POLAROGRAPHY

PREPARED BY
A.CAROLINE GRACE
ASSOCIATE PROFESSOR
SVCP

INTRODUCTION

- The value of current flowing through a cell at any applied voltage is measured with the help of an instrument known as polarograph and the curves obtained with it are known as polarogram.
- It is an electro analytical technique that deals with the effect of the potential of an electrode in an electrolysis cell on the current that flows through it.
- Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode.
- In polarography, the current flowing through the cell is measured as a function of the potential of the working electrode.
- This current is proportional to the concentration of the analyte usually.

- The basic idea of polarography is to pass the current between two electrodes, one large in area and other very small.
- The large electrode is a pool of mercury at the bottom of the cell and the small electrode is a drop of mercury coming out of a very fine capillary tube.
- The solution to be analysed is taken along with a suitable medium containing an excess of different electrolyte called base or supporting electrolyte.
- The purpose of this electrolyte is to carry the bulk of the current and to raise the conductivity of the solution.
- From the current voltage curve the nature and concentration of the material may be obtained.

Introduction

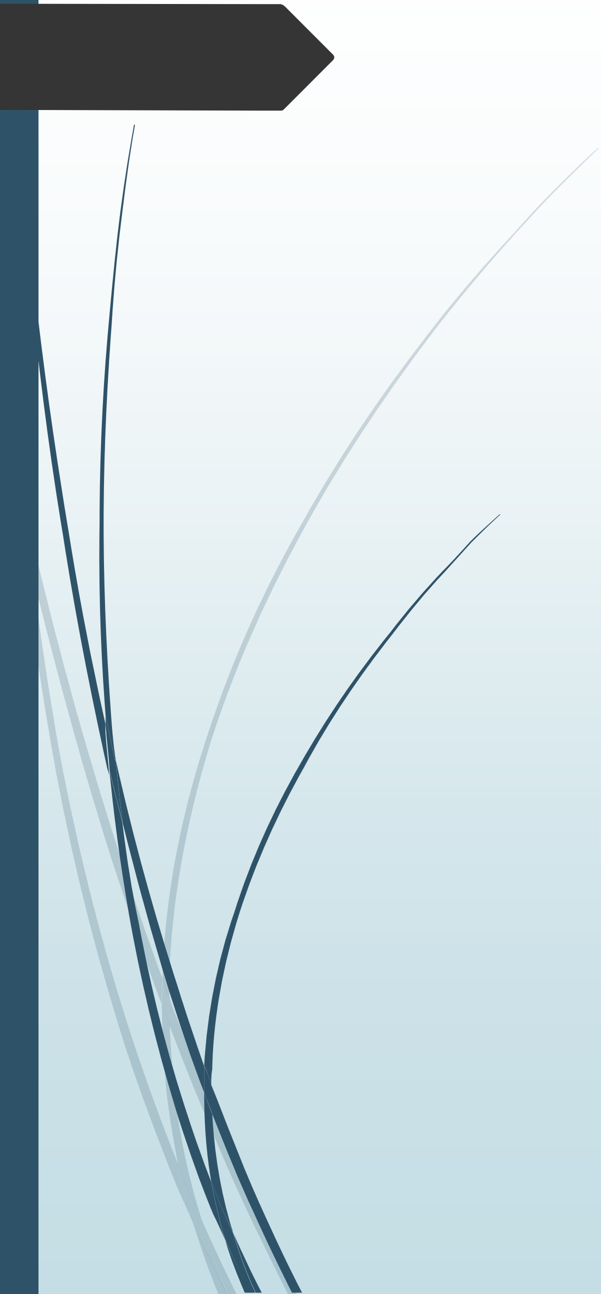
- Polarographic method has been developed by Jarslov Heyrovsky, in 1992.
- This method has acquired immense importance in analytical chemistry for determination of metal ions and other electroactive organic methods.
- Polarography is the study of the electrolysis of solutions of electrooxidizable and or electroreducible substances between a dropping mercury electrode (DME) and some reference electrode (RE) .

DEFENITION

- Polarography is an electromechanical technique of analysing solutions that measure 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 it’s nature.

PRINCIPLE

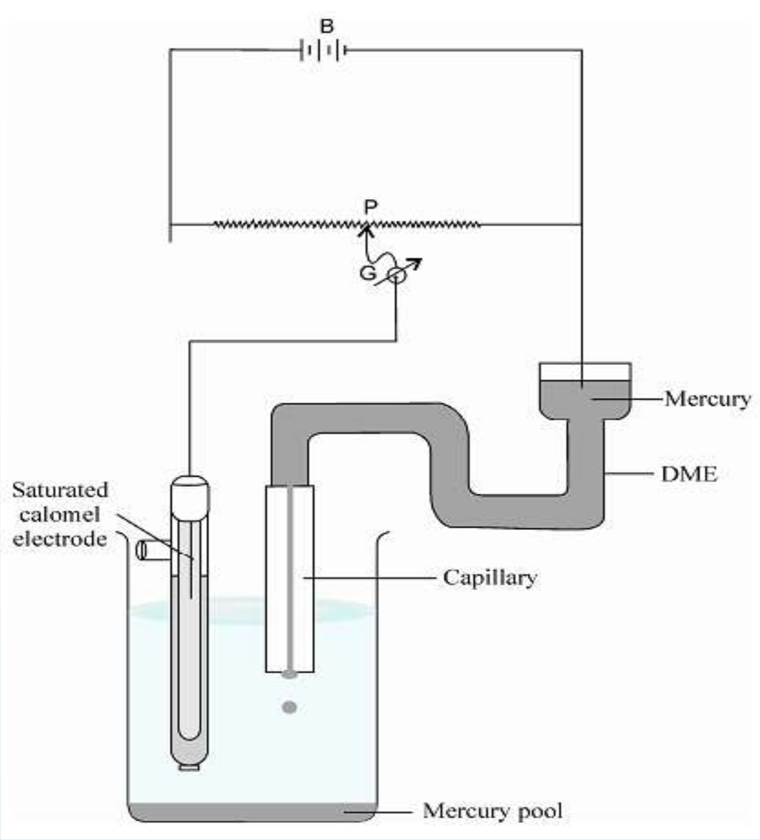
- Polarography is the study of the electrolysis of solutions of electrooxidizable and or electroreducible substances between a **dropping mercury electrode (DME-Polarized or indicator electrode) and** reference electrode such as saturated calomel electrode (**Depolarized electrode**).
- The potential between these electrodes is varied and the consequent changes in the flow of current is measured .
- On plotting the changes in current flow versus the potential difference, one obtains an **curve known as polarogram.**
- From the measurements of the current - potential curves resulting from electron transfer processes at the surface of a **DME, the identity and concentration of the reactant** substance can be determined.



