ELECTROCHEMISTRY
CONTENTS

JEE(Advanced) Syllabus

Electrochemical cells and cell reactions; Electrode potentials; Nernst equation and its relation to ΔG; Electrochemical series, emf of galvanic cells; Faraday's laws of electrolysis; Electrolytic conductance, specific, equivalent and molar conductance, Kohlrausch's law; Concentration cells.

JEE(Main) Syllabus

Electrolytic and metallic conduction, conductance in electrolytic solutions, specific and molar conductivities and their variation with concentration: Kohlrausch's law and its applications. Electrochemical cells-Electrolytic and Galvanic cells, different types of electrodes, electrode potentials including standard electrode potential, half-cell and cell reactions, EMF of a Galvanic cell and its measurement; Nernst equation and its applications; Relationship between cell potential and Gibbs' energy change; Dry cell and lead accumulator; Fuel cells; Corrosion and its prevention.

ELECTROCHEMISTRY

1.   SECTION (A) : GALVANIC CELL, ITS REPRESENTATION & SALT BRIDGE

1.1.   Introduction :

Batteries are everywhere in modern societies. They provide the electric current to start our automobiles and to power a host of products such as pocket calculator, digital watches, heart pacemaker, radio, and tape recorders.

Electrochemistry is the area of chemistry concerned with the interconversion of chemical energy and electrical energy. A battery is an electrochemical cell, a device for interconverting chemical and electrical energy. A battery takes the energy released by a spontaneous chemical reaction and uses it to produce electricity.

Electrochemical cell:
It is device for converting chemical energy in to electrical energy.

Electrochemical cell are of two types

Galvanic cells or Voltaic cell
● A spontaneous chemical reaction generates an electric current.

Electrolytic cell
● An electric current drives a nonspontaneous reaction.

Thus the two types of cells are reverse of each other.

1.2.   Construction/ Working principle

Whenever a metal strip is put in an electrolyte the process of oxidation and reduction takes place simultaneously within the system. Due to this there is a potential difference between the metal phase and the liquid phase.

On joining the metal strips through a wire (of negligible resistance) the current flows as long as the potential difference exists between the metal phase and the liquid phase.

I.   Anode:
Some metals (which are reactive) are found to have tendency to go into the solution phase when these are placed in contact with their ions or their salt solution.

For example: Zn rod is placed in $ZnSO_4$ solution.

Figure : 1   Figure : 2   Figure : 3

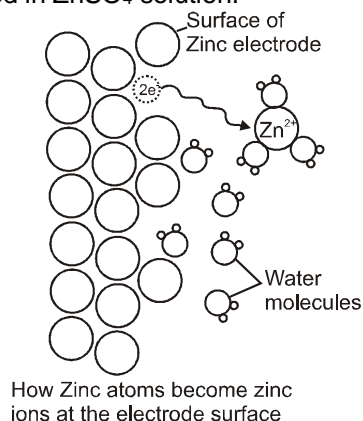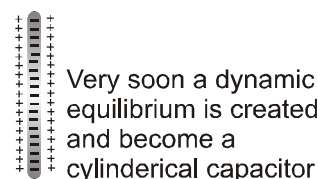| ![Resonance logo] Resonance® Educating for better tomorrow | **Reg. & Corp. Office :** CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.)– 324005
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Toll Free : 1800 258 5555 **| CIN :** U80302RJ2007PLC024029 | **ADVECH - 1** |
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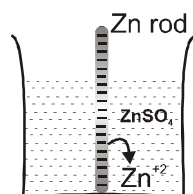
The Zn atom or metal atoms will move in the solution to form Zn^{+2}. After some time following equilibrium will be established. $Zn(s) \rightleftharpoons Zn^{2+} + 2e^-$

There will be accumulation of sufficient negative charge on the rod which will not allow extra zinc ions to move in the solution. i.e. solution will be saturated with Zn^{+2} ions.

The extra positive charge of the solution will be more concentrated around the negatively charged rod. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode potential.

This particular electrode is known as anode :

● On anode oxidation will take place. (Release of electron).

● To act as source of electrons.

● It is of negative polarity.

● The electrode potential is represented by $E_{Zn(s)/Zn^{2+}(aq)}$

II.   Cathode :

Copper ion shed its solvating water accepts two electron and become a netural copper of the electrode.

Very soon a dynamic equilibrium is created and it become a cylinderical capacitor

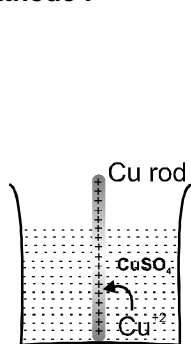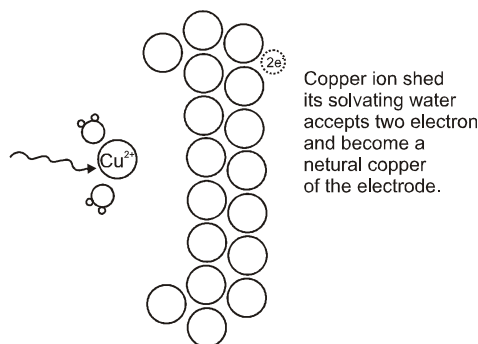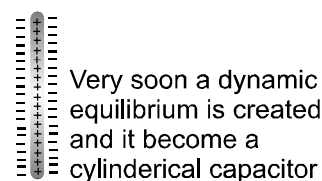**Figure : 1**   **Figure : 2**   **Figure : 3**

Some metals (Cu, Ag, Au etc.,) are found to have the opposite tendency i.e., when placed in contact with their aqueous ions, the ions from the solution will get deposited on the metal rod.

The following equilibrium will be established : $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$.

So rod will have deficiency of electron (positive charge). Extra negative charge will surround this positively charged rod and form double layer. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode potential. This will be known as cathode.
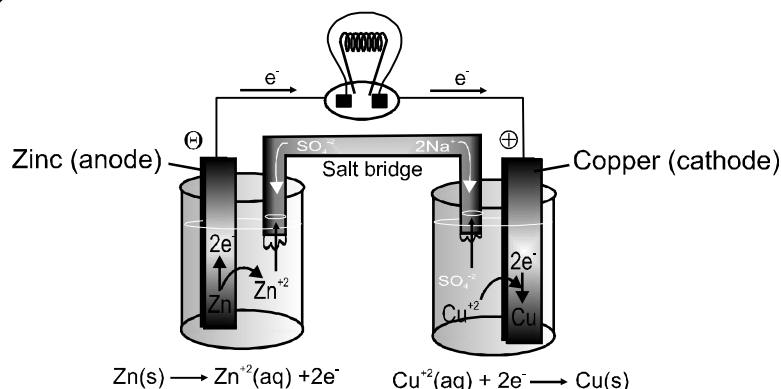
● At cathode reduction will take place. (Gain of e^- will take place)

● To act as sink of electron.

● Positive polarity will be developed.

● Their electrode potential can be represented by : $E_{Cu^{2+}(aq)/Cu(s)}$

Anode : $\begin{cases} \text{Is where oxidation occurs} \\ \text{Is where electrons are produced} \\ \text{Has a negative sign} \end{cases}$ **Cathode :** $\begin{cases} \text{Is where reduction occurs} \\ \text{Is where electrons are consumed} \\ \text{Has a positive sign} \end{cases}$

1.3.   Construction of Cell :

● It has two **half-cells, each** having a beaker containing a metal strip that dips in its aqueous solution.

● The metal strips are called **electrodes** and are connected by an conducting wire.

● Two solutions are connected by a **salt bridge.**

● The oxidation and reduction half reactions occur at a separate electrodes and electric current flows through the wire.

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

Selection of electrolyte for Salt Bridge :

- The electrolyte in salt bridge should be such that speed of its cation equals speed of its anion in electrical field.
- For that charge and sign of the ions should be almost equal. Transport number of cation = Transport number of anion

  or   Mobility of cation = Mobility of anion

  KCl is generally preferred but KNO_3 or NH_4NO_3 can also be used.
- If Ag^+, Hg_2^{2+}, Pb^{2+}, Tl^+ ions are present in a cell then in salt bridge KCl is not used because there can be formation of precipitate of $AgCl$, Hg_2Cl_2, $PbCl_2$ or $TlCl$ at mouth of tube which will prevent the migration of ions and its functioning will stop.
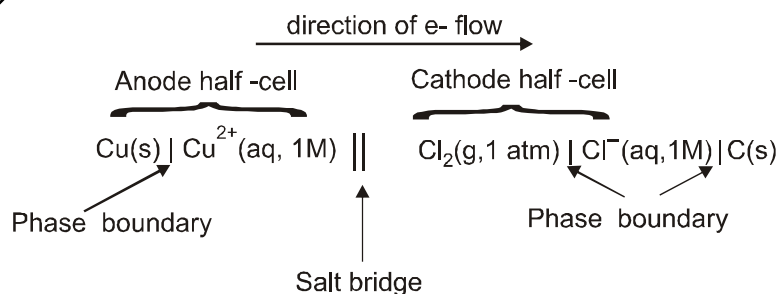
Functions of Salt Bridge :

- A **salt bridge** is a U–shaped inverted tube that contains a gel permeated with an inert electrolyte.
- It connects the solution of two half-cell to complete the circuit.
- It minimize the liquid junction potential. The potential difference between the junction of two liquids.
- It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current.
- "The simultaneous electrical neutrality of the anodic oxidation chamber and cathodic reduction chamber is due to same mobility or velocity of K^+ and NO_3^- ions taken into salt bridge.
- If the salt bridge is removed then voltage drops to zero.
- The ions of the inert electrolyte do not react with other ion in the solution and the ions are not oxidised or reduced at the electrodes.
- Generally tube is filled with a paste of agar-agar powder with a natural electrolyte/generally not common to anodic/cathodic compartment with porous plugs at each mouth of tube.
- It prevents mechanical mixing of two electrolytic solution.

Liquid-Liquid Junction Potential :

The potential difference which arises between two solutions (during the progress of reaction) when in contact with each other.

Shorthand Notation for Galvanic Cells

- We require two half cells to produce an electrochemical cell, which can be represented by following few rules;
- The anode half-cell is always written on the left followed on the right by cathode half-cell.
- The separation of two phases (state of matter) is shown by a vertical line.
- The various materials present in the same phase are shown together using commas.
- The salt bridge is represented by a double slash (||).
- The significant features of the substance viz. pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.
- For a gas electrode, the gas is indicated after the electrode for anode and before the electrode in case of cathode. (i.e. $Pt \, H_2/H^+$ or $H^+/H_2 \, Pt$)

direction of e- flow

Anode half -cell   Cathode half -cell

$Cu(s) \mid Cu^{2+}(aq, 1M) \parallel Cl_2(g, 1\ atm) \mid Cl^-(aq, 1M) \mid C(s)$

Phase boundary   Phase boundary

Salt bridge

Solved Example

Example 1.   Write short hand notation for the following reaction, $Sn^{2+}(aq) + 2Ag^+(aq) \longrightarrow Sn^{4+}(aq) + 2Ag(s)$.

Solution: The cell consists of a platinum wire anode dipping into an Sn^{+2} solution and a silver cathode dipping into an Ag^+ solution therefore $Pt(s) \mid Sn^{2+}(aq), Sn^{4+}(aq) \parallel Ag^+(aq) \mid Ag(s)$.

Example 2.   Write the electrode reaction and the net cell reaction for the following cells. Which electrode would be the positive terminal in each cell ?

(a) $Zn \mid Zn^{2+} \parallel Br^-, Br_2 \mid Pt$

(b) $Cr \mid Cr^{3+} \parallel I^-, I_2 \mid Pt$

(c) $Pt \mid H_2, H^+ \parallel Cu^{2+} \mid Cu$

(d) $Cd \mid Cd^{2+} \parallel Cl^-, AgCl \mid Ag$

Solution:

(a)   Oxidation half cell reaction, $Zn \longrightarrow Zn^{2+} + 2e^-$

Reduction half cell reaction, $Br_2 + 2e^- \longrightarrow 2Br^-$

Net cell reaction $Zn + Br_2 \longrightarrow Zn^{2+} + 2Br^-$ (Positive terminal : cathode Pt)

(b)   Oxidation half reaction, $[Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$

Reduction half reaction, $[I_2 + 2e^- \longrightarrow 2I^-] \times 3$

Net cell reaction $2Cr + 3I_2 \longrightarrow 2Cr^{3+} + 6I^-$ (Positive terminal : cathode Pt)

(c)   Oxidation half reaction, $H_2 \longrightarrow 2H^+ + 2e^-$

Reduction half reaction, $Cu^{2+} + 2e^- \longrightarrow Cu$

Net cell reaction $H_2 + Cu^{2+} \longrightarrow Cu + 2H^+$ (Positive terminal : cathode Cu)

(d)   Oxidation half reaction, $Cd \longrightarrow Cd^{2+} + 2e^-$

Reduction half reaction, $[AgCl + e^- \longrightarrow Ag + Cl^-] \times 2$

Net cell reaction $Cd + 2AgCl \longrightarrow Cd^{2+} + 2Ag + 2Cl^-$

(Positive terminal : cathode Ag)

2.   SECTION (B) : ELECTROCHEMICAL SERIES & ITS APPLICATIONS

2.1.   Electrode Potential :

●   The driving force that pushes the negative charge electrons away from the anode and pulls them towards the cathode is an electrical potential called **electromotive force** also known as **cell potential** or the **cell voltage.** Its unit is volt

●   The potential difference developed between metal electrode and its ions in solution in known as electrode potential.

●   Electrode potential depends upon :

   ○   Concentration of the solution.

   ○   Nature of the metal.

   ○   Nature of the electrolyte.

   ○   Pressure temperature conditions.

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- The potential difference developed between metal electrodes and the solution of its ions at 1 M concentration at 1 bar pressure and at a particular temperature is known as standard electrode potential.
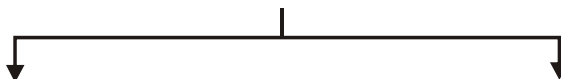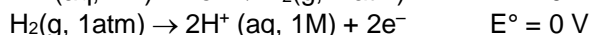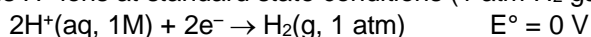
Oxidation Potential (O.P.)	Reduction Potential (R.P.)
The electrode potential for oxidation half reaction.	The electrode potential for reduction half reaction.
Tendency to get oxidised.	Tendency to get reduced.
Greater the O.P. then greater will be tendency to get oxidised.	**Greater the R.P. greater will be tendency to get reduced.**

	Type of Electrode	Electrode reaction in standard condition	Representation
1	Metal electrode (Zn electrode, Cu electrode etc.)	Reduction : $Zn^{2+} + 2e^- \rightarrow Zn(s)$	$E^0_{Zn^{2+}/Zn(s)}$ (SRP)
		Oxidation : $Zn(s) \rightarrow Zn^{2+} + 2e^-$	$E^0_{Zn(s)/Zn^{2+}}$ (SOP)
2	Hydrogen peroxide electrode	Reduction : $2e^- + 2H^+ + H_2O_2 \rightarrow 2H_2O$	$E^0_{H_2O_2/H_2O}$
		Oxidation : $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	$E^0_{H_2O_2/O_2}$
3	Redox electrode	Reduction : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	$E^0_{MnO_4^-/Mn^{2+}}$
4	Metal-Metal insoluable salt electrode	Reduction : $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$	$E^0_{AgCl(s)/Ag(s)/Cl^-}$
		Oxidation : $Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$	$E^0_{Ag(s)/AgCl(s)/Cl^-}$

2.2. Reference electrode :

- The potential of a single electrode cannot be determined what were the potential difference between two electrodes can be accurately measured using a reference electrode.
- An electrode is chosen as a reference with respect to which all other electrodes are valued.
- Standard Hydrogen Electrode **(SHE)** is taken as standard reference electrode. Its electrode potential is arbitrarily assumed to be 0.00 volt.
- Standard Hydrogen Electrode **(SHE)** consists of a platinum electrode in contact with H_2 gas and aqueous H^+ ions at standard state conditions (1 atm H_2 gas, 1 M H^+ (aq),).

  $2H^+(aq, 1M) + 2e^- \rightarrow H_2(g, 1 atm)$ $E° = 0$ V

  $H_2(g, 1atm) \rightarrow 2H^+ (aq, 1M) + 2e^-$ $E° = 0$ V

2.3. Cell potential :

- The difference in electrode potentials of the two half cell reactions (oxidation half cell and reduction half cell) is known as emf of the cell or cell potential.

  The emf of the cell or cell potential can be calculated from the values of electrode potential of the two half cell constituting the cell. The following three method are in use:
- When oxidation potential of anode and reduction potential of cathode are taken into account:

  $E°_{cell}$ = oxidation potential of anode + reduction potential of cathode

       $= E°_{ox}(anode) + E°_{red}(cathode)$
- When reduction potential of both electrodes are taken into account :

  $E°_{cell}$ = Reduction potential of cathode – Reduction potential of anode

       $= E°_{cathode} – E°_{anode}$ both are reduction potential.
- When oxidation potential of both electrodes are taken into account :

  $E°_{cell}$ = oxidation potential of anode – Oxidation potential of cathode

       $= E°_{ox} (anode) – E°_{ox} (cathode)$

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- The standard cell potential E° is the cell potential when both reactants and products are in their standard states–solutes at 1 M concentration, gases at a partial pressure of 1 atm, solids and liquids in pure from, with all at a specified temperature, usually 25° C.
- E°$_{cell}$ is intensive property so on multiplying/Dividing cell reaction by any number, the E°$_{cell}$ value would not change.

Calculation of electrode potential :

At Anode

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

- Oxidation potential O.P. = $E_{H_2(g)/H^+(aq.)}$
- Under standard state
- $E^0_{H_2(g)/H^+(aq.)}$ = SOP

At Cathode

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

- Reduction Potential (R.P.) $E_{H^+/H_2(g)}$ = RP
- Under standard state.
- $E^0_{H^+/H_2(g)}$ = SRP

Hydrogen Electrode
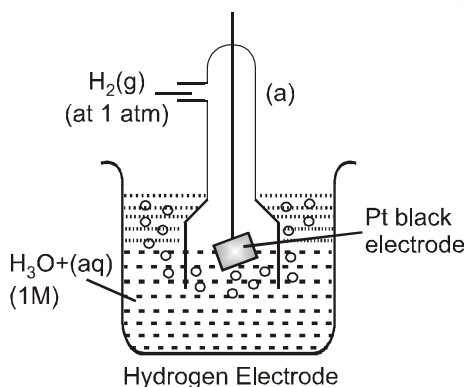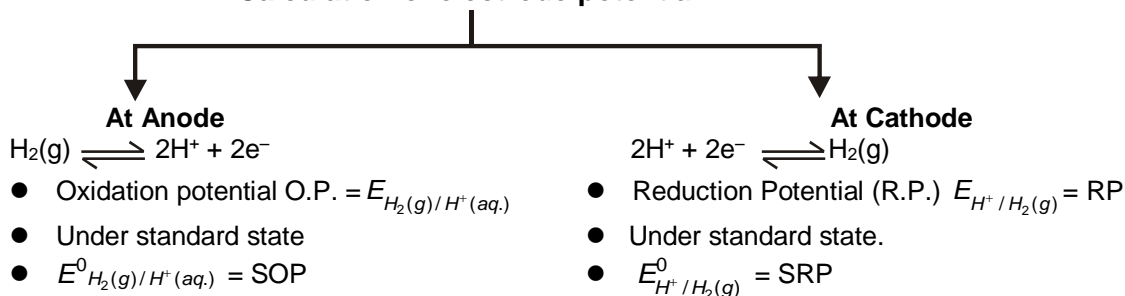
- For SHE reference potential is taken to be zero at all temperature.

    SOP = – SRP = 0 for SHE.

- To calculate standard potential of any other electrode a cell is coupled with standard hydrogen electrode (SHE) and its potential is measured that gives the value of electrode potential of that electrode.

    Anode   :   Zinc electrode

    Cathode :   SHE

    Cell   :   Zinc electrode || SHE

    Cell potential :

    $E_{cell} = E_{H^+/H_2(g)} - E°_{Zn^{2+}/Zn}$

    = 0.76 V (at 298 K experimentaly)

    So, $E^0_{Zn^{2+}/Zn} = -0.76$ V (SRP)

    $E^0_{Zn/Zn^{2+}(aq)} = 0.76$ V(SOP)

A galvanic cell measuring the Zn^{2+} |Zn half-cell potential
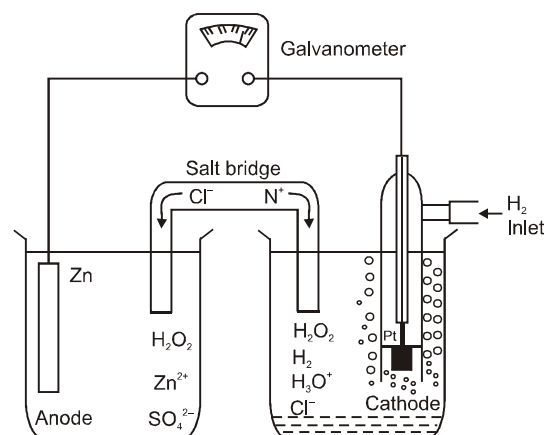
- So, w.r.t. H$_2$, Zn has greater tendency to get oxidised.

In similar manner reduction potentials (SRP) at 298 K for many other electrodes are calculated and are arranged in a series increasing order known as electrochemical series.

Electrochemical Series :

	Electrode	Reaction	SRP (at 298 K)
	*Li	$Li^+ + e^- \rightarrow Li(s)$	– 3.05 V
	K	$K^+ + e^- \rightarrow K(s)$	– 2.93 V
	Ba		
	Ca	$Ca^{+2} + 2e^- \rightarrow Ca(s)$	– 2.87 V
	Na	$Na^+ + e^- \rightarrow Na(s)$	– 2.71 V
	Mg	$Mg^{+2} + 2e^- \rightarrow Mg(s)$	– 2.37 V
	Al		
	* Electrolytes (H_2O)	$H_2O(l) + e^- \rightarrow \frac{1}{2}H_2 + OH^-$	– 0.828 V
	*Zn	$Zn^{+2} + 2e^- \rightarrow Zn(s)$	– 0.76 V
	Cr	$Cr^{+3} + 3e^- \rightarrow Cr(s)$	– 0.74 V
	*Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	– 0.44 V
	Cd	$Cd^{+2} + 2e^- \rightarrow Cd(s)$	– 0.40 V
	Co		
	Ni	$Ni^{+2} + 2e^- \rightarrow Ni(s)$	– 0.24 V
	Sn	$Sn^{+2} + 2e^- \rightarrow Sn(s)$	– 0.14 V
	Pb	$Pb^{+2} + 2e^- \rightarrow Pb(s)$	– 0.13 V
	*H_2	$2H^+ + 2e^- \; H_2(g)$	0.00 V
	Cu	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34 V
	I_2		
	Fe	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77 V
	Hg	$Hg_2^{2+} + 2e^- \rightarrow Hg(l)$	0.79 V
	Ag	$Ag^+ + e^- \rightarrow Ag$	
	Hg	$Hg^{2+} \rightarrow Hg(l)$	
	Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	1.06 V
	* Electrolytes	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O(\ell)$	1.23 V
	*	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$	1.33 V
	*	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36 V
	*	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51 V
	*	$F_2 + 2e^- \rightarrow 2F^-$	2.87 V

Increasing strength of reducing agent (left vertical arrow, pointing up)

Increasing strength of oxidising agent (right vertical arrow, pointing down)

Solved Examples

Example 1. Calculate E^0_{cell} of (at 298 K), Zn(s) / ZnSO₄(aq) || CuSO₄(aq) / Cu(s)
Given that $E^0_{Zn/Zn^{2+}(aq)} = 0.76$ V, $E^0_{Cu(s)/Cu^{2+}(aq)} = -0.34$ V

Solution: $E^0_{cell} = (S.R.P)_{cathode} - (S.R.P)_{anode}$
$= 0.34 - (-0.76) = 1.1$ V

Example 2. Given the cell Ag AgCl(s) | NaCl (0.05 M) || Ag NO₃ (0.30 M) | Ag
(a) Write half reaction occurring at the anode.
(b) Write half reaction occurring at the cathode.
(c) Write the net ionic equation of the reaction.
(d) Calculate E^0_{cell} at 25°C.
(e) Does the cell reaction go spontaneous as written ?
(Given $E°_{AgCl,Cl} = +0.22$ volt) ; $E^0_{Ag^+/Ag} = +0.80$ volt)

Solution: (a) LHS electrode is anode and half reaction is oxidation.
$Ag^+ + Cl^- \longrightarrow AgCl(s) + e^-$ ... (i)
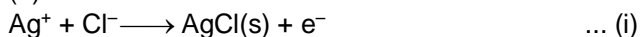
(b) RHS electrode is cathode and half reaction is reduction.

$Ag + e \longrightarrow Ag(s)$ ... (ii)

(c) From equation (i) and (ii) cell reaction is : Cl^- (0.05 M) + Ag^+ (0.30 M) AgCl(s)

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

     = (0.80 – 0.22 volt = 0.58 volt

(e) Yes, the e.m.f. value is positive, the reaction will be spontaneous as written in the cell reaction.

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3.   SECTION (C) : CONCEPT OF ΔG

3.1.   Free energy changes for cell reaction :

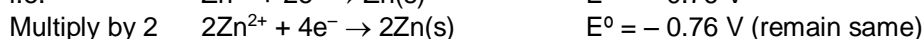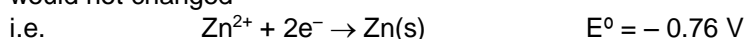- The free energy change ΔG (a thermochemical quantity) and the cell potential E(an electrochemical quantity) both measure the driving force of a chemical reaction.
- The values of ΔG and E are directly proportional and are related by the equation,

       ΔG = –nFE

where   n = Number of moles of electron transferred in the reaction.

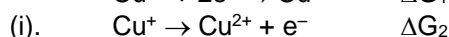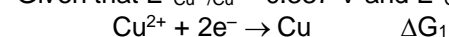   F = Faraday constant = 96485 C/mole e⁻ 96500 C/mole e⁻

- **Calculation of Electrode Potential of unknown electrode with the help of given (two) electrode.**
- Obtain the reaction of the 3ʳᵈ electrode with the help of some algebraic operations on reactions of the given electrodes.
- Then calculate ΔG⁰ of the 3ʳᵈ reaction with the help of some algebaric operations of ΔG⁰ of 1ˢᵗ and 2ⁿᵈ reactions.
- Use ΔG⁰ = –nF E⁰_elec. to calculate unknown E.P.
- E^0_{cell} is intensive property so if we multiply/Divide electrode reaction by any number the E^0_{cell} value would not changed

   i.e. $Zn^{2+} + 2e^- \rightarrow Zn(s)$ E^0 = – 0.76 V

   Multiply by 2 $2Zn^{2+} + 4e^- \rightarrow 2Zn(s)$ E^0 = – 0.76 V (remain same)

Solved Example

Example 1.   Given that $E^0_{Cu^{2+}/Cu}$ = 0.337 V and $E^0_{Cu^+/Cu^{2+}}$ = – 0.153 V. Then calculate $E^0_{Cu^+/Cu}$.

Solution: $Cu^{2+} + 2e^- \rightarrow Cu$ ΔG_1

        (i). $Cu^+ \rightarrow Cu^{2+} + e^-$ ΔG_2

        After adding $Cu^+ + e^- \rightarrow Cu$

                 $\Delta G_1 + \Delta G_2 = \Delta G_3$

                 $-2F\ E^0_1 - F\ E^0_2 = -F\ E^0_3$

                 $E_3 = 2\ E^0_1 + E^0_2$ = 2 × 0.337 – 0.153 = 0.674 – 0.153 = 0.521 V

Example 2. $E^0_{Mn^{2+}/MnO_4^-}$ = –1.51 V   ; $E^0_{MnO_2/Mn^{+2}}$ = + 1.23 V

           $E^0_{MnO_4^-/MnO_2}$ = ?   (All in acidic medium)

Solution: $4H_2O + Mn^{2+} \rightarrow Mn\ O_4^- + 8H^+ + 5e^-$ ΔG_1

        (i). $Mn\ O_4^- + 8H^+ + 5e^- \rightarrow 4H_2O + Mn^{2+}$ $-\Delta G_1$

              $2e^- + MnO_2 + 4H^+ \rightarrow Mn^{2+} + 2H_2O$ ΔG_2

        (ii). $2H_2O + Mn^{2+} \rightarrow MnO_2 + 4H^+ + 2e^-$ $-\Delta G_2$

        (iii). $4H^+ + Mn\ O_4^- + 3e^- \rightarrow MnO_2 + 2H_2O$ ΔG_3

           (i) + (ii) = (iii)
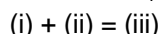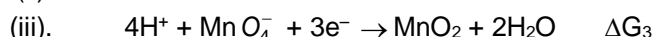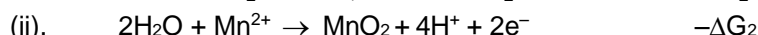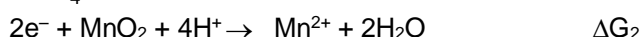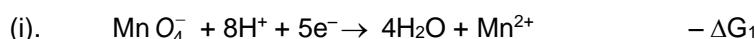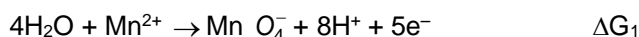
           $\Delta G_3 = -\Delta G_1 - \Delta G_2$

           $-3E_3F = 5\ E^0_1\ F + 2\ E^0_2\ F$

           $E = \dfrac{-[5E_1 + 2E_2]}{3} = \dfrac{-[5(-1.51) + 2(1.23)]}{3} = \dfrac{-[-7.55 + 2.46]}{3} = \dfrac{+5.09}{3}$ = 1.69 V

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Example 3. Will Fe^{2+} disproportionate or not

$$Fe^{3+} \xrightarrow[\text{anode}]{0.77\,V} Fe^{2+} \xrightarrow[\text{cathode}]{-0.44\,V} Fe$$

-0.036
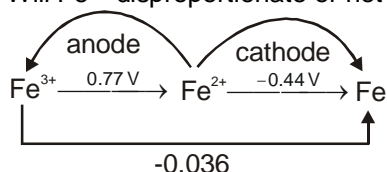
Solution: This is known as **latimer diagram.**
S.R.P to right of the species greater than SRP of it's left species will undergo disproportionation.

4. SECTION (D) : NERNST EQUATION & ITS APPLICATIONS (INCLUDING CONCENTRATION CELLS)

4.1. Nernst Equation :

- Cell potentials depend on temperature and on the composition of the reaction mixtures.
- It depends upon the concentration of the solute and the partial pressure of the gas, if any.
- The dependence upon the concentration can be derived from thermodynamics.
  From thermodynamics
  $\Delta G = \Delta G° + RT \ln Q$
  $- nFE = - nFE° + 2.303\,R\,T \log Q$

  $E = E° - \dfrac{2.303RT}{nF} \log Q$

  Take $T = 298\,K$, $R = 8.314\,J/mol\,K$, $F = 96500\,C$

  Now we get, $E = E° - \dfrac{0.059}{n} \log Q$

  Where n = number of transfered electron, Q = reaction quotient
- Nernst equation can be used to calculate cell potentials for non standard conditions also.
- Nernst equations can be applied to half cell reactions also.

4.2. Applications of Nernst equation

- **Nernst Equation for Electrode Potential**

  $$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$
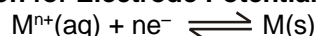
  $$E_{Redn} = E_{red}^0 - \dfrac{RT}{nF} \ell n \left[\dfrac{M(s)}{M^{n+}} \right]$$

  $$E_{Redn} = E_{red}^0 - \dfrac{2.303\,RT}{nF} \log \left[\dfrac{M(s)}{M^{n+}} \right]$$

  At 298K, $\quad E_{Redn} = E_{Re\,d^n}^0 - \dfrac{0.059}{n} \log \left[\dfrac{1}{M^{n+}} \right]$

- **Hydrogen Electrode**

  $$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$$
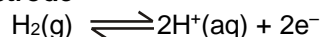
  $$E = E^0 - \dfrac{0.0591}{2} \log \left[\dfrac{(H^+)^2}{P_{H_2}} \right]$$

- **Metal–metal soluble salt electrode.**

  $$Zn^{2+} + 2e^- \rightarrow Zn(s)$$
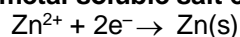
  $$E_{Redn} = E_{Re\,d^n}^0 - \dfrac{2.303\,RT}{nF} \log \left(\dfrac{1}{Zn^{+2}} \right) \text{ at 298K}$$

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$$E_{Redn} = E_{red}^0 - \frac{0.059}{2} \log \left(\frac{1}{Zn^{+2}} \right)$$

- **Gas – electrode Hydrogen electrode.**

$$2H^+ + 2e^- \rightarrow H_2(g)$$
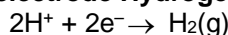
$$E_{Redn} = E_{Red^n}^0 - \frac{0.059}{2} \log \left(\frac{P_{H_2}}{[H^+]^2} \right)$$

- **Redox electrode**

$$4H_2O + Mn^{2+} \rightarrow MnO_4^- + 8H^+ + 5e^-$$

$$E_{OX} = E_{ox}^0 - \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{+2}]}$$

Solved Examples

Example 1. Calculate R.P. of hydrogen electrode at 298K which is prepared with the help of aq. solution of acetic acid with 0.1 M concentration at 1 atm pressure Ka = 1.8×10^{-5}.

Solution: $[H^+] = \sqrt{Ka \times c} = \sqrt{1.8 \times 10^{-5} \times 10^{-1}} = \sqrt{1.8 \times 10^{-6}}$

$$2H^+ + 2e^- \rightarrow H_2$$

$$E_{Redn} = E_{red}^0 - \frac{0.059}{2} \log \frac{P_{H_2}}{[H^+]^2} \qquad (E^0{}_{Redn} = 0)$$

$$E_{Redn} = -\frac{0.059}{2} \log \left(\frac{1}{1.8 \times 10^{-6}} \right) = -\frac{0.059}{2} [6 - \log (1.8)]$$

$$E_{Redn} = -\frac{0.059}{2} \times 5.74 = -0.169 \text{ V}$$

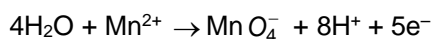**Example 2.** Which is stronger oxidizing agent
(i) $K_2Cr_2O_7$ in solution in which $[Cr_2O_7{}^{2-}] = 0.1$ M, $[Cr^{3+}] = 10^{-2}$ M and $[H^+] = 10^{-1}$ M
(ii) $KMnO_4$ in a solution in which $[MnO_4^-] = 10^{-1}$M, $[Mn^{2+}] = 10^{-2}$M, $[H^+] = 10^{-2}$ M
$E^0{}_{Cr_2O_7{}^{2-}/Cr^{+3}} = 1.33$ V $E^0{}_{MnO_4^-/Mn^{+2}} = 1.51$ V

Sol.

(i) $14H^+ + Cr_2O_7{}^{2-} \rightarrow 2Cr^{+3} + 7H_2O + 6e^-$
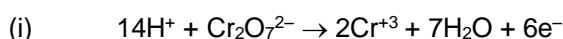
$$E_{Redn} = 1.33 - \frac{0.059}{6} \log \left[\frac{10^{-4} \times 10}{10^{-14}} \right] = 1.33 - \frac{0.059}{6} \times 11$$

$$E_{Redn} = 1.33 - \frac{0.649}{6} = 1.330 - 0.108 = 1.222 \text{ V}$$

(ii) $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

$$E_{Redn} = 1.51 - \frac{0.059}{5} \log \left[\frac{10^{-2}}{10^{-16} \times 10^{-1}} \right] = 1.51 - 0.059 \times 3 = 1.51 - 0.18 = 1.33 \text{ V}$$

E_{Redn} is more so, good oxidising agent

4.3. Nernst Equation for cell Potential :

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

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln Q$$

n – no. of electrons which gets cancelled out while making cell reaction.

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Equilibrium in electrochemical cell

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

$$\mathbf{\Delta G = - nF \, E_{cell}}$$

From thermodynamics

$$\Delta G = \Delta G^0 + RT\ell nQ$$

at chemical equilibrium $\Delta G = 0$

$E_{cell} = 0 \rightarrow$ cell will be of no use

so, $\Delta G^0 = - RT\ell n \, K_{eq}$

at equilibrium $- nF \, E^0_{cell} = -2.303 \, RT \log (K_{eq})$

$$\log K_{eq} = \frac{nF}{2.303 \; RT} \, E^0_{cell}$$

at 298 K and R = 8.314 J/mol K

$$\log K_{eq} = \frac{n}{0.059} \, E^0_{cell}$$

Solved Examples

Example 1. Calculate E_{cell} of Pt(s) $\begin{vmatrix} Cl_2(g) \\ 0.1 \ atm \end{vmatrix} \begin{vmatrix} Cl^-(aq) \\ 10^{-2}M \end{vmatrix} \begin{vmatrix} Cr_2O_7^{2-}, Cr^{+3} (in \ H_2SO_4) = 0.05M \\ 0.01 \ M \qquad\qquad 0.1 \ M \end{vmatrix}$ Pt

Given that $E^0_{Cr_2O_7^{2-}/Cr^{+3}}$ = 1.33 V ; $E^0_{Cl^-/Cl_2}$ = −1.36 V

Sol. $6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$

$[2Cl^- \rightarrow Cl_2 + 2e^-] \times 3$

$14H^+ + 6Cl^- + Cr_2O_7^{2-} \rightarrow 3Cl_2 + 2Cr^{+3} + 7H_2O$
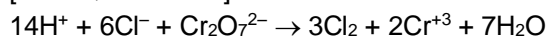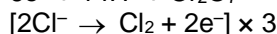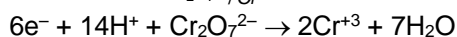
E^0_{cell} = 1.33 − (+1.36) = − 0.03

$$E_{cell} = - 0.03 - \frac{0.059}{6} \ \log \frac{[Cr^{3+}]^2[P_{Cl_2}]^3}{[H^+]^{14}[Cl^-]^6[Cr_2O_7^{2-}]} = - 0.03 - \frac{0.059 \times 23}{6}$$

E_{cell} = − 0.26 V

Example 2. The E°$_{cell}$ for the reaction Fe + Zn^{2+} $\rightleftharpoons$ Zn + Fe^{2+}, is − 0.32 volt at 25°C. What will be the equilibrium concentration of Fe^{2+}, when a piece of iron is placed in a 1 M Zn^{2+} solution ?

Sol. We have the Nernst equation at equilibrium at 25°C

$$E° = \frac{0.0591}{n} \log K \qquad\qquad\qquad ... (i)$$

Since E°$_{Cell}$ for the given reaction is negative, therefore, the reverse reaction is feasible for which E°$_{cell}$ will be + 0.32 V, Thus for

Zn	+	Fe^{2+}	$\rightleftharpoons$	Fe	+	Zn^{2+}	;	E°$_{Cell}$ + 0.32 V
−		x		−		(1–x)		
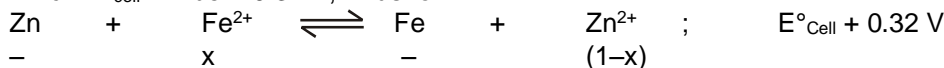
Now, $E° = \dfrac{0.0591}{n} \log \dfrac{[Zn^{2+}]}{[Fe^{2+}]}$ or $0.32 = \dfrac{0.0591}{2} \log \dfrac{[Zn^{2+}]}{[Fe^{2+}]}$

$\log = \dfrac{[Zn^{2+}]}{[Fe^{2+}]} - 10.829$ Taking antilog,

$[Fe^{2+}] = 1.483 \times 10^{-11}$ M

4.4. Work done by a cell :

(i) Let 'n' faraday charge be taken out of a cell of EMF 'E'; then work done by the cell will be calculated as :
work = Charge × Potential = nFE

(ii) Work done by cell = Decrease in free energy
so $- \Delta G = nFE$ or $W_{max} = + nFE°$ where E° is standard EMF of the cell.

Solved Examples

Example 1. Calculate the maximum work that can be obtained from the Daniel cell given below -
Zn(s) | Zn^{2+} (aq) || Cu^{2+} (aq) | Cu (s). Given that $E^0_{Zn^{2+}/Zn}$ = – 0.76 V and $E^0_{Cu^{2+}/Cu}$ = + 0.34 V.

Solution: Cell reaction is : Zn(s) + Cu^{2+} (aq) $\longrightarrow$ Cu(s) + Zn^{2+} (aq) Here n = 2
$E^0_{cell} = E^0_{cathode} - E^0_{anode}$ (On the basis of reduction potential)
= + 0.34 – (0.76) = 1.10 V
We know that :
$W_{max} = \Delta G^0 = - nFE^0$
= – (2 mol) × (96500 C mol) × (1.10 V) = – 212300 C.V. = – 212300 J
or W_{max} = – 212300 J

4.5. Concentration cells :

- A concentration cell consists of two electrodes of the same material, each electrode dipping in a solution of its own ions and the solution being at different concentrations.
- The two solutions are separated by a salt bridge.
e.g. Ag(s) | Ag$^+$ (a$_1$) || Ag$^+$ (a$_2$) | Ag(s) $\longrightarrow$ (a$_1$ < a$_2$) a$_1$, a$_2$ are concentrations of each half cell
At LHS electrode anode : Ag (s) $\longrightarrow$ Ag$^+$(a$_1$) + e$^-$
At RHS electrode cathode : Ag$^+$(a$_2$) + e$^-$ $\longrightarrow$ Ag(s)
The net cell reaction is : Ag$^+$ (a$_2$) $\longrightarrow$ Ag$^+$ (a$_1$)
The nernst eq. is

$$E_{cell} = - \frac{0.059}{n} \log \frac{a_1}{a_2} \text{ (Here n = 1, Temp, 298 K)}$$

- Likewise, the e.m.f. of the cell consisting of two hydrogen electrodes operating at different pressure P_1 and P_2 ($P_1 > P_2$) and dipping into a solution HCl is :

$$E_{cell} = \frac{0.059}{2} \log \frac{P_1}{P_2} \text{ (at 298 K)}$$

5. SECTION (E) : ELECTROLYSIS

5.1. Electrolysis & Electrolytic cell :

Electrolysis :
- Electrolyte is a combination of cations and anions which in fused state or in aqueous solution can conduct electricity.
- This is possible due to the movement of ions from which it is made of.
- The process of using an electric current to bring about chemical change is called electrolysis.
- Electrolysis is a process of oxidation and reduction due to current in the electrolytic solution.
- The product obtained during electrolysis depends on following factors.
○ The nature of the electrolyte
○ The concentration of electrolyte
○ The charge density flowing during electrolysis.
○ The nature of the electrode

5.2. Active vs Inactive electrodes :

- The metal electrodes in the cell that are active, because the metals themselves are components of the half reactions.
- As the Daniel cell operates, the mass of the zinc electrode gradually decreases, and the [Zn^{2+}] in the anode half – cell increases. At the same time, the mass of the copper electrode increases and the [Cu^{2+}] in the cathode half – cell decreases; we say that the Cu^{2+} "plates out" on the electrode.

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- For many redox reactions, however, there are no reactants or products capable of serving as electrodes. Inactive electrodes are used, most commonly rods of graphite or platinum, materials that conduct electrons into or out of the cell but cannot take part in the half -reactions.
- In a voltaic cell based on the following half reactions, for instance, the species cannot act as electrodes:

$$2I^-(aq) \longrightarrow I_2(s) +2e^- \text{ [anode ; oxidation]}$$
$$MnO_4^- (aq) + 8H^+ (aq) + 5e^- \longrightarrow Mn^{2+} (aq) + 4H_2O(\ell) \text{ [cathode ; reduction]}$$
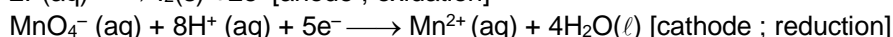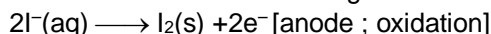
  Therefore, each half–cell consists of inactive electrodes immersed in an electrolyte solution that contains all the species involved in that half -reaction. In the anode half-cell, I^- ions are oxidized to solid I_2. The electrons released flow into the graphite anode, through the wire, and into the graphite cathode. From there, the electrons are consumed by MnO_4^- ions as they are reduced to Mn^{2+} ions.

  Examples of Electrolysis

- Using inert (Pt/graphite) electrodes.

Cathode (red):	$Pb^{2+} + 2e^- \rightarrow Pb(s)$	$E^0 = 0.126V$
Anode :	$2Br^- \rightarrow Br_2 + 2e^-$	$E^0 = -1.08$ V

  $$E_{cell} = -0.126 - (0.108) \times 10 = -1.206 \text{ V}$$
  $$E_{ext} > 1.206 \text{ V}$$

- Electrolysis of $CuSO_4$ molten

Cathode :	$Cu^{2+} + 2e^- \rightarrow Cu$	$E^0 = +0.34$ V
Anode :	$2 SO_4^{2-} \rightarrow S_2 O_8^{2-} + 2e^-$	$E^0 = -2.05$ V

  $H_2S_2O_8$ – Marchall's acid peroxy disulphuric acid.

  $$E_{cell} = 0.34 - (2.05) = -1.71 \text{ V (negative } \therefore \text{ not feasible)}$$

- Electrolysis of aq $CuSO_4$

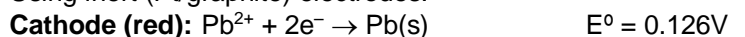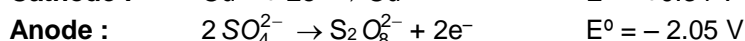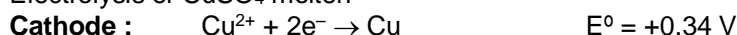 | | | |
  |---|---|---|
  | **Cathode :** | $Cu^{2+} + 2e^- \rightarrow Cu(s)$ | $E^0 = 0.34$ V |
  | | $2e + 2H_2O(\ell) \rightarrow H_2(g) + 2OH^-(aq)$ | $E^0 = -0.83V$ |
  | **Anode :** | $2 SO_4^{2-} \rightarrow S_2 O_8^{2-} + 2e^-$ | $E^0 = -2.05$ V |
  | | $2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$ | $E^0 = -1.23$ V |
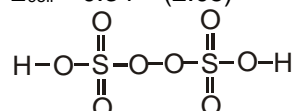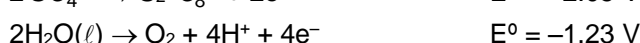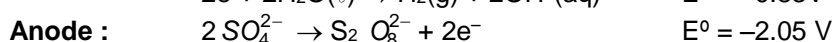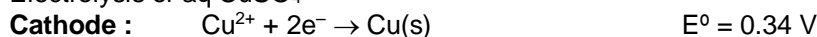
- Electrolysis of aq NaBr solution (initially PH = 7)

Cathode :	$Na^+(aq) + e^- \rightarrow Na(s)$	$E^0 = -2$ V
	$2e^- + 2H_2O(\ell) \rightarrow H_2 + 2OH^-$	$E^0 = -0.83$ V
Anode :	$2Br^- \rightarrow Br_2 + 2e^-$	$E^0_{OX} = -1.08$ V
	$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$	$E^0_{OX} = -1.23$ V

- Electrolysis of aq NaCl

Cathode :	$Na^+ + e^- \rightarrow Na$	$E^0 = -2V$
	$2e^- + 2H_2O(\ell) \rightarrow H_2(g) + 2OH^-$	$E^0 = -0.83$ V
Anode :	$2Cl^- \rightarrow Cl_2 + 2e^-$	$E^0_{OX} = -1.30$ V
	$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$	$E^0_{OX} = -1.23$ V
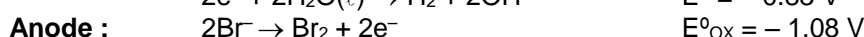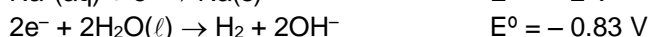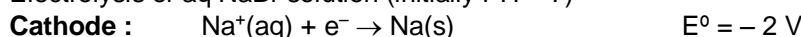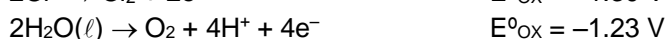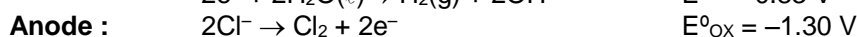
  Rate of production of Cl_2 is more than rate of production of O_2 gas.

- Electrolysis of CH_3COONa

Cathode :	$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$	
Anode :	$2CH_3COO^- \rightarrow 2CO_2 + C_2H_6 + 2e^-$	
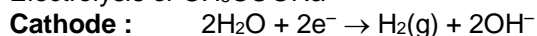
Note : According to thermodynamics, oxidation of H_2O to produce O_2 should take place on anode but experimentally (experiment from chemical kinetics) the rate of oxidation of water is found to be very slow. To increase its rate, the greater potential difference is applied called over voltage or over potential but because of this oxidation of Cl^- ions also become feasible and this takes place on anode.

