POLAROGRAPHY

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UNIT 4: POLAROGRAPHY

- Introduction to voltametric methods of analysis
- Principles of polarographic analysis
- Dropping Mercury Electrode
- Instrument and working of polarographic apparatus
- Ilkovic equation and quantitative analysis
- Polarogram and chemical analysis
- Analysis of mixture of cations
- Factors affecting polarographic wave
- Applications

INTRODUCTION TO VOLTAMETRIC METHODS OF ANALYSIS

- Voltammetry refers to electrochemical methods in which a specific voltage profile is applied to a working electrode as a function of time and the current produced by the system is measured.

- This is commonly done with an instrument called a potentiostat, which for these measurements is capable of applying variable potentials to the working electrode relative to a reference electrode (like Ag/AgCl) while measuring the current that flows as a result of the electrode reaction.

- Voltametry = current voltage technique

- Depending on the particular method, it is possible to apply reducing and/or oxidizing potentials.
- When a reduction occurs, the current is called a cathodic current.
- When an oxidation occurs, the current is called an anodic current.
- Different voltammetric methods involve different voltage profiles.
- Voltammetric methods are among some of the most common electrochemical methods in use today.
- There are a variety of voltammetric methods.
- Major of these methods: anodic stripping voltammetry (ASV), linear sweep voltammetry, and cyclic voltammetry (CV).

POLAROGRAPHY

- Polarography is a branch of voltametry
- It is differing from potentiometry
- In potentiometry the potential difference between the two electrodes is measured while the current flowing between the electrodes is held constant (usually at about zero)
- Polarographic technique was discovered by J. Heyrovsky

PRINCIPLES OF POLAROGRAPHIC ANALYSIS

- In polarography, microelectrolysis is carried out with the help of two electrodes.

These two electrodes are –

- Reference electrode
- Indicator electrode

Reference electrode

- This electrode has a comparatively large surface area
- This is the nonpolarisable (constant potential) electrode
- This generally acts as an anode and may be a pool of mercury or a saturated calomel electrode

Indicator electrode

- This electrode has a comparatively small surface area
- This is the polarisable electrode
- An electrode is considered to be polarised when it adopts a potential impressed upon it with little or no change of current.
- This is generally functioning as a cathode and is dropping mercury electrode (DME).
- This is also called as microelectrode or working electrode.

- Polarography involves the study of the correlation between the electric current passing through the cell and the voltage applied between the electrodes.

- The potential is varied in some preselected manner during the current measurement.

- The graphical representation of the measurements (current vs voltage) is called as polarogram and the apparatus used for these measurements is called as polarograph.

- The polarogram gives both qualitative and quantitative information about the solution under test.

DROPPING MERCURY ELECTRODE

- Mercury continuously drops from reservoir through capillary tube into the solutions
- The optimum interval between drops for most analysis is between 2 to 5 seconds.

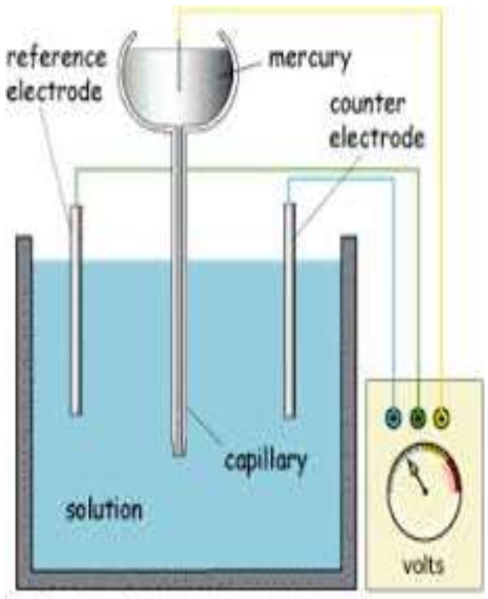
- Why mercury? Mercury as a working electrode is useful because :
  - It displays a wide negative potential range.
  - It's surface is readily regenerated by producing a new drop or film

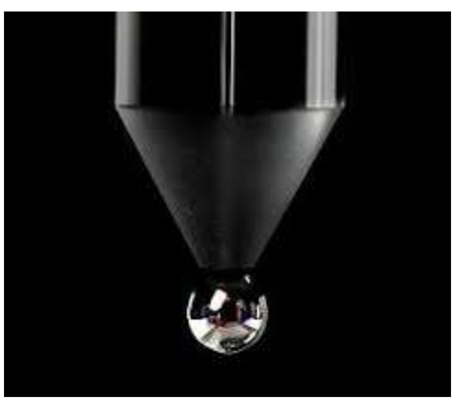
- Mercury flows continuously through the capillary and adds to the growing drop at the end of the capillary that serves as the working electrode.

