POLAROGRAPHY

- Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode.
- It is the technique that deals with the effect of the potential of an electrode on the current that flows through it. The electrode whose potential is varied is called the indicator electrode.
- The potential between reference and indicator electrodes is varied and the consequent change in the flow of current is measured.

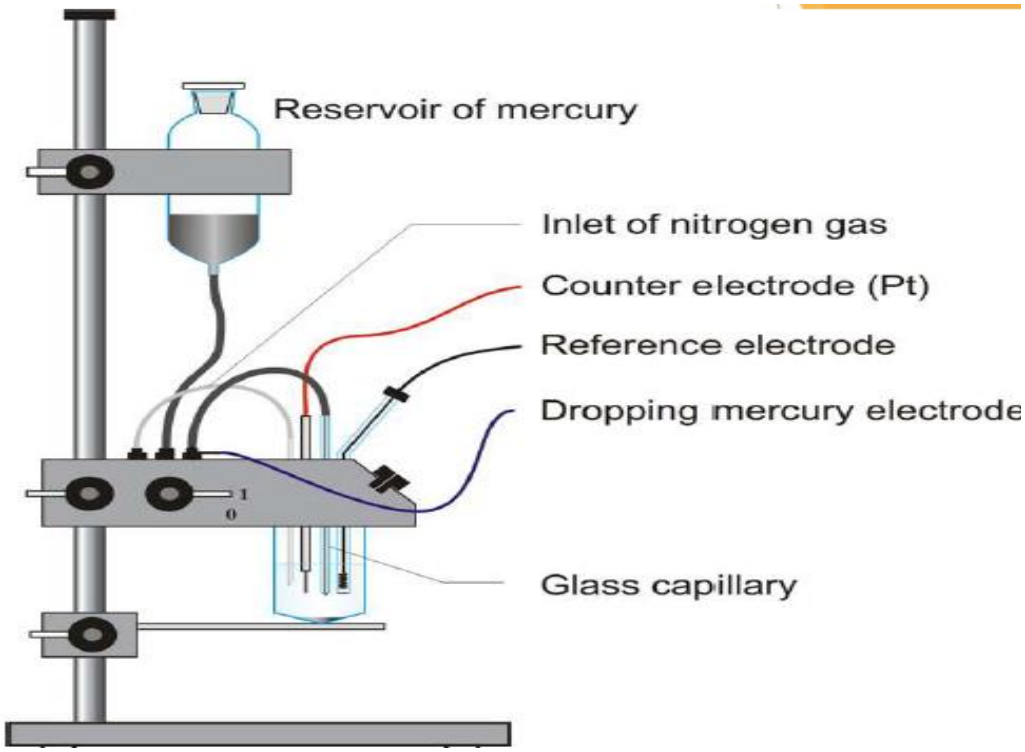
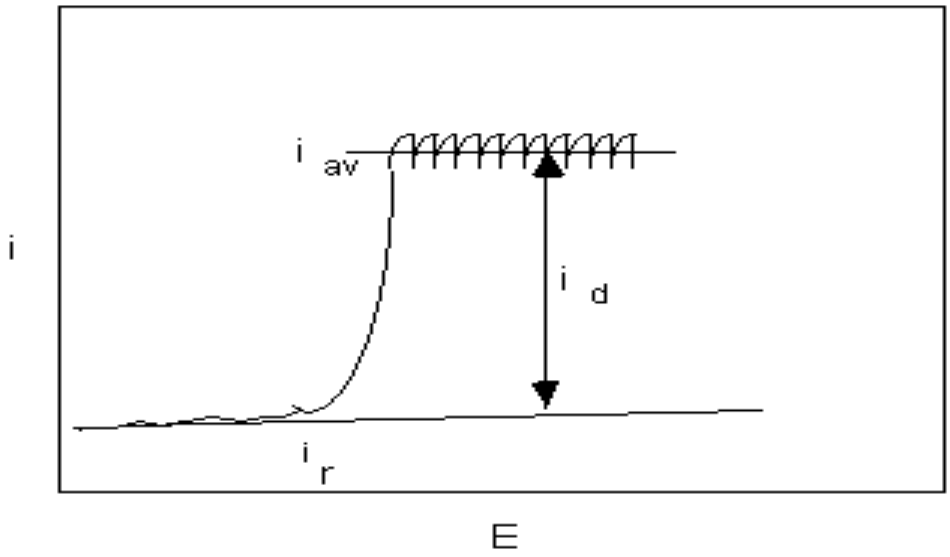