5.3. Electrolysis using attackable (reactive) electrodes.

- Electrolysis of aq. $CuSO_4$ using Cu electrode.

Cathode (reduction) :	$Cu^{2+} + 2e^- \rightarrow Cu$	$E^0 = +0.34$ V
	$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-$	$E^0 = -0.83$ V
Anode (oxidation) :	$SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$	$E^0_{OX} = -2.05$ V
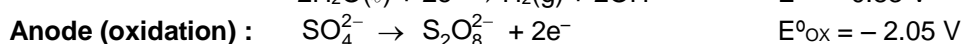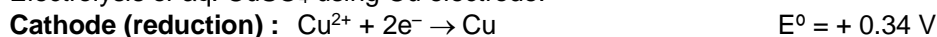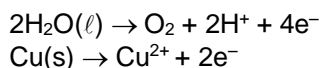
$2H_2O(\ell) \rightarrow O_2 + 2H^+ + 4e^-$		$E^0 = 1.23$ V
$Cu(s) \rightarrow Cu^{2+} + 2e^-$		$E^0 = -0.34$ V

Electrolytic refining

- $AgNO_3(aq)$ using Cu cathode & Ag anode.

Cathode : $Ag^+ + e^- \rightarrow Ag(s)$ $E^0 = 0.8$ V

                   $2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^0 = -0.83$ V

Anode : $NO_3^- \rightarrow X$ (No reaction)

                   $2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$ $E^0 = -1.23$ V

                   $Ag(s) \rightarrow Ag^+(aq) + e^-$ $E^0 = -0.80$ V
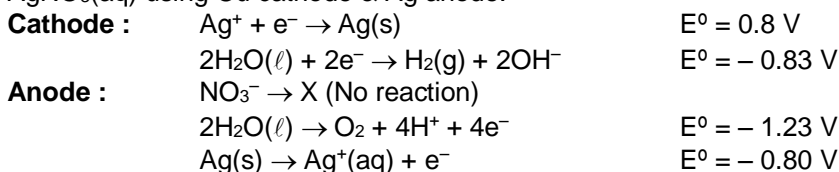
6.   SECTION (F) : FARADAY LAWS & ITS APPLICTIONS

6.1.   Faraday's Law of Electrolysis :

- **1st Law :** The mass deposited/released/produced of any substance during electrolysis is proportional to the amount of charge passed into the electrolyte.

$$W \propto Q$$
$$W = ZQ$$

Z – electrochemical equivalent of the substance.

Unit of Z = $\dfrac{mass}{coulomb}$ = Kg/C or g/C

Z = Mass deposited when 1 C of charge is passed into the solution.

Equivalent mass (E) : mass of any substance produced when 1 mole of e^- are passed through the solution during electrolysis.

$$E = \frac{\text{Molar mass}}{\text{no. of } e^- \text{ involved in oxidation / reduction}}$$

e.g. $Ag^+ + e^- \rightarrow Ag$ $E = \dfrac{M}{1}$

         $Cu^{2+} + 2e^- \rightarrow Cu(s)$ $E = \dfrac{M}{2}$

         $Al^{3+} + 3e^- \rightarrow Al(s)$ $E = \dfrac{M}{3}$
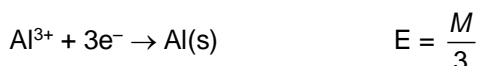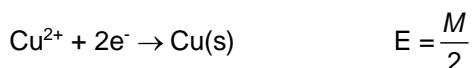
1 mole of e^- = 1 Faraday of charge.

∵   96500 C – Charge deposit E gram metal charge

∴ $1C \rightarrow \left(\dfrac{E}{96500}\right)$ g $Z = \dfrac{E}{96500}$

$$W = \frac{EQ}{96500} = \frac{\text{Molar mass}}{(\text{no. of } e^- \text{ involved})} \times \frac{Q}{96500}$$

$$\int dQ = i \int dt \qquad Q = it \qquad W = \frac{i \times t}{96500} \times \frac{\text{Molar mass}}{(\text{no. of } e^- \text{ involved})}$$

- **2nd Law :** When equal charge is passed through 2 electrolytic cells and this cells are connected in series then mass deposited at electrode will be in the ratio of their electrochemical equivalents or in the ratio of their equivalent masses.

$$W = ZQ = \frac{EQ}{96500}$$

$$\frac{W_1}{W_2} = \frac{z_1}{z_2} = \frac{E_1}{E_2} \text{ (Q = same)}$$

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Current Efficiency :

$$\text{Current efficiency} = \frac{\text{charge actually used in electricity}}{\text{charge passed}} \times 100$$

$$\text{Current efficiency} = \frac{\text{mass actually produced}}{\text{mass that should have been produced}} \times 100$$

Solved Examples

Example 1. Calculate volume of the gases liberated at STP if 1 L of 0.2 molar solution of $CuSO_4$ is electrolysed by 5.79 A current for 10000 seconds.

Sol. No. of moles of e^- = $\frac{5.79 \times 10000}{96500}$ = $\frac{579}{965}$ = 0.6

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

0.2 mole 0.4 mole

$2H_2O(\ell) + 2e^- \rightarrow H_2 + 2OH^-$

0.2 mole of $e^- \rightarrow$ 0.1 mole of H_2 at S.T.P.

Anode : $2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$

4 mole of $e^- \rightarrow$ 1 mole of O_2

0.6 mole of $e^- \rightarrow$ 0.15 mole of O_2

so, total moles = 0.25 mole

Total volume = 5.6 Ltr.

Example 2. The electrochemical equivalent of copper is 0.0003296 g coulomb^{-1}. Calculate the amount of copper deposited by a current of 0.5 ampere flowing through copper sulphate solution for 50 minutes.

Sol. According to Faraday's first law, W = Zit

W = 0.5 × 50 × 60 × 0.003296 = 0.4944 g

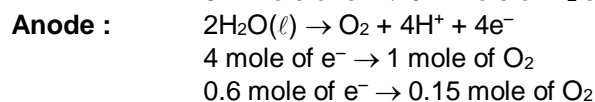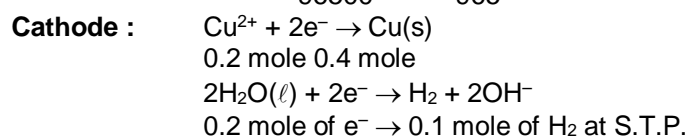**Example 3.** An electric current is passed through three cells connected in series containing $ZnSO_4$, acidulated water and $CuSO_4$ respectively. What amount of Zn and H_2 are liberated when 6.25 g of Cu is deposited? Eq. wt. of Cu and Zn are 31.70 and 32.6 respectively.

Sol. ∵ Eq. of Cu = Eq. of Zn = Eq. of H_2

$$\frac{6.25}{31.70} = \frac{W_{Zn}}{32.6} = \frac{W_{H_2}}{1}$$

Example 4. The cell consists of three compartments separated by porous barriers. The first contains a cobalt electrode in 5.00 L of 0.100 M cobalt (II) nitrate; the second contains 5.00 L of 0.100 M KNO_3 and third contains 0.1 M $AgNO_3$. Assuming that the current within the cell is carried equally by the positive and negative ions, tabulate the concentrations of ions of each type in each compartment of the cell after the passage of 0.100 mole electrons.

Given : $Co^{2+} + 2e^- \rightarrow Co$ $\quad E^0 = -.28$ V

$Ag^+ + e^- \rightarrow Ag$ $\quad E^0 = 0.80$ V

0.20 M NO_3^-	0.10 M NO_3^-	0.10 M NO_3^-
Co		Ag
0.10 M Co^{2+}	0.10 M K^+	0.10 M Ag^+
5.0 L	5.0 L	5.0 L
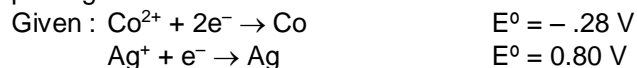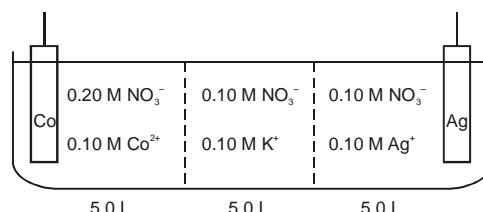
Sol. Spontaneous reaction is : $2Ag^+ + Co \rightarrow Co^{2+} + 2Ag$ $\quad E^0 = 1.08$

In the left compartment. Cobalt will be oxidized to cobalt (II) ion. In the right compartment, silver ion will be reduced to silver. The passage of 0.100 mol electrons will cause the following quantities of change.

	Compartment 1	Compartment 2	Compartment 3
Effect of electrode	+ 0.0500 mol Co^{3+}		– 0.100 mol Ag^+
Positive ion movement	–0.0250 mol Co^{2+}	+ 0.0250 mol Co^{2+}	+ 0.0500 mol K^+
			– 0.0500 mol K^+
Negative ion movement	+0.0500 mol NO_3^-		– 0.0500 mol NO_3^-

Changing the numbers of mol to concentrators in 5.0 L compartments and adding or subtracting yields the following results :

Final concentrations (M)					
0.0800	Co^{2+}	0.015	Co^{2+}	0.00500	Ag^+
0.0900	NO_3^-	0.210	K^+	0.090	NO_3^-
	NO_3^-	0.100	K^+	0.0100	

7. SECTION (G) : COMMERCIAL CELLS & CORROSION

7.1. Some Primary Cells

- **Primary cells :** These cells cannot be recharge i.e., dry cell (lechlanche cells) mercury cells (miniature cell used in the electronic devices)
  E_{cell} = constant
  as all substances used are either pure solids or pure liquids.

7.2. DRY CELLS and alkaline batteries :

- Cell potential = 1.5 V
- Anode : $Zn (s) \longrightarrow Zn^{+2}(aq) + 2e^-$
- Cathode : $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$
  $Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$
- Alkaline batteries contain basic material inside it.
- NaOH / KOH is used instead of the acidic salt NH_4Cl
- **Cathode :** $2MnO_2(s) + H_2O(\ell) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$
- **Anode :** $Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O(\ell) + 2e^-$
- Voltage produced by these cells = 1.54 V
- The cell potential does not decline under high current loads because no gases are formed.

7.3. Hg cell :

- Suitable for law current devices - Hearingaeds, watches
- **Anode :** $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$
  Cathode : $HgO + H_2O + 2e^- \longrightarrow Hg(\ell) + 2OH^-$
  Cell reaction : $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(\ell)$
- Cell potential = 1.35 V and remains constant.
- **Secondary cells :** Lead storage batteries used is automobiles (Cars/bikes)
  Anode : Pb(s)
  Cathode : $PbO_2(s)$
  H_2SO_4(conc.) about 38% solution of H_2SO_4 is taken.
  Anode : $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

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

  $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4 + 2e^-$
  Most of the $PbSO_4(s)$ ppt sticks to the lead rod.
  Cathode : $2e^- + 4H^+ + PbO_2(s) \longrightarrow Pb^{2+}(aq) + 2H_2O(\ell)$

  $Pb^{2+}(aq) + SO_4^{2-}(aq) + 4H^+ + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(\ell)$
  $PbSO_4(s)$ sticks to cathode rod.

  $Pb(s) + PbO_2 + 4H^+ + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(\ell)$
  E_{cell} = 2.05 V

Note : During the working of the cell or discharge H_2SO_4 will be consumed so it's concentration in the solution hence density of the solution will decrease, during charging of the cell $PbSO_4$ will get converted into Pb(s) and, $PbO_2(s)$ and H_2SO_4 will be produced.

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Nickel – cadmium battery.
E_{cell} = constant as cell reaction has pure solid/liquids only.
Anode : Cd(s)
Cathode : $NiO_2(s)$
Electrolyte : KOH

$$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$$
$$\underline{2e^- + NiO_2 + 2H_2O \rightarrow Ni(OH)_2(s) + 2OH^-}$$
$$Cd(s) + NiO_2(s) + 2H_2O(\ell) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$
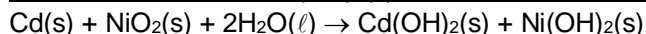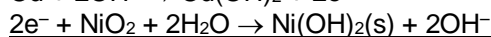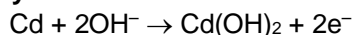
Fuel cells (H_2–O_2 cell) :
Anode : $\quad H_2 \rightarrow 2H^+ + 2e^- \times 2$
Cathode : $\quad \underline{4e^- + 4H^+ + O_2 \rightarrow 2H_2O}$
$$\qquad\quad 2H_2 + O_2 \rightarrow 2H_2O(\ell)$$
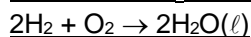
CH_4–O_2 fuel cells :
Anode : $\quad 2H_2O + CH_4 \rightarrow CO_2 + 8H^+ + 8e^-$
Cathod : $\quad \underline{4e^- + 4H^+ + O_2 \rightarrow 2H_2O}$
$$\qquad\quad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(\ell)$$
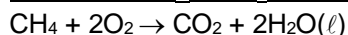
Mechanism of corrosion
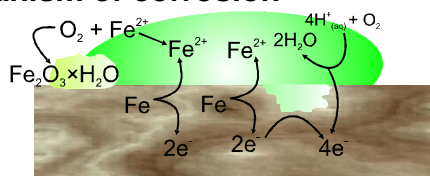
Oxidation : $\quad Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
Reduction : $\quad 2O^{2-}(g) + 4H^+(aq) \rightarrow 2H_2O(l)$
Atmospheric
Oxidation : $\quad 2Fe^{2+}(aq) + 2H_2O(l) + 1/2O_2 \rightarrow Fe_2O_3(s) + 4H^+(aq)$

Solved Examples

Example 1. During the discharge of a lead storage battery the density of H_2SO_4 falls from ρ_1 g/cc to ρ_2 g/C, H_2SO_4 of density of ρ_1 g/C. C is X% by weight and that of density of ρ_2 g/c.c is Y% by weight. The battery holds V litre of acid before discharging. Calculate the total charge released at anode of the battery. The reactions occurring during discharging are.

At anode : $\quad Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

At cathode : $\quad PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$
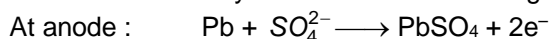
Sol. Mass of acid solution before discharge of lead storage battery (LSB) = $(V \times 10^3 \times \rho_1)$ g
$$= (1000 \times V\rho_1)g$$

Mass of H_2SO_4 before discharge of LSB = $\left(1000 \times V\rho_1 \times \dfrac{X}{100}\right)$ g = $(10 \times V\rho_1 X)$g

Net reaction during discharging : $Pb + PbO_2 + 2H_2SO_4 \longrightarrow PbSO_4 + 2H_2O$
From the reaction, it is evident that the moles of electron exchanged (lost at anode and gain at cathode) is equal to the moles of H_2SO_4 consumed or moles of H_2O produced. Let the moles of H_2SO_4 produced be x, then
Mass of H_2O produced during discharge of LSB = (18x) g
Mass of H_2SO_4 consumed during discharge of LSB = (98x) g
Mass of H_2SO_4 after discharge of LSB = $[(10V\rho_1 X)] – 98x]$ g
Mass of acid solution after discharge of LSB = $[(1000 V\rho_1) – 98x + 18x] = [(1000 V\rho_1) – 80x]$g

% of H_2SO_4 after discharge of LSB = $\dfrac{\text{Mass of } H_2SO_4 \text{ after discharge}}{\text{Mass of acid solution after discharge}} \times 100$

Y = $\dfrac{[(1000 \times V\rho_1) – 98x]}{[(1000 \times V\rho_1) – 80x]} \times 100$ x can be calculated as all other quantities are known.

Total charge released at cathode, Q = nF = xF.

Example 2.

A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6% by weight (density 1.261 g ml^{-1} at 25°C) to one of 27% by weight. The original volume of electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as H_2SO_4 is used up. Over all reaction is.

$$Pb(s) + PbO_2(s) + 2H_2SO_4(\ell) \longrightarrow 2PbSO_4(s) + 2H_2O(\ell)$$
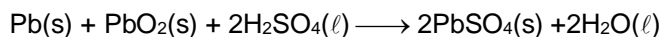
Sol. Before the discharge of lead storage battery,

Mass of solution = 1000 × 1.261 = 1261 g

Mass of H_2SO_4 = $\dfrac{1261 \times 34.6}{100}$ = 436.3 g.

Mass of water = 1261 − 436.3 = 824.7 g

After the discharge of lead storage battery,

Let the mass of H_2O produce as a result of net reaction during discharge

$(Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O)$ is x g

Moles of H_2O produced = $\dfrac{x}{18}$ = moles of H_2SO_4 consumed

Mass of H_2SO_4 consumed = $\dfrac{x}{18}$ × 98

Now, mass of solution after discharge = $1261 - \dfrac{98x}{18} + x$

% by the mass of H_2SO_4 after discharge = $\dfrac{\text{Mass of } H_2SO_4 \text{ left}}{\text{Mass of solution after discharge}}$ × 100 = 27

$$= \dfrac{436.3 - \dfrac{98x}{18}}{1261 - \dfrac{98x}{18} + x} \times 100 = 27 \qquad\qquad x = 22.59 \text{ g}$$

8. SECTION (H) : ELECTRICAL CONDUCTANCE

8.1. Electrolytic Conductance :

Conductors

Metallic Conductors
1. Charge carries are e$^-$
2. No chemical changes
3. No transfer of mass
4. Resistance is because of collision of e$^-$ s with fixed metal atoms.
5. Temp ↑ R ↑
6. Low resistance generally good conductor.

Electrolytic Conductors
1. Charge carries ions (cations/ anions)
2. Decomposition of electrolyte takes place.
3. Transfer of mass
4. Resistance is because of collision of ions with solvent molecules & because of interionic force of attraction
5. Temp ↑ R ↓
6. High resistance generally

8.2. Factors Affecting Conductance & Resistance :

1. **Solute :** Solute interactions (Inter–Ionic force of attraction) Greater the force of attraction, greater will be the resistance.
Force ∝ Charge

2. **Solute :** Solvent Interaction (Hydration/Solvation of Ions)
Greater the solvation

Solvation ∝ Charge ∝ $\dfrac{1}{size}$ greater will be resistance

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Li⁺ (Hydrated largest)   Cs⁺ (Hydrated smallest)

Resistance of LiCl > Resistance of CsCl

3. **Solvent –** Solvent interaction (Viscosity): greater the viscosity greater will be resistance

4. Temperature

$T\uparrow$ $R\downarrow$

5. Nature of electrolyte

Weak electrolyte – High resistance   Strong electrolyte – Low resistance

Resistance :

$R = \dfrac{V}{I}$ (Ohm's law (Ω))

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

ρ – resistivity / specific resistance

– resistance of unit length wire of unit area of cross section = constant = (Ω m)

$\rho = \dfrac{RA}{\ell}$

Resistivity of a solution is defined as the resistance of the solution between two electrodes of 1 cm² area of cross section and 1 cm apart.

or

Resistance of 1 cm³ of solution will be it's resistivity.

Conductance :

$C = \dfrac{1}{R}$ = mho = Ω^{-1}

= S (Siemens)

Conductivity/specific conductance

$\kappa = \dfrac{1}{\rho} = \dfrac{\ell}{RA} = \rho\dfrac{\ell}{A}$ unit $^{-1}\Omega$ cm^{-1}

= conductivity of 1 cm³ of solution

α concentration of ions

$\kappa = \dfrac{1}{\rho}$ $C = \dfrac{1}{R}$

$\kappa \propto$ (no. of ions) no. of charge carriers

- Since conductivity or resistivity of the solution is dependent on its concentration, so two more type of conductivities are defined for the solution.

8.3. Molar conductivity/molar conductance (Λ_m) :

Conductance of a solution containing 1 mole of an electrolyte between 2 electrodes which are unit length apart.

- Let the molarity of the solution 'C'

C moles of electrolyte are present in 1 Lt. of solution.

so molar conductance = Λ_m

$\Lambda_m = \kappa V$ $\Lambda_m = \dfrac{\kappa \times 1000}{C}$ $\Rightarrow$ $\Lambda_m = \dfrac{\kappa \times 1000}{\text{molarity}}$

- Its units are Ohm^{-1} cm² mol^{-1}

- **Equivalent conductance :** Conductivity of a solution containing 1 g equivalent of the electrolyte.

Λ_{eq} – equivalent conductivity/conductance.

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

- Its units are Ohm^{-1} cm² eq^{-1}

8.4.   Ionic Mobility

- Ionic Mobility = speed of the ion per unit electrical field

$$\mu = \frac{speed}{electrical\ field} = \frac{speed}{potential\ gradient}$$

- Its units are $V^{-1}\ cm^2\ sec^{-1}$

Ionic mobility = u = $\dfrac{\Lambda_M^0}{96500} = \dfrac{\Lambda_M^0}{F}$

- **Transport Number**
  Transport Number of any ion is fraction of total current carried by that ion.

Transport Number of cation = $\dfrac{\Lambda_M^0}{\Lambda_M^0 electrolyte}$

Solved Examples

Example 1.   If resistivity of 0.8 M KCl solution is 2.5×10^3 cm calculate Λ_m of the solution.
Sol. $\rho = 2.5 \times 10^{-3}\,\Omega$ cm

$$K = \frac{10^3}{2.5} = 4 \times 10^2 \qquad \Rightarrow \qquad \Lambda_m = \frac{4 \times 10^2 \times 1000 \times 10}{0.8} = 5 \times 10^5\ \Omega^{-1}\ cm^2\ mole^{-1}$$

8.5.   Variation of conductivity and molar conductivity with concentration

- Conductivity always decreases with the decrease in concentration both for weak and strong electrolytes.
- The number of ions per unit volume that carry the current in a solution decreases on dilution.
- Molar conductivity increases with decreases in concentration. This is because the total volume, V of solution containing one mole of electrolyte also increases.
- Molar conductivity is the conductance of solution.
- When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol Λ^0.

8.6.   Strong Electrolytes :

- For strong electrolytes. Λ increases slowly with dilution and can be represented by the equation $\Lambda = \Lambda^0 - A\ C^{1/2}$
- The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e. the charges on the cations and anion produced on the dissociation of the electrolyte in the solution.

Example :   Thus NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1 , 2-1 and 2-2 electrolyte respectively.

- All electrolytes of a particular type have the same value for 'A'.

Variation of Λ against $c^{1/2}$
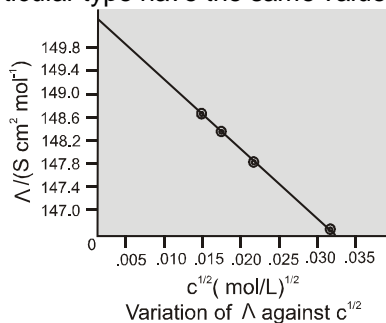
8.7. Weak electrolytes

- Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change in Λ with dilution is due to increases in the number of ions in total volume of solution that contains 1 mol of electrolyte.
- At infinite dilution (i.e. concentration c $\rightarrow$ zero) electrolyte dissociates completely ($\alpha = 1$), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately.
- Molar conductivity versus c$^{1/2}$ for acetic acid
  (weak electrolyte) and potassium chloride
  (strong electrolyte in aqueous solutions.
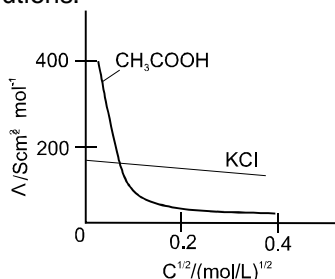
9. SECTION (I) : KOHLRAUSCH LAW AND ITS APPLICATIONS

9.1. Kohlarausch's Law :

- "At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions." i.e., $\Lambda_\infty = \Lambda_+ + \Lambda_-$

- At infinite dilution or near zero concentration when dissociation is 100%, each ion makes a definite contribution towards molar conductivity of electrolyte irrespective of the nature of the other ion. (because interionic forces of attraction are zero)

$$\Lambda^0_{m\ electrolyte} = {}_m^0 \nu_+ \Lambda^0_m + \nu_- \Lambda^0_{m-}$$

ν_+ = no. of cation in one formula unit of electrolyte

ν_- = no. of anions in one formula unit of electrolyte

For NaCl, $\nu_+ = 1$ $\nu_- = 1$

For Al$_2$(SO$_4$)$_3$, $\nu_+ = 2$ $\nu_- = 3$

$$\Lambda^0_{eq\ electrolyte} = \Lambda^\infty_{eq+} + \Lambda^\infty_{eq-}$$

$$\Lambda^0_{eq+} = \frac{\Lambda^0_m}{\text{charge on the cation}} \qquad\qquad \Lambda^0_{eq}.Al^{3+} = \frac{\Lambda^0_m Al^{3+}}{3}$$

$$\Lambda^0_{eq} = \frac{\Lambda^0_m}{\text{charge on the anion}} \qquad\qquad \Lambda^0_{eq}, \text{electrolyte} = \frac{\Lambda^0_m\ \text{electrolyte}}{\text{total + ve charge on cation}}$$

$$\text{or}$$

$$\text{total} - \text{ve charge on anion}$$

$$\Lambda^0_{eq}\ Al_2(SO_4)_3 = \Lambda^0_{eq}\ Al^{3+} + \Lambda^0_{eq}\ SO_4^{2-}$$

$$= \frac{\Lambda^0_m Al^{3+}}{3} + \frac{\Lambda^0_m SO_4^{2-}}{2}$$

$$\Lambda^0_{eq}\ Al_2(SO_4)_3 = \frac{2\Lambda^0_{mAl^{3+}} + 3\Lambda^0_{mSO_4^{2-}}}{6}$$

Solved Example

Example 1. Λ_m^0 Na$^+$ = 150 Ω^{-1} cm^2 mole^{-1}; Λ_{eq}^0 Ba^{2+} = 100 Ω^{-1} cm^2 eq^{-1}; Λ_{eq}^0 SO_4^{2-} = 125 Ω^{-1} cm^2 eq^{-1}; Λ_m^0 Al^{3+} = 300 Ω^{-1} cm^2 mole^{-1}; Λ_m^0 NH_4^+ = 200 Ω^{-1} cm^2 mole^{-1}; Λ_m^0, Cl$^-$ = 150 Ω^{-1} cm^2 mole^{-1}

Then calculate :

(a) Λ_{eq}^0, Al^{3+}

(b) Λ_{eq}^0, Al$_2$(SO$_4$)$_3$

(c) Λ_m^0, (NH$_4$)$_2$SO$_4$

(d) Λ_m^0, NaCl, BaCl$_2$. 6H$_2$O

(e) Λ_m^0, (NH$_4$)$_2$ SO$_4$ Al$_2$(SO$_4$)$_3$. 24H$_2$O

(f) Λ_{eq}^0, NaCl

Solution:

(a) Λ_{eq}^0 Al^{3+} = $\dfrac{300}{3}$ = 100

(b) Λ_{eq}^0 Al$_2$(SO$_4$)$_3$ = 100 + 125 = 225

(c) Λ_m^0 (NH$_4$)$_2$SO$_4$ = 2 × 200 + 2 × 125 = 650

(d) Λ_m^0 NaCl.BaCl$_2$.6H$_2$O = 150 + 200 + 3 × 150 = 800 r^{-1}

(e) Λ_m^0 (NH$_4$)$_2$ SO$_4$ Al$_2$(SO$_4$)$_3$.24H$_2$O = 400 + 600 + 4 × 250 = 2000

(f) Λ_{eq}^0 NaCl = 300 Ω^{-1} cm^2 eq^{-1}

Example 2. To calculate Λ_m^0 or Λ_{eq}^0 of weak electrolyte

Sol. $\Lambda_{mCH_3COOH}^0 = \Lambda_{mCH_3COO^-}^0 + \Lambda_m^0 H^+$

$= (\Lambda_{mCH_3COO^-}^0 + \Lambda_{mNa^+}^0) - \Lambda_{mNa^+}^0 + \Lambda_{mH^+}^0 + \Lambda_{mCl^+}^0 - \Lambda_{mCl^-}^0$

$\Lambda_{CH_3COOH}^0 = \Lambda_{mCH_3COONa}^0 + \Lambda_{mHCl}^0 - \Lambda_{mNaCl}^0$

Example 3. Calculate Λ_m^0 of oxalic acid, given that

Λ_{eq}^0 Na$_2$C$_2$O$_4$ = 400 Ω^{-1} cm^2 eq^{-1}, Λ_m^0 H$_2$SO$_4$ = 700 Ω^{-1} cm^2 mole^{-1}, Λ_{eq}^0 Na$_2$SO$_4$ = 450 Ω^{-1} cm^2 eq^{-1}

Sol. Λ_m^0 H$_2$C$_2$O$_4$ = 700 + 800 − 900 = 600 Ω^{-1} cm^2 mole

Λ_{eq}^0 = 400 + $\dfrac{700}{2}$ − 450 ; $\dfrac{\Lambda_m}{2}$ = 350 − 50 = 300

Λ_m = 600

9.2. Applications of Kohlaraushch's law

- Calculate $\Lambda°$ for any electrolyte from the $\Lambda°$ of individual ions.
- Determine the value of its **dissociation constant** once we known the $\Lambda°$ and Λ at a given concentration c.
- **Degree of dissociation :** At greater dilution the ionization become 100%, therefore called infinite dilution.
  At lower dilution the ionization (dissociation into ions) is less than 100% and equivalent conductance become lower,
  i.e., $\Lambda_{eq} < \Lambda°_{eq}$
  degree of dissociation

$$\alpha = \frac{\Lambda_{eq}}{\Lambda_{eq}^0} = \frac{equivalent \quad conductance \quad at \quad a \quad given \quad concentration}{equivalent \quad conductance \quad at \quad at \quad \inf inite \quad dilution}$$

- **Dissociation constant** of weak electrolyte:

$K_C = \dfrac{C\alpha^2}{1-\alpha}$; α = degree of dissociation, C = concentration

- The degree of dissociation then it can be approximated to the ratio of molar conductivity Λ_c at the concentration c to limiting molar conductivity, Λ^0. Thus we have :

$\alpha = \Lambda/\Lambda^0$

But we known that for a weak electrolyte like acetic acid.

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{c\Lambda^2}{\Lambda^\circ(1 - \Lambda/\Lambda^\circ)} = \frac{c\Lambda^2}{\Lambda^\circ(\Lambda - \Lambda^\circ)}$$

- **Solubility(s) and K_{SP} of any sparingly soluble salt.**

Sparingly soluble salt = Very small solubility

Solubility = molarity = 0

so, solution can be considered to be of zero conc or infinite dilution.

Λ_m, saturated = $\Lambda_M^\infty = \dfrac{K \times 1000}{Solubility}$ S = $\dfrac{K \times 1000}{\Lambda_M^0}$ $K_{SP} = S^2$ (for AB type salt)

Solved Example

Example 1. If conductivity of water used to make saturated solution of AgCl is found to be $3.1 \times 10^{-5\,-1}$ cm^{-1} and conductance of the solution of AgCl = $4.5 \times 10^{-5\,-1}$ cm^{-1}

If Λ_M^0 AgNO$_3$ = $200\,\Omega^{-1}$ cm^2 mole^{-1}, Λ_M^0 NaNO$_3$ = $310\,\Omega^{-1}$ cm^2 mole^{-1}

Calculate K_{SP} of AgCl

Solution: Λ_M^0 AgCl = 140   Total conductance = 10^{-5}

$$S = \frac{140 \times 4 \times 10^{-5} \times 1000}{140} = \frac{1.4 \times 10^{-4}}{14} \; ; \;\; S = 5.4 \times 10^{-4} ; \;\;\; S^2 = 1 \times 10^{-8}$$

Example 2. To calculate K_W of water

Solution: $H_2O(\ell) + H_2O(\ell) \rightarrow H_2O^+(aq) + OH^-(aq)$

$\Lambda_m = \Lambda_{M,H_2O}^0 = \Lambda_M^0 H^+ + \Lambda_M^0 OH^-$

$= \dfrac{K \times 1000}{molarity}$ - Concentration of water molecules 100% dissociated Ask

Molarity = [H$^+$] = [OH$^-$] = $\dfrac{K \times 1000}{\lambda_M^\infty}$

$K_W = [H^+][OH^-] = \left[\dfrac{K \times 1000}{\lambda_M^0} \right]^2$ K_a or $K_b = \dfrac{[H^+][OH^-]}{H_2O}$

Variation of κ, Λ_m & Λ_{eq} of solutions with Dilution

$\kappa \propto$ conc. of ions in the solution. In case of both strong and weak electrolytes on dilution the concentration of ions will decrease hence κ will decrease.

Λ_m or Λ_{eq} $(\kappa \propto C)$ strong electrolyte

$\Lambda_m = \dfrac{1000 \times \kappa}{molarity}$ $(\kappa \propto \sqrt{K_aC}\,)$ weak electrolyte.

$\Lambda_{eq} = \dfrac{1000 \times \kappa}{normality}$

For strong electrolyte $\Lambda_m \propto \dfrac{\kappa}{C} \propto \dfrac{C}{C}$ = constant

For weak electrolyte $\Lambda_m \propto \dfrac{\kappa}{C} \propto \dfrac{\sqrt{K_aC}}{C} \propto \dfrac{1}{\sqrt{C}}$

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SUMMARY

Electrochemistry is the area of chemistry concerned with the interconversion of chemical and electrical energy. Chemical energy is converted to electrical energy in a galvanic cell, a device in which a spontaneous redox reaction is used to produce an electric current. Electrical energy is converted to chemical energy in an electrolytic cell, a cell in which an electric current drives a nonspontaneous reaction. It's convenient and reduction occur at separate electrodes.

The electrode at which oxidation occurs is called the anode, and the electrode at which reduction occurs is called the cathode. The cell potential E (also called the cell voltage or electromotive force is an electrical measure of the driving force of the cell reaction. Cell potentials depend on temperature, ion concentrations, and gas pressure. The standard cell are in their standard states. Cell potentials are related to free-energy changes by the equations $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$, where F = 96,500 C/mol e^- is the **faraday,** the charge on 1 mol of electrons.

The standard reduction potential for the a half-reaction is defined relative to an arbitrary value of 0 V for the standard hydrogen electrode (S.H.E.) : $2H^+(aq, 1\ M) + 2\ e^- \rightarrow H_2(g,\ 1\ atm)$ $E^0 = 0\ V$

Tables of standard reduction potentials--- are used to arrange oxidizing and reducing agents in order of increasing strength, to calculate E^0 values for cell reactions, and to decide whether a particular redox reaction is spontaneous.

Cell potential under nonstandard-state conditions can be calculated using the Nernst equation,

$$E = E^0 - \frac{0.0592}{n} \log Q \text{ in volts, at } 25^oC$$

where Q is the reaction quotient. The equilibrium constant K and the standard cell potential E^0 are related by the equation $E^0 = \dfrac{0.0592}{n} \log K$ in volts, at 25^oC

A battery consists of one or more galvanic cells. A fuel cell differs from a battery in that the reactants are continuously supplied to the cell. **Corrosion** of iron (rusting) is an electrochemical process surface and oxygen is reduced in a cathode region. Corrosion can be prevented by covering iron with another metal, such as zinc, in the process called **galvanizing,** or simply by putting the iron in electrical contact with a second metal that is more easily oxidized, a process called **cathodic protection.**

Electrolysis, the process of using an electric current to bring about chemical change, is employed to produce sodium, chlorine, sodium hydroxide, and aluminum (Hall-Heroult process) and is used in electrorefining and electroplating. The product obtained at an electrode depends on the reduction potentials and overvoltage. The amount of product obtained is related to the number of moles of electrons passed through the cell, which depends on the current and the time that the current flows.

Electrochemistry

relates

Chemical energy   Electrical energy

Electrore fining and electroplating

Batteries

used in

interconverted in

used in

Shorthand notation

represented using

Galvanic cells (Voltaic cells)

Electroytic cells

process called

Electrolysis

having

reaction are

reaction are

Standard cell potential, E°

Spontaneous oxidation-reduction

Nonspontaneous oxidation-reduction

related to

producing

requiring

1) Free energy change, G°
2) Equilibrium constant, K

$\Delta G = -$
$E = +$

Electric current

$\Delta G = (+)$
$E = (-)$

oxidation half-reaction occurring at the

reducing half-reaction occurring at the

Anode

Cathode

calculate from

used in

Standard reduction potentials

Nernst equation

$$E = E° - \frac{.0592}{n} \log \frac{(Products)}{(Reactants)} \qquad \Rightarrow \qquad E = E° - \frac{.0592}{n} \log \frac{(Anodic\ ion\ concentration)}{(Cathodic\ ion\ concentration)}$$

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

Problem 1   Na-amalgam is prepared by electrolysis of NaCl solution using liquid Hg as cathode. How long should the current of 10 amp. is passed to produce 10% Na–Hg on a cathode of 10 g Hg. (Atomic mass of Na = 23).

(A) 7.77 min   (B) 9.44 min.   (C) 5.24 min.   (D) 11.39 min.

Solution: **(A)**   90 g Hg has 10 g Na

∴   10 g Hg = $\dfrac{10}{90}$ × 10 = $\dfrac{10}{9}$ g Na

∴   Weight of Na = $\dfrac{M}{n}$ × $\dfrac{i \times t}{96500}$

$\dfrac{10}{9}$ = $\dfrac{23}{1}$ × $\dfrac{10 \times t}{96500}$ [∴ $Na^+ + e \rightarrow Na$]

∴   t = $\dfrac{10 \times 96500}{9 \times 10 \times 23}$ = 7.77 min

Problem 2   We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution then the conductivity of this solution in terms of 10^{-7} Sm^{-1} units will be

[Given $\Lambda^0_{(Ag^+)}$ = 4×10^{-3} Sm^2 mol^{-1}, $\Lambda^0_{(Br^-)}$ = 6×10^{-3} S m^2 mol^{-1}, $\Lambda^0_{(NO_3^-)}$ = 5×10^{-3} Sm^2 mol^{-1}]

(A) 39   (B) 55   (C) 15   (D) 41

Solution: **(A)**

The solubility of AgBr in presence of 10^{-7} molar $AgNO_3$ is 3×10^{-7} M.

Therefore $[Br^-]$ = 3×10^{-4} m^3, $[Ag^+]$ = 4×10^{-4} m^3 and $[NO_3^-]$ = 10^{-4} m^3

Therefore κ_{total} = κ_{Br^-} + κ_{Ag^+} + $\kappa_{NO_3^-}$ = 39 Sm^{-1}

Problem 3   A hydrogen electrode X was placed in a buffer solution of sodium acetate and acetic acid in the ratio a : b and another hydrogen electrode Y was placed in a buffer solution of sodium acetate and acetic acid in the ratio b : a. If reduction potential values for two cells are found to be E_1 and E_2 respectively w.r.t. standard hydrogen electrode, the pK_a value of the acid can be given as

(A) $\dfrac{E_1 - E_2}{0.118}$ (B) $-\dfrac{E_1 + E_2}{0.118}$ (C) $\dfrac{E_1}{E_2} \times 0.118$ (D) $\dfrac{E_2 - E_1}{0.118}$

Solution: **(B)**

$H^+ + e^- \Rightarrow \dfrac{1}{2} H_2(g)$

E_1 = 0 – 0.0591 log $\dfrac{1}{(H^+)_1}$
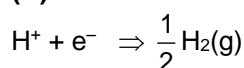
E_1 = 0 + 0.0591 log $[H^+]_1$ = –0.0591 pH_1

E_2 = – 0.0591 pH_2

pH_1 = pk_a + log $\dfrac{Salt}{Acid}$

pH_1 = pk_a + log $\dfrac{a}{b}$ .... (1)

pH_2 = pk_a + log $\dfrac{b}{a}$

pH_2 = pk_a – log $\dfrac{a}{b}$ .... (2)

Add (1) & (2) $pH_1 + pH_2 = 2 pk_a$

$2pk_a$ = $-\dfrac{E_1}{0.0591} - \dfrac{E_2}{0.0591}$ ⇒ pk_a = $-\left[\dfrac{E_1 + E_2}{0.118}\right]$

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Problem 4 At what $\dfrac{[Br^-]}{\sqrt{[CO_3^{2-}]}}$ does the following cell have its reaction at equilibrium?

$Ag(s) \mid Ag_2CO_3(s) \mid Na_2CO_3\,(aq) \mid\mid KBr(aq) \mid AgBr(s) \mid Ag(s)$
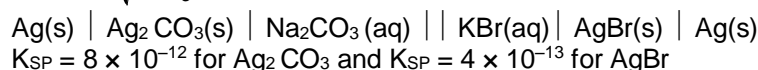
$K_{SP} = 8 \times 10^{-12}$ for Ag_2CO_3 and $K_{SP} = 4 \times 10^{-13}$ for AgBr

(A) $\sqrt{1} \times 10^{-7}$ (B) $\sqrt{2} \times 10^{-7}$ (C) $\sqrt{3} \times 10^{-7}$ (D) $\sqrt{4} \times 10^{-7}$

Solution: **(B)** Anode : $Ag(s) \longrightarrow Ag^+\,(aq) + 1e^-$

Cathode : $Ag^+(aq) + 1e^- \longrightarrow Ag$

Net : $Ag^+_{(AgBr)} \xrightarrow{\;1e^-\;} Ag^+_{(Ag_2CO_3)}$
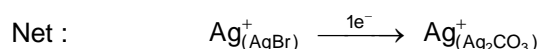
$0 = 0 + \dfrac{0.059}{1} \log \dfrac{\left(\dfrac{K_{SP}AgBr}{[Br^-]}\right)}{\sqrt{\dfrac{K_{SP}Ag_2CO_3}{[CO_3^{2-}]}}}$ $\Rightarrow$ $\dfrac{K_{SP}\;AgBr}{[Br^-]} = \sqrt{\dfrac{K_{SP}\;Ag_2CO_3}{[CO_3^{2-}]}}$

$\Rightarrow$ $\dfrac{4 \times 10^{-13}}{\sqrt{8 \times 10^{-12}}} = \dfrac{[Br^-]}{\sqrt{[CO_3^{2-}]}}$ $\Rightarrow$ $\dfrac{[Br^-]}{\sqrt{[CO_3^{2-}]}} = \sqrt{2} \times 10^{-7}$

Problem 5

A resistance of $50\,\Omega$ is registered when two electrodes are suspended into a beaker containing a dilute solution of a strong electrolyte such that exactly half of the them are submerged into solution. If the solution is diluted by adding pure water (negligible conductivity) so as to just completely submerge the electrodes, the new resistance offered by the solution would be

(A) $50\,\Omega$ (B) $100\,\Omega$

(C) $25\,\Omega$ (D) $200\,\Omega$

Solution: **(A)**

$R = \dfrac{1}{k}\;\dfrac{\ell}{A}$

The k is halved while the A is doubled. Hence R remains $50\,\Omega$.
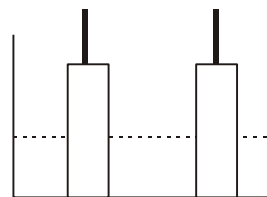
Problem 6 Calculate the cell EMF in mV for

$Pt \mid H_2\,(1atm) \mid HCl\,(0.01\,M) \mid\mid AgCl(s) \mid Ag(s)$ at 298 K

If $\Delta G_f°$ values are at 25°C.

$-109.56\,\dfrac{kJ}{mol}$ for AgCl(s) and $-130.79\,\dfrac{kJ}{mol}$ for $(H^+ + Cl^-)$ (aq)

(A) 456 mV   (B) 654 mV   (C) 546 mV   (D) None of these

Solution: **(A)**

$\Delta G^0_{cell\ reaction} = 2\,(-130.79) - 2\,(-109.56) = -42.46\ kJ/mole$

(for $H_2 + 2AgCl \longrightarrow 2Ag + 2H^+ + 2Cl^-$)
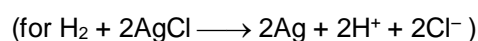
$\therefore$ $E^0_{cell} = \dfrac{-42460}{-2 \times 96500} = +0.220\ V$

Now $E_{cell} = +0.220 + \dfrac{0.059}{2}\ \log \dfrac{1}{(0.01)^4} = 0.456\ V = 456\ mV$.

Problem 7 Consider the cell $Ag(s) \mid AgBr(s) \mid Br^-(aq) \mid\mid AgCl(s) \mid Cl^-(aq) \mid Ag(s)$ at 25ºC. The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10}. For what ratio of the concentrations of Br^- & Cl^- ions would the emf of the cell be zero ?

(A) 1 : 200   (B) 1 : 100   (C) 1 : 500   (D) 200 : 1

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Solution: **(A)** $E^0_{Br^-/AgBr/Ag} = E^0_{Ag^+/Ag} + \dfrac{0.059}{1} \log K_{SP} AgBr = E^0_{Ag^+/Ag} - 0.7257$

and $\quad E^0_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} + \dfrac{0.059}{1} \log K_{SP} AgCl = E^0_{Ag^+/Ag} - 0.59$

Now cell reaction is

$Ag + Br^- \longrightarrow AgBr + 1e^-$

$\underline{AgCl + 1e^- \longrightarrow Ag + Cl^-}$

$Br^- + AgCl \longrightarrow Cl^- + AgBr$
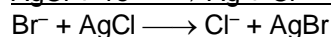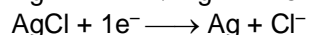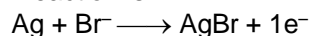
$0 = (0.7257 - 0.59) + \dfrac{0.059}{1} \log \dfrac{[Br^-]}{[Cl^-]} \quad \Rightarrow \quad \dfrac{[Br^-]}{[Cl^-]} = 0.005$

Problem 8 The conductivity of a solution may be taken to be directly proportional to the total concentration of the charge carries (ions) present in it in many cases. Using the above find the percent decrease in conductivity (k) of a solution of a weak monoacidic base BOH when its 0.1 M solution is diluted to double its original volume. ($K_b = 10^{-5}$ for BOH) (Take $\sqrt{50} = 7.07$) (Mark the answer to nearest integer),

Solution: Initially $[OH^-] = \sqrt{10^{-5} \times 0.1} = 10^{-3}$

$[ions]_{total} = 2 \times 10^{-3}$ M

later $\quad [OH^-] = \sqrt{10^{-5} \times \dfrac{1}{20}} = \sqrt{50} \times 10^{-4}$ M

$\therefore \quad [ions]_{total} = 2\sqrt{50} \times 10^{-4}$ M

$\therefore \quad$ % change on $[ions]_{total} = \dfrac{2\sqrt{50} - 20}{20} \times 100 = -29.29\%$ **Ans. 29**

Problem 9 At 0.04 M concentration the molar conductivity of a solution of a electrolyte is 5000 Ω^{-1} cm^2 mol^{-1} while at 0.01 M concentration the value is 5100 Ω^{-1} cm^2 mol^{-1}. Making necessary assumption (Taking it as strong electrolyte) find the molar conductivity at infinite dilution and also determine the degree of dissociation of strong electrolyte at 0.04 M.

Solution: From the graph we can see the λ_M^∞ value of 5200 Ω^{-1} cm^2 mol^{-1}. Hence
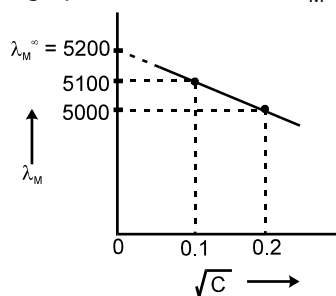
$\alpha = \dfrac{5000}{5200} = 0.9615 \approx 0.96$ **Ans. 96**

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Exercise-1

✎ **Marked Questions may have for Revision Questions.**

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Galvanic cell, its Representation & salt bridge

Commit to memory :

Notation for Galvanic cell :

Anode half cell   Cathode half cell

$$M(s) \mid M^{2+}(aq, C_1) \parallel N^{2+}(aq, C_2) \mid N(s)$$

↓   ↓   ↓

Phase boundary   Salt bridge   Phase boundary

→   LOAN ≡ left oxidation- Anode-negative
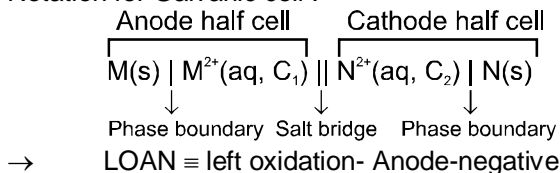
A-1. ✎ In the galvanic cell $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$, the electrons flow from Cu-electrode to Ag-electrode. Answer the following questions regarding this cell :
(a) Which is the anode ?
(b) Which is the cathode ?
(c) What happens at anode-reduction or oxidation ?
(d) What happens at cathode-oxidation or reduction ?
(e) Which electrode loses mass ?
(f) Which electrode gains mass ?
(g) Write the electrode reactions.
(h) Write the cell reaction
(i) Which metal has greater tendency to loss electron-Cu or Ag ?
(j) Which is the more reactive metal-Cu or Ag ?
(k) What is the function of salt bridge represented by the symbol $\parallel$?