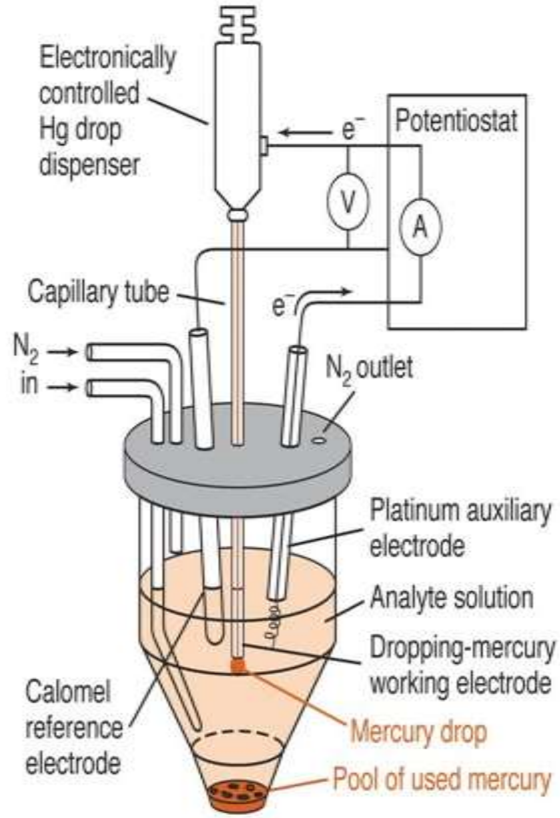
- As the drop grows, its surface area increases. There is an increase in current due to electrical double-layer formation (i.e.more and more counter-ions move in to surround the exposed mercury drop surface as it grows).

- The charging current follows the rate of growth of the drop surface (not it's volume)

INSTRUMENTATION







Polarography apparatus featuring a dropping- mercury working electrode.

ADVANTAGES OF DME

- The surface area of mercury drop is smooth, continuously renewed and surface area is reproducible. This eliminates passivity and poisoning effects.
- Mercury forms amalgams with many metals.
- Mercury has a high hydrogen over voltage
- The surface area of the mercury drop can be calculated from the weight of the drop.
- Since the electrode is continuously renewed, series of reducible species can be estimated in given solution
- The diffusion current assumes a steady value immediately after each change of the applied potential and is reproducible.
- It can be used over the range of +0.4 volts to -2.0 volt with reference to the saturated calomel electrode.

