Electrochemistry

General Introduction Redox reactions



Oxidation and reduction

	Property	Oxidation	Reduction
1	Hydrogen	Loss	Gain
2	Oxygen	Gain	Loss
3	Electron	Loss	Gain
4	Oxidation No.	Increase	Decrease

	Oxidising agent or oxidant	Reducing agent or reductant
1	Under goes reduction	Undergoes oxidation
2	Gain electrons	Donates electrons
3	Oxidation no. of its atoms increases	Oxidation no. of its atoms decreases

For example, consider the reaction

 $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

Or $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ (i) Zn is oxidized on Zn²⁺ ions while Cu²⁺ has been

reduced to Cu.

Similarly in the reaction

 $Cu(s) + 2 AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2 Ag(s)$ Or $Cu(s) + 2 Ag^+ \rightarrow Cu^{2+}(aq) + 2 Ag(s)$ (ii) Cu has been oxidized to Cu²⁺ ions while Ag+ has been reduced to Ag.

Concept Ladder



Displacement reactions and can't be redox reactions. Single displacement reactions are redox reactions where as double displacement reactions are not redox reactions.

Again in the reaction

 $Zn(s) + H_2 SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$

 $Or \qquad Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_{2}(g) \quad \dots \quad (iii)$

Zn has been oxidized to Zn^{2+} whereas H^+ ions have been reduced to H_{a} gas.

The substance which gets reduced oxidizes the other substance and is called **oxidizing agent** or **oxidant** while the substance which gets oxidized reduces the other substance and is called **reducing agent** or **reductant**. Thus, oxidizing agent is a substance which gains electrons while reducing agent is a substance which loses electrons.

Redox reaction is defined as the reaction which is considered to be made up of two half reactions, one involving oxidation, i.e. loss of electrons and the other involving reduction, i.e., gain of electrons. These are known as **oxidation half-reaction** and **reduction half-reaction**. For example, the reaction (i) may be split into two half reactions as under:

 $Zn \longrightarrow Zn^{2^{+}} + 2e^{-} (oxidation half-reaction)$ $Cu^{2^{+}} + 2e^{-} \longrightarrow Cu (Reduction half-reaction)$ $Zn + Cu^{2^{+}} \longrightarrow Zn^{2^{+}} + Cu$

Electrochemistry

Electrochemistry is defined as the branch of physical chemistry, which deals with the study of conversion of electrical energy from chemical energy which is produced in a redox reaction or how to get redox reaction by using electrical energy, which is otherwise non-spontaneous.

Previous Year's Question

In acidic medium H_2O_2 changes $Cr_2O_7^{2-}$ to CrO_5 which has two (-0-0-) bonds. Oxidation state of Cr in CrO_5 is **[NEET-2014]** (1) +5 (2) +3 (3) +6 (4) -10

Concept Ladder





Definition

Electrochemistry deals with relationship between electrical and chemical energy





• This reaction happens by its own. Therefore its Gibb's free energy is negative.

 $\Delta G < 0$ $\Delta G > 0$ (spontaneous) (Non spontaneous

- Work done by the system in electrochemical process
 Work done = −∆G
- Electrical work = Charge × potential
 Difference

Definition

The device in which chemical energy is converted into electrical energy by spontaneous redox reaction is called Galvanic cell Or Voltaic cell



Galvanic Cell Or Voltaic Cell

In the above cell, the zinc ion solution begins to build up a positive charge. Similarly, as copper ions plate on as copper, the solution builds up a negative charge. The half cell reactions will stop unless positive ions can move from the zinc half-cell to the copper half cell, and negative ions from the copper half-cell can move to the zinc half-cell. It is necessary that these ion flow occur without mixing of the zinc ion and copper ion solutions. If copper ion comes in contact with the zinc metal.

Concept Ladder



In a galvanic cell, reduction potential of reduction half cell reaction is always greater than oxidation half cell reaction.

Types of Conductors

	Electronic conductors or Metallic conductors	Electrolytic Conductors or Solution Conductors
1	It allows current to pass in metallic lattice by the	It allows current to pass in molten state or in
	movement of electron. e.g., Cu, Ag, etc.	aq. solution of electrolytes by movement of
		ions. e.g., NaCl(aq) or NaCl (fused).
2	There is only physical change occur during	There is physical as well as chemical changes
	passage of current.	occurs during passage of current.
3	It generally shows no transfer of matter.	It involves transfer of matter in form of ions.
4	During the passage of current, resistance	During the passage of current, resistance
	increases due to increase in temperature.	generally decreases as there is decreases in
	Thermal motion of metal ions which results in	degree of hydration of ions and viscosity of the
	hindrance in the flow of electrons increases with	medium with increase in temperature.
	increase in temperature.	
5	The conducting power of metal is usually high.	The conducting power of electrolytic conductors

Electrolytes and Electrolysis

(1) Definition : When current is passed through the aqueous solution of a substance and the substance decomposed of into its ions then the substance is termed as electrolyte and this process is known as electrolytic decomposition or electrolysis.

> Examples of electrolytes are solutions of bases, acids, fused salts and salts in water etc. Electrolytes may be strong or weak. Solutions of alcohol, glycerine, cane sugar etc., are examples of non-electrolytes.

Strong and Weak Electrolytes

(i) The extent or degree of dissociation of different electrolytes in solution is different.

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is relatively low.



An aqueous solution and copper sulfate is electrolysed using platinum electrodes in another case. Will the products of electrolysis be same of different?

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Higher is the value of dissociation constant greater is the degree of dissociation and stronger is the electrolyte.

- (ii) Strong electrolytes are the substances which are largely dissociated and form a highly conducting liquid in water. e.g., All salt (except CdBr₂, HgCl₂), mineral acids like HCl, H₂SO₄, NHO₃, etc., and bases like KOH, NaOH, etc., are strong electrolytes. They are almost 100% ionized at normal dilution.
- (iii) Weak electrolytes are the substances which are low conducting liquid formed to a small extent in aqueous solution, e.g., all organic acids (except sulfonic acids), inorganic acids like H3BO3, HCN etc., and bases like ammonia, amines etc., are weak electrolytes.

Factors Influencing Degree of Dissociation

The degree of dissociation (α) of an electrolyte in solution is given by:

Mole dissoicated at any time

 $\alpha = \frac{1}{\text{Total mole present at t} = 0 \text{ or dissolved initially}}$ The variation of α of an electrolyte is directed by

- (i) Nature of solute : All ionic compounds (strong electrolytes) have α ~ 1 at normal dilution. Most of the polar covalent compounds (weak electrolytes) have α<<1.
- (ii) Nature of solvent : Solvent having high dielectric constants are themselves feebly ionized but an electrolyte in high dielectric constant solvent (say water) show higher degree of dissociation than in a solvent of low dielectric constant (say methanol).
- (iii) Dilution : The extent of dissociation of an electrolyte increases with dilution of solution.

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Mineral acids have covalent bond, still they are strong electrolytes. Why?

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Dilution of solute follows ostwald's law of dilution for weak electrolytes.

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A solution of NaCl is initially at 50°C and temperature is increased to 100°C. would there be change in ionisation?

- (iv) Temperature : the extent of dissocation of an electrolyte also increases with an increase in temperature.
- (v) Addition of other species : Addition of another solute having an ion common to that of weak electrolyte shows a decrease in degree of dissociation of weak electrolyte (see common ion effect).

Electrical energy $\xrightarrow{\text{Electrolysis}}$ Chemical energy Chemical energy $\xrightarrow{\text{Electromotive}}$ Electrical energy

- (2) Electrolytic cell or Voltameter : The device which carries the process of electrolysis or electrolytic decomposition is known as electrolytic cell or voltameter.
 - (i) Voltameter convert electrical energy into chemical energy.
 - (ii) Anode (or +ve pole) is an electrode where reduction takes place whereas cathode (or -ve pole) is an electrode where oxidation takes place
 - (iii) Anions are discharged on anode and cations on cathode, during the electrolysis in voltameter.
 - (iv) In voltameter, flow of electrons is from anode to cathode and current will flow from cathode to anode outside the electrolyte.

