloride solution which of the half cell reaction will occur at anode?
(a) $Na^+(aq) + e^- \longrightarrow Na(s)\,;\ \overset{\circ}{E}_{cell} = -2.71V$
(b) $2H_2O(l) \to O_2(g) + 4H^+(aq) + 4e^-\,;\ \overset{\circ}{E}_{cell} = 1.23V$
(c) $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g);\ \overset{\circ}{E}_{cell} = 0.00\ V$
(d) $Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-;\ \overset{\circ}{E}_{cell} = 1.36\ V$

NEET/AIPMT (2013-2017) Questions

18. A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode would be ? ***[2013]***
(a) 0.59 V (b) 0.118 V
(c) 1.18 V (d) 0.059 V

19. At 25°C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is 9.54 $ohm^{-1}\,cm^2mol^{-1}$ and at infinite dilution its molar conductance is 238 $ohm^{-1}\,cm^2\,mol^{-1}$. The degree or ionisation of ammonium hydroxide at the same concentration and temperature is : ***[2013]***
(a) 20.800% (b) 4.008%
(c) 40.800% (d) 2.080%

20. A button cell used in watches functions as following

$$Zn(s) + Ag_2O(s) + H_2O(l) \rightleftharpoons 2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq)$$

If half cell potentials are :
$Zn^{2+}(aq) + 2e^- \to Zn(s);\ E^o = -0.76\ V$
$Ag_2O(s) + H_2O\,(l) + 2e^- \to 2Ag(s) + 2OH^-(aq);\ E^o = 0.34\ V$
The cell potential will be : ***[2013]***
(a) 0.42 V (b) 0.84 V
(c) 1.34 V (d) 1.10 V

21. How many grams of cobalt metal will be deposited when a solution of cobalt (II) chloride is electrolyzed with a current of 10 amperes for 109 minutes (1 Faraday = 96,500 C; Atomic mass of Co = 59 u) ***[NEET Kar. 2013]***
(a) 0.66 (b) 4.0
(c) 20.0 (d) 40.0

22. Consider the half-cell reduction reaction :
$Mn^{2+} + 2e^- \to Mn,\ E° = -1.18\ V$
$Mn^{2+} \to Mn^{3+} + e^-,\ E° = -1.51\ V$
The E° for the reaction $3Mn^{2+} \to Mn^0 + 2Mn^{3+}$, and possibility of the forward reaction are, respectively ***[NEET Kar. 2013]***
(a) – 2.69 V and no (b) – 4.18 V and yes
(c) + 0.33 V and yes (d) + 2.69 V and no

23. When 0.1 mol MnO_4^{2-} is oxidised the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is: ***[2014]***
(a) 96500 C (b) 2×96500 C
(c) 9650 C (d) 96.50 C

24. The weight of silver (at wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be : ***[2014]***
(a) 5.4 g (b) 10.8 g
(c) 54.9 g (d) 108.0 g

25. A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as : ***[2015]***
(a) Electrolytic cell (b) Dynamo
(c) Ni-Cd cell (d) Fuel Cell

26. Aqueous solution of which of the following compounds is the best conductor of electric current ? ***[2015 RS]***
(a) Acetic acid, $C_2H_4O_2$
(b) Hydrochloric acid, HCl
(c) Ammonia, NH_3
(d) Fructose, $C_6H_{12}O_6$

27. The pressure of H_2 required to make the potential of H_2-electrode zero in pure water at 298 K is : ***[2016]***
(a) 10^{-14} atm (b) 10^{-12} atm
(c) 10^{-10} atm (d) 10^{-4} atm

28. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field ? ***[2017]***
(a) K (b) Rb
(c) Li (d) Na

29. In the electrochemical cell :- ***[2017]***
$Zn\,|\,ZnSO_4\,(0.01M)\,||\,CuSO_4\,(1.0\ M)\,|\,Cu$, the emf of this Daniel cell is E_1. When the concentration of $ZnSO_4$ is changed to 1.0M and that of $CuSO_4$ changed to 0.01M, the emf changes to E_2. From the followings, which one is the relationship between E_1 and E_4?

(Given, $\frac{RT}{F} = 0.059$)
(a) $E_1 < E_2$ (b) $E_1 > E_2$
(c) $E_2 = 0 \neq E_1$ (d) $E_1 = E_2$

Hints & Solutions

EXERCISE - 1

1. (b) Charge passed

$= 30 \times 60 \times 2 = 3600$ coulombs

Chlorine liberated

$$= \frac{35.5 \times 3600}{96500} = 1.32\text{gm}$$

2. (a) NH_4^+ is conjugate acid of NH_3 as it is capable of giving H^+ ion.

$$\underset{\text{Base}}{NH_3} + H^+ \longrightarrow \underset{\text{Conjugate acid}}{NH_4^+}$$

3. (d) Molarity = 0.01 M ; Resistance = 40 ohm;

Cell constant $\frac{l}{A} = 0.4\,\text{cm}^{-1}$.

Specific conductivity (κ)

$$= \frac{\text{cell constant}}{\text{resistance}} = \frac{0.4}{40} = 0.01\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

Molar conductance ($\wedge_m$) $= \frac{1000\kappa}{\text{Molarity}}$

$$= \frac{1000 \times 0.01}{.01} = 10^3\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

4. (b) Specific conductance of the solution (κ) = 0.012 $\text{ohm}^{-1}\ \text{cm}^{-1}$ and resistance (R) = 55 ohm.

Cell constant = Specific conductance × Observed resistance

$= 0.012 \times 55 = 0.66\text{cm}^{-1}$.

5. (a) Difluoroacetic acid being strongest acid will furnish maximum number of ions showing highest electrical conductivity.

6. (c) Volume of 1×10^{-5} gm of hydrogen

$$= \frac{22400 \times 10^{-5}}{2}\ \text{c.c.}$$

When 0.5 amp flows for 2 hours, charge passed

$= 0.5 \times 60 \times 60 \times 2 = 3600$ coulomb

Now 1 coulomb of electricity releases

$$= \frac{22400 \times 10^{-5}}{2}\ \text{c.c. of gas}$$

3600 coulomb of electricity releases,

$$= \frac{22400 \times 10^{-5}}{2} \times \frac{3600}{10^3}\ \text{litres} = 0.4\ \text{litres}$$

7. (b) $\Lambda^{\infty}_{HCl} = 426.2$ (i)

$\Lambda^{\infty}_{AcONa} = 91.0$ (ii)

$\Lambda^{\infty}_{NaCl} = 126.5$ (iii)

$$\Lambda^{\infty}_{AcOH} = \text{(i)} + \text{(ii)} - \text{(iii)} = [426.2 + 91.0 - 126.5] = 390.7$$

8. (b) $\text{ohm}^{-1}\ \text{cm}^2\ (\text{geq})^{-1}$

9. (a) $\Lambda_{eq} = \kappa \times \frac{1000}{N} = \frac{1}{R} \times \frac{l}{a} \times \frac{1000}{N}$

$$= \frac{1}{R} \times \text{cell constant} \times \frac{1000}{N}$$

$$= \frac{1}{220} \times 0.88 \times \frac{1000}{0.01} = 400\ \text{mho cm}^2\ \text{g eq}^{-1}$$

10. (c) Charge = $1 \times 30 \times 60 = 1800$ coulomb

96500 liberates 35.5 gm of Cl

1800 coulomb liberates

$$\frac{35.5 \times 1800}{96500} = 0.66\ \text{gm of Cl}$$

11. (b) Here, R = 31.6 ohm

$$\therefore \text{Conductance} = \frac{1}{R} = \frac{1}{31.6}\ \text{ohm}^{-1} = 0.0316\ \text{ohm}^{-1}$$

Specific conductance = conductance × cell constant.

