PROBLEM-SOLVING TACTICS

(a) Related to electrolysis: Electrolysis comprises of passing an electric current through either a molten salt or an ionic solution. Thus the ions are "forced" to undergo either oxidation (at the anode) or reduction (at the cathode). Most electrolysis problems are really stoichiometry problems with the addition of some amount of electric current. The quantities of substances produced or consumed by the electrolysis process is dependent upon the following:

(i) Electric current measured in amperes or amps

(ii) Time measured in seconds

(iii) The number of electrons required to produce or consume 1 mole of the substance

(b) To calculate amps, time, coulombs, faradays and moles of electrons:

Three equations related these quantities:

(i) Amperes × time = Coulombs

(ii) 96,485 coulombs = 1 Faraday

(iii) 1 Faraday = 1 mole of electrons

The through process for interconverting amperes and moles of electrons is:

Amps and time $\longleftrightarrow$ Coulombs $\longleftrightarrow$ Faradays $\longleftrightarrow$ Moles of electrons

Use of these equations are illustrated in the following sections.

(c) To calculate the quantity of substance produced or consumed: To determine the quantity of substance either produced or consumed during electrolysis, given the time a known current flowed:

(i) Write the balanced half-reactions involved.

(ii) Calculate the number of moles of electrons that were transferred.

(iii) Calculate the number of moles of substance that was produced/consumed at the electrode.

(iv) Convert the moles of substance to desired units of measure.

(d) Determination of standard cell potentials: A cell's standard state potential is the potential of the cell under standard state conditions, and it is approximated with concentrations of 1 mole per liter (1 M) and pressures of 1 atmosphere at 25°C.

(i) To calculate the standard cell potential for a reaction.

(ii) Write the oxidation and reduction half-reactions for the cell.

(iii) Look up the reduction potential, $E^\circ_{reduction,}$ for the reduction half-reaction in a table of reduction potentials.

(iv) Look up the reduction potential for the reverse of the oxidation half-reaction and reverse the sign to obtain the oxidation potential. For the oxidation half-reaction, $E^\circ_{oxidation} = -E^\circ_{reduction}$.

(v) Add the potentials of the half-cells to get the overall standard cell potential.

$$E^\circ_{cell} = -E^\circ_{reduction} + E^\circ_{oxidation}$$

(e) For determining non-standard state cell potentials: To determine the cell potential when the conditions are other than standard state (concentrations not 1 molar and/or pressures not 1 atmosphere):

(i) Determine the standard state cell potential.

(ii) Determine the new cell potential resulting from the changed conditions.

(iii) Determine Q, the reaction quotient.

(iv) Determine n, the number of electrons transferred in the reaction "n".

(v) Determine E_{cell}, the cell potential at the non-standard state conditions using the Nernst equation.

$$E_{cell} = E^{\circ}_{cell} - (RT/nF)\ln Q$$

E_{cell} = cell potential at non-standard state conditions; E°_{cell} = standard state cell potential

R = constant (8.31 J/mole K); T = absolute temperature (Kelvin scale)

F = Faraday's constant (96,485 C/mole e^-)

n = Number of moles of electrons transferred in the balanced equation for the reaction occurring in the cell;

Q = Reaction quotient for the reaction. $aA + bB \rightarrow cC + dD$, $Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

If the temperature of the cell remains at 25°C, the equation simplifies to:

$E_{cell} = E^{\circ}_{cell} - (0.0257/n)\ln Q$ or in terms of $\log_{10}$; $E_{cell} = E^{\circ}_{cell} - (0.0592/n)\log Q$