Anode Flow of electrons Flow of current Cathode

For voltameter, E_{cell} = -ve and ΔG = +ve.

(v) Neutral atoms are converted from the anions after reaching the anode by giving up their electrons.

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Common ion effect involves the presence of similer type of ions in two different compound present in the same solution only for weak electrolytes. Example may insicde the soltuion of CH₃COOH and CH₃COONa

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During Faraday's time, there were no devices available which could supply constant current Hence, the quantity of electrochemistry passed was measured by putting apparatus called an coulometer (Coulomb measures) in the cirrcuit which is simply a standard electrolytic cell.

At Anode :

 $A^- \longrightarrow A + e^-$ (Oxidation)

(vi) Neutral atoms can also be converted from cations when electrons supplied by the battery are reaching to the cathode.

At Cathode :

 $B^+ + e^- \longrightarrow B$ (Reduction)

Products formed in above reactions at cathode and anode are known as primary products and the overall change takes place is known as primary change.

Secondary products are the molecules or compounds formed due to furthur change in primary products and this further change is known as secondary change.

(3) Preferential discharge theory : According to this theory " The ion is discharged on one which occur low in the electrochemical series or which requires least energy or ions with lower discharge potential then at either electrode more than one type of ion is attracted".

> The potential at which the ion is deposited or discharged on the appropriate electrode is defined as the discharge or deposition potential (D.P.). The values of discharge potential will be different for different ions.

> The increase in order of deposition of some of the ions or the decrease in order of discharge potential is given below,

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Voltage (v) supplied in an electrical circuit is obtained from the equation of emf. E = V + Ir = V = E - Ir Where E = emf of cell r = Internal resistance

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On Electrolysis of brine, NaOH, H_2 and Cl_2 are obtained. H_2 is obtained at cathode and Cl_2 at anode. Why Na is not obtained at cathode?

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To obtained the products of electrolysis from aqueous solution, the process is for more complicated in comparison to the electrolysis products from molten state.

For cations :

Li⁺, K⁺, Na⁺, Ca²⁺, Mg²⁺, Al³⁺, Zn²⁺, Fe²⁺, Ni²⁺, H⁺, Cu²⁺, Hg²⁺, Ag⁺, Au³⁺

For Anion :

 $SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$

- (4) Application of electrolysis : It has wide applications in major industries. Given below are some of the important applications :
 - (i) Production of hydrogen by electrolysis of water.
 - (ii) Manufacture of heavy water (D_2O) .
 - (iii) The metals like Al, Mg, K, Na, etc. are obtained by electrolysis of fused electrolytes.
 - (iv) Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.
 - (v) In this method the metal ions Ag, Cu etc. contained in the solution, pure metal is deposited at cathode.
 - (vi) Electroplating : It is the process in which superior metal is coated over an inferior metal by electrolysis. To prevent inferior metal from corrosion and making it more attractive in appearance electroplating is done. Cathode of an electrolytic cell is made by the object to be plated, the solution is made by the ions of the metal to be deposited.

Concept Ladder

Compounds like NaOH, KOH, Na₂CO₃, KClO₃ white lead, KMnO₄ etc. are synthesised by electrosynthesis method.

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When will be the conducting power of strong electrolyte greater than weak electrolyte?

Concept Ladder

techanique of The electrolysis is used in the refining of Cu. The impure Cu(95%) is made anode and thin a sheet of pure Cu is made cathode, and electrolysis is carried out to get pure Cu. The electrolyte is CuSO, solution acidified with dilute H₂SO₄. Impurities fall down as anode mud.

Faraday's laws of electrolysis

These laws are given by Michael Faraday in 1833. The Faraday's laws of electrolysis governs that, during the process of electrolysis when the substances (in the form of ions) are depositaed on electrodes.

- (1) Faraday's first law : It states that, "The mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed." i.e., W ∝ Q Where, W = Mass of ions liberated in gm,
 - Q = Quantity of electricity passed in

Coulombs

= Current in Amperes (I) × Time in second (t)

 \therefore W \propto I × t or W = Z × I × t

In case current efficiency (η) is given, then

$$W = Z \times I \times t \times \frac{\eta}{100}$$

where, Z is constant, called as electrochemical equivalent (ECE) of the ion deposited.

When a current of 1 A is passed for 1 sec. (i.e., Q = 1), then, W = Z

Therefore, electrochemical equivalent (ECE) may be defined as when a current of 1 amp. is passed through the mass of the ion deposited for a second.

It's unit is gram per coulomb.

Coulomb is the unit of electrical charge.

96500 Coulombs 6.023 × 10^{23}

electrons = 1 mole electrons

1 coulomb = $\frac{6.023 \times 10^{23}}{96500}$ = 6.28 × 18¹⁸ electrons

or 1 electronic charge = 1.6 × 10⁻¹⁹ Coulomb

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Mass of substance is deposited at electrode. Can this method be used to address corrosion?

Concept Ladder Electr chemical Equivalent = Weight deposited by 1 colomb $= \frac{Eq.wt \text{ of substance}}{96500}$



Calculate the quantity of electricity that would be required to reduce 12.3 gram of nitrobenzene to online if the current efficiency for the process is 50 percent. If the process drop across the cell is 3 volts, how

much energy will be consumed?

[NEET-2014]

(1) 347kJ	(2) 447kJ
(3) 397kJ	(4) 497kJ

(2) 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

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \text{ or } \frac{Z_1 I t}{Z_2 I t} = \frac{E_1}{E_2} \text{ or } \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

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

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

where,

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

1F = Charge on an electron × Avogadro's number.

 $|f = e^- \times N = (1.602 \times 10^{-19} \text{ c}) \times (6.023 \times 10^{23} \text{ mol}^{-1})$

Number of Faraday

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

(3) Faraday's law for gaseous electrolytic

product For the gases, we use

$$v = \frac{It V_e}{96500}$$

where, V = Volume of gas evolved at an electrode at S.T.P.

V_e = Equivalent volume = Vol. of gas evolved at S.T.P. at an electrode by 1 Faraday charge

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Magnitude of charge carried by 1 mole of electrons is 96487 C(6 × 10²³ × 1.6 × 10⁻¹⁹ = 96487C). It is also known as one faraday, i.e., 1F = 96500C.





Why oxidation potential of H₂O is greater than fluoride ion?

Concept Ladder



Reduction potential of H_2O > (×) Reduction potential of cations of 1, 2 and 13 groups of periodic table, e.g., Na⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺, etc. so reduction of H_2O occurs at cathode.

Electrical Resistance and Conductance

• Resistance (R) :-

 $R = \frac{V}{I}$ is expressed in ohms.

• Conductance (G) :-

Conductance is the property of material by virtue of which it favours flow of current.

$$G = \frac{1}{R}$$

[unit of G is **mho** or **ohm**⁻¹ or **Siemens** (S)]

Specific resistance/Resistivity (ρ) :-The resistance (R) of a conductor is directly proportional to its length(*l*) and inversely proportional to its area of cross section (A).

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

Previous Year's Question

Zinc can be coated on iron to produce galvanised iron but the reverse is not possible. It is becasue. **[NEET 2016]**

- (1) Zinc is lighter than iron
- (2) Zinc has lower melting point than iron
- (3) Znc has lower negative electrode potential than iron
- (4) Zinc has higher electrode potential than iron



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

If l = 1 cm, A= 1 cm², therefore $\rho = R$

\therefore V = A × l = 1 cm³

Therefore resistance offered by 1 cm³ electrolytic solution is known as resistivity. [Unit of $\rho \rightarrow \text{ohm cm}^{-1}$]

(d) Specific conductance/ Conductivity (κ) :-

Conductivity is defined as the reciprocal of

specific resistance,
$$\kappa = \frac{1}{2}$$

$$\mathsf{R} = \frac{\rho \ell}{\mathsf{A}} \qquad \qquad \frac{1}{\rho} = \frac{1}{\mathsf{R}} \cdot \frac{\ell}{\mathsf{A}}$$

 $\kappa = G \times G^*$

Specific conductance = Conductance × Cell constant [Unit of K is ohm⁻¹ cm⁻¹] Hence specific conductivity of a solution is defined as the conductance offered by 1 cm³ of electrolytic solution.