A-2. Write cell reaction of the following cells :
(a) $Cu \mid Cu^{2+}(aq) \parallel Ag^+(aq) \mid Ag$ (b) $Pt \mid Fe^{2+}, Fe^{3+} \parallel MnO_4^-, Mn^{2+}, H^+ \mid Pt$
(c) $Pt, Cl_2 \mid Cl^-(aq) \parallel Ag^+(aq) \mid Ag$ (d) $Cd \mid Cd^{2+}(aq) \parallel H^+(aq) \mid H_2 \mid Pt$

A-3. Write cell notation of each cell with following cell reactions :
(a) $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
(b) $2Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq)$
(c) $Pb(s) + Br_2(l) \rightarrow Pb^{2+}(aq) + 2Br^-(aq)$

Section (B) : Electrochemical series & its Applications

Commit to memory :

$$SRP \propto \text{Oxidising power} \propto \frac{1}{\text{reducing power}} \propto \text{Non-metallic character} \propto \frac{1}{\text{Metallic character}}$$

B-1. The reduction potential values are given below
$Al^{3+}/Al = -1.67$ volt, $Mg^{2+}/Mg = -2.34$ volt, $Cu^{2+}/Cu = +0.34$ volt, $I_2/I^- = +0.53$ volt.
Which one is the best reducing agent ?

B-2. ✎ The standard reduction potential value of the three metallic cations X, Y and Z are 0.52, –3.03 and –1.18 V respectively. Write the decreasing order of reducing power of the corresponding metals :

B-3. ✎ **(i)**   Which of the following oxides is reduced by hydrogen ?
         MgO, CuO and Na_2O
     (ii)   Which of the following oxides will decompose most easily on heating ?
         ZnO, CuO, MgO and Ag_2O
     (iii)   The value of E^0_{OX} for electrode reactions,
         $Fe \longrightarrow Fe^{2+} + 2e^-$, $Cu \longrightarrow Cu^{2+} + 2e^-$ and $Zn \longrightarrow Zn^{2+} + 2e^-$
         are 0.444, –0.337 and 0.763 volt respectively. State which of these metals can replace the other two from the solution of their salts ?

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B-4. For the cell reaction $2Ce^{4+} + Co \rightarrow 2Ce^{3+} + Co^{2+}$, E^0_{Cell} is 1.89 V. If $E^{\circ}_{Co^{2+}|Co}$ is $-$ 0.28 V, what is the value of $E^{\circ}_{Ce^{4+}|Ce^{3+}}$?

B-5. Determine the standard reduction potential for the half reaction :

$Cl_2 + 2e^- \rightarrow 2Cl^-$

Given $Pt^{2+} + 2Cl^- \rightarrow Pt + Cl_2$, $E^0_{Cell} = -$ 0.15 V

       $Pt^{2+} + 2e^- \rightarrow Pt$ $E^{\circ} = 1.20$ V

B-6. What is E^0_{Cell} if :

$2Cr + 3H_2O + 3OCl^- \rightarrow 2Cr^{3+} + 3Cl^- + 6 OH^-$

$Cr^{3+} + 3e^- \rightarrow Cr$, $E^{\circ} = -$ 0.74 V

$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ $E^{\circ} = 0.94$ V
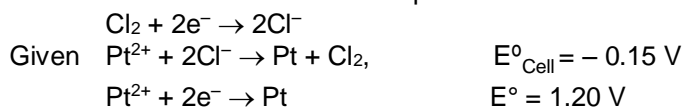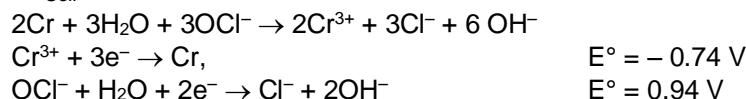
Section (C) : Concept of ∆G

Commit to memory :

E^0_{cell} is an intensive property, so on multiplying or dividing electrode reaction, E^0_{cell} remains same.

Calcualte E^0_{cell} for 3rd reaction with the help of 1st and 2nd reaction using $\Delta G^0 = -nF\, E^0_{cell}$.

$E^0_{target} = \dfrac{n_1 E_1 + n_2 E_2}{n_{target}}$ where n_1 = electrons participating in 1st reaction.

                                     n_2 = electrons participating in 2nd reaction.

                                     n_{target} = electrons participating in target reaction.

C-1. If $E^{\circ}_{Fe^{2+}|Fe} = -0.44$ V, $E^{\circ}_{Fe^{3+}|Fe^{2+}} = 0.77$ V. Calculate $E^{\circ}_{Fe^{3+}|Fe}$

C-2. Consider the standard reduction potentials (in volts) as shown in Fig. Find E^0.

$$SO_4^{2-} \xrightarrow{\;-0.936\;} SO_3^{2-} \xrightarrow{\;-0.576\;} \frac{1}{2}S_2O_3^{2-}$$

$$\lfloor \underline{\hspace{3cm} E^{\circ} = ?\hspace{3cm}} \uparrow$$
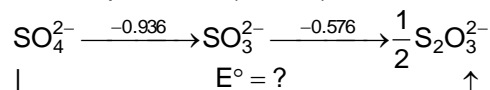
C-3. The standard oxidation potentials for Mn^{3+} ion acid solution are $Mn^{2+} \xrightarrow{\;-1.5\;V\;} Mn^{3+} \xrightarrow{\;-1.0\;V\;} MnO_2$.

Is the reaction $2\,Mn^{3+} + 2\,H_2O \longrightarrow Mn^{2+} + MnO_2 + 4H^+$ spontaneous under conditions of unit activity ? What is the change in free energy ?

C-4. Using the ΔG^0 for the reactions

     $C + O_2 \rightarrow CO_2$ $\Delta G^0 = -395$ kJ / mole,

     $2Al(\ell) + 3/2O_2 \rightarrow Al_2O_3(s)$ $\Delta G^0 = -1269$ kJ/mole

     $Al_2O_3(s) \rightarrow Al_2O_3$ (melt) $\Delta G^0 = 16$ kJ/mole
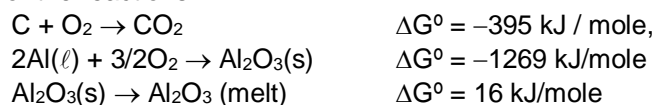
Calculate the EMF for the cell reaction $2Al_2O_3$ (melt) $+ 3C \rightarrow 4Al(\ell) + 3CO_2(g)$. The number of electrons involved in the reaction is 12.

Section (D) : Nernst equation & its Applications (including concentration cells)

Commit to memory :

Nernst equation : $E_{cell} = E^0_{cell}\,\dfrac{RT}{nf} - \ln Q$

At 25ºC, $E_{cell} = E^0_{cell} - \dfrac{0.0591}{n}\log Q$

where, n = number of transferred electron, Q = reaction quotient.

For concentration cell $E^0_{cell} = 0$

D-1. Calculate the oxidation potential of a hydrogen electrode at pH = 1 (T = 298 K).

D-2. Calculate the equilibrium constant for the reaction :

$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$, [Given $E^0_{Ce^{4+}/Ce^{3+}} := 1.61$ V; $E^0_{Fe^{3+}/Fe^{2+}} = 0.77$V]

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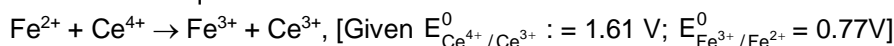
D-3. The standard reduction potential of Cu^{2+} / Cu couple is 0.34 V at 25°C. Calculate the reduction potential at pH = 14 for this couple.
(Given : K_{sp}, Cu $(OH)_2$ = 1.0×10^{-19}).

D-4. The EMF of the cell M |M^{n+} (0.02 M) || H^+ (1M) | H_2 (g) (1 atm), Pt at 25°C is 0.81V. Calculate the valency of the metal if the standard oxidation potential of the metal is 0.76V.

D-5. Consider the following electrochemical cell :
(a) Write a balanced net ionic equation for the spontaneous reaction that take place in the cell.
(b) Calculte the standard cell potential E^0 for the cell reaction.
(c) If the cell emf is 1.6 V, what is the concentration of Zn^{2+} ?
(d) How will the cell potential be affected if KI is added to Ag^+ half-cell ?
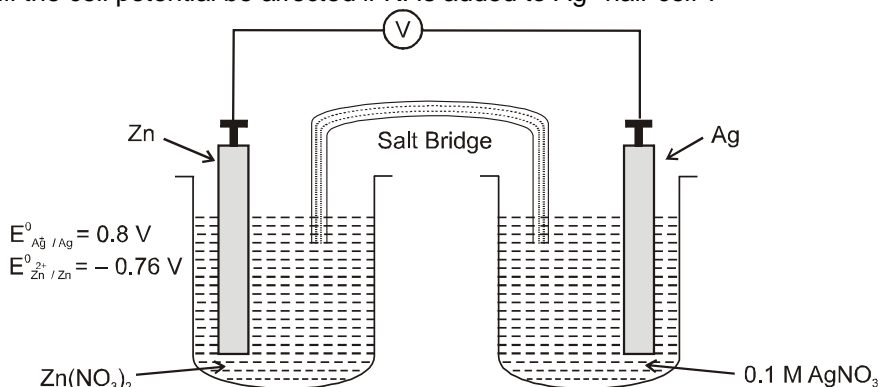
D-6. $NO_3^- \longrightarrow NO_2$ (acid medium), E^0 = 0.790 V
$NO_3^- \longrightarrow NH_3OH^+$ (acid medium), E^0 = 0.731 V.
At what pH, the above two will have same E value? Assume the concentration of all other species NH_3OH^+ except [H^+] to be unity.

D-7. The standard oxidation potential of Zn referred to SHE is 0.76V and that of Cu is –0.34V at 25ºC. When excess of Zn is added to $CuSO_4$, Zn displaces Cu^{2+} till equilibrium is reached. What is the approx value of $\log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$ at equilibrium?

Section (E) : Electrolysis

> **Commit to memory :**
> Higher SOP means higher tendency of oxidation.
> Higher SRP means higher tendency of reduction.
> SOP order : SO_4^{2-} < NO_3^- < Cl^- < H_2O < Br^- < Ag < I^- < OH^- < Cu.....< Li
> SRP order : Follow ECS

E-1.

	ELECTROLYTE	ANODE Product	CATHODE Product
1	NaCl (Molten) with Pt electrode		
2	NaCl (aq) with Pt electrode		
3	Na_2SO_4 (aq) with Pt electrode		
4	$NaNO_3$ (aq) with Pt electrode		
5	$AgNO_3$ (aq) with Pt electrode		
6	$CuSO_4$ (aq) with Inert electrode		
7	$CuSO_4$ (aq) with Copper electrode		

Section (F) : Faraday laws & its Applictions

> **Commit to memory :**
> Faraday's law of electrolysis :
> Ist law $\qquad$ W = ZQ = $\dfrac{EQ}{96500}$
> $\qquad\qquad$ Q = it

2nd law	$\dfrac{W_1}{W_2} = \dfrac{Z_1}{Z_2} = \dfrac{E_1}{E_2}$ (Q = same)	

Current efficiency (η) = $\dfrac{\text{actual amount of product}}{\text{theortical amount of product}} \times 100$

$W_{actual} = \left(\dfrac{E \times Q}{96500}\right)\dfrac{\eta}{100}$

F-1. Find the number of electrons involved in the electro−deposition of 63.5 g of copper from a solution of copper sulphate is :

F-2. A current 0.5 ampere when passed through $AgNO_3$ solution for 193 sec. deposited 0.108 g of Ag . Find the equivalent weight of Ag :

F-3. A certain metal salt solution is electrolysed in series with a silver coulometer. The weights of silver and the metal deposited are 0.5094 g and 0.2653g. Calculate the valency of the metal if its atomic weight is nearly that of silver.

F-4. 3A current was passed through an aqueous solution of an unknown salt of Pd for 1Hr. 2.977g of Pd^{+n} was deposited at cathode. Find n. (Given Atomic mass of Pd = 106.4)

F-5. How long a current of 2A has to be passed through a solution of $AgNO_3$ to coat a metal surface of $80cm^2$ with $5\mu m$ thick layer? Density of silver = $10.8g/cm^3$.

F-6. A certain electricity deposited 0.54g of Ag from $AgNO_3$ Solution. What volume of hydrogen will the same quantity of electricity liberate at STP (V_m = 22.4 L/mol).

F-7. A current of 3.7A is passed for 6hrs. between Ni electrodes in 0.5L of 2M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?

F-8. Cd amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. How long should a current of 5A be passed in order to prepare 12% Cd-Hg amalgam when 2 g Hg is used as cathode (atomic weight of Cd = 112.4)

F-9. Electrolysis of a solution of HSO_4^- ions produces $S_2O_8^{2-}$. Assuming 75% current efficiency, what current should be employed to achieve a production rate of 1 mole of $S_2O_8^{2-}$ per hour ?

Section (G) : Commercial Cells & Corrosion

Commit to memory :
At STP, V_m (molar volume of the gas) = 22.4 L/mol
Volume of gas required at STP = moles of gas × 22.4

G-1. A fuel cell uses $CH_4(g)$ and forms CO_3^{2-} at the anode. It is used to power a car with 80 Amp. for 0.96 hr. How many litres of $CH_4(g)$ (STP) would be required ? (V_m = 22.4 L/mol) (F = 96500). Assume 100% efficiency.

G-2. Find E^0 of cell formed for rusting of iron ?

$E^0_{Fe/Fe^{2+}} = +0.44$ V

$E^0_{H_2O|O_2|H^+} = -1.23$ V

Section (H) : Electrical Conductance

Commit to memory :
Conductivity (κ) = $C \times \dfrac{\ell}{A} = \dfrac{1}{R} \times \dfrac{\ell}{A}$

where, $\dfrac{\ell}{A}$ = cell constant, C = conductance, R = resistance.

A = surface area of electrodes, ℓ = distance between electrodes.

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Molar conductance $(\Lambda_m) = \dfrac{\kappa \times 1000}{M}$ S cm^2 mol^{-1}

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

where, M = molarity, N = normality and N = M × valence factor

H-1. The resistance of a M/10 KCl solution in 245 ohms. Calculate the specific conductance and the molar conductance of the solution if the electrodes in the cell are 4 cm apart and each having an area of 7.0 sq. cm.

H-2. The equivalent conductance of 0.10 N solution of MgCl$_2$ is 97.1 mho cm^2 eq.$^{-1}$ at 25°C. A cell with electrodes that are 1.50 cm^2 in surface area and 0.50 cm apart is filled with 0.1N MgCl$_2$ solution. How much current will flow when the potential difference between the electrodes is 5 volts ?

H-3. The specific conductance of a N/10 KCl solution at 18°C is 1.12 × 10^{-2} mho cm^{-1}. The resistance of the solution contained in the cell is found to be 65 ohms. Calculate the cell constant.

Section (I) : Kohlrausch law and its applications

Commit to memory :

Kohlrausch law : At infinite dilution, $\Lambda^0_{m,\ electrolyte} = \nu_+ \Lambda^0_{m^+} + \nu_- \Lambda^0_{m^-}$

where, ν_+ = number of cations in one formula unit of electrolyte.
          ν_- = number of anions in one formula unit of electrolyte.

At infinite dilution equivalent conductance : $\Lambda^0_{eq,\ electrolyte} = \Lambda^0_{eq+} + \Lambda^0_{eq-}$

Degree of dissociation (D.O.D.) = $\alpha = \dfrac{\Lambda_m}{\Lambda^0_m} = \dfrac{\Lambda_{eq}}{\Lambda^0_{eq}}$

For weak electrolyte, dissociation constant $(K_a) = \dfrac{C\alpha^2}{1-\alpha}$, where, C = concentration of electrolyte.

Solubility (s) = $\dfrac{\kappa \times 1000}{\Lambda^0_m}$ and $K_{sp} = S^2$ for AB type salt.

I-1. The molar conductance of an infinitely dilute solution of NH$_4$Cl is 150 and the ionic conductances of OH$^-$ and Cl$^-$ ions are 198 and 76 respectively. What will be the molar conductance of the solution of NH$_4$OH at infinite dilution. If the molar conductance of a 0.01 M solution NH$_4$OH is 9.6, what will be its degree of dissociation?

I-2. Given the molar conductance of sodium butyrate, sodium chloride and hydrogen chloride as 83, 127 and 426 mho cm^2 mol^{-1} at 25°C respectively. Calculate the molar conductance of butyric acid at infinite dilution.

I-3. Calculate K$_a$ of acetic acid if its 0.05 N solution has equivalent conductance of 7.36 mho cm^2 at 25°C. $(\lambda^\infty_{CH_3COOH} = 390.7)$.

I-4. The specific conductance of a saturated solution of AgCl at 25°C after subtracting the specific conductance of conductivity of water is 2.28 × 10^{-6} mho cm^{-1}. Find the solubility product of AgCl at 25°C. $(\lambda^\infty_{AgCl} = 138.3$ mho cm$^2)$

Section (J) : Conductometric Titration

Commit to memory :
H$^+$ and OH$^-$ ions are highly conducting.

J-1. Draw approximate titration curve for following –
(1) HCl(aq) is titrated with NaOH
(2) CH$_3$COOH(aq) is titrated with NaOH
(3) Equimolar mixture of HCl and HCN titrated withNaOH
(4) NH$_4$Cl(aq) is titrated withNaOH

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PART - II : ONLY ONE OPTION CORRECT TYPE

* Marked Questions are having more than one correct option.

Section (A) : Galvanic cell, its Representation & salt bridge

A-1. In a galvanic cell
(A) Chemical reaction produces electrical energy   (B) electrical energy produces chemical reaction
(C) reduction occurs at anode   (D) oxidation occurs at cathode

A-2.✎ Which of the following is/are function(s) of salt-bridge ?
(A) It completes the electrical circuit with electrons flowing from one electrode to the other through external wires and a flow of ions between the two compartments through salt - bridge
(B) it minimises the liquid - liquid junction potential
(C) both correct
(D) none of these

A-3. Salt bridge contains :
(A) calomel   (B) sugar   (C) H_2O (D) agar-agar paste

A-4.✎ The emf of the cell, Ni | Ni^{2+} (1.0 M) || Ag^+ (1.0M) | Ag [E° for Ni^{2+} / Ni = –0.25 volt, E° for Ag^+/Ag = 0.80 volt] is given by -
(A) –0.25 + 0.80 = 0.55 volt   (B) –0.25 – (+0.80) = –1.05 volt
(C) 0 + 0.80 – (–0.25) = + 1.05 volt   (D) –0.80 – (–0.25) = – 0.55 volt

Section (B) : Electrochemical series & its Applications

B-1.✎ E^0 for $F_2 + 2e \longrightarrow 2F^-$ is 2.8 V, E^0 for $\frac{1}{2} F_2 + e \longrightarrow F^-$ is

(A) 2.8 V   (B) 1.4 V   (C) – 2.8 V   (D) – 1.4 V

B-2. Consider the cell potentials = $E^o_{Mg^{2+}|Mg}$ – 2.37 V and $E^o_{Fe^{3+}|Fe}$ = – 0.04 V. The best reducing agent would be
(A) Mg^{2+} (B) Fe^{3+} (C) Mg   (D) Fe

B-3.✎ If a spoon of copper metal is placed in a solution of ferrous sulphate -
(A) Cu will precipitate out   (B) iron will precipitate
(C) Cu and Fe will precipitate   (D) no reaction will take place

B-4.✎ The position of some metals in the electrochemical series in decreasing electropositive character is given as Mg > Al > Zn > Cu > Ag. What will happen if a copper spoon is used to stir a solution of aluminium nitrate ?
(A) The spoon will get coated with aluminium   (B) An alloy of aluminium and copper is formed
(C) The solution becomes blue   (D) There is no reaction

B-5. For Zn^{2+} / Zn, E° = –0.76 V, for Ag^+/Ag E° = 0.799 V. The correct statement is -
(A) the reaction Zn getting reduced Ag getting oxidized is spontaneous
(B) Zn undergoes reduction and Ag is oxidized
(C) Zn undergoes oxidation Ag^+ gets reduced
(D) No suitable answer

B-6.✎ Electrode potential data are given below.
Fe^{3+} (aq) + e^- $\longrightarrow$ Fe^{2+} (aq); E^0 = + 0.77
Al^{3+} (aq) + $3e^-$ $\longrightarrow$ Al (s); E^0 = – 1.66 V
Br_2 (aq) + $2e^-$ $\longrightarrow$ $2Br^-$ (aq) ; E^0 = + 1.08 V
Based one the data given above, reducing power of Fe^{2+}, Al and Br^- will increase in the order :
(A) Br^- < Fe^{2+} < Al   (B) Fe^{2+} < Al < Br^- (C) Al < Br^- < Fe^{2+} (D) Al < Fe^{2+} < Br^-

B-7.✎ KCl can be used in salt bridge as electrolyte in which of the following cells?
(A) Zn | $ZnCl_2$ || $AgNO_3$ | Ag   (B) Pb | $Pb(NO_3)_2$ || $Cu(NO_3)_2$ | Cu
(C) Cu | $CuSO_4$ || $AuCl_3$ | Au   (D) Fe | $FeSO_4$ || $Pb(NO_3)_2$ | Pb

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B-8. Consider the following E^0 values :
$$E^0_{Fe^{3+}/Fe^{2+}} = + 0.77 \text{ V} \qquad ; \qquad E^0_{Sn^{2+}/Sn} = - 0.14 \text{ V}$$

Under standard conditions the potential for the reaction is
$$Sn\ (s) + 2\ Fe^{3+}\ (aq) \rightarrow 2Fe^{2+}\ (aq) + Sn^{2+}\ (aq)$$
(A) 1.68V   (B) 1.40 V   (C) 0.91 V   (D) 0.63 V
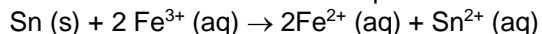
Section (C) : Concept of ΔG

C-1. Given standard electrode potentials :
$$Fe^{3+} + 3e^- \longrightarrow Fe\ ; \qquad E° = -0.036 \text{ volt}$$
$$Fe^{2+} + 2e^- \longrightarrow Fe; \qquad E° = -0.440 \text{ volt}$$
The standard electrode potential $E°$ for $Fe^{3+} + e^- \longrightarrow Fe^{2+}$
(A) –0.476 volt   (B) –0.404 volt   (C) 0.440 volt   (D) 0.772 volt
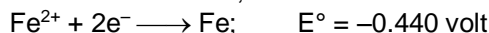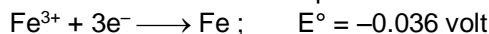
C-2. $Cu^+ + e^- \longrightarrow Cu, E° = x_1$ volt; $Cu^{2+} + 2e^- \longrightarrow Cu, E° = x_2$ volt, then for $Cu^{2+} + e^- \longrightarrow Cu^+, E°$ (volt) will be -
(A) $x_1 – 2x_2$ (B) $x_1 + 2x_2$ (C) $x_1 – x_2$ (D) $2x_2 – x_1$

C-3. Which of the following statements about the spontaneous reaction occurring in a galvanic cell is always true?
(A) $E^0_{cell} > 0, \Delta G^0 < 0,$ and $Q < K$ (B) $E^0_{cell} > 0, \Delta G^0 < 0,$ and $Q > K$
(C) $E^0_{cell} > 0, \Delta G^0 > 0,$ and $Q > K$ (D) $E_{cell} > 0, \Delta G < 0,$ and $Q < K$

Section (D) : Nernst equation & its Applications (including concentration cells)

D-1. The standard emf for the cell reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ is 1.10 volt at 25°C. The emf for the cell reaction when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solutions are used at 25°C is
(A) 1.10 volt   (B) 0.110 volt   (C) –1.10 volt   (D) –0.110 volt

D-2. Consider the cell $\begin{vmatrix} H_2(Pt) \\ 1\ atm \end{vmatrix} \begin{vmatrix} H_3O^+ (aq) \\ pH\ =\ 5.03 \end{vmatrix} \begin{vmatrix} Ag^+ \\ x\ \ M \end{vmatrix}$ Ag. The measured EMF of the cell is 1.0 V. What is the value of x ? $E^0_{Ag^+,Ag} = + 0.8$ V. [T = 25°C] ; $E^0_{Ag^+,Ag} = + 0.8$ V. [T = 25°C]
(A) 2×10^{-2} M   (B) 2×10^{-3} M   (C) 1.5×10^{-3} M   (D) 1.5×10^{-2} M

D-3. $Zn\ |\ Zn^{2+}\ (C_1)||\ Zn^{2+}\ (C_2)|Zn.$ for this cell ΔG is negative if -
(A) $C_1 = C_2$ (B) $C_1 > C_2$ (C) $C_2 > C_1$ (D) None

D-4. Pt $\begin{vmatrix} H_2 \\ (p_1) \end{vmatrix} \begin{vmatrix} H^+ \\ (1\ M) \end{vmatrix} \begin{vmatrix} H^+ \\ (1\ M) \end{vmatrix} \begin{vmatrix} H_2 \\ (p_2) \end{vmatrix}$ Pt (where p_1 and p_2 are pressures) cell reaction will be spontaneous if :
(A) $p_1 = p_2$ (B) $p_1 > p_2$ (C) $p_2 > p_1$ (D) $p_1 = 1$ atm

D-5. Pt | (H_2) | pH = 1 || pH = 2 | (H_2)Pt
     1 atm   1 atm
The cell reaction for the given cell is :
(A) spontaneous   (B) non - spontaneous   (C) equilibrium   (D) none of these

D-6. The EMF of a concentration cell consisting of two zinc electrodes, one dipping into $\dfrac{M}{4}$ sol. of zinc sulphate & the other into $\dfrac{M}{16}$ sol. of the same salt at 25^0 C is
(A) 0.0125 V   (B) 0.0250 V   (C) 0.0178 V   (D) 0.0356 V

Section (E) : Electrolysis

E-1. In an electrolytic cell of $Ag/AgNO_3/Ag$, when current is passed, the concentration of $AgNO_3$
(A) Increases   (B) Decreases   (C) Remains same   (D) None of these

E-2. If 0.224 L of H_2 gas is formed at the cathode, the volume of O_2 gas formed at the anode under identical conditions, is
(A) 0.224 L   (B) 0.448 L   (C) 0.112 L   (D) 1.12 L

E-3. The two aqueous solutions, A ($AgNO_3$) and B (LiCl) were electrolysed using Pt. electrodes. The pH of the resulting solutions will
(A) increase in A and decrease in B   (B) decrease in both
(C) increase in both   (D) decrease in A and increase in B.

E-4. In the electrolysis of aqueous $CuBr_2$ using Pt electrodes :
(A) Br_2 gas is not evolved at the anode
(B) Cu (s) is deposited at the cathode
(C) Br_2 gas is evolved at anode and H_2 gas at cathode
(D) H_2 gas is evolved at anode.

E-5. During electrolysis of $CuSO_4$ using Pt-electrodes, the pH of solution
(A) increases   (B) decreases   (C) remains unchanged   (D) cannot be predicted

Section (F) : Faraday laws & its Applictions

F-1. How many faradays are required to reduce one mol of MnO_4^- to Mn^{2+} -
(A) 1   (B) 2   (C) 3   (D) 5

F-2. Three faradays of electricity was passed through an aqueous solution of iron (II) bromide. The mass of iron metal (at. mass 56) deposited at the cathode is -
(A) 56 g   (B) 84 g   (C) 112 g   (D) 168 g

F-3. A current of 2 A was passed for 1 h through a solution of $CuSO_4$ 0.237 g of Cu^{2+} ions were discharged at cathode. The current efficiency is
(A) 42.2%   (B) 26.1%   (C) 10%   (D) 40.01%

F-4. A current of 9.65 ampere is passed through the aqueous solution NaCl using suitable electrodes for 1000 s. The amount of NaOH formed during electrolysis is
(A) 2.0 g   (B) 4.0 g   (C) 6.0 g   (D) 8.0 g

F-5. Salts of A (atomic mass 15), B (atomic mass 27) and C (atomic mass 48) were electrolysed using same amount of charge. It was found that when 4.5 g of A was deposited, the mass of B and C deposited were 2.7g and 9.6 g. The valencies of A, B and C respectively.
(A) 1, 3 and 2   (B) 3, 1 and 3   (C) 2, 6 and 3   (D) 3, 1 and 2

Section (G) : Commercial Cells & Corrosion

G-1. During discharge of a lead storage cell the density of sulphuric acid in the cell :
(A) Increasing   (B) decreasing
(C) remians unchanged   (D) initially increases but decrease subsequently

G-2. In H_2-O_2 fuel cell the reaction occuring at cathode is :
(A) $2\,H_2O + O_2 + 4\,e^- \longrightarrow 4\,OH^-$ (B) $2H_2 + O_2 \longrightarrow 2H_2O\,(l)$
(C) $H^+ + OH^- \longrightarrow H_2O$ (D) $H^+ + e^- \longrightarrow \dfrac{1}{2}\,H_2$.

G-3. Which is not correct method for prevention of iron from Rusting -
(A) Galvanisation   (B) Connecting to sacrificial electrode of Mg
(C) Making medium alkaline   (D) Making medium acidic

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Section (H) : Electrical Conductance

H-1. Which of the following curve represents the variation of Λ_M with $\sqrt{C}$ for $AgNO_3$?

(A) Λ_M / $\sqrt{C}$
(B) Λ_M / $\sqrt{C}$
(C) Λ_M / $\sqrt{C}$
(D) Λ_M / $\sqrt{C}$
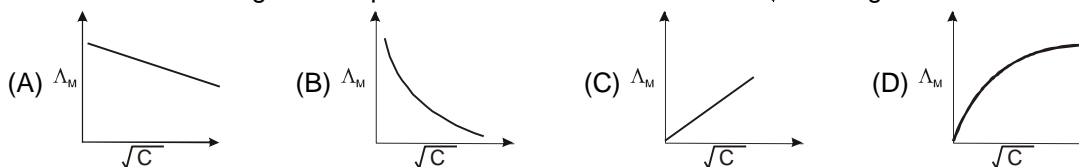
H-2. Which has maxmium conductivity :

(A) $[Cr(NH_3)_3 Cl_3]$ (B) $[Cr(NH_3)_4 Cl_2]Cl$ (C) $[Cr(NH_3)_5Cl]Cl_2$ (D) $[Cr(NH_3)_6]Cl_3$

H-3. Resistance of decimolar solution is 50 ohm. If electrodes of surface area 0.0004 m² each are placed at a distance of 0.02 m then conductivity of solution is :

(A) 1 s cm⁻   (B) 0.01 s cm⁻   (C) 0.001 s cm⁻   (D) 10 s cm⁻

Section (I) : Kohlrausch law and its applications

I-1. The ionization constant of a weak electrolyte (HA) is 25×10^{-6} while the equivalent conductance of its 0.01 M solution is 19.6 S cm² eq⁻¹. The equivalent conductance of the electrolyte at infinite dilution (in S cm² eq⁻¹) will be

(A) 250   (B) 196   (C) 392   (D) 384

I-2. The conductivity of a saturated solution of $BaSO_4$ is 3.06×10^{-6} ohm⁻¹ cm⁻¹ and its equivalent conductance is 1.53 ohm⁻¹ cm² equiv⁻¹. The K_{sp} for $BaSO_4$ will be

(A) 4×10^{-12} (B) 2.5×10^{-13} (C) 25×10^{-9} (D) 10^{-6}

I-3. Molar conductance of 0.1 M acetic acid is 7 ohm⁻¹ cm² mol⁻¹. If the molar cond. of acetic acid at infinite dilution is 380.8 ohm⁻¹ cm² mol⁻¹, the value of dissociation constant will be :

(A) 226×10^{-5} mol dm⁻³   (B) 1.66×10^{-3} mol dm⁻¹

(C) 1.66×10^{-2} mol dm⁻³   (D) 3.442×10^{-5} mol dm⁻³

I-4. The conductivity of a solution of AgCl at 298 K is found to be 1.382×10^{-6} Ω^{-1} cm⁻¹. The ionic conductance of Ag^+ and Cl^- at infinite dilution are 61.9 Ω^{-1} cm² mol⁻¹ and 76.3 Ω^{-1} cm² mol⁻¹, respecitvley. The solubility of AgCl is

(A) 1.4×10^{-5} mol L⁻¹   (B) 1×10^{-2} mol L⁻¹   (C) 1×10^{-5} mol L⁻¹   (D) 1.9×10^{-5} mol L⁻¹

I-5. 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) $\dfrac{[x_1 + x_2 - x_3]}{2}$ (B) $\dfrac{[x_1 - x_2 - x_3]}{2}$ (C) $2 (x_1 + x_2 - 2x_3)$ (D) $\dfrac{[x_1 + x_2 - 2x_3]}{2}$

Section (J) : Conductometric Titration

J-1. 20 ml KOH solution was titrated with 0.2 mol/l H_2SO_4 solution in conductivity cell. Concentration of KOH solution was –

(A) 0.3 M

(B) 0.15

(C) 0.12

(D) None of these
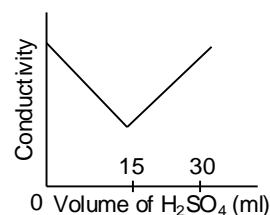
J-2. Following curve for conductometric titration is obtained when –

x = Equivalence point
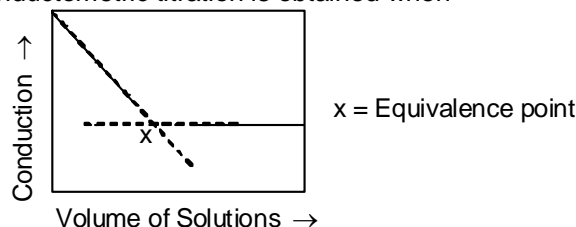
(A) NaOH solution is added in to HCl solution

(B) NaOH solution is added in to CH_3COOH solution

(C) NH_4OH solution is added in to HCl solution

(D) NH_4OH solution is added in to CH_3COOH solution

PART - III : MATCH THE COLUMN

1. Match the column

	Column I		Column II
(A)	$Zn \mid Zn^{+2} \mid\mid Mg^{2+} \mid Mg$ $\quad c_1 \quad\quad c_2 \quad (c_1 = c_2)$	**(p)**	$E_{cell} = 0$
(B)	$Zn \mid Zn^{+2} \mid\mid Ag^+ \mid Ag$ at. equilibrium	**(q)**	$E^0_{cell} = 0$
(C)	$Ag \mid Ag^+ \mid\mid Ag^+ \mid Ag$ $\quad c_1 \quad\quad c_2 \quad (c_1 = c_2)$	**(r)**	$E^0_{cell} = +ve$
(D)	$Fe \mid Fe^{+2} \mid\mid Ag \mid Ag^+$ $\quad c_1 \quad\quad c_2 \quad (c_1 = c_2)$	**(s)**	$E^0_{cell} = -ve$

2.^✎ Match Matrix $\left(E^0_{Ag^+/Ag} = 0.8\right)$.

	Column I		Column II
(A)	$Pt \mid H_2\ (0.1\ bar) \mid H^+\ (0.1\ M) \mid\mid H^+\ (1\ M) \mid H_2\ (0.01\ bar) \mid Pt$	**(p)**	Concentration cell
(B)	$Ag \mid Ag^+\ (10^{-9}\ M) \mid\mid Ag^+\ (10^{-2}\ M) \mid Ag$	**(q)**	$E_{cell} > 0$
(C)	$Cu \mid Cu^{2+}\ (0.1\ M) \mid\mid Cu^{2+}\ (0.01\ M) \mid Cu$	**(r)**	$E^0_{cell} = 0$ but cell is working.
(D)	$Pt \mid Cl_2\ (1bar) \mid HCl\ (0.1\ M) \mid\mid NaCl\ (0.1M) \mid Cl_2 \mid Pt\ (1\ bar)$	**(s)**	non working condition

Exercise-2

✎ **Marked Questions may have for Revision Questions.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1. Given : $E^0(Cu^{2+} \mid Cu) = 0.337$ V and $E^0 (Sn^{2+} \mid Sn) = -0.136$ V. Which of the following statements is correct?

(A) Cu^{2+} ions can be reduced by $H_2(g)$ (B) Cu can be oxidized by H^+

(C) Sn^{2+} ions can be reduced by $H_2(g)$ (D) Cu can reduce Sn^{2+}

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2. Using the standard potential values given below, decide which of the statements I, II, III, IV are correct. Choose the right answer from (a), (b), (c) and (d)

$Fe^{2+} + 2e^- = Fe$, $\qquad E^0 = -0.44$ V

$Cu^{2+} + 2e^- = Cu$, $\qquad E^0 = +0.34$ V

$Ag^+ + e^- = Ag$, $\qquad E^0 = +0.80$ V

I. Copper can displace iron from $FeSO_4$ solution

II. Iron can displace copper from $CuSO_4$ solution

III. Silver can displace Cu from $CuSO_4$ solution

IV. Iron can displace silver from $AgNO_3$ solution

(A) I and II   (B) II and III   (C) II and IV   (D) I and IV

3. Red hot carbon will remove oxygen from the oxide AO and BO but not from MO, while B will remove oxygen from AO. The activity of metals A, B and M in decreasing order is

(A) A > B > M   (B) B > A > M   (C) M > B > A   (D) M > A > B

4. Which statement is correct.

(A) In SHE, the pressure of dihydrogen gas should be low and pH of solution should be zero.

(B) In the reaction $H_2O_2 + O_3 \longrightarrow 2H_2O + 2O_2$, H_2O_2 is oxidised to H_2O.

(C) The absolute value of electrode potential cannot be determined.

(D) According to IUPAC conventions, the standard electrode potential pertains to oxidation reactions only.

5. The electrode oxidation potential of electrode $M(s) \longrightarrow M^{n+}(aq)$ (2M) $+ ne^-$ at 298 K is E_1. When temperature (in ^0C) is doubled and concentration is made half, then the electrode potential becomes E_2. Which of the following represents the correct relationship between E_1 and E_2 ?

(A) $E_1 > E_2$ (B) $E_1 < E_2$ (C) $E_1 = E_2$ (D) Cann't be predicted

6. A galvanic cell is composed of two hydrogen electrodes, one of which is a standard one. In which of the following solutions should the other electrode be immersed to get maximum emf ?

$K_a(CH_3COOH) = 2 \times 10^{-5}$, $K_a(H_3PO_4) = 10^{-3}$.

(A) 0.1 M HCl   (B) 0.1 M CH_3COOH (C) 0.1 M H_3PO_4 (D) 0.1 M H_2SO_4

7. Two weak acid solutions HA_1 and HA_2 each with the same concentration and having pK_a values 3 and 5 are placed in contact with hydrogen electrode (1 atm, 25^{0}C) and are interconnected through a salt bridge. The emf of the cell is :

(A) 0.21 V

(B) 0.059 V

(C) 0.018 V

(D) 0.021 V

8. A hydrogen electrode placed in a buffer solution of CH_3COONa and CH_3COOH in the ratios of x : y and y : x has electrode potential values E_1 volts and E_2 volts, respectively at 25^{0}C. The pK_a values of acetic acid is (E_1 and E_2 are oxidation potentials)

(A) $\dfrac{E_1 + E_2}{0.118}$ (B) $\dfrac{E_2 - E_1}{0.118}$ (C) $-\dfrac{E_1 + E_2}{0.118}$ (D) $\dfrac{E_1 - E_2}{0.118}$

9. What is the emf at 25° C for the cell, Ag, $\begin{vmatrix} AgBr & (s), & Br^- \\ & a = 0.34 \end{vmatrix} \begin{vmatrix} Fe^{3+} & , & Fe^{2+} \\ a = 0.1 & a = 0.02 \end{vmatrix}$ Pt

The standard reduction potentials for the half-reactions $AgBr + e^- \rightarrow Ag + Br^-$ and $Fe^{3+} + e^- \rightarrow Fe^{2+}$ are + 0.0713 V and + 0.770 V respectively.

(A) 0.474 volt   (B) 0.529 volt   (C) 0.356 volt   (D) 0.713 volt

10. When the sample of copper with zinc impurity is to be purified by electolysis, the appropriate electrode are

(A) pure zinc as cathode and pure copper as anode

(B) impure sample as cathode and pure copper as anode

(C) impure zinc as cathode and impure sample as anode

(D) pure copper as cathode and impure sample as anode

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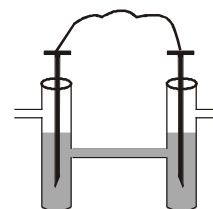
11. Four moles of electrons were transferred from anode to cathode in an experiment on electrolysis of water. The total volume of the two gases (dry and at STP) produced will be approximately (in litres)
    (A) 22.4   (B) 44.8   (C) 67.2   (D) 89.4

12. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2. Passing a current of 27A for 24 hours gives 1kg of MnO_2. The current efficiency in this process is :
    (A) 100%   (B) 95.185%   (C) 80%   (D) 82.951%

13. During the preparation of $H_2S_2O_8$ (per disulphuric acid) O_2 gas also releases at anode as byproduct, When 9.72 L of H_2 releases at cathode and 2.35 L O_2 at anode at STP, the weight of $H_2S_2O_8$ produced in gram is
    (A) 87.12   (B) 43.56   (C) 83.42   (D) 51.74

14. When the electric current is passed through a cell having an electrolyte, the positive ions move towards cathode and negative ions towards the anode. If the cathode is pulled out of the solution
    (A) the positive and negative ions will move towards anode
    (B) the positive ions will start moving towards the anode while negative ions will stop moving
    (C) the negative ions will continue to move towards anode while positive ions will stop moving
    (D) the positive and negative ions will start moving randomly

15. When iron is rusted, it is :
    (A) reduced   (B) oxidised   (C) evaporated   (D) decomposed

PART - II : NUMERICAL VALUE QUESTIONS

1.
$H_4XeO_6 + 2H^+ + 2e^- \longrightarrow XeO_3 + 3H_2O$ $E^0 = 3\ V$

$F_2 + 2e^- \longrightarrow 2F^-$ $E^0 = 2.87\ V$

$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$ $E^0 = 2.07\ V$

$Ce^{4+} + e^- \longrightarrow Ce^{3+}$ $E^0 = 1.67\ V$

$2HClO + 2H^+ + 2e^- \longrightarrow Cl_2 + 2H_2O$ $E^0 = 1.63\ V$

$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O$ $E^0 = 1.23\ V$

$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$ $E^0 = 0.89\ V$

$BrO^- + H_2O + 2e^- \longrightarrow Br^- + 2OH^-$ $E^0 = 0.76\ V$

$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$ $E^0 = 0.36\ V$

$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$ $E^0 = 0.36\ V$

Based on the above data, how many of the following statements are correct ?
(A) F_2 is better oxidizing agent than $H_4X_6O_6$.
(B) Ozone can oxidize Cl_2
(C) ClO_4^- is better oxidizing agent in basic medium than in acidic medium
(D) Ferrocyanide ion can be easily oxidized by ClO^-, Ce^{4+}, Li^+, BrO^-
(E) ClO^- can oxidize Br^- and ClO_3^- in basic medium
(F) Ce^{4+} can oxidize Cl_2 in acidic medium under standard conditions.

2. A hydrogen gas electrode is made by dipping platinum wire in a solution of NaOH of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode is 10x milivolt. Find x ? (Take $\dfrac{2.303\ RT}{F} = 0.059$)

3. Estimate the cell potential of a Daniel cell having 1.0M Zn^{2+} and originally having 1.0M Cu^{2+} after sufficient NH_3 has been added to the cathode compartment to make NH_3 concentration 2.0M at equilibrium. Given K_f for $[Cu(NH_3)_4]^{2+} = 1 \times 10^{12}$, $E°$ for the reaction, $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ 1.1V. (Take $\dfrac{2.303\ RT}{F} = 0.06$, log 6.25 = 0.8) Respond as 10 $\times$ your answer.

4. Molar conductivity of 0.04 $MgCl_2$ solution at 298 k is 200 Scm^2mole^{-1}. A conductivity cell which is filled with $MgCl_2$ have area of cross-section of electrode $4cm^2$ & distance between electrode is 8 cm. If potential difference between electrode is 10V then find current flow in miliampere.

5. The conductivity of a solution which is 0.1 M in $Ba(NO_3)_2$ and 0.2 M in $AgNO_3$ is 5.3 Sm^{-1}. If $\lambda^o_{(Ag^+)} =$ 6×10^{-3} Sm^2 mol^{-1} & $\lambda^o_{(Ba^{2+})} = 13 \times 10^{-3}$ Sm^2 mol^{-1}, determine $\lambda^o_{(NO_3^-)}$ in same unit. Report your answer after multiplying by 1000.

6. Λ^∞_m (weak mono basic HA acid) = 390.7 S cm^2 mol^{-1}

Λ_m of HA at 0.01 M is 3.907 S cm^2 mol^{-1}

Find pH of 0.01 M HA ?

7. For a saturated solution of AgCl at 25°C, $\kappa = 3.4 \times 10^{-6}$ ohm^{-1} cm^{-1} and that of $H_2O(\ell)$ used is 2.02×10^{-6} ohm^{-1} cm^{-1}. $\Lambda°_m$ for AgCl is 138 ohm^{-1} cm^2 mol^{-1} then the solubility of AgCl in mili moles per m^3 will be :

8. At 298 K, the conductivity of pure water is 5.5×10^{-6} S m^{-1}. Calculate the ionic product of water using the following data :

λ^o_m values (in S m^2 mol^{-1}) : $Ba(OH)_2$ = 5.3×10^{-2}, HCl = 4.25×10^{-2}, $BaCl_2$ = 2.8×10^{-2}.

Does your answer match with experimental value. Write 20 for yes & 40 for No.

9. How many of the following comparisons are correct with respect to their Λ^∞_m ?
(A) $K^+ > Na^+$ (B) $K^+ > H_3O^+$ (C) $Ca^{2+} > Na^+$ (D) $Mg^{2+} > NH_4^+$
(E) $H_3O^+ > Mg^{2+}$ (F) $K^+ > Mg^{2+}$

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Given $E^\circ_{Ag^+/Ag}$ = 0.80V, $E^\circ_{Mg^{2+}/Mg}$ = –2.37V, $E^\circ_{Cu^{2+}/Cu}$ = 0.34V, $E^\circ_{Hg^{2+}/Hg}$ = 0.79 V.

Which of the following statements is/are correct
(A) $AgNO_3$ can be stored in copper vessel (B) $Mg(NO_3)_2$ can be stored in copper vessel
(C) $CuCl_2$ can be stored in silver vessel (D) $HgCl_2$ can be stored in copper vessel

2. Any redox reaction would occur spontaneously, if :
(A) the free energy change (ΔG) is negative (B) the ΔG^o is positive
(C) the cell e.m.f. (E^o) is negative (D) the cell e.m.f. is positive

3. Consider an electrolytic cell E being powered by a galvenic cell G, as shown in the figure. Then :
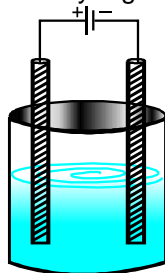
(A) Anode of E is connected to cathode of G (B) Anode of E is connected to anode of G
(C) Cathode of E is connected to anode of G (D) Cathode of E is connected to cathode of G

4. On electrolysis, in which of the following, O_2 would be liberated at the anode ?
(A) dilute H_2SO_4 with Pt electrodes (B) aqueous $AgNO_3$ solution with Pt electrodes
(C) dilute H_2SO_4 with Cu electrodes (D) aqueous NaOH with a Fe cathode & a Pt anode

5. A current of 2.68 A is passed for one hour through an aqueous solution of $CuSO_4$ using copper electrodes. Select the correct statement(s) from the following :

(A) increase in mass of cathode = 3.174 g

(B) decrease in mass of anode = 3.174 g

(C) no change in masses of electrodes

(D) the ratio between the change of masses of cathode and anode is 1 : 2.

6. Three moles of electrons are passed through three solutions in succession containing $AgNO_3$, $CuSO_4$ and $AuCl_3$, respectively. The molar ratio of amounts of cations reduced at cathode will be

(A) 1 : 2 : 3   (B) $\dfrac{1}{1} : \dfrac{1}{2} : \dfrac{1}{3}$ (C) 3 : 2 : 1   (D) 6 : 3 : 2

7. If same quantity of electricity is passed through three electrolytic cells containing $FeSO_4$, $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$, then

(A) the amount of iron deposited in $FeSO_4$ and $Fe_2(SO_4)_3$ are equal

(B) the amount of iron deposited in $FeSO_4$ is 1.5 times of the amount of iron deposited in $Fe(NO_3)_3$.

(C) the amount of iron deposited in $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$ are equal

(D) the same amount of gas is evolved in all three cases at the anode.

8. When a lead storage battery is discharged then :

(A) SO_2 is evolved   (B) lead sulphate is produced at both electrodes

(C) sulphuric acid is consumed   (D) water is formed

9. Mark out the correct statement(s) regarding electrolytic molar conductivity.

(A) It increase as temperature increases.

(B) It experiences resistance due to vibration of ion at the mean position.

(C) Increase in concentration decreases the electrolytic molar conductivity of both the strong as well as the weak electrolyte.

(D) Greater the polarity of solvent, greater is the electrolytic molar conduction.

10. On increasing dilution following will increase :

(A) Equivalent conductivity   (B) Conductivity

(C) Molar conductivity   (D) All of these

11. The resistances of following solutions of KCl were measured using conductivity cells of different cell constants, at same temperature. (Consider that at concentration less than 0.1 M, the specific conductivity of solution is directly proportional to the concentration of solution.)

