

Crash Course for NEET 2020

KEY NOTES ON ELECTROCHEMISTRY

Biomentors Classes Online, Mumbai

NCERT Based - Very Important Points

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Electrochemistry :

It is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Differences between electrochemical cell and electrolytic cell :

Electrochemical cell (Galvanic or Voltaic cell)	Electrolytic cell
1. It is a device which converts chemical energy into electrical energy.	1. It is a device which converts electrical energy into chemical energy.
2. It is based upon the redox reaction which is spontaneous. <i>i.e.</i> , $\Delta G = -ve$	2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied. <i>i.e.</i> , $\Delta G = +ve$
3. Two electrodes are usually set up in two separate beakers.	3. Both the electrodes are suspended in the solution or melt of the electrolyte in the same beaker.
4. The electrolytes taken in the two beakers are different.	4. Only one electrolyte is taken.
5. The electrodes taken are of different materials.	5. The electrodes taken may be of the same or different materials.
6. The electrode on which oxidation takes place is called the <i>anode</i> (or -ve pole) and the electrode on which reduction takes place is called the <i>cathode</i> (or +ve pole)	6. The electrode which is connected to the -ve terminal of the battery is called the <i>cathode</i> ; the cations migrate to it which gain electrons and hence, a reduction takes place, the other electrode is called the <i>anode</i> .

- Faraday's first law of electrolysis :** The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

$$w \propto Q \text{ or } w = ZQ = Z \times I \times t$$

Where Z is the electrochemical equivalent of the substance deposited and

$$Z = \frac{\text{Eq.Wt of Substance}}{96500}$$

- Faraday's second law :** It states that,

"When the same quantity of electricity is passed through different electrolytes, the masses of different ions liberated at the electrodes are directly proportional to their chemical equivalents (Equivalent weights)." *i.e.*,

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \text{ or } \frac{Z_1 It}{Z_2 It} = \frac{E_1}{E_2} \text{ or } \frac{Z_1}{Z_2} = \frac{E_1}{E_2} \quad (\because W = ZIt)$$

Thus the electrochemical equivalent (Z) of an element is directly proportional to its equivalent weight (E), i.e.,

$$E \propto Z \text{ or } E = FZ \text{ or } E = 96500 \times Z$$

where, F = Faraday constant = 96500 C mol^{-1}

So, 1 Faraday = $1F$ = Electrical charge carried out by one mole of electrons.

$1F$ = Charge on an electron \times Avogadro's number.

$$1F = e^- \times N = (1.602 \times 10^{-19} \text{ C}) \times (6.023 \times 10^{23} \text{ mol}^{-1}).$$

$$\text{Number of Faraday} = \frac{\text{Number of electrons passed}}{6.023 \times 10^{23}}$$

Conductance in electrolytic solutions :

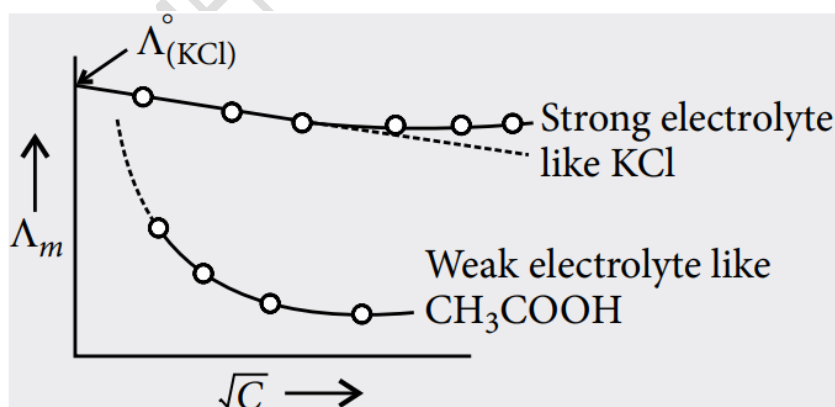
Property	Formula	Units	Effect of dilution
Conductance (G)	$\frac{1}{R} = \frac{a}{\rho l} = \frac{\kappa a}{l}$	$\text{Ohm}^{-1} (\Omega^{-1})/\text{Siemens (S)}$	Increases as larger number of ions are produced.
Specific conductance (κ) or conductivity	$\frac{1}{\rho}$ or $G \frac{l}{a}$	$\text{Ohm}^{-1} \text{ cm}^{-1}/\text{S m}^{-1}$	Decreases as number of ions per cm^3 decreases.
Equivalent conductivity (Λ_{eq})	$\kappa \times V$ or $\kappa \times \frac{1000}{N}$	$\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}/\text{S m}^2 \text{ eq}^{-1}$	Increases with dilution due to large increase in V .
Molar conductivity (Λ_m)	$\kappa \times V$ or $\kappa \times \frac{1000}{M}$	$\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}/\text{S m}^2 \text{ mol}^{-1}$	Increases with dilution due to large increase in V .