Cell constant :

$$G^* = \frac{\ell}{A}$$
 : its unit is cm⁻¹

(e) Molar conductivity or Molar conductance :

$$\Lambda_{\rm m} = \kappa \times V$$

$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M}$$

[Unit \rightarrow ohm⁻¹ cm² mol⁻¹]

(f) Equivalent conductivity or Equivalent conductance (Λ_{eq} or λ_{eq})

$$\Lambda_{eq} = \kappa \times V$$

$$\Lambda_{\rm eq} = \frac{\kappa \times 1000}{N}$$

Relation between $\Lambda_{_{\text{eq}}}$ and $\Lambda_{_{\text{m}}}$

$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{{\sf M}} \text{ and } \Lambda_{\rm eq} = \frac{\kappa \times 1000}{{\sf N}}$$

Previous Year's Question

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

[NEET 2010]

- Increase in both i.e. number of ions and ionic mobility of ions
- (2) Increase in ionic mobility of ions
- (3) 100% ionisation of electrolyte at normal dilution.
- (4) increase in number of ions

Concept Ladder

Resistivity is the measure of resisting power of a specified material to the flow of an electric current. It only depends only on nature of material 1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 50 ohm. Calculate the

A.1 Given l = 2.1 cm, a = 4.2 sq. cm, R = 50 ohm Specific conductance, Specific conductance, $\kappa = \frac{l}{a} \cdot \frac{1}{R}$

equivalent conductivity of the solution.

Or
$$\kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1}$$

Equivalent conductivity = $\kappa \times V$ V = the volume containing 1 g equivalent = 1000 ml So Equivalent conductivity = 0.01 × 1000 = 10 ohm⁻¹ cm² equiv⁻¹

Q.2 At 298 K $\frac{1}{50N}$ KCl is field in a cell of Its specific conductance is 0.001735 ohm⁻¹

 $\rm cm^{-1}$ and resistance is 100 ohm then calculate

(i) Cell const.

(ii) Molar conductivity (or) Molar conductance

A.2 (i)
$$K = \frac{1}{R} \cdot \frac{l}{A}$$
 = 0.001735 = $\frac{1}{100 \text{ ohm}} \times \frac{l}{A}$ = 5 cm⁻¹
= $\frac{l}{A}$ = 0.1735 cm⁻¹
(ii) $\Lambda_m = \frac{K \times 1000}{m} = \frac{0.001735 \times 1000}{\frac{1}{50}} \begin{bmatrix} N = Mn_f \\ n_f = 1 \\ M \Rightarrow \frac{1}{50} \end{bmatrix}$
= 86.75 S cm² mol⁻¹

2.3 Specific conductance of an electrolyte is 3.825 S cm⁻¹. If limiting molar conductivity is 425 S cm²mol⁻¹, then calculate molarity of electrolyte of it is 90% dissociated :

=

$$\wedge_{\rm m} = \frac{3.825 \times 1000}{M} \left[\alpha = \frac{\wedge_{\rm m}}{\wedge_{\rm m}^0} \right]$$

 $0.4 \times 425 = \Lambda_m$ = 382.5 S cm² mol⁻¹

$$382.5 = \frac{3.825 \times 100}{M}$$

Molarity = 10 M

DETERMINATION OF $\Lambda^{0}_{\ \mbox{m}}$ OR Λ^{0}

A plot of $\Lambda_{\rm m}$ vs $\sqrt{C}\,$ as found experimentally is as shown below graphically.



Debye Huckel Onsager equation -

Λ_m = Λ_m[∞] - b√C [only for strong electrolyte]
 When values of Λ_m are plotted against C then a straight line is obtained. This induced to zero concentration. The point where the straight line intersects Λ_m⁰ axis is of the strong electrolyte.

Previous Year's Question

8

Molar conductivites (Λ^0_m) at infinite dilution of NaCl, HCl and CH₃COONa are 126.4, 425.9 and 91.0 S cm² mol⁻¹ respectively for CH₃COOH will be

[NEET 2012]

- (1) 425.5 S cm² mol⁻¹
 (2) 180.5 S cm² mol⁻¹
 (3) 290.8 S cm² mol⁻¹
- (4) 390.5 S cm² mol⁻¹

Concept Ladder

There is avery large increase in conductance with dilution especially near infinite delution. As concentration of the weak electrolyte is Reduced, more of it ionizes. But the non linearity of curve in case of weak electrolyte shoots up suddenly for some low concentration and assumes the shape of straight line parallel to Λ_m axis. Hence extrapolation in this case is impossible. Thus, experimentally also the value of Λ_o of a weak electrolyte cannot be determined. However, it can be done with the help of Kohlrausch's law to be discussed later.

Kohlrausch's Law of Independent Migration of Ions

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte regardless of the nature of the other ion which with it is associated and that the molar conduction at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. $\wedge_m^0 = \wedge_+^0 + \wedge_-^0$, \wedge_+^0 the contribution of the cation \wedge_-^0 is the contribution of the anion

APPLICATION OF KOHLRAUSCH'S LAW

• Determination of \wedge^{0}_{m} of a weak electrolyte:

 $(CH_{3}COOH) = (HCl) + \wedge_{m}^{0} (CH_{3}COONa) - \wedge_{m}^{0} (NaCl)$

• Determination of degree of dissociation (α)

No. of molecules ionised Total number of molecules dissolved

$$=\frac{\Lambda_{m}}{\Lambda^{0}}$$

 $\alpha = -$

 Determination of solubility of sparingly soluble salt

$$\wedge_{\rm m}^{\rm 0} = \frac{1000 {\rm K}}{{\rm C}}$$

where C is termed as molarity of solution and hence the solubility.

Previous Year's Question



Which of the following expression correctly represent the equivalent conductance at of infinite dilution of $Al_2(SO_4)$? Given that $^{\wedge}_{SO_4^{2-}}$ and $^{\wedge}_{Al^{3+}}$ are the

equivalent conductances at infitite dilution of respective ions [NEET 2010]

(1)
$$2 \Lambda_{Al^{3+}}^{0} + 3 \Lambda_{SO_4^{2-}}^{0}$$

(2)
$${}^{0}_{\Lambda_{Al^{3+}} + \Lambda_{SO_4^{2-}}}$$

(3)
$$\begin{pmatrix} 0 & 0 \\ \Lambda_{Al^{3+}} + \Lambda_{SO_4^{2-}} \end{pmatrix} \times 6$$

$$(4) \ \frac{1}{3} \frac{{}^{0}_{\Lambda_{Al^{3+}}}}{\Lambda_{Al^{3+}}} + \frac{1}{2} \frac{{}^{0}_{\Lambda_{SO_{4}^{2-}}}}{\Lambda_{SO_{4}^{2-}}}$$



Concept Ladder



Ionic mobility is defined as the speed of the ion cm/sec at infinite dilution under a potential gradient of 1 volt/ cm.

Ionic Mobility = $\frac{\text{Ionic conductance}}{96500}$

.4	Compare the conductance in following		
	$Cl_3 C CH_2 COOH$	CH ₃ CH ₂ COOH	
	(a)	(b)	

- A.4 $a > b \rightarrow$ degree of dissociation of a > degree of dissociation of b
 - Calculate solubility product of $BaSO_4$ If its conductivity and molar conductance at saturation are 3.06 × 10⁻⁶ S cm⁻¹ and 153 S cm² mol⁻¹ respectively.

.5
$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

 $s \qquad s \qquad s$
 $K_{SP} = s^2 \qquad K \times 1000$
 $s = \qquad \frac{K \times 1000}{N_m^0} \qquad = \qquad \left(\frac{3.06 \times 10^{-6} \times 1000}{153 \ \text{S cm}^2 \text{mol}^{-1}}\right)$
 $K_{SP} = (2 \times 10^{-5})^2 \qquad = 2 \times 10^{-5} \text{ mol/lit} \qquad = 4 \times 10^{-10}$

The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and 91.0 ohm⁻¹ cm² equiv⁻¹, respectively at 25°C. Calculate the equivalent conductance of acetic acid at infinite dilution.