Instrumentation

A polarography consist of 3 components

- A potentiometer (for providing a known PD across the electrodes in a polarographic cell).
- A electrolytic or a polarographic cell.
- A galvanometer or an ammeter (for measuring electrolysis current).



A POTENTIOMETER

- A potentiometer consists of an electrolytic cell and a resistance(R) Connected in series.
- The required PD is set across the electrodes in a polarographic cell by adjusting the position of movable jockey connected to a galvanometer.
- A résistance wire(R) is present.
- The potential difference across resistance (R) wire is equal to electromotive force (e.m.f,E) or voltage of galvanic cell.
- The point which is at positive potential i.e which connected to positive electrode of a galvanic cell and next point is at negative potential i.e connected to negative electrode.
- Thus potential drops from positive to negative value as one moves from first point to next point.

- If the length of wire is 10 units ,then a potential drops per unit length of resistance wire is EMF/10.The position of the pointer on the resistance wire decides the potential of negative electrode of an electrolytic cell.
- Thus the change in the position of the pointer on the resistance wire provides the varying PD across the electrodes of an electrolytic cell. Hence change in PD across electrodes reflects the change in potential of negative electrode.

THE POLAROGRAPHIC CELL OR ELECTROLYTIC CELL

- A polarographic cell is H shaped .
- One arm of H shaped cell contains the solution of a sample to be analysed and another arm contains saturated KCl solution or KCl solution of known strength .
- Two types of polarographic cells are usually used:
  - **Dropping Mercury Electrode (DME)**
  - **Saturated calomel Electrode (SCE)**

DME (dropping mercury electrode)

- Normally electrodes are used in the form of solid rods or solid plates.
- DME exist in form of small droplets of mercury formed at the tip of a capillary.
- It consist of a short length of glass capillary tubing having internal diameter in the range of 0.03 to 0.05 mm.
- Capillary tubing is attached to a short but large bore glass tubing, which is connected to a mercury reservoir via a piece of rubber tubing.
- Height of mercury column above the tip of the capillary tubing is maintained by changing the level of mercury reservoir bulb.

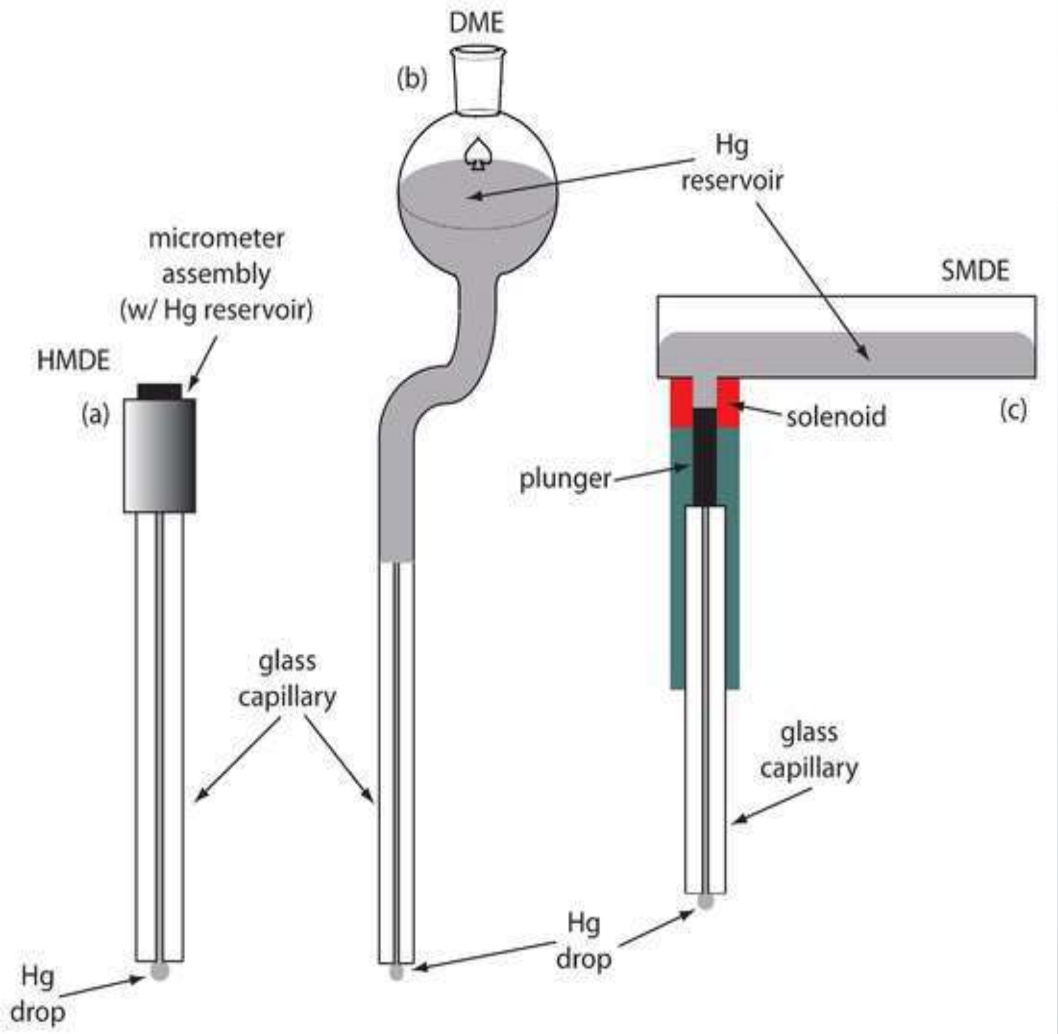
- Constant height of the mercury column above the tip of the capillary tubing is essential in order to maintain the flow rate of mercury or to determine the no. of droplets of mercury formed per unit time.
- Each droplet goes through a definite sequence at the tip of the capillary, then the droplet slowly grows in size, attains a critical mass and then detaches from the capillary.
- Negative potential is applied to mercury droplets by introducing a platinum wire in Hg reservoir .Platinum wire is maintained at negative potential by connecting it to an anode of a galvanic cell ,which acts as a source of electrons to it.

