19CH201 - ENGINEERING CHEMISTRY

UNIT-1 - ELECTROCHEMISTRY

1.8. Measurement of EMF - Electrolytic cell

EMF OF A CELL

Definition

Electromotive force is defined as, "the difference of potential which causes flow of current from one electrode of higher potential to the other electrode of lower potential.

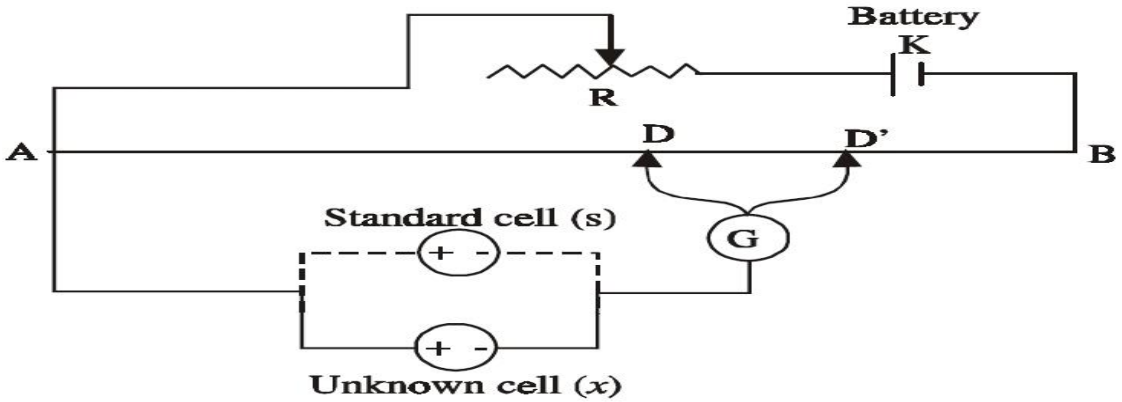
Thus, the emf of a galvanic cell can be calculated using the following relationship.

$$EMF = \left\{\begin{matrix}\text{Standard reduction}\\ \text{potential of right hand}\\ \text{side electrode}\end{matrix}\right\} - \left\{\begin{matrix}\text{Standard reduction}\\ \text{potential of left}\\ \text{hand side electrode}\end{matrix}\right\}$$

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

Measurement of emf of a cell

The potential difference or emf of a cell can be measured on the basis of poggendorff's compensation principle. Here the emf of the cell is just opposed or balanced by an emf of standard cell (external emf), so that no current flows in the circuit.



The potentiometer consists of a uniform wire AB (Fig. 1.8). A storage battery (K) is connected to the ends A and B of the wire through a rheostat (R). The cell of unknown emf (x) is connected in the circuit by connecting its positive pole to A and the negative pole is connected to a sliding contact (D) through a galvanometer G. The sliding contact is freely moved along the wire AB till no current flows through the galvanometer. Then the distance AD is measured. The emf of unknown cell is directly proportional to the distance AD.

$$E_x \propto AD$$

Then the unknown cell (x) is replaced by a standard cell (s) in the circuit. The sliding contact is again moved till there is null deflection in the galvanometer. Then the distance AD′ is measured. The emf of standard cell Es is directly proportional to the distance AD′.

$$E_s \propto AD'$$

Then, the emf of the unknown cell can be calculatedfrom the following equation.

$$\frac{\text{Emf of the unknown cell x}}{\text{Emf of the standard cell s}} = \frac{\text{Length AD}}{\text{Length AD'}}$$

$$\frac{E_x}{E_s} = \frac{AD}{AD'}$$

$$\therefore \text{Emf of the unknown cell} = E_x = \frac{AD}{AD'} \text{ X } E_s$$

Factors affecting emf of a cell

1. Nature of the electrolytes and electrodes.
2. Concentration and composition of the electrolytes.
3. pH and temperature of the solution.

Differences between electrolytic cells and electrochemical cells

Sl. No.	Electrolytic cell	Electrochemical cell
1.	Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
2.	The anode carries positive charge.	The anode carries negative charge.
3.	The cathode carries negative charge.	The cathode carries positive charge.
4.	Here the electrons are supplied to the cell from the external battery. i.e., electrons move in through cathode and comes out from anode.	But, electrons are drawn from the cell. i.e., electrons move from anode to cathode through the external circuit.
5.	Amount of the electricity passed during electrolysis is measured by coulometer.	The e.m.f. produced in the cell is measured by potentiometer.
6.	The extent of chemical reaction occurring at the electrodes is governed by the Faradays's law of electrolysis.	The e.m.f. of the cell depends on the concentration of the electrolytes and the chemical nature of the electrode.

7.

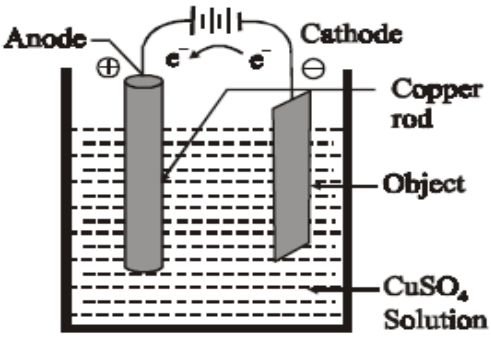


Fig. 1.9 Electrolytic Cell

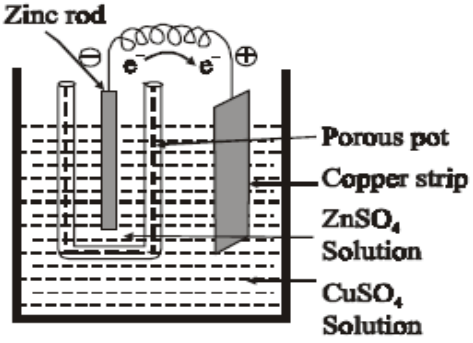


Fig 1.10 Electrochemical Cell