$= 0.0316\ \text{ohm}^{-1} \times 0.367\ \text{cm}^{-1} = 0.0116\ \text{ohm}^{-1}\ \text{cm}^{-1}$

Now, molar concentration = 0.5M (given)

$= 0.5 \times 10^{-3}$ mole cm^{-3}

$$\therefore \text{Molar conductance} = \frac{\kappa}{C} = \frac{0.0116}{0.5 \times 10^{-3}}$$

$$= 23.2\ \text{S cm}^2\ \text{mol}^{-1}$$

12. (b) For the given cell

$M|M^+\|X^-|X$, the reaction can be given by

R.H.S. : Reduction -

$$X + e^- \rightarrow X^-\ ;\ E^0 = 0.33\ \text{V}$$

L.H.S. : Oxidation

$$M \rightarrow M^+ + e^-;\ E^0 = 0.49\ \text{V}$$

Adding both half cell reactions, we get

$$M + X \rightarrow M^+ + X^-$$

$$E^{\circ}_{cell} = E^{\circ}_{RHS} - E^{\circ}_{LHS} = 0.33 - 0.44 = -0.11\ \text{V}$$

Since E_{Cell} = –ve, the reaction can not be spontaneous in forward direction but can proceed spontaneously if the direction is reversed.

13. (b) Given current (i) = 0.5 amp;

Time (t) = 100 minutes × 60 = 6000 sec

Equivalent weight of silver nitrate (E) = 108.

According to Faraday's first law of electrolysis

$$W = \frac{Eit}{96500} = \frac{108 \times 0.5 \times 6000}{96500} = 3.3575\ \text{g.}$$

14. (c) According to Faraday's law of electrolysis, the amount of metal deposited on an electrode is directly proportional to the amount of electricity passed and equivalent weight of metal. Now equivalent weight of

sodium is 23, magnesium is $\frac{24.3}{2}$ i.e. 12.15 and of aluminium is $\frac{27}{3}$ i.e. 9. So, sodium which has highest equivalent weight among Na, Mg and Al, is deposited to highest extent during electrolysis.

15. (d) 1 mole of $e^- = 1F = 96500$ C
27g of Al is deposited by 3×96500 C
5120 g of Al will be deposited by
$$= \frac{3 \times 96500 \times 5120}{27} = 5.49 \times 10^7 \text{ C}$$

16. (a) $2H^+ + 2e^- \longrightarrow H_2$
$$E_H \text{ (Eq. wt)} = \frac{2}{2} = 1 \text{ g}$$
$$= \frac{22400}{2} = 11200 \text{ ml (STP)}$$
$$\text{Total charge passed} = \frac{96500 \times 112}{11200} = 965$$
$$Q = It = 965$$
$$I = \frac{965}{965} = 1 \text{amp.}$$

17. (d) $\frac{W_A}{E_A} = \frac{W_B}{E_B}; \ \frac{1.6}{8} = \frac{\text{Wt. of Ag}}{108}$
$\therefore$ Wt. of Ag = 21.6 g

18. (b) Here Ag^+ acts as oxidising agent and Co^{2+} acts as reducing agent. So, cell can be represented as
$Co^{2+} | Co^{3+}(aq.) || Ag^+(aq.) | Ag$
Using Nernst equation,
$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \left| \frac{[Co^{3+}(aq)][Ag]}{[Ag^+(aq)][Co^{2+}]} \right|$$
So, lesser the logarithmic term higher will be the value of E_{cell}. Among the given combinations logarithmic term is lesser for 0.1 M Co^{3+} and 2M Ag^+ and hence it will form a cell of highest voltage.

19. (b) $Cu^{+2} + \quad 2e^- \quad \rightarrow Cu(s)$
$\qquad 2 \times 96500 \text{ C} \quad 63.6\text{g}$
$$9650 \text{ C will deposit} = \frac{63.6}{2 \times 96500} \times 9650 = 3.18 \text{ g}$$

20. (a) Charge = 0.2 × 1 Faraday
= 0.2 × 96500 coulombs
= $19300 = 1.93 \times 10^4$ coulombs

21. (b) Magnesium which is more electropositive than iron prevents the rusting of iron by converting themselves into positive ion and thus reverses the process of conversion of iron to Fe^{3+} ion.

22. (d) $Ag^+ + e^- \longrightarrow Ag$
96500 coulombs deposit = 108 g of Ag
$$\therefore \text{ 965 coulombs deposit} = \frac{108}{96500} \times 965 = 1.08 \text{ g Ag}$$

23. (a) Total charge on one mole of monovalent metal ion = Charge on N_0 electrons
$1F = 96500 \text{ coulombs} = 9.65 \times 10^4$ coulombs.

24. (c) Using Faraday's second law of electrolysis,
$$\frac{\text{Weight of Cu deposited}}{\text{Weight of Ag deposited}} = \frac{\text{Equ. wt. of Cu}}{\text{Equ. wt. of Ag}}$$
$$\Rightarrow \frac{w_{Cu}}{0.18} = \frac{63.5}{2} \times \frac{1}{108}$$
$$\Rightarrow w_{Cu} = \frac{63.5 \times 18}{2 \times 108 \times 100} = 0.0529 \text{ g.}$$

25. (a) Charge passed = $25 \times 10^{-3} \times 60$
$= 15 \times 10^{-1} = 1.5$ coulomb
$Ca^{2+} + 2e \longrightarrow Ca$
Now for calcium ion,
2 × 96500 coulomb is required for
6.02×10^{23} atoms
$$\text{0.3 coulomb will be required for } \frac{6.02 \times 10^{23} \times 1.5}{2 \times 96500}$$
$= 4.68 \times 10^{18}$

26. (a) For deposition of silver, reaction is
$Ag^+ + e^- \longrightarrow Ag$
1 mol of Ag will be deposited by
$= 1 \text{ F} = 96500 \text{ C} = 9.65 \times 10^4 \text{ C}$
Since 1 equivalent weight of Ag is also equal to the weight of its 1 mol, hence 1 equivalent weight of Ag will be deposited by = 9.65×10^4 C

27. (c) According to the definition 1 F or 96500 C is the charge carried by 1 mol of electrons when water is electrolysed
$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$
So, 4 Faraday of electricity liberate = 32 g of O_2.
Thus 1 Faraday of electricity liberate
$$= \frac{32}{4} \text{g of } O_2 = 8 \text{ g of } O_2$$

28. (a) Charging increases the voltage. When the discharged cell is recharged, it acts as electrolytic cell.

29. (b) A current of 96500 coulombs liberate 1 mole of O_2.
⇒ 96500 C liberates = 22.4 L of O_2 at NTP
$$\Rightarrow 9650 \text{ C liberates} = \frac{22.4}{96500} \times 9650$$
$= 2.24$ L of O_2 at NTP

30. (b) $Fe^{2+} + 2e^- \rightarrow Fe; E_{Fe} = \frac{56}{2} = 28$
1 Faraday liberates = 28 g of Fe
3 Faraday liberates = 3 × 28 = 84 gm

31. (c)

32. (b) Amount of silver present in 125 ml of 1 M. $AgNO_3$
$$= \frac{108}{1000} \times 125 \text{ g}$$

Q needed for deposition of 108 g (1 g equivalent of Ag) $= 1\,F = 96500\,C$

$\therefore$ Q needed for deposition of

$$\frac{108}{1000} \times 125 \text{ g Ag} = \frac{1}{108} \times \frac{108}{1000} \times 125 \text{ F} = 0.125 \text{ F}$$

$$= 0.125 \times 96500 \text{ C}$$

Since, $Q = i \times t$

$$\therefore \; t = \frac{0.125 \times 96500}{241.25} = 50 \text{ s}$$

[Given: $i = 241.25$ amperes]

33. (d) Charge (Coulombs) pass per second $= 10^{-6}$
number of electrons passed per second

$$= \frac{10^{-6}}{1.602 \times 10^{-19}} = 6.24 \times 10^{12}$$

34. (c) $$E^\circ_{cell} = \frac{2.303RT}{nF} \log K_{eq} = \frac{.0591}{n} \log K_{eq}$$

$$= \frac{.0591}{2} \log 10^6 = .0591 \times 3 = 0.1773 \text{ V}$$

35. (a) $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$
O.S. of Cr changes from +3 to +6 by loss of electrons. At anode oxidation takes place.

36. (d) In electrolysis of dilute H_2SO_4, O_2 is liberated at anode. It can be summarised as follows :-
$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$
$H_2O \rightleftharpoons H^+ + OH^-$
During electrolysis, the hydrogen ions migrate towards the cathode and are collected here in the form of hydrogen gas.
Following reactions take place
At cathode : $2H^+ + 2e^- \longrightarrow H_2$
$4H^+ + 4e^- \longrightarrow 2H_2$
At anode : $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$
Overall reaction is
$4H^+ + 2H_2O \rightleftharpoons 2H_2 + O_2 + 4H^+$
Thus, we see that hydrogen is produced at cathode and oxygen at anode during electrolysis.

