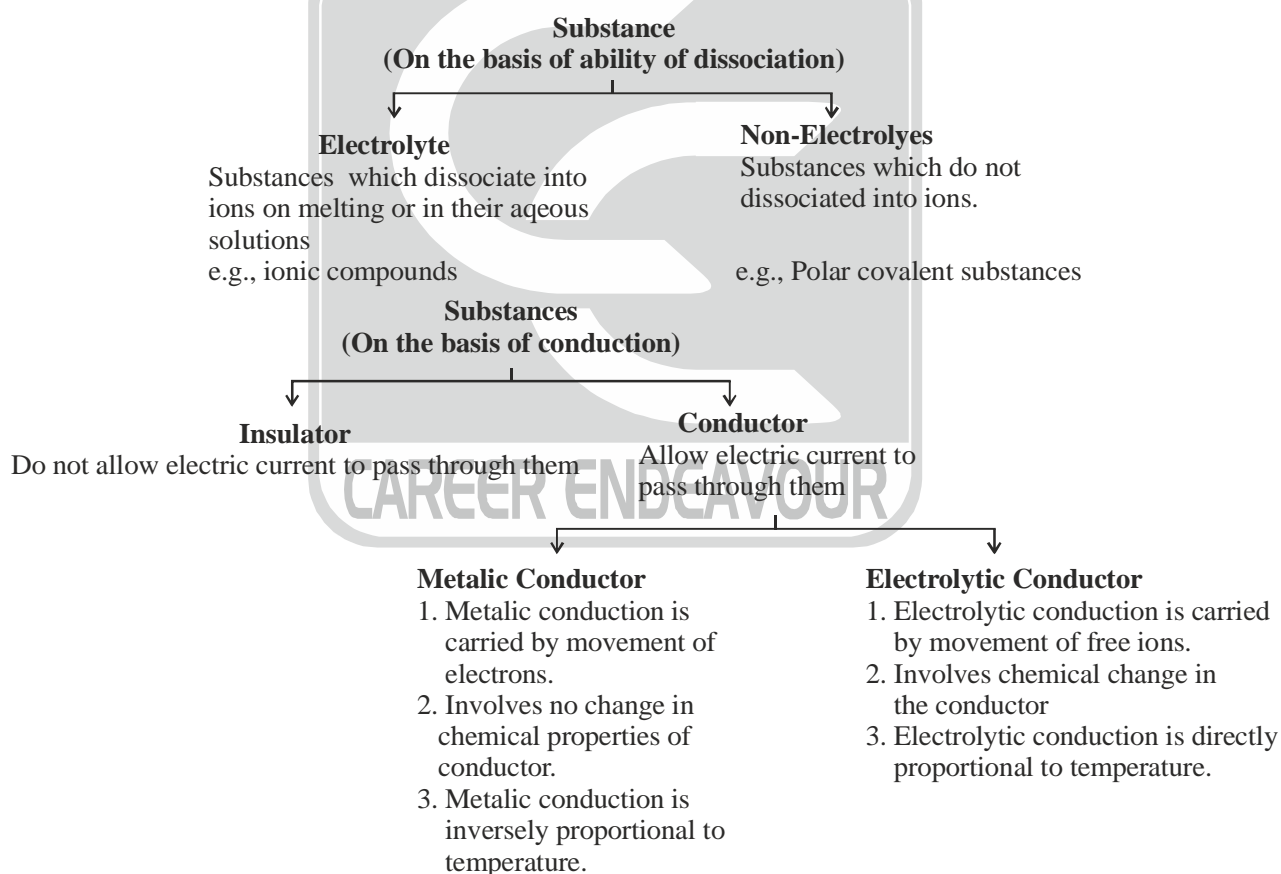


ELECTROCHEMISTRY

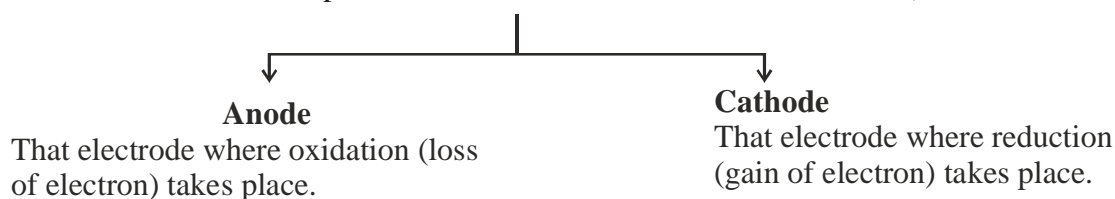
Introduction :

