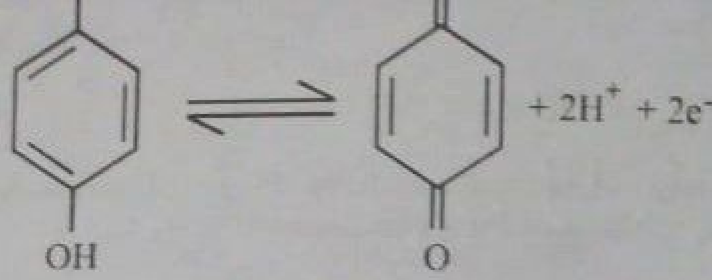

or simply

$$QH_2 \rightleftharpoons Q + 2H^+ + 2e^-$$

10.6. ELECTROMOTIVE FORCE AND ITS MEASUREMENT

When a cell is connected in series with a galvanometer and the circuit is closed, the galvanometer is deflected, indicating that a current is flowing through the circuit. The flow of current from one electrode to the other is evidence for the existence of a potential difference between them. This difference of potential which causes a current to flow from the electrode of higher potential to the one of lower is called the *electromotive force* of the cell. It is abbreviated as emf and is expressed in volts (V).

The most common method of determining the potential difference between any two points in an electric circuit is to connect a voltmeter across the two points. The potential difference or voltage is read then directly from the instrument. A serious objection to the use of voltmeter is that, it draws some current from the cell during measurements. When some current is drawn from the cell reaction products are formed at the electrode surfaces which cause concentration change of the electrolyte around the electrodes. This polarization of the electrodes changes the emf of the cell. Again with appreciable current flow, part of the emf will have to be utilized to overcome the internal resistance of the cell, and hence the potential measured on voltmeter will not be the total cell emf. Hence potential measuring devices like potentiometers which require only small currents are suitable for accurate measurements and other instruments like voltmeter, etc. which draw appreciable currents from the cell are unsuitable for emf measurements.

Potentiometers for emf measurements operate on the *Poggendorff compensation principle*. In this method the unknown emf is opposed by another known emf until the two are equal. Figure 10.3 gives a basic circuit diagam of a direct reading potentiometer. *ab* is the slide wire of uniform cross sectional area having high resistance. A cell W, usually a storage battery of constant emf larger than the emf of the cell to be measured, is connected in series with the resistance across the terminal of resistance wire ab. The cell X of unknown emf is connected to 'a' with poles in the same direction as the cell W. The other terminal of the cell is connected through the galvanometer G to the sliding wire by a double-pole double throw key, D. The position of the terminal is moved along the sliding wire and the rheostat is adjusted until at S' no current flows through the galvanometer. At this point the potential difference between 'a' and S' just balances the emf E_X of the cell X. Next the standard cell S.C. with emf E_S is connected to the sliding wire by means of D. The null point S on the sliding wire is again determined. The fall in potential along aS' is exactly compensated by the emf of the standard cell, E_S. Since the cross sectional areas of the wire is uniform, hence we have

$$\frac{E_X}{E_S} = \frac{\text{Drop of potential from } a \text{ to } S'}{\text{Drop of potential from } a \text{ to } S} = \frac{\text{Length } aS'}{\text{Length } aS}$$

Knowing the emf of S.C., we can calculate the emf of experimental cell X.

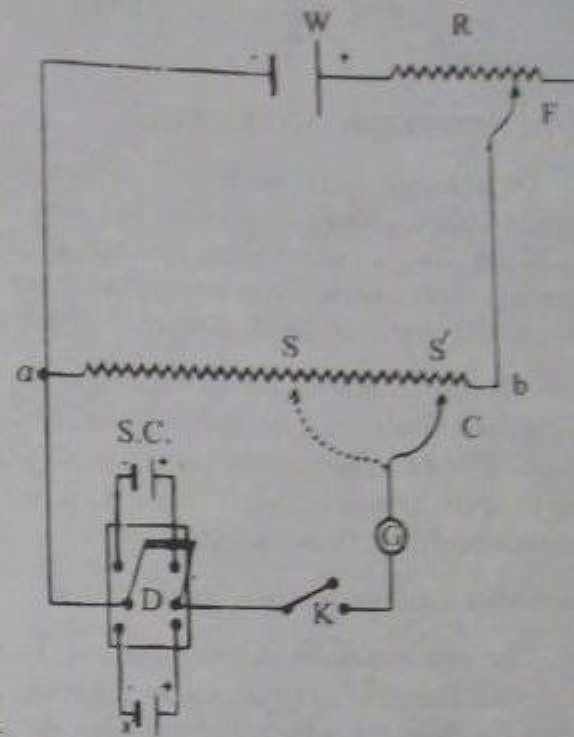

Fig. 10.3. Principle of direct reading potentiometer.

The standard cell should be capable of giving a constant and reproducible emf. The most widely used standard cell is a Weston Cell (Fig. 10.4). It consists of a H-shaped glass vessel containing in each arm one of the electrodes and filled throughout with the electrolyte. The positive electrode consists of mercury covered with a paste of mercury-mercurous sulphate and the negative electrode is a 12.5% cadmium amalgam. A saturated solution of cadmium sulphate ($CdSO_4 \cdot \frac{8}{3} H_2O$) is placed over the electrode. The cell reactions when it operates spontaneously are:

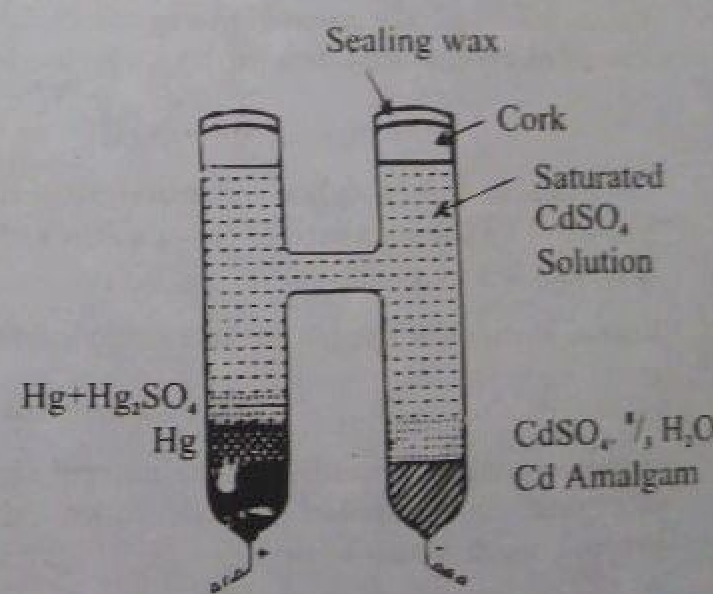

Fig. 10.4. Saturated Weston standard cell

Anode reaction: $Cd(Hg) \rightleftharpoons Cd^{2+} + Hg + 2e^-$

Cathode reaction: $Hg_2SO_4 + 2e^- \rightleftharpoons 2Hg + SO_4^{2-}$

Overall reaction: $Cd(Hg) + Hg_2SO_4 \rightleftharpoons Cd^{2+} + 3Hg + SO_4^{2-}$