INSTRUMENT AND WORKING OF POLAROGRAPHIC APPARATUS

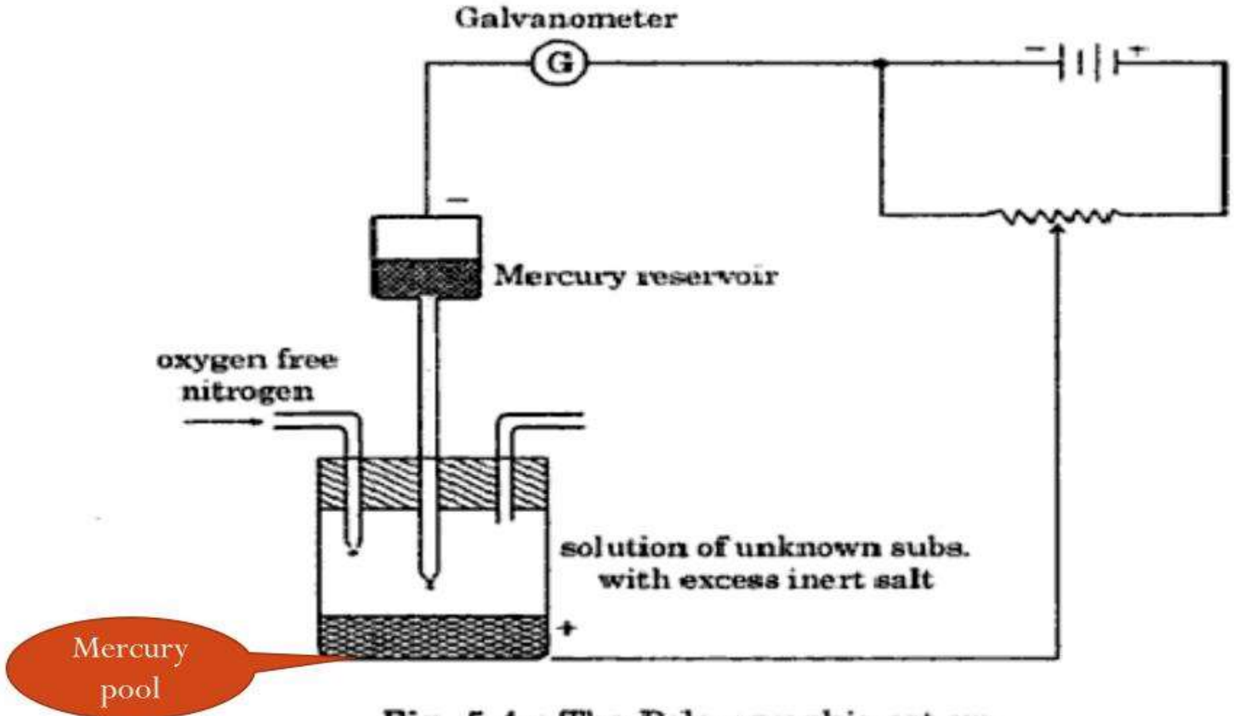


Fig. 5.4 : The Polarographic set up.

INSTRUMENT AND WORKING

- A polarographic cell consists of a smell easily polarisable microelectrode or indicator electrode, a non polarisable reference electrode and the solution – electrolyte to be analyzed.

The cell consists of –

- **The Cathode**
- **The Anode**
- **The Electrolyte solution**

The Cathode -

- The dropping mercury electrode acts as a cathode.
- It acts as a indicator electrode.

The Anode -

- Large amount of mercury is placed at the bottom of the cell and the electrolyte solution is placed above it.
- This pool of mercury acts as an anode having area comparatively large.
- It is a non-polarisable electode
- Its potential remains constant.