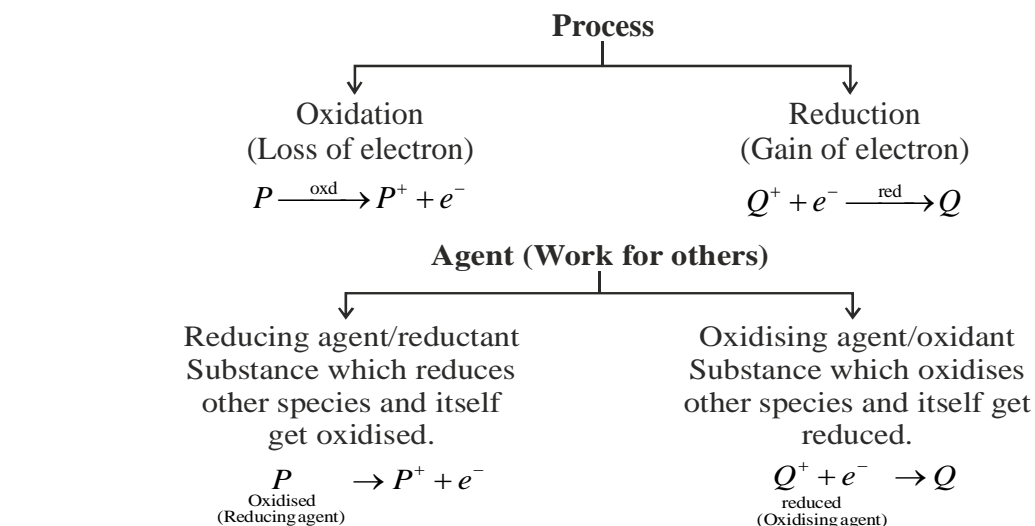
Electrochemical cell can be broadly classified into two categories, viz., electrolytic cell and galvanic (or voltaic) cells. In the former, a chemical reaction (more precisely electrolysis) is carried out with the help of an electrical current, whereas in the latter an electrical current is produced as a result of some spontaneous chemical reaction. In other words, an electrolytic cell is a device to convert electrical energy into chemical energy whereas in the galvanic cell, the reverse process takes place. In this section, we will outline the working of these two types of cells along with their sign conventions.



Electrode

(A rod or a piece of conducting substance dipped in an electrolyte solution for deposition or liberation of substance is electrode)





Cell

(A device which consists of two electrodes dipped in electrolyte solution to convert chemical energy into electric energy or vice versa)

Electrochemical/Galvanic/Voltaic cell

1. Chemical energy \rightarrow Electrical energy.
2. Voltmeter $\left(\text{⊗}\right)$ is used in the cell.
3. Anode is given **negative** polarity
cathode is given **positive** polarity.

Electrolytic cell

1. Electrical energy \rightarrow chemical energy
2. Battery $\left(\text{+||-}\right)$ is used in such cells.
3. Anode is given **positive** polarity
Cathode is given **negative** polarity.

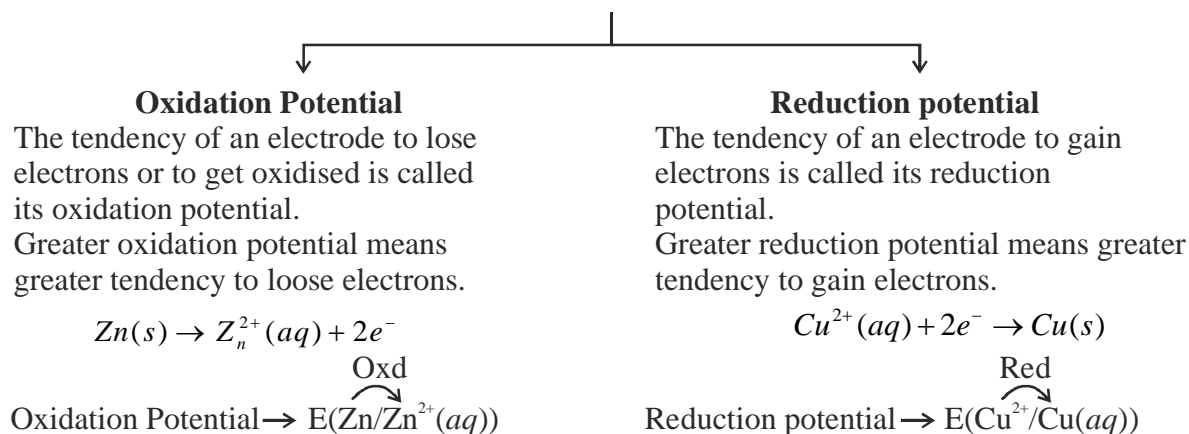
Salt bridge : It is an inverted U-shaped tube filled with saturated concentrated solution of KCl or KNO_3 or NH_4NO_3 in agar-agar jell or gelatin.

Function : 1. It completes the electrical circuit.

2. It maintain the electrical neutrality of the two half cell

Electrode Potential (E)

(The potential developed at an electrode dipped in an electrolyte solution i.e., known as electrode potential. It arises either due to oxidation or reduction).



$$\text{Oxidation potential} = - \text{Reduction potential}$$

The electrode potential depends upon :

- (i) Nature of the metal and its ions.
- (ii) Concentration of the ions in the solution.
- (iii) Temperature.

Standard electrode potential (E°) : The electrode potential of a metal electrode is determined with respect to a standard hydrogen electrode is called standard electrode potential.

Electrochemical series : The arrangement of elements in order of their increasing reduction potential values is called electrochemical series.

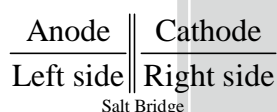
Formulation of a Galvanic cell :

An electrochemical cell requires two electrodes for a reaction to occur. The assembly comprising the electrode and the reagents is called the half-cell and the component of the total chemical reaction that occurs in the half-cell is the half-cell reaction or electrode reaction. Thus, we require two half-cells to produce an electrochemical cell. A half-cell or an electrochemical cell can be briefly represented following a few rules given below.

- (i) The separation of two phases is shown by a vertical line.
- (ii) The various materials present in the same phase are shown together with the help of commas.
- (iii) The two half-cells are joined with the help of double vertical lines.
- (iv) The significant features of the substances such as pressure of gas, concentration of ion, etc., are indicated in brackets drawn immediately after writing the substance.

We represent the cell as $Zn | Zn^{2+}(c_1) || Cu^{2+}(c_2) | Cu$.

