POLAROGRAPHY

ADVANCED INVENTION

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INTRODUCTION

- Polarographic Analysis.
- Is a method of analysis based on the measurement of current electrolysis of an electroactive species at a given electrode potential under controlled conditions.
- It is the branch of voltammetry where the working electrode is a dropping mercury electrode (DME) or a static mercury drop electrode (SMDE), which useful for their wide cathodic ranges and renewable surfaces.

POLAROGRAPHY

- In 1922, Polarography was developed by (zech chemist, Jaroslav Heyrovsky , who won the noble prize for his discovery.

- An electromechanical techniques of analysing solutions that measure the current flowing between two electrodes in the solution as well as gradually increasing applied voltage to determine respectively the concentration of a solute and its nature.

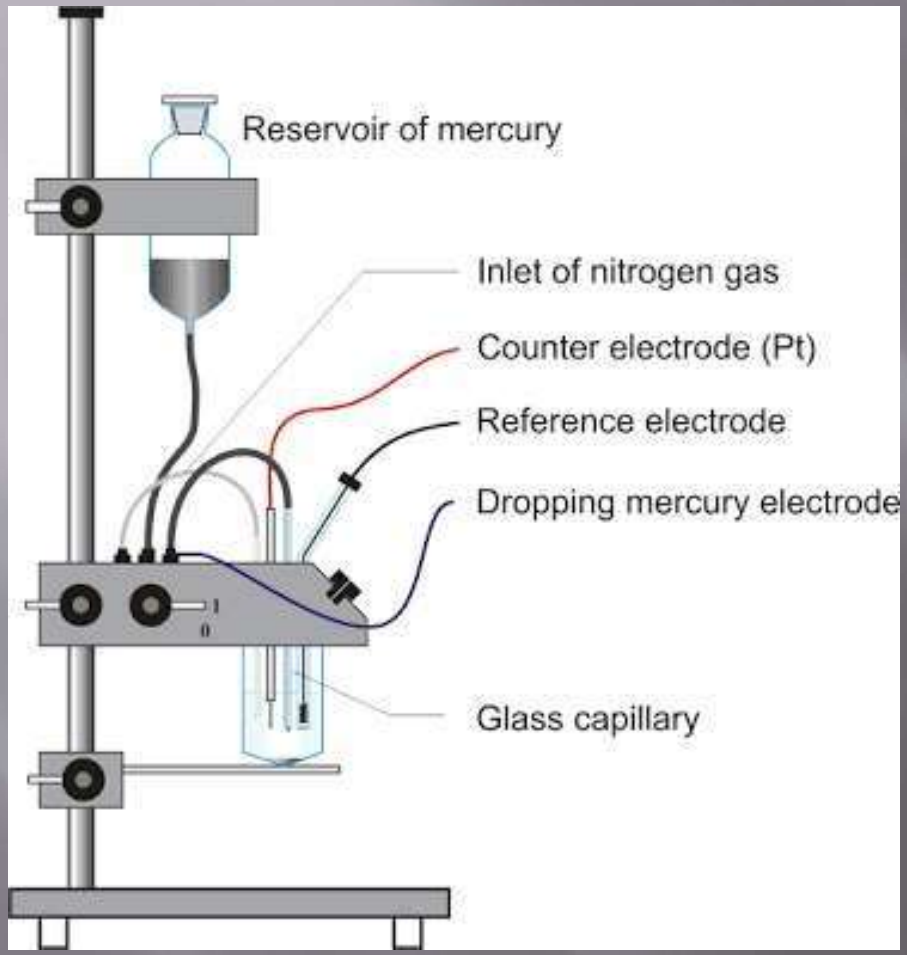
Polarographic Analysis

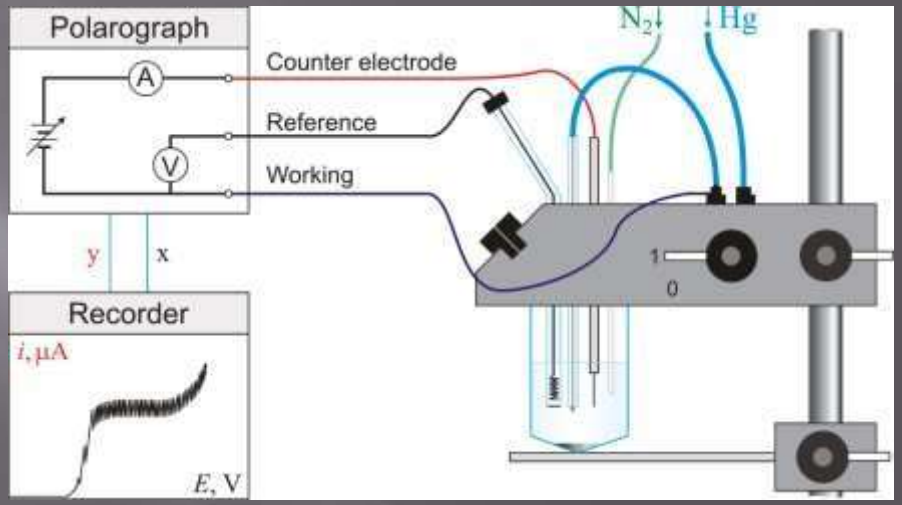
- Is a method of analysis in which the solution to be analysed is electrolysed in such a way that the graph of current against voltage shows what is in solution and how much is present.
- In this method, a reference electrode and an indicator electrode are required.

- Reference elecrode – acts to maintain a constant potential throught the measurement.

- Indicator electrode – acts to maintain a constant potential impressed upon it from an external source.