37. (d) Calomel electrode is used as reference electrode.

38. (b) Electrode potential is considered as zero

39. (a) Ag is easiest to be reduced among the given choices because its reduction potential is highest among the given choices.

40. (d) $$\overbrace{Zn^{2+} + 2e^- \longrightarrow Zn}^{\text{Reduction}}$$ It shows reduction reaction.

41. (b) $2AgCl_{(s)} + H_{2(g)} \rightarrow 2HCl_{(aq)} + 2Ag_{(s)}$
The activities of solids and liquids are taken as unity and at low concentrations, the activity of a solute is approximated to its molarity.
The cell reaction will be

$$Pt_{(s)} \mid H_{2(g)}, 1\text{bar} \mid H^+_{(aq)} 1M \mid AgCl_{(aq)}\ 1M \mid Ag_{(s)}$$

42. (a)

43. (a) $$k = \frac{\text{Cell constant}}{R} = \frac{1.15}{250}$$

$$\Lambda_{eq} = \frac{1.15}{250} \times \frac{1000}{1} = 4.6$$

44. (c) Molar conductance of solution is related to specific conductance as follows :

$$\wedge_m = K \times \frac{1000}{C} \qquad \text{....(1)}$$

where C is molar concn.
Putting $K = 6.3 \times 10^{-2}$ ohm^{-1} cm^{-1} and $C = 0.1M$ in equ (1), we get

$$\wedge_m = (6.3 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}) \times \frac{1000}{(0.1 \text{mol}/\text{cm}^3)}$$

$= 6.3 \times 10^{-2} \times 10^4$ ohm^{-1}cm^2 mol^{-1}
$= 630$ ohm^{-1} cm^2 mol^{-1}

45. (a) Anode has negative polarity.

46. (b) Reduction occurs at cathode. Among the given choices, the reaction shown in option (b) is the reduction of Ag^+ to Ag. So, it occurs at cathode.

47. (a) Cell reaction

cathode :

$$H_2O(\ell) + \frac{1}{2}O_2(g) + 2e^- \longrightarrow 2OH^-(aq)$$

anode : $$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$$

$$H_2O(\ell) + \frac{1}{2}O_2(g) + H_2(g) \longrightarrow 2H^+(aq) + 2OH^-(aq)$$

Also we have

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)\,;\ \Delta G_f^\circ = -237.2 \text{ kJ/mole}$$

$$H_2O(\ell) \longrightarrow H^+(aq) + OH^-(aq);$$

$\Delta G^\circ = 80$ kJ/mole

Hence for cell reaction

$\Delta G^\circ = -237.2 + (2 \times 80) = -77.20$ kJ/mole

$$\therefore\ E^\circ = -\frac{\Delta G^\circ}{nF} = \frac{77200}{2 \times 96500} = 0.40\text{V}$$

48. (b) (i) $A^{3+} + e^- \longrightarrow A^{2+}$, $\Delta G_1 = -1\,F\,y_2$
(ii) $A^{2+} + 2e^- \longrightarrow A$, $\Delta G_2 = -2F(-y_1) = 2Fy_1$
Add, (i) and (ii) we get
$A^{3+} + 3e^- \longrightarrow A$;
$\Delta G_3 = \Delta G_1 + \Delta G_2$
$-3FE^\circ = -Fy_2 + 2Fy_1$
$-3FE^\circ = -F(y_2 - 2y_1)$

$$E^\circ = \frac{y_2 - 2y_1}{3}$$

49. (a) In the electrolysis of cupric sulphate, the reaction that occurs at cathode is

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

Thus 2F or 2×96500 C of electricity is required to deposit

= 1 mol of Cu = 63.5 g of Cu

It means that to deposit 63.5 g of Cu, the amount of electricity required = 2 × 96500 C

So, to deposit 0.634 g of Cu, the amount of electricity

$$\text{required} = \frac{2 \times 96500}{63.5} \times 0.634 \approx 1930\,\text{C}$$

50\. (b) Without losing its concentration $ZnCl_2$ solution cannot kept in contact with Al because Al is more reactive than Zn due to its highly negative electrode reduction potential.

51\. (c) $$2\,Cu^+ \longrightarrow Cu^{+2} + Cu$$

$$2\,e^- + Cu^{+2} \longrightarrow Cu\,;\; E_1^\circ = 0.34\text{V}; \quad \text{...(i)}$$

$$e^- + Cu^{+2} \longrightarrow Cu^+\,;\; E_2^\circ = 0.15\text{V}; \quad \text{...(ii)}$$

$$Cu^+ + e^- \rightarrow Cu;\; E_3^\circ = ? \quad \text{... (iii)}$$

Now, $\Delta G_1^\circ = -nFE_1^\circ = -2 \times 0.34\text{F}$

$\Delta G_2^\circ = -1 \times 0.15\text{F}$, $\Delta G_3^\circ = -1 \times E_3^\circ\text{F}$

Again, $\Delta G_1^\circ = \Delta G_2^\circ + \Delta G_3^\circ$

$\Rightarrow -0.68\text{F} = -0.15\text{F} - E_3^\circ\text{F}$

$\Rightarrow E_3^\circ = 0.68 - 0.15 = 0.53\text{V}$

$E_{cell}^\circ = E_{\text{cathode}}^\circ(Cu^+/Cu) - E_{\text{anode}}^\circ(Cu^{+2}/Cu^+)$
$= 0.53 - 0.15 = 0.38$ V.

52\. (d) In the silver plating of copper, $K[Ag(CN)_2]$ is used instead of $AgNO_3$. Copper being more electropositive readily precipitate silver from their salt solution

$$Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + Ag$$

whereas in $K[Ag(CN)_2]$ solution a complex anion $[Ag(CN)_2]^-$ is formed and hence Ag^+ are less available in the solution and therefore copper cannot displace Ag from its complex ion.

53\. (b) I = 1A, t = 16 min. 5 sec = 965 sec

Quantity of electricity pased,

Q = It = 1 × 965 C = 965 C

The reaction involved at the cathode is

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

Thus, 2F (= 2 × 96500 C) deposits

= 1 mol of Cu = 63.5g Cu

$$\Rightarrow \quad 965\text{ C deposits} = \frac{63.5 \times 965}{2 \times 96500}\text{ g Cu} = 0.3125\text{ g Cu}$$

Now, Normality of the solution

$$= \frac{0.3125}{(63.5/2)} \times \frac{1000}{1000} = 0.01\text{ N}$$

54\. (d) $$E^\circ = \frac{0.0591}{n}\log K$$

Here, $n = 2, E^\circ = 0.295$

$$\therefore \log K = \frac{2 \times 0.295}{0.0591} = 9.98 \approx 10 \text{ or } K = 10^{10}$$

55\. (b) RHS : $2H^+ + 2e^- \rightleftharpoons H_2\,(P_2)$

LHS : $H_2(P_1) \rightleftharpoons 2H^+ + 2e^-$

overall reaction : $H_2\,(P_1) \rightleftharpoons H_2(P_2)$

$$E = E^\circ - \frac{RT}{nF}\ell n\frac{P_2}{P_1} = 0 - \frac{RT}{nF}\ell n\frac{P_2}{P_1} = \frac{RT}{nF}\ell n\frac{P_1}{P_2}$$

56\. (a) $$Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}][H_2]}{[H^+]^2}$$

Addition of H_2SO_4 will increase $[H^+]$and E_{cell} will also increase and the equilibrium will shift towards RHS

57\. (c) According to Faraday's law of electrolysis

W = ZQ

where W is weight of substance liberated at an electrode, Z is electrochemical equivalent and Q is quantity of electricity passed.