Fig. Polarographic setup/experiment

- Mercury continuously drops from reservoir through a capillary tube into the solution. The optimum interval between drops for most analyses is between 2 and 5 seconds.
- In polarography, changes in current resulting from the electrolysis of the solution under study are investigated using the indicator electrode (cathode).
- The anode of the electrolytic cell called the reference electrode consists of either a mercury pool at the bottom of the cell or a calomel electrode.
- Data/ Results are obtained from an automatic recording instrument is called a polarogram, and the trace is called a polarographic wave.
- Polarogram is a graph of current (i) versus potential in a polarographic analysis.

1. **i_r (residual current)** which is the current obtained when no electrochemical change takes place.

2. **i_{av} (average current/limiting current)** is the current obtained by averaging current values throughout the life time of the drop.
3. **i_d (diffusion current)** which is the current resulting from the diffusion of electroactive species to the drop surface.



Dropping mercury electrode

- The figure given below shows a typical dropping mercury electrode (DME). It consists of roughly 10 cm of a fine capillary tubing (inside diameter 5 ± 0.05 mm).
- The diameter of the capillary is such that a new drop forms and breaks every 2 to 6 s. The diameter of the drop is 0.5 to 1 mm and is highly reproducible.
- In some applications, the drop time is controlled by a mechanical knocker that removes the drop at a fixed time after it begins to form. Furthermore, a fresh metallic surface is formed by simply producing a new drop. The fresh reproducible surface is important because the currents measured are very sensitive to cleanliness and freedom from disturbances.

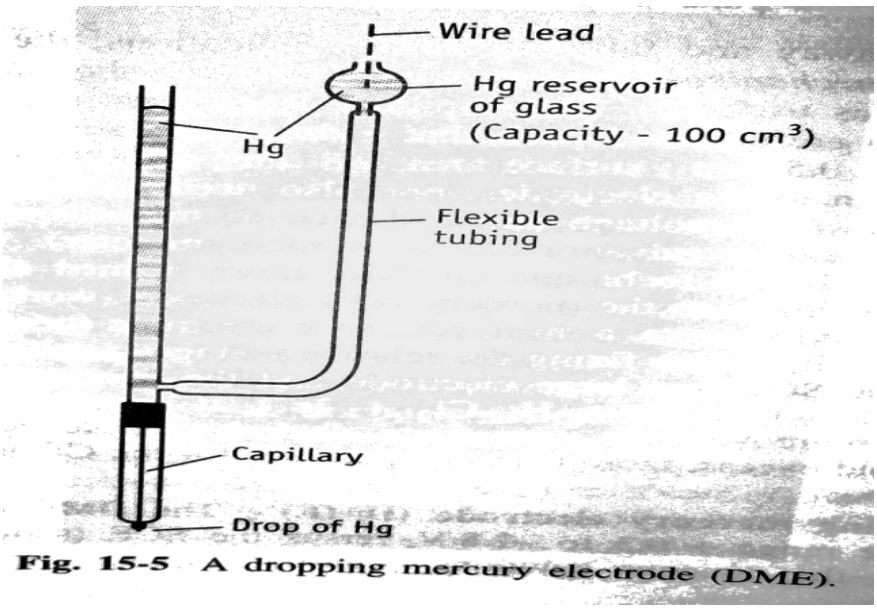


Fig. 15-5 A dropping mercury electrode (DME).

- The following equation is called as Ilkovic equation

$$i_d = 708\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}$$

i_d = Average diffusion current
n = Number of Faradays per mol involved in the electrode reaction
D = Diffusion coefficient of the electroactive material
C = Concentration of the electroactive material, (millimoles/litre)
m = rate of flow of mercury through the capillary
t = time between successive drops of mercury

Applications of Polarography

- The most important advantage of polarography is the determination of two or more substances by obtaining a single current-potential curve.
- In addition to analytical uses, polarography is one of the most fruitful techniques of research in physical, inorganic and organic chemistry.
- It is being used to study diverse topics as hydrolysis, solubility, complex formation, and adsorption, kinetics of chemical reactions, the effects of structure on reactivity and many others.