The Weston cadmium cell will be written as $Pt | Hg | Cd(Hg) | CdSO_4 \cdot \frac{8}{3} H_2O(s) |$ saturated solution of $CdSO_4 | CdSO_4 \cdot \frac{8}{3} H_2O(s) | Hg_2SO_4, Hg | Pt$

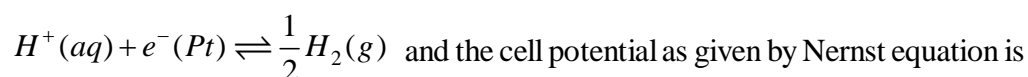
**DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIALS :**

In this section, we consider various types of half-cells that are employed and the expressions which relate the half-cell potential with the concentrations and pressures of the constituents of the half-cell.

Gas - ion half-cell :

If the gas-ion half-cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half-cell is the hydrogen gas-hydrogen ion half-cell. In this half-cell, purified hydrogen gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.

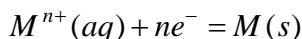
The expression of $E_{\text{half-cell}}$ can be derived by considering the reversible reduction reaction that occurs at the electrode. For the present case, the half-cell reaction is



$$E_{H^+|H_2|Pt} = E^\circ_{H^+|H_2|Pt} - \frac{RT}{F} \ln \frac{(pH_2)^{1/2}}{[H^+]}$$

Metal-Metal Ion Half-Cell :

Metal - metal ion half-cell consists of a bar metal M in contact with a solution containing M^{n+} ions. Examples include zinc-zinc ion, copper-cupric ion, silver-silver ion and gold-auric ion half-cell. The equilibrium reaction at the electrode is

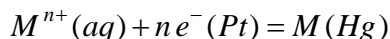


and the cell potential as given by Nernst equation is

$$E_{M^{n+}|M} = E_{M^{n+}|M}^{\circ} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

METAL AMALGAM - METAL ION HALF-CELL :

In this electrode, metal amalgam is placed in contact with a solution containing metal ion. Electrical contact is made by a platinum wire dipping into the amalgam pool. The equilibrium reaction at the electrode is



and the cell potential is given by

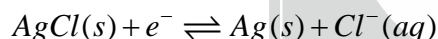
$$E_{M^{n+}|M(Hg)Pt} = E_{M^{n+}|M(Hg)Pt}^{\circ} - \frac{RT}{nF} \ln \frac{[M(Hg)]}{[M^{n+}]}$$

where $E_{M^{n+}|M(Hg)Pt}^{\circ}$ is the standard potential of the given metal amalgam.

Metal-Insoluble Salt-Anion Half-Cell :

In this half-cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. Four such half-cells are described below.

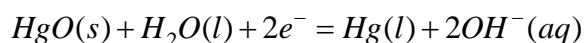
Silver-Silver Chloride-Chloride Half-Cell : The half-cell is represented as $Cl^{-} | AgCl | Ag$. The equilibrium reaction that occurs at the electrode is



and the cell potential is

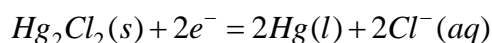
$$E_{Cl^{-}|AgCl|Ag} = E_{Cl^{-}|AgCl|Ag}^{\circ} - \frac{RT}{F} \ln [Cl^{-}]$$

Mercury-Mercuric Oxide-Hydroxide Ion Half-Cell : In this half-cell, a pool of mercury is covered with a paste of solid HgO and a solution of a base. The equilibrium reaction that takes place at the platinum electrode is



$$E_{OH^{-}|HgO|Hg} = E_{OH^{-}|HgO|Hg}^{\circ} - \frac{RT}{F} \ln [OH^{-}]$$

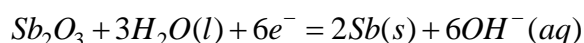
Mercury-Mercurous Chloride-Chloride Ion Half-Cell : This half-cell is known as calomel half-cell. The equilibrium reaction is



Its Nernst equation is

$$E_{Cl^{-}|Hg_2Cl_2|Hg} = E_{Cl^{-}|Hg_2Cl_2|Hg}^{\circ} - \frac{RT}{F} \ln [Cl^{-}]$$

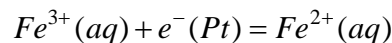
Antimony-Antimony Oxide-Hydroxide Ion Half-Cell : The equilibrium reaction that takes place in the half-cell is



Its Nernst equation is

$$E_{OH^-|Sb_2O_3|Sb} = E_{OH^-|Sb_2O_5|Sb}^\circ - \frac{RT}{F} \ln[OH^-]$$

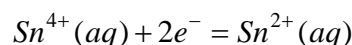
Oxidation-Reduction Half-Cell : An oxidation-reduction half-cell has an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation. One of the examples is ferric-ferrous half-cell. The equilibrium reaction to be considered is



The Nernst equation is

$$E_{Fe^{3+}, Fe^{2+}|Pt} = E_{Fe^{3+}, Fe^{2+}|Pt}^\circ - \frac{RT}{F} \ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

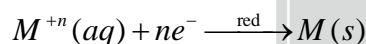
Another example is stannic-stannous half-cell where the reduction reaction to be considered is



and the Nernst equation is

$$E_{Sn^{4+}, Sn^{2+}|Pt} = E_{Sn^{4+}, Sn^{2+}|Pt}^\circ - \frac{RT}{2F} \ln \frac{[Sn^{2+}]}{[Sn^{4+}]}$$

Nernst equation for an electrode : Electrode potentials depend on the concentration of the electrolyte solutions. Nernst gave a relationship between electrode potentials and concentrations of the electrolyte solutions.



$$E(M^{+n}/M) = E^\circ(M^{+n}/M) - \frac{2.303RT}{nF} \log \frac{[M(s)]}{[M^{+n}(aq)]}$$

$$\text{at } 298k, \frac{2.303RT}{F} = \frac{2.303 \times 8.314 \times 298}{96500} = 0.0591$$