	Concentration of Solution	Cell Constant
1.	0.1 M	$1 \ cm^{-1}$
2.	0.01 M	$10 \ cm^{-1}$
3.	0.005 M	$5 \ cm^{-1}$
4.	0.0025 M	$25 \ cm^{-1}$

Which of the following comparisons between their conductances (G) is/are correct ?

(A) G_1 is maximum   (B) G_4 is minimum   (C) $G_3 >> G_2$ (D) G_4 is maximum

12. Identify correct statements :

(A) Kohlraush law is applicable only on weak electrolyte.

(B) On increasing dilution conductance, molar conductivity, equivalent conductivity increases but conductivity decreases.

(C) $\Lambda_m = \dfrac{K}{C}$ following formula has units $\Lambda_m \to \Omega^- \ dm^2/mol$, $K \to \Omega^- \ dm^{-1}$, $C \to mol/\ell$.

(D) Equation $\Lambda_m = \Lambda_m^\infty - b\sqrt{C}$ is applicable on weak as well as strong electrolyte.

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13. Select the correct option(s):

(A) $\dfrac{\lambda^{\circ}_{eq}\ (Al^{3+})}{3} = \lambda^{\circ}_{m}\left(Al^{3+}\right)$ & $\dfrac{\lambda^{\circ}_{eq}\ (SO_4^{2-})}{2} = \lambda^{\circ}_{m}\ (SO_4^{2-})$

(B) $\lambda^{\circ}_{eq}\ (Al^{3+}) = \dfrac{\lambda^{\circ}_{m}\left(Al^{3+}\right)}{3}$ & $\lambda^{\circ}_{eq}\ (SO_4^{2-}) = \dfrac{\lambda^{\circ}_{m}\ (SO_4^{2-})}{2}$

(C) $\lambda^{\circ}_{eq}\ (Al_2(SO_4)_3) = \dfrac{\lambda^{\circ}_{m}\ (Al^{3+})}{3} + \dfrac{\lambda^{\circ}_{m}\ (SO_4^{2-})}{2}$

(D) $\lambda^{\circ}_{m}\ (Al_2(SO_4)_3) = 6 \times \lambda^{\circ}_{eq}\ (Al_2(SO_4)_3)$

14. Which of the following order is correct related to their mobility in solution:

(A) $Cs^+_{aq} > Rb^+_{aq} > K^+_{aq} > Na^+_{aq} > Li^+_{aq}$ (B) $Be^{+2}_{aq} > Li^+_{aq} > Cs^+_{aq}$

(C) $H^+_{aq} > Li^+_{aq} > Be^{+2}_{aq} > Na^+_{aq} > Mg^{+2}_{aq}$ (D) $H^+_{(aq)} > Na^+_{(aq)} > Li^+_{(aq)} > Be^{+2}_{(aq)}$

15. For strong electrolyte Λ_M increases slow with dilution and can be represented by the equation
$\wedge_M = \wedge^{0}_M - AC^{½}$
Select correct statement

(A) Plot of $\wedge_M$ against $C^{½}$ is obtain a straight line with intercept $\wedge^{0}_M$ & and slope '–A'
(B) Value of A depends upon temperature solvent and nature of electrolyte.
(C) NaCl and KCl have different value of constant 'A'
(D) NaCl and MgSO₄ have different value of constant 'A'

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

If an element can exist in several oxidation states, it is convenient to display the reduction potentials corresponding to the various half reactions in diagrammatic form, known as Latimer diagram. The Latimer diagram for chlorine in acid solution is

$ClO_4^- \xrightarrow{+1.20\ V} ClO_3^- \xrightarrow{+1.18\ V} HClO_2 \xrightarrow{+1.60\ V} HClO \xrightarrow{1.67\ V} Cl_2 \xrightarrow{1.36\ V} Cl^-$

in basic solution.

$ClO_4^- \xrightarrow{0.37\ V} ClO_3^- \xrightarrow{0.30\ V} ClO_2^- \xrightarrow{0.68\ V} ClO^- \xrightarrow{0.42\ V} Cl_2 \xrightarrow{1.36\ V} Cl^-$
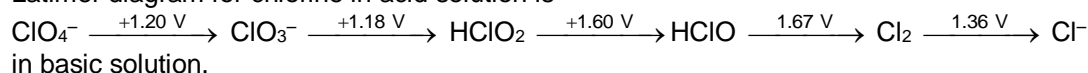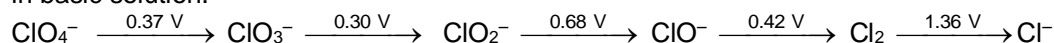
The standard potentials for two nonadjacent species can also be calculated by using the concept that $\Delta G°$ as an additive property but potential is not an additive property and $\Delta G° = - nFx^0$. If a given oxidation state is a stronger oxidising agent than in the next higher oxidation state, disproportionation can occur. The reverse of disproportionation is called comproportionation. The relative stabilities of the oxidation state can also be understood by drawing a graph of $\Delta G°/F$ against oxidation state, known as Frost diagram, choosing the stability of zero oxidation state arbitrarily as zero. The most stable oxidation state of a species lies lowest in the diagram. Disproportionation is spontaneous if the species lies above a straight line joining its two product species.

1. Which of the following couple have same value of potential at pH = 0 and pH = 14?

(A) $\dfrac{ClO_4^-}{ClO_3^-}$ (B) $\dfrac{ClO_2^-}{Cl_2}$ (C) $\dfrac{ClO^-}{Cl_2}$ (D) $\dfrac{Cl_2}{Cl^-}$
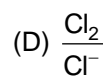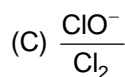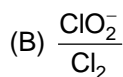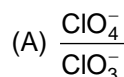
2. What is the potential of couple $\dfrac{ClO^-}{Cl^-}$ at pH = 14 ?

(A) 1.78 V   (B) – 0.94 V   (C) 0.89 V   (D) – 0.89 V

3. Which of the following statement is correct ?
(A) Cl₂ undergoes disproportionation into Cl⁻ and ClO⁻ both at pH = 0 and pH = 14.
(B) Cl₂ undergoes disproportionation into Cl⁻ and ClO⁻ at pH = 14 but not at pH = 0.
(C) Cl₂ undergoes disproportionation into Cl⁻ and ClO⁻ at pH = 0 but not at pH = 14.
(D) None of these

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4. For a hypothetical element, the Frost diagram is shown in figure?
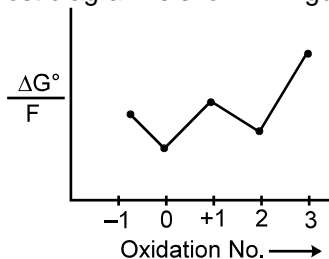
Which of the following oxidation state is least stable?

(A) – 1   (B) 0   (C) + 2   (D) + 3

5. Which of the following statement is correct ? According to Q.4

(A) A^{+1} undergoes disproportionation into A and A^{2+}.

(B) A^{2+} undergoes disporportionation in A and A^{3+}.

(C) A undergoes comporportionation in A^{+1} and A^{-1}.

(D) All of the above.

Comprehension # 2

The molar conductance of NaCl varies with the concentration as shown in the following table and all values follows the equation

$$\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$$ Where λ_m^C = molar specific conductance

λ_m^∞ = molar specific conductance at infinite dilution

C = molar concentration

Molar Concentration of NaCl	Molar Conductance in ohm^{-1} cm^2 mole^{-1}
4×10^{-4}	107
9×10^{-4}	97
16×10^{-4}	87

When a certain conductivity cell (C) was filled with 25×10^{-4} (M) NaCl solution. The resistance of the cell was found to be 1000 ohm. At Infinite dilution, conductance of Cl^- and SO_4^{-2} are 80 ohm^{-1} cm^2 mole^{-1} and 160 ohm^{-1} cm^2 mole^{-1} respectively.

6. What is the molar conductance of NaCl at infinite dilution ?

(A) 147 ohm^{-1} cm^2 mole^{-1} (B) 107 ohm^{-1} cm^{2}s mole^{-1}

(C) 127 ohm^{-1} cm^2 mole^{-1} (D) 157 ohm^{-1} cm^2 mole^{-1}

7. What is the cell constant of the conductivity cell (C)

(A) 0.385 cm^{-1} (B) 3.85 cm^{-1} (C) 38.5 cm^{-1} (D) 0.1925 cm^{-1}

8. If the cell (C) is filled with 5×10^{-3} (N) Na_2SO_4 the observed resistance was 400 ohm. What is the molar conductance of Na_2SO_4.

(A) 19.25 ohm^{-1} cm^2 mole^{-1} (B) 96.25 ohm^{-1} cm^2 mole^{-1}

(C) 385 ohm^{-1} cm^2 mole^{-1} (D) 192.5 ohm^{-1} cm^{2}s mole^{-1}

9. If a 100 mL solution of 0.1M HBr is titrated using a very concentrated solution of NaOH, then the conductivity (specific conductance) of this solution at the equivalence point will be (assume volume change is negligible due to addition of NaOH) . Report your answer after multipling it with 10 in Sm^{-1}.

[Given $\lambda^0_{(Na^+)} = 8 \times 10^{-3}$ Sm^2 mol^{-1} , $\lambda^0_{(Br^-)} = 4 \times 10^{-3}$ S m^2 mol^{-1}]

(A) 6   (B) 12   (C) 15   (D) 24

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Comprehension # 3

Answer 10, Q.11 and Q.12 by appropriately matching the information given in the three columns of the following table.

The curves in Column 1 shows the variation of conductivity during different titrations. The analyte and titrants has been listed in Column 2 & Column 3 respectively.

Column-1		Column-2 (Titrate)		Column-3 (Titrant)	
(I)	Conductivity decreases initially then increases slowly then increases rapidly	(i)	$(C_2H_5)_2NH$	(P)	HCl
(II)	Conductivity decreases initially then increases	(ii)	CH_3COOH	(Q)	NaOH
(III)	Conductivity decreases initially then remains approximately same	(iii)	HBr	(R)	CH_3COOH
(IV)	Conductivity increases initially then remains approximately same	(iv)	NaOH	(S)	NH_4OH

10. Which of the following is an incorrect combination of curves in Column 1.
(A) (II) (iii) (Q)   (B) (I) (i) (P)   (C) (I) (iii) (S)   (D) (I) (ii) (Q)

11. The correct combination for a titration in which conductance at equivalent point is lower than initial
(A) (I) (ii) (Q)   (B) (I) (iii) (S)   (C) (III) (iv) (R)   (D) (IV) (ii) (S)

12. Select the correct combination
(A) (I) (iii) (Q)   (B) (IV) (ii) (S)   (C) (I) (iii) (S)   (D) (I) (iv) (R)

Exercise-3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

* Marked Questions are having one or more than one correct options.

1. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below :   **[JEE 2002, 3/84]**

$MnO_4^-(aq.) + 8H^+(aq.) + 5e^- \rightarrow Mn^{2+}(aq.) + 4H_2O(\ell)$ E^0 = 1.51 V
$Cr_2O_7^{2-}(aq.) + 14H^+(aq.) + 6e^- \rightarrow 2Cr^{3+}(aq.) + 7H_2O(\ell)$ E^0 = 1.38 V
$Fe^{3+}(aq.) + e^- \rightarrow Fe^{2+}(aq.)$ E^0 = 0.77 V
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq.)$ E^0 = 1.40 V

Identify the only INCORRECT statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$:
(A) MnO_4^- can be used in aqueous HCl.   (B) $Cr_2O_7^{2-}$ can be used in aqueous HCl.
(C) MnO_4^- can be used in aqueous H_2SO_4.   (D) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4.

2. Two students use the same stock solution of $ZnSO_4$ and different solutions of $CuSO_4$ to make Daniel cell. The emf of one cell is 0.03 V higher than the other. The concentration of $CuSO_4$ solution in the cell with higher emf value is 0.5 M. Find out the concentration of $CuSO_4$ solution in the other cell.

$\left(\text{Given} : \dfrac{2.303 \ RT}{F} = 0.06 \right)$.   **[JEE 2003, 2/60]**

3. The emf of the cell, $Zn \mid Zn^{2+}(0.01 \text{ M}) \parallel Fe^{2+}(0.001 \text{ M}) \mid Fe$ at 298 K is 0.2905 V. Then the value of equilibrium constant for the cell reaction is :   **[JEE 2004, 3/84]**

(A) $e^{\frac{0.32}{0.0295}}$ (B) $10^{\frac{0.32}{0.0295}}$ (C) $10^{\frac{0.26}{0.0295}}$ (D) $10^{\frac{0.32}{0.059}}$

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4. Find the equilibrium constant at 298 K for the reaction : **[JEE 2004, 4/60]**

$$Cu^{2+}(aq) + In^{2+}(aq) \rightleftharpoons Cu^+(aq) + In^{3+}(aq)$$

Given that $E^0_{Cu2+ / Cu+}$ = 0.15 V, $E^0_{In3+ / In+}$ = − 0.42 V, $E^0_{In2+ / In+}$ = − 0.40 V.

5. The half cell reactions for rusting of iron are :

$$2H^+ + \frac{1}{2} O_2 + 2e^- \longrightarrow H_2O; \ E^0 = +1.23 \ V \ \& \ Fe^{2+} + 2e^- \longrightarrow Fe ; \ E^0 = - 0.44 \ V$$

ΔG^0 (in kJ/mol) for the overall reaction is : **[JEE 2005, 3/84]**
(A) − 76   (B) − 322   (C) − 122   (D) − 176

Comprehension # 1

Tollen's reagent is used for the detection of aldehyde. When a solution of $AgNO_3$ is added to glucose with NH_4OH, then gluconic acid is formed.

$$Ag^+ + e^- \longrightarrow Ag ; \qquad\qquad\qquad E^0_{red} = 0.8 \ V$$
$$C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7 \ (Gluconic \ acid) + 2H^+ + 2e^- ; \qquad E^0_{oxd} = - 0.05 \ V$$
$$Ag(NH_3)_2^+ + e^- \longrightarrow Ag(s) + 2NH_3 ; \qquad\qquad E^0 = - 0.337 \ V$$

[Use $2.303 \times \dfrac{RT}{F}$ = 0.0592 and $\dfrac{F}{RT}$ = 38.92 at 298 K]
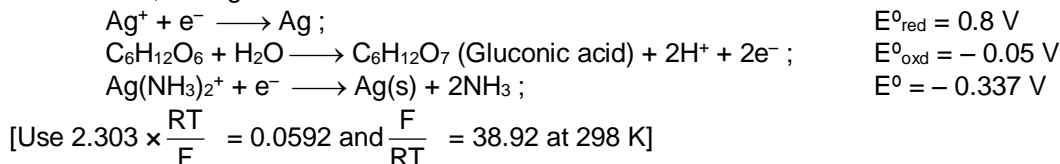
Now answer the following three questions :

6. $2Ag^+ + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$
Find ln K of this reaction : **[JEE 2006, 5/184]**
$2Ag^+ + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$
(A) 66.13   (B) 58.38   (C) 28.30   (D) 46.29

7. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much : **[JEE 2006, 5/184]**
(A) E_{oxd} will increase by a factor of 0.65 for E^0_{oxd} (B) E_{oxd} will decrease by a factor of 0.65 for E^0_{oxd}
(C) E_{red} will increase by a factor of 0.65 for E^0_{red} (D) E_{red} will decrease by a factor of 0.65 for E^0_{red}

8. Ammonia is always is added in this reaction. Which of the following must be INCORRECT :
(A) NH_3 combines with Ag^+ to form a complex. **[JEE 2006, 5/184]**
(B) $Ag(NH_3)_2^+$ is a weaker oxidising reagent than Ag^+.
(C) In absence of NH_3, silver salt of gluconic acid is formed.
(D) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode.

9. We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution, find conductivity (specific conductance) of this solution in terms of 10^{-7} Sm^{-1}.
Given : $\Lambda^0_{(Ag+)} = 6 \times 10^{-3} \ Sm^2mol^{-1}$, $\Lambda^0_{(Br-)} = 8 \times 10^{-3} \ Sm^2mol^{-1}$, $\Lambda^0_{(NO3^-)} = 7 \times 10^{-3} \ Sm^2mol^{-1}$.
[JEE 2006, 6/184]

Comprehension # 2

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with its atomic/molecular masses. To handle such large number conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes.
(Given : Atomic masses : Na = 23, Hg = 200 ; 1 Faraday = 96500 coulombs)
Now answer the following three questions :

10. The total number of moles of chlorine gas evolved is : **[JEE 2007, 4/162]**
(A) 0.5   (B) 1.0   (C) 2.0   (D) 3.0

11. If the cathode is Hg electrode, the maximum weight (in g) of amalgam formed from this solution is : **[JEE 2007, 4/162]**
(A) 200   (B) 225   (C) 400   (D) 446

12. The total charge (in coulombs) required for complete electrolysis is : **[JEE 2007, 4/162]**
(A) 24125   (B) 48250   (C) 96500   (D) 193000

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Comprehension # 3

Redox reactions play a pivoted role in chemistry and biology. The values of standard redox potential (E^0) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below is a set of half-cell reactions (acidic medium) along with their E^0 values with respect to normal hydrogen electrode. Using this data, obtain the correct explanations to questions 13 - 14.

$$I_2 + 2e^- \longrightarrow 2I^- \qquad E^0 = 0.54 \text{ V}$$
$$Cl_2 + 2e^- \longrightarrow 2Cl^- \qquad E^0 = 1.36 \text{ V}$$
$$Mn^{3+} + e^- \longrightarrow Mn^{2+} \qquad E^0 = 1.50 \text{ V}$$
$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E^0 = 0.77 \text{ V}$$
$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \qquad E^0 = 1.23 \text{ V}$$
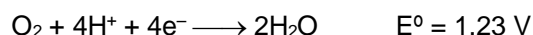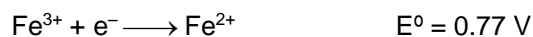
13. Among the following, identify the correct statement : **[JEE 2007, 4/162]**
(A) Chloride ion is oxidised by O_2 	(B) Fe^{2+} is oxidised by iodine
(C) Iodine ion is oxidised by chlorine 	(D) Mn^{2+} is oxidised by chlorine

14. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution, because : **[JEE 2007, 4/162]**
(A) O_2 oxidises Mn^{2+} to Mn^{3+} 	(B) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(C) Fe^{3+} oxidises H_2O to O_2 	(D) Mn^{3+} oxidises H_2O to O_2

15. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milliampere current. The time required to liberate 0.01 mole of H_2 gas at the cathode is : (1 Faraday = 96500 C)
    [JEE 2008, 3/163]
(A) 9.65×10^4 sec 	(B) 19.3×10^4 sec 	(C) 28.95×10^4 sec 	(D) 38.6×10^4 sec

16.* For the reduction of NO_3^- ion in an aqueous solution, E^0 is +0.96 V. Values of E^0 for some metal ions are given below :

$$V^{2+}(aq) + 2e^- \longrightarrow V \qquad E^0 = -1.19 \text{ V}$$
$$Fe^{3+}(aq) + 3e^- \longrightarrow Fe \qquad E^0 = -0.04 \text{ V}$$
$$Au^{3+}(aq) + 3e^- \longrightarrow Au \qquad E^0 = +1.40 \text{ V}$$
$$Hg^{2+}(aq) + 2e^- \longrightarrow Hg \qquad E^0 = +0.86 \text{ V}$$
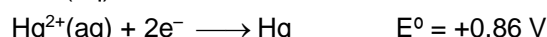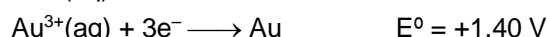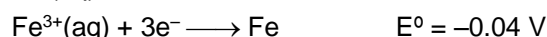
The pair(s) of metals that is(are) oxidized by NO_3^- in aqueous solution is(are) : **[JEE 2009, 4/160]**
(A) V and Hg 	(B) Hg and Fe 	(C) Fe and Au 	(D) Fe and V

Comprehension # 4

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is :
M(s) | M$^+$(aq ; 0.05 molar) || M$^+$(aq ; 1 molar) | M(s)
For the above electrolytic cell, the magnitude of the cell potential is | E_{cell} | = 70 mV.
Now answer the following two questions :
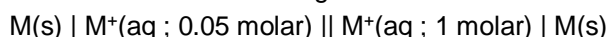
17. For the above cell : **[JEE 2010, 3/163]**
(A) $E_{cell} < 0$; $\Delta G > 0$ 	(B) $E_{cell} > 0$; $\Delta G < 0$ 	(C) $E_{cell} < 0$; $\Delta G^0 > 0$ 	(D) $E_{cell} > 0$; $\Delta G^0 < 0$

18. If the 0.05 molar solution of M$^+$ is replaced by a 0.0025 molar M$^+$ solution, then the magnitude of the cell potential would be : **[JEE 2010, 3/163]**
(A) 35 mV 	(B) 70 mV 	(C) 140 mV 	(D) 700 mV

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19. $AgNO_3$(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 : **[JEE 2011, 3/180]**

(P)   (Q)   (R)   (S)

(A) (P)   (B) Q   (C) (R)   (D) (S)
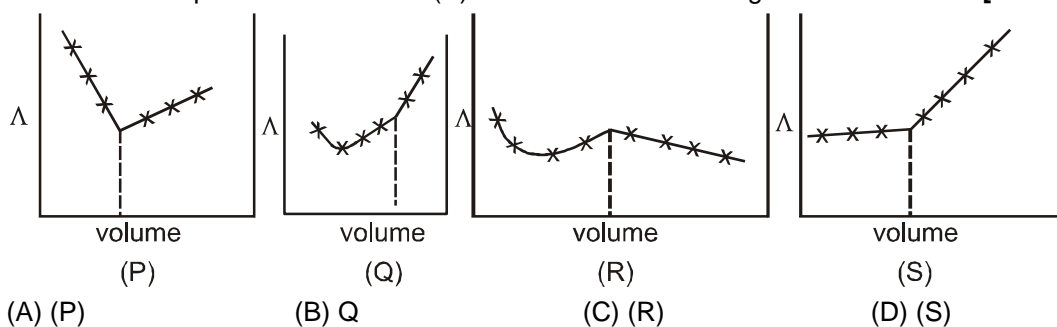
20. Consider the following cell reaction : **[JEE 2011, 3/180]**

$$2Fe\ (s) + O_2\ (g) + 4H^+\ (aq) \longrightarrow 2Fe^{2+}\ (aq) + 2H_2O\ (l) \qquad E^0 = 1.67\ V$$
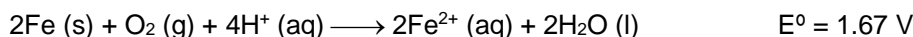
At $[Fe^{2+}] = 10^{-3}$ M, $P(O_2) = 0.1$ atm and pH = 3, the cell potential at 25°C is :

(Take $\dfrac{2.303\ R\ (298)}{F} = 0.06$)

(A) 1.47 V   (B) 1.77 V   (C) 1.87 V   (D) 1.57 V

Comprehension # 5

The electrochemical cell shown below is a concentration cell.

M|M^{2+} (saturated solution of a sparingly soluble salt,MX_2)|| M^{2+} (0.001 mol dm^{-3}) |M

The emf of the cell depends on the difference in concetration of M^{2+} ions at the two electrodes. The emf of the cell at 298 is 0.059 V.

21. The solubility product (K_{sp} ; in mol^3 dm^{-9}) of MX_2 at 298 K based on the information available in the given concentration cell is : (Take $2.303\times R \times 298/F = 0.059$ V) **[IIT-JEE 2012, 3/66]**

(A) 1×10^{-15} (B) 4×10^{-15} (C) 1×10^{-12} (D) 4×10^{-12}

22. The value of ΔG (in kJ mol^{-1}) for the given cell is : (Take 1F = 96500 C mol^{-1}) **[IIT-JEE 2012, 3/136]**

(A) – 5.7   (B) 5.7   (C) 11.4   (D) –11.4

23. An aqueous solution of **X** is added slowly to an aqueous solution of **Y** as shown in list I. The variation in conductivity of these reactions is given in List II. Match List I with List II and select the correct answer using the code given below the lists : **[JEE(Advanced) 2013, 3/120]**

	List I		List II
P.	$(C_2H_5)_3N + CH_3COOH$ X Y	1.	Conductivity decreases and then increases
Q.	KI (0.1M) + $AgNO_3$(0.01M) X Y	2.	Conductivity decreases and then does not change much
R.	$CH_3COOH + KOH$ X Y	3.	Conductivity increases and then does not change much
S.	NaOH + HI X Y	4.	Conductivity does not change much and then increases

Codes :

	P	Q	R	S			P	Q	R	S
(A)	3	4	2	1		(B)	4	3	2	1
(C)	2	3	4	1		(D)	1	4	3	2

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24. The standard reduction potential data at 25°C is given below. **[JEE(Advanced) 2013, 3/120]**

E^0 ($Fe^{3+}.Fe^{2+}$) = + 0.77 V; E^0 ($Fe^{2+}.Fe$) = – 0.44 V;

E^0 ($Cu^{2+}.Cu$) = + 0.34 V; E^0 ($Cu^+.Cu$) = + 0.52 V;

E^0 ($O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$) = + 1.23 V; E^0 ($O_2(g) + 2H_2O + 4e^- \rightarrow 4OH$) = + 0.40 V

E^0 ($Cr^{3+}.Cr$) = – 0.74 V; E^0 ($Cr^{2+}.Cr$) = – 0.91 V

Match E^0 of the rebox pair in List I with the values given in List II and select the correct answer using the code given below the lists :

	List I		List II
P.	E^0 (Fe^{3+}, Fe)	1.	– 0.36 V
Q.	E^0 ($4H_2O \rightleftharpoons 4H^+ + 4OH^-$)	2.	–0.4 V
R.	E^0 ($Cu^{2+} + Cu \rightarrow 2Cu^+$)	3.	–0.04 V
S.	E^0(Cr^{3+}, Cr^{+2})	4.	–0.83 V

Codes :

	P	Q	R	S			P	Q	R	S
(A)	4	1	2	3		(B)	2	3	4	1
(C)	1	2	3	4		(D)	3	4	1	2

25. In a galvanic cell, the salt bridge **[JEE(Advanced) 2014, 3/120]**
(A) does not participate chemically in the cell reaction.
(B) stops the diffusion of ions from one electrode to another.
(C) is necessary for the occurrence of the cell reaction.
(D) ensures mixing of the two electrolytic solutions.

26. All the energy released from the reaction X → Y, $\Delta_r G^0$ = –193 kJ mol⁻¹ is used for oxidizing M⁺ as M⁺ → M^{3+} + 2e⁻ , E^0 = – 0.25 V. Under standard conditions, the number of moles of M⁺ oxidized when one mole of X is converted to Y is : [F = 96500 C mol⁻¹] **[JEE(Advanced) 2015, 4/168]**

27. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$, the difference in their pK_a values, pK_a (HX) – pK_a (HY), is (consider degree of ionization of both acids to be <<1)

[JEE(Advanced) 2015, 4/168]

28. For the following electrochemical cell at 298 K,

Pt(s) | H₂(g, 1 bar) | H⁺(aq, 1 M) || M^{4+}(aq) | M^{2+}(aq) | Pt(s), E_{cell}= 0.092 V when $\dfrac{\left[M^{2+}(aq)\right]}{\left[M^{4+}(aq)\right]}$ = 10^x.
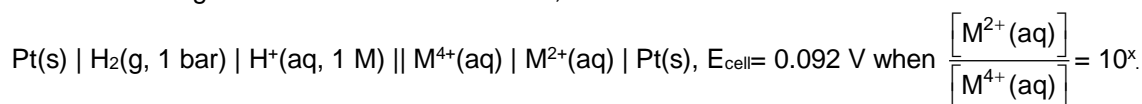
Given : $E^0_{M^{4+}/M^{2+}}$ = 0.151 V; 2.303 $\dfrac{RT}{F}$ = 0.059 V

The value of x is : **[JEE(Advanced) 2016, 3/124]**
(A) –2   (B) –1   (C) 1   (D) 2

29. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm². The conductance of this solution was found to be 5 × 10⁻⁷ S. The pH of the solution is 4. The value of limiting molar conductivity (Λ^0_m) of this weak monobasic acid in aqueous solution is Z × 10² S cm⁻¹ mol⁻¹. The value of Z is **[JEE(Advanced) 2017, 3/122]**

30. For the following cell, Zn(s) | ZnSO₄(aq) || CuSO₄ (aq) | Cu(s) when the concentration of Zn^{2+} is 10 times the concentration of Cu^{2+}, the expression for ΔG (in J mol⁻¹) is : **[JEE(Advanced) 2017, 3/122]**
[F is Faraday constant; R is gas constant; T is temperature; E°(cell) = 1.1 V]
(A) 2.303 RT + 1.1 F   (B) 1.1 F   (C) 2.303 RT – 2.2 F   (D) –2.2 F

31. For the electrochemical cell,   Mg(s) | Mg^{2+} (aq,1 M) || Cu^{2+} (aq,1M) | Cu(s)
the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to *x* M, the cell potential changes to 2.67 V at 300 K. The value of *x* is ____. (Given, $\dfrac{F}{R}$ = 11500 K V⁻¹, where F is the Faraday constant and R is the gas constant, ln(10) = 2.30). **[JEE(Advanced) 2018, 3/120]**

32. Consider an electrochemical cell : A(s) | A^{n+}(aq, 2 M) || B^{2n+}(aq, 1 M) | B(s). The value of ΔH° for the cell reaction is twice that of ΔG° at 300 K. If the emf of the cell is zero, the ΔS°(in J K⁻¹mol⁻¹) of the cell reaction per mole of B formed at 300 K is____.
(Given : ln (2) = 0.7, R(universal gas constant) = 8.3 J K⁻¹ mol⁻¹. H, S and G are enthalpy, entropy and Gibbs energy, respectively.) **[JEE(Advanced) 2018, 3/120]**

PART - II : JEE (MAIN) ONLINE PROBLEMS (PREVIOUS YEARS)

1. The standard electrode potentials $\left(E^{\circ}_{M^+/M}\right)$ of four metals A, B, C and D are –1.2 V, 0.6 V, 0.85 V and – 0.76 V, respectively. The sequence of deposition of metals on applying potential is :
[JEE(Main) 2014 Online (09-04-14), 4/120]

(1) A, C, B, D   (2) B, D, C, A   (3) C, B, D, A   (4) D, A, B, C

2. A current of 10.0 A flows for 2.00 h through an electrolytic cell containing a molten salt of metal X. This results in the decomposition of 0.250 mol of metal X at the cathode. The oxidation state of X in the molten salt is : (F = 96,500 C)   **[JEE(Main) 2014 Online (09-04-14), 4/120]**

(1) 1 +   (2) 2 +   (3) 3 +   (4) 4 +

3. Given : Fe^{3+} (aq) + e⁻ → Fe^{2+} (aq) ; E⁰ = + 0.77 V

Al^{3+} (aq) + 3e⁻ → Al(s); E⁰ = –1.66 V

Br_2 (aq) + 2e⁻ → 2Br⁻ ; E⁰ = +1.09 V

Considering the electrode potentials, which of the following represents the correct order of reducing power?
[JEE(Main) 2014 Online (11-04-14), 4/120]

(1) Fe^{2+} < Al < Br⁻   (2) Br⁻ < Fe^{2+} < Al   (3) Al < Br⁻ < Fe^{2+} (4) Al < Fe^{2+} < Br⁻

4. How many electrons would be required to deposit 6.35 g of copper at the cathode during the electrolysis of an aqueous solution of copper sulphate ? (Atomic mass of copper = 63.5 u, N_A = Avogadro's constant).   **[JEE(Main) 2014 Online (12-04-14), 4/120]**

(1) $\dfrac{N_A}{20}$ (2) $\dfrac{N_A}{10}$ (3) $\dfrac{N_A}{5}$ (4) $\dfrac{N_A}{2}$

5. A variable, opposite external potential (E_{ext}) is applied to the cell Zn|Zn^{2+} (1 M) || Cu^{2+} (1M) | Cu, of potential 1.1 V. When E_{ext} < 1.1 V and E_{ext} > 1.1 V respectively electrons flow from :
[JEE(Main) 2015 Online (10-04-15), 4/120]

(1) Cathode to anode in both cases   (2) cathode to anode and anode to cathode

(3) anode to cathode and cathode to anode   (4) anode to cathode in both cases

6. At 298 K, the standard reduction potentials are 1.51 V for MnO_4^- |Mn^{2+}, 1.36 V for Cl_2|Cl⁻ , 1.07 V for Br_2|Br, and 0.54 V for I_2|I⁻. At pH = 3, permanganate is expected to oxidize : $\left(\dfrac{RT}{F} = 0.059\,V\right)$

[JEE(Main) 2015 Online (11-04-15), 4/120]

(1) Cl⁻, Br⁻ and I⁻   (2) Br⁻ and I⁻   (3) Cl⁻ and Br⁻   (4) I⁻ only

7. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M $ZnSO_4$?
[JEE(Main) 2016 Online (09-04-16), 4/120]

(1) The copper metal will dissolve and zinc metal will be deposited.

(2) The copper metal will dissolve with evolution of oxygen gas.

(3) The copper metal will dissolve with evolution of hydrogen gas.

(4) No reaction will occur.

8. Identify the correct statement: **[JEE(Main) 2016 Online (10-04-16), 4/120]**

(1) Corrosion of iron can be minimized by forming an impermeable barrier at its surface.

(2) Iron corrodes in oxygen-free water.

(3) Iron corrodes more rapidly in salt water because its electrochemical potential is higher.

(4) Corrosion of iron can be minimized by forming a contact with another metal with a higher reduction potential.

9. What is the standard reduction potential (E⁰) for Fe^{3+} → Fe ?

Given that :   **[JEE(Main) 2017 Online (08-04-17), 4/120]**

Fe^{2+} + 2e⁻ → Fe; $E^{\circ}_{Fe^{2+}/Fe}$ = – 0.47 V

Fe^{3+} + e⁻ → Fe^{2+} ; $E^{\circ}_{Fe^{2+}/Fe}$ $E^{\circ}_{Fe^{2+}/Fe^{2+}}$ = + 0.77 V

(1) + 0.30 V   (2) – 0.057 V   (3) + 0.057 V   (4) – 0.30 V

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10. Consider the following standard electrode potentials (E^0 in volts) in aqueous solution :

Element	M^{3+} / M	M^+ / M	**[JEE(Main) 2017 Online (08-04-17), 4/120]**
Al	−1.66	+ 0.55	
Tl	+1.26	− 0.34	

Based on these data, which of the following statements is **correct** ?

(1) Al^+ is more stable than Al^{3+} (2) Tl^{3+} is more stable than Al^{3+}

(3) Tl^+ is more stable than Al^{3+} (4) Tl^+ is more stable than Al^+

11. Which of the following ions does not liberate hydrogen gas on reaction with dilute acids ?

[JEE(Main) 2017 Online (09-04-17), 4/120]

(1) Mn^{2+} (2) Ti^{2+} (3) V^{2+} (4) Cr^{2+}

12. To find the standard potential of M^{3+}/M electrode, the following cell is constituted : Pt / M / M^{3+} (0.001 mol L^{-1}) / Ag^+ (0.01 mol L^{-1}) / Ag

The emf of the cell is found to be 0.421 volt at 298 K. The standard potential of half reaction $M^{3+} + 3e^- \longrightarrow$ M at 298 K will be : **[JEE(Main) 2017 Online (09-04-17), 4/120]**

(Given $E^-_{Ag^+/Ag}$ at 298 K = 0.80 volt)

(1) 0.32 Volt   (2) 0.66 Volt   (3) 0.38 Volt   (4) 1.28 Volt

13. When an electric current is passed through acidified water, 112 mL of hydrogen gas at N.T.P was collected at the cathode in 965 seconds. The current passed, in ampere, is :

[JEE(Main) 2018 Online (15-04-2018), 4/120]

(1) 2.0   (2) 0.1   (3) 0.5   (4) 1.0

14.^ When 9.65 ampere current was passed for 1.0 hour into nitrobenzene in acidic medium, the amount of p-aminophenol produced is : **[JEE(Main) 2018 Online (16-04-2018), 4/120]**

Note : Nitrobenzene actually convert into aniline in reduction in acidic medium.

(1) 109.0 g   (2) 98.1 g   (3) 9.81 g   (4) 10.9 g

15. The anodic half–cell of lead–acid battery is recharged using electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolyzed in g during the process is : (Molar mass of $PbSO_4$ = 303 g mol^{-1})

[JEE(Main) 2019 Online (09-01-2019), 4/120]

(1) 15.2   (2) 22.8   (3) 7.6   (4) 11.6

16. If the standard electrode potential for a cell is 2 V at 300 K, the equilibrium constant (K) for the reaction

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

at 300 K is approximately (R = 8 JK^{-1}mol, F = 96000 C mol^{-1})

[JEE(Main) 2019 Online (09-01-2019), 4/120]

(1) e^{320} (2) e^{-80} (3) e^{160} (4) e^{-160}

17. Consider the following reduction processes :

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

$Ca^{2+} + 2e^- \rightarrow Ca(s)$; $E^0 = -2.86$ V

$Mg^{2+} + 2e^- \rightarrow Mg(s)$; $E^0 = -2.36$ V

$Ni^{2+} + 2e^- \rightarrow Ni(s)$; $E^0 = -0.25$ V

The reducing power of the metals increases in the order: **[JEE(Main) 2019 Online (10-01-2019), 4/120]**

(1) Ca < Mg < Zn < Ni   (2) Ni < Zn < Mg < Ca   (3) Ca < Zn < Mg < Ni   (4) Zn < Mg < Ni < Ca

18. In the cell,   Pt(s) | H_2(g,1bar) | HCl(aq) | AgCl (s) | Ag(s)| Pt(s)

The cell potential is 0.92 V when a 10^{-6} molal HCl solution is used. The standard electrode potential of

(AgCl / Ag, Cl^{-}) electrode is : $\left\{ \text{Given}, \dfrac{2.303RT}{F} = 0.06 \text{Vat} 298k \right\}$

[JEE(Main) 2019 Online (10-01-2019), 4/120]

(1) 0.76 V   (2) 0.20 V   (3) 0.94 V   (4) 0.40 V

19. The electrolytes usually used in the electroplating of gold and silver, respectively, are:

[JEE(Main) 2019 Online (10-01-2019), 4/120]

(1) $[Au(CN)_2]^-$ and $[AgCl_2]^-$ (2) $[Au(NH_3)_2]^+$ and $[Ag(CN)_2]^-$

(3) $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$ (4) $[Au(OH)_4]^-$ and $[Ag(OH)_2]^-$

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20. For the cell Zn(s) | Zn^{2+} (aq)||M^{x+} (aq) |M(s), different half cells and their standard electrode potentials are given below :

M^{x+}(aq)/M(s)	Au^{3+}(aq)/ Au(s)	Ag^+(aq)/Ag(s)	Fe^{3+}(aq)/Fe^{2+}(aq)	Fe^{2+}(aq)/Fe(s)
$E^{\circ}_{M^{x+}/M}$ (V)	1.40	0.80	0.77	−0.44

If $E^{\circ}_{Zn^{2+}/Zn}$ = −0.76 V, which cathode will give a maximum value of E°_{cell} per electron transferred ?

[JEE(Main) 2019 Online (11-01-2019), 4/120]

(1) Au^{3+} / Au   (2) Fe^{3+} / Fe^{2+} (3) Fe^{2+} / Fe   (4) Ag^+ / Ag

21. Given the equilibrium constant : K_C of the reaction Cu(s) + $2Ag^+$(aq) → Cu^{2+} (aq) + 2Ag(s) is 10×10^{15}, caluclate the E^0_{cell} of this reaction at 298 K : $\left[2.303\dfrac{RT}{F} \text{at} 298K = 0.059 \text{ V} \right]$

[JEE(Main) 2019 Online (11-01-2019), 4/120]

(1) 0.4736 mV   (2) 0.04736 V   (3) 0.4736 V   (4) 0.04736 mV

22. The standard electrode potential E^{Θ} and its temperature coefficient $\left(\dfrac{dE^{\Theta}}{dT} \right)$ for a cell are 2 V and −5 × 10^{-4} VK^{-1} at 300 K respectively. The cell reaction is

$$Zn(s) + Cu^{2+} (aq) \rightarrow Zn^{2+} (aq) + Cu(s)$$
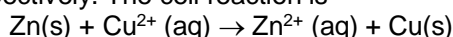
The standard reaction enthalpy (Δ_rH^{Θ}) at 300 K in kJ mol^{-1} is :
(Use R = 8JK^{-1} mol^{-1} and F = 96,000 $Cmol^{-1}$)   **[JEE(Main) 2019 Online (12-01-2019), 4/120]**
(1) 206.4   (2) −384.0   (3) 192.0   (4) −412.8

23. Λ^0_m for NaCl, HCl and NaA are 126.4, 425.9 and 100.5 S cm^2mol^{-1}, respectively. If the conductivity of 0.001 M HA is 5 × 10^{-5} S cm^{-1}, degree of dissociation of HA is:

[JEE(Main) 2019 Online (12-01-2019), 4/120]

(1) 0.125   (2) 0.50   (3) 0.75   (4) 0.25

24. Given that, $E^{\Theta}_{O_2/H_2O} = +1.23V$

$E^{\Theta}_{S_2O_8^{2-}/SO_4^2} = 2.05V$

$E^{\Theta}_{Br_2/Br^-} = +1.09V;$

$E^{\Theta}_{Au^{3+}/Au} = +1.4V$

The strongest oxidizing agent is :   **[JEE(Main) 2019 Online (08-04-19)S1, 4/120]**
(1) O_2 (2) Br_2 (3) Au^{3+} (4) $S_2O_8^{2-}$

25. Calculate the standard cell potential (in V) of the cell in which following reaction takes place :
Fe^{2+} (aq) + Ag^+ (aq) → Fe^{3+} (aq) + Ag(s)
Given that
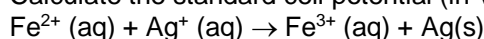
$E^0_{Ag^+/Ag} = xV$

$E^0_{Fe^{2+}/Fe} = yV$

$E^0_{Fe^{3+}/Fe} = zV$ **[JEE(Main) 2019 Online (08-04-19)S2, 4/120]**

(1) x – z   (2) x – y   (3) x + y – z   (4) x + 2y – .3z

26. The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K is :
Zn(s) + Cu^{2+}(aq) → Zn^{2+}(aq) + Cu(s).
E^0 = 2 V at 298 K
(Faraday's constant, F = 96000 C mol^{-1})   **[JEE(Main) 2019 Online (09-04-19)S1, 4/120]**
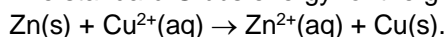
27. A solution of Ni(NO₃)₂ is electrolyzed between platinum electrodes using 0.1 Faraday electricity. How many mole of Ni will be deposited at the cathode?

[JEE(Main) 2019 Online (09-04-19)S2, 4/120]

(1) 0.20   (2) 0.15   (3) 0.10   (4) 0.05

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28. Consider the statements Statement-1 and Statement-2 :
Statement-1 : Conductivity always increases with decrease in the concentration of electrolyte.
Statement-2 : Molar conductivity always increase with decrease in the concentration of electrolyte.
The correct option among the following is :
[JEE(Main) 2019 Online (10-04-19)S1, 4/120]
(1) Both Statement-1 and Statement-2 are correct
(2) Both Statement-1 and Statement-2 are wrong
(3) Statement-1 is wrong and Statement-2 is correct
(4) Statement-1 is correct and Statement-2 is wrong

29. Which one of the following graphs between molar conductivity (A_m) versus $\sqrt{C}$ is correct?
[JEE(Main) 2019 Online (10-04-19)S2, 4/120]
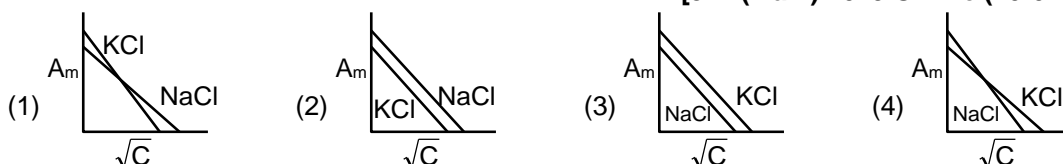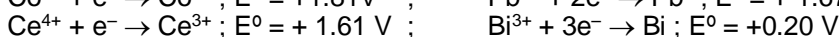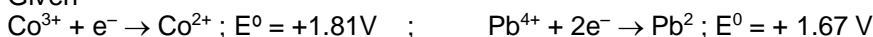
30. Given
$Co^{3+} + e^- \rightarrow Co^{2+}$; $E^0 = +1.81V$; $Pb^{4+} + 2e^- \rightarrow Pb^2$; $E^0 = +1.67$ V
$Ce^{4+} + e^- \rightarrow Ce^{3+}$; $E^0 = +1.61$ V ; $Bi^{3+} + 3e^- \rightarrow Bi$; $E^0 = +0.20$ V
Oxidizing power of the species will increase in the order :**[JEE(Main) 2019 Online (12-04-19)S1, 4/120]**
(1) $Ce^{4+} < Pb^{4+} < Bi^{3+} < Co^{3+}$
(2) $Bi^{3+} < Ce^{4+} < Pb^{4+} < Co^{3+}$
(3) $Co^{3+} < Pb^{4+} < Ce^{4+} < Bi^{3+}$
(4) $Co^{3+} < Ce^{4+} < Bi^{3+} < Pb^{4+}$

31. The decreasing order of electrical conductivity of the following aqueous solution is :
[JEE(Main) 2019 Online (12-04-19)S2, 4/120]
0.1 M Formic acid (A) ; 0.1 M Acetic acid (B) ; 0.1 M Benzoic acid (C)
(1) A > B > C
(2) A > C > B
(3) C > A > B
(4) C > B > A

32. Given that the standard potentials ($E°$) of Cu^{2+}/Cu and Cu^+/Cu are 0.34 V and 0.522 V respectively, the $E°$ of Cu^{2+}/Cu^+ is:
[JEE(Main) 2020 Online (07-01-20)S1, 4/120]
(1) +0.158 V
(2) –0.182 V
(3) 0.182 V
(4) –0.158 V

33. The equation that is incorrect is:
[JEE(Main) 2020 Online (07-01-20)S2, 4/120]

(1) $\left(\Lambda^0_m\right)_{NaBr} - \left(\Lambda^0_m\right)_{NaI} = \left(\Lambda^0_m\right)_{KBr} - \left(\Lambda^0_m\right)_{NaBr}$

(2) $\left(\Lambda^0_m\right)_{H_2O} = \left(\Lambda^0_m\right)_{HCl} + \left(\Lambda^0_m\right)_{NaOH} - \left(\Lambda^0_m\right)_{NaCl}$

(3) $\left(\Lambda^0_m\right)_{KCl} - \left(\Lambda^0_m\right)_{NaCl} = \left(\Lambda^0_m\right)_{KBr} - \left(\Lambda^0_m\right)_{NaBr}$

(4) $\left(\Lambda^0_m\right)_{NaBr} - \left(\Lambda^0_m\right)_{NaCl} = \left(\Lambda^0_m\right)_{KBr} - \left(\Lambda^0_m\right)_{KCl}$

34. What would be the electrode potential for the given half cell reaction at pH = 5 ?
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$; $E^0_{red} = 1.23$ V ($R = 8.314$ J mol^{-1} K^{-1} ; Temp = 298 K ; oxygen under std. pressure of 1 bar)
[JEE(Main) 2020 Online (08-01-20)S1, 4/120]
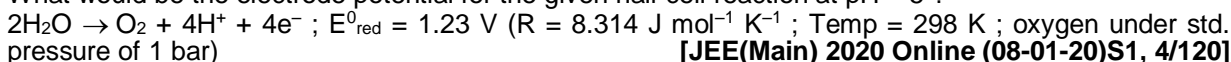
35. For an electrochemical cell
[JEE(Main) 2020 Online (08-01-20)S2, 4/120]

$Sn(s)|Sn^{2+}(aq, 1M)||Pb^{2+}(aq, 1M)|Pb(s)$ the ratio $\dfrac{[Sn^{2+}]}{[Pb^{2+}]}$ when this cell attains equilibrium is _____

$\left(\text{Given}:E^°_{Sn^{2+}|Sn} = -0.14V, E^°_{Pb^{2+}|Pb} = -0.13V, \dfrac{2.303RT}{F} = 0.06 \right)$

36. 108 g of silver (molar mass 108 g mol^{-1}) is deposited at cathode from $AgNO_3$(aq) solution by a certain quantity of electricity. The volume (in L) of oxygen gas produced at 273 K and 1 bar pressure from water by the same quantity of electricity is _____
[JEE(Main) 2020 Online (09-01-20)S1, 4/120]

37. Amongst the following, the form of water with the lowest ionic conductance at 298 K is:
[JEE(Main) 2020 Online (09-01-20)S2, 4/120]
(1) distilled water
(2) sea water
(3) water from a well
(4) saline water used for intravenous injection

Answers

EXERCISE - 1

PART - I

A-1. (a) Cu   (b) Ag   (c) oxidation   (d) reduction

(e) Cu   (f) Ag   (g) anode-Cu $\longrightarrow Cu^{2+} + 2e^-$; cathode-$Ag^+ + e^- \longrightarrow Ag$

(h) $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$ (i) Cu   (j) Cu

(k) to complete circuit and maintain electrical neutrality in solution

A-2. (a) $2Ag^+ + Cu \longrightarrow 2Ag + Cu^{2+}$ (b) $8H^+ + MnO_4^- \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

(c) $2Ag^+ + 2Cl^- \longrightarrow 2Ag + Cl_2$ (d) $Cd + 2H^+ \longrightarrow Cd^{2+} + H_2$

A-3. (a) $Zn \mid Zn^{2+} \mid\mid H^+ \mid H_2 \mid Pt$ (b) $Pt \mid Sn^{2+}, Sn^{4+} \mid\mid Fe^{3+}, Fe^{2+} \mid Pt$ (c) $Pb \mid Pb^{2+} \mid\mid Br^- \mid\mid Br_2 \mid Pt$

B-1. Mg   **B-2.** Y > Z > X

B-3. **(i)** CuO **:** Cu is below hydrogen in series, so it can reduce from CuO to Cu.