POINTS TO REMEMBER

S.No.		Description
1	Electrolyte	Any substance which dissolves in water to form a solution that will conduct an electric current (ionic substances).Electrolytes may be classified as strong (NaCl, HCl, NaOH) or weak (NH_4OH, CH_3COOH, HF). Solutions that do not conduct electricity at all are called non-electrolytes.
2	Strong and Weak Electrolytes	**Strong electrolyte** - Solutions in which the substance dissolved (solute) is present entirely as ions. **Weak electrolyte** - A solute that yields a relatively low concentration of ions in solution.
3	Dissociation	The separation of ions that occurs when an ionic substance dissolves: $CaCl_2(s) + H_2O \rightarrow Ca^{+2}(aq) + 2Cl^-(aq)$.
4	Electrochemical Cells	A system of electrodes and electrolytes in which a spontaneous or non-spontaneous redox reaction occurs.
5	Components of Electrochemical cells	a. Electrode: An electrical conductor (metal strip) used to establish contact with a non-metallic part of the circuit (usually an electrolyte). b. Anode: The electrode at which oxidation occurs. c. Cathode: The electrode at which reduction occurs. d. Electrolyte: A liquid, paste, or gel that serves to conduct charge by moving ions in the cell. e. Half-cell: A single electrode immersed in a solution of its ions. f. Salt bridge: A device (porous disk or bridge i.e. U-tube containing inert electrolytic solution, KCl, NH_4NO_3, etc.) placed between the cells which maintains electrical neutrality by allowing ions to migrate between the cells. g. External circuit: The part of the cell where charge is conducted as a current of moving electrons. h. Standard Electrode Reduction Potential E°: The measurement, in volts, of the tendency for a half reaction to occur as a reduction half reaction.

S.No.		Description
6	Voltaic/Galvanic Cells	Redox reactions are spontaneous and chemical energy is transformed into electrical energy. The cell potential $E°$ is positive and the anode is the negative electrode. i.e. batteries $Zn(s) \mid Zn^{+2}(1M) \mid\mid Cu^{+2}(1M) \mid Cu(s)$ anode $\mid\mid$ cathode
7	Electrolytic Cells	Cell in which an external electric current is required to drive a non-spontaneous redox reaction. The cell potential ($E°$) is negative and the anode is the positive electrode. i.e. electrolysis, electroplating, etc. $Cu(s) \mid Cu^{+2}(1M) \mid\mid Cu^{+2}(1M) \mid Cu(s)$ anode $\mid\mid$ cathode

8	Quick Comparison of Electrolytic Cells		**Galvanic/Voltaic**	**Electrolytic**
		Type of redox reaction cell potential ($E°_{cell}$) Electron flow	Spontaneous	Non-spontaneous
			($E°_{cell}$ is positive)	($E°_{cell}$ is negative)
		Site of oxidation	Creates one	Requires one
		Site of reduction	Anode	Anode
		Positive electrode	Cathode	Cathode
		Negative electrode	Cathode	Anode
		Flow of electrons	Anode	Cathode
			Anode to cathode	Anode to cathode
			(negative to positive)	(positive to negative)
			Batteries	Electrolysis, electroplating

9	Faraday's First law of Electrolysis	The amount of electrolyte discharged at an electrode is directly proportional to the quantity of electricity passed: $\quad W \propto Q \qquad$ where, $= I. t$ $\quad I$ = Current strength in ampere $\quad T$ = time in seconds $\Rightarrow \quad W = ZQ = Zit$ $\quad Z$ is a constant called electrochemical equivalence (ECE)
10	Electrochemical Equivalent	It is the amount of an electrolyte discharged on passing one coulomb of electricity.
11	Faraday's Constant	It is the charge possessed by 1.0 mole of electrons and it is equal to 96500 coulombs (approx.). In terms of faraday's constant the number of gram equivalent of electrolyte discharged at an electrode is equal to the number of faraday's passed. $\Rightarrow \quad W = E \left(\dfrac{Q}{96500} \right)$ where, E = Equivalent weight
12	Faraday's Second Law	**Second Law:** If same quantity of electricity is passed through different cells connected in series, same number of gram equivalent of electrolytes are discharged at each of the electrodes: $\Rightarrow \qquad \dfrac{W_1}{W_2} = \dfrac{E_1}{E_2}$ Where, W_1 and W_2 are the weights of electrolytes discharged at two different electrodes in two different cells connected in series and E_1 and E_2 are their respective equivalent weights.