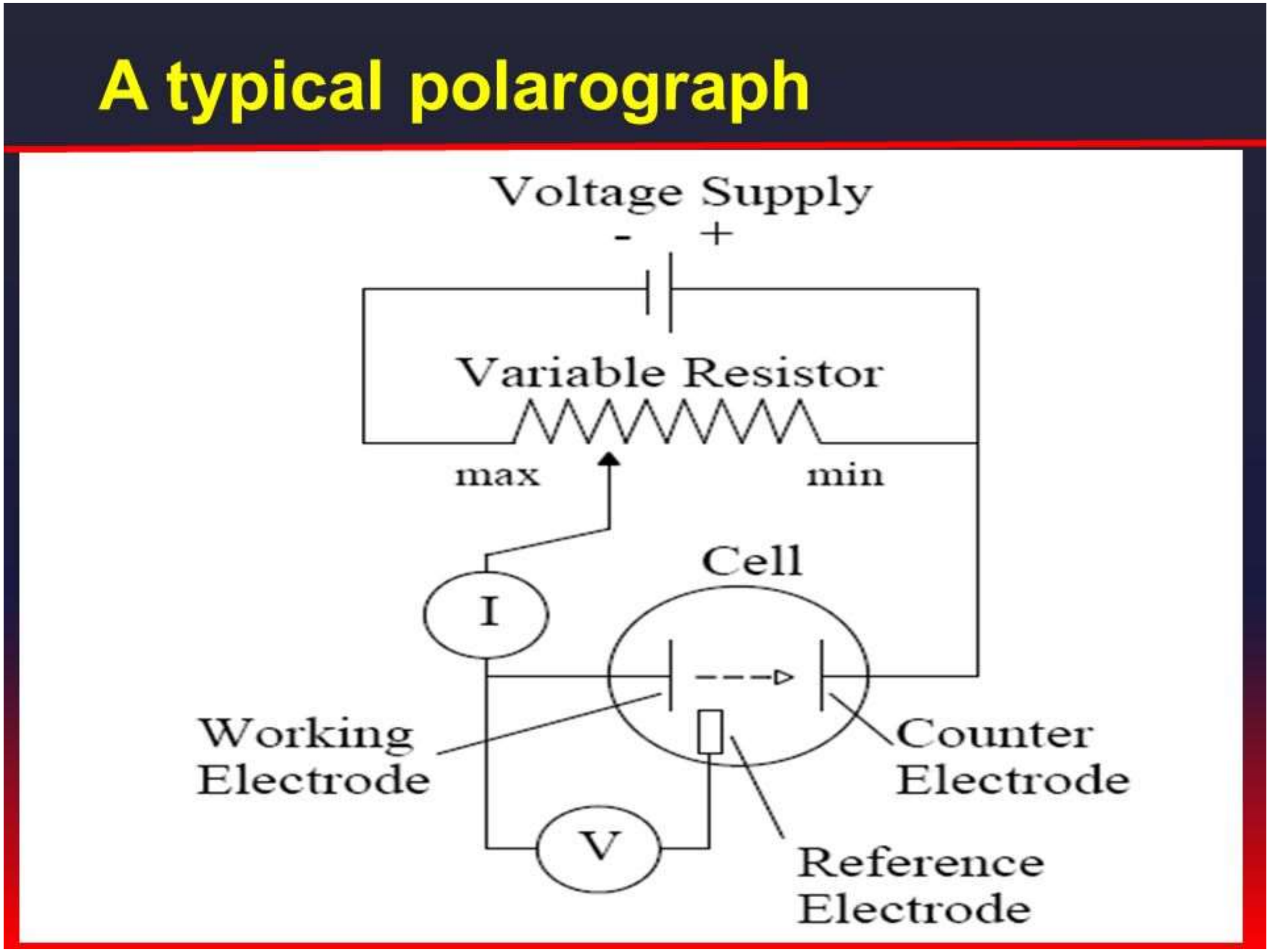
The Electrolyte solution

- The polarographic cell contains the solution of the substance to be analysed and large amount of KCL.
- Here KCL acts as a supporting electrolyte whose concentration is at least 100 times larger than that of analyte.
- In this solution, solution of maximum suppressor is added.

The removal of oxygen from the solution –

- The inert nitrogen gas is bubbled through the sample solution in a polarographic cell.
- It expels dissolved oxygen from the solution.
- N2 gas is bubbled through the solution before but not during actual measurement.

POLAROGRAPH



WORKING

- The test solution of supporting electrolyte and maximum suppressor is placed in the cell and nitrogen gas is bubbled through the solution to expel dissolved oxygen in it.
- The cell is fitted with DME which serves as a cathode and pool of mercury or SCE which acts as an anode.
- The drops of mercury are allowed to fall into the solution from DME.
- The applied voltage is increased slowly, measured by the potentiometer.
- When the applied potential of the DME is adjusted to the reduction potential of the metal ion in the solution, then the metal ions are reduced to metal by the reaction –

$$Mn^{+} + n\,e^{-} \rightleftharpoons M(s)$$
$$Cd^{2+} + 2\,e^{-} \rightleftharpoons Cd\,(s)$$

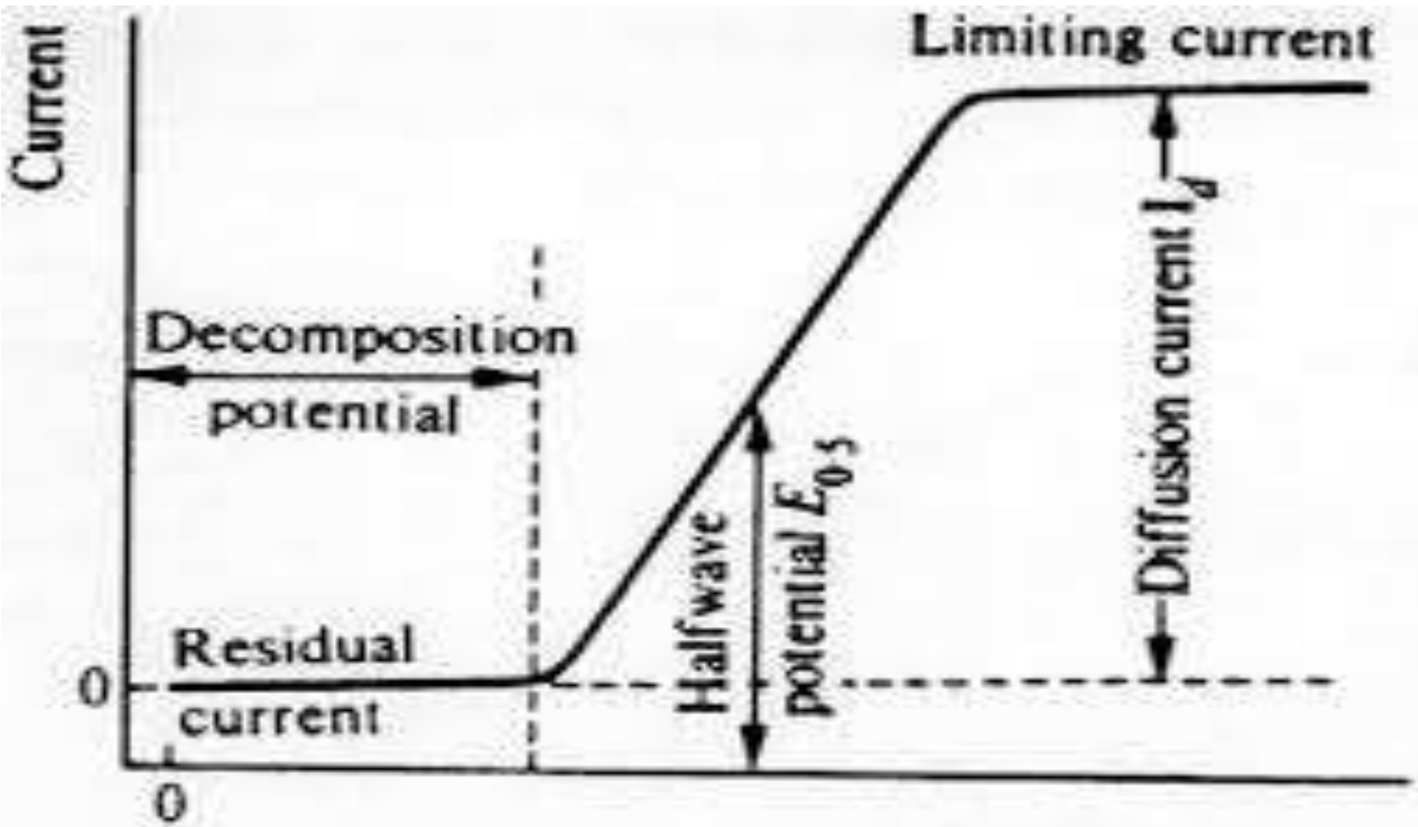
- Then the metal dissolves in the mercury drop to form an amalgam as,