A.6 According to Kohlrausch's law

Α

$\wedge_{\rm {}_{\infty}CH_{3}COONa} = \wedge_{\rm {}_{CH_{3}COO^{-}}} + \wedge_{\rm {}_{Na^{+}}} = 91.0$	1 ·
$\wedge_{{}_{\infty}HCl} = \wedge_{H^+} + \wedge_{Cl^-} = 426.16$	2
$\wedge_{\infty NaCl} = \wedge_{Na^+} + \wedge_{Cl^-} = 126.45$	3

By adding eq^{n} (1) and (2) and subtracting (3)

FACTORS AFFECTING ELECTROLYTIC CONDUCTANCE

- Inter ionic attraction :inter ionic attraction between ions of solute is more, then the conductance will be less.
- Polarity of solvent :-

If solvent has high-dielectric constant then the ionization and conductance will be higher.

• Viscosity of medium :-

On increasing the viscosity of medium, the conductance decreases.

• Temperature :-

As the temperature of electrolytic solution is increased, the conductance increases

- **Hydrated size :** Due to hydration of ions conductance decreases.
- Dilution :-
 - (i) On increasing the dilution conductance(G) increases.

For strong electrolyte on dilution interionic force of attraction decreases therefore conductance increases. For weak electrolyte with dilution degree of dissociation (α) increases therefore conductance increases.

- (ii) On dilution specific conductance decreases because on dilution number of ions in 1 ml solution decreases.
- (iii) On dilution equivalent and molar conductance increases because with dilution normality or molarity decreases.

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Conductivity of solution dependes upon the polarity of solvent. Would the solution of benzene and toluene conduct electrolysis?

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Transport number is the fraction of current carried by ion. Transport number =

Current carried by ion Total current carried

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Is there any relationship between molar conductance and dilution?

19.

Representation of a cell



Net reaction

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

Concept Ladder



In a galvanic cell, cathode is positive with respect to anode.

Give the cell reaction from the cell notation

$$Zn_{(s)} | Zn^{2+}_{(aq)} || Fe^{3+}_{(aq)} |, Fe^{2+}_{(aq)} | Pt$$

A.7 The half cell reactions are Anode $Zn(s) \rightarrow Zn^{2+} (aq) + 2e^{-}$ Cathode $Fe^{3+}_{(aq)} + e^{-} \rightarrow Fe^{2+}_{(aq)}$ and the cell reaction is : $Zn_{(s)} + 2Fe^{3+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$

Electrode potential

Metal acquires either a negative or positive charge w.r.t. the solution when it is placed in a solution of its ions. By this a definite potential is developed between the metal and the solution. This difference in potential is known as electrode potential. It depends on the concentration of ions, nature of electrode and temperature. **Condition in which the circuit stops working**

Concept Ladder



Decreasing order of metallic character is given below: K > Na > Ba > Ca > Mg > Al > Zn > Fe > Ni > Sn H > Cu > Hg > Ag > Au > Pt



• No current will flow. In this situation salt bridge is introduced.

Salt bridge construction :

- 1. It is inverted U-shaped tube
- Contains inert electrolyte like KCl, KNO₃, NH₄,Cl etc. in agar-agar gel & gelatin.
- 3. Ions of electrolyte do not react with ions of electrode solution.

Salt bridge functions :

- 1. To complete circuit.
- 2. To maintain electrical neutrality.

Standard Reduction Potential : Conditions:

Rack your Brain

On what criteria the sign convention of electrodes is decided ?

Concept Ladder



Another function of salt bridge is that it prevents liquid-liquid junction potential i.e., the potential difference that arises between the two solutions when they are directly in contact with each other



According to the IUPAC conventions, Standard electrode potential = Standard reduction potential

Cell potential Or emf of the cell (E_{cell})

The difference between electrode potential of two half cells is known as cell potential

$$\mathsf{E}_{\mathsf{cell}} = \left(\mathsf{E}_{\mathsf{OP}}\right)_{\mathsf{A}} + \left(\mathsf{E}_{\mathsf{RP}}\right)_{\mathsf{c}}$$

 $\mathsf{E}_{\mathsf{cell}} = \left(\mathsf{E}_{\mathsf{RP}}\right)_{\mathsf{C}} - \left(\mathsf{E}_{\mathsf{RP}}\right)_{\mathsf{A}}$

Q.8 For the cell reaction $2Ce^{4+} + Co \rightarrow 2Ce^{3+}$



+ Co^{2+}, E^0_{cell} is 1.89 V $E^0_{Co^{2+}|CO} is \ 0.28 \ V, \ what \ is \ the \ value \ of \ E^0_{Ce^{4+}|Ce^{3+}}$

A.8 $E_{cell}^{0} = E_{ce^{4+}|Ce^{3+}}^{0} - E_{Co^{2+}|CO}^{0}$ $1.89 = E_{Ce^{4+}|Ce^{3+}}^{0} - (-.28)$ $E_{Ce^{4+}|Ce^{3+}}^{0} = 1.61 V$

Rack your Brain



Which electrode of a galvanic cell corresponds to the higher potential energy.

Q.9	Which of the following metal displaces hydrogen from H ₂ SO ₄ solution or acidified		
	water?		
	(1) Mg	(2) Al	
	(3) Fe	(4) All of these	

Ε

(+)

(-)

0

A.9 (4)

Relationship between Gibb's free energy change and emf of cell

Work done = Decrease in free energy change Charge on 1 mole $e^- = N_A \times e^-$ = 6.023 × 10²³ × 1.6 × 10⁻¹⁹

= 96500 = 1 Faraday

- [1 Faraday = charge on 1 mole of electron]
- Charge of n moles of electron

Equilibrium

q = nF

Work done = charge × cell potential

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

$$\Delta G$$
Spontaneous
(-)
Non- spontaneous
(+)

Previous Year's Question

The pressure of H_2 required to make the potential of H_2 elctrode is zero in pure water at 298K is (1) 10⁻¹⁰ atm (2) 10⁻⁴ atm (3) 10⁻¹⁴ atm (4) 10⁻¹² atm

Concept Ladder



Electron flow from anode to cathode in the external circuit. Inner circuit is completed by the flow of ions through the salt bridge.

Electrochemical Series

Increasing strength of reducing agent

The elements arranged in the decreasing order of reduction potential, the series attained is known as Electrochemical series