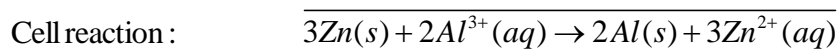
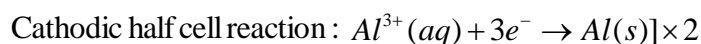
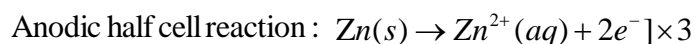
$$E_{(M^{+n}/M)} = E_{(M^{+n}/M)}^\circ - \frac{0.0591}{n} \log \frac{[M(s)]}{[M^{+n}(aq)]}$$

$$E_{(M^{+n}/M)} = \text{Electrode reduction potential (V)}$$

$$E_{(M^{+n}/M)}^\circ = \text{Standard electrode reduction potential (V).}$$

n = number of moles of electron in half cell

e.g., Zn – Al cell

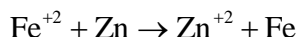


$$E_{cell} = E_{cell}^\circ - \frac{2.303RT}{nF} \log \frac{[Al(s)]^2 \cdot [Zn^{2+}(aq)]^3}{[Zn(s)]^3 \cdot [Al^{3+}(aq)]^2}$$

1. The values of standard reduction potential E^0 for the half reaction are



The EMF of the cell reaction



will be

- (a) -0.35 V (b) $+0.35 \text{ V}$ (c) $+1.17 \text{ V}$ (d) -1.17 V [JNU-2003]

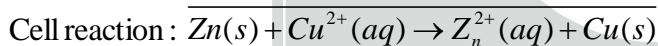
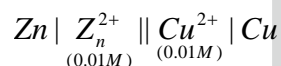
Soln. : $E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$
 $= -0.41 - (-0.76)$
 $= +0.35 \text{ V}$

Correct option (b)

2. The e.m.f. of $\text{Zn} | \text{Zn}^{2+} (0.01 \text{ M}) || \text{Cu}^{2+} (0.01 \text{ M}) | \text{Cu}$ cell will be (given standard oxidation potentials of Zn and Cu electrodes are 0.761 V and -0.337 V respectively) [JNU-2005]

- (a) 1.098 V (b) -1.098 V (c) 0.424 V (d) -0.424 V

Soln. : The given cell will be represented as



$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$= +0.337 + 0.761$$

$$= +1.098 \text{ V}$$

The e.m.f. of given cell:

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

at 298 K

$$\Rightarrow E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \Rightarrow E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{0.01}{0.01}$$

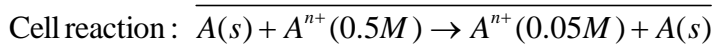
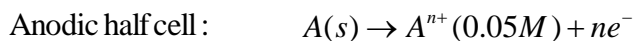
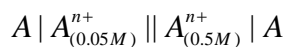
$$\Rightarrow E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log 1$$

$$\Rightarrow E_{\text{cell}} = E_{\text{cell}}^0 - 0 \Rightarrow E_{\text{cell}} = +1.098 \text{ V}$$

Correct option (a)

3. In a concentration cell, $A \left| A_{(0.05M)}^{n+} \right| \left| A_{(0.5M)}^{n+} \right| A$ at 25°C the $E = 0.029\text{ V}$. The number of electrons involved in the cell reaction is [JNU-2006]
- (a) 1 (b) 2 (c) 3 (d) 0

Soln. : The given cell will be represented as -



The e.m.f of given cell :

$$E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log \frac{[P]}{[R]}$$

At 298 K

$$E_{cell} = 0 - \frac{0.0591}{n} \log \frac{0.05}{0.5}$$

$$\because E_{cell}^{\circ} = 0$$

$$\Rightarrow 0.029 = -\frac{0.0591}{n} \log 10^{-1} \Rightarrow 0.029 = \frac{0.0591}{n} \Rightarrow n = \frac{0.0591}{0.029} \approx 2$$

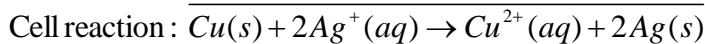
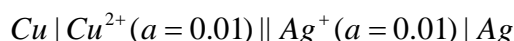
Correct option (b)

4. What would be the e.m.f. of the following cell? [JNU-2010]



- (a) 0.420 V (b) 0.390 V (c) -0.390 V (d) -0.420 V

Soln. : The given cell will be represented as -



$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = E_{\text{Ag}^+/\text{Ag}}^{\circ} - E_{\text{Cu}^{2+}/\text{Cu}}^{\circ}$$

$$= 0.79 - 0.34 = 0.45\text{ V}$$

The e.m.f. of given cell :

$$E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

At 298 K

$$\Rightarrow E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2} \quad \Rightarrow E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{(0.01)}{(0.01)^2}$$

$$\Rightarrow E_{cell} = 0.45 - \frac{0.0591}{2} \log 10^2 \quad \Rightarrow E_{cell} = 0.45 - \frac{0.0591}{2} \times 2$$

$$\Rightarrow E_{cell} = 0.45 - 0.0591 \quad \Rightarrow E_{cell} = 0.3909V$$

$$\Rightarrow E_{cell} \simeq 0.390V$$

Correct option (b)

Calculation of equilibrium constant :

Cell reaction : $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

Nernst equation -

$$E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log Q_c$$

At equilibrium $E_{cell} = 0, Q_c = K_c$

$Q_c \rightarrow$ Reaction quotient.

