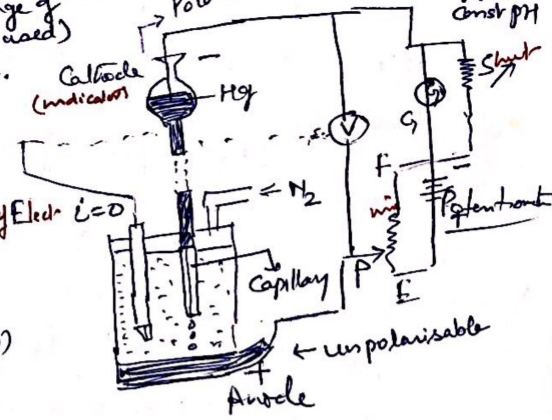
Polarography (Voltametry) C Vs V

- Measurement of potential difference as current flows in Soln. & the result obtained is in terms of nature & conc. of many subs.
- Value of current flowing through cell at applied Voltage is measured c̄ polarograph.
- Method in c̄ soln. is eletrolysed & the graph of current vs Voltage shows what is in soln & how much qty.
- Developed by Czech, Jaroslav Heyrovsky in 1922. Won Nobel prize. 1959
- I is passed b/w 2 electrodes one c̄ large area & other is very small.
- Both electrodes are of Hg
- Large electrode → pool of Hg at bottom of cell.
- Small " → Drop of Hg coming out of very fine capillary tube.
- If steady rising Voltage is applied to cell, a reproducible I vs V curve.
- Electrolyte is an electroactive dil. soln. of material c̄ is to be analysed in suitable medium containing an excess of diff. electrolyte known as base or supporting electrolyte.
- The supporting electrolyte → carry bulk of I & to raise conductivity of soln. (inert inactive) Not electroactive (with in range of potentials used) Maint. const Ionic str. To ↑ C of soln. Eliminate Transport of electroactive sp. × Ionic st. & Conductivity Much Larger Than EA. mat. To control EP.

Apparatus :-



DME → Hg reservoir, Hg drops as small drops thru' a capillary. (cathode) → indicator/micro electrode.

Hg pool at bottom of reservoir → large area, ∴ not polarised. ($i = 0$) (anode) — Reference electrode.

Connect → Cathode & anode to a battery

Apply voltage → can be changed by adjusting S along potentiometer wire EF. P — Potentiometer → EMF of 3 V (upto) applied to cell. G Galvanometer measures I. S shunt to adjust sensitivity of G.

Reservoir → Blowing N_2 provision → To remove dissolved O_2 from Sample.

EMF = +3 to − 2.0 V Vs SCE

At more −ve pot. than −1.8 V vs SCE H_2 evolves at −2.0 V Supp. E discharges. Above +0.4 V Hg dissolves Gives anodic wave due to Oxidn Hg (I) ion.