When Q coloumbs of electricity passed through molten Al_2O_3, the amount of Al liberated is

$W_{Al} = Z_{Al}\,Q$

$$\Rightarrow W_{Al} = \frac{\text{equ. wt of Al}}{96500}Q$$

$$\Rightarrow 1.8 = \frac{27}{3 \times 96500}Q \quad \text{.........(i)}$$

Similarly when Q cloumbs of electricity is passed through molten NaCl, the amount of Na liberated is

$$W_{Na} = \frac{23}{96500}Q \quad \text{........(ii)}$$

Divide (ii) by (i), we get

$$\frac{W_{Na}}{1.8} = \frac{23}{96500} \times \frac{96500 \times 3}{27}$$

$$\Rightarrow W_{Na} = 1.8 \times 3 \times \frac{23}{27} = 4.6\text{ g.}$$

58\. (d) $$E_{cell} = E_{cell}^\circ - \frac{RT}{nF}\ln Q$$

At equilibrium,

$E_{cell} = 0$ and $Q = K_c$

$\therefore \quad E_{cell} \neq E_{cell}^\circ$

59\. (b) A current of 96500 coulombs liberate 1 mole of O_2.

$\Rightarrow$ 96500 C liberates = 22.4 L of O_2 at NTP

$\Rightarrow$ 9650 C liberates = 2.24 L of O_2 at NTP

60\. (d) Here Ni is anode and Au is cathode

Given $E^\circ_{Ni^{2+}/Ni} = -0.25\text{V}$ and $E^\circ_{Au^{3+}/Au} = +1.5\text{ V}$

$$E^\circ_{cell} = E^\circ_C - E^\circ_A = 1.5 - (-0.25) = 1.5 + 0.25 = 1.75\text{ V}$$

61. (c) $E^\circ_{Cr^{3+}/Cr} = -0.74$ V, $E^\circ_{Co^{2+}/Co} = -0.28$ V

The given cell reaction is

$Cr \mid Cr^{3+}(1.0\ M) \parallel Co^{2+}\ (1.0\ M) \mid Co$

∴ Cr is anode and Co is cathode

$$E^\circ_{cell} = E^\circ_C - E^\circ_A = -0.28 - (-0.74)$$
$$= -0.28 + 0.74 = +0.46\ V$$

62. (a) On removing the salt bridge between the two half cells the circuit is broken. Hence, emf becomes zero.

63. (c) The E°_{cell} is given by

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_{eq}$$

$$\therefore\ 0.591 = \frac{0.0591}{1}\log K_{eq}$$

$$\text{or } \log K_{eq} = \frac{0.591}{0.0591} = 10$$

$$\text{or } K_{eq} = 1 \times 10^{10}$$

64. (a) Given : $[Fe^3 + e^- \longrightarrow Fe^{2+}] \times 2$

$E^\circ = 0.771 \times 2\ V = 1.542\ V$

$2I^- \longrightarrow I_2 + 2e^- \qquad E^\circ = -0.536\ V$

$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

$E^\circ_{cell} = 1.542 - 0.536 = 1.006\ V$

65. (b) For the given cell

$$E_{cell} = E^\circ_{cell} - \frac{0.059V}{2}\log\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$$

The cell potential will decreases with increase in $[Zn^{2+}\ (aq)]$ and will increases with increase in $[Cu^{2+}(aq)]$.

66. (b) Fe is above Pb in the electrochemical series i.e. E°_{oxid} of Fe (+ 0.44 V) is higher than E°_{oxid} of Pb (+ 0.129 V). Hence, on addition of powdered Fe and Pb to a solution of Fe^{++} ion and Pb^{++} ion, the following reaction will take place :

$$Fe(s) + Pb^{++}(aq) \longrightarrow Fe^{++}(aq) + Pb(s)$$

So, more Pb and Fe^{++} ions will be formed.

67. (b) Maximum work done = W_{max}

$$= -nFE^\circ_{cell} = -2 \times 96500 \times 1.10 = -212.30\ KJ$$

68. (c) pH changes from 0 to 7.

∴ $[H^+]$ changes from 1 to 10^{-7} M.

$$\text{Accordingly } E_{red.} = \frac{-0.059}{n}\log\frac{1}{[H^+]}$$
$$= 0.059 \log 10^{-7}$$

i.e., $0.059 \times (-7) = -0.41$ volt.

69. (a) $2Ag^+ + H_2 \longrightarrow 2H^+ + 2Ag$

$$E = E^\circ - \frac{0.0591}{2}\log\frac{[H^+]^2}{P_{H_2} \times [Ag^+]^2}$$

$$0.222 = 0.7995 - \frac{0.0591}{2}\log\frac{1}{[Ag^+]^2}$$

$[Ag^+] = 10^{-9.8}$

$K_{sp} = [Ag^+]\,[Cl^-] = (10^{-9.8}) \times (1) = 10^{-9.8}$

70. (b) Nernst equation is

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

When E_{cell} drops to zero the concentration of ions will be equilibrium concentrations. We have for general cell reaction

$$aA + bB \rightleftharpoons cC + dD$$

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

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

[Since at equilibrium $E_{cell} = 0$]

$$E^o_{cell} = \frac{0.0591}{n}\log K_c \text{ at 298K.}$$

71. (a) Apply Nernst equation to the reaction

$Pb + Sn^{2+} \rightarrow Pb^{2+} + Sn$

$$\text{or } E^\circ + \frac{0.059}{2}\log\frac{[Sn^{2+}]}{[Pb^{2+}]} = E_{cell}$$

$$\text{or } \log\frac{[Sn^{2+}]}{[Pb^{2+}]} = \frac{0.01 \times 2}{0.059} = 0.3\ \ (\because E_{cell} = 0)$$

$$\text{or } \frac{[Sn^{2+}]}{[Pb^{2+}]} = \text{antilog } (0.3)$$

72. (d) For a concentration cell having different concentrations of ions.

$$E = \frac{0.0591}{n}\log\frac{c_1}{c_2}$$

If all the concentrations are identical then obviously the cell voltage is zero. But as the pH of 0.1 M HCl (strong acid) and pH of 0.1M CH_3COOH is (weak acid) not same, therefore the cell voltage is not zero.

73. (b) Electricity required = No. of g equiv. × 96500 coulombs

$= 0.5 \times 96500 = 48250$ C

74. (b) $\Delta G = -nE^\circ F$

For concentration cell, $E = \frac{RT}{nF}\ln\frac{C_2}{C_1}$

In it R, T, n and F are constant

So E is based upon $ln\,\frac{C_2}{C_1}$

$$\text{Now } \Delta G = -nEF = -nF \times \frac{RT}{nF}\ln C_2/C_1$$
$$= -RT\,ln\,C_2/C_1$$

At constant temperature ΔG is a function of $ln\ C_2/C_1$.

75. (d) This is because zinc has higher oxidation potential than Ni, Cu and Sn. The process of coating of iron surface with zinc is known as galvanization. Galvanized iron sheets maintain their lustre due to the formation of protective layer of basic zinc carbonate.

76. (b) $H^+ + e^- \longrightarrow \frac{1}{2}H_2;\ E_H = \frac{1}{2} \times 2 = 1;$

$$Cu^{2+} + 2e^- \longrightarrow Cu;\ E_{Cu} = \frac{63.5}{2} = 31.75$$

$$\frac{W_{Cu}}{E_{Cu}} = \frac{W_H}{E_H} \text{ or } W_{Cu} = \frac{0.504}{1} \times 31.75 = 16 \text{ g}$$

77. (b) Magnesium provides cathodic protection and prevent rusting or corrosion.

78. (b) In $H_2 - O_2$ fuel cell, the combustion of H_2 occurs to create potential difference between the two electrodes

79. (b) During charging, the lead storage battery behaves like an electrolytic cell. So, at anode the reaction is

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

80. (d) At cathodes : $Fe^+ + 2e^- \longrightarrow Fe;$

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

$$(E_{Fe})_1 = \frac{\text{At. wt.}}{2};\ (E_{Fe})_2 = \frac{\text{At. wt.}}{3}$$

Hence, $\frac{(E_{Fe})_1}{(E_{Fe})_2} = \frac{3}{2}$

81. (c) $2NH_4Cl + Zn \to 2NH_3 + ZnCl_2 + H_2 \uparrow.$

82. (d) $Pb + PbO_2 + 2H_2SO_4 \underset{\text{Recharge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O.$

Sulphuric acid is consumed on discharging.