Limiting molar conductivity

When concentration approaches zero i.e. ; at infinite dilution, the molar conductivity is known as limiting molar conductivity (Λ_m°).

Variation of molar conductivity with concentration :

For a strong electrolyte it is shown by DebyeHuckel Onsager equation as follows : $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$



Here, Λ_m° = Molar conductivity at infinite dilution (Limiting molar conductivity)

Λ_m = Molar conductivity at V -dilution

A = Constant which depends upon nature of solvent and temperature

C = Concentration

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$$

Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to Λ_m° and slope equal to $-A$.

Thus, Λ_m decreases linearly with \sqrt{C} , when $C = 0$, $\Lambda_m = \Lambda_m^\circ$ and Λ_m° can be determined experimentally.

For weak electrolytes :

There is a very large increase in conductance with dilution especially near infinite dilution as no. of ions increases. Λ_m increases as C decreases but does not reach a constant value even at infinite dilution. Hence, their Λ_m cannot be determined experimentally

For a strong electrolyte :

There is only a small increase in conductance with dilution. This is because a strong electrolyte is completely dissociated in solution and so, the number of ions remain constant and on dilution, interionic attractions decreases as ions move far apart.

Kohlrausch's law of independent migration of ions :

It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

$\Lambda_m^\circ = v_+\lambda_+^\circ + v_-\lambda_-^\circ$ where λ_+° and λ_-° are the limiting molar conductivities of the cation and anion respectively and v_+ and v_- are stoichiometric number of cations and anions respectively in one formula unit of the electrolyte.

Applications of Kohlrausch's law

(i) **Determination of Λ_m° for weak electrolytes** : The molar conductivity of a weak electrolyte at infinite dilution (Λ_m°) cannot be determined by extrapolation method. However, Λ_m° values for weak electrolytes can be determined by using the Kohlrausch's equation.

$$\Lambda_{CH_3COOH}^\circ = \Lambda_{CH_3COONa}^\circ + \Lambda_{HCl}^\circ - \Lambda_{NaCl}^\circ$$

(ii) **Determination of the degree of ionisation of a weak electrolyte** :

If λ_m^c is the molar conductivity of a weak electrolyte at any concentration C and, λ_m° is the molar conductivity of a electrolyte at infinite dilution. Then, the degree of ionisation is given by,

$$\alpha_c = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{\Lambda_m^c}{(v_+\lambda_+^\circ + v_-\lambda_-^\circ)}$$

Thus, knowing the value of Λ_m^c , and Λ_m° (From the Kohlrausch's equation), the degree of ionisation at any concentration (α_c) can be determined.

(iii) **Determination of the ionisation constant of a weak electrolyte** :

for a weak electrolyte AB , the ionisation equilibrium is, $AB \rightleftharpoons A^+ + B^-$; If C is the initial concentration of the electrolyte AB in solution, then the equilibrium concentrations of various species in the solution are, $[AB] = C(1 - \alpha)$, $[A^+] = C\alpha$ and $[B^-] = C\alpha$

Then, the ionisation constant of AB is given by, $K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)}$

We know, that at any concentration C , the degree of ionisation (α) is given by, $\alpha = \Lambda_m^c / \Lambda_m^\infty$

Then, $K = \frac{C(\Lambda_m^c / \Lambda_m^\infty)^2}{[1 - (\Lambda_m^c / \Lambda_m^\infty)]} = \frac{C(\Lambda_m^c)^2}{\Lambda_m^\infty (\Lambda_m^\infty - \Lambda_m^c)}$; Thus, knowing Λ_m^∞ and Λ_m^c at any concentration, the

ionisation constant (K) of the electrolyte can be determined.

(iv) **Determination of the solubility of a sparingly soluble salt :**

the molar conductivity of a sparingly soluble salt at infinite dilution (Λ_m^∞) can be obtained from the relationship,

$$\Lambda_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty \quad \dots\dots(i)$$

The conductivity of the saturated solution of the sparingly soluble salt is measured. From this, the conductivity of the salt (κ_{salt}) can be obtained by using the relationship, $\kappa_{\text{salt}} = \kappa_{\text{sol}} - \kappa_{\text{water}}$, where, κ_{water} is the conductivity of the water used in the preparation of the saturated solution of the salt.

$$\Lambda_{\text{salt}}^\infty = \frac{1000 \kappa_{\text{salt}}}{C_m} \quad \dots\dots(ii)$$

From equation (i) and (ii) ;

$$C_m = \frac{1000 \kappa_{\text{salt}}}{(\nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty)}, \quad C_m \text{ is the molar concentration of the sparingly soluble salt in its saturated}$$

solution. Thus, C_m is equal to the solubility of the sparingly soluble salt in the *mole per litre* units.