$K_c \rightarrow$ Equilibrium constant.

$$\Rightarrow 0 = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log K_c$$

$$\Rightarrow E_{cell}^{\circ} = \frac{2.303RT}{nF} \log K_c$$

At 298K

$$E_{cell}^{\circ} = \frac{0.0591}{n} \log K_c$$

Relationship between E_{cell}° and ΔG° :

At equilibrium

$$E_{cell}^{\circ} = \frac{2.303RT}{nF} \log K_c \quad \dots(1)$$

$$\Delta G^{\circ} = -2.303RT \log K_c \quad \dots(2)$$

From equation (1) and (2)

$$E_{cell}^{\circ} = \frac{-\Delta G^{\circ}}{nF}$$

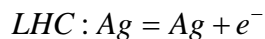
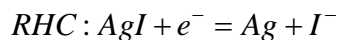
$$\Delta G^{\circ} = -nF E_{cell}^{\circ}$$

Solubility product :

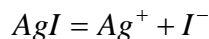
To measure the solubility product of silver iodide at 298 K.



The half-cell reactions are



The cell reaction is



The cell potential is given as

$$E_{cell} = E_{cell}^\circ - \frac{RT}{F} \ln [Ag^+][I^-]$$

At equilibrium, we will have

$$\frac{RT}{F} \ln K_{sp}^\circ (AgI) = E_{cell}^\circ = E^\circ (I^- | AgI | Ag) - E^\circ (Ag^+ | Ag)$$

At 298 K, we have

$$\log K_{sp}^\circ (AgI) = \frac{E_{cell}^\circ}{(2.303RT / F)} = \frac{(-0.151V) - (0.799V)}{0.05913V} = \frac{-0.950V}{0.05913V}$$

$$\text{Thus, } K_{sp}^\circ (AgI) = 8.58 \times 10^{-17}$$

FARADAY'S LAW OF ELECTROLYSIS :

First law : The amount of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolytic solution.

$$\therefore W \propto q \quad W = \text{mass of substance deposited or liberated in gm.}$$

$$W = Z \times q \quad I = \text{current in ampere 'A'}$$

t = time in second

$$W = \frac{E}{F} \times I \times t$$

Z = electrochemical equivalent (The electrochemical equivalent of a chemical element is the mass of that element (in grams) transported by 1 coulomb of electric charge)

E = equivalent mass

$$\therefore q = I \times t$$

M = atomic or molecular mass

n = total change in oxidation state for one mole of reactant

F = faraday's constant (96500 C mol⁻¹)

Second law : If the same quantity of electricity is passed through different electrolytes, the amount of different substance deposited or dissolved are proportional to their chemical equivalent masses.

$$\therefore W \propto E \qquad E = \frac{M}{n}$$

M = atomic or molecular mass

n = change in oxidation state

$$\boxed{\frac{W_A}{W_B} = \frac{E_A}{E_B}}$$

5. A current of 4.0 amperes deposits 0.8 g of sodium when passed through molten NaCl for 20 minutes. The electrochemical equivalent of sodium is **[JNU-2013]**

- (a) 1.0×10^{-2} g/C (b) 2.5×10^{-1} g/C (c) 4.16×10^{-4} g/C (d) 1.67×10^{-4} g/C

Soln. : $I = 4.0$ A

$$W_{Na} = 0.8 \text{ g}$$

$$t = 20 \text{ minutes}$$

$$= 1200 \text{ seconds}$$

Electrochemical equivalent (Z) = ?

$$\therefore w = Z \times q$$

$$\Rightarrow w = Z \times I \times t \Rightarrow 0.8 = Z \times 4 \times 1200$$

$$\Rightarrow Z = \frac{0.8}{4 \times 1200} = 1.67 \times 10^{-4} \text{ g/c}$$

Correct option (d)

Ohm's law :

$$V = IR$$

$$\Rightarrow R = \frac{V}{I} = \frac{\text{Work per unit charge}}{\text{Current}}$$

Resistance (R) : Obstruction in the flow of charge is called resistance. Unit of resistance is ohm.

Conductance (G) : The ease with which current flows is called conductance. It is reciprocal of resistance. Unit of conductance is mho or Ω^{-1} or S.

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

Current (I) : Charge flowing per unit time, unit of current is ampere (A).

$$\Rightarrow I = \frac{q}{t}$$

Resistivity or specific resistance (ρ) : Resistivity is defined as the resistance offered by 1 cm³ of the solution.

$$R \propto l \quad l \rightarrow \text{length of wire}$$

$$\propto \frac{1}{a} \quad a \rightarrow \text{cross sectional area of wire.}$$

$$R \rightarrow \text{resistance}$$

$$\Rightarrow R \propto \frac{l}{a} \quad \rho \rightarrow \text{Resistivity}$$

$$\boxed{R = \rho \frac{l}{a}} \quad \Rightarrow \rho = R \frac{a}{l} \text{ ohm cm}$$

Conductivity or specific conductance (κ) : Conductivity is defined as the conductance offered by 1 cm³ of the solution. It is reciprocal of resistivity.

$$\therefore \kappa = \frac{1}{\rho} S \text{ cm}^{-1}$$

Cell constant (G^*) : It is defined as the ratio of the length (l) between the electrodes and their area of cross section (a).

$$G^* = \frac{l}{a} \text{ cm}^{-1}$$

Molar conductivity (Λ_m) : Molar conductivity of a solution at a dilution 'V' is the conductance of all the ions produced by dissolving 1 mole of electrolyte in 'V' cm³ of the solution when the electrodes are 1 cm apart and area of the electrodes is so large that whole of the solution is contained between them.

$$\Lambda_m = \frac{\kappa \times 1000}{C_M}$$

$C_M \rightarrow$ Molarity of solution, $\kappa \rightarrow$ Specific conductivity

Unit of molar conductivity (Λ_m) is $S \text{ cm}^2 \text{ mol}^{-1}$.

