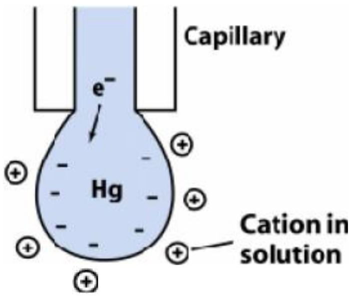
Polarography



Dropping Mercury Electrode (DME)

Polarography

❑ Polarography is one of the Voltametric methods of analysis; electrochemical methods where current voltage curves obtained at the surface of microelectrodes are studied.

❑In polarography the microelectrode is a dropping mercury electrode (DME).

❑The method is used for the analysis of electroreducible or oxidizable metal, ion or organic substance (electroactive species).

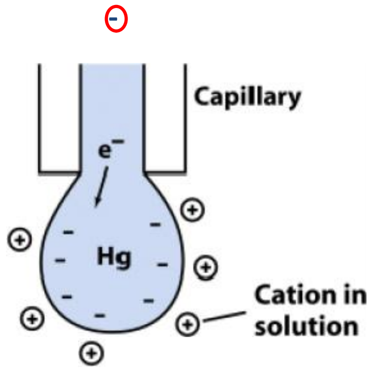
❑ Electroactive species is transferred into a polarographic cell (electrolytic cell) where voltage is applied to the electrodes

❑ One of the electrodes is a polarizable microelectrode (DME) while the other is reference non polarizable electrode

-DME is the cathode
(attached to the negative pole of the voltage supply)

-upon applying the voltage, electroactive species will move towards DME, electron transfer occurs and a current flows.

-The current produced is proportional to concentration of the electroactive species

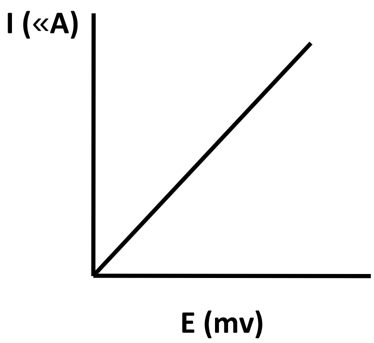


Polarization:

Ohm's law : $E_{cell} = I R$

$E \sim I$ (current)

If the increase in cell potential is not accompanied by increase in current it is called Polarization.



Modes of Transport of Electroactive species to DME

1-By Convection:

by **mechanical stirring** or by **heating**, as it increases current increases . This type can be **prevented by:**

-avoiding stirring

-controlling the temperature.

-adding gelatin to increase viscosity of medium

2-By electrostatic attraction :

between **positive species** and the **negative cathode**; The current produced here is known by **migration current**, it can be **minimized by**:

-adding large excess of inert electrolyte (not reducible) known by **supporting electrolyte** (50-100 times th analyte concentration)

3-By diffusion:

-occurs due to **concentration gradient of ions**

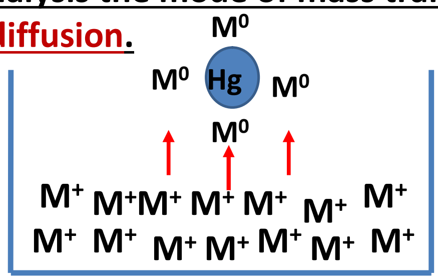
-The rate of mass transport by diffusion depends on **the concentration and the diffusion coefficient** (a constant value characteristic for the analyte)

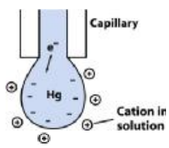
-the **transport (current) will depend on concentration.**

Small ion conc $\longrightarrow$ small inflection of curve

high ion conc $\longrightarrow$ large inflection of curve

in polarographic analysis the mode of mass transport should be **only by diffusion.**



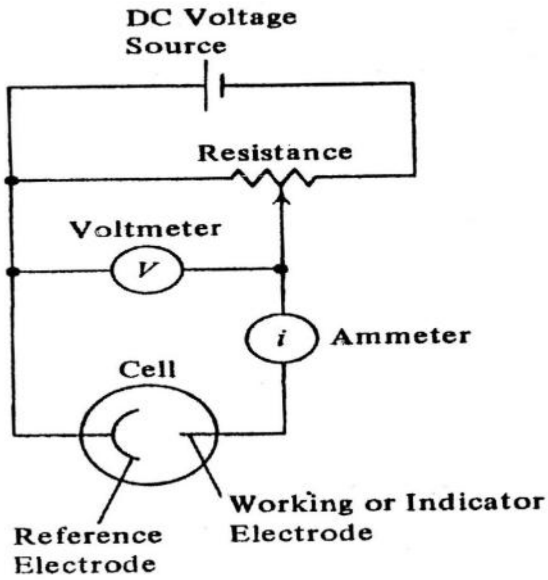


Instrument (Polarograph):