Electrode	Reaction	SRP(at 298K)
Li	$Li^{+} + e^{-} \rightarrow Li(s)$	-3.05 V
К	$K^{\scriptscriptstyle +}$ + $e^{\scriptscriptstyle -}$ $ ightarrow$ K(s)	–2.93 V
Ba	$Ba^{+2} + 2e^{-} \rightarrow Ba$	–2.91 V
Ca	Ca^{*2} + 2e ⁻ \rightarrow Ca(s)	–2.87 V
Na	$Na^{*} + e^{-} \rightarrow Na(s)$	–2.71 V
Mg	$Mg^{_{+2}} + 2e^- \rightarrow Mg(s)$	–2.36 V
Al	$Al^{3+} + 3e^- \rightarrow Al$	–1.66 V
Mn	${\sf Mn}^{{}^{\scriptscriptstyle+2}}$ + 2e $^{\scriptscriptstyle-}$ $ ightarrow$ Mn	–1.18 V
H₂O	$H_2O(\ell) + e^- \rightarrow \frac{1}{2}H_2 + OH^-$	-0.828 V
Zn	$Zn^{^{+2}} + 2e^{-} \rightarrow Zn(s)$	-0.76 V
Cr	$Cr^{*3} + 3e^- \rightarrow Cr(s)$	-0.74 V
Fe	$\mathrm{Fe}^{^{2+}}$ + 2e ⁻ \rightarrow Fe	-0.44V
Cd	$Cd^{_{+3}} + 2e^- \rightarrow Cd(s)$	-0.40 V
Co	$\mathrm{Co}^{^{+2}} + 2e^{-} \rightarrow \mathrm{Co}$	-0.28 V
Ni	$Ni^{*} + 2e^{-} \rightarrow Ni(s)$	–0.25 V
Sn	$\operatorname{Sn}^{^{+2}}$ + 2e ⁻ \rightarrow Sn(s)	-0.14 V
Pb	$Pb^{^{*2}}$ + 2e ⁻ \rightarrow Pb(s)	–0.13 V
H ₂	$2H^{+} + 2e^{-} \rightarrow H_2(s)$	0.00 V
Cu	Cu^{2*} + $2e^- \rightarrow Cu(s)$	0.34 V
I ₂	$I_2 + 2e^- \rightarrow 2I^-$	0.54 V
Fe	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77 V
Hg	Hg_{2}^{2+} +2e ⁻ $ ightarrow$ 2Hg(ℓ)	0.79 V
Ag	$Ag^{+} + e^{-} \rightarrow Ag$	0.80 V
Hg	Hg^{2*} + 2e ⁻ \rightarrow Hg(ℓ)	0.85 V
Br ₂	$Br_{_2} + 2e^- \rightarrow 2Br^-$	1.09 V
Pt	$Pt^{^{+2}} + 2e^{-} \rightarrow Pt$	1.20 V
0,	$\frac{1}{2}O_2+2H^++2^{e^-}\rightarrow H_2O(\ell)$	1.23 V
Cl2	Cl_2 + 2e ⁻ \rightarrow 2 Cl ⁻	1.36 V
Au	$Au^{_{+3}}$ + $3e^{_{-}} \rightarrow Au(s)$	1.40 V
F ₂	$F_2 + 2e^- \rightarrow 2F^-$	2.87 V



Electrochemistry

Q.10 If E₀ for Au⁺ + e⁻ → Au (s) is 1.69 V & E₀ for 3e⁻ + Au⁺³ → Au is 1.40 V, then E₀ will be
(1) 0.19 V
(2) 2.945 V
(3) 1.255 V
(4) none

A.10 (3)

Nernst equation:

When the concentration is not equal to 1 Molar. Then we use Nernst equation According to thermodynamics,

 $\Delta G = \Delta G^{\circ} + RT \ln Q$

$$(:-\Delta G = nFE \text{ and } -\Delta G^\circ = nFE^\circ)$$

 $-nFE = -nFE^{\circ} + RT lnQ$

$$E_{cell} = E_{cell}^{o} - \frac{2.303RT}{nF} \log Q$$

where E^{0} = standard electrode potential,

R = gas constant, T = temperature (in K)

- F = Faraday (96500 coulomb mol⁻¹),
- n = number of moles of e⁻ gained lost or transferred in balanced equation.

At 25°C, above equation may be written as $5 - 5^{\circ} = 0.0591_{1-3} = 0.0591_{1$

$$E_{cell} = E_{cell}^0 - \frac{n}{n} \log Q$$

$$E_{cell} = E_{cell}^{o} - \frac{0.0591}{n} log \frac{[P]}{[R]}$$





3

If the E^0_{cell} for a given reaction has a negative value, which of the following gives the correct relationship for the value of ΔG^0 and K_{eq} ?

[NEET 2016]

(1)
$$\Delta G^{\circ} > 0$$
; $K_{eq} < 1$
(2) $\Delta G^{\circ} > 0$; $K_{eq} > 1$
(3) $\Delta G^{\circ} < 0$; $K_{eq} > 1$
(4) $\Delta G^{\circ} < 0$; $K_{eq} < 1$

Q.11 Calculate the EMF of a Daniel cell when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001 M and 0.1 M respectively. The standard EMF of the cell is 1.1V

A.11 E = 1.159 V
Zn(S) + CuSO₄
$$\rightarrow$$
 ZnSO₄ + Cu
E_{cell} = E⁰_{cell} - $\frac{0.0591}{2} log \left[\frac{Zn^{2+}}{Cu^{2+}} \right] = 1.1 - \frac{0.0591}{2} log \frac{10^{03}}{10^7} = 1.159 V$

2.12 Calculate E⁰ and E for the cell Sn | Sn²⁺ (1M) || Pb²⁺(10⁻³M) | Pb, E0 (Sn²⁺| Sn)
 = -0.14V, E⁰ (Pb²⁺| Pb) = -0.13V. Is cell reaction is feasible?

A.12 No,
$$E_{cell} = -0.078V$$

 $E_{cell} = -E_{Sn^{2+}/Sn}^{0} + E_{Pb^{2+}/Pb}^{0} - \frac{0.059}{2} log \left[\frac{Sn^{2+}}{Pb^{2+}} \right] = +0.14 - 0.13 - \frac{0.059}{2} log 10^{13}$

Take =
$$+0.01 - \frac{0.059}{2} \times = -0.078$$
 V

Applications of Nernst Equation

(i) Calculation of electrode potential

 $(E_{RP} \text{ or } E_{OP})$

$$\mathsf{E}_{\mathsf{RP}} = \mathsf{E}_{\mathsf{RP}}^{0} - \frac{0.0591}{n} \log \frac{1}{[\mathsf{M}^{+n}]}$$

If $[M^{+n}]$ increases, then E_{RP} increases

(ii) Calculation of electrode potential and pH of hydrogen electrode -

$$2H^+ + 2e^- \rightarrow H_2(g)$$

$$\mathsf{E}_{\mathsf{RP}} = \mathsf{E}_{\mathsf{RP}}^{0} - \frac{0.0591}{2} \log \frac{\mathsf{P}_{\mathsf{H}_{2}}}{\left[\mathsf{H}^{+}\right]^{2}}$$

$$\therefore \qquad E_{RP}^{0} = 0 ; \ E_{RP} = E_{RP}^{0} - \frac{0.0591}{2} \log \frac{1}{[H^{+}]^{2}}$$

Previous Year's Question

6

Consider the half-cell reduction reaction

 $Mn^{2+} + 2e^{-} \rightarrow Mn, E^{0} = -1.18V$

 $Mn^{2+} \rightarrow Mn^{3+} + e^-, E^0 = -1.51V$ The E⁰ for the reaction,

 $3Mn^{2+} \rightarrow Mn^{0} + 2Mn^{+3}$ and possibility of the forward reaction are respectively?

[NEET 2016]

- (1) -4.18 V and yes
- (2) +0.33 V and Yes
- (3) +2.69 V and No
- (4) -2.69 V and No



Why Cu²⁺ dispropostionates in aqueous solution?

(iii) Calculation of equilibrium constant ($K_{_{eq}})$ and ΔG^{o}

From Nernst equation -

$$E_{cell} = E_{Cell}^{\circ} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

At equilibrium, $E_{cell} = 0$ and $\frac{[P]}{[R]} = K_{eq}$
 $E_{Cell}^{\circ} = \frac{0.0591}{n} \log K_{eq}$
 $E_{Cell}^{\circ} = \frac{2.303 \text{RT}}{nF} \log K_{eq}$
nF $E_{Cell}^{\circ} = 2.303 \text{ RT} \log K_{eq}$

 $\Delta G^{\circ} = -2.303 \text{ RT } \log \text{K}_{eq}$

Previous Year's Question

In the electrochemical cell; Zn | ZnSO₄ (0.01M) || CuSO₄(1.0M) | Cu the emf of this Daniell cell is E_1 when the concentration of ZnSO₄ is changed to 1.0M and that of CuSO₄ changed to 0.01 M the emf changes to E_0 . From the followings, which one is the relationship between E_1 and E_2 ? [NEET 2017]

(1)
$$E_1 < E_2$$

(2) $E_1 > E_2$
(3) $E_2 = 0 \neq E_2$
(4) $E_1 = E_2$

Q.13 Calculate the equilibrium constant for the reaction $Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3++}, \ [E^{0}_{Ce^{4+}/Ce^{3+}} = 1.44V; E^{0}_{Fe^{3+}/Fe^{2+}} = 0.68V]$ $\frac{2.303 \text{ RT}}{F} = 0.06 \text{ at } 25^{\circ} \text{ C}, \log 4.68 = 0.67$

A.13
$$K_c = 4.68 \times 10^{12}$$

 $Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$
 $E^0 = 1.44 - 0.68 = 0.76 V = \frac{0.06}{1} \log K_c$
 $K_c = 4.64 \times 10^{12}$

CONCENTRATION CELL (E°_{Cell} = 0)

 Electrode Gas concentration cell : Pt, H₂ (P₁) | H⁺ (C) | H₂ (P₂), Pt At 25° C, [For spontaneity of such cell reaction, p₁ >p₂]



Will change in tempature affect E^{o}_{cell} ?

