

Unit –I Electrochemistry

(A) Galvanic cells, irreversible & reversible cells, e.m.f. of cell & its measurement, relation between electrical energy and chemical energy, calculation of thermodynamic quantities of a cell reactions (ΔG , ΔH & ΔS & equilibrium constant)

(B) Types of reversible electrodes : metal-metal ion electrode, gas electrode, metal insoluble salt anion electrode, redox electrodes, amalgam electrode, Nernst equation, calculation of cell e.m.f. from single electrode potential, reference electrodes, standard electrode potential, concentration cells with & without transference, liquid-junction potential, salt bridge & its functions. Applications of e.m.f. measurements in : (i) pH- determination using hydrogen electrode, quinhydrone electrode & glass electrode (ii) Potentiometric titration (Acid –Base and Redox titrations). Numericals Problems.

Electrochemical Cell & Galvanic Cell: Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes, which are joined by a salt bridge.

Electrochemical cell is of two types. (a) Electrolytic Cell (b) Galvanic Cell or Voltaic Cell

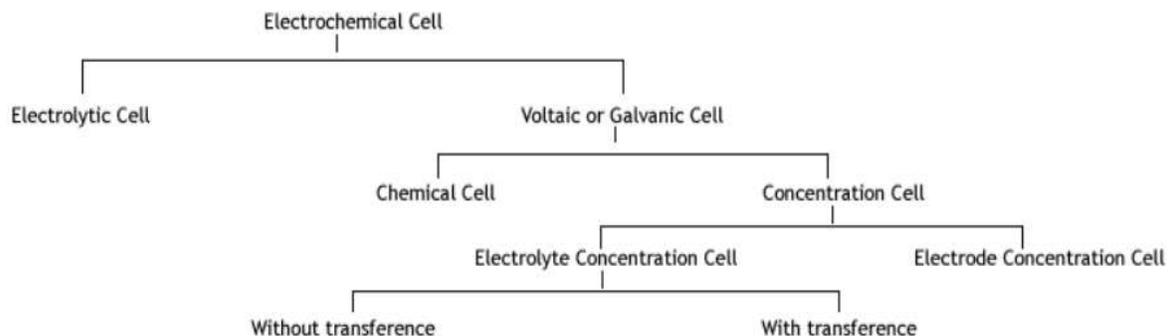
Electrolytic Cell: It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

Galvanic Cell: The device used to convert the chemical energy produced on a redox reaction into electrical energy is called an electrochemical cell or simply a chemical cell. These are also called galvanic cells or voltaic cell after the names of Luigi Galvanic and Alessandro Volta who were first to perform experiments on the conversion of chemical energy into electrical energy.

In electrochemical cell, a spontaneous redox reaction is carried out in an indirect manner and the decrease in free energy during chemical reaction appears as electrical energy. An indirect redox reaction is such that reduction and oxidation processes are carried out in two separate vessels called half-cells.

An electrode, i.e., a metallic conductor in contact with an electrolyte, develops an electrical potential called the electrode potential. In a galvanic or voltaic cell, the e.m.f. of the cell is the algebraic sum of the electrode potentials of the two electrodes with universally agreed sign conventions. Each of the electrodes in contact with the electrolyte solution is also called a half cell.

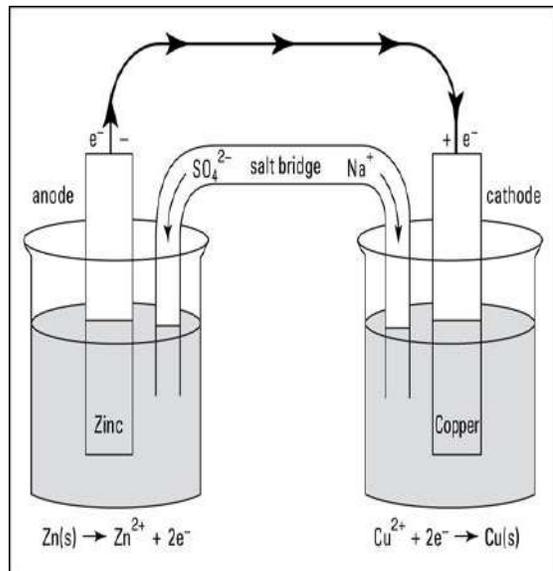
As a galvanic cell functions, i.e., delivers current, at the two electrodes spontaneous chemical reactions take place, which when combined gives the overall chemical reaction called the cell reaction. It is the energy of this chemical reaction that generates the e.m.f. of the cell. In such cases, the cell is called a chemical cell. In some cells there is no overall chemical reaction but the e.m.f. is generated because of the difference in the concentrations of either the electrolytes or the electrodes.



