Polarography

Polarography is an instrumental technique and consists in the measurement of applied potential versus current flow in solutions and the data so obtained can thus be interpreted in terms of the nature and behaviour of many substances and systems.

Heyrovsky (1923) devised polarographic method of analysis using dropping mercury electrode. The current potential curve was obtained by means of an automatic registering apparatus known as polarograph and the resulting curve is known as a polarogram.

Description of Polarograph

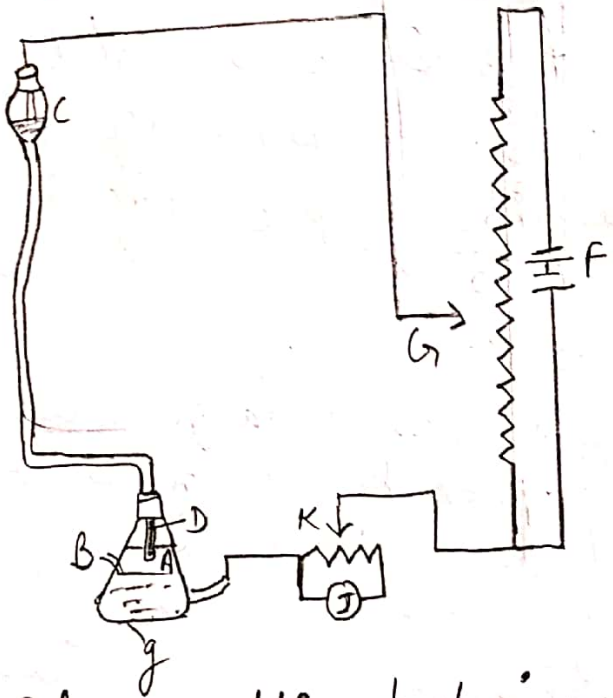

Fig. 1 — Polarographic technique

The complete digrammatic representation of the apparatus is shown in Fig-1. It consists of a flask A containing the experimental solutions, which can be saturated with hydrogen gas by passing the gas through a glass tube B. This reservoir C constitutes a part of the dropping mercury cathode, the drops of mercury failing at a rate 20-30 drops per minute from the end of a capillary tube D. The

anode consists of mercury pool at the bottom of the flask H, the connection is made by a seal in wire. The cathode C and the anode E are connected to the appropriate ends of a battery F. The applied voltage can be varied by means of a sliding contact G along a potentiometer wire HI. The potentiometer consists of a number of turns of wire wound around a rotating drum, the contact G being fixed. The only idea behind this is, that in this manner the applied E.M.F. is varied in a regular known manner. The current strength is indicated by a galvanometer I, across the terminals of which is connected a shunt K, so that the sensitivity of the instrument can be varied when desired. The corresponding current strength is registered photographically by the light reflected from mirror galvanometer on to a sheet of sensitized paper, attached to a rotating drum which is synchronized with the one carrying the potentiometer wire.

As the anode has a large area of surface and current is probably of the order of 10^{-6} amp., the polarisation at this electrode is negligible and the potential of anode may, therefore, be regarded as constant. If this potential is measured, by comparison with a standard reference electrode, the potential of cathode can thereby be determined, by measuring the total E.M.F. across the cell.

Though a number of other electrodes, such a streaming, hanging, rotating micro-electrodes, gold, graphite and carbon electrodes have also been

used, the dropping mercury electrode has its several advantages in comparison with the other electrodes. The dropping mercury electrode, usually abbreviated as d.m.e., is preferred because:

(1) Mercury can be easily purified by first running it through a column of 10% nitric acid several times and then through a column of distilled water and finally the dry metal is distilled under reduced pressure at least three times.
(2) The metal is noble.
(3) Mercury has a high overvoltage, which makes possible the description of ions difficult to reduce.
(4) The metal can easily be restored after its successive use.
(5) The diffusion current assumes steady value almost immediately and is reproducible.
(6) Its surface area is reproducible with any given capillary.