DIAGRAM:


Reservoir of mercury
Inlet of nitrogen gas
Counter electrode (Pt)
Reference electrode
Dropping mercury electrode
Glass capillary


Polarograph
A
V
y
x
Recorder
i, μA
E, V
Counter electrode
Reference
Working
N2
Hg

EXAMPLES OF MERCURY ELECTRODES:

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

Examples of electrodes

- **HMDE(HANGING MERCURY DROP ELECTRODE)-**We extrude the drop of Hg by rotating a micrometer screw that pushes the mercury from a reservoir through a narrow capillary.
- **DME(DROPING MERCURY ELECTRODE)-** mercury drops at the end of the capillary tube as a result of gravity. Unlike the HMDE , the mercury drop of a DME grows continuously as mercury flows from the reservoir under the influence of gravity and has a infinite of several seconds . At the end of its lifetime the mercury drop dislodged ,either manually or its own. and replaced by new drop.

- DSME (STATIC MERCURY DROP ELECTRODE)- uses a solenold driven plunger to control the flow of mercury. Activation of the solenold mometerily lifts the plumber , allowing mercury to flow through the capillary and forming a single,hanging Hg drop

ADVANTAGES OF DME:

- Surface area is reproducible
- Constant renewal of electrode surface eliminating poisoning effect
- Mercury forms amalgams with most metal ions and alkali metal ions which are reducible
- It is useful over the range of +0.4 to -1.8V

DISADVANTAGE OF DME

- Electrodes cannot be used above +0.4V
- Capillary is difficult to maintain sice dust or either particularly matter can be block the capillary
- Mercury can be easily oxidixied thus limit the feasible range of the electrode

PRINCIPLE

- Study of solutions or of electrode processes by means of electrolysis with two electrodes , one polarizable, the former formed by mercury regularly dropping from capillary tube.
- POLARIZED ELECTRODE : Dropping Mercury Electrode (DME)
- DEPOLARIZED ELECTRODE : Saturated Calomel Electrode

- Mercury continously drops from reservoir through a capillary tube into nthe solution
- The optimum interval between drops for most analysis is between 2 and 5 seconds.

WORKING (INSTRUMENT DIAG)

- It consist of polarsable elctrode (DME) and non polarsible electrode (saturated calomel electrode)
- Between these electrodes, the required potential range (0 to -3v) can be applied
- It consist of sample cell in which the sample solution to be analysied tis kept

- Sample cell made up of glass and has tampering edge to hold at the bottom to hold mercury – after the droplets have been formed
- The capillary is dipped into the solution to be analysed and the height of mercury reservoir is analysied in such a way drop time of about 2-7 sec is set
- Supporting electrolite be like kcl (50-100 times sample conc) is added to the sample solution to eliminate migration current.

- In polarographic analysis “ diffusion which is proportional to the conc of the electrolite and hence only the diffusion current has to be measured
- In normal condition , without the supporting electrolyte, migration current is also recorded which is not required
- Oxygen present in sample solution is removed by passing nitrogen or using alkaline pyrogallol solution . Maximum suppressors are added in the req conc.
- When all these things are done , initial and final potential is set in the instrument the current voltage cure is recorded

- From the current voltage curve , half wave potential & diffusion current is determined and thus qualitative and quantitative analysis is performed

POLAROGRAPHIC DATA

- Obtained from an automatic recording instrument is called a polarogram, and the trace a polarographic ware.

- POLAROGRAM

  It is a graph of current versus potential in a polarographic analysis.

3 categories:

A. Collectively referred to as residual current

B.Referred to as diffusion current resulting from the reduction of the sample

C. Called the limiting current

- The diffusion current of a known concentration of reference standard are first determined followed by the determination of the determination of the diffusion current of the unknown concentration.

POLAROGRAM

- (Residual current) which is the current obtained when no electrochemical change takes place.
- (Average current/limiting current)is the current obtained by average current values throuhtout the life time of the drop while
- (Diffusion current) which is the current resulting from the diffusion of electroactive species to the drop surface.

RESIDUAL CURRENT MIGRATION CURRENT

- It is the sum of the relativity larger condens current (charging current) and a very small faradic current.

- It is due to migration of cations from the bulk of the solution towards cathode due to diffusive force . Irrespective of concentration gradient

DIFFUSION CURRENT

- Diffusion current is due to the actual diffusion of electroreducible ion from the bulk of the sample to the surface of the mercury droplets due to concentration gradient

LIMITING CURRENT

- Beyond a certain potential , the current reach a steady value called as the limiting current

FACTORS AFFECTING DIFFUSION CURRENT

- **CONCENTRATION : ** Diffusion current is **directly proportional** to concentration of the electroreducible ions . This forms the basis quantitative analysis. i.e, if concentration is less , then diffusion current is less . If concentration is more then diffusion current also more

TEMPERATURE

- Diffusion of ions is being affected by temperature hence diffusion current also varies with respect is temperature (directly proportional)

ILKOVIC EQUVATION:

$$I_d = 708\, n\, C\, D^{1/2}\, m^{2/3}\, t^{1/6}$$

- I_d= diffusion current due to electro reducible ions.
- n =no of electrons involved in the reduction of one molecule.
- C =conc. Expressed in mmol/lit
- D = wt .of mercury flowing through capillary
- i = drop time in seconds.

QUALITATIVE ANALYSIS:

- Direct comparison method.
- CCM- calibration curve method.
- Internal standard or pilot ion.
- Method of standard addition.

INORGANIC ANALYSIS:

- composition of alloy.
- Purity of element.
- Analysis of trace trace elements like copper, Zn, iron, nickle, lead, manganese.
- Trace metals and metal containing drugs.
- Blood and serum cancer diagnosis.