WORKING

- Because of the availability of electrons at DME ,the positive ions of an analyte are attracted towards it during electrolysis .
- Once the cations of the analyte are in the vicinity of DME ,at a particular potential at DME ,cations are reduced .
- If $PbCl_2$ as an analyte ,Pb^{2+} ions are reduced to Pb atoms as shown in the following reaction.
- $Pb^{+2} + 2e^{-} \rightarrow Pb$
- Thus DME is used as a cathode in a polarographic cell

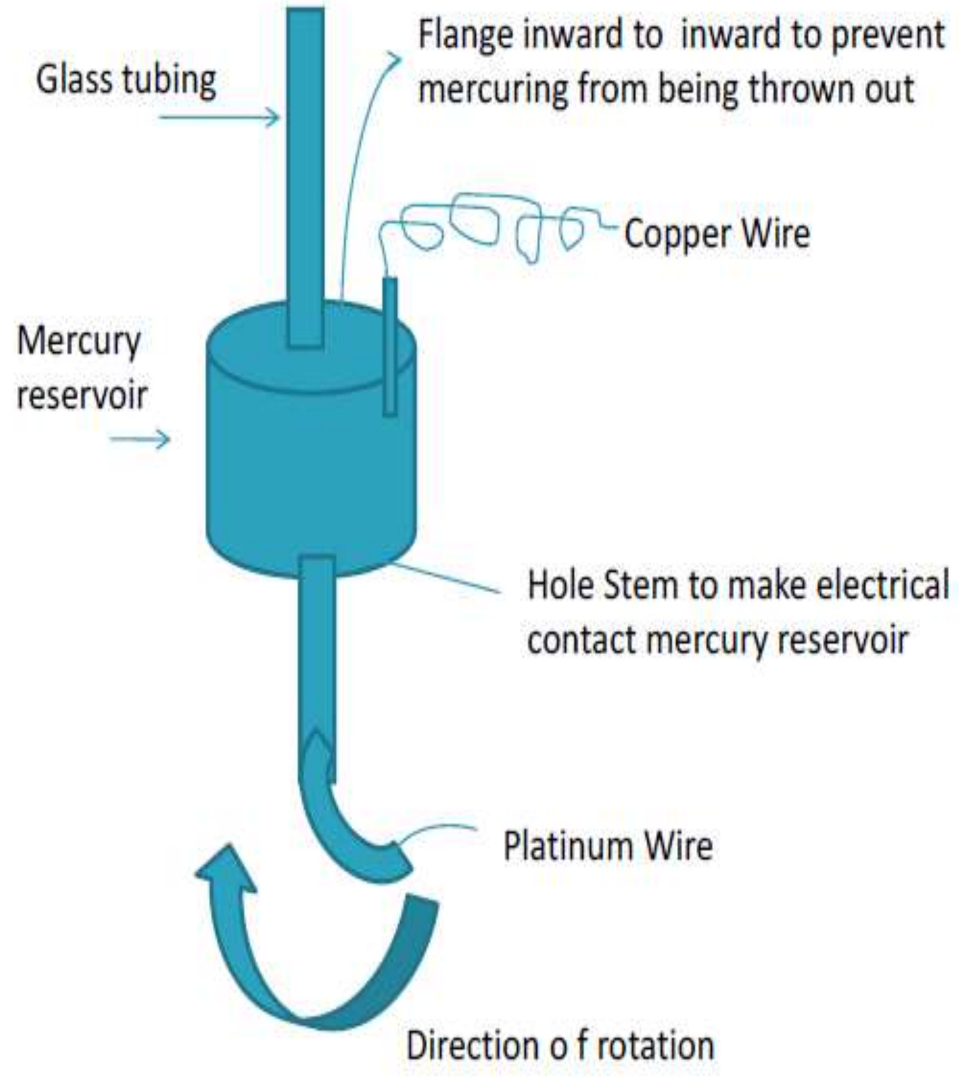
- In polarography, mercury is used as a working electrode, because mercury it is a liquid. The working electrode is often a drop suspended from the end of a capillary tube.

Mercury as working electrode is useful because:
It displays a wide negative potential range
 Its surface is readily regenerated by producing a new drop or film
Many metal ions can be reversibly reduced into it.



ROTATING PLATINUM ELECTRODE

- Mercury cannot be used as electrode at positive potentials because of its oxidation
- With platinum electrode the attainment of steady state diffusion current is slow
- One has to wait for a considerable time after each addition of reagent
- Therefore the platinum electrode is rotated at 600 rpm.



- It consist of a glass tube of length 15 – 20 cm in length and 6 mm in diameter.