Equivalent conductivity (Λ_{eq}) : Equivalent conductance of an electrolyte is defined as the conductance of a volume of solution containing one equivalent weight of dissolved substance when placed between two parallel electrodes 1 cm apart and large enough to contain between them all of the solution.

$$\Lambda_{eq} = \frac{\kappa \times 1000}{C_N}$$

$C_N \rightarrow$ Normality of solution

$\kappa \rightarrow$ Specific conductivity

$v \rightarrow$ Volume of solution in 'cm³' containing one gram equivalent of the electrolyte

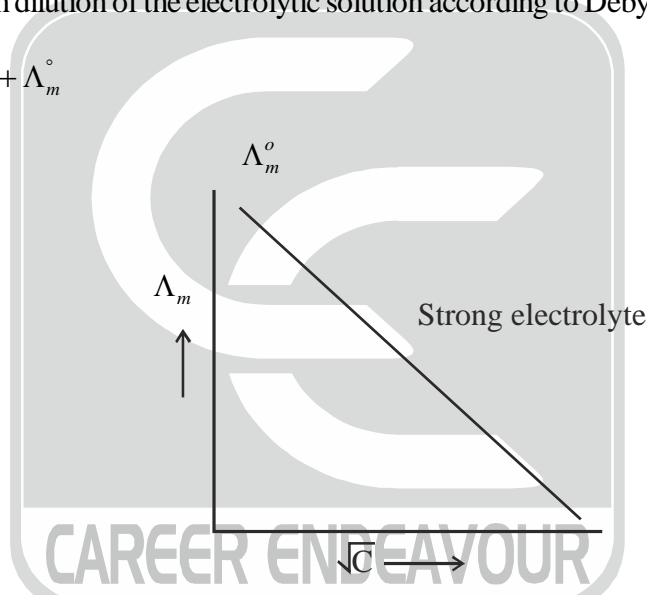
Variation of conductance (G), conductivity (κ) and molar conductivity (Λ_m) with dilution :

- Conductance of a solution depends on the number of ions in the solution and their mobility. Strong electrolytes are completely dissociated in solution and so the number of ions in the solution remains constant. When concentration is higher there are strong inter-ionic attractions due to which the mobility of ions is less. But on dilution these inter-ionic attractions decrease hence the ions can move more freely, which increases the conductance on dilution.
- On dilution number of ions present per cm^3 of the solution decrease hence specific conductivity (κ) decreases with dilution.
- On dilution concentration of the electrolytic solution decrease hence molar conductivity increase on dilution.

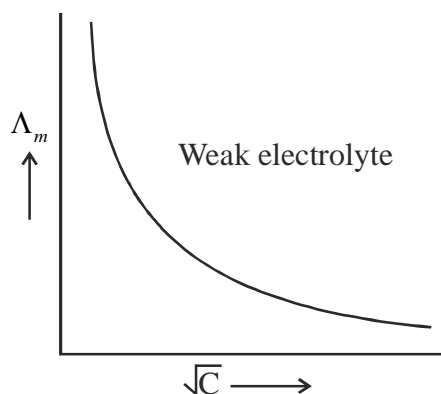
$$\therefore \Lambda_m = \frac{\kappa}{C_M} \Rightarrow \Lambda_m \propto \frac{1}{C_M}$$

Calculation of maximum molar conductance (Λ_m° or Λ_m^∞) : For strong electrolyte molar conductance increases linearly with dilution of the electrolytic solution according to Debye-Huckel equation.

$$\Lambda_m = -b\sqrt{c} + \Lambda_m^\circ$$

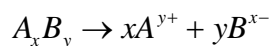


For weak electrolyte : In case of weak electrolyte, they do not get completely dissociated. Since on dilution the degree of dissociation (α_d) increase, hence on dilution, more number of ions are produced, due to which the conductance of the solution increase rapidly on dilution for weak electrolyte.



Kohlrausch's law of independent migration of ions : At infinite dilution when the dissociation of electrolyte is completed, each ion starts moving independent of each other and hence each ion contributes a definite proportion towards the molar conductance of electrolyte at infinite dilution.

Limiting molar conductivity at infinite dilution of A_xB_y .



$$\Lambda_m^\circ = x \times \lambda_{A^{y+}}^\circ + y \times \lambda_{B^{x-}}^\circ$$

Λ_m° = Limiting molar conductivity of electrolyte at infinite dilution.

$\lambda_{A^{y+}}^\circ$ = Limiting ionic conductivity for cation at infinite dilution.

$\lambda_{B^{x-}}^\circ$ = Limiting ionic conductivity for anion at infinite dilution.

Applications of Kohlrausch's law :

- (i) With the help of Kohlrausch's law we can determine the limiting molar conductance at infinite dilution (Λ_m°) for weak electrolyte by using limiting molar conductance at infinite dilution (Λ_m°) for strong electrolytes.
- (ii) Used to calculate degree of dissociation for weak electrolyte.

$$\therefore \alpha_d = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$

Λ_m° = molar conductivity of electrolyte at infinite dilution

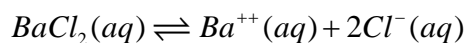
Λ_m^c = molar conductivity of electrolyte at concentration C.

α_d = degree of dissociation.

- (iii) Kohlrausch's law can be used to determine dissociation constant for acid (K_a) or base (K_b).