Daniel Cell:

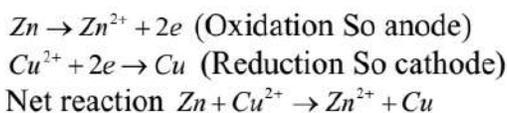
It consists of two half-cells. The left hand half-cell contains a zinc metal electrode dipped in ZnSO₄ solution. The half-cell on the right hand side consists of Cu metal electrode in a solution of CuSO₄. A salt bridge that prevents the mechanical mixing of the solution joins the half-cells. When the zinc and copper electrodes are joined by a wire the following observations are made.

- There is flow of electric current through the external circuit.
- The Zn rod loses its mass while copper rod gains in the mass.
- The concentration of ZnSO₄ solution increases while the concentration of CuSO₄ solution decreases.
- The solutions in both the compartments remain electrically neutral.



During the passage of electric current through external circuit, electrons flow from zinc electrode to the copper electrode. At the zinc electrode, zinc metal is oxidized to zinc ions, which go into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode where they are used in the reduction of Cu²⁺ ions to metallic copper which is deposited on the electrode.

Cell Reaction



At the zinc rod, oxidation occurs. So it is the anode of the cell and negatively charged.

Electrode Sign: The sign of the anode and cathode in the voltaic or galvanic cells are opposite to those in the electrolytic cells.

Reversible and irreversible cells : A cell is said to be reversible if the following two conditions are fulfilled

- The chemical reaction of the cell does not proceed further when an exactly equal external e.m.f. is applied.

(ii) Chemical reaction of the cell is reversed and current flows in opposite direction when external e.m.f. is slightly higher than that of cell.

Any other cell, which does not obey the above two conditions, is termed as irreversible cell.

Cell Potential or E.M.F. of a cell

Every galvanic or voltaic cell is made up of two half-cells, the oxidation half cell (anode) and the reduction half-cell (cathode). One of the electrodes must have a higher electrode potential (higher tendency to lose electrons) than the other electrode. As a result of this potential difference, the electrons flow from an electrode at a higher potential to the electrode at a lower potential.

The difference between the electrode potentials of the two half-cells is known as electromotive force (e.m.f.) of the cell or cell potential or cell voltage.

The e.m.f. of the cell or cell potential can be calculated from the values of electrode potential of the two half cells constituting the cell.

(i) When oxidation potential of anode and cathode are taken into account

$$E^0_{cell} = E^0_{anode} - E^0_{cathode}$$

(ii) When reduction potential of cathode and anode are taken into account

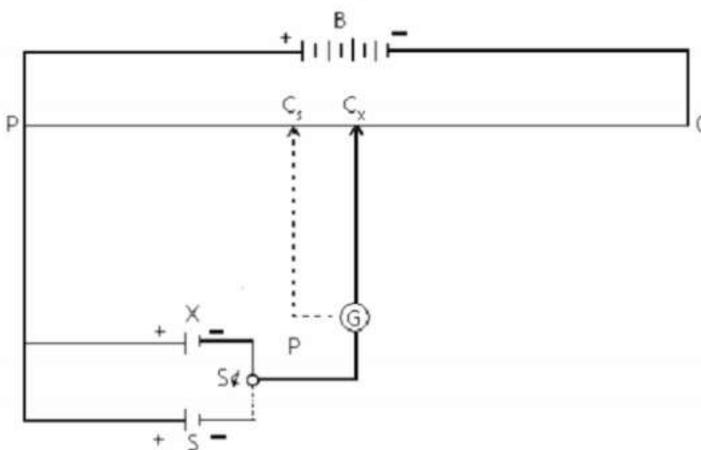
$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

Measurement e.m.f. of cell

Measurement of the e.m.f. of a reversible cell requires that during measurement only a very negligibly small current is drawn from the cell so that the electrode systems and the cell as a whole do not depart to any significant extent from their respective equilibrium states under the conditions of measurement. Obviously the reversible cell e.m.f (ideally, the open circuit e.m.f., i.e., when no current is drawn from the cell) cannot be measured by a voltmeter that will draw an appreciable current disturbing the equilibrium of the processes occurring in the cell. In order to avoid this, the measurement of the thermodynamic value (equilibrium value) of the e.m.f. of a galvanic cell is made using a potentiometer.