- Glass rod with a bent platinum wire at its tip The platinum wire extends 5-10 mm from the wall of glass tubing.

- The electrode is mounted on shaft of the motor and rotated at constant speed of 600 RPM .

- Electrical connection is made to the electrode by copper wire passing through the tubing to the mercury covering the platinum wire seal.

- Wire contacts are made through a mercury reservoir so that the potential can be applied and the current is measured.

- Nitrogen gas is bubbled through the titrate to remove oxygen

- Advantages:
- Diffusion current is 20 times larger than DME which allows to measure the small concentration of ion.
- The rotating platinum electrode can be used at positive potential up to + 0.9 Volt where as DME can be used only +0.4 volt to -2.0 Volt.
- The electrode is simple to construct.

CALOMEL ELECTRODE

CONSTRUCTION

- This electrode consist of pure mercury in contact with a mixture of mercury and calomel (Hg_2Cl_2) and a solution of KCl

WORKING

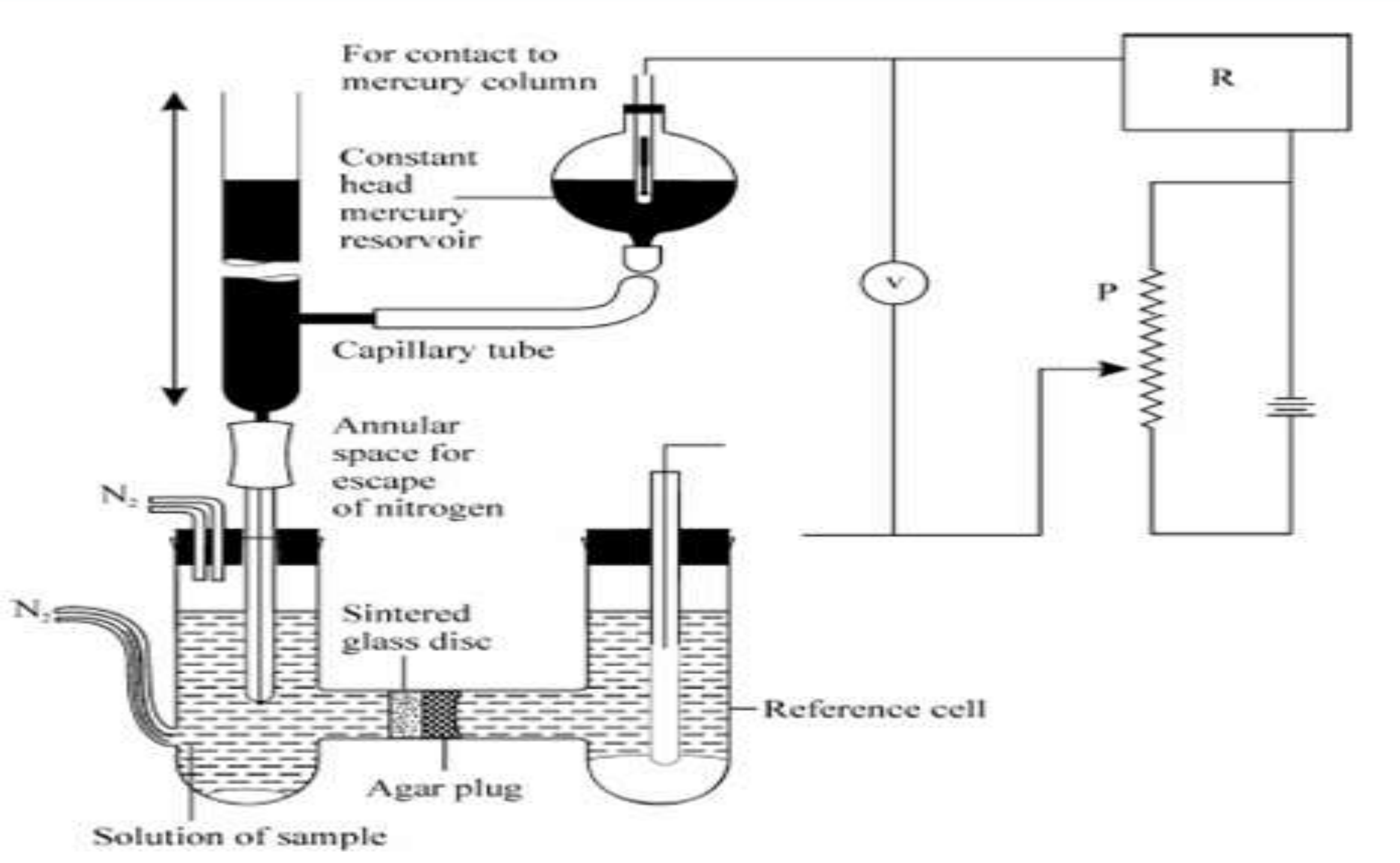
- The reaction which determines the potential of this electrode is given below

$$Hg_2Cl_2\,(s) + 2e \rightarrow 2Hg + 2Cl$$

- Commonly , 0.1N ,1N or Saturated solution of KCl is used for the polarographic studies . When the saturated solution is used in the preparation of calomel electrode , the electrode is called *saturated calomel electrode (SCE).*

POLAROGRAPHIC CELL OR ELECTROLYTIC CELL

- A polarographic cell is H shaped .
- One arm of H shaped cell contains the solution sample to be analysed and other arm contains saturated KCl solution of known strength.
- Dropping Mercury Electrode is used as cathode and is dipped in solution of an analyte.
- Saturated Calomel Electrode is used as an anode and is dipped in a saturated solution of KCl.


