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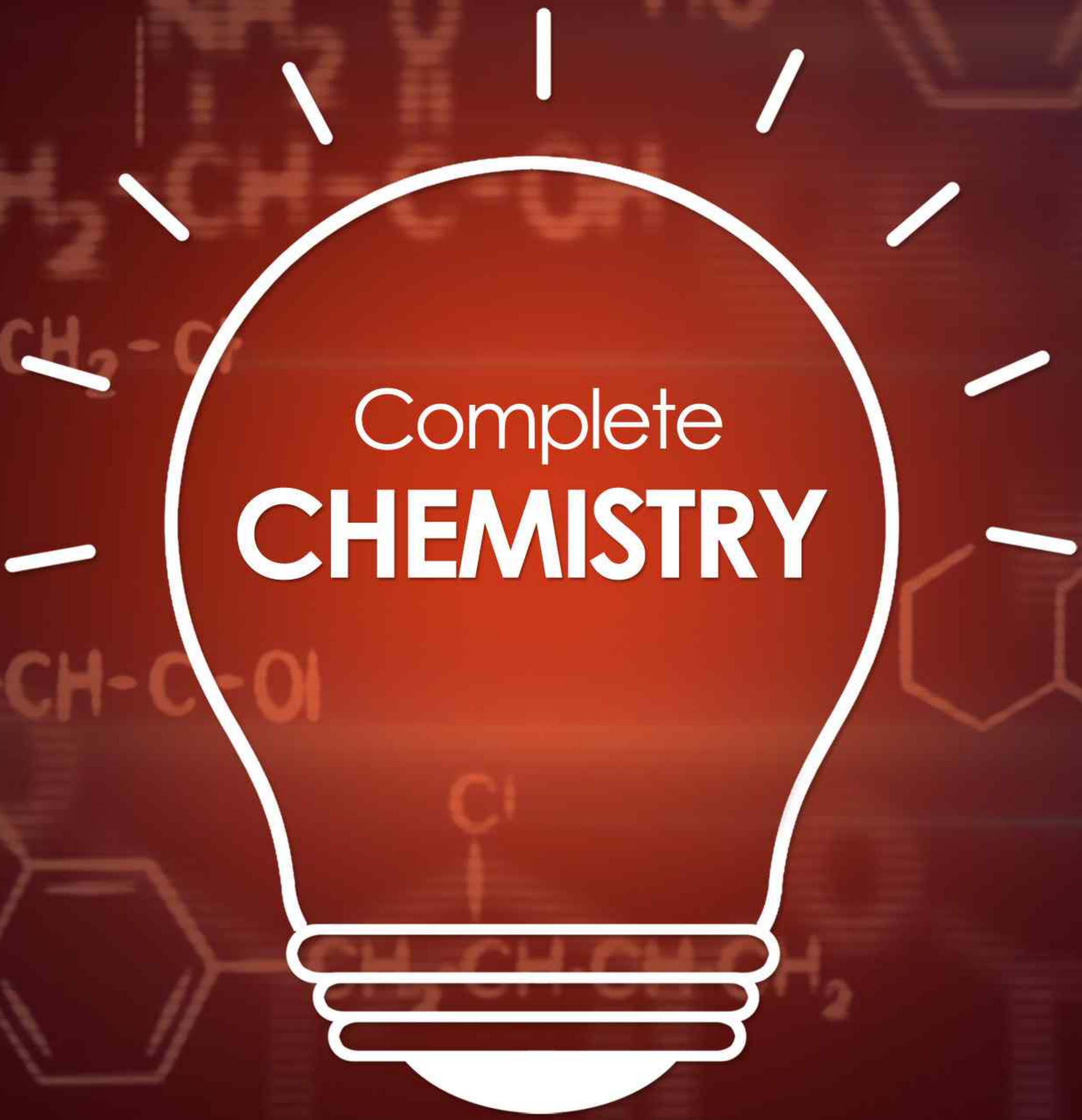


Complete
CHEMISTRY

IIT-JEE ·NEET ·CBSE eBOOKS

CLASS 11&12th

CLASS 12th

Electrochemistry

01. Electrochemical Cells

An electrochemical cell consists of two electrodes (metallic conductors)in contact with an electrolyte (an ionic conductor).

An electrode and its electrolyte comprise an Electrode Compartment.

Electrochemical Cells can be classified as:

(a) Electrolytic cells in which a non-spontaneous reaction is driven by an external source of current.

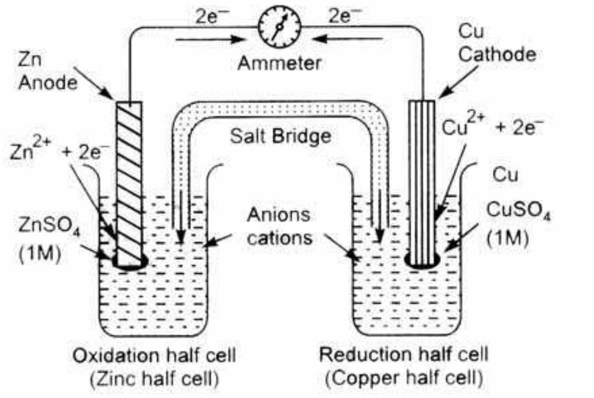
(b) Galvanic cells which produce electricity as a result of a spontaneous cell reaction.

An electrochemical cell is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses of generates an electric current.