83. (b) For spontaneous reaction E^0_{cell} must be positive.

$$Zn^{2+} \longrightarrow Zn;\ E^0 = -0.76V$$

$$Cu^{2+} \longrightarrow Cu;\ E^0 = -0.34V$$

Here Cu acts as cathode and zinc acts as anode.

$$E^\circ_{cell} = E^\circ_C - E^\circ_A = (-0.34) - (-0.76)$$
$$= 0.42 \text{ V.}$$

84. (b) Efficiency of a fuel cell $(\eta) = \frac{\Delta G}{\Delta H}$

85. (c) As $E^o_{cell} = \frac{0.0591}{n} \log K_c$

$$\therefore\ 0.46 = \frac{0.0591}{2} \log K_c$$

$$\therefore\ \log K_c = \frac{2 \times 0.46}{0.0591} = 15.57$$

or K_c = Antilog $15.57 = 3.7 \times 10^{15} \approx 4 \times 10^{15}$

86. (c) From the given data we find Fe^{3+} is strongest oxidising agent. More the positive value of E°, more is the tendency to get oxidized. Thus correct option is (c).

87. (d) Kohlrausch's Law states that at infinite dilution, each ion migrates independent of its co-ion and contributes to the total equivalent conductance of an electrolyte a definite share which depends only on its own nature. From this definition we can see that option (d) is the correct answer.

88. (c) Writing the equation for pentane-oxygen fuel cell at respective electrodes and overall reaction, we get

At Anode:

$$\underset{\text{(pentane)}}{C_5H_{12}} + 10H_2O \to 5CO_2 + 32H^+ + 32e^-$$

At Cathode:

$$8O_2 + 32H^+ + 32e^- \to 16H_2O$$
$$\text{Overall}: C_5H_{12} + 8O_2 \to 5CO_2 + 6H_2O$$

Calculation of $\Delta G°$ for the above reaction

$$\Delta G° = [5 \times (-394.4) + 6 \times (-237.2)] - [-8.2]$$
$$= -1972.0 - 1423.2 + 8.2 = -3387.0 \text{ kJ}$$
$$= -3387000 \text{ Joules.}$$

From the equation we find n = 32

Using the relation, $\Delta G° = -\ nFE^\circ_{cell}$ and substituting various values, we get

$$-3387000 = -32 \times 96500 \times E^\circ_{cell}\ (F = 96500C)$$

$$\text{or } E^\circ_{cell} = \frac{3387000}{32 \times 96500}$$

$$= \frac{3387000}{3088000} \text{ or } \frac{3387}{3088} V = 1.0968 V$$

Thus option (c) is correct answer.

89. (d) $Cu^{2+} + 2e^- \to Cu;$

$\Delta G^o = -nE^oF = -2 \times F \times 0.337 = -0.674 F$ ....(i)

$Cu^+ \to Cu^{2+} + e^-;$

$\Delta G^o = -nE^oF = -1 \times F \times -0.153 = 0.153 F$ ....(ii)

On adding eqn (i) & (ii)

$Cu^+ + e^- \to Cu;$

$\Delta G^o = -0.521 F = -nE^oF;$

Here n = 1 $\quad \therefore E^o = +0.52 V$

90. (a) $\because Q = i \times t$

$\therefore\ Q = 4.0 \times 10^4 \times 6 \times 60 \times 60 \text{ C} = 8.64 \times 10^8 \text{ C}$

$$Al^{3+} + \underset{3 \times 96500C}{3e^-} \longrightarrow \underset{27g}{Al}$$

[3 × 96500 C liberates = 27 g of Al]

∴ 96500 C liberates 9 g of Al

$$8.64 \times 10^8 \text{ C liberates} = \frac{9}{96500} \times 8.64 \times 10^8 \text{ g Al}$$
$$= 8.1 \times 10^4 \text{ g of Al}$$

91. (d) Degree of dissociation

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{8.0}{400} = 2 \times 10^{-2}$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \approx c\alpha^2 = \frac{1}{32} \times \left(2 \times 10^{-2}\right)^2 = 1.25 \times 10^{-5}$$

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

Here, $n = 2$, $E^\circ_{cell} = +0.46\,V$

$$\Delta G^\circ = -nE^\circ F = \frac{-2\times0.46\times96500}{1000}\,kJ \simeq -89\,kJ$$

93. (a) Dilution of strong electrolytes increases ionisation, hence ionic mobility of ions which in turn increases equivalent conductance of the solution.

94. (c) Conductivity of an electrolyte depends on the mobility of ions and concentration of ions. The motion of an ionic species in an electric field is retarded by the oppositely charged ions due to their interionic attraction. On dilution, concentration of electrolyte decreases and the retarding influence of oppositely charged ions decreases. Therefore mobility of ions increases.

95. (a) Option (ii) and (iv) are correct

96. (c) As the value of standard reduction potential decreases the reducing power increases i.e.,

$$\underset{(-3.0)}{Z} > \underset{(-1.2)}{X} > \underset{(+0.5)}{Y}$$

97. (b) $Cu^{2+} + 1e^- \rightarrow Cu^+ \quad E_1^o = 0.15V; \Delta G_1^o = -n_1E_1^oF$

$Cu^+ + 1e^- \rightarrow Cu \quad E_2^o = 0.50V; \Delta G_2^o = -n_2E_2^oF$

$Cu^{2+} + 2e^- \rightarrow Cu \qquad \Delta G^\circ = \Delta G^\circ{}_1 + \Delta G^\circ{}_2$

$-nE^\circ F = -1\, n_1\, E_1{}^o\, F + (-1)\, n_2\, E_2^oF$

$-nE^\circ F = -1\, (n_1\, E_1{}^o\, F + n_2\, E_2^oF)$

$$E^\circ = \frac{n_1E_1{}^o + n_2E_2^o}{n} = \frac{0.15\times1 + 0.50\times1}{2}$$

$E^\circ = 0.325\,V$

98. (b) Given $E_{Sn^{+4}/Sn^{+2}} = +0.15\,V$

$E_{Cr^{+3}/Cr} = -0.74\,V$

$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = 0.74 + 0.15 = 0.89\,V$

99. (d) Standard Gibbs free energy is given as $\Delta G^\circ = -nE^\circ F$

If $E^\circ_{cell} < 0$ i.e., – ve

$\Delta G^\circ > 0$

Further $\Delta G^\circ = -RT\ln K_{eq}$

$\therefore\ \Delta G^\circ > 0$ and $K_{eq} < 0$

100. (d) $\Lambda^\circ_{m(NH_4Cl)} = \Lambda^\circ_{m NH_4^+} + \Lambda^\circ_{m Cl^-}$

$\Lambda^\circ_{m(NaOH)} = \Lambda^\circ_{m Na^+} + \Lambda^\circ_{m OH^-}$

$\Lambda^\circ_{m(NaCl)} = \Lambda^\circ_{m Na^+} + \Lambda^\circ_{m Cl^-}$

$$\therefore\ \Lambda^\circ_{m\left(NH_4^+\right)} + \Lambda^\circ_{m\left(OH^-\right)}$$

$$= \Lambda^\circ_{m\left(NH_4^+\right)} + \Lambda^\circ_{m\left(Cl^-\right)} + \Lambda^\circ_{m\left(Na^+\right)} + \Lambda^\circ_{m\left(OH^-\right)} - \left[\Lambda^\circ_{m\left(Na^+\right)} + \Lambda^\circ_{m\left(Cl^-\right)}\right]$$

$$\Lambda^\circ_{m(NH_4OH)} = \Lambda^\circ_{m(NH_4Cl)} + \Lambda^\circ_{m(NaOH)} - \Lambda^\circ_{m(NaCl)}$$

EXERCISE - 2

1. (d) $\lambda_m^\infty(BaSO_4) = \lambda^\infty_{Ba^{2+}} + \lambda^\infty_{SO_4^{2-}}$

$= \lambda_m^\infty(BaCl_2) + \lambda_m^\infty(H_2SO_4)^- - 2\lambda^\infty_{(HCl)}$

$= x_1 + x_2 - 2x_3;\quad \lambda^\circ_e = \frac{1}{2}\lambda^\circ_m(BaSO_4)$

2. (a) Conductivity $(\kappa) = \frac{\ell}{R.a.}$

$\kappa = \frac{l}{R.a}$; cell constant. $\left(\frac{l}{a}\right) = 1.29\times100 = 129$

Again conductivity of 0.02M solution $\kappa = \frac{1}{520}\times129$

$$\Lambda_m = \frac{\kappa\times1000}{M} = \frac{129}{520}\times\frac{1000}{0.02} = 1.24\times10^{-4}\,S\,m^2mol^{-1}$$

3. (b) At Anode, $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$

Equivalent wt. of chlorine $(E_{Cl_2}) = \frac{35.5\times2}{2} = 35.5$

$$W_{Cl_2} = \frac{E_{Cl_2}\times I\times t}{96500} = \frac{35.5\times2\times30\times60}{96500} = 1.32\ gm.$$

4. (d)

5. (d) Charge on one mole of electrons = 96500 C

6. (a) By Faraday's I^st Law of electrolysis, $\frac{W}{E} = \frac{Q}{96500}$

(where Q = it = charge of ion)

We know that no. of gram equivalent

$$= \frac{W}{E} = \frac{it}{96500} = \frac{1\times965}{96500} = \frac{1}{100}$$

(where i = 1 A, $t = 16\times60+5 = 965$ sec.)