For contact to mercury column
Constant head mercury resorvoir
Capillary tube
Annular space for escape of nitrogen
N_2
N_2
Sintered glass disc
Agar plug
Solution of sample
Reference cell
R
V
P

A GALAVNOMETER OR AN AMMETER FOR MEASURING ELECTROLYSIS OF CURRENT

- When an external potential is applied to the electrode in polarographic cell ,the electrolysis of an analyte occurs.
- The current produced due to electrolysis is measured by galvanometer.
- A fast responding galvanometer records maximum current produced during electrolysis

- In polarography, the current flowing through the cell is measured as a function of the potential of the working electrode.
- Usually this current is proportional to the concentration of the analyte
- The working electrode is a dropping mercury electrode or a mercury droplet suspended from a bottom of a glass capillary tube.

- Analyte is either reduced (most of the cases) or oxidized at the surface of the mercury drop.

- The current –carrier auxiliary electrode is a platinum wire.

- SCE or Ag/AgCl reference electrode is used.

- The potential of the mercury drop is measured with respect to the reference electrode.

- ir (residual current) which is the current obtained when no electrochemical change takes place.
- iav (average current/limiting current)is the current obtained by averaging current values throughout the life time of the drop while
- id (diffusion current) which is the current resulting from the diffusion of electroactive species to the drop surface.

ILKOVIC EQUATION

- The diffusion current at the DME is given by Ilkovic equation:
- **$I_d = 607\, n\, D^{1/2}\, c\, m^{2/3}\, t^{1/6}$**

I_d = the average diffusion current during the life of drop,in amperes

607=a constant of various numerical factors including ∏,the Faraday constant ,density of mercury etc..

n= the number of electrons involved in the electron reaction.

D = The diffusion coffecient of the substance in cm^2 /sec.

C= the conc of substance in m moles /litre.

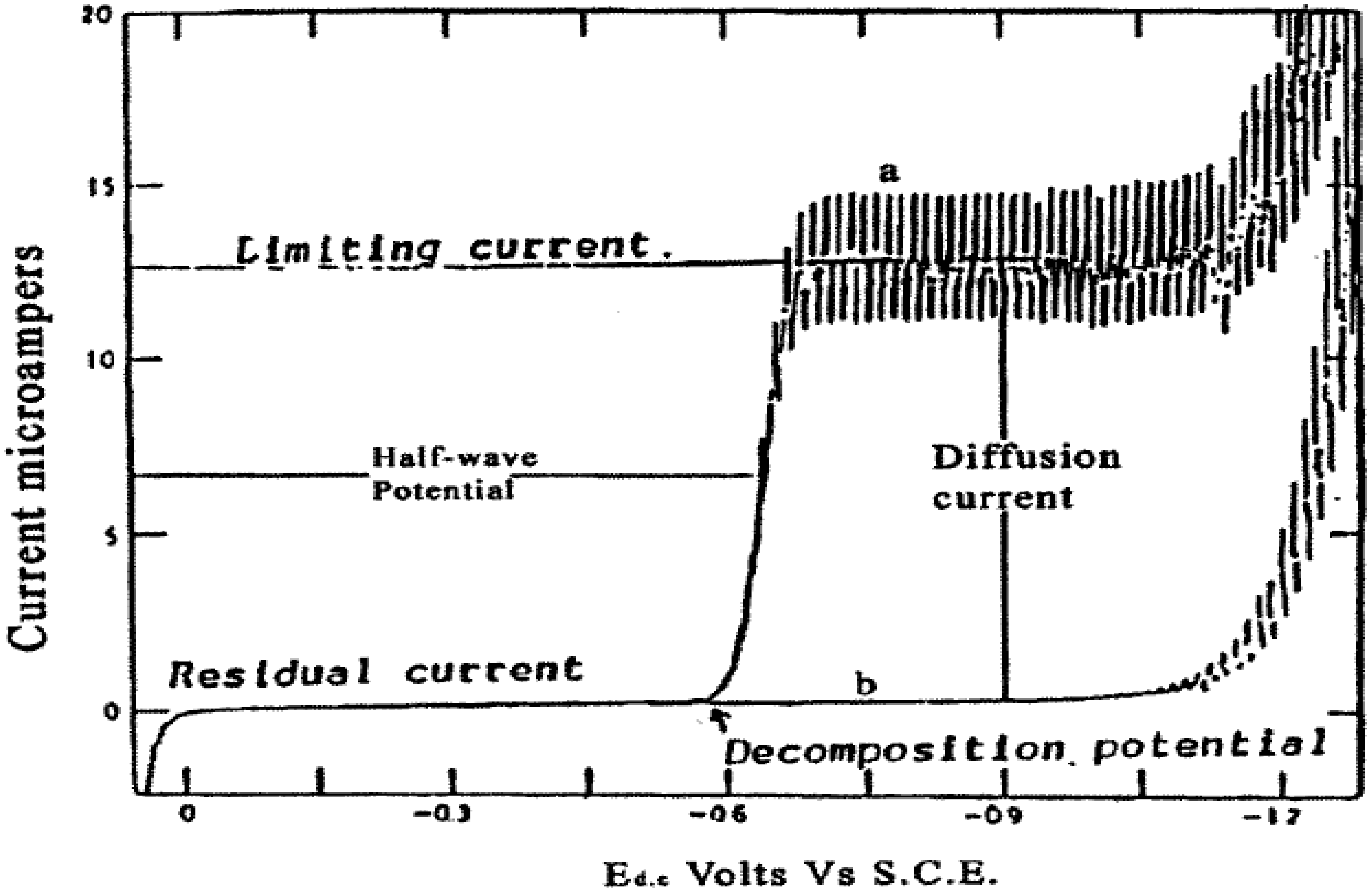
M = the rate of mercury flowing through the capillary in mg/sec

t= the drop time in seconds.