$$M(s) + Hg = M(Hg)$$
$$Cd\,(s) + Hg = Cd\,(Hg)$$

- The amalgam formed is removed from the electrode and settles down at the bottom of the cell.
- The resulting current flowing through the cell is measured with the help of galvanometer.
- The average current voltage curve is drawn by plotting applied emf values abscissa and current as ordinates. – Polarogram.

- https://youtu.be/C8CM7d5e5Vg
- https://youtu.be/AbemMe19fF4

IDEAL POLAROGRAPHIC WAVE



ILKOVIC EQUATION AND QUANTITATIVE ANALYSIS

- Ilkovic equation is a relation used in polarography relating the diffusion current (i_d) and the concentration of the depolarizer (c), which is the substance reduced or oxidized at the dropping mercury electrode.
- The Ilkovic equation has the form

$$i_d = k\, n\, D^{1/3} m^{2/3} t^{1/6} c$$

- Where
  - k is a constant which includes Faraday constant,
  - π and the density of mercury, and has been evaluated at 708 for max current and 607 for average current,
  - D is the diffusion coefficient of the depolarizer in the medium (cm^2/s),
  - n is the number of electrons exchanged in the electrode reaction,
  - m is the mass flow rate of Hg through the capillary (mg/sec), and
  - t is the drop lifetime in seconds, and c is depolarizer concentration in mol/cm^3.

- The equation is named after the scientist who derived it, the Slovak chemist, Dionýz Ilkovič 1907-1980).

FACTORS AFFECTING POLAROGRAPHIC WAVE

- **Residual current -**

  Residual current = Condenser current + Faradic current

(i) **Condenser current**

(ii) **Faradic current**

- **Migration current**
- **The supporting electrolyte**
- **Diffusion current**

http://yengage.yenepoya.edu.in/idata/YenepoyaUniversity/ilFile/4/55/file_45592/001/UNIT%20VII.pdf

http://vlab.amrita.edu/?sub=2&brch=190&sim=687&cnt=1

APPLICATIONS OF POLAROGRAPHY

- Polarography is used widely employed for the analysis of trace metals in the alloys including ultra-pure metals, minerals/metallurgy, environmental analysis, foodstuffs, beverages and body-fluids, toxicology and clinical analysis.
- In the biological systems it is used to determine vitamins, alkaloids, hormones, terpenoid substances and so on.
- In medical field polarography is used to analyze natural colouring substance of drugs and pharmaceutical preparations, determining pesticide or herbicide residues in food stuffs, and in the structure determination of many organic compounds.
- Since a fresh, smooth, reproducible drop is produced at regular intervals of time contamination or surface poisoning will be limited.