(ii) Ag_2O**:** Lower in series stability of oxide become lesser.

(iii) Lower S.R.P. metal can displace higher S.R.P. metals ions from solution.

B-4. 1.61 V   **B-5.** 1.35 V   **B-6.** 1.68 V   **C-1.** – 0.036 V

C-2. −0.756 V   **C-3.** Spontaneous, − 48250 J   **C-4.** −1.14 volt

D-1. 0.059 volt   **D-2.** 10^{14} **D-3.** – 0.2214 V   **D-4.** n = 2

D-5. (a) The spontaneous cell reaction: $Zn + 2Ag^+$ (aq) $\rightleftharpoons Zn^{2+}$ (aq) $+ 2Ag$ (s)

(b) 1.56 V   (c) $[Zn^{2+}] = 4 \times 10^{-4}$ M

(d) As we add KI to cathode chamber, some Ag^+ will precipitate out as:

$Ag^+ + I^- \longrightarrow AgI$

The above reaction reducing $[Ag^+]$ from cathode chamber. This will reduce E_{cell} according to Nernst's equation.

D-6. pH = 1.5.   **D-7.** log $[Zn^{2+}]/[Cu^{2+}] = 37.22$

E-1.

	ELECTROLYTE	ANODE Product	CATHODE Product
1	NaCl (Molten) with Pt electrode	$Cl_2(g)$	Na
2	NaCl (aq) with Pt electrode	$Cl_2(g)$	$H_2(g)$
3	Na_2SO_4 (aq) with Pt electrode	$O_2(g)$	$H_2(g)$
4	$NaNO_3$ (aq) with Pt electrode	$O_2(g)$	$H_2(g)$
5	$AgNO_3$ (aq) with Pt electrode	$O_2(g)$	Ag
6	$CuSO_4$ (aq) with Inert electrode	$O_2(g)$	Cu
7	$CuSO_4$ (aq) with Copper electrode	Cu dissolve	Cu

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F-1. 12.04×10^{23} **F-2.** 108. **F-3.** 2 **F-4.** n = 4 **F-5.** t = 193 sec.

F-6. $V_{(H_2)}$ = 56.0 mL. **F-7.** Ni^{2+} = 2M **F-8.** t = 93.65 sec. **F-9.** +71.5 amp

G-1. 8 **G-2.** 1.67 V **H-1.** 2.332×10^{-3} mho cm^{-1}, 23.32 mho cm^2 mol^{-1}.

H-2. 0.1456 amp **H-3.** 0.728 cm^{-1}. **I-1.** 272, 0.0353 **I-2.** 382 mho cm^2 mol^{-1}.

I-3. 1.76×10^{-5} mole/litre. **I-4.** 2.70×10^{-10} (mole/litre)^2.

J-1. (1) [Conductance vs Volume of NaOH graph] (2) [Conductance vs Volume of NaOH graph] (3) [Conductance vs Volume of NaOH graph] (4) [Conductance vs Volume of NaOH graph]
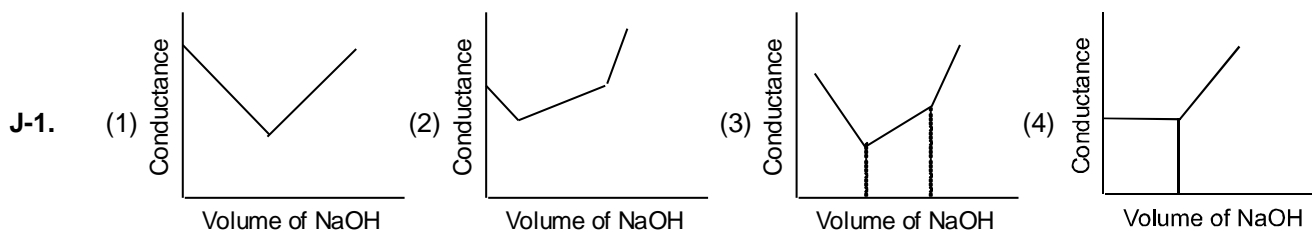
PART - II

A-1.	(A)	**A-2.**	(C)	**A-3.**	(D)	**A-4.**	(C)	**B-1.**	(A)
B-2.	(C)	**B-3.**	(D)	**B-4.**	(D)	**B-5.**	(C)	**B-6.**	(A)
B-7.	(C)	**B-8.**	(C)	**C-1.**	(D)	**C-2.**	(D)	**C-3.**	(D)
D-1.	(A)	**D-2.**	(A)	**D-3.**	(C)	**D-4.**	(B)	**D-5.**	(B)
D-6.	(C)	**E-1.**	(C)	**E-2.**	(C)	**E-3.**	(D)	**E-4.**	(B)
E-5.	(B)	**F-1.**	(D)	**F-2.**	(B)	**F-3.**	(C)	**F-4.**	(B)
F-5.	(C)	**G-1.**	(B)	**G-2.**	(A)	**G-3.**	(D)	**H-1.**	(A)
H-2.	(D)	**H-3.**	(B)	**I-1.**	(C)	**I-2.**	(D)	**I-3.**	(D)
I-4.	(C)	**I-5.**	(D)	**J-1.**	(A)	**J-2.**	(C)		

PART – III

1. (A - s) ; (B - p,r) ; (C - p,q) ; (D - r)   **2.** (A - p, q, r) ; (B - p, q, r) ; (C - p, s) ; (D - p, s)

EXERCISE - 2

PART - I

1.	(A)	**2.**	(C)	**3.**	(C)	**4.**	(C)	**5.**	(B)
6.	(B)	**7.**	(B)	**8.**	(A)	**9.**	(D)	**10.**	(D)
11.	(C)	**12.**	(B)	**13.**	(B)	**14.**	(D)	**15.**	(B)

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PART - II

1. 3 (B, E & F)   **2.** 59   **3.** $E° = 7$ V.   **4.** 40

5. $\lambda^o_{(NO_3^-)} = 7$ Sm^2 mol^{-1} **6.** 4   **7.** 10   **8.** 20   **9.** 4

PART - III

1. (BC)   **2.** (AD)   **3.** (AC)   **4.** (ABD)   **5.** (AB)

6. (BD)   **7.** (BCD)   **8.** (BCD)   **9.** (ACD)   **10.** (AC)

11. (AB)   **12.** (BC)   **13.** (BCD)   **14.** (A)   **15.** (ABD)

PART – IV

1. (D)   **2.** (C)   **3.** (B)   **4.** (D)   **5.** (A)

6. (C)   **7.** (D)   **8.** (D)   **9.** (B)   **10.** (C)

11. (C)   **12.** (B)

EXERCISE – 3

PART - I

1. (A)   **2.** 0.05 M   **3.** (B)   **4.** $K_C = 10^{10}$ **5.** (B)

6. (B)   **7.** (A)   **8.** (D)   **9.** 55 S m^{-1} **10.** (B)

11. (D)   **12.** (D)   **13.** (C)   **14.** (D)   **15.** (B)

16. (ABD)   **17.** (B)   **18.** (C)   **19.** (D)   **20.** (D)

21. (B)   **22.** (D)   **23.** (A)   **24.** (D)   **25.** (A)

26. 4   **27.** 3   **28.** (D)   **29.** 6   **30.** (C)

31. 10   **32.** -11.62 JK^{-1}mol^{-1}

PART – II

1. (3)   **2.** (3)   **3.** (2)   **4.** (3)   **5.** (4)

6. (2)   **7.** (4)   **8.** (1)   **9.** (2)   **10.** (4)

11. (1)   **12.** (1)   **13.** (4)   **14.** (3)   **15.** (3)

16. (3)   **17.** (2)   **18.** (2)   **19.** (3)   **20.** (1)

21. (3)   **22.** (4)   **23.** (1)   **24.** (4)   **25.** (4)

26. (2)   **27.** (4)   **28.** (3)   **29.** (3)   **30.** (2)

31. (2)   **32.** (1)   **33.** (1)   **34.** -0.93 to -0.94

35. 2.13 to 2.17   **36.** 5.66 to 5.68   **37.** (1)

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Additional Problems for Self Practice (APSP)

✎ Marked Questions may have for Revision Questions.

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Marks: 100   **Max. Time : 1 Hour**

Important Instructions:

A.   **General :**

1.   The test paper is of **1** hour duration.
2.   The Test Paper consists of **25** questions and each questions carries **4** Marks. Test Paper consists of **Two** Sections.

B.   **Test Paper Format and its Marking Scheme:**

1.   Section-1 contains **20** multiple choice questions. Each question has four choices (1), (2), (3) and (4) out of which **ONE** is correct. For each question in Section-1, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. In all other cases, minus one **(–1)** mark will be awarded.

2.   Section-2 contains **5** questions. The answer to each of the question is a **Numerical Value**. For each question in Section-2, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. No negative marks will be answered for incorrect answer in this section. In this section answer to each question is **NUMERICAL VALUE** with two digit integer and decimal upto two digit. If the numerical value has more than two decimal places   **truncate/round-off** the value to **TWO** decimal placed.

SECTION-1

This section contains **20** multiple choice questions. Each questions has four choices (1), (2), (3) and (4) out of which Only **ONE** option is correct.

1.✎ The standard electrode potentials (reduction) of Pt/Fe^{3+}, Fe^{2+} and Pt/Sn^{4+}, Sn^{2+} are + 0.77 V and 0.15 V respectively at 25° C. The standard EMF of the reaction $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$ is

(1) – 0.62 V   (2) – 0.92 V   (3) + 0.31 V   (4) + 0.85 V

2.✎ Which is/are correct among the following?

Given, the half cell emf's $E^0_{Cu^{+2} | Cu} = 0.337$, $E^0_{Cu^{+1} | Cu} = 0.521$

(1) Cu^{+1} disproportionates   (2) Cu and Cu^{2+} comproportionates.

(3) $E^0_{Cu | Cu^{+2}} + E^0_{Cu^{+1} | Cu}$ is positive   (4) (1) and (3) Both

3.   How many g of silver will be displaced from a solution of $AgNO_3$ by 4 g of magnesium?

(1) 18 g   (2) 4 g   (3) 36 g   (4) 16 g

4.   The electrode potentials for $Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)}$ and $Cu^+_{(aq)} + e^- \longrightarrow Cu_{(s)}$ are +0.15 V and + 0.50V respectively. The value of $E^0_{Cu^{2+}/Cu}$ will be :

(1) 0.500 V   (2) 0.325 V   (3) 0.650 V   (4) 0.150 V

5.✎ How much will the reduction potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralised to pH = 7 at 25ºC ?

(1) Increases by 0.059 V   (2) Decreases by 0.059 V

(3) Increases by 0.41 V   (4) Decreases by 0.41 V

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6. Consider the following Galvanic cell as shown in figure. By what will value the cell voltage change when concentration of ions in anodic and cathodic compartments are both increased by factor of 10 at 298 K
(1) + 0.591 V
(2) – 0.0591 V
(3) – 0.1182 V
(4) 0 V

7. In a cell that utilise the reaction : $Zn\ (s) + 2H^+\ (0.1M) \longrightarrow Zn^{2+}\ (aq) + H_2\ (g)$
addition of 0.1 M H_2SO_4 to cathode compartment will :
(1) increase the cell emf and shift equilibrium to the left.
(2) lower the cell emf and shift equilibrium to the right.
(3) increase the cell emf and shift equilibrium to the right.
(4) lower the cell emf and shift equilibrium to the left.

8. The chemical reaction, $2AgCl(s) + H_2\ (g) \longrightarrow 2HCl\ (aq) + 2Ag\ (s)$
taking place in a galvanic cell (under standard condition) is represented by the notation.
(1) $Pt(s) \mid H_2\ (g),\ 1\ bar \mid 1\ M\ KCl\ (aq) \mid AgCl(s) \mid Ag\ (s)$
(2) $Pt(s) \mid H_2\ (g),\ 1\ bar \mid 1\ M\ HCl\ (aq) \mid 1\ M\ Ag^+\ (aq) \mid Ag\ (s)$
(3) $Pt(s) \mid H_2\ (g),\ 1\ bar \mid 1\ M\ HCl\ (aq) \mid AgCl\ (s) \mid Ag\ (s)$
(4) $Pt(s) \mid H_2\ (g),\ 1\ bar \mid 1\ M\ HCl\ (aq) \mid Ag\ (s) \mid AgCl\ (s)$

9. For the cell, $Pt \mid H_2\ (g) \mid H^+\ (aq) \parallel Cu^{2+}\ (aq) \mid Cu\ (s)$; $E^0_{Cu/Cu^{2+}} = -0.34$ V.
Then calculate approximate value of K_{eq} ?
(1) 5×10^{12}　　　(2) 2×10^{11}　　　(3) 2×10^{-11}　　　(4) 5×10^{-12}

10. In the given figure, the electrolytic cell contains 1 L of an aqueous 1 M Copper (II) sulphate solution. If 0.4 mole of electrons are passed through cell, the concentration of copper ion after passage of the charge will be :
(1) 0.4 M
(2) 0.8 M
(3) 1.0 M
(4) 1.2 M

11. Cost of electricity for the production of 'X' litre H_2 at NTP at cathode is Rs. X. Then cost of electricity for the production 'X' litre O_2 gas at NTP at anode will : (assume 1 mole of electrons as one unit of electricity)
(1) 2X　　　(2) 4X　　　(3) 16X　　　(4) 32X

12. A current of 0.1 A was passed for 965 second through a solution of Cu^+ solution and 0.03175 g of copper was deposited on the cathode. Calculate the current efficiency for the copper deposition. (Cu – 63.5)
(1) 79%　　　(2) 39.5 %　　　(3) 63.25%　　　(4) 50%

13. A current of 9.95 amp following for 10 minutes, deposits 3 g of a metal. Equivalent weight of the metal is :
(1) 12.5　　　(2) 18.5　　　(3) 21.5　　　(4) 48.5

14. The specific conductance of a N/10 KCl at 25°C is 0.0112 $ohm^{-1}\ cm^{-1}$. The resistance of cell containing solution at the same temperature was found to be 55 ohms. The cell constant will be
(1) 6.16 cm^{-1}　　　(2) 0.616 cm^{-1}　　　(3) 0.0616 cm^{-1}　　　(4) 616 cm^{-1}

15. The equivalent conductance of a N/10 NaCl solution at 25°C is $10^{-2}\ Sm^2 eq^{-1}$. Resistance of solution contained in the cell is 50 Ω. Cell constant is:
(1) $50\ m^{-1}$　　　(2) $50 \times 10^{-6}\ m^{-1}$　　　(3) $50 \times 10^{-3}\ m^{-1}$　　　(4) $50 \times 10^3\ m^{-1}$

16. For an NaCl (aq.) solution, which of the following quantities go to zero as NaCl concentration goes to zero? (Assume the solvent's contribution to conductivity has been subtracted off).
(1) $\wedge_m$　　　(2) κ　　　(3) $\lambda_m\left(Na^+\right)$　　　(4) $\lambda_m\left(Cl^-\right)$

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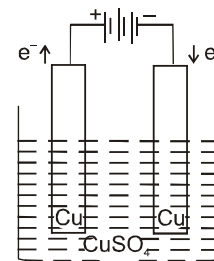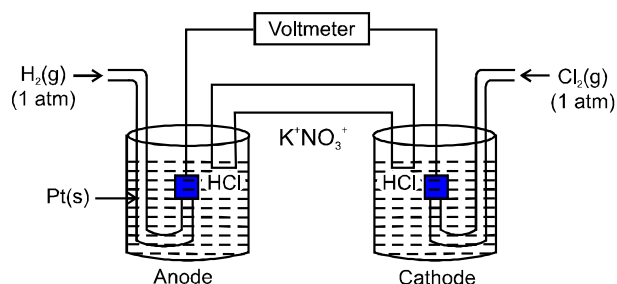
17. Find the value of λ^{α}_{eq} for potashalum.

Given : $\lambda^{\alpha}_{m(K^+)}= 73.5\ \Omega^{-1}cm^2\ mol^{-1}$, $\lambda^{\alpha}_{m(Al^{+3})} = 198\ \Omega^{-1}cm^2\ mol^{-1}$, $\lambda^{\alpha}_{m(SO_4^{-2})}= 160\ \Omega^{-1}cm^2\ mol^{-1}$

(1) $145.6\Omega^{-1}cm^2\ eq^{-1}$ (2) $1165\ \Omega^{-1}cm^2\ eq^{-1}$
(3) $532\ \Omega^{-1}cm^2\ eq^{-1}$ (4) $195.5\ \Omega^{-1}cm^2\ eq^{-1}$

18. A graph of molar conductivity of three electrolytes ($NaCl$, HCl and NH_4OH) is plotted against $\sqrt{C}$
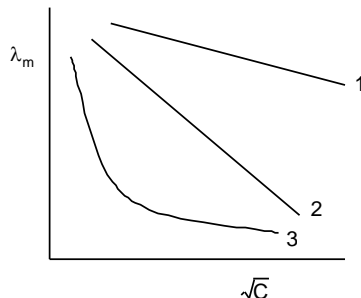
Which of the following options is correct ?

	(1)	(2)	(3)		(1)	(2)	(3)
(1)	NaCl	HCl	NH₄OH	(2)	NH₄OH	NaCl	HCl
(3)	HCl	NaCl	NH₄OH	(4)	NH₄OH	HCl	NaCl

19. 0.1 molar solution NaCl filled in different conductivity cell. Order of equivalent conductance of NaCl solution is :

	Cell – 1	**Cell – 2**	**Cell – 3**
A	5 cm²	6 cm²	10 cm²
l	2 cm	3 cm	4 cm²
Equivalents : conductance	a	b	c

A = Area of cross section, l = distance between two electrode.
(1) Cell – 1 > Cell – 2 > Cell – 3   (2) Cell – 1 = Cell – 2 = Cell – 3
(3) Cell – 1 > Cell – 3 < Cell – 2   (4) None of these

20. Acetic acid is titrated with NaOH solution. Which of the following statement is correct for this titration?
(1) conductance increases upto equivalence point, then it decreases
(2) conductance increases upto equivalence point, then it increases
(3) first conductance increases slowly upto equivalence point and then increases rapidly
(4) first conductance increases slowly upto equivalence point and then drops rapidly .

SECTION-2
This section contains **5** questions. Each question, when worked out will result in **Numerical Value**.

21.
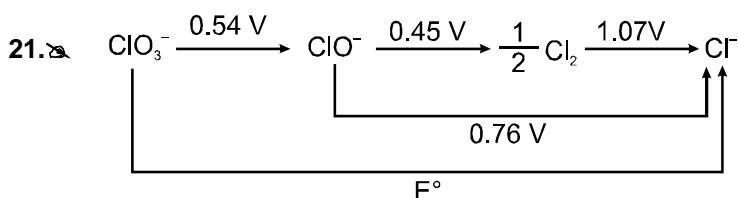
The E° in the given figure is X. Report the answer as 10X.

22. The standard reduction potential for Zn^{+2}/Zn ; Ni^{+2}/Ni ; and Fe^{+2}/Fe are –0.76V, –0.23V, –0.44V respectively. In how many of the following, the reaction $X + Y^{+2} \longrightarrow X^{+2} + Y$ will be non-spontaneous:

	X	Y
(I)	Ni	Fe
(II)	Ni	Zn
(III)	Fe	Zn
(VI)	Zn	Ni

23. A current is passed through 2 voltameters connected in series. The first voltameter contains XSO_4 (aq.) and second has Y_2SO_4 (aq.). The relative atomic masses of X and Y are in the ratio of 2 : 1. The ratio of the mass of X liberated to the mass of Y liberated is a : b. Find a + b

24. The ratio of wt. deposited of metal x, y, z on passing electric charge in ratio of 1 : 2 : 3 respectively is 3 : 2 : 1 then the ratio of equivalent weights for the above metals respectively is a : b : c. Find a + b + c

25. A resistance of 50Ω is registered when two electrodes are suspended into a beaker containing a dilute solution of a strong electrolyte such that exactly half of the them are submerged into solution as shown in figure. If the solution is diluted by adding pure water (negligible conductivity) so as to just completely submerge the electrodes, the new resistance offered by the solution would be :
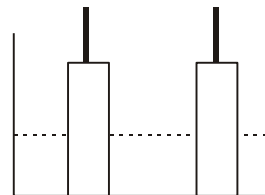
Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25					
Ans.										

PART - II : JEE (MAIN) / AIEEE OFFLINE PROBLEMS (PREVIOUS YEARS)

1. For the following cell with hydrogen electrodes at two different pressure p_1 and p_2,

Pt | $H_2(g)$ | $H^+(aq)$ | $H_2(g)$ | Pt
   p_1 1M p_2

emf is given by : **[AIEEE 2002, 3/225]**

(1) $\dfrac{RT}{F}\log_e \dfrac{p_1}{p_2}$ (2) $\dfrac{RT}{2F}\log_e \dfrac{p_1}{p_2}$ (3) $\dfrac{RT}{F}\log_e \dfrac{p_2}{p_1}$ (4) $\dfrac{RT}{2F}\log_e \dfrac{p_2}{p_1}$

2. Which of the following reactions is possible at anode : **[AIEEE 2002, 3/225]**
(1) $2 Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$ (2) $F_2 \rightarrow 2F^-$

(3) $\dfrac{1}{2}O_2 + 2H^+ \rightarrow H_2O$ (4) displacement reaction

3. For a cell given below : **[AIEEE 2002, 3/225]**
    Ag | Ag^+ || Cu^{2+} | Cu
       −   +
    $Ag^+ + e^- \longrightarrow Ag$ $E^0 = x$
    $Cu^{2+} + 2e^- \longrightarrow Cu$, $E^0 = y$
The value of E^0_{cell} is :
(1) x + 2y (2) 2x + y (3) y −x (4) y − 2x

4. For a cell reaction involving a two electron change, the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be : **[AIEEE 2003, 3/225]**
(1) 1×10^{-10} (2) 29.5×10^{-2} (3) 10 (4) 1×10^{10}

5. Standard electrode potentials of three metals A, B and C are +0.5 V, –3.0 V and –1.2 V respectively. The reducing power of these metals is in the order : **[AIEEE 2003, 3/225]**
(1) B > C > A (2) A > B > C (3) C > B > A (4) A > C > B

6. Consider the following E^0 values :

$E^0_{Fe^{3+}/Fe^{2+}}$ = + 0.77 V ; $\qquad$ $E^0_{Sn^{2+}/Sn}$ = – 0.14 V

Under standard conditions, the cell potential for the reaction given below is : **[AIEEE 2004, 3/225]**

$Sn_{(s)} + 2Fe^{3+}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$
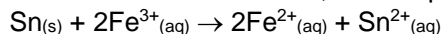
(1) 1.68 V $\qquad$ (2) 1.40 V $\qquad$ (3) 0.91 V $\qquad$ (4) 0.63 V

7. The limiting molar conductivities Λ^0 for NaCl, KBr and KCl are 126, 152 and 150 S cm^2 mol^{-1} respectively. The value of Λ^0 for NaBr is : **[AIEEE 2004, 3/225]**
(1) 128 S cm^2 mol^{-1} $\qquad$ (2) 176 S cm^2 mol^{-1} $\qquad$ (3) 278 S cm^2 mol^{-1} $\qquad$ (4) 302 S cm^2 mol^{-1}

8. In a cell that utilizes the reaction $\qquad$ $Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$,
addition of H$_2$SO$_4$ to cathode compartment will : **[AIEEE 2004, 3/225]**
(1) lower the E and shift equilibrium to the left.
(2) lower the E and shift the equilibrium to the right.
(3) increase the E and shift the equilibrium to the right.
(4) increase the E and shift the equilibrium to the left.

9. The $E^0_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are – 0.41, + 1.57, + 0.77 and + 1.97 V respectively. For which one of these metals, the change in oxidation state from +2 to +3 is easiest :**[AIEEE 2004, 3/225]**
(1) Cr $\qquad$ (2) Mn $\qquad$ (3) Fe $\qquad$ (4) Co

10. Aluminium oxide may be electrolysed at 1000ºC to furnish aluminium metal (At.Mass of Al = 27 amu ; 1 Faraday = 96,500 Coulombs). The cathode reaction is $Al^{3+} + 3e^- \rightarrow Al^0$. To prepare 5.12 kg of aluminium metal by this method, one would require : **[AIEEE–2005, 3/225]**
(1) 5.49 × 10^7 C of electricity $\qquad$ (2) 1.83 × 10^7 C of electricity
(3) 5.49 × 10^4 C of electricity $\qquad$ (4) 5.49 × 10^{10} C of electricity

11. The molar conductivities Λ^0_{NaOAc} and Λ^0_{HCl} at infinite dilution in water at 25°C are 91.0 and 426.2 Scm^2/mol respectively. To calculate Λ^0_{HOAc}, the additional value required is : **[AIEEE–2006, 3/165]**

(1) $\Lambda^0_{H_2O}$ $\qquad$ (2) Λ^0_{KCl} $\qquad$ (3) Λ^0_{NaOH} $\qquad$ (4) Λ^0_{NaCl}

12. Given data is at 25°C :
$Ag + I^- \rightarrow AgI + e^-$; E° = 0.152 V
$Ag \rightarrow Ag^+ + e^-$; E° = – 0.800 V

What is the value of log K$_{sp}$ for AgI : $\qquad$ (Take $\dfrac{0.474}{0.059}$ = 8.065) **[AIEEE–2006, 3/165]**

(1) – 8.12 $\qquad$ (2) + 8.612 $\qquad$ (3) – 37.83 $\qquad$ (4) – 16.13

13. 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 Sm^{-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 the electrolyte will be : (Take $\dfrac{129}{520}$ = 0.248) **[AIEEE–2006, 3/165]**

(1) 124 × 10^{-4} Sm^{2}mol^{-1} $\qquad$ (2) 1240 × 10^{-4} Sm^{2}mol^{-1}
(3) 1.24 Sm^{2}mol^{-1} $\qquad$ (4) 12.4 × 10^{-4} Sm^{2}mol^{-1}

14. The equivalent conductances of two strong electrolytes at infinite dilution in H$_2$O (where ions move freely through a solution) at 25°C are given below : **[AIEEE–2007, 3/120]**
$\Lambda^0_{CH_3COONa}$ = 91.0 Scm^2/equiv $\quad$ and $\qquad$ Λ^0_{HCl} = 426.2 Scm^2/equiv

What additional information/quantity one needs to calculate Λ^0 of an aqueous solution of acetic acid :

(1) The limiting equivalent conductance of H$^+$ ($\lambda^\circ_{H^+}$) $\qquad$ (2) Λ^0 of chloroacetic acid (ClCH$_2$COOH)

(3) Λ^0 of NaCl $\qquad$ (4) Λ^0 of CH$_3$COOK

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15. The cell Zn | Zn^{2+}(1M) || Cu^{2+}(1M) | Cu : (E°$_{cell}$ = 1.10V) was allowed to completely discharge at 298 K.

The relative concentration of Zn^{2+} to Cu^{2+} $\left(\dfrac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is : (Take $\dfrac{1.1}{0.059}$ = 18.65)   **[AIEEE–2007, 3/120]**

(1) $10^{37.3}$ (2) 9.65×10^4 (3) antilog (24.08)   (4) 37.3

16. Given : $E^0_{Cr^{3+}/Cr}$ = – 0.72, $E^0_{Fe^{2+}/Fe}$ = – 0.42 V

The potential for the cell Cr | Cr^{3+}(0.1 M) || Fe^{2+}(0.01 M) | Fe at 298 K is :

(Take $\dfrac{2.303\,R\,(298)}{F}$ = 0.06)   **[AIEEE–2008, 3/105]**

(1) 0.339 V   (2) – 0.339 V   (3) – 0.26 V   (4) 0.26 V

17. Given : $E^0_{Fe^{3+}/Fe}$ = – 0.036 V, $E^0_{Fe^{2+}/Fe}$ = – 0.439 V

The value of standard electrode potential for the change, $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$ will be :

(1) 0.385V   (2) 0.770V   (3) –0.270V   (4) –0.072V

18. The Gibbs energy for the decomposition of Al$_2$O$_3$ at 500ºC is as follows :   **[AIEEE–2010, 4/144]**

$\dfrac{2}{3}$ Al$_2$O$_3$ $\rightarrow$ $\dfrac{4}{3}$ Al + O$_2$; Δ_rG = + 966 kJmol^{-1}. The potential difference needed for electrolytic reduction of Al$_2$O$_3$ at 500ºC is at least :

(1) 4.5 V   (2) 3.0 V   (3) 2.5 V   (4) 5.0 V

19. The reduction potential of hydrogen half-cell will be negative, if :   **[AIEEE–2011(1), 4/120]**
(1) p(H$_2$) = 1 atm and [H$^+$] = 2.0 M   (2) p(H$_2$) = 1 atm and [H$^+$] = 1.0 M
(3) p(H$_2$) = 2 atm and [H$^+$] = 1.0 M   (4) p(H$_2$) = 2 atm and [H$^+$] = 2.0 M

20. 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+} $\rightarrow$ X^{2+} + Y will be spontaneous, when :   **[AIEEE 2012, 4/120]**
(1) X = Ni, Y = Fe   (2) X = Ni, Y = Zn   (3) X= Fe, Y = Zn   (4) X= Zn, Y = Ni

21. Given : $E^0_{Cr^{3+}/Cr}$ = –0.74 V ; $E^0_{MnO_4^-/Mn^{2+}}$ = 1.51 V

                 $E^0_{Cr_2O_7^{2-}/Cr^{3+}}$ = 1.33 V ; E^0_{Cl/Cl^-} = 1.36 V

Based on the data given above, strongest oxidising agent will be :   **[JEE(Main) 2013, 4/120]**
(1) Cl   (2) Cr^{3+} (3) Mn^{2+} (4) MnO$_4^-$

22. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.4 S m^{-1}. The resistance of 0.5 M solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in S m^2 mol^{-1} is :   **[JEE(Main) 2014, 4/120]**
(1) 5×10^{-4} (2) 5×10^{-3} (3) 5×10^3 (4) 5×10^2

23. The equivalent conductance of NaCl at concentration C and at infinite dilution are Λ_C and Λ_∞, respectively. The correct relationship between Λ_C and Λ_∞ is given as : (where the constant B is positive)
         [JEE(Main) 2014, 4/120]

(1) $\Lambda_C = \Lambda_\infty + (B)C$ (2) $\Lambda_C = \Lambda_\infty - (B)C$ (3) $\Lambda_C = \Lambda_\infty - (B) \sqrt{C}$ (4) $\Lambda_C = \Lambda_\infty + (B) \sqrt{C}$

24. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is :
         [JEE(Main) 2014, 4/120]

(1) Ag   (2) Ca   (3) Cu   (4) Cr

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25. Given below are the half-cell reactions : **[JEE(Main) 2014, 4/120]**

$Mn^{2+} + 2e^- \longrightarrow Mn$; $E^0 = -1.18$ V

$2(Mn^{3+} + e^- \longrightarrow Mn^{2+})$; $E^0 = +1.51$ V

The E^0 for $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ will be :

(1) –2.69 V ; the reaction will not occur (2) –2.69 V ; the reaction will occur

(3) –0.33 V ; the reaction will not occur (4) –0.33 V ; the reaction will occur

26. Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is : (at. mass of Cu = 63.5 amu) **[JEE(Main) 2015, 4/120]**

(1) 0 g (2) 63.5 g (3) 2 g (4) 127 g

27. Galvanization is applying a coating of : **[JEE(Main) 2016, 4/120]**

(1) Cr (2) Cu (3) Zn (4) Pb

28. Given

$E^o_{Cl_2/Cl^-} = 1.36$ V, $E^o_{Cr^{3+}/Cr} = -0.74$ V

$E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V, $E^o_{MnO_4^-/Mn^{2+}} = 1.51$ V

Among the following, the strongest reducing agent is : **[JEE(Main) 2017, 4/120]**

(1) Mn^{2+} (2) Cr^{3+} (3) Cl^- (4) Cr

29. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane? **[JEE(Main)-2018, 4/120]**

(Atomic weight of B = 10.8u)

(1) 3.2 hours (2) 1.6 hours (3) 6.4 hours (4) 0.8 hours

PART - III : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. The increase in the equivalent conductance of a salt solution on dilution is due to increase in the **[NSEC-2000]**

(A) attraction between the ions (B) degree of ionization of the salt

(C) molecular attraction (D) association of the salt

2. When 96500 coulombs of electricity are passed through a nickel sulphate solution, the amount of nickel deposited will be **[NSEC-2000]**

(A) 1.0 mol (B) 0.5 mol (C) 0.1 mol (D) 2.0 mol **[NSEC-2000]**

3. When a piece of copper wire is immersed in a silver nitrate solution, the colour of the solution turns blue due to **[NSEC-2000]**

(A) oxidation of silver (B) reduction of copper

(C) oxidation of copper (D) formation of soluble complex

4. The reduction potentials of Zn, Cu, Fe and Ag are in the order : **[NSEC-2001]**

(A) Zn,Cu,Fe,Ag (B) Cu,Ag,Fe,Zn (C) Ag,Cu,Fe,Zn (D) Fe,Zn,Cu, Ag

5. The standard reduction potentials of Cu^{2+}/Cu and Cu^+/Cu are 0.339 V and 0.518 V respectively. The standard electrode potential of Cu^{2+}/Cu^+ half cell is : **[NSEC-2001]**

(A) 0.16 V (B) 0.827 V (C) 0.184 V (D) 0.490 V

6. How many coulombs are required for oxidation of 1 mole of H_2O to O_2 ? **[NSEC-2001]**

(A) 3.86×10^5C (B) 9.65×10^4C (C) 1.93×10^5C (D) 4.825×10^4C

7. The metal which can not be obtained by electrolysis of its aqueous salt solution is : **[NSEC-2001]**

(A) Au (B) Al (C) Ag (D) Cu

8. The units of conductivity are : **[NSEC-2001]**

(A) Siemen^{-1}.cm^{-1}. (B) Siemen.cm (C) Siemen.cm^{-1} (D) Semen.cm^{-2}.mol^{-1}

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9. The calomel electrode used a reference elecrode contains :   **[NSEC-2001]**
    (A) PbO_2-$PbSO_4$ mixture   (B) $HgCl_2$
    (C) Hg_2Cl_2 (D) $ZnCl_2$

10. KCl is used in a salt bridge because :   **[NSEC-2001]**
    (A) it forms a good jelly with agar-agar
    (B) it is strong electrolyte
    (C) it is a good conductor of elelctric current
    (D) the transference number of K^+ and Cl^- ions are almost equal

11. During the electrolysis of fused NaCl, the reaction occurring at the anode is : **[NSEC-2001]**
    (A) reduction of Na^+ ions   (B) oxidation of Cl^- ions
    (C) oxidation of Na^+ ions   (D) reduction of Cl^- ions

12. On electrolysis, one mole of chromium ions will be deposited by :   **[NSEC-2001]**
    (A) three moles of electrons   (B) two moles of electrons
    (C) one mole of electrons   (D) six moles of electrons

13. The quantity of electricity which deposits 1.08 g of silver from $AgNO_3$ solution is :   **[NSEC-2002]**
    (A) 96500 coulombs   (B) 9650 coulombs   (C) 965 coulombs   (D) 96.5 coulombs.

14. In the conductometric titration of CH_3COOH vs NaOH, the titration curve obtained will be of the type
                                                                                   [NSEC-2002]

    (A)   (B)   (C)   (D)

15. The standared reduction potentials at 298 K for the half reactions are: **[NSEC-2002]**
    (a) $Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$; –0.762 V   (b) $Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$; – 0.740 V
    (c) $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$; 0.000 V   (d) $Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$; 0.770 V
    Which is the strongest reducing agent?
    (A) $Zn_{(s)}$ (B) $Cr_{(s)}$ (C) $H_{2(g)}$ (D) $Fe^{2+}_{(aq)}$.

16. The molar conductivities of H^+, Li^+ and Na^+ ions in aqueous solutions at infinite dilution are in the order :
                                                                                   [NSEC-2003]
    (A) $H^+ > Li^+ > Na^+$ (B) $H^+ < Li^+ < Na^+$ (C) $H^+ > Na^+ > Li^+$ (D) $Na^+ > H^+ > Li^+$.

17. $Fe^{2+} + 2e \rightarrow Fe$ .....(i)
    $Fe^{3+} + e \rightarrow Fe^{2+}$ .....(ii)
    The standard potentials (in volt) corresponding to the reactions (i) and (ii) are E_1 and E_2 respectively.
    The value (in volt) of the standard potential corresponding to the reaction $Fe^{3+} + 3e \rightarrow Fe$ is
                                                                                   [NSEC-2003]
    (A) (E_1+E_2) (B) $(2E_1+E_2)/3$ (C) $(E_1 +2E_2)/2$ (D) $(E_1+E_2)/3$.

18. The standard reduction potentials of Cu^{2+}, Zn^{2+}, Sn^{2+} and Ag^+ are 0.34, –0.76, –0.14 and 0.80 V
    respectively. The storage that is possible without any reaction is for   **[NSEC-2003]**
    (A) $CuSO_4$ solution in a zinc vessel   (B) $AgNO_3$ solution in a zinc vessel
    (C) $AgNO_3$ solution in a tin vessel   (D) $CuSO_4$ solution in a silver vessel.

19. A certain current passed through $CuSO_4$ solution for 100 seconds deposits 0.3175 g of copper. The
    current passed (in A) is   **[NSEC-2004]**
    (A) 4.83   (B) 9.65   (C) 0.963   (D) 0.483

20. The salt that can be used in the salt bridge of an electrochemical cell is   **[NSEC-2004]**
    (A) $FeCl_3$ (B) AgCl   (C) CH_3COONa (D) KNO_3.

21. The conductometric titration curve (of conductance vs mL of NaOH) obtained when acetic acid is titrated against NaOH is **[NSEC-2005]**

(A) (B) (C) (D)
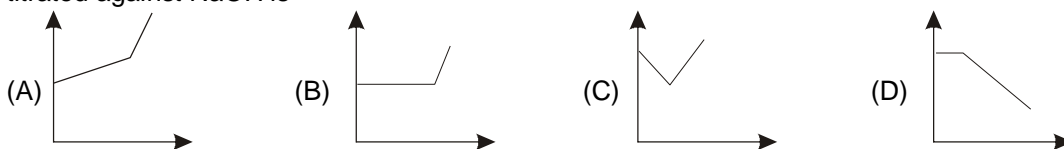
22. In an alkaline energy cell the overall cell reaction is as follows :
$$Zn(s) + 2MnO2(s) + 2H_2O \rightarrow Zn(OH)_2(s) + 2MnO(OH).$$
Which of the following reactions is taking place at the cathode? **[NSEC-2005]**
(A) $2MnO_{2(s)} + 2H_2O + 2e \rightarrow Zn(OH)_2(s) + 2MnO(OH)_{(s)}$
(B) $2MnO_{2(s)} + 2H_2O + 2e \rightarrow 2MnO(OH)_{(s)} + 2OH^-_{(aq)}$
(C) $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow Zn(OH)_2(s) + 2e$
(D) $Zn(OH)_{2(s)} + 2e \rightarrow Zn_{(s)} + 2OH^-_{(aq)}.$

23. What is the charge on an ion of tin if 7.42 g of metallic tin is deposited by passage of 24125 coulombs through a solution containing the ion ? **[NSEC-2005]**
(A) +1 (B) +3 (C) +2 (D) +4.

24. The cell potential (E) and free energy change (ΔG) accompanying an electrochemical reaction, are related by **[NSEC-2005]**
[NSEC-2005]

(A) $\Delta G = nFE$ (B) $\Delta G = nFE$ (C) $\Delta G = nFlogE$ (D) $\Delta G = nF \sqrt{logE}.$.

25. The mass of the copper, in grams, deposited during the passage of 2.5 ampere current through a Cu(II) sulphate solution for 1 hour is **[NSEC-2006]**
(A) 5.96 (B) 29.8 (C) 2.98 (D) 59.6

26. The standard reduction potentials of Fe^{2+}/Fe and Cu^{2+}/Cu electrodes are –0.44 and 0.34 volts, respectively. The following reaction would occur **[NSEC-2006]**
(A) copper will reduce Fe^{2+} ions (B) iron will reduce Cu^{2+} ions
(C) iron will oxidise copper metal (D) Cu^{2+} ions will reduce Fe^{2+}.

27. Rusting of iron is due to the formation of **[NSEC-2006]**
(A) hydrated ferrous oxide (B) hydrated ferric oxide
(C) only ferric oxide (D) a mixture of ferric oxide and $Fe(OH)_3$.

28. If the equilibrium constant of the disproportionation reaction
$$Hg_2^{2+} = Hg^0 + Hg^{2+}$$
at 298 K is 0.0795, the standard e.m.f. of the reaction is **[NSEC-2006]**
(A) –0.065 V (B) –0.212 V (C) 0.125 V (D) 0.110 V

29. The voltage for the cell: $Fe /Fe^{2+}(0.001M) // Cu^{2+}(0.10M) /Cu^{2+} (0.10 M) / Cu^{2+} (0.10 M) / Cu$ is 0.807 V at 25°C. What is the value of E° ? **[NSEC-2007]**
(A) 0.629 V (B) 0.689 V (C) 0.748 V (D) 0.866 V

30. A current of 2.0 A is used to plate Ni(s) from 500mL of a 1.0 M Ni^{2+} aqueous solution. What is the $[Ni^{2+}]$ after 3.0 hours ? **[NSEC-2007]**
(A) 0.39 M (B) 0.46 M (C) 0.78 M (D) 0.89 M

31. Nickel metal is added to a solution containing 1.0 M $Pb^{2+}_{(aq)}$ and 1.0 M $Cd^{2+}_{(aq)}$. Use the standard reduction potential to determine which of the following reaction (s) will occur. **[NSEC-2008]**
Reaction 1 : $Ni_{(s)} + Pb^{2+}_{(aq)} \rightarrow Pb_{(s)} + Ni^{2+}_{(aq)}$
Reaction 2 : $Ni_{(s)} + Cd^{2+}_{(aq)} Cd_{(s)} + Ni^{2+}_{(aq)}$
Reactions :
$$Pb^{2+}_{(aq)} + 2e = Pb_{(s)} \qquad E° = –0.13 V$$
$$Ni^{2+}_{(aq)} + 2e = Ni_{(s)} \qquad E° = –0.23 V$$
$$Cd^{2+}_{(aq)} + 2e = Cd_{(s)} \qquad E° = –0.40 V$$
(A) 1 only (B) 2 only (C) both 1 and 2 (D) neither 1 nor 2
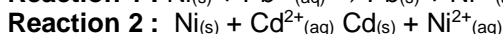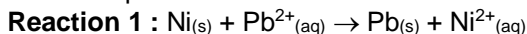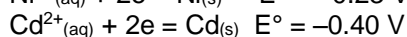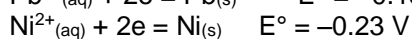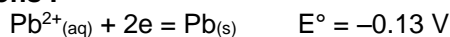
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32. An electrochemical cell constructed for the reaction, $Cu^{2+}_{(aq)} + M_{(s)} \rightarrow Cu_{(s)} + M^{2+}_{(aq)}$ has an $E° = 0.75$ V. The standard reduction potential for $Cu^{2+}_{(aq)}$ is 0.34 V. What is the standard reduction potential for $M^{2+}_{(aq)}$? **[NSEC-2008]**
(A) 1.09 V   (B) 0.410 V   (C) – 0410 V   (D) – 1.09 V

33. An electric current is passed through a silver voltameter connected to a water voltameter. 0.324 g of silver was deposited on the cathode of the silver voltameter. The volume of oxygen evolved at NTP is : **[NSEC-2009]**
(A) 5.6 cm³   (B) 16.8 cm³   (C) 11.2 cm³   (D) 22.4 cm³

34. The amount of copper (At. wt. 63.54) deposited by passing 0.2 faraday of electricity through copper sulphate is **[NSEC-2009]**
(A) 3.175 g   (B) 6.350 g   (C) 31.75 g   (D) 63.35 g

35. When aqueous solution of sodium chloride is electrolysed using platinum electrode the cathode reaction is, **[NSEC-2009]**

(A) $Na^+ + e^- \longrightarrow Na$ (B) $H_2O + e^- \longrightarrow \dfrac{1}{2} H_2 + OH^-$

(C) $Na^+ + OH^- \longrightarrow Na^+ + OH^- + e^-$ (D) $Na^+ + H_2O + e^- \longrightarrow Na + H^+ + OH^-$

36. The standard electrode potential values for four metals K, L, M and N are respectively, –3.05, –1.66, –0.40 and +0.80V. The best reducing agent is – **[NSEC-2009]**
(A) L   (B) K   (C) N   (D) M

37. $10Cl^- (aq) + 2MnO_4^- (aq) + 16H^+ (aq) \longrightarrow 5Cl_2 (g) + 2Mn^{2+} (aq) + 8H_2O (l)$ **[NSEC-2009]**
The value of E^0 for the above reaction at 25°C is 0.15V. Hence, the value of K for this reaction is:
(A) 2.4×10^{25} (B) 4.9×10^{12} (C) 1.2×10^5 (D) 3.4×10^2

38. Adding powdered Pb and Fe to a solution containing 1 M each of Pb^{2+} and Fe^{2+} ions would result in the formation of $– (E^0_{Pb^{2+}/Pb} = -0.126V$ and $E^0_{Fe^{2+}/Fe} = -0.44V)$ **[NSEC-2010]**
(A) more of Pb and Fe^{2+} ions   (B) more of Fe and Pb^{2+} ions
(C) more of Pb and Fe   (D) more of Pb^{2+} and Fe^{2+} ions

39. The cell $Al_{(s)}|Al^{3+}_{(aq)}$ (0.001 M) $||$ $Cu^{2+}_{(aq)}$ (0.10 M) $|$ $Cu_{(s)}$ has a standard cell potential $E^0 = 2.00$ V at 25°C. The cell potential at the given concentration will be : **[NSEC-2010]**
(A) 2.07 V   (B) 2.03 V   (C) 1.97 V   (D) 1.94 V

40. The mass of copper deposited when a current of 10A is passed through a solution of copper(II) nitrate for 30.6s is **[NSEC-2010]**
(A) 0.101 g   (B) 0.201 g   (C) 0.403 g   (D) 6.04 g

41. In the conductometric titration of silver nitrate against KCl, the graph obtained is **[NSEC-2011]**

42. Th emf of the cell (Zn | ZnSO₄(0.1M) || CdSO₄ (0.01M) | Cd) is **[NSEC-2011]**
$(E^o_{Zn^{2+}/Zn} = -0.76$ V, $E^o_{Cd^{2+}/Cd} = 0.40$ V at 298 K)
(A) +0.33 V   (B) +0.36 V   (C) +1.13 V   (D) –0.36 V

43. The conductivity of a metal decreases with increase in temperature because : **[NSEC-2012]**
(A) the kinetic energy of the electrons increases (B) the movement of electrons becomes haphazard
(C) the ions start vibrating   (D) the metal becomes hot and starts emiting radiation

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44. The amount of electricity required to deposit 1.0 mole of aluminium from a solution of $AlCl_3$ will be : **[NSEC-2012]**

(A) 1 faraday   (B) 3 faradays   (C) 0.33 faraday   (D) 1.33 faraday

45. Which is the strongest oxidising agent among the species given below? **[NSEC-2013]**

(i) In^{3+} $E^0 = -1.34V$ (ii) Au^{3+} $E^0 = 1.40V$
(iii) Hg^{2+} $E^0 = 0.867V$ (iv) Cr^{3+} $E^0 = -0.786V$
(A) Cr^{3+} (B) Au^{3+} (C) Hg^{2+} (D) In^{3+}

46. Which of the following aqueous solution has the lowest electrical conductance ? **[NSEC-2013]**

(A) 0.01M $CaCl_2$ (B) 0.01M KNO_2 (C) 0.01M CH_3COOH (D) 0.01M CH_3COCH_3

47. The value of the constant in Nernst equation

$$E = E^0 - \frac{constant}{n} \ln Q \text{ at } 25^0C \text{ is :}$$ **[NSEC-2013]**

(A) 0.592   (B) 0.0592   (C) 0.296   (D) 0.0296

48. When zinc rod is directly placed in copper sulphate solution **[NSEC-2013]**

(A) the blue colour of the solution starts intensifying
(B) the solution remains electrically neutral
(C) the temperature of the solution falls
(D) the weight of zinc rod starts increasing

49. For the following cell at 25^0C the E.M.F. is : [If $E^0_{M^{2+}/M} = 0.347$ V] **[NSEC-2014]**

$$M_{(S)} \mid M^{2+} (1M) \parallel M^{2+} (0.01M) \mid M_{(S)}$$

(A) 0.089V   (B) 0.598V   (C) 0.251V   (D) 0.764V

50. For a strong electrolyte, the change in the molar conductance with concentration is represented by : **[NSEC-2014]**

(I)   (II)   (III)   (IV)

(A) I   (B) II   (C) III   (D) IV

51. The specific conductance of 0.01M solution of the weak monobasic acid is 0.20×10^{-3} Scm^{-1}. The dissociation constant of the acid is   [Given: $\Lambda^0_{HA} = 400$ Scm^2mol^{-1}] **[NSEC-2014]**

(A) 5×10^{-2} (B) 2.5×10^{-5} (C) 5×10^{-4} (D) 2.5×10^{-11}

52. The reaction given below is the cell reaction in a galvanic cell.

$$Cd(s) + Sn^{2+}(aq) \rightarrow Cd^{2+}(aq) + Sn(s)$$

Where, $[Cd^{2+}] = 0.1$ M and $[Sn^{2+}] = 0.025$ M

Given: $E^0_{Cd^{2+}/Cd} = -0.403V$, $E^0_{Sn^{2+}/Sn} = -0.136V$, $F = 96485 Cmol^{-1}$

At 25^0C, the free energy change for this reaction is : **[NSEC-2014]**

(A) $-$ 48.05 KJ   (B) $-$ 54.96 KJ   (C) $-$ 100.58 KJ   (D) $-$ 107.46 KJ

53. A current of 5.0 A flows for 4.0 h through an electrolytic cell containing a molten salt of metal M. This results in deposition of 0.25 mol of the metal M at the cathode. The oxidation state of M in the molten salt is (1 Faraday = 96485 C mol^{-1}) **[NSEC-2015]**

(A) +1   (B) +2   (C) +3   (D) +4

54. The limiting molar conductivities of KCl, KNO_3, and $AgNO_3$ are 149.9, 145.0 and 133.4 S cm^2 mol^{-1}, respectively, at 25^0C. The limiting molar conductivity of AgCl at the same temperature in S cm^2 mol^{-1} is **[NSEC-2015]**

(A) 128.5   (B) 138.3   (C) 161.5   (D) 283.3

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55. The emf of a cell corresponding to the following reaction is 0.199 V at 298 K. **[NSEC-2015]**

$Zn (S) + 2 H^+ (aq) \rightarrow Zn^{2+} (0.1 M) + H_2 (g)$ $(E^o_{Zn/Zn^{2+}} = 0.76V)$

The approximate pH of the solution n at the electrode where hydrogen is being produced is ($p_{H2} = 1$ atm).

