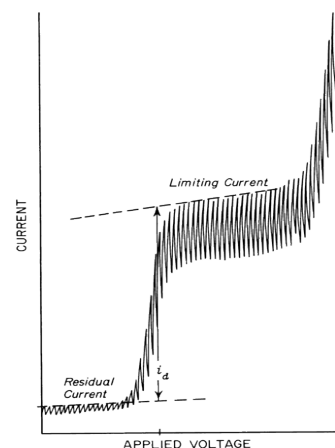


POLAROGRAPHY

Definition: Polarography is an electrochemical method of analysis based on the measurement of current flow resulting from the electrolysis of a solution at a polarisable microelectrode as a function of applied voltage.

Principle:

- Polarography is based upon the principle that gradually increasing voltage is applied between two electrodes, one of which is polarisable (dropping mercury electrode) and other is non-polarisable and current flowing between the two electrodes is recorded.
- A sigmoid shape current-voltage curve is obtained from which half wave potential as well as diffusion current is calculated.
- Diffusion current is used for determination of concentration of substance.
- Half wave potential is characteristic of every element.



Ilkovic Equation:

Ilkovic equation is a relation used in polarography relating the diffusion current (i_d) and the concentration of the non-polarisable electrode, i.e., the substance reduced or oxidised at the dropping mercury electrode (polarisable electrode).

$$i_d = 607 nD^{1/2} m^{2/3} t^{1/6} C$$

Where,

- i_d = Diffusion current in *microamperes*
- 607** = Constant of various **numerical factors** including: Faraday constant (Π), density of Hg, etc.,
- n = Number of electrons duly involved in the electrode reaction,
- D = Diffusion coefficient in $cm^2 \cdot sec^{-1}$,
- m = Weight of Hg flowing *via* the capillary in $mg \cdot sec^{-1}$,
- t = Drop time in *seconds*,
- C = Concentration in *mmol/L*.

The **Ilkovic Equation** holds good for the '**drop-time**' to vary between 2 to 8 seconds. In order to accomplish this aim and objective the following two critical adjustments may be done carefully:

- Length of capillary
- Manouvering the Hg-pressure to bring the drop time very much within the range (i.e., 2-8 sec)

There are four major governing factors that influence the Ilkovic equation:

1. Both 'm' and 't' shall change with the dimensions of the capillary (its length) and the applied pressure of Hg reservoir to form the 'drop'.
2. **Height of Hg column** must be maintained constantly as the 'drop time' solely depends upon the applied pressure by the **column of Hg** at the tip of **DME** and '**analyte**' **solution interface**.
3. **Applied voltage** in a DME-assembly is responsible for causing possible changes occurring in the prevailing '**surface tension**' of a **drop at the tip of electrode**.
4. Evidently, the variations in **temperature** and **viscosity** must be at bare minimum level because it disturbs the '**diffusion coefficient**' most significantly.

Definition:

1. Residual current (i_r):

The current that flows in the absence of the depolarizer (i.e. due to the supporting electrolyte) is called residual current. This has to be taken into consideration while interpreting the polarograms.

It is the sum of the relatively larger condenser current (i_c) and a very small faradic current (i_f).

$$i_r = i_f + i_c$$

i_c (**condenser current**) – is due to the formation of Helmholtz double layer at the mercury surface.

i_f (**faradic current**) – is due to the traces of impurities.

2. Migration current (i_m):

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

3. Diffusion current (i_d):

The difference between Residual current and Limiting current is called Diffusion Current (i_d).

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

4. Half wave potential

Half wave potential is the potential at which the concentration of oxidised and reduced forms at electrode surface is equal. i.e., 50% of oxidised and 50% of reduced forms are present.

5. Limiting current (i_l):

Beyond a certain potential, the current reaches a steady state value called as the limiting current. At this point, the rate of the diffusion of ions is equal to the rate of reduction of ions, and the state of electrode is said to be concentration polarised.

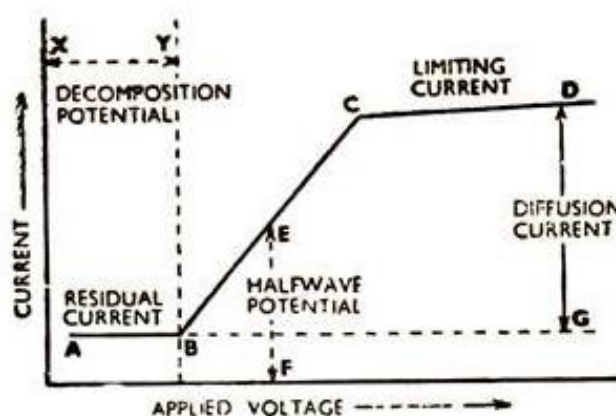
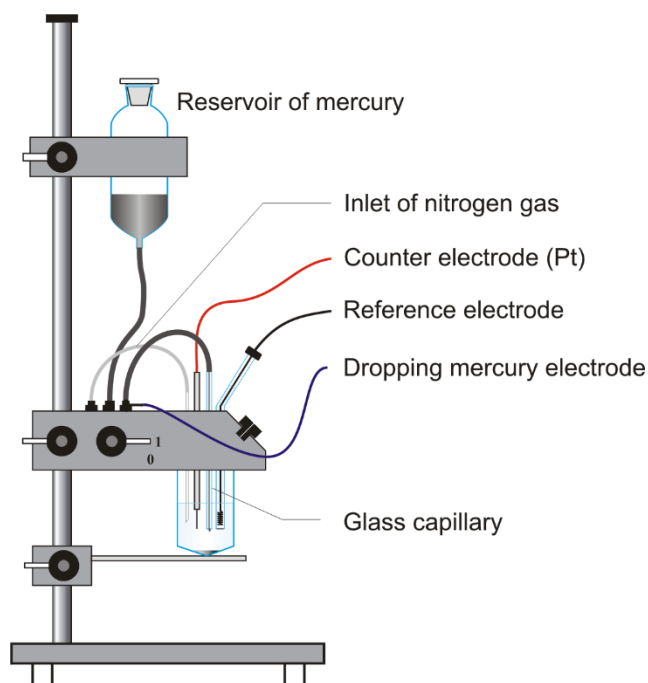