METHOD OF ANALYSIS

- The polarographic apparatus consists of a arisable electrode (DME) and a reference electrode (saturated calomel electrode) which is a non-polarisable electrode.
- Between these electrodes, the required potential range(0 to -3V) can be applied.
- It consist of a sample cell, in which the sample solution to be analysed is kept.
- Sample is made up of glass and has tapering edge at the bottom to hold the mercury   the droplets have been formed

POLOROGRAM


20
15
10
5
0
Current microampers
Limiting current.
a
Half-wave
Potential
Diffusion
current
Residual current
b
Decomposition potential
0
-0.3
-0.6
-0.9
-1.2
Ed.c Volts Vs S.C.E.

- The capillary is dipped into the solution to be analysed and the height of the mercury reservoir is adjusted in such a way that drop time of about 2-7 sec is set.

- Supporting electrolytes like potassium chloride (50-100 times the sample concentration) is added to the sample solution to eliminate migration current (KCL does not decompose at the operating voltage and hence diffusion current KCL is not recorded).

- In polarographic analysis, it is the diffusion current which is proportional to the concentration of the electrolyte and hence only the diffusion current has to be measured

- In normal conditions, without the supporting electrolyte, migration current is also recorded which is not required.
- Hence supporting electrolyte is added in large amounts which eliminates migration current.
- The oxygen present in the sample solution is removed by passing Nitrogen or using alkaline pyrogallol solution.
- Otherwise, curve due to oxygen is also recorded
- Maximum suppressors are added in the required concentration range

- When all these things are done, the initial and final potential is set in the instrument and the current voltage curve is recorded.
- From the current voltage curve, diffusion current is determined and thus qualitative and quantitative analysis is performed

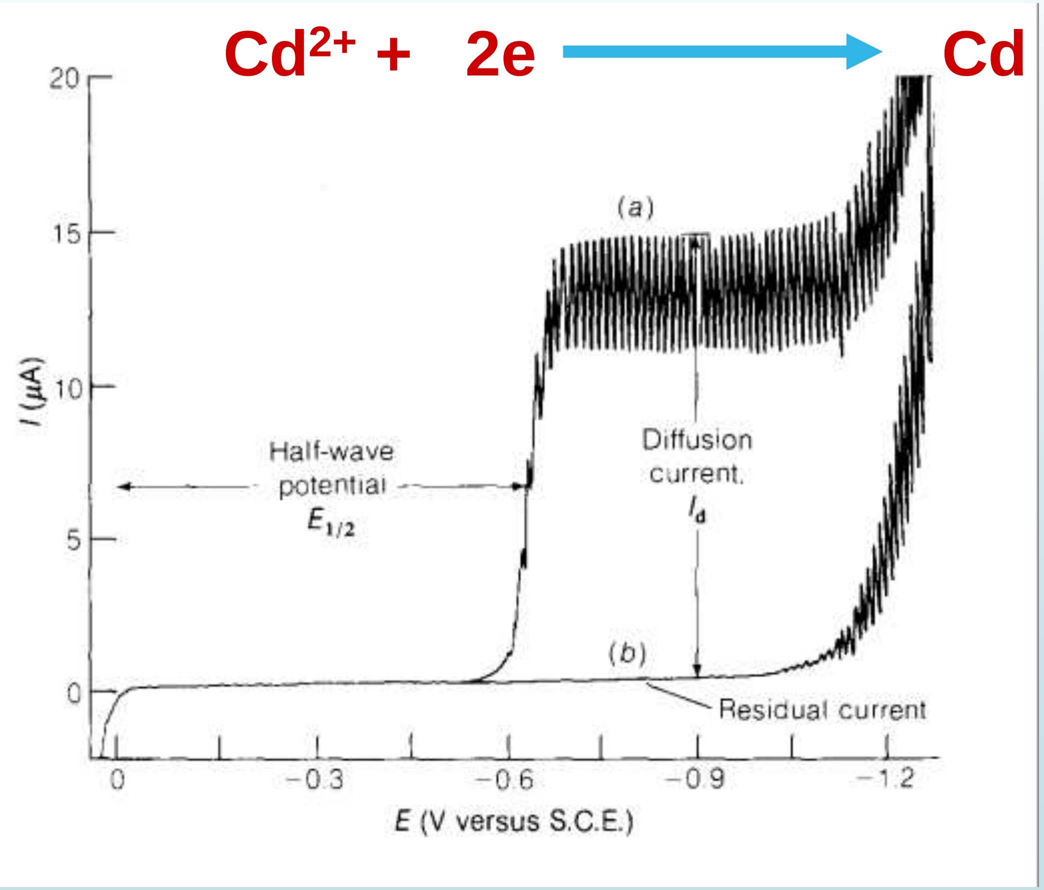
Residual Current

- Even in the absence of analyte, a small current flows through an electrochemical cell.
- This current, which is called the residual current, consists of two components: a faradaic current due to the oxidation or reduction of trace
  - ✓ a charging current. It is the current needed to charge or discharge the capacitor formed by the electrode surface-solution interface. This is called the condenser current or charging current.
  - ✓ It is present in all voltammetric and polarographic experiments, regardless of the purity of reagents.
  - ✓ As each drop of mercury falls, it carries its charge with it to the bottom of the cell. The new drop requires more current for charging.

SHAPE OF THE POLAROGRAM

A graph of current versus potential in a polarographic experiment is called a polarogram.

$Cd^{2+} + 2e \longrightarrow Cd$



- When the potential is only slightly negative with respect to the calomel electrode, essentially no reduction of Cd^{2+} occurs. Only a small residual current flows.
- At a sufficiently negative potential, reduction of Cd^{2+} commences and the current increases. The reduced Cd dissolves in the Hg to form an amalgam.
- After a steep increase in current, concentration polarization sets in: The rate of electron transfer becomes limited by the rate at which Cd^{2+} can diffuse from bulk solution to the surface of the electrode.
- The magnitude of this diffusion current I_d is proportional to Cd^{2+} concentration and is used for quantitative analysis. The upper trace in the Figure above is called a polarographic wave.