Pt | Cl₂ (g, P₂) | Cl⁻ (aq,C) || Cl⁻ (aq, C) | Cl₂ (g, P₁) | Pt EMF of cell is positive if (1) P₁ > P₂ (2) P₂ > P₁ (3) P₁ = P₂ (4) We cannot predict

A.14 For spontaneous reaction $P_1 > P_2$

Anode half cell

$$E_{ox} = E_{ox}^{0} - \frac{0.0591}{2} \log \frac{P_2}{C}$$
(1)

Cathode half cell

$$E_{red} = E_{red}^{-} - \frac{0.0591}{2} \log \frac{C}{P_1} \qquad \dots \dots (2)$$

$$E_{cell} = E_{ox} + E_{red}$$

$$= E_{ox}^{-} + E_{red}^{-} - \frac{0.0591}{2} \log \frac{P_2}{C} \cdot \frac{C}{P_1}$$

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

Rack your Brain



Why Pt electrodes are used with the combination of the gas when oxidised or reduced part is a gas?

Electrolyte concentration cells

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

$$\mathsf{E} = \frac{2.303\mathsf{RT}}{2\mathsf{F}}\mathsf{log}\left[\frac{\mathsf{C}_1}{\mathsf{C}_2}\right]$$

[For spontaneity of such cell reaction, $C_2 > C_1$]

Concept Ladder



A potential difference develops across the boundary of two solutions which is known has liquid junction potential of diffusion potential.



Electrolytic cell

NaCl(molten) \rightarrow Na $^{\scriptscriptstyle +}$ + Cl $^{\scriptscriptstyle -}$
Reactions at Anode (oxidation)
$2Cl^{-} \rightarrow Cl_{2}(g) + 2e^{-}$
Cathode (reduction)
2Na⁺ + 2e⁻ → 2Na(l)

Concept Ladder



The minimum voltage required for discharge of ions is called discharge potential

By electrolysis of aq. MgSO₄ with the help of inert electrode calculate ratio of moler of substance deposited at cathode and anode

(1) 1 : 4 (2) 1 : 2 (3) 2 : 1 (4) 4 : 1

A.15 At cathode $2H_2O + 2e^- \rightarrow H_2 + 2H^-$ At anode $n_f = 2$ $gm \text{ eq. } H_2 = \text{mol } H_2 \times 2$ $\frac{\text{mol } H_2}{\text{mol } O_2} = \frac{4}{2} = \frac{2}{1}$ At anode $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^$ $n_f = 2$ $gm \text{ eq. } H_2 = \text{mol } \times 4$

Aq. Na₂SO₄ is electrolysed then after electrolysis pH will be

- (1) increased
- (2) decreased
- (3) unchanged (4) None of these

A.16 (3)

Quantitative aspects of Electrolysis

Fe ⁺² + 2e ⁻¹	\rightarrow Fe
2 mole of e⁻	ightarrow 1 mol Fe
1 mole of e⁻	ightarrow 1/2 mol Fe

Equivalent weight of $Fe^{2+} = \frac{Molecular weight}{2}$

1 Faraday will discharge 1 Equivalent.

Faraday's law

(a) First law of electrolysis :

Amount of substance liberated or deposited at an electrode is proportional to value of charge passed (utilized) through the solution.

 $0 \propto W$

W = ZQ where Z = electrochemical equivalent then W = Z (when Q = 1 coulomb)

Amount of substance deposited or liberated by 1 coulomb charge is called electrochemical equivalent.

Let I ampere current is passed till 't' seconds Q = It

W = ZIt.

1 Faraday = 96500 coulomb = Charge on one mole electrons

Let 'E' is equivalent weight then 'E' gram will be liberated by 96500 coulombs.

 \therefore 1 Coulomb will liberate $\frac{E}{96500}$ gram;

Previous Year's Question



On electrolysis of dil. sulphuric using platinum acid (Pt) electrode, the product obtained at anode will be :

[NEET-2020]

- (1) Hydrogen gas
- (2) Oxygen gas
- (3) H₂S gas
- (4) SO₂ gas

Rack your Brain



Electrolysis of water is often done with a small amount of sulphuric acid added to water. Why?

Previous Year's Question

The weight of silver (at. wt = 108) displaced by a quantity of electricity which displaces 5600mL O_gO₂ at STP will be

[NEET-2014]

(1) 5.4 g	(2) 10.8
(3) 54.0 g	(4) 108.0

- g
- 0 g

$$Z = \frac{E}{96500} \qquad \therefore W = \frac{EIt}{96500}$$
$$\frac{W}{E} = \frac{It}{96500} = \text{number of g eq} = \text{number of faraday's}$$

7 How long a current of 2 A has to be passed through a solution of AgNO₃ to coat a metal surface of 80 cm² with 5 μm thick layer? Density of silver = 10.8 g/cm³.

A.17 d =
$$\frac{M}{V} \Rightarrow 10.8 = \frac{M}{80 \times 5 \times 10^{-4}} \Rightarrow M = 10.8 \times 400 \times 10^{-4}$$

W = $\frac{E \times I \times t}{96500} \Rightarrow 10.8 \times 400 \times 10^{-4} = \frac{108 \times 2 \times t}{96500} \Rightarrow t = 193 \text{ s}$

(b) Second law of electrolysis:

The weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights, when same amount of charge is passed through different electrolyte solutions connected in series.

i.e.
$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

18 One ampere current for how much time should be passed through Aq. Soln of 2 molar, 200 ml AgNO₃, so that 1 mol of Ag can be deposited

A.18 AgNO₃ \rightleftharpoons Ag⁺

$$\frac{W}{E} = \frac{i.t}{96500} \text{ molarity} = \frac{W}{E} = \frac{1 \times t}{9600} \Rightarrow 10^{-3} \times 1 = \frac{1 \times t}{96500}$$

T= 96.5 sec

When 1 M 2L Aq. AgNO₃ and 1 M, 2L aq NaCl are connected in units If 10.8 gm Ag deposited on cathode, then calculated volume of Cl₂ (at NTP) collected at anode





Can be used only once and can't be recharged. Ex. Dry cells and alkaline batteries

Secondary Batteries

Can be used more than once and can be recharged Ex. Nickel - Cadmium ("Ni - Cad") batteries lead storage batteries

Deniell cell

Deniell cell converts chemical energy liberated during the redox reaction to electrical energy and has an electrical potential equal to 1.1V when the concentration or activity of Zn²⁺ and Cu²⁺ ions is unity (1 mol dm⁻³).

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





Primary Batteries (Dry cells and alkaline batteries)

Cathode, reductions:

 $2NH_{4}^{\scriptscriptstyle +}\left(aq\right)+2e^{\scriptscriptstyle -} \rightarrow 2NH_{3}\left(g\right)+H_{2}\left(g\right)$

Anode Oxidation :

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

The pressure will be builded up and the cell is reptured by the formation of two gases at the cathode.

$$\begin{aligned} &Zn^{2+}\left(aq\right) + 2NH_{3}\left(g\right) + 2Cl^{-}\left(aq\right) \rightarrow Zn\left(NH_{3}\right)_{2}Cl_{2}\left(s\right) \\ &2MnO_{2}\left(s\right) + H_{2}\left(g\right) \rightarrow Mn_{2}O_{3}\left(s\right) + H_{2}O\left(l\right) \end{aligned}$$

Concept Ladder Mecury cell suitable for low current devices like hearing acids, watches, etc. con-

What is the most common

Rack your Brain

Primary Battery?

current devices like hearing acids, watches, etc. consists of zinc-mercury amalgam as anode and a paste of HgO and carbon as the cathode.