S.No.		Description
13	Nernst Equation	$E_{half-cell} = E^{\circ}_{half-cell} - \dfrac{2.303\ RT}{nF} \log \dfrac{[Reduced\ form]}{[Oxidised\ form]}$ At 298 K, the Nernst equation can be written as, $E_{half-cell} = E^{\circ}_{half-cell} - \dfrac{0.0591}{n} \log \dfrac{[Reduced\ form]}{[Oxidised\ form]}$

Solved Examples

JEE Main/Boards

Example 1: Zn and iron can replace Cu in a solution but Pt and Au cannot. Why?

Sol: Both Zn and iron have more E°_{OP} than Cu, whereas Pt and Au have less E°_{OP}

Example 2: Which of the following metals cannot be obtained by the electrolysis of their aqueous salt solution and why?

Al,   Na,   Cu,   Ag.

Sol: Al and Na cannot be obtained because they have higher E°_{OP} than H and thus, reduction of Cu^{2+} and Ag^{+} will give Cu and Ag.

Example 3: Calculate the no. of electron lost or gained during electrolysis of 2 g Cl^- from NaCl (aq) to give Cl_2 at anode.

Sol: First calculate the equivalent of Cl^- used during the reaction and on multiplying it with avogadro number will give us the no of electron lost during the reaction

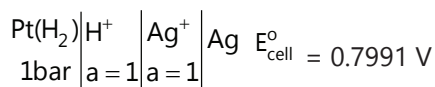$\because \quad 2Cl^- \rightarrow Cl_2 + 2e^-$
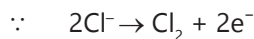
Eq. of Cl^- used = 2/35.5

$\because$ 1 eq. of an element involves 1 faraday charge or N electrons

$\therefore$ (2/35.5) eq. of an element involves

$= \dfrac{N \times 2}{35.5}$ electrons $= \dfrac{6.023 \times 10^{23} \times 2}{35.5}$

$= 3.4 \times 10^{22}$ electrons

Example 4: Evaluate the $E^{\circ}_{Ag^+/Ag}$ and $E^{\circ}_{Zn^{2+}/Zn}$ from the given values:

$$\begin{array}{c|c|c} Pt(H_2) & H^+ & Ag^+ \\ 1bar & a=1 & a=1 \end{array} Ag \quad E^o_{cell} = 0.7991\ V$$

Sol: Since platinum electrode has zero reduction potential the standard electrode potential will be equal to the standard electrode potential of the cell.

$E^{\circ}_{cell} = E^{\circ}_{OP_{H/H^+}} + E^{\circ}_{RP_{Ag^+/Ag}}$

Or $0.7991 = 0 + E^{\circ}_{RP_{Ag^+/Ag}}$ $\therefore E^{\circ}_{RP_{Ag^+/Ag}} = 0.7991\ V$

Example 5: Standard reduction potential of the Ag^+/Ag electrode at 298 K is 0.799 V. Given that for AgI, $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of I^- / AgI/Ag electrode.

Sol: Here solubility product is given from this calculate the concentration of silver ions. Now substituting this value in Nernst equation determine $E_{Ag^+/Ag}$

As we have found out $E_{Ag^+/Ag}$, $E^{\circ}_{I/AgI/Ag}$ can find out by using the value of solubility product.

$E_{Ag^+/Ag} = E^{\circ}_{Ag^+/Ag} + (0.059/1) \log [Ag^+]$ ... (i)

Also, $K_{sp_{AgI}} = [Ag^+][I^-]$

$\because [Ag]^+ = [I^-]$ (for a saturated solution)

$\therefore [Ag^+] = \sqrt{(K_{sp_{AgI}})} = \sqrt{(8.7 \times 10^{-17})}$

$= 9.32 \times 10^{-19}$ ... (ii)

$\therefore$ By Eq. (i),