6. The ionic conductances of Ba^{++} and Cl^- are respectively 127 and 76 $\text{ohm}^{-1}\text{cm}^2$ at infinite dilution. The equivalent conductance (in $\text{ohm}^{-1}\text{cm}^2$) of $BaCl_2$ at infinite dilution will be [JNU-2003]
- (a) 203 (b) 279 (c) 101.5 (d) 139.5

Soln. : Dissociation reaction of $BaCl_2$ is



$$\lambda_{Ba^{++}}^0 = 127 \text{ ohm}^{-1}\text{cm}^2$$

$$\lambda_{Cl^-}^0 = 76 \text{ ohm}^{-1}\text{cm}^2$$

The equivalent conductance (in $\text{ohm}^{-1}\text{cm}^2$) of $BaCl_2$ at infinite dilution is

$$\Lambda_{BaCl_2}^0 = \lambda_{Ba^{++}}^0 + 2\lambda_{Cl^-}^0$$

$$= 127 + 2 \times 76 = 127 + 152 = 279 \text{ ohm}^{-1}\text{cm}^2$$

Correct option (b)

7. The molar conductance at infinite dilution of Ag^+ is $61.92 \times 10^{-4} \text{ S} \cdot \text{mol}^{-1} \cdot \text{m}^2$ at 25°C . The ionic mobility of Ag^+ ion will be [JNU-2007]
- (a) 6.192 (b) 6.4×10^{-8} (c) 6.192×10^{-4} (d) 3.2×10^{-4}

Soln. : $\lambda_{(\text{Ag}^+)}^\infty = 61.92 \times 10^{-4} \text{ s mol}^{-1} \text{ m}^2$

$$u^\infty = ?$$

\therefore Ionic mobility at infinite dilution.

$$u^\infty = \frac{\lambda^\infty}{Z - F} = \frac{61.92 \times 10^{-4}}{1 - 96500} = 6.4 \times 10^{-8} \quad [Z(\text{Ag}^+) = 1]$$

Correct option (b)

8. At 25°C , the specific conductance of a 0.01 M aqueous solution of acetic acid is 0.163 mS m^{-1} . The molar conductance at infinite dilution is $390 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$. What is the degree of dissociation of the acid? [JNU-2013]
- (a) 0.017 (b) 0.0417 (c) 0.174 (d) 0.163

Soln. : $\kappa = 0.0163 \text{ S m}^{-1}$

$$c = 0.01 \text{ M} = 10 \text{ mol m}^{-3}$$

$$\Lambda^c = \frac{\kappa}{c} = \frac{0.0163}{10} = 163 \times 10^{-5} \text{ S m}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ = 390 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$\text{Degree of dissociation} = \frac{\text{Molar conductance at concentration } C}{\text{Molar conductance at infinite dilution}}$$

$$\alpha_a = \frac{\Lambda^c}{\Lambda^\circ} = \frac{163 \times 10^{-5}}{390 \times 10^{-4}} = 0.0417$$

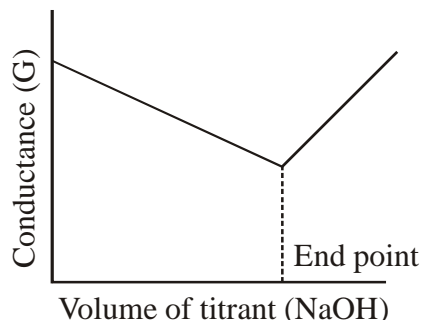
Correct option (b)

CONDUCTOMETRIC TITRATION

1. Strong Acid v/s Strong Base : $HCl + NaOH \rightarrow NaCl + H_2O$

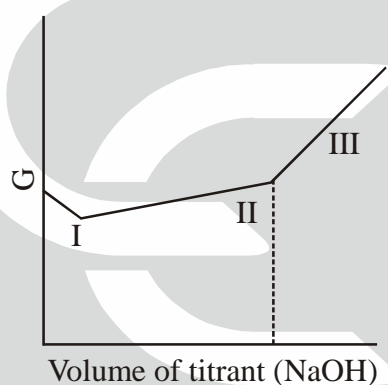
$\therefore HCl$ (analyte) v/s $NaOH$ (titrant) -

Here H^+ is replaced by Na^+ . So conductivity decreases.



(As HCl is converting to $NaCl$; Conductance decrease because HCl has higher conductance than $NaCl$ because H^+ has abnormally higher conductance than Na^+). But soon the conductance starts increasing by $NaOH$ having OH^- ions of higher conductance.

2. Weak Acid v/s Strong Base : $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ (strong electrolyte)

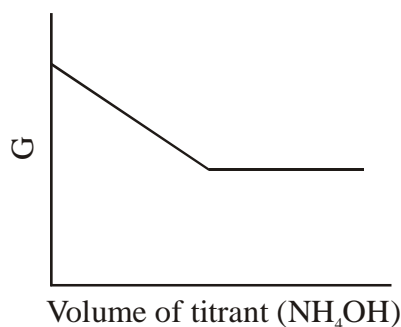


Part I : The small dip in part I is due to replacement of already present H^+ ion; by Na^+ ion.

Part II : The gradual increase in part II is due to the Replacement of acetic acid (weak electrolyte) by CH_3COONa (strong electrolyte).

Part III : The sharp increase in part III is due to addition of strong electrolyte $NaOH$ which has highly conducting OH^- ion.

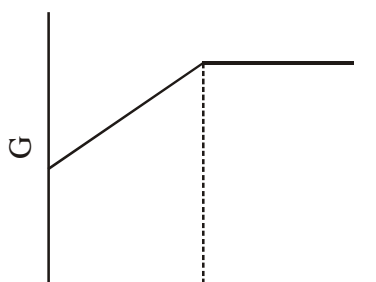
3. Strong acid v/s weak base : $HCl + NH_4OH \rightarrow NH_4Cl + H_2O$ (strong electrolyte)



After the end point; on adding NH_4OH ; the conductance remains almost constant because :

- NH_4OH is a weak electrolyte so it dissociates very less.
- The dissociation of NH_4OH is further suppressed by the common ion effect of NH_4^+ ion from NH_4Cl .