- When the potential is sufficiently negative around -1.2 V, reduction of H^+ begins and the curve rises steeply.
- At positive potentials (near the left side of the polarogram), oxidation of the Hg electrode produces a negative current. By convention, a negative current means that the working electrode is behaving as the anode with respect to the auxiliary electrode. A positive current means that the working electrode is behaving as the cathode.
- The oscillating current in the Figure above is due to the growth and fall of the Hg drops.
- As the drop grows, its area increases, more solute can reach the surface in a given time, and more current flows.
- The current increases as the drop grows until, finally, the drop falls off and the current decreases sharply.

Diffusion Current

When the potential of the working electrode is sufficiently negative, the rate of reduction of Cd^{2+} ions is governed by the rate at which Cd^{2+} can reach the electrode.

$$Cd^{2+} + 2e \longrightarrow Cd$$

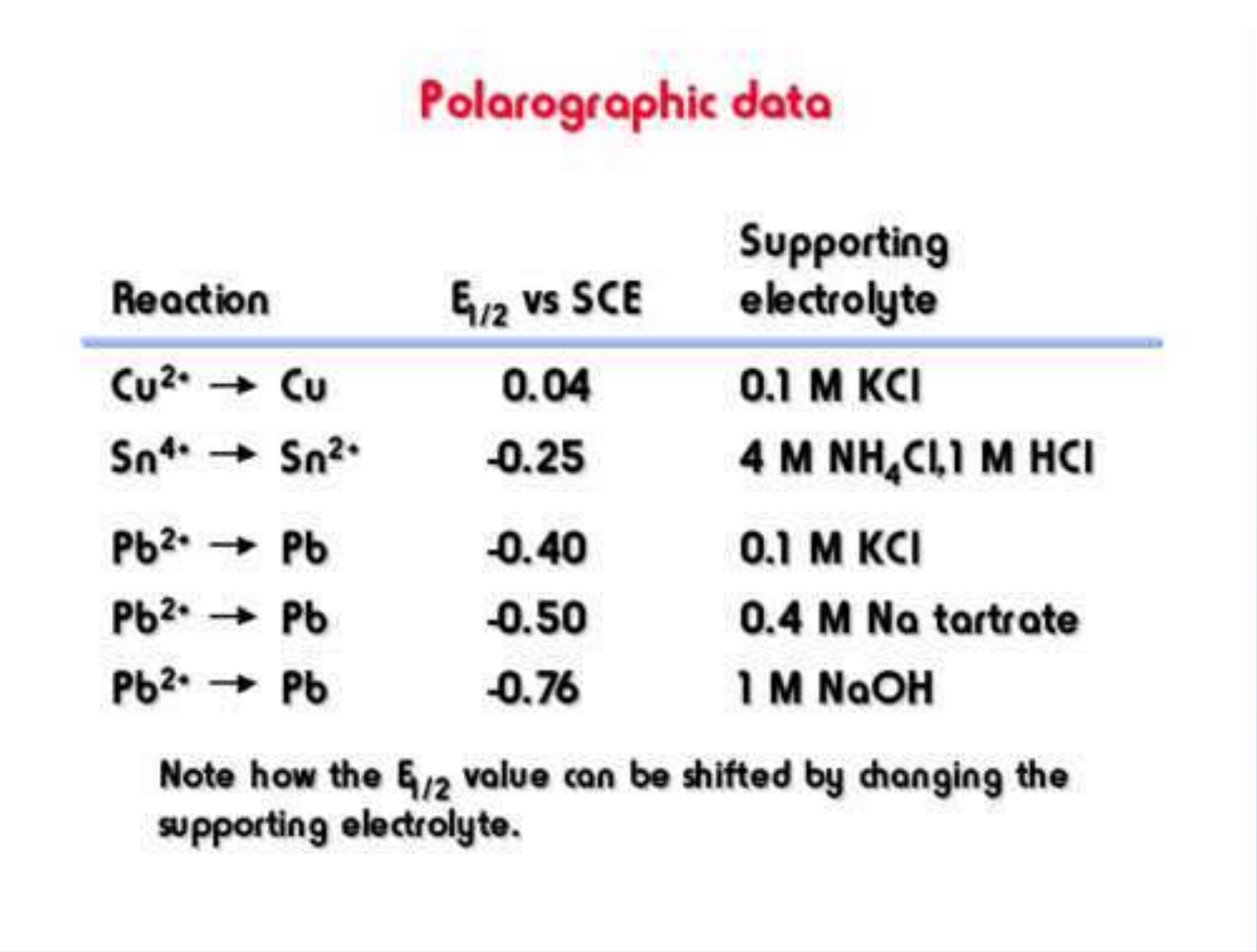
- In the Figure above, this occurs at potentials more negative than -0.7 V.
- In an unstirred solution, the rate of reduction is controlled by the rate of diffusion of analyte to the electrode.
- In this case, the limiting current is called the *diffusion current*.
- The solution must be perfectly quiet to reach the diffusion limit in polarography.
- Thus, the diffusion current is the limiting current when the rate of electrolysis is controlled by the rate of diffusion of species to the electrode.

Limiting current

- Beyond a certain potential , current value remains a a steady value is called limiting current.
- At this point rate of diffusion of ion = rate of reduction and state of electrode is said to be polarised.