A voltaic of galvanic cell is an electrochemical cell in which a spontaneous reaction generates an electric current.

A voltaic cell consists of two half-cells that are electrically connected. Each half cell is the portion of an electrochemical cell in which a half cell reaction take place.

In a voltaic cell, two half-cells are connected in such a way that electrons flow from one metal electrode to another through an external circuit, and ions flow from one half-cell to another through an internal cell connection. Figure given below illustrates an atomic view of a voltaic cell consisting of a zinc electrode and a copper electrode. As long as there is an external circuit, electrons can flow through it from one electrode to another. Because zinc tends to lose electrons more readily than copper, zinc atoms in the zinc electrode lose electrons to produce zinc ions. These electrons flow through the external circuit to the copper electrode, where they react with the copper ions to produce copper metal, and an electric current flows through the external circuit.



Daniell cell

The two half-cells of a voltaic cell are connected by a salt bridge. A salt bridge is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell; the salt bridge allows the flow of ions but prevents the mixing of the different solutions that would allow direct reaction of the cell reactants. The half-cells are connected externally so that an electric current flows.

The two half-cell reactions, as noted earlier, are

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad \text{(oxidation half cell-reaction)}$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad \text{(reduction half cell-reaction)}$$

Note that the sum of the two half cell-reaction

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

The net reaction that occurs in the voltaic cell, it is called the cell reaction.

NOTE ☞ (i) The salt-bridge contains solution of strong ionic salts like NaCl, $NaNO_3$, KNO_3, KCl etc., which is soaked in a colloidal solution of agar-agar gel which permits the movement of ions of salts only.

(ii) Salt bridge carries whole of the current across the boundary ; more over the K^+ and NO_3^- ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions completes the electrical circuit & permits the ions to migrate.

(iii) It maintains the electrical neutrality of the solutions in the two half-cells. In the absence of salt bridge, a reverse potential difference is set up in the two half-cells which results in breaking the continuous supply of voltage.

02. Representation of a cell (IUPAC Conventions)

Let us illustrate the convention taking the example of Daniel cell.

(i) Anodic half cell is written on left and cathodic half cell on right hand side.

$$Zn(s) \mid ZnSO_4(sol) \parallel CuSO_4(sol) \mid Cu(s)$$

(ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge of any type of porous partition.

(iii) EMF (electromotive force) may be written on the right hand side of the cell.

(iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

(v) Inert electrodes are represented in the bracket

$$Zn \mid ZnSO_4 \parallel H^+ \mid H_2,\ (Pt)$$

Example Write cell reaction of the following cells:

(i) $Ag \mid Ag^+(aq) \parallel Cu^{2+}(aq) \mid Cu$

(ii) $Pt \mid H_2 \mid H^+(aq) \parallel Cd^{2+}(aq) \mid Cd$

03. Electrode Potential

When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential.

The potential difference is established due to the formation of electrical double layer at the interface os metal and the solution. The development of negative charge (as on zinc plate) of positive charge (as on copper plate) can be explained in the following manner.

Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types :

Oxidation potential : When electrode is negatively charged with respect to solution, i.e., it acts as anode. Oxidation occurs.

$$M \longrightarrow Mn^{+} + ne^{-}$$

Reduction potential : When electrode is positively charged with respect to solution i.e., it acts as cathode. Reduction occurs.

$$Mn^{+} + ne^{-} \longrightarrow M$$

It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally.

04. Concept of Electromotive Force (EMF) of A Cell

Electron flows from anode to cathode in external circuit due to a pushing effect called or electromotive force (e.m.f.). EMF is called as cell potential. Unit of e.m.f. of cell is volt. EMF of cell may be calculated as:

E_{cell} = Reduction potential of cathode − Reduction potential of anode
Similarly, standard e.m.f. of the cell (E°) may be calculated as
E°_{cell} = Standard reduction potential of cathode − Standard reduction potential of anode

$$\begin{aligned} E_{cell} &= \text{R.P.(Cathode)} - \text{R.P.(Anode)} \\ &= \text{R.P.(Cathode)} - \text{O.P.(Anode)} \end{aligned}$$

Example For the cell reaction $2Ce^{4+} + Co \longrightarrow 2Ce^{3+} + Co^{2+}$
E°_{cell} is 1.89V. If $E^{o}_{Co^{2+}|Co}$ is−0.28V, what is the value of $E^{o}_{Co^{4+}|Ce^{3+}}$?

Solution

$$E^\circ_{cell} = E^{o}_{Co^{4+}/Ce^{3+}} - E^{o}_{Co^{2+}/Co}$$

$$1.89 = E^{o}_{Co^{4+}/Ce^{3+}} - (-.28)$$

$$E^{o}_{Co^{4+}/Ce^{3+}} = 1.61V$$

05. Relationship Between ΔG and Electrode Potential

Let n, Faraday charge is taken out from a cell of e.m.f.(E), than electrical work done by the cell my be calculated as,
Work done = Charge × Potential = nFE
From thermodynamics, we know that decrease in Gibbs free energy of a system is a measure of reversible or maximum obtainable work by the system
$\therefore\ \Delta G = -nFE$
Under standard state $\Delta G^{o} = -nFE^{o}$ (i)

(i) From thermodynamics we know, ΔG = negative for spontaneous process. Thus from eq.(i) it is clear that the EMF should be+be for a cell process to be feasible or spontaneous.
(ii) When ΔG = positive, E = negative and the cell process will be non spontaneous.