(A) 3 (B) 9 (C) 10 (D) 11

56. The standard electrode potentials, E^o of Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe at 300 K are +0.77 V and –0.44 V, respectively. The E^o of Fe^{3+}/Fe at the same temperature is **[NSEC-2015]**

(A) 1.21 V (B) 0.33 V (C) –0.036 V (D) 0.036 V

57. Three Faradays of electricity are passed through aqueous solutions of $AgNO_3$, $NiSO_4$ and $CrCl_3$ kept in three vessels using inert electrodes. The ratio (in moles) in which the metals Ag, Ni and Cr are deposited is : **[NSEC-2016]**

(A) 1 : 2 : 3 (B) 3 : 2 : 1 (C) 6 : 3 : 2 (D) 2 : 3 : 6

58. The standard potentials ($E°$) of MnO_4^-/Mn^{2+} and MnO_2/Mn^{2+} half cells in acidic medium are 1.51 V and 1.23 V respectively at 298 K. The standard potential of MnO_4^-/MnO_2 half-cell in acidic medium at the same temperature is : **[NSEC-2016]**

(A) 5.09 V (B) 1.70 V (C) 0.28 V (D) 3.34 V

59. Given the E_0 values for the half reactions :

$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$, 0.15 V

$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$, 0.92 V

$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$, 1.45 V

Which of the following statements is true? **[NSEC-2016]**

(A) Sn^{2+} is a stronger oxidizing agent than Pb^{4+} (B) Sn^{2+} is a stronger reducing agent than Hg_2^{2+}

(C) Hg^{2+} is a stronger oxidizing agent than Pb^{4+} (D) Pb^{2+} is a stronger reducing agent than Sn^{2+}

60. The conductivity of 0.10 M KCl solution at 298 K is 1.29×10^{-2} S cm^{-1}. The resistance of this solution is found to be 28.44 Ω. Using the same cell, the resistance of 0.10 M NH$_4$Cl solution is found to be 28.50 Ω. The molar conductivity of NH$_4$Cl solution in S cm^2 mol^{-1} is : **[NSEC-2016]**

(A) 0.130 (B) 13 (C) 130 (D) 1300

61. Which of the following statements is not correct regarding the galvanic cells ? **[NSEC-2016]**

(A) Oxidation occurs at the anode.

(B) Ions carry current inside the cell.

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

(D) When the cell potential is positive, the cell reaction is spontaneous.

62. When a medal is electroplated with silver (Ag) **[NSEC-2017]**

(A) The medal is the anode (B) Ag metal is the cathode

(C) The solution contains Ag$^+$ ions (D) The reaction at the anode is $Ag^+ + e^- \rightarrow Ag$

Use the table given below to answer questions 63 and 64

Reaction	E_0/V
$Ag \rightarrow Ag^+ + e^-$	–0.80
$Cr^{3+} + 3e^- \rightarrow 3Cr$	–0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
$I_2(s) + 2e^- \rightarrow 2 I^-$	0.54
$Co^{2+} + 2e^- \rightarrow Co$	–0.28
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.26

63. The best reducing agent among the following is **[NSEC-2017]**

(A) Ag$^+$ (B) Zn^{2+} (C) Cr^{3+} (D) I$^-$

64. E^o of the given cell is : **[NSEC-2017]**

Ni | (Ni^{+2}, 1.0 M) || (Co^{+2}, 1.0 M) | Co

(A) +0.02V (B) –0.02V (C) –0.54V (D) +0.54V

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65. The reduction of O_2 to H_2O in acidic solution has a standard reduction potential of 1.23 V. If the pH of the acid solution is increased by one unit, half cell potential will **[NSEC-2017]**

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$$

(A) decrease by 59 mV   (B) increase by 59 mV
(C) decrease by 236 mV   (D) increase by 236 mV

66. From the given standard electrode potentials **[NSEC-2018]**

$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ $E^0 = 0.15V$
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$ $E^0 = 1.07V$

The approximate free energy change of the process $2Br^-(aq) + Sn^{4+}(aq) \rightarrow Br_2(l) + Sn^{2+}(aq)$ is
(A) 117.6 kJ   (B) 355 kJ   (C) –177.6 kJ   (D) –355 kJ

67. Concentration of K^+ ions inside a biological cell was found to be 25 times higher than that outside. The magnitude of the potential difference between the two sides of the cell is close to (2.303 RT/F-can be taken as 59 mV; difference in concentrations of other ions can be taken as negligible) **[NSEC-2018]**
(A) 4.2 mV   (B) 195 mV   (C) 82 mV   (D) –82 mV

68. The standard redox potential for the reaction $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ is –1.23V. If the same reaction is carried out at 25ºC and at pH = 7, the potential will be **[NSEC-2018]**
(A) –0.82 V   (B) –3.28V   (C) 0.82V   (D) –1.18V

69. The standard electrode potential (E°) of the Daniel cell is 1.1 V and the overall cell reaction can be represented as $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$. Under which of the following conditions will the cell potential be higher than 1.1 V ? **[NSEC-2018]**
(A) 1.0 M Zn^{2+}, 1.0 M Cu^{2+} (B) 1.2 M Zn^{2+}, 1.2 M Cu^{2+}
(C) 0.1 M Zn^{2+}, 1.0 M Cu^{2+} (D) 1.0 M Zn^{2+}, 0.01 M Cu^{2+}

70. An electrochemical cell was constructed with Fe^{2+}/Fe and Cd^{2+}/Cd at 25ºC with initial concentrations of $[Fe^{2+}]$ = 0.800 M and $[Cd^{2+}]$ = 0.250 M. The EMF of the cell when $[Cd^{2+}]$ becomes 0.100 M is

Half cell	$E^0(V)$
$Fe^{2+}(aq)/Fe(s)$	– 0.44
$Cd^{2+}(aq)/Cd(s)$	– 0.40

[NSEC-2019]

(A) 0.013 V   (B) 0.011 V   (C) 0. 051 V   (D) 0.022 V

71. Molten NaCl is electrolysed for 35 minutes with a currect of 3.50 A at 40ºC and 1 bar pressure. Volume of chlorine gas evolved in this electrolysis is **[NSEC-2019]**
(A) 0.016 L   (B) 0.98 L   (C) 9.8 L   (D) 1.96 L

72. If the standard electrode potentials of Fe^{3+}/Fe and Fe^{2+}/Fe are –0.04 V and –0.44 V respectively then that of Fe^{3+}/Fe^{2+} is **[NSEC-2019]**
(A) 0.76 V   (B) –0.76 V   (C) 0.40 V   (D) –0.40 V

PART - IV : HIGH LEVEL PROBLEMS (HLP)

THEORY

Solubility product and EMF (Metal-Metal Insoluble Salt Electrode) :

● A half cell containing metal M and its sparingly soluble salt MA in a saturated solution.
i.e M(s) | MA (satd) or a metal, its sparingly soluble salt in contact with a solution of a soluble salt NaA of the same anion, i.e. M(s) | MA(s) | NaA is set up.

● The solubility product of a sparingly doubles salt is a kind of equilibrium constant.

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq) \qquad K_{sp} = [M^+][X^-]$$

At Anode
● $M(s) \rightleftharpoons M^+(aq) + e^-$

At Cathode
● $e^- + MX(s) \rightleftharpoons M(s) + X^-(aq)$

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Overall reaction	:	$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$
Cell representation	:	$M \mid M^+(\text{saturated sol.}) \parallel NaA \mid MX(s) \mid M(s)$

$E^0_{cell} = E^\circ_{red} - E^\circ_{ox}$
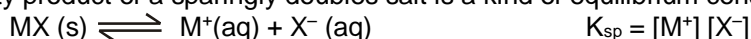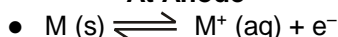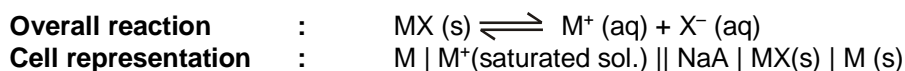
From thermodynamics $\Delta G^\circ = -nFE^\circ$

$\Delta G^\circ = -2.303\, RT \log K_{sp}$

combining both equations $-2.303\, RT \log K_{sp} = -nFE^\circ$

or $\quad E^\circ = \dfrac{2.303\ RT}{nF}\ \log K_{sp}$

$\quad E^\circ = \dfrac{0.0591}{n} \log K_{sp} \quad$ at 25°C

Solved Examples

Example Calculate K_{sp} if ($PbSO_4$) E_{cell} at 298 K of this electrode is 0.236 V

$Pb(s) \mid PbSO_4(s) \mid Na_2SO_4(aq) \parallel Pb(NO_3) \mid Pb(s)$
$\qquad\qquad\qquad$ 0.01 M $\qquad$ 0.1 M

$E_{cell} = E^0_{cell} - \dfrac{0.059}{2} \log \left[\dfrac{0.01}{0.1}\right]$

$0.236 = E^0_{cell} + \dfrac{0.059}{2}$

$E^0_{cell} = 0.236 - 0.03 = 0.206$

Solution I Let it be conc. cell

Anode $Pb(s) \rightarrow Pb^{2+}_{(a)} + 2e^-$

Cathode $Pb^{2+}_{(s)} + 2e^- \rightarrow Pb(s)$
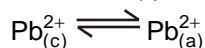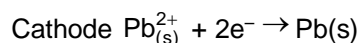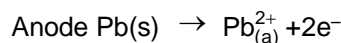
$Pb^{2+}_{(c)} \rightleftharpoons Pb^{2+}_{(a)}$

$E_{cell} = E^0_{cell} - \dfrac{0.059}{2} \log\left[\dfrac{(Pb^{2+})_a}{(Pb^{2+})_c}\right]$

$0.236 = \dfrac{0.059}{2} \log\left[\dfrac{(Pb^{2+})_a}{(Pb^{2+})_c}\right]$

$(Pb^{2+})_a = 10^{-9} M$

$K_{sp} = (Pb^{2+})_a (SO_4^{2-})_a = 10^{-11}$

Solution II **Let if it is not a conc cell**

Anode : $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

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

$\qquad Pb^{2+}(c) + SO_4^{2-}(a) \rightarrow PbSO_4(s)$

$E^0_{cell} = E^0_{Pb^{2+}/Pb} - E^0_{SO_4^{2-}\mid PbSO_4\mid Pb} = E^0_{Pb^{2+}\mid Pb} - \left[E^0_{Pb^{2+}\mid Pb^+} + \dfrac{0.059}{2}\log K_{sp}\right]$
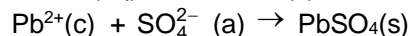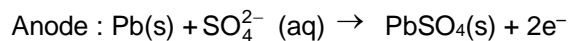
$E^0_{cell} = -\dfrac{0.059}{2}\ \log K_{sp}$

$0.236 = \dfrac{0.059}{2}\ \log K_{sp} - \dfrac{0.059}{2}\ \log\left[\dfrac{1}{(Pb^{2+})_c (SO_4^{2-})a}\right] = \log\left[\dfrac{K_{SP}}{0.1 \times 0.01}\right] = \log\left[\dfrac{K_{SP}}{10^{-3}}\right] \log 10^{-8}$

$K_{sp} = 10^{-11}$

Calomel Electrode :

- A calomel electrode consists of a platinum electrode dipping into mercury in contact with calomel (dimercury (I) chloride, Hg_2Cl_2) and potassium chloride solution.
- Usually the solution is saturated with potassium chloride.

- The cell has $E^0 = 0.28$ V (with respect of SHE) at 25°C

Standard (normal) calomel electrode when $[Cl^-] = 1M = 1N$

At Anode

$2Hg(\ell) \rightarrow Hg_2^{2+}$ (aq) + 2e$^-$

Hg_2^{2+} (aq) + 2Cl$^-$ $\rightarrow$ Hg$_2$Cl$_2$(s)

$2Hg(\ell) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2e^-$

- Cell representation

Pt(s) |Hg(ℓ) | Hg$_2$Cl$_2$(s) | Cl$^-$(aq)|| cathode

$E^0_{Hg\,|\,Hg_2Cl_2\,/\,Cl^-}$ = SOP

$E_{Cl^-\,/\,Hg_2Cl_2\,/\,Hg} = E^0_{Cl^-\,/\,Hg_2Cl_2\,/\,Hg} - \dfrac{RT}{F}\,\ell n[Cl^-]$

$E_{M^{n+}\,/\,M(Hg)Pt} = E^0_{M^{n+}\,/\,M(Hg)Pt} - \dfrac{RT}{F}\,\ell n[\dfrac{1}{M^{n+}}]$

At Cathode

$Hg_2^{2+} + 2e^- \rightarrow 2Hg(\ell)$

$Hg_2Cl_2 \rightarrow Hg_2^{2+}$ (aq) + 2Cl$^-$(aq)

$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(\ell) + 2Cl^-$

- Cell representation

(Anode) || Cl$^-$(aq) | Hg$_2$Cl$_2$|Hg(ℓ) | Pt(s)

$E^0_{Cl^-|Hg_2Cl_2|Hg(\ell)}$ = SRP
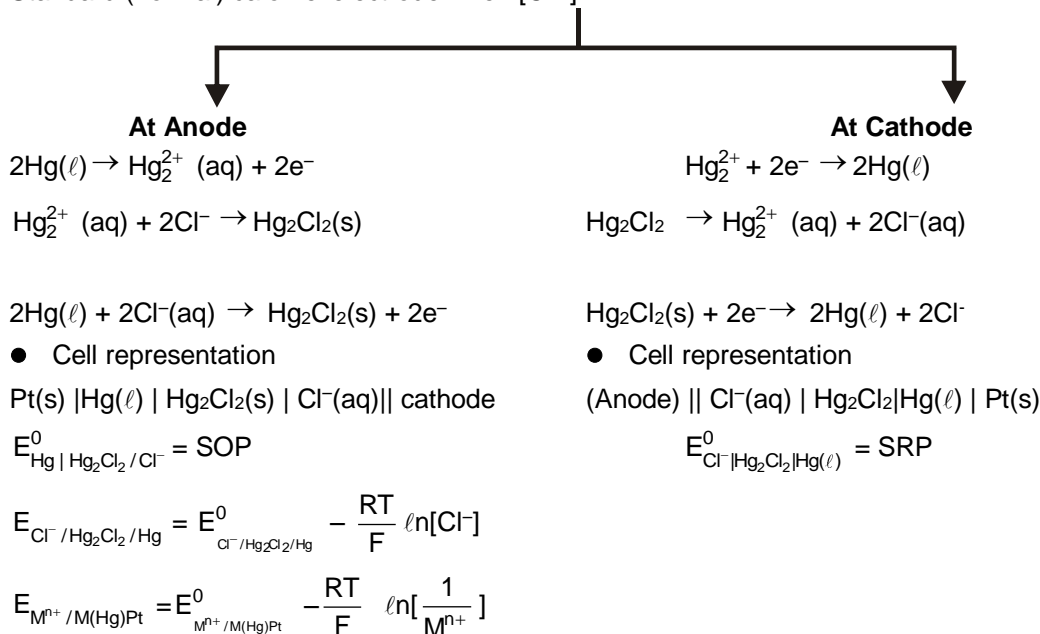
Thermodynamics of Cell Potential :

We know that :

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

$\Delta G = -nFE_{cell}$

$G = H - TS$

From thermodynamics H = E + PV enthalpy function.

Substituting G = E + PV – TS

By partial differentiation

dG = dE + PdV + VdP – TdS – SdT   ...... (i)

according to **1st law** of thermodynamics

E = q + W   dW = –PdV

dE = dq – PdV

dq = dE + PdV   ...... (ii)

according to **2nd law**

ds = $\dfrac{dq}{T}$ = dq = Tds   ...... (iii)

From (i), (ii) and (iii)

dG = VdP – SdT

at constant pressure, which is actually the condition for all normal cell reaction.

dG = –SdT

$S = \dfrac{-dG}{dT}$

$\Delta S = -\dfrac{d(\Delta G)}{dT}$

$\Delta G = - nFE_{cell}$

$\Delta S = +nF \dfrac{dE_{cell}}{dT}$

$\dfrac{dE_{cell}}{dT}$ = temperature cofficient of cell reaction.

$\Delta G = \Delta H - T\Delta S$

$\Delta H = - nF E_{cell} + nFT \dfrac{dE_{cell}}{dT}$

Kirchoff's equation

$\Delta Cp = \dfrac{d}{dT} (\Delta H)$

$\Delta Cp = Cp \text{ (of producits)} - Cp \text{ (of reactants)} = \dfrac{-nFdE_{cell}}{dT} + nFT \dfrac{d^2E_{cell}}{dT^2} + \dfrac{+nFdE_{cell}}{dT}$

$\Delta Cp = nFT \dfrac{d^2E_{cell}}{dT^2}$

SUBJECTIVE QUESTIONS

1. Determine range of E° values for this reaction $X^{2+}_{aq.} + 2e^- \longrightarrow X(s)$ for given conditions:
(a) If the metal X dissolve in HNO_3 but not in HCl it can displace Ag^+ ion but not Cu^{2+} ion.
(b) If the metal X in HCl acid producing $H_2(g)$ but does not displace either Zn^{2+} or Fe^{2+}.

Given : $\quad E^o_{Ag^+/Ag} = 0.8V$, $\qquad\qquad E^o_{Fe^{2+}/Fe} = -0.44V$,

$\quad\qquad\quad E^o_{Cu^{2+}/Cu} = 0.34V$, $\qquad\qquad E^o_{NO_3^-/NO} = 0.96V$, $\qquad\qquad E^o_{Zn^{2+}/Zn} = -0.76V$

2. The standard reduction potential of TiO^{2+} and Ti^{3+} are given by
$TiO^{2+} + 2H^+ + e^- \longrightarrow Ti^{3+} + H_2O \qquad\qquad E^0 = 0.10$ V
$Ti^{3+} + 3e^- \longrightarrow Ti \qquad\qquad\qquad\qquad\qquad E^0 = -1.21$ V
Find the standard reduction potential of TiO^{2+} to Ti.

3. The standard oxidation potential for the half−cell
$\qquad NO_2^- (g) + H_2O \longrightarrow NO_3^-(aq) + 2H^+ (aq) +2e$ is −0.78 V.
Calculate the reduciton potential in 9 molar H^+ assuming all other species at unit concentration. What will be the reduction potential in neutral medium ?

4. Calculate the electrode potential at 25^0C of Cr^{3+}, $Cr_2O_7^{2-}$ electrode at pOH = 11 in a solution of 0.01 M both in Cr^{3+} and $Cr_2O_7^{2-}$.
$\qquad Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O \quad E^0 = 1.33$ V.

5. An electrochemical cell is constructed with an open switch as shown below:

0.5 M Sn^{2+} $\qquad\qquad\qquad$ 0.1 M X^{n+}

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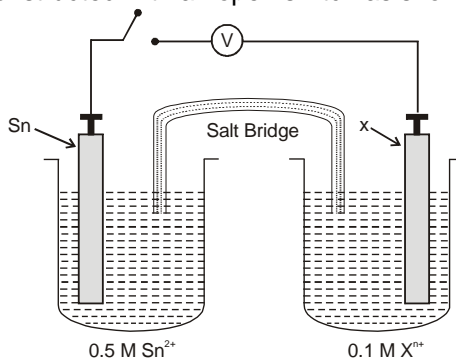
When the switch is closed, mass of tin-electrode increase. If E^0 (Sn^{2+} / Sn) = $-$ 0.14 V and for E^0 (X^{n+} / X) = $-$ 0.78 V and initial emf of the cell is 0.65 V, determine n and indicate the direction of electron flow in the external circuit.

6. Equinormal Solutions of two weak acids, HA (pK_a = 3) and HB (pK_a = 5) are each placed in contact with standard hydrogen electrode at 25°C (T = 298 K). When a cell is constructed by interconnecting them through a salt bridge find the e.m.f. of the cell.

7. In two vessels each containing 500ml water, 0.5m mol of aniline (K_b = 10^{-9}) and 25 m mol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.

8. Write cell reaction from given cell diagrams
(A) $Cu\,|\,Cu^{2+}\,\|\,Cl^-\,|\,Hg_2Cl_2\,|\,Hg\,|\,Pt$
(B) Ag (s) | $AgIO_3$ (s)|Ag^+, HIO_3 || Zn^{2+} | Zn (s)
(C) Mn (s) | Mn $(OH)_2$ (s) Mn^{2+}, OH^- || Cu^{2+}|Cu (s)

9. For the galvanic cell : Ag | AgCl (s)|KCl (0.2M) || KBr (0.001M) |AgBr (s) |Ag,
Calculate the EMF generated? (Take $\dfrac{2.303RT}{F}$ = 0.06)
[$K_{sp(AgCl)}$= 10^{-10} ; $K_{sp(AgBr)}$=10^{-13}]

10. Given, E° = $-$0.27 V for the Cl^- | $PbCl_2$ |Pb couple and $-$ 0.12 V for the Pb^{2+} | Pb couple, determine K_{sp} for $PbCl_2$ at 25°C ? (Take $\dfrac{2.303RT}{F}$ = 0.06)

11. The pK_{sp} of AgI is 16. if the E° value for Ag^+ | Ag is 0.8 V. Find the E° for the half cell reaction AgI(s) + $e^- \rightarrow$ Ag + I^- ? (Take $\dfrac{2.303RT}{F}$ = 0.06)

12. The EMF of the standard weston cadmium cell Cd (12.5%) in Hg | $3CdSO_4$, $8H_2O$ (solid) | saturated solution of $CdSO_4$ || Hg_2SO_4(s) | Hg is 1.0180 volts at 25° C and the temperature coefficient of the cell, $\left(\dfrac{\partial E}{\partial T}\right)_P$ = $-$ 4.0 × 10^{-5} V/degree. Calculate ΔG, ΔH and ΔS for the reaction in the cell when n = 2.

13. ΔH for the reaction Ag(s) + $\dfrac{1}{2}$ $Hg_2 Cl_2$ (s) $\longrightarrow$ AgCl(s) + Hg(ℓ) is +1280 cal at 25°C. This reaction can be conducted in a cell for which the emf = 0.0455 volt at this temperature. Calculate the temperature coefficient of the emf.

14. The standard electromotive force of the cell :
Fe | Fe^{2+} (aq) | | Cd^{2+} | Cd is 0.0372 V
The temperature coefficient of e.m.f. is –0.125 V K^{-1}. Calculate the quantities ΔG^0, ΔH^0 and ΔS^0 at 25ºC.

15. The voltage of a certain cell has standred potential at 25ºC and 20ºC are 0.3525 V and 0.3533 V respectively. If the number of electrons involved in the overall reactions are two, calculate ΔG^0, ΔS^0 and ΔH^0 at 25ºC.

16. A metal is known to form fluoride MF_2. When 10A of electricity is passed through a molten salt for 330 sec., 1.95g of metal is deposited. Find the atomic weight of M. What will be the quantity electricity required to deposit the same mass of Cu from $CuSO_4$?

17. Find the volume of gases evolved by passing 0.965 A current for 1 hr through an aqueous solution of CH_3COONa at 250ºC and 1 atm.

18. One of the methods of preparation of per disulphuric acid, $H_2S_2O_8$, involve electrolytic oxidation of H_2SO_4 at anode ($2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of H_2 and 2.35L of O_2 were generated at STP. What is the weight of $H_2S_2O_8$ formed ?

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19. The standard reduction potential values, E^0 (Bi^{3+} / Bi) and E^0 (Cu^{2+} /Cu) are 0.226V and 0.344V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolysed at 25°C. To what value can $[Cu^{2+}]$ be brought down before bismuth starts to deposit, in electrolysis.

20. Calculate the dissociation constant ($k_{dissociation}$) of water at 25°C from the following data :

Specific conductance of H_2O = 5.8 × 10^{-8} mho cm^{-1}, $\lambda^{\infty}_{H^+}$ = 350.0 and $\lambda^{\infty}_{OH^-}$ = 198.0 mho $cm^2\,mol^{-1}$

21. **(a)** Calculate ΔG^0 of the following reaction :
$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$
Given : $\Delta G^0(AgCl)$ = – 109 kJ/mole, $\Delta G^0(Cl^-)$ = – 129 kJ/mole, $\Delta G^0(Ag^+)$ = 77 kJ/mole.
Represent the above reaction in form of a cell.
Calculate E^0 of the cell. Find $\log_{10} K_{sp}$ of AgCl at 25°C.
(b) 6.539 × 10^{-2} g of metallic Zn (atomic mass = 65.39 amu) was added to 100 mL of saturated solution of AgCl.

Calculate $\log_{10} \dfrac{[Zn^{2+}]}{[Ag^+]^2}$ at equilibrium at 25°C, given that :

$$Ag^+ + e^- \longrightarrow Ag \qquad\qquad E^0 = 0.80\ V$$
$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad\qquad E^0 = -\,0.76\ V$$

Also find how many moles of Ag will be formed. (Take $\dfrac{114}{193}$ = 0.59, $\dfrac{1.56}{0.059}$ = 26.44) **[JEE 2005, 6/60]**

ONLY ONE OPTION CORRECT TYPE

22. The standard potential of the reaction $H_2O + e^- \to \dfrac{1}{2} H_2 + OH^-$ at 298 K by using K_w (H_2O) = 10^{-14}, is :

(A) – 0.828 V   (B) 0.828 V   (C) 0 V   (D) – 0.5 V

23. Given : $Hg_2^{2+} + 2e \longrightarrow 2\,Hg$, E^0 = 0.789 V & $Hg^{2+} + 2e \longrightarrow Hg$, E^0 = 0.854 V,
calculate the equilibrium constant for $Hg_2^{2+} \longrightarrow Hg + Hg^{2+}$.
(A) 3.13 × 10^{-3} (B) 3.13 × 10^{-4} (C) 6.26 × 10^{-3} (D) 6.26 × 10^{-4}

24. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$,
If H^+ concentration is decreased from 1 M to 10^{-4} M at 25°C, where as concentration of Mn^{2+} and MnO_4^- remain 1 M.
(A) the potential decreases by 0.38 V with decrease in oxidising power
(B) the potential increases by 0.38 V with increase in oxidising power
(C) the potential decreases by 0.25 V with decrease in oxidising power
(D) the potential decreases by 0.38 V without affecting oxidising power
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$,

25. At equimolar concentrations of Fe^{2+} and Fe^{3+}, what must $[Ag^+]$ be so that the voltage of the galvanic cell made from the (Ag^+ | Ag) and (Fe^{3+} | Fe^{2+}) electrodes equals zero?
$$Fe^{2+} + Ag^+ \rightleftharpoons Fe^{3+} + Ag$$
$$E^0_{Ag^+|Ag} = 0.7991\ ;\ E^0_{Fe^{3+}|Fe^{2+}} = 0.771$$
(A) 0.34   (B) 0.44   (C) 0.47   (D) 0.61

26. The cell Pt (H_2) (1 atm) | H^+(pH = ?) || I^- (a = 1) | AgI(s), Ag(s) | Pt has emf, E_{298K} = 0. The standard electrode potential for the reaction $AgI + e^- \to Ag + I^\ominus$ is – 0.151 volt. Calculate the pH value.
(A) 3.37   (B) 5.26   (C) 2.56   (D) 4.62

27. Using the information in the preceding problem, calculate the solubility product of AgI in water at 25°C $[E^o_{(Ag^+,\ Ag)}$ = + 0.799 volt]
(A) 1.97 × 10^{-17} (B) 8.43 × 10^{-17} (C) 1.79 × 10^{-17} (D) 9.17 × 10^{-17}

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28. The solubility product of silver iodide is 8.3×10^{-17} and the standard reduction potential of Ag, Ag^+ electrode is $+ 0.8$ volts at $25°$ C. The standard reduction potential of Ag,AgI/I^- electrode from these data is

(A) $– 0.30$ V (B) $+ 0.15$ V (C) $+ 0.10$ V (D) $– 0.15$ V

29. The efficiency of an hypothetical cell is about 84% which involves the following reaction :

$A (s) + B^{2+} (aq) \longrightarrow A^{2+} (aq) + B (s) : \Delta H = – 285$ kJ

Then, the standard electrode potential of the cell will be

(A) 1.20 (B) 2.40 V (C) 1.10 V (D) 1.24 V

30. The temperature coefficient, of the emf i.e. $\dfrac{dE}{dT} = – 0.00065$ volt. deg^{-1} for the cell Cd | CdCl$_2$ (1M) ||

AgCl (s) | Ag at 25°C. Calculate the entropy changes ΔS_{298K} for the cell reaction, $Cd + 2AgCl \rightarrow Cd^{2+} + 2Cl^- + 2Ag$

(A) $– 105.5$ JK^{-1} (B) $– 150.2$ JK^{-1} (C) $– 75.7$ JK^{-1} (D) $– 125.5$ JK^{-1}

31. The standard emf of the cell, Cd(s) $|$ CdCl$_2$(aq) (0.1 M) $||$ AgCl(s) $|$ Ag(s) in which the cell reaction is, Cd(s) $+ 2AgCl(s) \longrightarrow 2Ag(s) + Cd^{+2} (aq) + 2Cl^-(aq)$ is 0.6915 V at 0°C and 0.6753 V at 25°C. The ΔH^0 of the reaction at 25°C is :

(A) $– 176$ kJ (B) $– 234.7$ kJ (C) $+ 123.5$ kJ (D) $– 167.26$ kJ

32. The potential of the Daniell cell, Zn $\left| \begin{array}{c} ZnSO_4 \\ (1 \ M) \end{array} \right| \left| \begin{array}{c} CuSO_4 \\ (1 \ M) \end{array} \right|$ Cu was reported by Buckbee, Surdzial and

Metz as $E° = 1.1028 – 0.641 \times 10^{-3}$ T $+ 0.72 \times 10^{-5}$ T^2, where T is the temperature in degree celsius. Calculate $\Delta S°$ for the cell reaction at 25°C :

(A) $– 45.32$ EU (B) $– 34.52$ EU (C) $– 25.43$ EU (D) $– 54.23$ EU

33. Using the data in the preceding problem, calculate the equilibrium constant of the reaction at 25°C.

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu, \quad K = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

(A) 8.314×10^{24} (B) 4.831×10^{31} (C) 8.314×10^{36} (D) 4.831×10^{44}

34. $\Delta G = \Delta H – T\Delta S$ and $\Delta G = \Delta H + T \left[\dfrac{d(\Delta G)}{dT} \right]_p$ then $\left(\dfrac{dE_{cell}}{dT} \right)$ is :

(A) $\dfrac{\Delta S}{nF}$ (B) $\dfrac{nE}{\Delta S}$ (C) $– nFE_{cell}$ (D) $+ nEF_{cell}$

35. One g equivalent of Na metal is formed from electrolysis of fused NaCl. No. of mole of Al from the fused Na$_3$AlF$_6$ with the same current passed is :

(A) 1 (B) 3 (C) 1/3 (D) 2

36. The specific conductivity of a saturated solution of AgCl is 3.40×10^{-6} ohm^{-1} cm^{-1} at 25 ºC. If $\Lambda_{Ag^+} = 62.3$ ohm^{-1} cm^2 mol^{-1} & $\Lambda_{Cl^-} = 67.7$ ohm^{-1} cm^2 mol^{-1}, the solubility of AgCl at 25 ºC is :

(A) 2.6×10^{-5} M (B) 4.5×10^{-3} M (C) 3.6×10^{-5} M (D) 3.6×10^{-3} M

37.

List-1	List-II
(P) Conductivity does not change much then increases	(1) NH$_3$ is added in C$_6$H$_5$COOH
(Q) Conductivity increases then does not change much	(2) CH$_3$COOH is added in NaOH
(R) Conductivity decreases then does not change much	(3) KOH is added in HCl
(S) Conductivity decreases then increases	(4) Conc. KCl is added in dilute AgNO$_3$
(T) Conductivity tends to zero at the end point	(5) MgSO$_4$ is added in Ba(OH)$_2$

	(P)	(Q)	(R)	(S)	(T)		(P)	(Q)	(R)	(S)	(T)
(A)	4	2	1	5	3	(B)	1	2	3	4	5
(C)	5	4	3	2	1	(D)	4	1	2	3	5

38. The standard reduction potentials E° of the following systems are

	System	E°(volts)
(i)	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	1.51
(ii)	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	0.15
(iii)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	1.33
(iv)	$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	1.61

The oxidising power of the various species decreases in the order
(A) $Ce^{4+} > Cr_2O_7^{2-} > Sn^{4+} > MnO_4^-$ (B) $Ce^{4+} > MnO_4^- > Cr_2O_7^{2-} > Sn^{4+}$
(C) $Cr_2O_7^{2-} > Sn^{4+} > Ce^{4+} > MnO_4^-$ (D) $MnO_4^- > Ce^{4+} > Sn^{4+} > Cr_2O_7^{2-}$

39. Consider the reaction : (T = 298 K)
$Cl_2(g) + 2Br^-$ (aq) $\longrightarrow 2Cl^-$ (aq) $+ Br_2$ (aq.)
The emf of the cell, when $[Cl^-] = [Br_2] = [Br^-] = 0.01M$ and Cl_2 gas is at 1 atm pressure, will be :
(E° for the above reaction is = 0.29 volt)
(A) 0.54 volt   (B) 0.35 volt   (C) 0.24 volt   (D) –0.29 volt

40. $2Ce^{4+} + Co \longrightarrow 2Ce^{3+} + Co^{2+}$, E^0_{cell} = 1.89 V, $E^0_{Co^{2+}/Co}$ = – 0.277 V hence, $E^0_{Ce^{4+}/Ce^{3+}}$ is :
(A) 0.805 V   (B) 1.62 V   (C) – 0.805 V   (D) – 1.61 V

41. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$; E^0 = 1.51 V ; $\Delta G^0_1 = -5 \times 1.51 \times F$

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$; E^0 = 1.23 V ; $\Delta G^0_2 = -2 \times 1.23 \times F$

$E^0_{MnO_4^- | MnO_2}$ is
(A) 1.70 V   (B) 0.91 V   (C) 1.37 V   (D) 0.548 V

42. ΔG is the available energy (energy produced) during the electrochemical reaction in galvanic cell which can be converted into useful work. In the light of second law of thermodynamics in the cell the change in electrode potential with temperature will be equal to
(A) $\dfrac{\Delta S}{nF}$ (B) $\dfrac{nF}{\Delta S}$ (C) – 2.303 RT log K_C (D) $\dfrac{-2.303 \quad RT}{nF}$

43. The reduction potential of hydrogen electrode when placed in a buffer solution is found to be – 0.413V. The pH of the buffer is -
(A) 10   (B) 4   (C) 7   (D) 12

44. A gas Cl_2 at 1 atm is bubbled through a solution containing a mixture of 1 M Br^{-1} and 1 M F^{-1} at 25ºC. If the reduction potential is F > Cl > Br, then :
(A) Cl will oxidise Br and not F   (B) Cl will oxidise F and not Br.
(C) Cl will oxidise both Br and F   (D) Cl will reduce both Br and F

45. The oxidation potentials of Zn, Cu, Ag, H_2 and Ni are 0.76, –0.34, –0.80, 0.00, 0.25 volt, respectively. Which of the following reactions will provide maximum voltage ?
(A) $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$ (B) $Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$
(C) $H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu$ (D) $H_2 + Ni^{2+} \longrightarrow 2H^+ + Ni$

46. The reduction potential of a half-cell consisting of a Pt electrode immersed in 1.5 M Fe^{2+} and 0.015 M Fe^{3+} solution at 25°C is $\left(E^0_{Fe^{3+}/Fe^{2+}} = 0.770 \quad V \right)$.
(A) 0.652 V   (B) 0.88 V   (C) 0.710 V   (D) 0.850 V

47. $Zn + Cu^{2+}$ (aq) $\rightleftharpoons Cu + Zn^{2+}$ (aq) Reaction quotient is Q = $\dfrac{[Zn^{2+}]}{[Cu^{2+}]}$. E^0_{cell} = 1.10 V. E_{cell} will be 1.1591

V when :
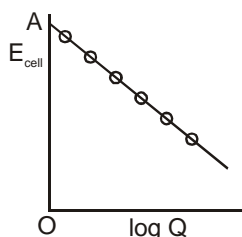
(A) $[Cu^{2+}]/[Zn^{2+}]$ = 0.01   (B) $[Zn^{2+}]/[Cu^{2+}]$ = 0.01 (C) $[Zn^{2+}]/[Cu^{2+}]$ = 0.1   (D) $[Zn^{2+}]/[Cu^{2+}]$ = 1

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48. Pure water is saturated with pure solid AgCl, a silver rod is placed in the solution and the potential is measured against normal calomel electrode at 25°C. This experiment is then repeated with a saturated solution of AgI. If the difference in potential in the two cases is 0.177 V, what is the ratio of solubilty product (K_{sp}) of AgCl and AgI at the temperature of the experiment ? (In both cases normal calomel electrode is cathod)

(A) 10^3 (B) 10^6 (C) 10^{-3} (D) 10^{-6}

49. Conductance measurements can be used to detect the end point of acid-base titrations. Which of the following plots correctly represent the end point of the titration of strong acid and a strong base ?
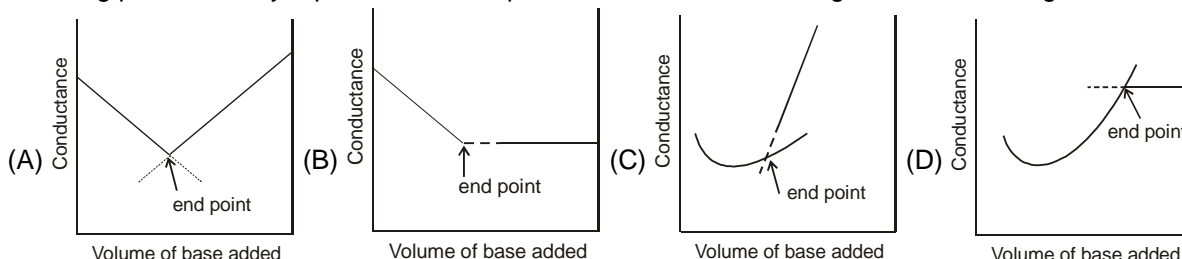
50. Which one of the following will increase the voltage of the cell ? (T = 298 K)

$$Sn + 2Ag^+ \longrightarrow Sn^{2+} + 2Ag$$

(A) increase in the size of silver rod   (B) increase in the concentration of Sn^{+2} ions

(C) increase in the concentration of Ag^+ ions   (D) none of the above

51. In a $H_2 - O_2$ fuel cell, 6.72 L of hydrogen at NTP reacts in 15 minutes, the average current produced in amperes is

(A) 64.3 amp   (B) 643.3 amp   (C) 6.43 amp   (D) 0.643 amp

52. The standard reduction potential of a silver chloride electrode is 0.2 V and that of a silver electrode is 0.79 V. The maximum amount of AgCl that can dissolve in 10^6 L of a 0.1 M AgNO$_3$ solution is

(A) 0.5 mmol   (B) 1.0 mmol   (C) 2.0 mmol   (D) 2.5 mmol

53. A cell   Cu | Cu^{++} || Ag$^+$ | Ag initially contains 2M Ag$^+$ and 2M Cu^{2+} ions in 1 L electrolyte. The change in cell potential after the passage of 10 amp current for 4825 sec during usage of cell is: (Take $\dfrac{2.303RT}{F} = 0.06$)

(A) – 0.009 V   (B) – 1.00738 V   (C) – 0.0038 V   (D) –1.2 V

54. At 27°C $\left(\dfrac{\partial E^o}{\partial T}\right)_P = -1.45 \times 10^{-3}$ V K^{-1} and $E^0 = 1.36$ V

For the cell Pt | H$_2$ (g) | HCl (aq) | Cl$_2$ | Pt. Calculate entropy and enthalpy change in this standard state.

(A) –962.48 JK^{-1}, –346.435 KJ   (B) –279.85 JK^{-1}, –346.453 KJ

(C) –1326.23 JK^{-1}, –346.435 KJ   (D) –280.24 KJK^{-1}, –346.435 KJ.

55. If K_{sp} values of AgCl, AgBr & AgI at 298 K are 10^{-10}, 10^{-13} & 10^{-17} respectively,

Compare $E^o_{Cl^-/AgCl/Ag}$, $E^o_{Br^-/AgBr/Ag}$ & $E^o_{I^-/AgBr/Ag}$:

(A) $E^o_{Cl^-/AgCl/Ag}$ will have the least value and its value will be less than $E^o_{Ag^+/Ag}$

(B) $E^o_{I^-/AgBr/Ag}$ will have the least value and its value will be more than $E^o_{Ag^+/Ag}$

(C) $E^o_{Cl^-/AgCl/Ag}$ will have the least value and its value will be more than $E^o_{Ag^+/Ag}$

(D) $E^o_{I^-/AgBr/Ag}$ will have the least value and its value will be less than $E^o_{Ag^+/Ag}$

NUMERICAL VALUE QUESTIONS

56. Consider the cell Ag|AgBr(s)| Br$^-$ || Cl$^-$ | AgCl(s)| Ag at 25°C. The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10}. For what ratio of the concentrations of Br$^-$ & Cl$^-$ ions would the e.m.f. of the cell be zero ? Report as 1000 × your answer.

57. A silver coulom meter is in series with a cell electrolyzing water. In a time of 1 minute at a constant current, 1.08 g silver got deposited on the cathode of the coulometer. What total volume **(in mL)** of the gases would have produced in other cell if in this cell the anodic and cathodic efficiencies were 90% and 80% respectively. Assume STP conditions and the gases collected are dry. (Ag – 108) (Molar volume of any ideal gas at STP = 22.4 L). Report as (your answer ÷ 10)

58. During electrolysis of $CH_3COONa_{(aq)}$, the mole ratio of gases formed at anode and cathode is :

59. Calculate the emf of the cell in mV

$$Ag\,(s),\ AgIO_3\,(s)\ \Big|\ Ag^+(xM),\ HIO_3\ (1\ M)\ \Big|\Big|\ Zn^{+2}(1\ M)\Big|\ Zn(s)$$

If $K_{sp} = 3 \times 10^{-8}$ for $AgIO_3$ and $K_a = \dfrac{1}{6}$ for HIO_3 and E^0_{cell} for $2Ag + Zn^{+2} \longrightarrow 2Ag^+ + Zn$ is – 1.56 V.

(log 3 = 0.48) (Take $\dfrac{2.303\ RT}{F} = 0.06$) **(Write magnitude of first two digits of your answer)**

60. A saturated solution of MX is prepared K_{SP} of MX is a × 10^{-b}. If 10^{-7} mol of MNO_3 are added in 1 ℓ of this solution conductivity of this solution is 55×10^{-7} S m^{-1} :

$$\lambda^\circ_{m^+} = 6 \times 10^{-3}\ S\ m^2\ mol^{-1}\ ;\ \lambda^\circ_{x^-} = 8 \times 10^{-3}\ ;\ \lambda^\circ_{NO_3^-} = 7 \times 10^{-3}$$

Find the value of (a + b) ? Given that 10 < a < 100

61. $Zn^{2+}(aq) + 4OH^-(aq) \longrightarrow Zn(OH)_4^{2-}(aq)$

Value of equilibrium constant (K_f) for above reaction is 10^x then find x:

Given : $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s);\ E^o = -0.76V$

$Zn(OH)_4^{2-}(aq) + 2e^- \rightarrow Zn(s) + 4OH^-(aq);\ E^o = -1.36V$

$2.303\dfrac{RT}{F} = 0.06$

62. A cell reaction, $Zn + 2Fe^{3+} \rightleftharpoons 2Fe^{2+} + Zn^{2+}$, works at 25°C with the cell emf 1.2 volt and at 45°C with the cell emf 1.718 volt. Assuming ΔS^o to be constant in this temperature range, calculate ΔS^o in kJ/K. (Give your answer in the nearest integer).

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

63. Which of the following statements is wrong about galvanic cells ?
(A) Cathode is the positive electrode
(B) Cathode is the negative electrode
(C) Electrons flow from cathode to anode in the external circuit
(D) Reduction occures at cathode

64. When a cleaned strip of zinc metal is placed in a solution of $CuSO_4$, a spontaneous reaction occurs. Which of the following observation(s) is/are made ?
(A) the mass of zinc metal decreases gradually
(B) the copper metal starts depositing on either zinc plate or settles down to the vessel
(C) the solution remains electrically neutral
(D) the temperature of the solution decreases as it is an endothermic reaction.

65. Mark out the correct statement(s)

(A) Copper metal cannot reduce iron (II) ions in acidic solutions.

(B) Sodium can be obtained by the electrolysis of aqueous solution of NaCl using Pt electrodes.

(C) The current carrying ions in an electrolytic cell are not necessarily discharged at the electrodes.

(D) Cations having more negative oxidation potential than –0.828 V are reduced in preference to water.

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66. When a lead storage battery is recharged

(A) $PbSO_4$ is formed   (B) Pb is formed   (C) SO_2 is consumed   (D) H_2SO_4 is formed

67. Which of the following statements is / are correct ?

(A) The conductance of one cm^3 (or 1 $unit^3$) of a solution is called conductivity.

(B) Specific conductance increases while molar conductivity decreases on progressive dilution.

(C) The limiting equivalent conductivity of weak electrolyte cannot be determine exactly by extraplotation of the plot of Λ_{eq} against $\sqrt{c}$.

(D) The conductance of metals is due to the movement of free electrons.

68. Peroxodisulphate salts ($Na_2S_2O_8$) are strong oxidizing agents used as bleaching agents for fats, oil etc. Given

$O_2(g) + 4H^{\oplus}(aq) + 4e^- \longrightarrow 2H_2O(\ell)$ $E^0 = 1.23$ V

$S_2O_8^{-2} + 2e^- \longrightarrow 2SO_4^{-2}$ (aq) $E^0 = 2.01$ V

Which of the following statements is (are) correct ?

(A) Oxygen gas can oxidize sulphate ion to per-oxo disulphate ion ($S_2O_8^{-2}$) in acidic solution.