Since, we know that

$$\text{Normality} = \frac{\text{No. of gram equivalent}}{\text{Volume (in litre)}} = \frac{\frac{1}{100}}{1} = 0.01\,N$$

7. (b) In electrolysis of NaCl when Pt electrode is taken then H_2 liberated at cathode while with Hg cathode it forms sodium amalgam because more voltage is required to reduce H^+ at Hg than Pt.

8. (c) As per reaction in (c), reduction occurs at iodine electrode and oxidation at bromine electrode.

Hence, $E^\circ_{cell} = E^\circ_{I_2/I^-} - E^\circ_{Br_2/Br^-}$

$= 0.54 - 1.09 = -0.55V$

The negative cell potential suggests the non-spontaneity of the reaction. In other cases E_{cell} will be positive.

9. (b) $Sn^{4+} 2e^- \longrightarrow Sn^{2+}\quad E^\circ = 0.13V$

$Br_2 + 2e^- \longrightarrow 2Br^-\quad E^\circ = 1.08V$

E° value shows Br_2 has higher reduction potential. Hence

$E_{cell} = E_{Br_2/Br^-} - E_{Sn^{+4}/Sn^{+2}}$

$= 1.08 - 0.13 = 0.95\ V$

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

$n = 2, F = 96500.$

$-\Delta G = 2 \times 96500 \times 0.95\ kJ/mol.$

Also, $\Delta G = -2.303\,RT \log K_{eq}$

$$\log K_{eq} = -\frac{\Delta G}{2.303 \times R \times T} = \frac{-(-2 \times 96500 \times 0.95)}{2.303 \times 8.314 \times 298}$$

$= 32.13$

$K_{eq} = \text{antilog } 32.682 \approx 10^{32}$

10. (b) Cell reaction is, $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ell n \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Greater the factor $\left[\dfrac{(Zn^{2+})}{(Cu^{2+})}\right]$, less is the EMF

Hence $E_1 > E_2$

11. (b)

12. (b) It is the correct statement.

13. (b) $\Lambda^\circ_{Na^+} + \Lambda^\circ_{OH^-} = 248 \times 10^{-4} Sm^2mol^{-1}$

$\Lambda^\circ_{Na^+} + \Lambda^\circ_{Cl^-} = 126 \times 10^{-4} Sm^2mol^{-1}$

$\Lambda^\circ_{Ba^{2+}} + \Lambda^\circ_{2Cl^-} = 280 \times 10^{-4}\ S\ m^2mol^{-1}$

Now, $\Lambda^\circ_{Ba(OH)_2} = \Lambda^\circ_{BaCl_2} + 2\Lambda^\circ_{NaOH} - 2\Lambda^0_{NaCl}$

$\Lambda^\circ_{Ba(OH)_2} = 280 \times 10^{-4} + 2 \times 248 \times 10^{-4} - 2 \times 126 \times 10^{-4}$

$\Lambda^\circ_{Ba(OH)_2} = 524 \times 10^{-4} Sm^2mol^{-1}.$

14. (b) $\kappa = \frac{1}{R} \times \text{Cell constant}$

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

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

16. (b) For this cell, reaction is; $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

$$E = E^\circ - \frac{0.0591}{n}\log\frac{c_1}{c_2};\ E^\circ = E + \frac{0.0591}{n}\log\frac{c_1}{c_2}$$

$$= 0.2905 + \frac{0.0591}{2}\log\frac{10^{-2}}{10^{-3}} = 0.32\ V.$$

$$E^\circ = \frac{0.0591}{2}\log K_c;\ \log K_c = \frac{0.32 \times 2}{0.0591} = \frac{0.32}{0.0295}$$

$\therefore K_c = 10^{\frac{0.32}{0.0295}}.$

17. (b) 18. (c)

19. (a) An oxidising agent with a higher reduction potential will oxidise only reducing agent with a lower reduction potential.

20. (a) 27 gm of Al is obtained by charge of 3×96500 C.

$\because$ 1 gm of Al is obtained by charge of $3 \times \frac{96500}{27}$C.

$\therefore$ 5.12×10^3 gm of Al is obtained by charge of $3 \times \frac{96500}{27} \times 5.12 \times 1000 = 5.49 \times 10^7$C.

21. (b) $\Delta E = E^\circ - \frac{0.059}{2}\log[H^+]^2$

$= 1.30 - \frac{0.059}{2}\log(10^{-2})^2 = 1.418\ V$

22. (d) $E_{cell} = 0$; when cell is completely discharged.

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

$$\text{or } 0 = 1.1 - \frac{0.059}{2}\log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

$$\log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right) = \frac{2 \times 1.1}{0.059} = 37.3$$

$$\therefore \frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37.3}$$

23. (d) From the given representation of the cell, E_{cell} can be found as follows.

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

[Nernst -Equ.]

$$= -0.42 - (-0.72) - \frac{0.059}{6}\log\frac{(0.1)^2}{(0.01)^3}$$

$$= -0.42 + 0.72 - \frac{0.059}{6}\log\frac{0.1 \times 0.1}{0.01 \times 0.01 \times 0.01}$$

$$= 0.3 - \frac{0.059}{6}\log\frac{10^{-2}}{10^{-6}} = 0.3 - \frac{0.059}{6} \times 4$$

$= 0.30 - 0.0393 = 0.26\ V$

Hence option (d) is correct answer.

24. (c) $CH_3OH\,(l)+\frac{3}{2}O_2\,(g)\rightarrow CO_2\,(g)+2H_2O\,(l)$

$$\Delta G_r=[\Delta G_f(CO_2,g)+2\Delta G_f(H_2O,\ell)]-\left[\Delta G_f(CH_3OH,\ell)+\frac{3}{2}\Delta G_f(O_2,g)\right]$$

$$=-394.4+2\,(-237.2)-(-166.2)-0$$
$$=-394.4-474.4+166.2=-702.6\text{ kJ}$$

$$\%\text{ efficiency}=\frac{702.6}{726}\times100=97\%$$

25. (c) $\Delta G=-nFE$

For 1 mol of Al, n = 3

For $\frac{4}{3}$ mol of Al, $n=\frac{4}{3}\times3=4$

or $E=\dfrac{\Delta G}{-nF}=\dfrac{966\times10^3}{-4\times96500}=-2.5\text{ V}$

∴ The potential difference needed for the reduction =2.5 V.

26. (a) The value of $E^\circ_{M^{2+}/M}$ for given metal ions are

$E^\circ_{Mn^{2+}/Mn}=-1.18\text{ V}$,

$E^\circ_{Cr^{2+}/Cr}=-0.9\text{ V}$,

$E^\circ_{Fe^{2+}/Fe}=-0.44\text{ V}$ and

$E^\circ_{Co^{2+}/Co}=-0.28\text{ V}$.

The correct order of $E^\circ_{M^{2+}/M}$ values without considering negative sign would be

$Mn^{2+}>Cr^{2+}>Fe^{2+}>Co^{2+}$.