SECONDARY OR RECHARGABLE BATTERIES The lead storage battery – Discharging reaction :

 $\label{eq:pb} \begin{array}{l} \mathsf{Pb}(s) + \mathsf{PbO}_2(s) + 2\mathsf{H}_2\,\mathsf{SO}_4 \to \mathsf{PbSO}_4(s) + 2\mathsf{H}_2\,\mathsf{O} \end{array}$ Cathode reduction :

$$2MnO_{2}(s) + H_{2}(g) \rightarrow Mn_{2}O_{3}(s) + H_{2}O(l)$$

Anode Oxidation

$$\mathsf{PbO}_{2}\left(s\right) + 4\mathsf{H}^{\scriptscriptstyle +}\left(aq\right) + \mathsf{SO}_{4}^{2^{\scriptscriptstyle -}}\left(aq\right) + 2e^{\scriptscriptstyle -} \rightarrow \mathsf{PbSO}_{4}\left(s\right) + 2\mathsf{H}_{2}\mathsf{O}\left(l\right)$$

Net Cell reaction

 $\mathsf{Pb}\left(s\right) + \mathsf{SO}_{\mathsf{4}}^{\mathsf{2-}}\left(\mathsf{aq}\right) \to \mathsf{PbSO}_{\mathsf{4}}\left(s\right) + 2\mathsf{e}^{-}$

Charging reaction is reverse of discharging reaction with the reaction on anode will be written on cathode and vice versa

Concept Ladder



The discharging process of the storage cell is based on the principles of electrochemical cell, whereas the charging process is based upon the principles of electrolytic cells.



What is end life of the battery?



Nickel - Cadmium ("Ni - Cad") batteries

Cathode (Reduction) :

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

Anode (Oxidation):

 $Cd + 2OH^{-} \rightarrow Cd(OH)_2 + 2e^{-}$

Net cell reaction :

 $\text{NiO}_2(\text{OH}) + \text{Cd} + \text{H}_2\text{O} \rightarrow 2\text{Ni(OH)}_2 + \text{Cd(OH)}_2$



Fuel Cell



Cathode, reduction :

 $O_2(g)$ + 2 $H_2O(l)$ + 4e⁻ → 4OH⁻ (aq) E° = 1.23 V

Anode, Oxidation :

 $H_2(g) \rightarrow 2H^+(aq) + 2e^ E^\circ = 0 V$

Corrosion Cells and Reactions

A corrosion system can be regarded as a shortcircuited electrochemical cell in which the anodic process is something like

 $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$

and the cathodic steps can be given as

$$\begin{array}{l} \mathsf{O_2} + 2\mathsf{H_2O} + 4\mathsf{e}^- \rightarrow 4\mathsf{OH}^- \\ \\ \mathsf{2H^+} + 2\mathsf{e}^- \rightarrow \mathsf{H_2} \ (\mathsf{g}) \\ \\ \mathsf{M^{2^+}} + 2\mathsf{e}^- \rightarrow \ \mathsf{M}(\mathsf{s}) \end{array}$$

Concept Ladder

Efficiency of a Fuel Cell

$$\eta = \left| \frac{\Delta G}{\Delta H} \right| = \left| \frac{nFE}{\Delta H} \right|$$

Previous Year's Question

A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as [2015, Cancelled]

- (1) Dynamo
- (2) Ni-Cd cell
- (3) Fuel cell
- (4) Electrolytic cell

2

Control of Corrosion

• Sacrificial coatings

When coating of more active metal is applied on another metal, negative charge is supplied to the metal.



Sacrificial protection of iron by zinc

Cathodic Production

By maintaining a continuous supply of negative electrical charge on a metal for inhabitation for dissolution of positive ions.

Concept Ladder

In a galvanic cell, cathode is positive with respect to anode.

37.

- **2.20** Compare the conductance in following Colour of KI solution containing starch turns blue when Cl, water is added. Explain.
- A.20 Chlorine placed below iodine in electrochemical series having more reduction potential and thus shows reduction whereas I⁻ undergoes oxidation. The I₂ so formed get absorbed in starch to give blue colour.

 $\begin{array}{c} 2\mathsf{I}^{-} & \longrightarrow 2\mathsf{e}^{-} \\ \hline \\ \hline \mathsf{C}\mathsf{l}_{2} + 2\mathsf{e}^{-} & \longrightarrow 2\mathsf{C}\mathsf{l}^{-} \\ \hline \\ \hline \mathsf{C}\mathsf{l}^{-} + 2\mathsf{I}^{-} & \longrightarrow \mathsf{I}_{2} + 2\mathsf{C}\mathsf{l}^{-} \end{array}$

- **Q.21** How many moles of electrons are needed for the reduction of 20 mL of 0.5M solution of KMnO₄ in acid medium ?
- A.21 Moles of $KMnO_4 = M \times V(L) = 0.5 \times 20 \times 10^{-3} = 10^{-2} [\because Mn7^+ + 5e^- \rightarrow Mn^{2+}]$ $\therefore 1 \text{ mol } KMnO_4 \text{ required} = 5 \text{ mol } e^ \therefore 10^{-2} \text{ mol } KMnO_4 \text{ required} = 5 \times 10^{-2} \text{ mol } e^-$
- Q.22 Which cells were used in te Apollo space program? What was the product used for?
- A.22 H,—O, fuel cell. The product H,O was used for drinking by the astronauts.
- Q.23 An aqueous solution of NaCl is electrolysed with inert electrodes. Write the equations for the reactions taking place at cathode and anode. What happens if NaNO₃(aq.) is used instead of NaCl ?
- A.23 For NaCl(aq.)anode : $2Cl^- \rightarrow Cl_2 + 2e^$ cathode : $2H^+ + 2e^- \rightarrow H_2$ For NaNO3 (aq.) anode : $2OH^- \rightarrow H_2O + 1/2 O_2 + 2e^$ cathode : $2H^+ + 2e^- \rightarrow H_2$

- Q.24 The value of μ[∞] for NH₄Cl, NaOH and NaCl are 129.8, 248.1 and 126.4 ohm⁻¹ cm² mol⁻¹ respectively. Calculate μ[∞] for NH₄OH solution.
- A.24 $\mu^{\infty}_{NH_4OH} = \mu^{\infty}_{NH_4Cl} + \mu^{\infty}_{NaOH} \mu^{\infty}_{NaCl} = 129.8 + 248.1 126.4 = 251.5 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
- Q.25 Given the standard electrode potentials ; K⁺/K = -2.93 V, Ag⁺/Ag = 0.80 V, Hg²⁺/Hg = 0.79 V, Mg²⁺/Mg = -2.37 V, Cr³⁺/Cr = -0.74V. Arrange these metals in their increasing order of reducing power.
- **A.25** More is E°RP, hence more is the oxidising power or more is the tendency to get reduced or lesser is reducing power. Ag < Hg < Cr < Mg < K
- Q.26 Iron does not rust even if zinc coating on its surface is broken but the same is not true when coating is of tin.
- A.26 Zn is more reactive than Fe, this implies that if a crack appears on the surface of Fe coated with Zn even then Zn will take part in the redox reaction and not Fe. In other words, Zn will be corroded in preference to Fe, but same is not in the case with Sn. It is less reactive than Fe, when a crack appears on the surface of Fe coated with Sn, then Fe will take part in the redox reaction and not Sn. Therefore, Fe will be corroded under these circumstances.
- Q.27 How will show that Faraday's second law of electrolysis is simply corollary of the first law.
- A.27 According to Faraday's first law of electrolysis. $w = Z \times Q$ If same quantity of electricity is passed through two electrolytes, i.e., $Q_1 = Q_2 = Q$, then In case of first electrolyte,

 $w_{_1}$ = $Z_{_1} \times Q$ and In case of second electrolyte, $w_{_2}$ = $Z_{_2} \times Q$