The solubility of the salt in *gram per litre* units can be obtained by multiplying C_m with the molar mass of the salt.

Types of cells

Dry cell, lead accumulator and fuel cells

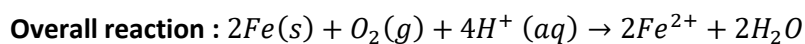
	Dry cell	Lead storage battery	Fuel cell
Anode	Zinc	Lead	Porous carbon containing catalysts (H ₂ passed)
Cathode	Graphite	Lead dioxide	Porous carbon containing catalysts (O ₂ passed)
Electrolyte	MnO ₂ + C (touching cathode) NH ₄ Cl + ZnCl ₂ (touching anode)	H ₂ SO ₄ (38%)	Conc. aqueous KOH
Anode reaction	Zn _(s) → Zn ²⁺ _(aq) + 2e ⁻	Pb _(s) + SO ₄ ²⁻ _(aq) → PbSO _{4(s)} + 2e ⁻	H _{2(g)} + 2OH ⁻ _(aq) → 2H ₂ O _(l) + 2e ⁻
Cathode reaction	MnO _{2(s)} + NH ₄ ⁺ _(aq) + e ⁻ → MnO(OH) _(s) + NH _{3(g)}	PbO _{2(s)} + SO ₄ ²⁻ _(aq) + 4H ⁺ + 2e ⁻ → PbSO _{4(s)} + 2H ₂ O _(l)	O _{2(g)} + 2H ₂ O _(l) + 4e ⁻ → 4OH ⁻ _(aq)

Corrosion : The slow eating away of metals when exposed to the atmosphere is called corrosion.

Corrosion of iron (Rusting) : It is an electrochemical phenomenon which occurs in the presence of moisture and oxygen.

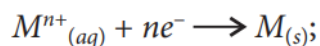
At anode: $2Fe(s) \rightarrow 2Fe^{2+}(aq) + 4e^-$

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



Method used for prevention of corrosion : Barrier protection, sacrificial protection, anti-rust solutions

Nernst equation for reduction reaction



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}_{(aq)}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}_{(aq)}]}$$

Product of electrolysis of various electrolytes

Electrolyte	Products		Reactions involved	
	At cathode	At anode	At cathode	At anode
Molten NaCl	Na metal	Cl ₂ gas	$Na^+_{(l)} + e^- \longrightarrow Na_{(l)}$	$Cl^-_{(l)} \longrightarrow \frac{1}{2} Cl_{2(g)} + e^-$
Aqueous NaCl	H ₂ gas	Cl ₂ gas	$H_2O_{(l)} + e^- \longrightarrow \frac{1}{2} H_{2(g)} + OH^-_{(aq)}$	$Cl^-_{(aq)} \longrightarrow \frac{1}{2} Cl_{2(g)} + e^-$
Dil. H ₂ SO ₄	H ₂ gas	O ₂ gas	$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2} H_{2(g)}$	$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$
Conc. H ₂ SO ₄	H ₂ gas	S ₂ O ₈ ²⁻	$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2} H_{2(g)}$	$2SO_4^{2-}_{(aq)} \longrightarrow S_2O_8^{2-}_{(aq)} + 2e^-$

Types of commercial cells : There are mainly two types of commercial cells,

Primary cells : In these cells, the electrode reactions cannot be reversed by an external electric energy source. In these cells, reactions occur only once and after use they become dead. Therefore, they are **not chargeable**. Some common example are, dry cell, mercury cell, Daniell cell and alkaline dry cell

(i) **Voltaic cell**

Cathode : Cu rod

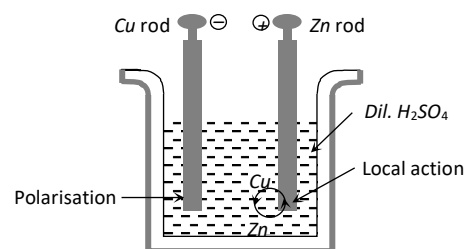
Anode : Zn rod

Electrolyte : dil. H₂SO₄ **Emf :** 1.08 V

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

At Anode : $Zn \rightarrow Zn^{2+} + 2e^-$

Over all reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$



(ii) Daniel cell

Cathode : Cu rod

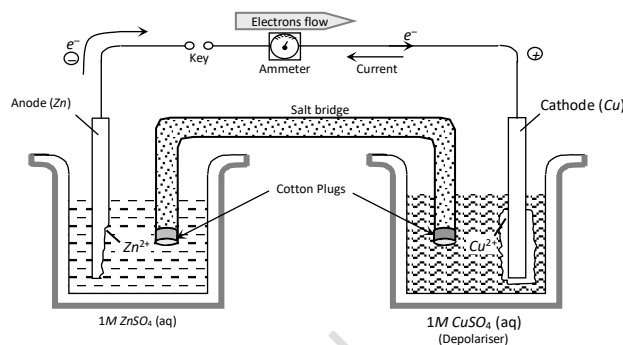
Anode : Zn rod

Electrolyte : dil. H_2SO_4 **Emf** : 1.1 V

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

At Anode : $Zn \rightarrow Zn^{2+} + 2e^-$

Over all reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$



(iii) Leclanche cell (Dry cell)