1-electric circuit
2-polarographic cell

1-electric circuit

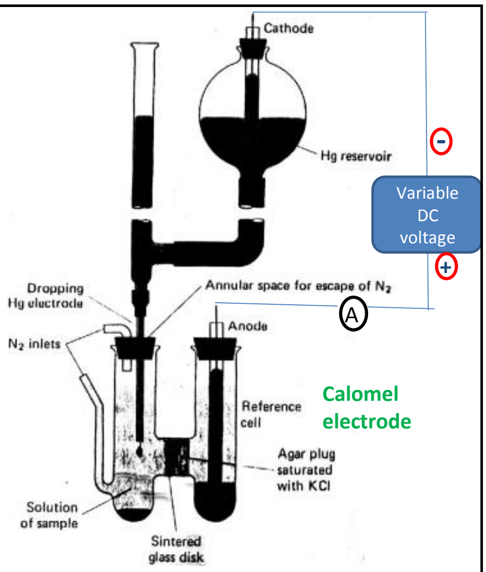
-increasingly negative potential from +0.5 to -2.5 volt at a definite rate of millivolt.



2-Polarographic cell

-lifetime of a drop from 2 to 6 seconds

- Nitrogen is bubbled through the solution for five minutes to expel oxygen. Also kept at the surface

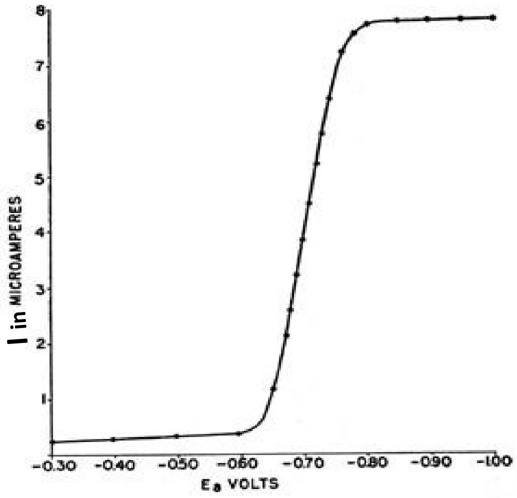


Polarographic cell

Polarogram

-a plot of **current** as a function of applied **potential**

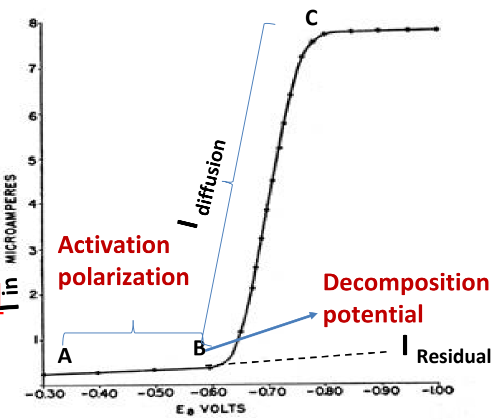
-The applied potential is given a **negative sign** as the microelectrode is connected to the **negative terminal** of the power supply.



A-B : Activation polarization

Increase in volt not accompanied by increase in current , additional potential is needed to overcome the energy barrier

small current passing through the cell is known by residual current i_r



B : Decomposition potential

Potential once exceeded, reduction begins

B-C :

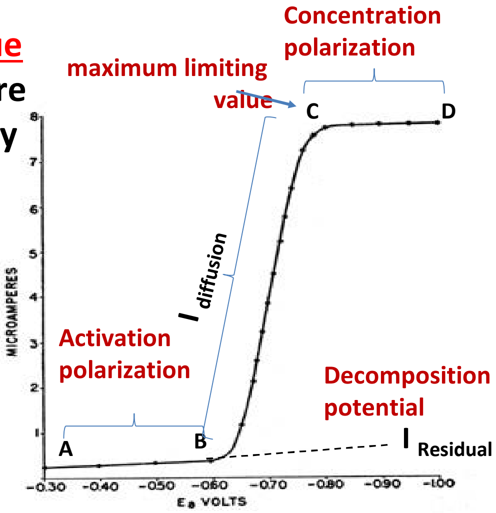
Increase in volt is accompanied by increase in current (diffusion current)

C : maximum limiting value

The point after which there is no increase in current by increase of potential;

C-D : Concentration polarization

When the rate of electron transfer is maximum and the current is maximum.