PQ is nothing but a long wire (Fig.) of considerably high resistance. The resistance per unit length of the wire is accurately known at the experimental temperature and does not vary to any significant extent due to slight changes in temperature. B represents a battery of cells (storage cells, usually) of a fixed e.m.f. joined across PQ. X is the cell, the e.m.f. of which is to be determined. S is a standard cell, the e.m.f. of which is not only accurately reproducible but

remains constant over considerable period of time and has a low temperature coefficient. S' is a two way switch by which either the cell X or the cell S can be brought into the circuit. The e.m.f. of B is opposed by either X or S depending on whether X or S is brought into the circuit, through the galvanometer G to a sliding contact C_x or C_s on PQ. The contact points, C_x or C_s, is adjusted to a null, i.e., no current flows through the galvanometer. This is very nearly as good as an open circuit. At the null point, the fall of potential (E_x) between P and C_x (when X is in the circuit) due to B is accurately compensated by the e.m.f. of the cell, X, under study. Likewise when S is brought into the circuit, the fall of potential (E_s) between P and C_s due to B is accurately compensated by the e.m.f. of the standard cell, S.



So

$E_x / E_s = (\text{Resistance of the part of PQ between P and } C_x / \text{Resistance of the part of PQ between P and } C_s)$

$= (\text{The length } PC_x / \text{The length } PC_s)$

Since the e.m.f., E_s , of the standard cell and the resistance per unit length of the potentiometer wire (PQ) are accurately known, E_x can be calculated. The method as described above is known as Poggendorf's compensation method.

Relation between electrical energy and chemical energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in **coulombs (C)**, an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in **amperes (A)**.

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1

mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday. ($1F = 96500 \text{ C}$)

$$\begin{aligned} F &= (1.602 \times 10^{-19} \text{ C})(6.022 \times 10^{23} \text{ J/mol e}^-) \\ &= 9.648 \times 10^4 \text{ C/mol e}^- \\ &\approx 96,485 \text{ J/(V} \cdot \text{mole}^-) = 96500 \text{ C.} \end{aligned}$$

he total charge transferred from the reductant to the oxidant is therefore nF , where n is the number of moles of electrons.

The maximum amount of work that can be produced by an electrochemical cell (w_{\max}) is equal to the product of the cell potential (E_{cell}^0) and the total charge transferred during the reaction (nF):

$$w_{\max} = n \cdot F \cdot E_{\text{cell}}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{\max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG ; this relationship is as follows:

$$\Delta G = -n \cdot F \cdot E_{\text{cell}}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E_{cell}^0 , consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E_{cell}^0 is as follows:

$$\Delta G^\circ = -n \cdot F \cdot E_{\text{cell}}^0$$

A spontaneous redox reaction is characterized by a negative value of ΔG° , which corresponds to a positive value of E_{cell}^0 .

Calculation of thermodynamic quantities of cell reactions (ΔG , ΔH & ΔS & equilibrium constant)

The relationship between the potential of an electrochemical cell and ΔG is given as

$$\Delta G = -n \cdot F \cdot E$$

where n is the number of faradays of electricity delivered by the cell. E is positive by convention and being an intensive quantity, does not depend on how the stoichiometric equation for the spontaneous overall cell reaction is written. But ΔG being an extensive quantity does depend on

how the overall cell reaction is written. The same is true about the corresponding enthalpy and the entropy changes (ΔH and ΔS). These thermodynamic quantities are usually expressed in kJ mol^{-1} (ΔS in $\text{J K}^{-1} \text{mol}^{-1}$) when these become intensive quantities.

From thermo dynamics we have,

$$\Delta S = - \left[\frac{\partial \Delta G}{\partial T} \right]_p$$

$$\text{or } \Delta S = n.F \left[\frac{\partial E}{\partial T} \right]_p$$

$$\text{since } -\Delta G = n.F.E$$

The temperature coefficient of the cell e.m.f., $(\partial E / \partial T)_p$ can be obtained by determining the e.m.f at various temperatures. Again from thermodynamics we have,

$$\Delta G = \Delta H - T\Delta S$$

$$\text{or } -n.F.E = \Delta H - T\Delta S$$

$$\text{or } \Delta H = -n.F.E + T\Delta S$$

$$\Delta H = -n.F.E + T.n.F \left[\frac{\partial E}{\partial T} \right]_p$$

Thus the enthalpy change associated with the overall cell reaction for a reversible cell can be determined from the reversible e.m.f. (E) and the temperature coefficient of the reversible e.m.f. of the cell, .The equilibrium constant is related to standard Gibbs free energy, ΔG^0 (or $-n.F.E^0$).

Hence we get

$$\text{Since } \Delta G^0 = -RT \ln K$$

$$\text{or } -n.F.E^0 = -RT \ln K$$

$$E^0 = - (RT/n.f) \ln K$$

$$\ln K = - \left[\frac{n.F E^0}{RT} \right]$$

The above equation is used to calculate the equilibrium constant of an overall cell reaction at a given temperature from the experimentally determined value of the standard e.m.f. of the cell at the same temperature.