(B) $O_2(g)$ is reduced to water

(C) Water is oxidised to O_2

(D) $S_2O_8^{-2}$ ions are reduced to SO_4^{-2} ions.

69. 0.1 molar solution of NaBr solution is electrolysed by passing 965 column charge. After electrolysis which statement is correct for resulting solution.

(A) Specific conductance increases   (B) molar conductance increases

(C) No change in molar conductance.   (D) Specific resistance increases.

70. A beaker contains a small amount of iron Fe(s). Which of the following aqueous solution, when added to the beaker, would dissolve the iron i.e. convert Fe(s) to Fe^{2+} (aq) ?

Half cells	E^0 at 25ºC
$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76
$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.41
$Al^{3+} + 3e^- \longrightarrow Al$	–1.66
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	0.70
$Cr_2O_7^{2-} + 6e^- + H^+ \longrightarrow 2Cr^{3+}$	1.23
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.30

(A) $Cr_2O_7^{2-}$ (acidic solution)   (B) H_2O_2 (acidic solution)

(C) Al^{3+} (D) Zn^{2+}

COMPREHENSION

Comprehension # 1

1 L, 2 M $ZnSO_4$ 1 L, 0.2 M $CuSO_4$
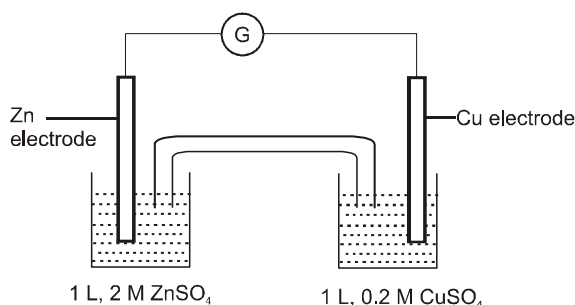
Given $E^0_{Zn^{+2}|Zn} = -0.76$ V K_f $[Cu(NH_3)_4]^{+2} = 4 \times 10^{11}$

$E^0_{Cu^{+2}|Cu}$ $= 0.34$ V

Answer the following.

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71. The emf of cell at 200 k is [Given : $\dfrac{2.303 \times R}{F}$ = 2 × 10^{-4} and assume that E^0 values are independent on temperature.]

(A) 1.7 V   (B) 1.08 V   (C) 1.09 V   (D) 1.10 V

72. When 1 mole NH$_3$ added to cathode compartment than emf of cell is (at 298K)

(A) 0.81 V   (B) 1.91 V   (C) 1.1 V   (D) 0.72 V

73. At what conc of Cu^{+2} emf of the cell will be zero (at 298K) and conc. of Zn^{+2} is remain same

(A) 1.19 × 10^{-37} (B) 1. 19 × 10^{-20} (C) 3.78 × 10^{-4} (D) 0.0068

Comprehension # 2

Strong Acid Versus Strong Base

The principle of conductometric titrations is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that the conductivity of the solution varies during the course of the titration. Take, for example, the titration between a strong acid, say HCl, and a strong base, say NaOH. Before NaOH is added, the conductance of HCl solution has a high value due to the presence of highly mobile hydrogen ions. As NaOH is added, H$^+$ ions are replaced by relatively slower moving Na$^+$ ions. Consequently, the conductance of the solution decreases and this continues right upto the equivalence point where the solution contains only NaCl. Beyond the equivalence point, if more of NaOH is added, then the solution contains an excess of the fast moving OH$^-$ ions with the result that its conductance is increased and it continues to increase as more and more of NaOH is added.

If we plot the conductance value versus the amount of NaOH added, we get a curve of the type shown in **Fig**.
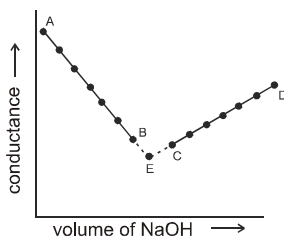
The descending portion AB represents the conductances before the euivalence point (solution contains a mixture of acid HCl and the salt NaCl) and the ascending portion CD represents the conductances after the equivalence point (solution contains the salt NaCl and the excess of NaOH). The point E which represents the minium conductance is due to the solution containing only NaCl with no free acid or alkali and thus represents the equivalence point. This point can, however, be obtained by the extrapolation of the lines AB and DC, and therefore, one is not very particular in locating this point experimentally as it is in the case of ordinary acid-base titrations involving the acid-base indicators.

Weak Acid versus Strong Base

Let us take the specific example of acetic acid being titrated against NaOH. Before the addition of alkali, the solution shows poor conductance due to feeble ionization of acetic acid. Initially the addition of alkali casue not only the replacement of H$^+$ by Na$^+$ but also suppresses the dissociation of acetic acid due to the common ion Ac$^-$ and thus the conductance of the solution decreases in the beginning. But very soon the conductance starts increasing as addition of NaOH neutralizes the undissociated HAc to Na$^+$Ac$^-$ thus causing the replacement of non-conducting HAc with strong-conducting electrolyte Na$^+$Ac$^-$. The increase in conductance continunes right up to the equivalence point. Beyond this point conductance increases more rapidly with the addition of NaOH due to the highly conducting OH$^-$ ions. The graph near the equivalence point is curved due to the hydrolysis of the salt NaAc. The actual equivalence point can, as usual, be obtained by the extrapolation method.

In all these graphs it has been assumed that the volume change due addition of solution from burrette is negligible, hence volume change of the solution in beaker the conductance of which is measured is almost constant throughout the measurement.

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74. The nature of curve obtained for the titration **between weak acid versus strong base as described in the above passage will be :**

(A) Conductance vs volume of NaOH

(B) Conductance vs volume of NaOH

(C) Conductance vs volume of NaOH

(D) Conductance vs volume of NaOH
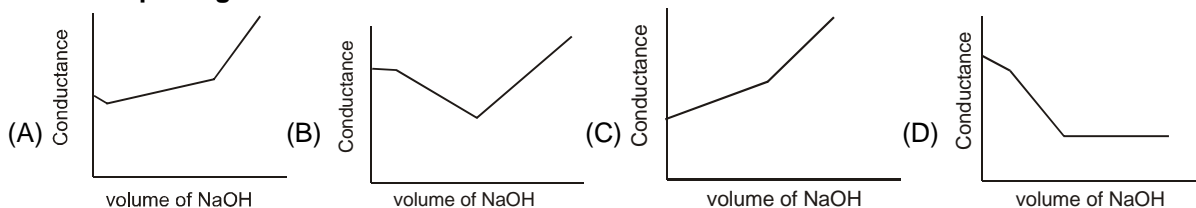
75. The most appropriate titration curve obtained when a mixture of a strong acid (say HCl) and a weak acid (say CH_3COOH) is titrated with a strong base(say NaOH) will be

(A) Conductance vs volume of NaOH, minimum at $V_1 + V_2$

(B) Conductance vs volume of NaOH, flat between V_1 and V_2

(C) Conductance vs volume of NaOH, minimum at V_1, kink at V_2

(D) Conductance vs volume of NaOH, kink at V_1, minimum at V_2
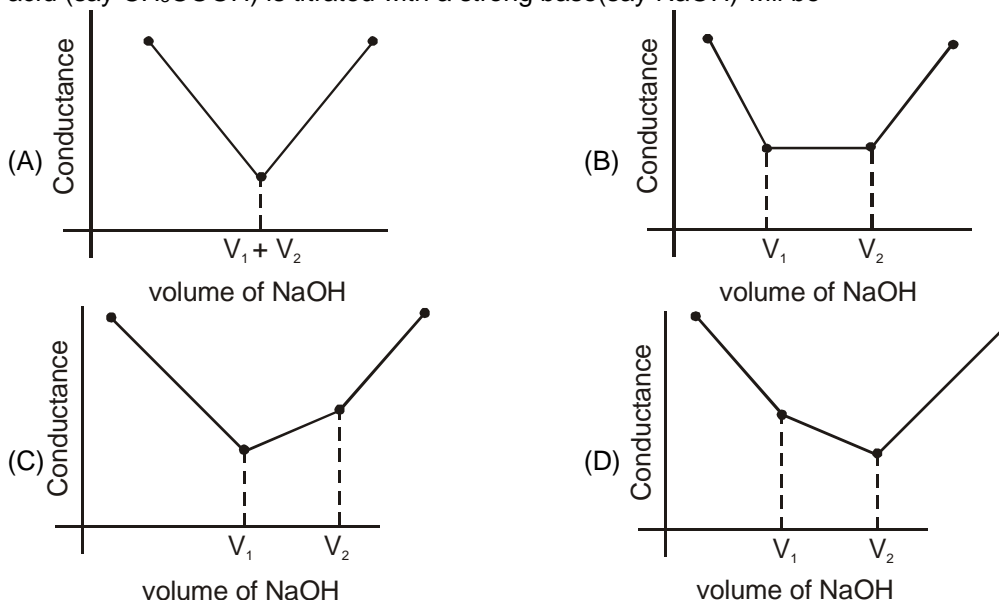
PART - V : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.   **Max. Marks : 66**

Important Instructions

A. General :

1. The test is of 1 hour duration.
2. The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format

3. Each part consists of five sections.
4. Section 1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5. Section 2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6. Section 3 contains 6 questions. The answer to each of the questions is a numerical value, ranging from 0 to 9 (both inclusive).
7. Section 4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8. Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme

9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.

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10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.

11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)
This section contains 10 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

---

1. An initial solution of x M, 1L Fe^{+2} was reduced to Fe(s) on passage of 1 A current for 965 seconds. If after electrolysis 0.1M, 10 ml acidified $KMnO_4$ solution was required to oxidize remaining Fe^{+2} solution then the value of 'x' is -
(A) 10^{-2} (B) 10^{-3} (C) 5×10^{-3} (D) 5×10^{-2}

2. A solution of 100 mL, 0.2 M CH_3COOH is mixed with 100 mL, 0.2 M NaOH solution. The molar conductance for 0.1 M CH_3COOH at infinite dilution is 200 S cm^2 mol^{-1} and at any concentration is 2.0 S cm^2 mol^{-1}. Then calculate pH of the solution?
(A) 7 (B) 8 (C) 5 (D) 9

3. The specific conductance of saturated solution of silver bromide is K (Ω^{-1} cm^{-1}). The limiting ionic conduction of Ag^+ and Br^- ions are a & b respectively. The solubility of AgBr in g lit^{-1} is:
(Molar mass of AgBr = 188g mol^{-1})

(A) $K \times \dfrac{1000}{a-b}$ (B) $\dfrac{K}{a+b} \times 188$ (C) $\dfrac{K \times 1000 \times 188}{a+b}$ (D) $\dfrac{a+b}{K} \times \dfrac{1000}{188}$

4. The conductance ratio $\dfrac{\lambda}{\lambda^\circ}$ = 0.936 given this for a certain solution of KCl and λ = 122 $\Omega^{-1}cm^2$ eq^{-1} and

$\dfrac{\lambda^\circ_+}{\lambda^\circ} = \dfrac{0.98}{1.98}$. Calculate the limiting values of Ionic conductance of $K^\oplus$ and Cl^- ions in $\Omega^{-1}cm^2$ eq^{-1}.
(A) 64.51, 65.83 (B) 74.60, 26.40 (C) 30.31, 69.69 (D) 70.12, 29.88

5. Osmotic pressure of 0.1 M weak acid HA is 3 atm. If molar conductance of 0.1 M HA is $30\Omega^{-1}cm^2mol^{-1}$. than molar conductance at infinite dilution is :
(A) 150 $\Omega^{-1}cm^2$ $mole^{-1}$ (B) 300 $\Omega^{-1}cm^2$ $mole^{-1}$
(C) 100 $\Omega^{-1}cm^2$ $mole^{-1}$ (D) 200 $\Omega^{-1}cm^2$ $mole^{-1}$

6. The molar conductivity of 0.05 M solution of $MgCl_2$ in a cell with electrodes of 1.5 cm^2 surface area and 0.5cm apart and 0.15 amphere current flow when a potential difference of 5 volt is applied between two electrodes –
(A) $200\Omega^{-1}$ cm^2 mol^{-1} (B) 195.6 Ω^{-1} cm^2 mol^{-1}
(C) 149.8 Ω^{-1} cm^2 mol^{-1} (D) 169.5 Ω^{-1} cm^2 mol^{-1}

7. 5 litre solution of 0.4 M $CuSO_{4(aq)}$ is electrolyzed using Pt electrode. A current of 482.5 ampere is passed for 4 minutes. The concentration of $CuSO_4$ left in solution is (Assume volume of solution to be remained unchanged):
(A) 0.16 M (B) 0.28 M (C) 0.34 M (D) 0.40 M

8. For a concentration cell :
Pt | Ag (s) | Ag^+ (aq., C_1) || Ag^+ (aq., C_2) | Ag (s) | Pt

EMF of the cell is X volt then calculate the ratio of $\dfrac{C_2}{C_1}$?

(A) anti log $\left(\dfrac{x}{0.059}\right)$ (B) anti log $\left(\dfrac{x}{2 \times 0.059}\right)$ (C) anti log $\left(\dfrac{4x}{0.059}\right)$ (D) None of these

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9. A saturated solution of $Fe(OH)_3$ is present in a solution of pH = 12, what is the reduction potential of Fe^{3+}/Fe in solution ($E^0_{Fe^{3+}/Fe}$ = –0.036V, K_{sp} of $Fe(OH)_3$ = 10^{-26}), $[\frac{2.303 \times RT}{F} = 0.06]$

(A) –0.436V (B) 0.39V (C) + 0.36V (D) – 1.2 V

10. Under which of the following condition direction of flow of current will be opposite i.e. from Zn electrode to Cu electrode at 298 K : [Given : $\frac{2.303 \times RT}{F} = 0.06$] ; E^0_{cell} for $Zn|Zn^{2+}||Cu^{2+}|Cu$ = 1.1 V

(A) $[Zn^{2+}] > e^{84.4} [Cu^{2+}]$ (B) $[Zn^{2+}] < e^{84.4} [Cu^{2+}]$
(C) $[Zn^{2+}] = e^{84.4} [Cu^{2+}]$ (D) $[Cu^{2+}] = e^{84.4} [Zn^{2+}]$

Section-2 : (One or More than one options correct Type)
This section contains 6 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

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11. Two test tubes I & II contain solutions of sodium salts of halide in water. When Br_2 was added to both the solutions then following observations were noted.

Test Tube	Observation
I	Violet vapous emerged
II	No reaction occurred

If halides in the tubes I & II are X^- and Y^- (and their molecular forms being X_2 & Y_2 respectively) then the true options would be :
(A) SRP of Br_2 is more than the SRP of X_2 (B) SRP of Br_2 is more than the SRP of Y_2
(C) Y_2 can oxidize X^- into X_2 (D) Y_2 can oxidize Br^- into Br_2.

12. In the concentration cell

$$Pt \left| H_2(g) \left| \begin{matrix} HA \\ NaA \end{matrix} \right| \left| \begin{matrix} HA \\ NaA \end{matrix} \right| H_2(g) \right| Pt$$

Value of cell potential will depend on –
(A) Value of pKa of HA (B) Temperature
(C) Concentration of HA in two electrodes (D) Concentration of NaA in two electrodes

13. 20 millimolar solution of aq. $CuSO_4$ (500 ml) is electrolysed with sufficient amount and a total of 0.04 faraday of electricity is supplied. Then :
(A) Total volume of gases evolved at STP = 224 ml
(B) Total volume of gases evolved at STP = 448 ml
(C) Total volume of gases evolved at STP = 672 ml
(D) Resulting solution after electrolysis becomes acidic

14. Emf of cell $Ag|Ag^+$ (saturated solution of Ag_2CrO_4) || Ag^+(0.1 M) | Ag is 0.164 volt at 298 K. Then
(A) K_{sp} of Ag_2CrO_4 in water is nearly 2.3×10^{-12}
(B) Given cell is a concentration cell
(C) K_{sp} of Ag_2CrO_4 can't be determined by given data.
(D) Concentration of Ag^+ ion in anode compartment when EMF is 0.164 volt is nearly 1.66×10^{-4} M

15. $E^0_{Mg^{2+}/Mg} = -2.4V$, $E^0_{Sn^{4+}/Sn^{2+}} = 0.1$ V , $E^0_{MnO_4^-, H^+/Mn^{2+}} = 1.5$ V, $E^0_{I_2/I^-} = 0.5$ V

Here,
(A) MnO_4^- is the strongest Oxidizing Agent and Mg is the strongest Reducing Agent.
(B) $Sn^{4+} + 2I^- \longrightarrow Sn^{2+} + I_2$ is a nonspontaneous reaction.
(C) $Mg^{2+} + Sn^{2+} \longrightarrow Mg + Sn^{4+}$ is a spontaneous reaction.
(D) Here, Weakest oxidizing agent is Sn^{4+} and weakest reducing agent is Mn^{2+}

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16. The following diagram shows an electrochemical cell in which the respective half cells contain aqueous 1.0 M solutions of the salts XCl_2 and YCl_3. Given that:

$$3X(s) + 2Y^{3+}(aq) \longrightarrow 3X^{2+}(aq) + 2Y(s) \quad E_{cell} > 0$$

Which of the following statements is correct?

(A) The electrode made from metal X has positive polarity.

(B) Electrode Y is the anode

(C) The flow of electrons is from Y to X

(D) The reaction at electrode X is an oxidation

Section-3 : (Numerical Value Questions)

This section contains 6 questions. Each question, when worked out will result in a numerical value from 0 to 9 (both inclusive)

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17. By how many of the following actions, can the E_{cell} be increased ($\Delta S = +\,ve$) for the cell reaction

$A \mid A^+ (aq) \parallel Cl^- \mid Cl_2(g) \mid Pt$

(a) By dilution of anodic solution.

(b) By dilution of cathodic soltuion.

(c) By decreasing temperature.

(d) By increasing pressure of Cl_2 in cathodic compartment.

(e) By increasing the mass of anode (A(s))

(f) By increasing temperature

18. At infinite dilution the molar conductance for CH_3COONa is 150 S cm^2 mol^{-1}, for HCl is 200 S cm^2 mol^{-1} and for NaCl is 125 S cm^2 mol^{-1}. Then calculate pH of 0.001 M CH_3COOH ?

(Given : Molar conductance of CH_3COOH at 0.001 M concentration is 2.25 S cm^2 mol^{-1}).

19. The conductivity of an aqueous solution of a weak monoprotic acid is 0.000032 ohm^{-1}cm^{-1} at a concentration, 0.2 M. If at this concentration the degree of dissociation is 0.02, calculate the value of Λ_0 (ohm^{-1} cm^2 /eqt).

20. $Pt, H_2(g) \mid 2\,M\ CH_3COONH_4(aq) \parallel 2\,M\ NaCl(aq) \mid H_2(g), Pt$

  20 atm   0.2 atm

Given $pK_a(CH_3COOH) = 4.74$ $pK_b = (NH_4OH) = 4.74$

If E is emf of the cell in volt, calculate 1000 E.   [Take : $\dfrac{2.303\ RT}{F} = 0.059$]

21. EMF of the following cell is 0.634 volt at 298 K $Pt \mid H_2$ (1 atm) $\mid H^+ (aq) \parallel Hg_2^{2+}(aq., 1N) \mid Hg(\ell)$. The pH of anode compartment is :

Given $E^0_{Hg_2^{2+}|Hg} = 0.28$ V and $\dfrac{2.303\ RT}{F} = 0.059$

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SECTION-4 : Comprehension Type (Only One options correct)

This section contains 2 paragraphs, each describing theory, experiments, data etc. 6 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph For Questions 22 to 24

Consider the cell :

Pt | H_2 | NaOH (aq), NaCl (aq) | AgCl (s) | Ag

      (0.01 M)   (0.012 M)
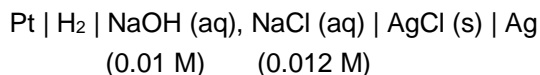
at T°C

E_{cell} = 1.05 V   and $E^o_{AgCl/Ag}$ = 0.22 V

Using this knowledge ; and taking $\dfrac{RT}{F}$ = 0.06 (log 1.2 = 0.08)

Answer the following questions.

22. Which of the following is overall cell reaction for the given reaction ?

(A) $\dfrac{1}{2}H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Cl^-$ (aq) + Ag

(B) $H_2(g) + 2OH^-$ (aq) + 2AgCl(s) $\longrightarrow$ $2H_2O + 2Ag(s) + 2Cl^-$ (aq)

(C) $H_2 + 2Ag^+ \longrightarrow 2H^+ + Ag$

(D) $H_2 + 2OH^- + 2Ag^+ \longrightarrow 2Ag + 2H_2O$

23. Find the value of pK_w of water at T°C.

(A) 14.91   (B) 12.91   (C) 13.91   (D) 14.15

24. What can be said about the temperature T°C ?

(A) It is greater than 25°C   (B) It is smaller than 25°C

(C) It is equal to 25°C   (D) Nothing can be said from given information

Paragraph For Questions 25 to 27

The specific conductance of 0.001 M Na_2SO_4 solution is 2.6 $\times$ 10^{-2} $\Omega^{-1}m^{-1}$ and it increases to 7$\times10^{-2}$ $\Omega^{-1}m^{-1}$ when the solution becomes also saturated with $CaSO_4$. The limiting molar conductance of Na^+ & Ca^{2+} are 0.005 $\Omega^{-1}m^2 mol^{-1}$ and 0.006 $\Omega^{-1}m^2 mol^{-1}$.

25. Limiting molar conductivity of SO_4^{2-} is -

(A) 0.006 $\Omega^{-1}m^2 mol^{-1}$ (B) 0.016 $\Omega^{-1}m^2 mol^{-1}$ (C) 0.012 $\Omega^{-1}m^2 mol^{-1}$ (D) 0.01 $\Omega^{-1}m^2 mol^{-1}$

26. Concentration of SO_4^{2-} & Ca^{2+} in the given solutions is -

(A) $[SO_4^{2-}]$ = 0.002 mol/lt, $[Ca^{2+}]$ = 0.002 mol/lt   (B) $[SO_4^{2-}]$ = 0.001 mol/lt, $[Ca^{2+}]$ = 0.002 mol/lt

(C) $[SO_4^{2-}]$ = 0.003 mol/lt, $[Ca^{2+}]$ = 0.002 mol/lt   (D) $[SO_4^{2-}]$ = 0.001 mol/lt, $[Ca^{2+}]$ = 0.001 mol/lt

27. Solubility product of $CaSO_4$ is -

(A) 6 $\times$ 10^{-6} (B) 4 $\times$ 10^{-6} (C) 2 $\times$ 10^{-6} (D) 10^{-6}

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SECTION-5 : Matching List Type (Only One options correct)
This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

28.

List-I			List-II	
(P)	Molar conductivity	(1)	$\dfrac{\text{Conductivity}}{\text{Molarity}}$	
(Q)	Conductivity	(2)	$\dfrac{\text{Conductivity}}{\text{Limiting molar conductivity}}$	
(R)	Degree of dissociation	(3)	$\dfrac{\text{Molar conductivity}}{\text{Limiting molar conductivity}}$	
(S)	Solubility of sparingly soluble salt	(4)	Decreases with dilution	

Codes :

	P	Q	R	S		P	Q	R	S
(A)	4	1	2	3	(B)	2	3	4	1
(C)	1	2	3	4	(D)	1	4	3	2

Practice Test-2 (IIT-JEE (ADVANCED Pattern))
OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28		
Ans.										

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APSP Answers

PART - I

1.	(1)	**2.**	(4)	**3.**	(3)	**4.**	(2)	**5.**	(4)
6.	(3)	**7.**	(3)	**8.**	(3)	**9.**	(2)	**10.**	(3)
11.	(1)	**12.**	(4)	**13.**	(4)	**14.**	(2)	**15.**	(1)
16.	(2)	**17.**	(1)	**18.**	(3)	**19.**	(2)	**20.**	(3)
21.	6	**22.**	3 (I, II, III)	**23.**	2	**24.**	13	**25.**	50

PART - II

1.	(2)	**2.**	(1)	**3.**	(3)	**4.**	(4)	**5.**	(1)
6.	(3)	**7.**	(1)	**8.**	(3)	**9.**	(1)	**10.**	(1)
11.	(4)	**12.**	(4)	**13.**	(1)	**14.**	(3)	**15.**	(1)
16.	(4)	**17.**	(2)	**18.**	(3)	**19.**	(3)	**20.**	(4)
21.	(4)	**22.**	(1)	**23.**	(3)	**24.**	(2)	**25.**	(1)
26.	(2)	**27.**	(3)	**28.**	(4)	**29.**	(1)		

PART - III

1.	(B)	**2.**	(B)	**3.**	(C)	**4.**	(C)	**5.**	(A)
6.	(C)	**7.**	(B)	**8.**	(C)	**9.**	(C)	**10.**	(D)
11.	(B)	**12.**	(A)	**13.**	(C)	**14.**	(B)	**15.**	(A)
16.	(C)	**17.**	(B)	**18.**	(D)	**19.**	(B)	**20.**	(D)
21.	(A)	**22.**	(B)	**23.**	(D)	**24.**	(A)	**25.**	(C)
26.	(B)	**27.**	(D)	**28.**	(A)	**29.**	(C)	**30.**	(C)
31.	(A)	**32.**	(C)	**33.**	(B)	**34.**	(B)	**35.**	(B)
36.	(B)	**37.**	(A)	**38.**	(A)	**39.**	(B)	**40.**	(A)
41.	(B)	**42.**	(C)	**43.**	(B)	**44.**	(B)	**45.**	(B)
46.	(D)	**47.**	(D)	**48.**	(B)	**49.**	()	**50.**	(B)
51.	(B)	**52.**	(A)	**53.**	(C)	**54.**	(B)	**55.**	(C)
56.	(C)	**57.**	(C)	**58.**	(B)	**59.**	(B)	**60.**	(C)
61.	(C)	**62.**	(C)	**63.**	(D)	**64.**	(B)	**65.**	(A)
66.	(A)	**67.**	(C)	**68.**	(A)	**69.**	(C)	**70.**	(B)
71.	(B)	**72.**	(A)						

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PART - IV

1. (a) $0.34 < E° < 0.8$; (b) $-0.44 < E° < 0$ **2.** -0.8825 volt

3. 0.836 volt, 1.1937 volt **4.** 0.936V

5. n = 3, Since mass of Sn increasing, Sn - electrode is working as cathode and X - metal electrode anode and electrons are flowing from X-electrode to Sn-electrode in the external circuit.

6. E = 0.059 V **7.** E = 0.395 V **9.** -0.042 V **10.** $K_{SP} = 10^{-5}$ **11.** -0.16V

12. $\Delta G = -196.5$ kJ ; $\Delta H = 198.8$ kJ ; $\Delta S = -7.72$ J d_{eg-1} **13.** 3.389×10^{-4} volt deg^{-1}

14. $\Delta S^0 = -24.125$ kJ K^{-1} ; $\Delta G^0 = -7179.6$ J ; $\Delta H^0 = -7196.43$ kJ

15. $\Delta S^0 = -30.88$ JK^{-1} $\Delta H^0 = -77.23$ kJ $\Delta G^0 = -68.03$ kJ

16. A = 114, Q = 5926.8C. **17.** V = 1.763 L **18.** 43.456 g

19. $[Cu^{2+}] = 10^{-4}$ M. **20.** 2×10^{-16} mole / litre.

21. (a) $E^0 = 0.59$ V, $\log_{10}K_{sp} = -10$; (b) 52.88, 10^{-6} mole.

22.	(A)	**23.**	(C)	**24.**	(A)	**25.**	(A)	**26.**	(C)
27.	(B)	**28.**	(D)	**29.**	(D)	**30.**	(D)	**31.**	(D)
32.	(D)	**33.**	(C)	**34.**	(A)	**35.**	(C)	**36.**	(A)
37.	(D)	**38.**	(B)	**39.**	(B)	**40.**	(B)	**41.**	(A)
42.	(A)	**43.**	(C)	**44.**	(A)	**45.**	(B)	**46.**	(A)
47.	(B)	**48.**	(B)	**49.**	(A)	**50.**	(C)	**51.**	(A)
52.	(B)	**53.**	(A)	**54.**	(B)	**55.**	(D)	**56.**	5
57.	14	**58.**	3	**59.**	11	**60.**	26	**61.**	20
62.	5	**63.**	(BC)	**64.**	(ABC)	**65.**	(ACD)	**66.**	(BD)
67.	(ACD)	**68.**	(CD)	**69.**	(AB)	**70.**	(AB)	**71.**	(B)
72.	(A)	**73.**	(A)	**74.**	(A)	**75.**	(C)		

PART - V

1.	(A)	**2.**	(D)	**3.**	(C)	**4.**	(A)	**5.**	(A)
6.	(A)	**7.**	(B)	**8.**	(A)	**9.**	(A)	**10.**	(A)
11.	(ACD)	**12.**	(BCD)	**13.**	(BD)	**14.**	(AD)	**15.**	(AB)
16.	(D)	**17.**	4 (a, b, d, f)	**18.**	5	**19.**	8	**20.**	59
21.	6	**22.**	(B)	**23.**	(C)	**24.**	(A)	**25.**	(B)
26.	(C)	**27.**	(A)	**28.**	(D)				

APSP Solutions

PART - I

1. $E_{cell} \Rightarrow E^0_{Sn^{4+}/Sn^{2+}} + E^0_{Fe^{2+}/Fe^{3+}}$ $\Rightarrow$ $0.15 — 0.77 = – 0.62$ V

2. $2Cu^{+1} \longrightarrow Cu + Cu^{+2}$

$2Cu^{+1} + 2e \longrightarrow 2Cu$

$Cu – 2e \longrightarrow Cu^{+2}$

——————————————

$2Cu^{+1} \longrightarrow Cu^{+2} + Cu$

——————————————

$\therefore$ $E° = \dfrac{2 \times 0.521 + 2(–0.337)}{2} = 0.184$

3. $\dfrac{W_1}{E_1} = \dfrac{W_2}{E_2}$; $\dfrac{4}{12} = \dfrac{W_{Ag}}{108}$; $W_{Ag} = 36$

4. $Cu^{2+} + 1e^- \rightarrow Cu^+$ $E^0_1 = 0.15$ v $\Delta G^0_1 = - n_1 E^0_1 F$

$Cu^+ + 1e^- \rightarrow Cu$ $E^0_2 = 0.50$ v $\Delta G^0_2 = – n_2 E^0_2 F$

$Cu^{2+} + 2e^- \rightarrow Cu$ $\Delta G^0 = \Delta G^0_1 + \Delta G^0_2$

$(–1) n E^0 F = (–1) n_1 E^0_1 F + (–1) n_2 E^0_2 F$

$E^0 = \dfrac{n_1 E^0_1 + n_2 E^0_2}{n} = \dfrac{0.15 \times 1 + 0.50 \times 1}{2} = 0.325V$

5. $H^+ + e^- \longrightarrow \dfrac{1}{2} H_2$. $E = 0 - \dfrac{.0591}{1} \log_{10} \dfrac{1}{[H^+]} = + 0.0591 \log_{10}[H^+]$.

$E_1 = 0$ {pH = 0}.

$E_2 = + 0.0591 \log_{10}[10^{-7}] = – .0591 \times 7$ {at pH = 7} $= – 0.41$ V.

6. $E_{cell} = E^0_{cell} - \dfrac{0.0591}{1} \log_{10}[H^+] [Cl^-]$ and $E'_{cell} = E^0_{cell} - \dfrac{0.0591}{1} \log_{10} 100[H^+] [Cl^-]$.

$E'_{cell} - E_{cell} = – 2 \times 0.0591 = – 0.1182$.

8. Cell notation is anode || cathode.

9. $0.34 = \dfrac{0.06}{2} \log K_{eq}$

$\log K_{eq} = 11.3$ or $K_{eq} = 2 \times 10^{11}$

10. Number of moles of Cu^{2+} produced from anode = number of moles of Cu^{2+} deposited at cathode.

11. For same charge passed mole of H_2 produced = 2 × moles of O_2 produced.

13. $\dfrac{W}{E} = \dfrac{it}{96500}$ $\Rightarrow$ $\dfrac{3}{E} = \dfrac{9.95 \times 10 \times 60}{96500} \Rightarrow$ $E = 48.5$

14. $K = \dfrac{1}{R}\left(\dfrac{\ell}{a}\right) \Rightarrow$ $0.0112 = \dfrac{1}{55}\left(\dfrac{\ell}{a}\right) \Rightarrow$ $\dfrac{\ell}{a} = 0.616$

15. $\lambda_{eq} = \dfrac{\left(\dfrac{1}{R} \times G^*\right) \times 10^{-3}}{N}$ $\therefore 10^{-2} = \dfrac{\left(\dfrac{1}{50} \times G^*\right) \times 10^{-3}}{1/10}$ $\therefore G^* = 50$ m^{-1}

16. $\Lambda_m(NaCl)$, $\lambda_m(Na^+)$, $\lambda_m(Cl^-)$ keep on increasing as concentration decreases but κ keeps on decreasing with dilution.

17. **(i)** $K_2SO_4.\ Al_2(SO_4).\ 24\ H_2O \Rightarrow 2\ K^+_{aq} + 2\ Al^{+3}_{aq} + 4\ SO^{-2}_{aq}$.
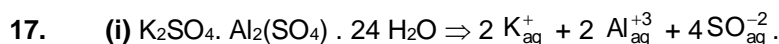
$$\lambda^\alpha_{m(Potash\ alum)} = 2\ \lambda^\alpha_{m(K^+)} + 2\ \lambda^\alpha_{m(Al^{+3})} + 4\ \lambda^\alpha_{m(SO_4^{-2})}$$

$$= 2 \times 73.5 + 2 \times 189 + 4 \times 160$$

$$= 1165\ \Omega^-.cm^2.mol^{-1}$$

V.F. for Potash alum = 8 . (total Positive charge)

$$\lambda^\alpha_{eq(Potash\ alum)} = \frac{\lambda^\alpha_{eq(Potash\ alum)}}{8} = \frac{1165}{8} = 145.6\ \Omega^-\ cm^2\ eq^{-1}$$

$$\frac{\lambda^\alpha_{m(Potash\ alume\ )}}{\lambda^\alpha_{eq(Potash\ alume\ )}} = \frac{1165}{145.6} = 8 : 1$$

(ii) $\dfrac{\lambda^\alpha_m}{\lambda^\alpha_{eq}}$ = V.F. of Compound, V.F. of Potash alume = 8.

18. $\begin{array}{l} HCl \rightarrow H^\oplus + Cl^- \\ (SA) \end{array}$ $\begin{array}{l} NaCl \rightarrow Na^\oplus + Cl^- \\ (SASB) \end{array}$
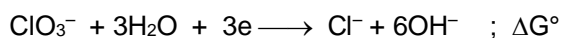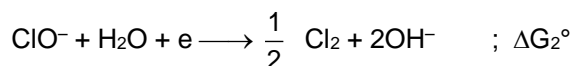
H^+ have highest mobility in comparison with $Na^\oplus$, both compound 100% dissociate.

because Molar mass of H^+ is less than $Na^\oplus$ ion and NH_4OH is weak basic.

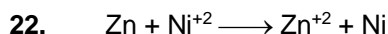**19.** Equivalent conductance in different cell is equal :

$$\lambda_{eq} = \frac{K \times 1000}{N}$$ K and N are constant

20. $CH_3COOH + NaOH \longrightarrow Na^+ + CH_3COO^- + H_2O$ Conductance I^{st} increases slowly since no. of ions increases. After end point it increases sharply due to OH^- ions.

21. $ClO_3^- + 2H_2O + 4e \longrightarrow ClO^- + 4OH^-$; ΔG_1°

$ClO^- + H_2O + e \longrightarrow \dfrac{1}{2}\ Cl_2 + 2OH^-$; ΔG_2°

$\dfrac{1}{2}\ Cl_2 + e \longrightarrow Cl^-$; ΔG_3°

_____

$ClO_3^- + 3H_2O + 3e \longrightarrow Cl^- + 6OH^-$; ΔG°

_____

$\therefore$ $\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ + \Delta G_3^\circ$

$- 6FE^\circ = - 4F \times 0.54 - 1F \times 0.45 - 1F \times 1.07$

$\therefore$ $E^\circ = + \dfrac{3.68}{6} = + 0.61\ V$

22. $Zn + Ni^{+2} \longrightarrow Zn^{+2} + Ni$

$E^0 = E^o_{Ni^{+2}/Ni} - E^o_{Zn^{+2}/Zn}$

$= -0.23 - (-0.76) = + 0.53\ V$

Positive value shows that the process is spontaneous.

Rest of all (I) (II) (III) combination have negative E^0 value.

(I) $E^0 = -0.44 - (-0.23) = -0.21\ V$

(II) $E^0 = -0.76 - (-0.23) = -0.53\ V$

(III) $E^0 = -0.76 - (-0.44) = -0.32\ V$

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23. $\dfrac{m_X}{m_Y} = \dfrac{\dfrac{A_X}{2} \times Q}{\dfrac{A_Y}{1} \times Q} \Rightarrow \qquad \dfrac{m_X}{m_Y} = 1 \qquad \because \qquad A_X = 2A_Y$

24. Let wt of metal deposited for x, y, z is 3a, 2a, a respectively & let moles of e^- passing for x, y, z be 1, 2 and 3 respectively then the wt of x, y, z deposited is E_x, $2E_y$, $3E_z$ (where E_x, E_y, E_z are equivalent wt. of x, y, z)

$\therefore \quad E_x = 3a$

$2E_y = 2a \Rightarrow E_y = a \qquad\qquad \& \qquad 3E_z = a \Rightarrow \qquad E_z = \dfrac{a}{3}$

$\therefore \quad E_x : E_y : E_z$

$= \quad 3a : a :$

$= \quad 9 : 3 : 1$

25. $R = \dfrac{1}{k} \ \dfrac{\ell}{A}$

Dilution upto twice of initial volume just complete submerge of electrodes, k becomes half and A becomes double. Hence R remains 50 Ω.

PART - II

1. The E^o of cell will be zero.

2. Here Cr^{3+} is oxidised to $C_2O_7^{2-}$

3. At LHS (oxidation) $2 \times (Ag \longrightarrow Ag^+ + e^-)$ $\qquad E^0_{ox} = -x$

At RHS (reduction) $Cu^{2+} + 2e^- \longrightarrow Cu$ $\qquad E^0_{red} = + y$

$2Ag + Cu^{2+} \longrightarrow \ Cu + \ 2Ag^+, \qquad\qquad E^0_{red} = (y - x)$

4. $0 = 0.295 - \dfrac{0.059}{2} \log K \qquad ; \qquad \log K = 10 \qquad ; \qquad K = 10^{10}.$

5.
	A	B	C
E^o_{red}	+0.5 V	–3.0 V	–1.2 V

The reducing power follows the following order: B > C > A.

6. $E^0_{cell} = 0.77 + 0.14 = 0.91$ volt.

7. $\overset{0}{\wedge}_{NaBr} = 126 + 152 - 150 = 128 \ S \ cm^2 \ mol^{-1}.$

8. $Zn + 2H^+_{(aq)} \longrightarrow Zn^{2+} (aq) + H_2 (g)$

$E = E^o - \dfrac{0.0591}{2} \log \dfrac{[Zn^{2+}] \ pH_2}{[H^+]^2}$

Adding H_2SO_4 means increasing H^+ and therefore E_{cell} will increase and reaction will shift to forward direction.

9. $Cr^{2+} \,|\, Cr^{3+} = +0.41V \qquad\qquad\qquad Mn^{2+} \,|\, Mn^{3+} = -1.57V$

$Fe^{2+} \,|\, Fe^{3+} = -0.77V \qquad\qquad\qquad Co^{2+} \,|\, Co^{3+} = -1.97V$

As Cr will have maximum oxidation potential value, therefore its oxidation will be easiest.

10. $Al^{3+} + 3e^- \longrightarrow \ Al.$

$\dfrac{5.12 \times 10^3}{27} = 189.62$ mol.

Charge $= 189.62 \times 3 \times 96500 = 5.489 \times 10^7$ coulomb.

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11. $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$ From the reaction,

$\Lambda^0_{CH_3COONa} + \Lambda^o_{HCl} = \Lambda^0_{CH_3COOH} + \Lambda^o_{NaCl}$ or $\Lambda^0_{CH_3COOH} = \Lambda^0_{CH_3COONa} + \Lambda^o_{HCl} - \Lambda^o_{NaCl}$

Thus to calculate the value of one should know the value of Λ^o_{NaCl} along with and Λ^o_{HCl}.

12. $0.152 = -0.8 - \dfrac{0.059}{1} \log K_{SP}$; $\log K_{SP} = -16.11$.

13. $C = 0.1\,M$, $R = 100\,\Omega$

$K = 1.29\,Sm^{-1} = \dfrac{1}{100} \times \dfrac{\ell}{A}$.

$C = 0.02\,M$, $R = 520\,\Omega$.

$K = \dfrac{1}{520} \times 129$ $\Rightarrow$ $\mathring{A}_M = \dfrac{\frac{1}{520} \times 129}{1000 \times 0.02} = 124 \times 10^{-4}\,Sm^2mol^{-1}$.

14. According to Kohlrausch's law the molar conductivity at infinite diluation (Λ^o) for weak electrolyte CH_3COOH is

$\Lambda^o_{CH3COOH} = \Lambda^o_{CH3COONa} + \Lambda^o_{HCl} - \Lambda^o_{NaCl}$

So for calculating the value of $\Lambda^o_{CH3COOH}$, value of Λ^o_{NaCl} should also be known.

15. $0 = +1.1 - \dfrac{0.0591}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$; $\log \dfrac{[Zn^{2+}]}{[Cu^{2+}]} = 37.3$.   ; $\dfrac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37.3}$ **Ans.**

16. $E_{cell} = E^0_{cell} - \dfrac{0.059}{6} \log \dfrac{[Cr^{+3}]^2}{[Fe^{+2}]^3} = 0.3 - \dfrac{0.056}{6} \log \dfrac{(0.1)^2}{(0.01)^3} = 0.3 - 0.04 = 0.26\,V$

17. $Fe^{3+} + 3e^- \longrightarrow Fe$ $\Delta G_1 = -3 \times F \times E^0_{Fe^{3+}/Fe}$

$Fe^{2+} \longrightarrow Fe$ $\Delta G_2 = -2 \times F \times E^0_{Fe^{2+}/Fe}$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\Delta G = \Delta G_1 - \Delta G_2$

$\Delta G = 3 \times 0.036F - 2 \times 0.439 \times F = -1 \times E^0\,(Fe^{3+}/Fe^{+2}) \times F$

$E^0\,(Fe^{3+}/Fe^{+2}) = 2 \times 0.439 - 3 \times 0.036 = 0.878 - 0.108 = 0.770\,V$

18. $\dfrac{2}{3} Al_2O_3 \longrightarrow \dfrac{4}{3} Al + O_2$

$\Delta_r G = +966\,kJ\,mol^{-1} = 966 \times 10^3\,J\,mol^{-1}$

$\Delta G = -nFE_{cell}$

$966 \times 10^3 = -4 \times 96500 \times E_{cell}$

$E_{cell} = 2.5\,V$

19. $2H^+\,(aq) + 2e^- \longrightarrow H_2\,(g)$

$E_{red} = E^0_{red} - \dfrac{0.0591}{n} \log \dfrac{P_{H_2}}{(H^+)^2}$; $E_{red} = 0 - \dfrac{0.0591}{2} \log \dfrac{2}{(1)^2}$; $E_{red} = -\dfrac{0.0591}{2} \log 2$

$\therefore$ E_{red} is forund to be negative for (3) option.

20. $X + Y^{2+} \longrightarrow X^{2+} + Y$

For reaction to be spontaneous E^o must be positive.

$E^o_{Zn/Zn+2} + E^o_{Ni2+/Ni} = 0.76 + (-0.23) = +0.53$ (positive)

21. Higher the SRP, better is oxidising agent

Hence MnO_4^- is strongest oxidising agent

22. $x = 1.4\,S/m$.

$R = 50\,\Omega$

$M = 0.2$

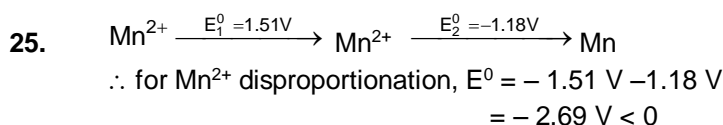$K = \dfrac{1}{R} \times \dfrac{\ell}{A} \quad \Rightarrow \dfrac{\ell}{A} = 1.4 \times 50 \text{ m}^{-1}.$

Now, new soltuion has M = 0.5, R = 280 Ω

$\Rightarrow K = \dfrac{1}{R} \times \dfrac{\ell}{A} = \dfrac{1}{280} \times 1.4 \times 50 = \dfrac{1}{4} \Rightarrow \Lambda_M = \dfrac{K}{1000 \times M} = \dfrac{\frac{1}{4}}{1000 \times 0.5} = \dfrac{1}{2000} = 5 \times 10^{-4}$
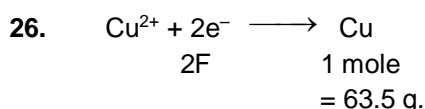
23. $\lambda_c = \lambda_\infty - B\sqrt{C}$ (Debye Huckel onsagn equation)

24. **Reason:** Higher the position of element in the electrochemical series, more difficult is the reduction of its cations.

If Ca^{2+} (aq) is electrolysed, water is reduced in preference to it. Hence it cannot be reduced electrolytically from an aqueous solutions.

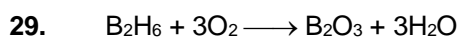**25.** $Mn^{2+} \xrightarrow{E_1^0 = 1.51V} Mn^{2+} \xrightarrow{E_2^0 = -1.18V} Mn$

$\therefore$ for Mn^{2+} disproportionation, $E^0 = -1.51$ V -1.18 V
$$= -2.69 \text{ V} < 0$$

Reaction is non-spontaneous.

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

     2F   1 mole
             = 63.5 g.

27. Galvanization is applying a coating of Zn.

28. For strongest reducing agent E_{OP}° should be maximum.

$E_{OP\ Cr/Cr^{+3}}^\circ = 0.74$ V

Whereas,

$E_{OP\ Mn^{2+}/MnO_4^-}^\circ = -1.51$ V $\Rightarrow$ $E_{OP\ Cr^{3+}/Cr_2O_7^{-2}}^\circ = -1.33$ V $\Rightarrow$ $E_{OP\ Cl^-/Cl_2}^\circ = -1.36$ V

29. $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$

1 mol   3 mol

3 mol O_2 is required for Burning 1 mol B_2H_6

$H_2O \xrightarrow{Electrolysis} H_2 + \dfrac{1}{2}O_2$ (V.F. of O_2 = 4)
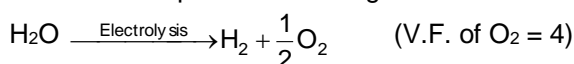
$\dfrac{\text{Equivalent of } O_2}{\text{V.F. of } O_2} = \text{mol of } O_2 = 3$

$\left[\dfrac{(100A) \times t\ sec.}{96500}\right] \times \dfrac{1}{4} = 3$ $\Rightarrow$ $\therefore t = \dfrac{3 \times 96500 \times 4}{100 \times 3600}$ hr. = 3.22 hrs.

PART - IV

1. (a) Metal should below hydrogen and Cu^{2+} but should above Ag^+ in series.

(b) Metal should above hydrogen but should below from Zn^{2+} and Fe^{2+} both.

2. $TiO^{2+} + 2H^+ + e^- \longrightarrow Ti^{3+} + H_2O$, 0.1 V $\Delta G_1^0 = -2 \times F \times 0.1$

$Ti^{3+} + 3e^- \longrightarrow Ti - 1.21$ V $\Delta G_2^0 = -3 \times (-1.21) \times F$

$TiO^{2+} + 2H^+ + 4e^- \longrightarrow Ti + H_2O$

$-4 \times E^0 \times F = -1 \times 0.1 \times F + -3 \times (-1.21) \times F$

$E^0 = \dfrac{0.1 - 3.63}{4} = -0.8825$ volt.
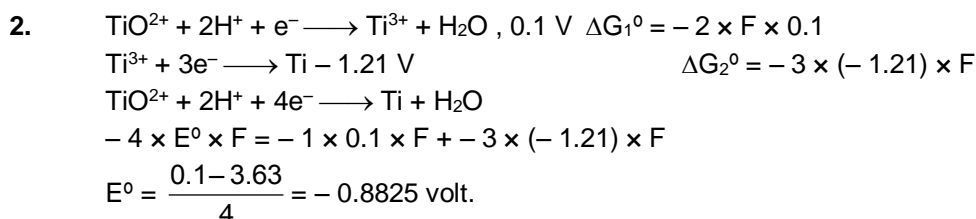
3. $E_{oxidation} = -0.78 - \dfrac{0.0591}{2} \log 9^2$ $\qquad = -0.78 - \dfrac{0.0591}{2} \times 2 \times \log 9 = -0.836$ volt

$E_{reduction} = -E_{oxidation} = 0.836$ volt

In neutral medium,

$E_{Oxidation} = -0.78 - \dfrac{0.0591}{2} \log (10^{-7})^2 = -1.1937$ volt

4. $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$, 1.33 volt

$E = 1.33 - \dfrac{0.0591}{6} \log \dfrac{(0.01)^2}{(0.01) \times (10.^{-3})^{14}} = 1.33 - \dfrac{0.0591}{6} \log 10^{-2} \times 10^{42}$
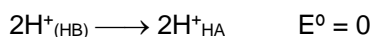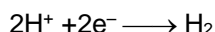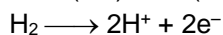
$= 1.33 - \dfrac{0.0591}{6} \times \log 10^{40} = 1.33 - \dfrac{0.0591}{6} \times 40 = 0.936$ volt

5. $0.65 = E_{oxid} + E_{red} = \left\{ 0.78 - \dfrac{0.0591}{n} \log (0.1) \right\} + \left\{ 0 - 0.14 - \dfrac{0.0591}{2} \log \dfrac{1}{0.5} \right\}$

$0.01 = -\dfrac{0.0591}{n} \times (-1) - \dfrac{0.0591}{2} \times 0.301 = 0.0591 \left(\dfrac{1}{n} - \dfrac{0.301}{2} \right)$ n = 3

Electrons flow from X electrode to Zn electrode.