Cathode : Graphite rod

Anode : Zn pot

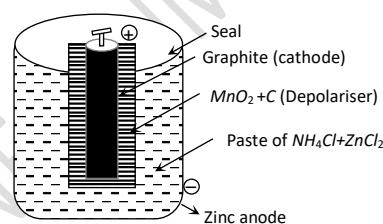
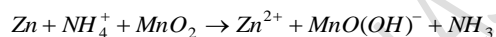
Electrolyte : Paste of $NH_4Cl + ZnCl_2$ in starch

Emf : 1.2 V to 1.5 V

At cathode : $NH_4^+ + MnO_2 + 2e^- \rightarrow MnO(OH)^- + NH_3$

At Anode : $Zn \rightarrow Zn^{2+} + 2e^-$

Over all reaction :



(iv) Mercury cell

Cathode : Mercury (II) oxide

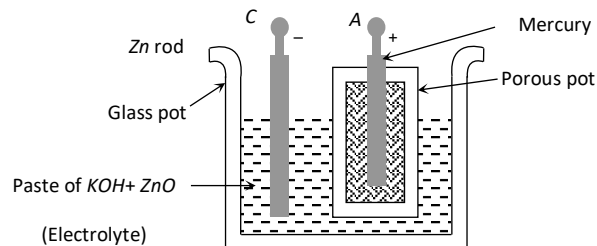
Anode : Zn rod

Electrolyte : Paste of $KOH + ZnO$ **Emf** : 1.35 V

At cathode : $HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH_{(aq)}^-$

At Anode : $Zn_{(s)} + 20H_{(aq)}^- \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$
(amalgam)

Over all reaction : $Zn_{(s)} + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$



(2) **Secondary cells** : In the secondary cells, the reactions can be reversed by an external electrical energy source. Therefore, these cells can be **recharged** by passing electric current and used again and again. These are also called **storage cells**. Examples of secondary cells are, lead storage battery and nickel – cadmium storage cell.

n charged	Lead storage cell	Alkali cell
	<p>Glass vessel PbO₂ Pb dil. H₂SO₄</p>	<p>Ni(OH)₂ Fe(OH)₂ Perforated steel grid KOH 20% + LiOH 1%</p>
Positive electrode	Perforated lead plates coated with PbO ₂	Perforated steel plate coated with Ni(OH) ₂
Negative electrode	Perforated lead plates coated with pure lead	Perforated steel plate coated with Fe
Electrolyte	dil. H ₂ SO ₄	20% solution of KOH + 1% LiOH
During charging	<p>Chemical reaction At anode : PbSO₄ + 2H⁺ + 2e⁻ → Pb + H₂SO₄ At cathode : PbSO₄ + SO₄²⁻ + 2H₂O - 2e⁻ → PbO₂ + 2H₂SO₄</p> <p>Specific gravity of H₂SO₄ increases and when specific gravity becomes 1.25 the cell is fully charged. Emf of cell: When cell is fully charged then E = 2.2 volt</p>	<p>Chemical reaction At anode : Ni(OH)₂ + 2OH⁻ - 2e⁻ → Ni(OH)₄ At cathode : Fe(OH)₂ + 2K⁺ + 2e⁻ → Fe + 2KOH Emf of cell : When cell is fully charged then E = 1.36 volt</p>
During discharging	<p>Chemical reaction At anode : Pb + SO₄²⁻ - 2e⁻ → PbSO₄ At cathode : PbO₂ + 2H⁺ + 2e⁻ + H₂SO₄ → PbSO₄ + 2H₂O</p> <p>Specific gravity of H₂SO₄ decreases and when specific gravity falls below 1.18 the cell requires recharging. Emf of cell : When emf of cell falls below 1.9 volt the cell requires recharging.</p>	<p>Chemical reaction At anode : Fe + 2OH⁻ - 2e⁻ → Fe(OH)₂ At cathode : Ni(OH)₄ + 2K⁺ + 2e⁻ → Ni(OH)₂ + 2KOH</p> <p>Emf of cell : When emf of cell falls below 1.1 V it requires charging.</p>
Efficiency	80%	60%

Fuel cells

These are Voltaic cells in which the reactants are continuously supplied to the electrodes. These are designed to convert the energy from the combustion of fuels such as H₂, CO, CH₄, etc. directly into electrical energy. The common example is **hydrogen-oxygen fuel cell** as described below,

In this cell, The reactions are