27. (c) $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

$$E=E^\circ-\frac{0.059}{1}\log\frac{[P(H_2)]^{1/2}}{[H^+]}$$

Now if $p_{H_2}=2$ atm and $[H^+]=1M$

then $E=0-\dfrac{0.059}{1}\log\dfrac{2^{1/2}}{1}=\dfrac{-0.059}{2}\log2$

28. (d) Here $n=4$, and $[H^+]=10^{-3}$ (as pH = 3)

Applying Nernst equation

$$E=E^\circ-\frac{0.059}{n}\log\frac{[Fe^{2+}]^2}{[H^+]^4(p_{O_2})}$$

$$=1.67-\frac{0.059}{4}\log\frac{(10^{-3})^2}{(10^{-3})^4\times0.1}$$

$$=1.67-\frac{0.059}{4}\log10^7=1.67-0.103=1.567$$

29. (a) $\kappa=\dfrac{1}{R}\times\dfrac{\ell}{A}$

$1.3=\dfrac{1}{50}\times\dfrac{\ell}{A}$

$\dfrac{\ell}{A}=65\text{ m}^{-1}$

$\Lambda=\dfrac{\kappa\times1000}{\text{molarity}}$

[molarity is in moles/litre but 1000 is used to convert liter into cm^3]

$$=\frac{\left(\frac{1}{260}\times65\text{ m}^{-1}\right)\times1000\text{ cm}^3}{0.4\text{ moles}}$$

$$=\frac{650\text{ m}^{-1}}{260\times4\text{ mol}}\times\frac{1}{1000}\text{ m}^3=6.25\times10^{-4}\text{ S m}^2\text{ mol}^{-1}$$

30. (d) For a spontaneous reaction ΔG must be –ve

Since $\Delta G=-nFE^\circ$

Hence for ΔG to be -ve ΔE° has to be positive. Which is possible when X = Zn, Y = Ni

$Zn+Ni^{++}\longrightarrow Zn^{++}+Ni$

$E^\circ_{Zn/Zn^{+2}}+E^\circ_{Ni^{2+}/Ni}=0.76+(-0.23)$

$=+0.53$

(positive)

31. (b) $H_2O \rightleftharpoons H^+ + OH^-$

$H^+ + e^- \longrightarrow \frac{1}{2}H_2$

∴ 0.5 mole of H_2 is liberated by 1 F = 96500 C

0.01 mole of H_2 will be liberated by

$=\dfrac{96500}{0.5}\times0.01\quad=1930\text{ C}$

$Q=I\times t$

$t=\dfrac{Q}{I}=\dfrac{1930\text{ C}}{10\times10^{-3}\text{ A}}=19.3\times10^4\text{ sec}$

32. (d) $AgNO_3(aq)+KCl(aq)\longrightarrow AgCl(s)+KNO_3(aq)$

Conductivity of the solution is almost compensated due to formation of $KNO_3(aq)$. However, after end point, conductivity increases more rapidly due to addition of excess $AgNO_3$ solution.

33. (d) Higher the value of standard reduction potential, stronger is the oxidising agent, hence MnO_4^- is the strongest oxidising agent.

34. (d) $E^\circ_{Cr^{3+}/Cr^{2+}}=-0.41\text{ V}$ $E^\circ_{Fe^{3+}/Fe^{2+}}=+0.77\text{ V}$

$E^\circ_{Mn^{3+}/Mn^{2+}}=+1.57\text{ V}$, $E^\circ_{Co^{3+}/Co^{2+}}=+1.97\text{ V}$

35. (c) Given $Fe^{+3}/Fe^{2+} = +0.77$ V

and $I_2/2I^- = 0.536V$

$$2\,(e^- + Fe^{+3} \longrightarrow Fe^{+2}) \qquad E^\circ = 0.77\,V$$

$$2I^- \longrightarrow I_2 + 2e^- \qquad E^\circ = -0.536\,V$$

$$2Fe^{+3} + 2I^- \longrightarrow 2Fe^{+2} + I_2$$

$E^\circ = E^\circ_{ox} + E^\circ_{red}$

$= 0.77 - 0.536$

$= 0.164\,V$

$\therefore$ Since value of E° is + ve reaction will take place.

36. (a) Higher the value of reduction potential higher will be the oxidising power whereas the lower the value of reduction potential higher will be the reducing power.

37. (d) $\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COONa} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$

$= 91 + 425.9 - 126.4 = 390.5\ S\,cm^2mol^{-1}$

38. (b) According to Kohlrausch's law, molar conductivity of weak electrolyte acetic acid (CH_3COOH) can be calculated as follows:

$$\Lambda^\circ_{CH_3COOH} = \left(\Lambda^\circ_{CH_3COONa} + \Lambda^\circ_{HCl}\right) - \Lambda^\circ_{NaCl}$$

$\therefore$ Value of Λ°_{NaCl} should also be known for calculating value of $\Lambda^\circ_{CH_3COOH}$.

39. (b) Given

$Fe^{3+} + 3e^- \rightarrow Fe,$

$E^\circ_{Fe^{3+}/Fe} = -0.036\,V$ ...(i)

$Fe^{2+} + 2e^- \rightarrow Fe,$

$E^\circ_{Fe^{2+}/Fe} = -0.439V$ ...(ii)

we have to calculate

$Fe^{3+} + e^- \rightarrow Fe^{2+},\ \Delta G = ?$

To obtain this equation subtract equ (ii) from (i) we get

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ ...(iii)

As we know that $\Delta G = -nFE$

Thus for reaction (iii)

$\Delta G = \Delta G_1 - \Delta G_2$

$-nFE^\circ = -nFE_1 - (-nFE_2)$

$-nFE^\circ = nFE_2 - nFE_1$

$-1FE^\circ = 2\times(-0.439) - 3\times(-0.036)$

$-1\,FE^\circ = -0.770\,F$

$\therefore\ E^\circ = +0.770V$

40. (d) $E_{red} = E^o_{red} + \dfrac{0.591}{n}\log[M^{n+}]$

Lower the concentration of M^{n+}, lower is the reduction potential.

Hence order of reduction potential is :

$Q > R > S > P$

41. (d) Electrolysis of both KCl and NaCl liberates H_2 at the cathode and Cl_2 at the anode. But the resulting solutions will be different.

42. (c) The oxidation states of X and Y are X^{3+} and Y^{2+}. Given atomic masses are in the ratio of 1 : 2

$$\because \text{Eq. mass} = \frac{\text{Atomic mass}}{\text{Oxidation state}}$$

$\therefore$ Equivalent masses are in the ratio

$$\frac{1}{3} : \frac{2}{2} \text{ or } \frac{1}{3} : 1 \text{ or } 1:3$$

43. (b) For $Zn^{2+} \rightarrow Zn$

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{2.303RT}{nF}\log\frac{[Zn]}{[Zn^{2+}]}$$

$$= -0.76 - \frac{0.06}{2}\log\frac{1}{[0.1]} = -0.76 - 0.03$$

$$E_{Zn^{2+}/Zn} = -0.79V$$

44. (d) Cell constant = *l/a*

Unit = $m/m^2 = m^{-1}$.

45. (d) Larger the size, lower the speed.

46. (d) $2H^+ + 2e^- \longrightarrow H_2$

$E_{cell} = 0.06\log[H^+] = 0.06 \times \log\sqrt{K_aC}$

$= 0.06 \times \log 10^{-3} = -0.18$ V

47. (b) Given I = 3.86 amp

t = 41 min 40 seconds = 2500 seconds

Mass deposited = ZIt

Where

$$Z = \frac{\text{Equivalent weight}}{96500}$$

Equivalent weight of Ca $= \dfrac{40}{2}\ (Ca^{2+} \rightarrow Ca) = 20$

$$Z = \frac{20}{96500} \times 3.86 \times 2500 = 2$$

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

49. (d) The specific conductivity decreases while equivalent and molar conductivities increase with dilution.

