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POLAROGRAPHY - PRINCIPLE, ILKOVIC EQUATION

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POLAROGRAPHY

- **An electromechanical technique of analyzing solutions that measures the current flowing between two electrodes in the solution as well as the gradually increasing applied voltage to determine respectively the concentration of a solute and its nature.**
- **Polarography is a subclass of voltametry where the working electrode is a dropping mercury electrode (DME). It is current versus potential are recorded when gradual changing current is take place when current applied to cell.**



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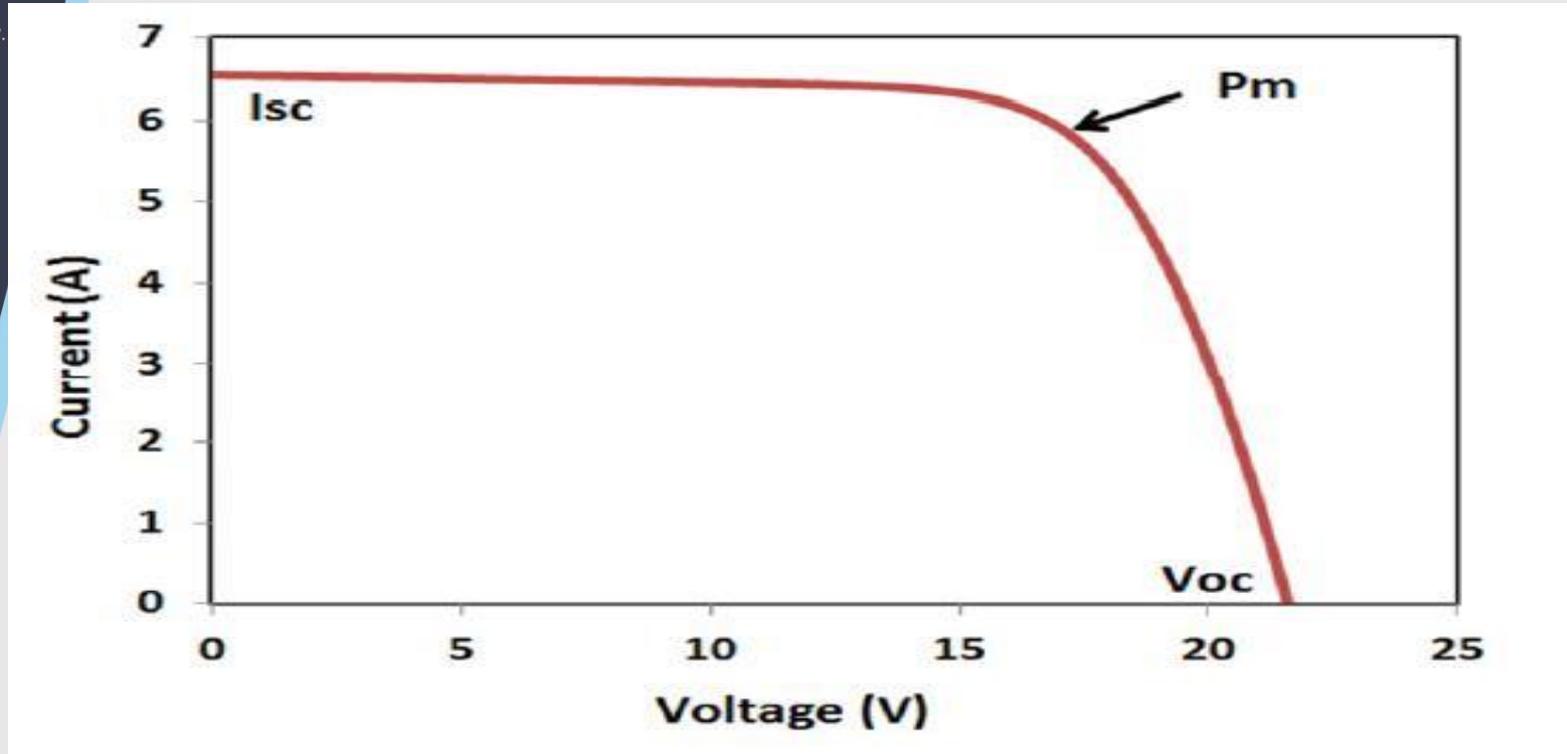
PRINCIPLE

- **A steadily increasing voltage is applied to a cell incorporating a mercury anode and a minute mercury cathode (composed of a succession of small mercury drops falling slowly from a fine capillary tube).**
- **The electrolyte is a dilute solution of the material under examination (which must be electro-active) in a suitable medium containing an excess of an indifferent electrolyte to carry the bulk of the current and raise the conductivity of the solution, thus ensuring that the material to be determined, if charged, does not migrate to the dropping mercury cathode. From an examination of the current-voltage curve, information as to the nature and concentration of the material may be obtained .**



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CURRENT-VOLTAGE CURVE



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- **The total current flowing will in fact be equal to the current carried by the ions undergoing normal electrolytic migration, plus the current due to the diffusion of ions:**

- **$I = I_d + I_m$ where I is the total current,**

I_d the diffusion current, and I_m the migration current.

- **From the current voltage curve both qualitative and quantitative analysis can be done.**
- **From the half wave potential qualitative analysis(identify a compound) and from the diffusion current quantitative analysis (determine conc. Can be done.**



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HALF WAVE POTENTIAL- Where an ion is present in 50% oxidised form and 50% reduced form



DIFFUSION CURRENT-

- It is due to the actual diffusion of ions from the anode to the electrode through out the process.
- Ilkovic examined the various factors which govern the diffusion current and deduced the following equation;



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$I_d = 607nDl/2Cm^{2/3}t^{1/6}$ where

I_d = the average diffusion current in microamperes during the life of the drop;

n = the number of electricity required per mole of the electrode

D = the diffusion coefficient of the reducible or oxidisable substance

C = its concentration in m mol L^{-1} ;

m = the rate of flow of mercury from the dropping electrode expressed in mg s^{-1} ; and

t = drop time in s.



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THANK YOU