6. $Pt / H_2O / H^+ (HA) // H^+ (HB) / H_2 / Pt$

$\qquad H_2 \longrightarrow 2H^+ + 2e^-$

$\qquad 2H^+ + 2e^- \longrightarrow H_2$

$\qquad 2H^+_{(HB)} \longrightarrow 2H^+_{HA}$ $\qquad E^0 = 0$

$E = 0 - \dfrac{0.0591}{2} \log \dfrac{[H^+]^2_{HA}}{[H^+]^2_{HB}}$ $\qquad$ But $Ka = \dfrac{[H^+]^2}{C}$

$= -\dfrac{0.0591}{2} \log \dfrac{10^{-3} \times C}{10^{-5} \times C}$ $\qquad = -0.0591$

the cell is constructed in reversed direction.

$E_{cell} = 0.0591$ volt.

7. $Pt / H_2 / H^+ (C_6H_5NH_{2(C)} // H^+_{(HCl)} / H_2 / Pt$

$H_2 \longrightarrow 2H^+_{(10-8M)} + 2e^-$, $\qquad\qquad C_6H_5NH_2 + H_2O \longrightarrow C_6H_5NH_3^+ + OH^-$

$2H^+ + 2e^- \longrightarrow H_2$ $\qquad K_b = \dfrac{(OH^-)^2}{\frac{5 \times 10^{-4}}{0.5}}$

$2H^+_{(5 \times 10-2)} \longrightarrow 2H^+_{(10-8)}$
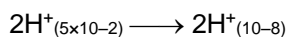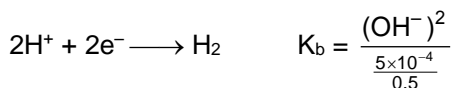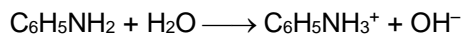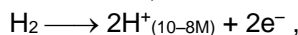
$E = 0 - \dfrac{0.0591}{2} \log \dfrac{(10^{-8})^2}{(5 \times 10^{-2})^2} = -\dfrac{0.0591}{2} \log 10^{-14} \times 4 = \dfrac{0.0591}{2} . [\log 4 - 14] = 0.396$ volt

8. (A) $Hg_2Cl_2(s) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Cl^- (aq) + 2Hg(l)$

(B) $2Ag_{(s)} + 2IO_3^- + Zn^{2+} \longrightarrow 2AgIO_{3(g)} + Zn_{(s)}$

(C) $Mn_{(s)} + 2OH^- + Cu^{2+} \longrightarrow Mn(OH)_{2(s)} + Cu_{(s)}$
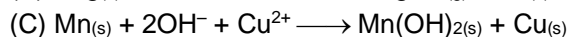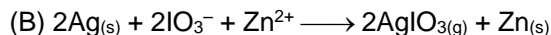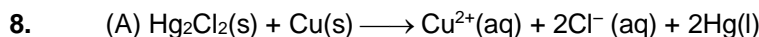
9. $E = 0 - \dfrac{.06}{1} \log \dfrac{10^{-10}/0.2}{10^{-13}/10^{-3}} = -0.042$ V

10. $E^0_{cell} = \dfrac{.06}{2} \log \dfrac{1}{K_{SP}}$ $\quad \Rightarrow \quad -0.12 + 0.27 = .03 \log \dfrac{1}{K_{SP}}$ $\quad \Rightarrow \quad K_{SP} = 10^{-5}$

11. $E^0_{Cell} = 0.06(-\log K_{SP})$ $\quad \Rightarrow \quad 0.8 - E^0_{I^-/AgI/Ag} = 0.96$ $\quad \Rightarrow \quad E^0_{I^-/AgI/Ag} = 0.16$V

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12. Cd (12.5%) in Hg / 3Cd SO$_4$, 8H$_2$O (solid) / satd sol of CdSO$_4$ || Hg$_2$SO$_{4(s)}$ | Hg, E = 1.018 volt

$\left(\dfrac{dE}{dT}\right)_P = -4 \times 10^{-5}$ volt d$_{eg-1.}$

$\Delta G = -nEF = -2\ 1.018 \times 96500 = -196.474$ kJ

$\Delta S = nF.\left(\dfrac{dE}{dT}\right)_P = 2 \times 96500 \times (-4 \times 10^{-5}) = -7.72$ JK^{-1}.

$\Delta G = \Delta H - T\Delta S$

$\Delta H = -196.474 + \dfrac{298 \times (-7.72)}{1000} = -196.474 - 2.3 = 198.774$ kJ

13. Ag(s) $+ \dfrac{1}{2}$ Hg$_2$Cl$_2$(s) $\longrightarrow$ AgCl$_{(s)}$ + Hg(l), $\Delta H = 1280$ cal.

E = 0.0455 volt

$\Delta H = -nEF + nF.T.\dfrac{dE}{dT}$

$1280 \times 4.18 = -1 \times 0.0455 \times 96500 + 1 \times 96500 \times 298 \times \dfrac{dE}{dT}$. $\Rightarrow$ $\dfrac{dE}{dT} = 3.387 \times 10^{-4}$ volt deg^{-1}.

14. $\dfrac{dE}{dT} = -0.125$ VK^{-1}. $E^0 = 0.0372$ volt

$\Delta G^0 = -nEF = -2 \times 0.0372 \times 96500 = -7.1796$ kJ.

$\Delta S^0 = nF \times \left(\dfrac{dE}{dT}\right)_P = 2 \times 96500 \times (-0.125) = -24.125$ kJ K^{-1}.

$\Delta H^0 = \Delta G^0 + T\Delta S^0 = -7.1796 - 298 \times 24.125 = -7196.43$ kJ

15. $E^0_{25^\circ C} = 0.3525$ volt $E^0_{20^\circ C} = 0.3533$ volt   n = 2

$\dfrac{dE}{dT} = \left(\dfrac{E^0_{25^\circ C} - E^0_{20^\circ C}}{T_2 - T_1}\right) = \dfrac{0.3525 - 0.3533}{25 - 20} = -1.6 \times 10^{-4}$ volt deg^{-1}.

$\Delta G^0_{25} = \Delta H^0_{25} - 298 \times \Delta S^0_{25} = -2 \times 0.3525 \times 96500 = -68.03$ kJ

$\Delta S^0 = 2 \times 96500 \times (-1.6 \times 10^{-4}) = -30.88$ Jk.

$\Delta H^0 = \Delta G^0 + T\Delta S^0 = -68.03 - 298 \times \dfrac{30.88}{1000} = -77.23$ kJ

16. v.f. of metal = 2.

w = Zit.

$1.95 = \dfrac{E}{96500}$ it $= \dfrac{M \times it}{v.f. \times 96500}$ $\Rightarrow$ M = 114 g.

अब Cu के लिए, $w = \dfrac{63.5 \times (it)}{2 \times 96500}$ $\Rightarrow$ $1.95 = \dfrac{63.5 \times (it)}{2 \times 96500}$ $\Rightarrow$ it = 5926.77 C.

17. 2CH$_3$COONa $\xrightarrow{\text{Electrolysis}}$ $\underset{\text{at anode}}{C_2H_6 + 2CO_2}$ + $\underset{\text{Cathode}}{H_2}$

Electric supplied $= \dfrac{0.965 \times 60 \times 60}{96500} = 3.6 \times 10^{-3}$ F

$V_{H2} = \dfrac{3.6 \times 10^{-3}}{2} \times \dfrac{0.0821 \times 298}{1} = 0.44$ lit ; $V_{total} = V_{C_2H_4} + V_{CO_2} + V_{H2} = 4 \times 0.44 = 1.76$ lit.

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18. Reaction at anode $\quad\quad 2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$

$H_2S_2O_8$, O_2 are the product at anode.

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

Reaction at cathode $\quad\quad 2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Eq. of H_2 = Eq. of O_2 + Eq. of $H_2S_2O_8$

$\dfrac{9.722}{22.4} \times 2 = \dfrac{2.35}{22.4} \times 4 + x \times 2 \quad\quad\quad \Rightarrow \quad\quad x = 0.244 \text{ mole} \Rightarrow \quad\quad W_{H_2S_2O_8} = 43.49 \text{ g.}$

19. $E^0 \ Bi^{3+}/Bi = 0.226$ volt $\quad\quad\quad E^0 \ Cu^{2+}/Cu = 0.344$ volt

$0.226 = 0.344 \ \dfrac{0.0591}{2} \log \dfrac{1}{[Cu^{2+}]} \quad\quad\quad \Rightarrow \quad\quad - \log [Cu^{2+}] = 4 \ [Cu^{2+}] = 10^{-4} \text{ M.}$

20. $K = 5.8 \times 10^{-8} \text{ Scm}^{-1}, \quad\quad\quad \Lambda^o_{H^+} = 350 \text{ Scm}^2 \quad\quad\quad \Lambda^o_{OH^-} = 198 \text{ Scm}^2$

$\Lambda_{H_2O} = \dfrac{1000 \times 5.8 \times 10^{-8}}{55.5} ; \quad\quad \alpha = \dfrac{\Lambda_{H_2O}}{\Lambda^o_{H_2O}} = \dfrac{(1000 \times 5.8 \times 10^{-8})}{55.5 \times (350 + 198)} = 0.1907 \times 10^{-8} = 1.907 \times 10^{-9}$

$K_a = C\alpha^2 = 55.55 \times (1.907)^2 \times 10^{-18} = 2.02 \times 10^{-16}.$

21. **(a)** $\Delta G^0_r = - 109 + 129 - 77 = - 57 \text{ kJ/mol}$

Cell representation : $Ag \mid AgCl \mid\mid Cl^- \mid Ag^+ \mid Ag.$

$- 1 \times 96500 \times E^0 = - 57 \times 10^3.$

$E^0 = 0.59$ volt.

$0 = 0.59 - \dfrac{0.059}{1} \log \dfrac{1}{K_{SP}} .$

$\log K_{SP} = \mathbf{- 10.}$

(b) $\quad\quad Zn \longrightarrow Zn^{2+} + 2e^-, \quad\quad 0.76$ volt.

$\quad\quad 2Ag^+ + 2e^- \longrightarrow 2Ag, \quad\quad 0.80$ volt.

$\overline{\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad}$

$\quad\quad Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag, \quad\quad\quad\quad E^0_{cell} = 1.56$ volt.

$\overline{\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad}$

$n_{Zn} = \dfrac{6.539 \times 10^{-2}}{65.39} = 10^{-3} \text{ mol}, \quad\quad\quad [Ag^+] = \sqrt{K_{sp}} = 10^{-5} \text{ M.}$

$0 = 1.56 - \dfrac{0.059}{2} \log K \quad\quad\quad\quad\quad n_{Ag+} = 10^{-5} \times 0.1 = 10^{-6} \text{ M.}$

$n_{Ag} = 10^{-6} \text{ mol.} \quad\quad\quad\quad\quad \Rightarrow \quad \mathbf{\log K = 52.8.}$

22. $H^+ + e^- \longrightarrow \dfrac{1}{2} H_2 , \ E° = 0 , \Delta G° = 0$

$H_2O \rightleftharpoons H^+ + OH^- , \ \Delta G° = - 8.314 \times 298 \ln 10^{-14}$

$H_2O + e^- \longrightarrow \dfrac{1}{2} H_2 + OH^- , \ -1 \times E° \times 96500 = -8.314 \times 298 \ln 10^{-14}$

$E° = - 0.828$ Volt.

23. $Hg_2^{2+} + 2e^- \longrightarrow 2Hg , \ 0.789$ Volt

$Hg \longrightarrow Hg^{2+} + 2e^- , \ -0.854$ Volt

$Hg_2^{2+} \longrightarrow Hg + Hg^{2+} , \ -0.065$ Volt

$\Delta G = - 2 \times (- 0.065) \times 96500 = -8.314 \times 298 \ln K_{eq.} \quad ; \quad\quad K_{eq.} = 6.3 \times 10^{-3}$

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24. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
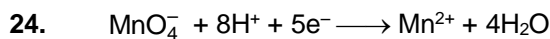
$$E_1 = E° - \frac{0.0591}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-] \times 1^8}$$

$$E_2 = E° - \frac{0.0591}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-] \times \left(10^{-4}\right)^8} = -\frac{0.0591}{5} \times 32 \quad = -0.37824 \qquad E_1 - E_2 = 0.38 \text{ Volt.}$$

25. $0 = (-0.771 + 0.7991) - \dfrac{0.0591}{1} \log \dfrac{1}{x} \quad \Rightarrow \quad 0 = 0.0281 + 0.0591 \log x$

$\log x = -\dfrac{0.0281}{0.0591} \qquad \Rightarrow \qquad x = 0.335 \text{ M}$

26. $0 = (-0.151 - 0) - \dfrac{0.0591}{1} \log [H^+].$

$0.0591 \times \log[H^+] = -0.151 \qquad ; \qquad pH = \dfrac{0.151}{0.0591} = 2.56$

27. $E^0_{Ag \mid Ag\,I \mid I^-} = E^0_{Ag^+ \mid Ag} - \dfrac{0.0591}{1} \log \dfrac{1}{K_{SP}}$

$-0.151 = 0.799 - \dfrac{0.0591}{1} \log \dfrac{1}{K_{sp}}$

$0.0591 \log K_{sp} = -0.151 - 0.799$
$\log K_{sp} = -16.074$
$K_{sp} = 8.43 \times 10^{-17}$

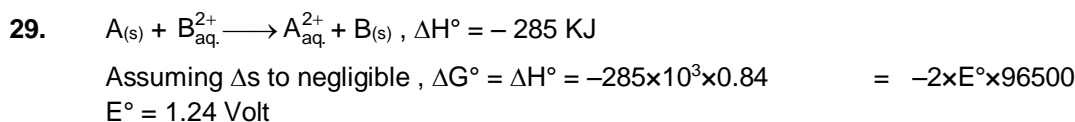**28.** $E_{I^- / AgI / Ag} = 0.8 - \dfrac{0.0591}{1} \log \dfrac{1}{K_{sp}}$

$\qquad = 0.8 + 0.0591 \times \log 8.3 \times 10^{-17} = -0.15 \text{ Volt}$
$\qquad$ or

$E°_{Ag / AgI / I^-} = E°_{Ag / Ag^+} + \dfrac{RT}{F} \cdot \ln \dfrac{1}{k_{sp}} = -0.8 - \dfrac{8.31 \times 298 \times 2.303}{96500} \log k_{sp}$

$\qquad = -0.8 - 0.0591 . \log 8.3 \times 10^{-17} = -0.8 + 0.095 = 0.15 \text{ V.}$

29. $A_{(s)} + B^{2+}_{aq.} \longrightarrow A^{2+}_{aq.} + B_{(s)}$, $\Delta H° = -285$ KJ

Assuming Δs to negligible , $\Delta G° = \Delta H° = -285 \times 10^3 \times 0.84 \qquad = -2 \times E° \times 96500$
$E° = 1.24$ Volt

30. $\dfrac{d\varepsilon}{dt} = -0.00065$ Vol deg^{-1}

$\Delta S_{298} = n.F. \dfrac{dE}{dT} \qquad = 2 \times 96500 \times (-0.00065) = -125.5$ J/K.

31. $\dfrac{dE}{dT} = \dfrac{(0.6753 - 0.6915)}{(25 - 0)} = -6.48 \times 10^{-4}$ V deg^{-1}

$\Delta H_{298} = -neF + nFT \dfrac{dE}{dT} = -2 \times 0.6753 \times 96500 + 2 \times 96500 \times 298 \times (-6.48 \times 10^{-4})$

$= 2 \times 96500 (-0.6753 - 0.1931) = -167.6$ KJ.

32. $E° = 1.1028 - 0.641 \times 10^{-3}\,T + 0.72 \times 10^{-5}\,T^2$

$\left(\dfrac{dE°}{dT}\right)_{2S} = -0.641 \times 10^{-3} + 2 \times 0.72 \times 10^{-5}\,T \qquad = (-0.641 + 0.36) \times 10^{-3} = -0.281 \times 10^{-3}$

$\Delta S° = nF\,\dfrac{dE°}{dT} = 2 \times 96500 \times (-281 \times 10^{-3}) = -54.23\ EU$

33. $E_{298}^{°} = 1.1028 - 0.641 \times 10^{-3} \times 25 + 0.72 \times 10^{-5} \times (25)^2 = 1.091275\ Volt$

$= -8.314 \times 298\ \ln K = -2 \times 1.091275 \times 96500$

$K = 10^{36.91} = 8.128 \times 10^{36}.$

34. $\Delta S = -\left\{\dfrac{d}{dT}(\Delta G)\right\}_p = +nF\left(\dfrac{dE}{dT}\right)_p$

$\left(\dfrac{dE}{dT}\right)_p = \dfrac{\Delta S}{nF}$

35. $Na^+ + e^- \longrightarrow Na(s)$

1mole   1 Faraday

$Al^{3+} + 3e^- \longrightarrow Al(s)$

1 Faraday

No. of mole of Al $= \dfrac{1}{3}$ mole.

36. $\Lambda_{Ag^+} = 62.3\ Scm^2\,mol^{-1}$, $\Lambda_{Cl^-} = 67.7\ Scm^2\,mole^{-1}$

$K_{AgCl} = 3.4 \times 10^{-6}\ Scm^{-1}$

$\wedge_{AgCl}^{\infty} = (62.3 + 67.5) = \dfrac{1000 \times 3.4 \times 10^{-6}}{S}$

$S = \dfrac{3.4 \times 10^{-3}}{(62.3 + 67.5)} = 2.6 \times 10^{-5}\ M$

38. Higher the std. reduction potential, higher is the oxidising power.

39. $E_{cell} = 0.29 - \dfrac{0.059}{2}\ \log\ \dfrac{0.01 \times (0.01)^2}{(0.01)^2 \times 1}$ or $\qquad E_{cell} = 0.35\ volt$

40. $E°_{cell} = 1.89$; $E°_{Ce4+/Ce3+} + E°_{Co/Co2+} = E + 0.277 \Rightarrow E = 1.62\ V$

41. $E°_{MnO_4^-/MnO_2} = \dfrac{5 \times 1.5 - 2 \times 1.23}{3} = 1.7\ volt$

42. $\Delta S = \dfrac{nFd\ E_{cell}}{d\ t}$ $\qquad$ or $\qquad$ $\dfrac{d\ E_{cell}}{d\ t} = \dfrac{\Delta\ S}{n\ F}$

43. $-0.413 = 0 - 0.059\ \log\ \dfrac{1}{[H^+]}$ or $\qquad \dfrac{0.414}{0.059} = -\log\ H^+ = pH$ $\qquad$ or $\qquad$ pH = 7

44. $Z > Y > X$ (Non metals like $F_2 > Cl_2 > Br_2$)

So, Y will oxidise X^- but not Z^-

Z will oxidise both X^- and Y^-

X can't oxidise Y^- or Z^-.

45. $E°_{cell} = 0.8 - (-0.76) = 1.56\ V$

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46. $E_{cell} = 0.77 - \dfrac{0.059}{1} \log \dfrac{1.5}{0.015} = 0.652$ V

47. $1.1591 = 1.1 - \dfrac{0.059}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$ or $\dfrac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{-2} = 0.01$

48. $Ag \longrightarrow Ag^+ + e^-$
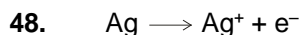
$E_1 = E_{oxid} + E_{calomel}$

$= E' - \dfrac{0.0591}{1} \log \sqrt{K_{sp_1}} + E_{calomel}$
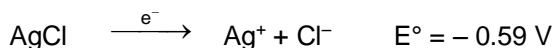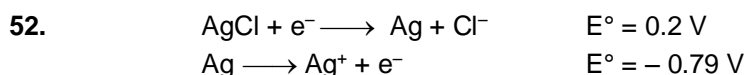
$E_2 = E' - \dfrac{0.0591}{1} \log \sqrt{K_{sp_2}} + E_{calomel}$ $\Rightarrow$ $E_2 - E_1 = 0.177 = 0.0591 \log \sqrt{\dfrac{K_{sp_1}}{K_{sp_2}}}$

$\dfrac{K_{sp_1}}{K_{sp_2}} = 10^6$.

49. $H^+ + Cl^- + NaOH \longrightarrow Na^+ + Cl^- + H_2O$ to conductance I^{st} decreases since no. of ions decreases after end point it inceases.

50. $E_{cell} = E^0_{cell} - \dfrac{0.059}{2} \log \dfrac{[Sn^{2+}]}{[Ag^+]^2}$ Ag^+ increase, E_{cell} increase.

51. $\dfrac{i \times 15 \times 60}{96500} = \dfrac{6.72}{22.4} \times 2 \Rightarrow$ $i = 64.3$ amp.

52. $AgCl + e^- \longrightarrow Ag + Cl^-$ $E° = 0.2$ V
          $Ag \longrightarrow Ag^+ + e^-$ $E° = -0.79$ V
———————————————————————————

$AgCl \xrightarrow{\ e^-\ } Ag^+ + Cl^-$ $E° = -0.59$ V

$E° = \dfrac{0.059}{n} \log K$ $\Rightarrow$ $-0.59 = \dfrac{0.059}{1} \log K_{SP}$ $\Rightarrow$ $K_{SP} = 10^{-10}$

Now solubility of AgCl in 0.1 M AgNO$_3$
   $S(S + 0.1) = 10^{-10}$ $\Rightarrow$ $S = 10^{-9}$ mol/L
Hence 1 mole dissolves in 10^9 L solution
hence in 10^6 L amount that dissolves in 1 m mol.

53. $Q = 10 \times 4825 = 48250$ C

no. of faraday $= \dfrac{48250}{96500} = 0.5$

$Ag + \dfrac{1}{2} Cu^{++} \longrightarrow Ag^+ + \dfrac{1}{2} Cu$
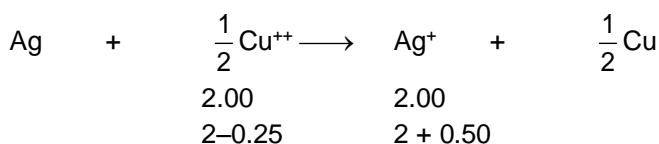
        2.00   2.00
        2–0.25   2 + 0.50

$E_{cell} = E^0_{Cell} - \dfrac{0.0591}{1} \log \dfrac{[Ag^+]}{[Cu^{++}]^{1/2}}$

$E_1 = E^0_{Cell} - \dfrac{0.0591}{1} \log \dfrac{2.00}{(2.00)^{1/2}}$

$E_2 = E^0_{Cell} - \dfrac{0.0591}{1} \log \dfrac{2.50}{(1.75)^{1/2}}$

$$\Delta E = E_2 - E_1 = \frac{0.0591}{1}\left[\log\sqrt{2} - \log\frac{2.50}{\sqrt{1.75}}\right] = \frac{0.0591}{1}[\log 1.41 - \log 1.88]$$

$$= \frac{0.0591}{1}[0.1492 - 0.2742] = -\frac{0.0591}{1} \times 0.125 = -0.00738 \text{ V.}$$

54. $nF\left(\dfrac{\partial E^o}{\partial T}\right) = \Delta S^o = -2 \times 96500 \times 1.45 \times 10^{-3} = -279.85 \text{ JK}^{-1}$

$\Delta G^o = -nFE^o = -2 \times 1.36 \times 96500 = -262.48 \text{ KJ.}$

$\Delta H^o = \Delta G^o + T\Delta S^o$

$\quad = -262.48 \times 10^3 - 300 \times 279.85$

$\quad = -262480 - 83955 = -346.435 \text{ KJ}$

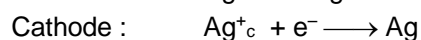**55.** $E^o_{X^-/AgX/Ag} = E^o_{Ag^+/Ag} + \dfrac{0.059}{1}\log_{10} K_{sp}(AgX)$

Thus, salt having least value of K_{sp} will have least value of $E^o_{X^-/AgX/Ag}$ and all values will be less than

$E^o_{Ag^+/Ag}$ (since 2nd term will always have a negative values).

**56.** If cell is taken to be conc cell, $E^o_{cell} = 0$

Anode : $\qquad Ag \longrightarrow Ag^+_a + e^-$

Cathode : $\qquad Ag^+_c + e^- \longrightarrow Ag$

$\qquad\qquad\qquad \overline{\qquad\qquad\qquad\qquad}$

$\qquad\qquad Ag_c^+ \rightleftharpoons Ag_a^+$

From Nernst eq,

$E_{cell} = E^o_{cell} - \dfrac{0.059}{1}\log\dfrac{[Ag^+]_a}{[Ag^+]_c} \qquad\Rightarrow\qquad 0 = 0 - \dfrac{0.059}{1}\log\dfrac{[Ag^+]_a}{[Ag^+]_c}$

$\therefore [Ag^+]_a = [Ag^+]_c \Rightarrow \dfrac{K_{sp}\text{ of }AgBr}{[Br^-]} = \dfrac{K_{sp}\text{ of }AgCl}{[Cl^-]}$ or, $\dfrac{5 \times 10^{-13}}{10^{-10}} = \dfrac{[Br^-]}{[Cl^-]} = \dfrac{[Br^-]}{[Cl^-]} = \dfrac{1}{200}$.

57. Charge passed = 0.01 Faraday

At the anode $\left(H_2O \longrightarrow \dfrac{1}{2}O_2 + 2H^+ + 2e^-\right)$ with 90 % efficientcy 0.01×0.9 F have been used and will

produce $\dfrac{1}{4} \times 0.01 \times 0.9$ mole of O_2 i.e. 0.00225 mol O_2.

At the cathode $2H_2O \xrightarrow{\;+2e^-\;} H_2 + 2OH^-$
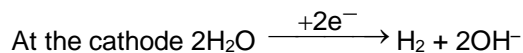
moles of H_2 produced = $\dfrac{0.01 \times 0.8}{2}$ mol = 0.004 mol

Total moles produced of gases = 0.004 + 0.00225 = 0.00625 mol

vol. at STP = 0.00625×22400 mL = 140 mL

59. $K_a = \dfrac{C\,\alpha^2}{1-\alpha} \qquad\Rightarrow\qquad \dfrac{1}{6} = \dfrac{\alpha^2}{1-\alpha}$

$\Rightarrow \qquad \alpha = \dfrac{-1 \pm \sqrt{(1)^2 + 4 \times 6 \times 1}}{12} = \dfrac{-1 \pm \sqrt{1+24}}{12} = \dfrac{1}{3}$

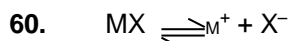$\therefore \qquad [IO_3^-] = 1 \times \dfrac{1}{3} = \dfrac{1}{3}M$

$\Rightarrow \qquad [Ag^+] = \dfrac{3 \times 10^{-8}}{\dfrac{1}{3}} = 9 \times 10^{-8}$ M

Now $2Ag + Zn^{+2} \xrightarrow{\;2e^-\;} 2Ag^+ + Zn$
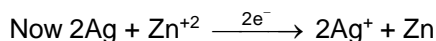
Gives: $\qquad E = -1.56 + \dfrac{0.06}{2} \log \dfrac{1}{(9 \times 10^{-8})^2} = -1.1376$ V

Ans. 11

60. $MX \rightleftharpoons M^+ + X^-$

$\quad\quad a + 10^{-7} \quad\quad a$

$K_{SP} = (a + 10^{-7})\, a$

$\dfrac{55 \times 10^{-7}}{1000} = (6 \times 10^{-3}\,(a + 10^{-7}) + 8 \times 10^{-3}\,a + 7 \times 10^{-3} \times 10^{-7})$

$55 \times 10^{-10} = 6 \times 10^{-3}\,a + 6 \times 10^{-10} + 8 \times 10^{-3}\,a + 7 \times 10^{-10}$

$42 \times 10^{-10} = 14 \times 10^{-3}\,a$

$\quad\quad\quad a = 3 \times 10^{-7}$

$K_{SP} = 12 \times 10^{-14}$

61. $E^o_{cell} = E^o_{RP(RHS)} - E^o_{RP(LHS)}$

$\quad\quad = -0.76 - (-1.36) = 0.6$

$\Delta_r G^o = -RT \ln K_{eq};$

or $\log K_{eq} = \dfrac{nFE^o}{RT \times 2.303} = \dfrac{2 \times 0.6}{0.06} = 20 \qquad \Rightarrow \qquad \dfrac{2 \times 0.6}{0.06} \Rightarrow 20; \; K_f = 10^{20}$

62. $\Delta S^o = nF \dfrac{dE}{dt} = 2 \times 96500 \times \dfrac{1.718 - 1.2}{20} = 5000$ Joule/K.

63. Reduction and electronation take place at cathode elctrode, so it become positive electrode.

64. (A, B, C) Reduction Potential of Ce is higher than that of Zn.

65. (A) because $E^o_{Cu^{2+}/Cu} > E^o_{Fe^{2+}/Fe}$.

66. Recharging reaction: $2PbSO_4\,(s) + 2H_2O. \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4\,(aq)$

67. On dilution specific conductance decreases while molar conductivity increases.

68. Create a cell with required cell reaction
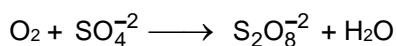
$O_2 + SO_4^{-2} \longrightarrow S_2O_8^{-2} + H_2O \qquad\qquad E^o_{cell} = 1.23 - 2.01 < 0$

$\Rightarrow$ Nonspontaneous cell reaction

69. Electrolysis of NaBr Solution

At Anode $\qquad 2Br^- \longrightarrow Br_2 + 2e^-$

at cathode $\qquad 2H_2O \xrightarrow{\;+2e^-\;} H_2 + 2OH^-$
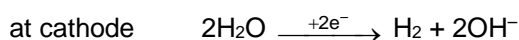
It is clear that Br^- ion are replaced by OH^-.

Hence molar conductance & specific conductance increases.

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70. (A) For $Cr_2O_7^{2-}$ (acidic solution)

$E^0 = 1.23$ which is greater than $E^o_{(Fe^{2+}/Fe)}$ hence it can oxidize Fe

(B) $H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$ $E^0 = -0.70$ V

    $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $E^0 = 1.30$ V

    $H_2O_2 + 2H^+ \longrightarrow 2H_2O$ $E^0 = \dfrac{(-0.70 \times 2) + (4 \times 1.30)}{2} = 1.9$
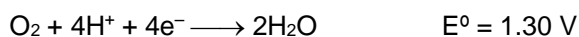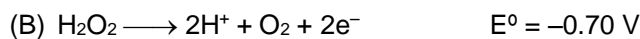
Here E^0 is grater than $E^o_{(Fe^{2+}/Fe)}$ hence H_2O_2 in acidic medium can oxides Fe.

71. $E_{cell} = E^0_{cell} - \dfrac{2.303 \; RT}{nF} \log \dfrac{(Zn^{+2})}{(Cu^{+2})} = 0.76 + 0.34 - \dfrac{2.303 \times 8.31 \times 200}{2 \times 96500} \log \dfrac{2}{0.2} = 1.08$ volt.

72. $Cu^{+2} + 4\, NH_3 \rightleftharpoons [Cu\,(CH_3)_4]^{+2}$

    0.2   1   0

    x   1−0.8   0.2

         $k_f = 4.0 \times 10^{11} = \dfrac{0.2}{x \times (0.2)^4} = \dfrac{1}{x \times (0.2)^3}$
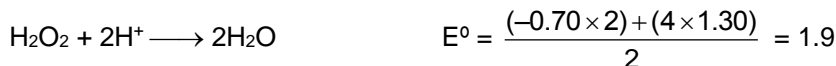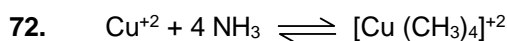
         $x = \dfrac{10^{-11}}{(0.2)^3 \times 4} \quad \Rightarrow \quad x = 3.125 \times 10^{-10}$ $[Cu^{+2}] = 3.125 \times 10^{-10}$

   $E_{cell} = 0.75 + 0.34 - \dfrac{0.0591}{2} \log \dfrac{2}{3.125 \times 10^{-10}}$

        $= 1.1 - \dfrac{0.0591}{2}(10 - 0.194) = 1.1 - 0.29 = 0.81$ volt

73. $E_{cell} = 1.1 - \dfrac{0.0591}{2} \log \dfrac{[2]}{[Cu^{+2}]} = 0$

$\log \dfrac{[2]}{[Cu^{+2}]} = \dfrac{1.1 \times 2}{0.0591} = 37.23 \quad \Rightarrow \quad \dfrac{2}{[Cu^{+2}]} = 1.68 \times 10^{37} \quad \Rightarrow \quad [Cu^{+2}] = 1.19 \times 10^{-37}$

74. First conductance decreases due to nutralisation of free H^+ ions of weak acid, then it increases due to formation of salt and after equivalence point it increases more fastly due to increasing of OH^- ions.

75. First conductance decreases due to nutralisation of strong acid H^+ ion then after it increases due to nutralisation of weak acid and after equivalence point it increases more fastly.

PART - V

1. $Fe^{+2} + 2e^- \longrightarrow Fe$
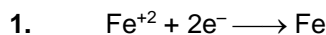
Number of milimoles of e^- passed $= \dfrac{(965)(1)}{96500} \times 1000 = 10$

∴   Milimoles of Fe^{+2} reduced = 5

∴   Milimoles of Fe^{+2} left = 1000 x – 5

∴   By equating mili equivalent = (1000x – 5) × 1 = (0.1)(10)(5) $\Rightarrow$ x = 10^{-2}

2. $CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

milli moles   100×0.2   100×0.2   –   –

              0   0   100×0.2

Then,

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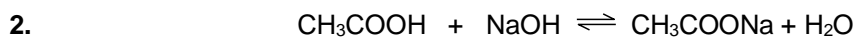
$$[CH_3COONa] = \frac{100 \times 0.2 \times 10^{-3}}{200} \times 1000 = 0.1 \Rightarrow \text{D.O.D }(\alpha) \text{ for } CH_3COOH = \frac{\Lambda_m}{\Lambda_m^0} = \frac{2.0}{200} = 10^{-2}$$

Then, K_a of $CH_3COOH = C\alpha^2 = 0.1 \times (10^{-2})^2 = 10^{-5}$

$\Rightarrow$ $pKa = 5$ for CH_3COOH.

So, pH of CH_3COONa salt is :

$$pH = 7 + \frac{1}{2} pKa + \frac{1}{2} \log C. \quad = 7 + \frac{1}{2} \times 5 + \frac{1}{2} \log 0.1 = 9.$$

3. $\Lambda_m^\infty = \Lambda_{Ag^+}^\infty + \Lambda_{Br^-}^\infty$

$\qquad = a + b$

$\Lambda_m^\infty = K \times \dfrac{1000}{S}$ $\qquad\qquad \Rightarrow \qquad S = \dfrac{K}{\Lambda_m^\infty} \times 1000 \qquad \Rightarrow \qquad S \text{ (g/lit)} = \dfrac{K}{a+b} \times 1000 \times 188$

4. $\dfrac{\lambda}{\lambda^\circ} = \dfrac{122}{\lambda^\circ} = 0.936$

$\lambda^\circ = 130.34 \ \Omega^{-1} cm^2 \ eq^{-1}$

$\dfrac{\lambda_+^\circ}{\lambda^\circ} = \dfrac{0.98}{1.98}$ $\qquad\qquad \Rightarrow \qquad \dfrac{\lambda_+^\circ}{130.34} = \dfrac{0.98}{1.98}$

$\lambda_{K+}^\circ = \lambda_+^\circ = 64.51 \ \Omega^{-1} cm^2 \ eq^{-1}$

And

$\dfrac{\lambda_-^\circ}{\lambda^\circ} = 1 - \dfrac{\lambda_+^\circ}{\lambda^\circ}$ $\qquad\qquad \Rightarrow \qquad \dfrac{\lambda_+^\circ}{\lambda^\circ} = 1 - \dfrac{0.98}{1.98}$

$\dfrac{\lambda_-^\circ}{130.34} = \dfrac{1}{1.98}$ $\qquad\qquad \Rightarrow \qquad \lambda_-^\circ = \dfrac{130.34}{1.98} = 65.83 \ \Omega^{-1} cm^2 \ eq^{-1}$

5. $\Pi = iCRT$

$3 = i \times 0.1 \times \dfrac{1}{12} \times 300$

$i = 1.2$

$i = 1 + \alpha(n-1)$

$1.2 = 1 + \alpha(2-1) = 0.2$

$0.2 = \dfrac{30}{\lambda_m^\infty}$ $\qquad\qquad \Rightarrow \qquad \lambda_m^\infty = 150 \ \Omega^{-1} cm^2 \ mol^{-1}$

6. $V = iR \qquad\qquad R = \dfrac{V}{i} = \dfrac{5}{0.15} = \dfrac{100}{3} \Omega$

$K = \dfrac{1}{R} \times \dfrac{\ell}{a} = \dfrac{3}{100} \times \dfrac{0.5}{1.5} = 10^{-2}$

$\Lambda_M = \dfrac{K \times 1000}{M} = 10^{-2} \times \dfrac{1000}{0.05} = 200 \ \Omega^{-1} cm^2 \ mol^{-1}$

7. $Cu^{2+} \qquad\qquad + \qquad 2e^- \qquad \rightarrow \qquad Cu$

$\qquad\quad 2mol \qquad\qquad \dfrac{482.5 \times 4 \times 60}{96500} \ mol$
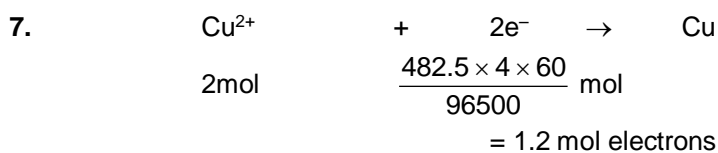
$\qquad\qquad\qquad\qquad\qquad = 1.2 \ mol \ electrons$

2 mole electrons then Cu^{+2} reacted = 1 mole

When 1.2 mole electrons then Cu^{+2} reacted $= \dfrac{1}{2} \times 1.2 = 0.6$

so, remaining Cu^{+2} moles $= 2 - 0.6 = 1.4$ moles

Remaining $[CuSO_4] = \dfrac{1.4}{5} = 0.28$ M.

8. For concentration cell $E^0_{cell} = 0$

$Ag\,(s) \longrightarrow Ag^+\,(C_1) + e^-$

$Ag^+\,(C_2) + e^- \longrightarrow Ag\,(s)$

_____

$Ag^+\,(C_2) \longrightarrow Ag^+\,(C_1)$
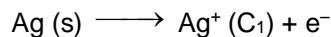
Then, $E_{cell} = X = 0 - 0.059 \log\left(\dfrac{C_1}{C_2}\right)$

$\Rightarrow \log\left(\dfrac{C_2}{C_1}\right) = \dfrac{X}{0.059}$

$\Rightarrow \dfrac{C_2}{C_1} = \text{anti log}\left(\dfrac{x}{0.059}\right)$

9. $Fe(OH)_3 \rightleftharpoons Fe^{+3} + 3OH^- \quad ; \quad [Fe^{+3}] = \dfrac{K_{sp}}{[OH^-]^3} = \dfrac{10^{-26}}{(10^{-2})^3} = 10^{-20}$

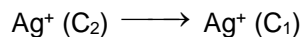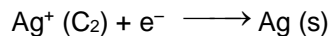$E_{Fe^{+3}/Fe} = E^0_{Fe^{+3}/Fe} - \dfrac{0.06}{3} \log \dfrac{1}{[Fe^{+3}]} = -0.036 - \dfrac{0.06}{3} \times 20 = -0.036 - 0.4 = -0.436$

10. For cell reaction to take place in opposite direction. E_{cell} must be negative.

$E_{cell} \quad < \quad 0$

$E^0_{cell} - \dfrac{0.06}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]} \quad < \quad 0$

$1.1 - \dfrac{0.06}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]} \quad < \quad 0$

$\dfrac{0.06}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]} \quad > \quad 1.1$

$\log \dfrac{[Zn^{2+}]}{[Cu^{2+}]} \quad > \quad 36.67$

$\ell n \dfrac{[Zn^{2+}]}{[Cu^{2+}]} \quad > \quad 84.4$

$[Zn^{2+}] > [Cu^{2+}]e^{84.4}$

11. X^- is I^-

Y^- is Cl^-

SRP $Cl_2 > Br_2 > I_2$

12. $E_{cell} = -\dfrac{RT}{nF} \ell n \dfrac{[H^+]_{anode}}{[H^+]_{cathode}} = -\dfrac{RT}{nF} \ell n \dfrac{\dfrac{K_a[HA]_{anode}}{[NaA]_{anode}}}{\dfrac{K_a[HA]_{cathode}}{[NaA]_{cathode}}}$

13.   Anode : $2H_2O \longrightarrow O_2\uparrow + 4OH^- + 4e^-$

                              0.01 mol   0.04 F

      Cathode : $Cu^{2+} +$ $2e^-$ $\longrightarrow$ $Cu(s)$

                  $20\times10^{-3}\times0.5$ 0.04 faraday

                  $= 10^{-2}$ mol -0.02

                  $= 0.01$ mol $= 0.02$ F

$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-$

            0.02F   0.01 mol

Total volume of gases evolved at STP = $(0.01 + 0.01) \times 22.4 = 448$ ml

14. $0.164 = 0 + \dfrac{0.0591}{1}\log_{10}\dfrac{0.1}{[Ag^+]_{anode}}$

$\Rightarrow$ $[Ag^+]_{anode} = 1.66 \times 10^{-4}$ M.

$K_{sp} = [Ag^+]^2 \times [CrO_4^{2-}] = 1.66 \times 10^{-4} \times \left(\dfrac{1.66 \times 10^{-4}}{2}\right)$

15.   **Hint:** Reverse of (B) & (C) is spontaneous; weakest Oxidizing Agent here is Mg^{2+}]

17.   (a, b, d, f) $E = E^0 - \dfrac{0.6}{n}\log\dfrac{[A^+][Cl^-]}{P_{Cl_2}}$

18. $\Lambda^0_{CH3COOH} = \Lambda^0_{CH3COONa} + \Lambda^0_{HCl} - \Lambda^0_{NaCl}$

            $= 150 + 200 - 125 = 225$ S cm^2 mol^{-1}.

$\Lambda^c_{CH3COOH} = 2.25$ S cm^2 mol^{-1}.

$\alpha = \dfrac{\Lambda^c_{CH_3COOH}}{\Lambda^0_{CH_3COOH}} = \dfrac{2.25}{225} = 10^{-2}$

Then $[H^+]$ for $CH_3COOH = C\alpha = 0.001 \times 10^{-2} = 10^{-5}$

$\Rightarrow$ $pH = -\log[H^+] = -\log(10^{-5}) = 5$

19. $K = 3.2 \times 10^{-5}\ \Omega^{-1}.cm^{-1}$

            $\Lambda = \dfrac{10^3 K}{C}$

            $\Lambda = \dfrac{3.2 \times 10^{-2}}{0.2} = 16 \times 10^{-2}$

            $\alpha = \dfrac{\Lambda}{\Lambda_\infty}$

$\therefore$ $\Lambda_\infty = \dfrac{\Lambda}{\alpha} = \dfrac{16 \times 10^{-2}}{0.02} = 8$

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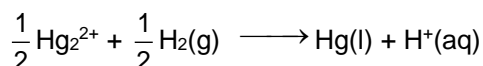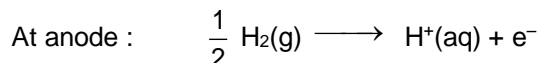**Toll Free :** 1800 258 5555 | CIN: U80302RJ2007PLC024029

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20. $E = E^0_{cell} - \dfrac{0.059}{2} \cdot \log Q$

$Q = \dfrac{(10^{-7})^2}{20} \times \dfrac{0.2}{(10^{-7})^2} = \dfrac{1}{100}$

$E = 0 - \dfrac{0.059}{2} \cdot \log \dfrac{1}{100} = \dfrac{0.059}{2} \times 2 = 0.059$

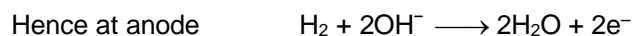$\Rightarrow \quad 1000E = 1000 \times 0.059 = 59$

21. At cathode : $\qquad \dfrac{1}{2} Hg_2^{2+} + e^- \longrightarrow Hg(l)$

At anode : $\qquad \dfrac{1}{2} H_2(g) \longrightarrow H^+(aq) + e^-$

$\rule{8cm}{0.4pt}$

$\qquad \dfrac{1}{2} Hg_2^{2+} + \dfrac{1}{2} H_2(g) \longrightarrow Hg(l) + H^+(aq)$

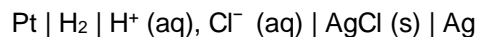$\qquad E_{cell} = E^0_{cell} - \dfrac{0.059}{1} \log [H^+]$

or $\qquad 0.634 = (0.28 - 0) + 0.059 \, pH$

or $\qquad pH = \dfrac{0.634 - 0.28}{0.059} = 6$

22. Overall reaction should be the one which is written in term of species present in the given electrode/cell.
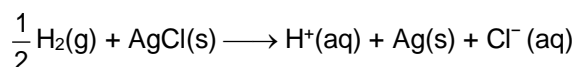
Hence at anode $\qquad H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$

At cathode $\qquad 2AgCl + 2e^- \longrightarrow 2Ag + Cl^-$

23. We can assume the given cell to be:

Pt | H$_2$ | H$^+$ (aq), Cl$^-$ (aq) | AgCl (s) | Ag

With this assumption, $E^o_{cell} = E^o_{AgCl/Ag^-} - E^o_{SHE}$

$\qquad\qquad\qquad\qquad = 0.22 \, V$

And cell reaction is :

$\qquad \dfrac{1}{2} H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Ag(s) + Cl^-(aq)$

$\Rightarrow \quad E_{cell} = E^o_{cell} - \dfrac{0.06}{1} \log (H^+)(Cl^-)$

$\qquad 1.05 = 0.22 - 0.06 \log \dfrac{K_w}{(OH^-)} (Cl^-)$

$\qquad 0.83 = 0.06 \left(-\log K_w - \log \dfrac{(Cl^-)}{(OH^-)} \right)$

$\qquad \dfrac{83}{6} = pK_w - \log \dfrac{0.012}{0.01}$

$\qquad \dfrac{83}{6} = pK_w - \log(1.2)$

$\Rightarrow \quad pK_w = \dfrac{83}{6} + \log(1.2) = 13.91$

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24. $pK_w = 13.91$

i.e. $K_w > 10^{-14}$

Hence T is greater than 25ºC.

25. For the solution of Na_2SO_4

$$\wedge = \frac{K}{C} = \frac{2.6 \times 10^{-2}}{1}$$

$$2\lambda^o_{Na^+} + \lambda^o_{SO_4^{2-}} = 0.026$$

$$\lambda^o_{SO_4^{2-}} = 0.026 - 0.01 = 0.016\ \Omega^{-1}\ m^2\ mol^{-1}$$

26. For the Na_2SO_4 solution saturated with $CaSO_4$ (Let x $\dfrac{mol}{m^3}$ be the solubility of $CaSO_4$)

$$K_{solution} = K_{Na^+} + K_{SO_4^{2-}} + K_{Ca^{2+}}$$

$$0.07 = (\lambda^o_{Na^+} \times [Na^+]) + (\lambda^o_{SO_4^{2-}} \times [SO_4^{2-}]) + (\lambda^o_{Ca^{2+}} \times [Ca^{2+}])$$

$$= (0.005 \times 2) + 0.016(1 + x) + (0.006x)$$

$$0.07 = 0.01 + 0.016 + 0.016x + 0.006x$$

$$X = 2\ mol/m^3$$

$\therefore$ $[Ca^{2+}] = 0.002\ mol/lt$, $[SO_4^{2-}] = 0.003\ mol/lt$

27. Solubility product of $CaSO_4 = [Ca^{2+}][SO_4^{2-}] = 0.002 \times 0.003 = 6 \times 10^{-6}$