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

EXERCISE - 3

Exemplar Questions

1. (c) Standard electrode potential of copper electrode can be calculated by constructing a concentration cell composed of two half cell reactions in which concentration of species on left hand and right hand side are unity.

$$\underbrace{Pt(s)\,|\,H_2(g, 1\text{ bar})\,||\,H^+(aq., 1\text{ M})}_{\text{Oxidation half cell}}\,||\,\underbrace{Cu^{2+}(aq, 1\text{ M})\,|\,Cu}_{\text{Reduction half cell}}$$

2. Electrode potential for Mg electrode varies according to the equation :

$$E_{Mg^{2+}/Mg} = E^\circ_{Mg^{2+}/Mg} - \frac{0.059}{2}\log\frac{1}{[Mg^{2+}]}$$

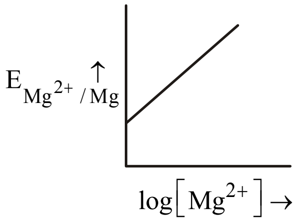
$$E_{Mg^{2+}/Mg} = E^\circ_{Mg^{2+}/Mg} + \frac{0.059}{2}\log\left[Mg^{2+}\right]$$

$$E_{Mg^{2+}/Mg} = \frac{0.059}{2}\log\left[Mg^{2+}\right] + E^\circ_{Mg^{2+}/Mg}$$

This equation represents equation of straight line.

Hence intercept (c) = $E^\circ_{Mg^{2+}/Mg}$ and slope = $\frac{0.059}{2}$

Thus, equation can be diagrammatically represented as:



3. (c) E_{cell} is an intensive property as it is independent of the mass of species but $\Delta_r G$ of cell reaction is an extensive property because this depends upon mass of species.
4. (b) Cell emf is the difference between the electrode potential of two electrodes when no current is drawn through the cell.
5. (d) Inert electrode does not participate in redox reaction and acts only as source or sink for electrons. It provides surface either for oxidation or for reduction reaction.
6. (c) If an external opposite potential is applied on the galvanic cell and increased slowly. It is observed that the reaction continues to take place till the opposing voltage reaches the value 1.1V. At this stage no current flow through the cell. Any further increase in the external potential restarts the reaction but in the opposite direction.

   Hence, now the cell will behave like an electrolytic cell.
7. (c) Greater the solvation of ions of an electrolyte lesser will be the electrical conductivity of the solution.
8. (b) Among the given options chromium has highest negative value of E° hence, it is the most strongest reducing agent.
9. (c) Higher the positive value of standard reduction potential of metal ion higher will be its oxidising capacity.

   Since, $E^\circ_{MnO_4^-/Mn^{2+}}$ has highest positive value hence it is the strongest oxidising agent.
10. (b) On moving down in electrochemical series reducing power decreases as the value of electrode potential decreases.
11. (d) $E^\circ_{MnO_4^-/Mn^{2+}}$ has highest positive value. So Mn^{2+} is most stable ion in its reduced form.
12. (d) $E^\circ_{Cr^{3+}/Cr}$ has the lowest value of SRP. Hence, Cr^{3+} is the most stable oxidised species.
13. (c) $Al^{3+}(aq) \xrightarrow{+3e} Al(s)$

    Hence, total 3F is required.
14. (d) Cell constant (G) = $\frac{l}{A}$

    where l = length of object and A = area of cross section Since, l and A remain constant for any particular object hence value of cell constant always remains constant.
15. (a) When the lead storage battery is recharged the reaction occurring on cell is reversed and $PbSO_4$ (s) on anode and cathode is converted into Pb and PbO_2 respectively

    The electrode reactions are as follows

    Anode reaction:

    $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$ (Reduction)

    Cathode reaction:

    $PbSO_4(s) + 2H_2O \rightarrow PbO_2(s) + SO_4^{2-} + 4H^+ + 2e^-$ (Oxidation)

    Net reaction:

    $2PbSO_4(s) + 2H_2O \rightarrow Pb(s) + PbO_2(s) + 4H^+(aq.) + 2SO_4^{2-}(aq.)$
16. (b) $\overset{\circ}{\Lambda}_{m(NH_4Cl)} = \overset{\circ}{\lambda}_{(NH_4^+)} + \overset{\circ}{\lambda}_{(Cl^-)}$ ...(i)

    $\overset{\circ}{\Lambda}_{m(NaOH)} = \overset{\circ}{\lambda}_{(Na^+)} + \overset{\circ}{\lambda}_{(OH^+)}$ ...(ii)

    $\overset{\circ}{\Lambda}_{m(NaCl)} = \overset{\circ}{\lambda}_{(Na^+)} + \overset{\circ}{\lambda}_{(Cl^-)}$ ...(iii)

    On adding (i) & (ii) and subtract (iii), we get :

    $\overset{\circ}{\Lambda}_{m(NH_4Cl)} + \overset{\circ}{\Lambda}_{m(NaOH)} - \overset{\circ}{\Lambda}_{m(NaCl)} = \overset{\circ}{\Lambda}_{m(NH_4OH)}$
17. (d) In the electrolysis of aqueous NaCl, following reactions are possible at anode.

    At anode; $Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-$;

    $\overset{\circ}{E}_{cell} = 1.36V$

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

    $\overset{\circ}{E}_{cell} = -1.23\ V$

    The reaction at anode with lower value of E° is preferred and therefore water should get oxidised in preference to $Cl^-_{(aq)}$. However on account of overpotential of oxygen reaction (d) is preferred.

NEET/AIPMT (2013-2017) Questions

18. (a) $H_2 \longrightarrow 2H^+ + 2e^-$

    1 atm 10^{-10}

    $$E_{H_2/H^+} = 0 - \frac{0.059}{2}\log\frac{\left(10^{-10}\right)^2}{1}$$

    $$E_{H_2/H^+} = +0.59\ V$$
19. (b) $\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{9.54}{238} = 0.04008 = 4.008\,\%.$

20. (d) $E°_{Cell} = E°_{OP} + E°_{RP}$

$= 0.76 + 0.314 = 1.10\,V$

21. (c) Applying,

$$w = Zit \;= \frac{Eit}{96500}$$

Equivalent weight of cobalt (II) = 59/2

I = 10 A

Time (t) = 109 min = 109 × 60 sec

Substituting these values we get,

$$w = \frac{59 \times 10 \times 109 \times 60}{2 \times 96500} = 20.0$$

22. (a) $\Delta E° = E^{\circ}_{red} + E^{\circ}_{oxd}$

$= -1.81 - 1.51 = -2.69$

Since $\Delta E°$ is negative

$\therefore \Delta G = -nFE°$, ΔG will have positive value so, forward reaction is not possible.

23. (c) $$\underset{0.1\text{ mole}}{\overset{(+6)}{Mn}O_4^{2-}} \longrightarrow \overset{(+7)}{MnO_4^-} + e^-$$

Quantity of electricity required = 0.1F

$= 0.1 \times 96500 = 9650\,C$

24. (d) $w_{O_2} = n_{O_2} \times 32$

$$w_{O_2} = \frac{5600}{22400} \times 32 = 8g \;= 1 \text{ equivalent of } O_2$$

= 1 equivalent of Ag = 108

25. (d) A device that converts energy of combustion of fuels, directly into electrical energy is known as fuel cell.

26. (b) HCl completely dissociates to give H^r and Cl^s ions, hence act as very good electrolyte. While others are non- electrolytes.

27. (a) $2H^+(aq) + 2e^- \rightarrow H_2(g)$

$$\therefore \; E = E^0 - \frac{0.0591}{2}\log\frac{P_{H_2}}{[H^+]^2}$$

$$0 = 0 - 0.0295 \log \frac{P_{H_2}}{(10^{-7})^2}$$

$$\frac{P_{H_2}}{(10^{-7})^2} = 1$$

$P_{H_2} = 10^{-14}$ atm

28. (c) Li^+ being smallest, has maximum charge density.

$\therefore$ Li^+ is most heavily hydrated among all alkali metal ions. Effective size of Li^+ in aqueous solution is therefore, largest. So, moves slowest under electric field.

29. (b) For cell,

$Zn|ZnSO_4(0.01\,M)\,||\,CuSO_4(1.0\,M)|Cu$

$$E_{cell} = E°_{cell} - \frac{2.303RT}{nF}\frac{\log[Zn^{2+}]}{[Cu^{2+}]}$$

$$\therefore \; E_1 = E°_{cell} - \frac{2.303RT}{2 \times F} \times \log\frac{(0.01)}{1}$$

When concentrations are changed for $ZnSO_4$ and $CuSO_4$, we can write

$$E_2 = E°_{cell} - \frac{2.303RT}{2F} \times \log\frac{1}{0.01}$$

$\therefore \; E_1 > E_2$