Fig. 1. Current-applied voltage curve (Polarogram)

Dropping Mercury Electrode (DME):

Dropping mercury electrode (DME) is a working electrode arrangement for polarography in which mercury continuously drops from a reservoir through a capillary tube (internal diameter 0.03 - 0.05 mm) into the solution. The optimum interval between drops for most analyses is



between 1 and 5 s. The unique advantage to the use of the DME is that the constant renewal of the electrode surface, exposed to the test solution, eliminates the effects of electrode poisoning.

Construction:

- The assembly consists of a mercury reservoir.
- It consists of fine capillary having bore size ranged from 20-50 μ and 10-15 cm long.
- The capillary is connected to mercury reservoir by rubber tubing.
- A small glass electrolysis cell in which the unknown solution is placed.
- The height of the mercury reservoir is adjusted such that drop time is 1-5 seconds.

Working:

- Dropping mercury electrode (DME) is a polarisable electrode and can act as both anode and cathode.
- The pool of mercury acts as counter electrode, i.e., anode if DME is cathode or cathode if DME is anode.
- The counter electrode is a non-polarisable electrode.
- To the analyte solution, electrolyte like KCl is added i.e., 50-100 times of sample concentration.
- Pure nitrogen or hydrogen gas is bubbled through the solution, to expel (remove) out oxygen.
- Eg: If the analyte solution contains cadmium ions, then cadmium ions are discharged at cathode.
$$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$$
- Then, gradually increasing voltage is applied to the polarographic cell and current is recorded.
- Graph is plotted between voltage applied and current. This graph is called Polarograph and the apparatus is known as Polarogram.
- The diffusion current produced is directly proportional to concentration of analyte and this is used in quantitative analysis.
- The half wave potential is characteristic of every compound and this is used in qualitative analysis.

Advantages:

1. Surface area is reproducible.

2. Electrode can be renewed and thus eliminates poisoning effect.
3. Mercury forms amalgam (solid solutions) with many metals.
4. The surface area can be calculated from the weight of the drop.

Disadvantages:

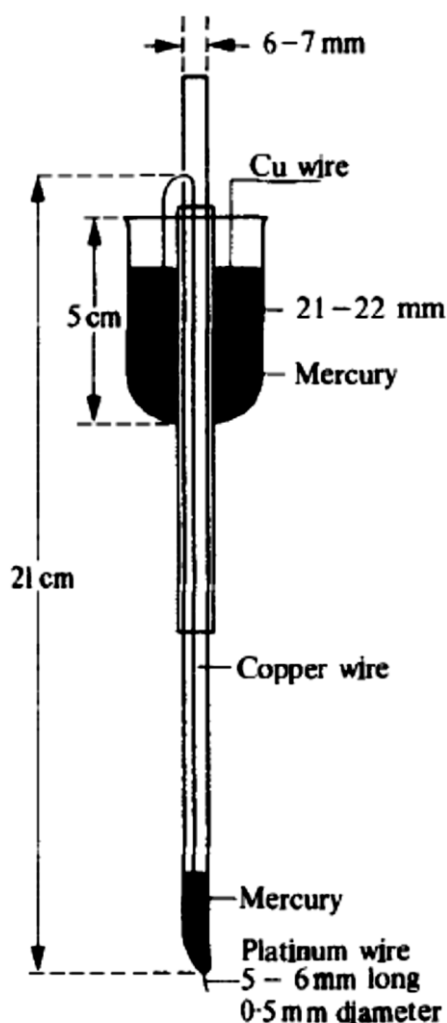
1. Capillary is very small and thus can be easily blocked.
2. Mercury is very toxic.
3. Surface area of each drop of mercury is never constant.
4. It cannot be used at higher positive potential due to oxidation of mercury.

Rotating Platinum Electrode:

DME has disadvantage that it cannot be used at high potential due to oxidation of mercury. Therefore, platinum electrode is used in such cases.

Why the platinum electrode is rotated?

If the platinum electrode is stationary then diffusion current will be slowly attained, so to overcome this problem platinum electrode rotated at constant speed, which results in increasing sensitivity and rate of attaining steady diffusion current.



Construction:

The construction of the rotating platinum electrode is evident from the figure.

The electrode is constructed from a standard 'mercury seal'.

It consists of about 5mm platinum wire having 0.5mm diameter below standard mercury seal by passing through small hole.

A wire from mercury seal is connected to the source that applies voltage.

The tubing forms the stem of the electrode which is rotated at a constant speed of 600 rpm.

Working:

Rotating platinum electrode is used as an indicator electrode. To the analyte solution supporting electrolyte like KCl is added i.e., 50-100 times of sample concentration.

Pure nitrogen gas is bubbled through the solution to expel out the dissolved oxygen.

Potential is applied across the electrodes and titration is started.

A graph is plotted between the volume of solution added v/s diffusion current and end point is detected.