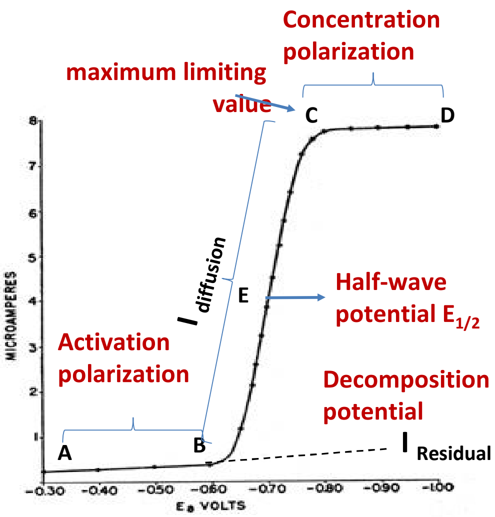


If potential is increased above this value it will not be accompanied by increase in the current and polarization takes place,

This type of polarization depends on the concentration of the electroactive species

E : half wave potential

the potential at the mid point of the steeply rising portion of the curve. It is characteristic for each substance under specific conditions



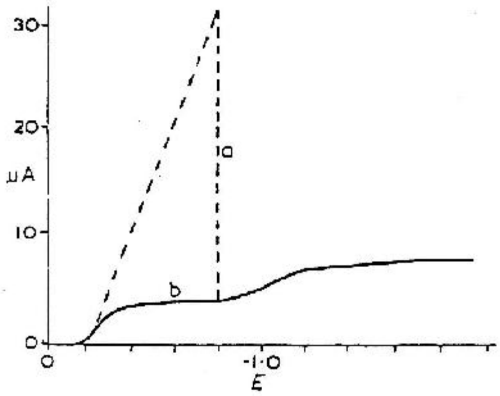
It does not depend on the concentration of the electroactive species

At this potential the [oxidized species] = [reduced species] and used for its identification.

Polarographic Maxima

-abnormal peak appears on the polarogram usually in concentrated solution

-Can be suppressed by addition of gelatin which is called maxima suppressor



Reduction of oxygen (a) in absence, (b) in presence of maximum suppressor

Effect of dissolved oxygen:

Oxygen is an electroreducible species its presence in solution produces a double wave in the range of 0 to -1.0 V due reduction reacti

$O_2 + 2H^+ + 2e \longrightarrow H_2O_2$

$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O$

This wave interferes with the analyte wave.

Thus oxygen must be removed by bubbling nitrogen through the solution for five minutes to expel oxygen.

Ilkovič Equation:

$$I_d = 607\, n\, D^{1/2}\, C\, m^{2/3}\, t^{1/6}$$

I_d average diffusion current
n number of electron in reduction of a molecule
D diffusion coefficient
C concentration
m rate of the mercury flow in capillary
t lifetime of a drop of mercury (2 to 7 sec.).

n,D,m and t are constants
($i_d = k\,C$)

$m^{2/3}\, t^{1/6}$ is known by the capillary characteristics it depends on
1- the mercury column height above the capillary tube
2- the internal capillary dimensions.

Advantages of DME:

1-The current voltage curve shows only the process occuring at the DME
2- can be done in acidic solutions as Large overvoltage is needed for reduction of H^+
3- reproducible results are obtained as Mercury electrode surface is continuously renewed, smooth surface of the mercury drop which allows reproducible rapid electron transfer. .
4- several runs can be performed using the same solution as the surface area of the electrode is very small the amount electrolyzed is negligible and the concentration of the original solution nearly remains the same
5- The reduced metals at the electrode surface form amalgum.

Disadvantage of the DME:

1-potential above 0.4 \ Hg metal is oxidized with a production of a wave that interferes with the analyte.

2-The drop surface area is changeable

3-The drop surface area change by change of potential

Application of polarography

Inorganic
Polarography

-Cations
-Anions
-Molecules

organic
Polarography

1- Cations

a- No interference in $E_{1/2}$:

-Mixture of Cu^{+}, Cu^{2+}, Cd^{2+} Ni^{2+} Zn^{2+} Mn^{2+} is determined simultaneously in 0.5 M NH_4OH, O.5 M NH_4Cl as each cation has its characteristic $E_{1/2}$ and shows separate wave.

b- interference in $E_{1/2}$:

1-Pb^{2+}, Ti^{+} and Sn^{2+} the same $E_{1/2}$ (-0.5V) in neutral and acidic medium. Use NaOH medium:

- Pb^{2+} form a complex with $E_{1/2}$ -0.8 V
- Sn^{2+} can be oxidized to Sn^{4+} which is reduced at -0.35 V
- Ti^{+} is reduced at -0.49.

2- Cu^{2+} and Bi^{3+} both are reduced at -0.25 in HNO_3 .

Use tartarate at pH 2 - 5 the potential is altered to -0.15 for Cu^{2+} and - 0.37 for Bi^{3+}