HALF WAVE POTENTIAL

- Half wave potential, $E_{1/2}$ is an important feature that can be derived from the polarogram.
- It is the potential corresponding to one half the limiting current i.e. $i_d/2$.
- $E_{l/2}$ is a characteristic for each element and thus used for qualitative analysis



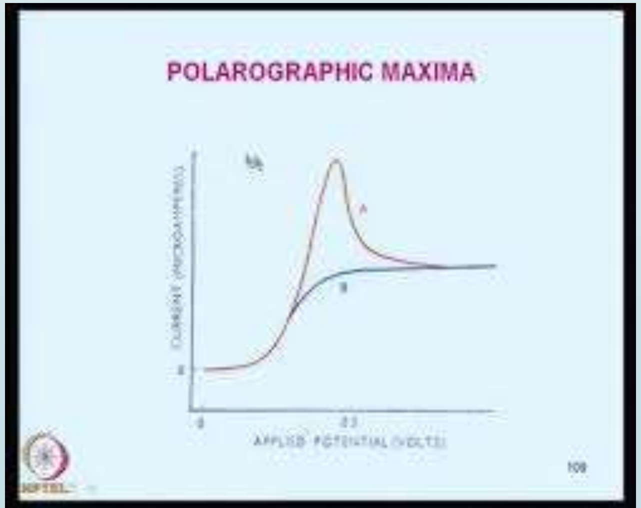
Polarographic data

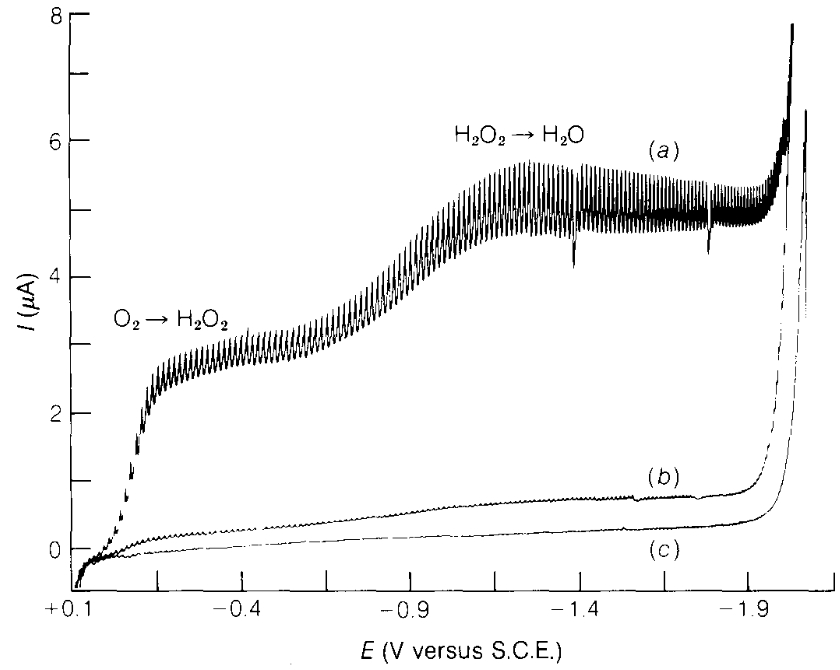
Reaction	$E_{1/2}$ vs SCE	Supporting electrolyte
$Cu^{2+} \rightarrow Cu$	0.04	0.1 M KCl
$Sn^{4+} \rightarrow Sn^{2+}$	-0.25	4 M NH_4Cl,1 M HCl
$Pb^{2+} \rightarrow Pb$	-0.40	0.1 M KCl
$Pb^{2+} \rightarrow Pb$	-0.50	0.4 M Na tartrate
$Pb^{2+} \rightarrow Pb$	-0.76	1 M NaOH

Note how the $E_{1/2}$ value can be shifted by changing the supporting electrolyte.

Polarographic Maxima and Its Suppression

- The current voltage curves obtained during polarographic analysis are not always well defined, S shaped curve as expected by the theory.
- But frequently the current keeps on increasing on the rising portion of the curve to much a higher value and falls on suddenly to attain steady limiting current. It is known as maxima.
- The maxima can be eliminated by adding surface acting agent like gelatin or triton X-100. These substances are called as maxima suppressor. The proper amount or maxima must be determined by trial and error.





Polarogram of 0.1 M KCl. (a) Saturated with air. (b) After partial deaeration. (c) After further deaeration. [L. Meites, *Polarographic Techniques*, 2nd ed. (New York: Wiley, 1965).]

Effect of Dissolved Oxygen

- Oxygen dissolved in the solution will be reduced at the DME leading to two well defined waves which were attributed to the following reactions:
- $O_2(g) + 2H^+ + 2e^- <====> H_2O_2$; $E_{1/2} = -0.1V$
- $H_2O_2 + 2H^+ + 2e^- <====> 2H_2O$; $E_{1/2} = -0.9V$
- $E_{1/2}$ values for these reductions in acid solution correspond to -0.05V and -0.8V versus SCE.
- This indicates that dissolved oxygen interferes in the determination of most metal ions.
- Therefore, dissolved O_2 has to be removed by bubbling nitrogen free oxygen into the solution before recording the polarogram.

APPLICATIONS

Qualitative and quantitative analysis of mixtures of organic or inorganic samples can be done even in low concentration without separation. They are given in detail as follows:

- Inorganic applications(qualitative and quantitative)
  - Composition of alloys
  - Purity of elements
  - Analysis of trace elements like copper, zinc, iron, lead, nickel, manganese etc

- Organic applications
- Electroreducible or oxidisable functional groups can be determined by polarographic technique
- Eg:- functional groups like Nitro and Nitroso groups, azo and diazo compounds, aldehydes, ketones, organic peroxides, lactones organic halogen compounds, disulphides, activated C=C, some acids and organo metallic compounds.
- Functional group can be inferred from half potential and the quantity of the substance can be determined from fusion current measurement

- Multi stage reduction of groups like nitro to nitrous to Hydroxylamine, amino group can also be achieved

RNO_2 -> R-NO -> R-NHOH -> $R-NH_2$

Examples of groups analysed by Polarography

Nitro groups:-

Chloramphenicol, nifedipine, felodipine, amlodipine, nimodipine

Aldehydes and ketones:-

vanillin, p-benoquionone, vitamin k and its derivatives, keto steroids

THANK YOU