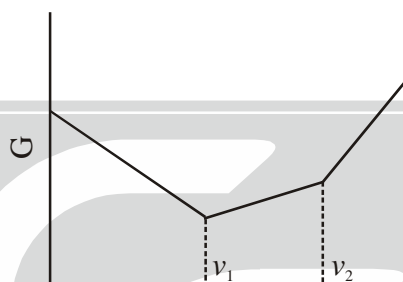
4. **Weak acid v/s weak base :** $CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$
 (weak acid) (Strong electrolyte)
 weak electrolyte



Volume of titrant (NH_4OH)

The reason for constant give after end point is same as the previous one.

5. **Strong acid + weak acid v/s strong base :** $HCl + CH_3COOH$ v/s $NaOH$



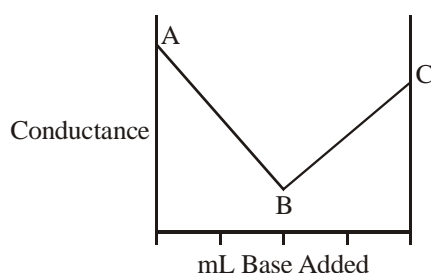
Volume of titrant ($NaOH$)

Volume (v_1) represent amount of $NaOH$ required to neutralise HCl only. Volume (v_2) represents the amount of $NaOH$ required to neutralise HCl as well $HCl + CH_3COOH$.

Volume ($v_2 - v_1$) represents. The amount of $NaOH$ required to neutralise acetic acid only.

- Weak acid v/s weak base titration can be performed with help of conductometric titration. But they cannot be performed in case of indicator based titration.
- Conductometric titration have high sensitivity (more accuracy) and it needs no indicator.

9. A sample of HCl is titrated with a standard solution of $NaOH$ and the reaction followed by monitoring the conductance of the solution. Which of the following statements based on this data is NOT TRUE :



- (a) The measured conductance increases after B because the overall concentration of ions increases as $NaOH$ is added after this point [TIFR-2015]
- (b) Point B is the End Point of the titration
- (c) H_3O^+ has a lower conductance than Na^+
- (d) $|\text{slope AB}| > |\text{slope BC}|$

Soln. : H_3O^+ has higher conductance than Na^+ .

Correct option (c)

PRACTICE SET

Multiple Choice Questions (MCQ)

- The unit of molar conductivity is :
 - $\text{ohm}^{-1}\text{cm}^{-1}$
 - $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
 - $\text{ohm cm}^{-2}\text{mol}^{-1}$
 - $\text{ohm cm}^2\text{mol}^{-1}$
- Pure water does not conduct electricity because of
 - is neutral
 - equal amount of positive and negative charge
 - is almost unionised
 - is readily decomposed
- The conductivity of a strong electrolyte
 - decrease on dilution
 - does not change considerably on dilution
 - increase on dilution
 - depends on density
- Doubling all the coefficient in the equation for a cell reaction
 - doubles both E° and ΔG°
 - double ΔG° , but does not change E°
 - double E° , but does not change ΔG°
 - does not change E° and ΔG°
- Given the standard reduction potentials at 25°C $E^\circ(A^+, A) = 0.7\text{V}$ and $E^\circ(B^+, B) = 0.8\text{V}$. Predict the spontaneous reaction at 25°C from the following
 - $A + B^+ \rightarrow A^+ + B$
 - $A^+ + B^+ \rightarrow A^{2+} + B$
 - $A^+ + B^+ \rightarrow A + B^{2+}$
 - $A^+ + B \rightarrow A + B^+$
- Number of moles of $K_2Cr_2O_7$ reduced by one mole of Pb
 - 6
 - $\frac{1}{6}$
 - $\frac{1}{3}$
 - 3
- The quantity of electricity required to deposit 190.62 gm of copper is :
 - 3 Faraday
 - 6 Coulombs
 - 1 Ampere
 - 6 Faraday
- The standard electrode potential of three metals A, B and C are -1.32V, 0.55V and -2.50V respectively. The reducing power of these metals follow the order
 - $C > A > B$
 - $B > A > C$
 - $A > B > C$
 - $A > C > B$
- Arrange the following in the order of their decreasing electrode potential: F, O, Ca and Mg.
 - O, Ca, Mg, F
 - F, O, Ca, Mg
 - O, Ca, F, Mg
 - Mg, Ca, O, F
- The standard potential of the cell, $Zn / Zn^{2+} || Ag^+ / Ag$ ($E^\circ_{Zn^{2+}/Zn} = -0.76\text{V}$ and $E^\circ_{Ag^+/Ag} = 0.799\text{V}$) is:
 - 1.559V
 - 1.559V
 - 0.039V
 - 2.358V

ANSWER KEY**PART-A [Multiple Choice Questions]**

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (b) | 2. (c) | 3. (c) | 4. (b) | 5. (a) |
| 6. (c) | 7. (d) | 8. (a) | 9. (b) | 10. (a) |

Part-B [Multiple selective questions]

- | | | | |
|------------|------------|------------|---------------|
| 11. (a, b) | 12. (a, c) | 13. (b, c) | 14. (a, b, d) |
| 15. (b, c) | | | |

PART-C [Numerical Answer Type]

- | | | |
|-------------|-------------|-------------|
| 16. (1.096) | 17. (76.65) | 18. (-0.91) |
| 19. (2.5) | 20. (395.5) | |