On diving
$$\frac{W_1}{W_2} = \frac{Z_1}{Z_2} = \frac{E_1 / 96500}{E_2 / 96500} = \frac{E_1}{E_2}$$

Where $\rm E_{1}$ and $\rm E_{2}$ are their equivalent masses

Q.28 Calculate the equilibrium constant for the reaction at 298 K $Zn(s) + Cu^{2+} (aq) \Longrightarrow Zn^{2+} (aq) + Cu(s)$ Given $E_{zn^{2+}/Zn}^{0} = -0.76V$ and $E_{Cu^{2+}/Cu}^{0} = +0.34V$

A.29 We know that
$$\log = \frac{nE_{cell}^0}{0.0591}$$

$$E_{cell}^{0} = \left[E_{cathode}^{0} - E_{anode}^{0}\right] = \left[(+0.34 \text{ V}) - (-0.76 \text{ V})\right] = 1.10 \text{ V}, \text{ n} = 2,$$

$$\log K_{c} = \frac{2 \times (1.10 \text{ V})}{(0.0591 \text{ V})} = 37.29 \implies K_{c} = \text{Antilog } 37.29 = 1.95 \times 1037$$

Q.30 Given that,
$$Co^{3+} + e^- \longrightarrow Co^{2+} E^\circ = + 1.82V$$

 $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$; $E^\circ = -1.23V$.
Explain why Co^{3+} is not stable in aqueous solutions

A.30 4
$$[Co^{+3} + e^{-} \longrightarrow Co^{2^+}]$$
; E° = + 1.82V
2H₂O $\longrightarrow O_2 + 4H^+ + 4e^-$; E° = - 1.23 V

E° for first reaction is positive, hence cell reaction is spontaneous. This implies Co³⁺ ions will take part in the reaction. Therefore, Co³⁺ is not stable.

Q.31 The measured e.m.f. at 25°C for the cell reaction, $Zn (s) + Cu^{2+} (1.0M) \longrightarrow Cu (s) + Zn^{2+} (0.1 M)$ is 1.3 volt Calculate E° for the cell reaction. **A.31** Using Nernst equation (at 298 K), $E_{cell} = E_{cell}^{0} - \frac{0.0591 V}{2} \log \frac{[Zn^{2+} (aq)]}{[Cu^{2+} (aq)]}$ Substituting the values $1.3V = E_{cell}^{0} - \frac{0.0591V}{2} \log \frac{0.1}{1.0} \Rightarrow 1.3V = E_{cell}^{0} - 0.02955 V \log 10^{-1}$ $1.3V = E_{cell}^{0} + 0.02955 V \log 10 \Rightarrow E_{cell}^{0} = 1.3 V - 0.02955 = 1.27 V$

Q.32 The resistance of a 0.01 N solution of an electrolyte was found to 210 ohm at 298 K using a conductivity cell with a cell constant of 0.88 cm⁻¹. Calculate specific conductance and equivalent conductance of solution

4.32 Given for 0.01 N solution. R = 210 ohm $\frac{\ell}{A} = 0.88 \text{ cm}^{-1}$ $\therefore K = \frac{1}{R} \times \frac{\lambda}{A} \Rightarrow K = \frac{1}{210} \times 0.88 = 4.19 \times 10^{-3} \text{ mho cm}^{-1}$ $\lambda_{eq} = \frac{k \times 1000}{N} \Rightarrow \lambda_{eq} = \frac{4.19 \times 10^{-3} \times 1000}{0.01} \Rightarrow \lambda_{eq} = 419 \text{ mho cm}^2 \text{eq}^{-1}$

Chapter Summary

• An electrochemical cell contains two electrodes (metallic conductors) in contact with an electrolyte.

An electrode and its electrolyte comprise an Electrode Compartment. Electrochemical Cells can be classified as:

- (i) Electrolytic Cells in which external source of current drives a non-spontaneous reaction
- (ii) Galvanic Cells which generates electricity as a result of a spontaneous cell reaction
- A voltic cell is a cell in which a spontaneous reaction generates an electric current.

In a galvanic cell, cathode is positive with respect to anode.

The salt-bridge having solution of strong ionic salts like KNO3, KCl, NaNO3, , NaCl etc., which is soaked in a colloidal soln of agar-agar gel which permits the movement of ions of salts only.

REPRESENTATION OF A CELL (IUPAC CONVENTIONS)

Anodic half-cell is written on left and cathodic half-cell on R.H.S.

 $Zn(s) | ZnSO_4 (sol) || CuSO_4 (sol) | Cu(s)$

The net reaction that occurs in the galvanic cell, it is called the cell reaction.. $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

- A metal and the solution develops definite potential difference between them. This potential difference is called electrode potential.
 - (i) Oxidation potential : When electrode is negatively charged w.r.t. solution, i.e., it acts as anode. Oxidation occurs. $M \rightarrow Mn^+ + ne^-$
 - (ii) Reduction potential : When electrode is positively charged w.r.t. solution. i.e., it acts as cathode. Reduction occurs. Mn+ + ne⁻ \rightarrow M
 - The magnitude of potential depends on the given below factors :
 - (i) Nature of the electrode
 - (ii) Concentration of the ion in solution
 - (iii) Temperature

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- Concept for Electromotive force (EMF) of a
 - $E_{cel}l = R.P.$ (Cathode) R.P. (Anode)

= R.P. (Cathode) + O.P (Anode)

• Electrolytic Cell : This cell changes EE to chemical energy. Electrolytic cell is defined to be the entire setup except external battery.

Electrolysis of molten sodium Chloride NaCl(molten) → Na+ + Cl-

rxns atanode (oxidation):cathode (reduction) $2Cl^- \rightarrow Cl^2$ (g) + 2e^- : $2Na^+ + 2e^- \rightarrow 2Na(l)$

• Relationship Between ∆G & Electrode Potential

	Reactions	$\Delta \mathbf{G}$	Е
1	Spontaneous	(-)	(+)
2	Non-spontaneous	(+)	(-)
3	Equilibrium	0	0

 Nernst Equation : aA + bB → cC + dD,

$$\mathsf{E}_{\text{cell}} = \mathsf{E}_{\text{cell}}^{o} - \frac{0.0591}{n} \text{log} \frac{\left[\mathsf{C}\right]^{c} \left[\mathsf{D}\right]^{d}}{\left[\mathsf{A}\right]^{a} \left[\mathsf{B}\right]^{b}}$$

 Concentration Cell : For such cell, E°_{cell} = 0.
 Electrode Gas concentration cell : For spontaneity of such cell reaction, p₁>p₂
 Electrolyte concentration cells: For spontaneity of such cell reaction, C₂>C₁

• Commercial Voltaic Cells :

After even recharging Primary batteries cannot be returned to their original state, so the battery is "dead" and must be discarded when the reactants are consumed,. Secondary batteries are also called rechargeable or storage batteries. The batteries can be recharged by reversing its reactions.

- The discharging process of the storage cell is based on the principles of electrochemical cell, whereas the charging process is based upon the principles of electrolytic cells.
- Faraday's laws of Electrolysis :
- **First law of electrolysis :** Amount of substance liberated or deposited at an electrode is proportional to value of charge passed (utilized) through the solution.
- **Second law of electrolysis :** The weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights, when same amount of charge is passed through different electrolyte solutions connected in series.
- i.e. $w_1 / w_2 = E_1 / E_2$

Conductance

Inverse of resistance is called as conductance and inverse of specific resistance is called as specific conductance.

$\mathsf{E}^{\mathsf{O}}_{\mathsf{cell}}$

• Equivalent Conductance

 $\mathsf{E}^{0}_{\mathsf{CO}^{2^{+}}|\mathsf{CO}}$

Molar Conductance

$${\sf E}^{0}_{{\sf C}e^{^{4+}}|{\sf C}e^{^{3+}}}$$

Relation between

- Kohlrausch's Law of Independent Migration of Ions
 - $\mathsf{E}^{0}_{\mathsf{CO}^{2+}|\mathsf{CO}}$