



**Construction of DME based Polarographic instrument**

- Electrodes: Indicator (DME) and Reference Electrode (Mercury Pool)
- Voltmeter and Voltage Source
- Recorder

**Electrodes:**

In all electro-analytical methods discussed here, at least two-electrodes are used: an **indicator electrode** and **reference electrode**. When it is necessary to eliminate the role of resistance between the electrodes, a third working (counter) electrode is used.

**Indicator electrode:** on which electrochemical changes in solution composition occur. The solution to be analyzed is placed into an electrolytic cell into which the indicator electrode is immersed.

The surfaces of the electrodes used in the first group are continuously renewed. A representative of such an electrode is the dropping mercury electrode (DME). In this electrode, the mercury is regularly and continuously dropping from the orifice of a glass capillary connected to a reservoir of mercury. A typical lifetime of a mercury drop is between 2 and 5's. **Polarizable electrode – Drop of Mercury available at Mercury reservoir**

**Reference electrode:** The most important part of a cell is its **reference electrode**. The potential of this should remain constant in the course of the experiment. Two kinds of reference electrodes, **“internal”** and **“external”** are in general use. An **internal electrode** is in direct contact with the solution being studied, while an **external electrode** is separated from it by a salt bridge or a porous membrane.

Here in case of mercury pool is used as **internal reference electrode**, since it is non-polarizable its potential largely remains constant. **Non-Polarizable electrode- Mercury Pool at bottom** (Acting as reference electrode)

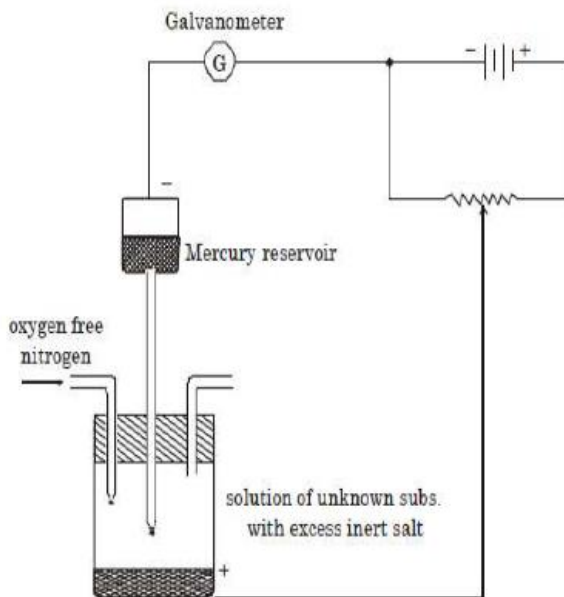
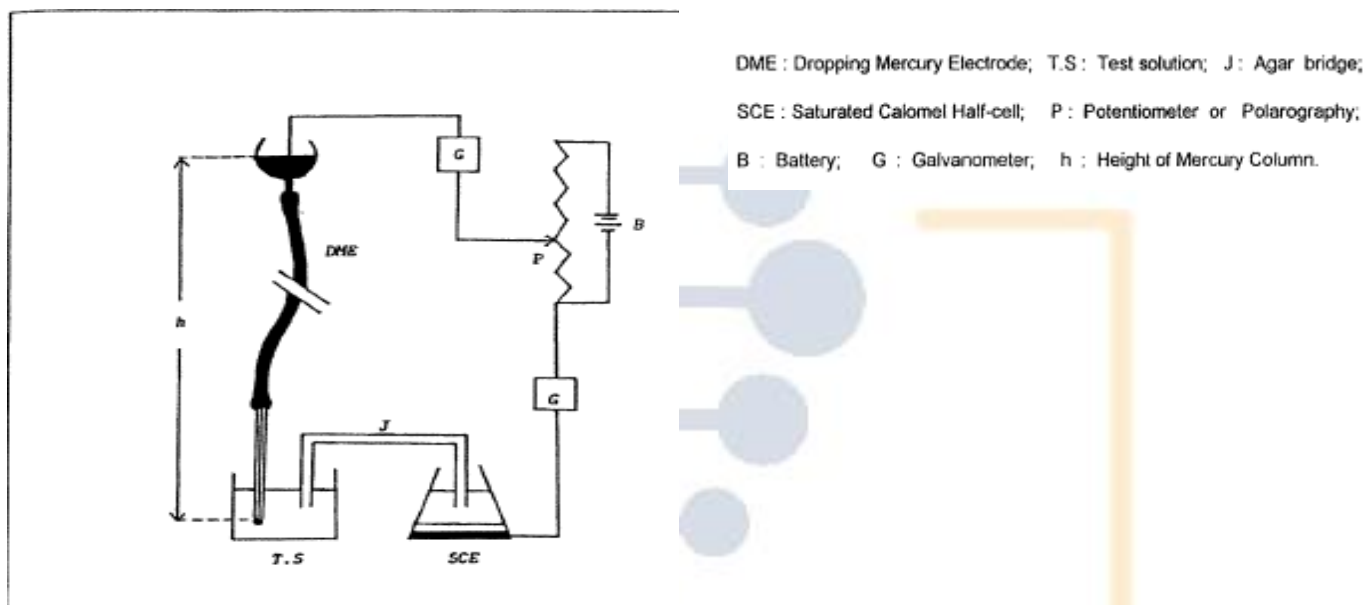


Fig. 1.2: Experimental set up in Polarographic Experiment

The **External reference electrode** is often separated from the investigated solution, either by a liquid/liquid junction or by a porous, chemically inactive material. For example SCE is attached to system. As shown below:



## Voltage source and Digital voltmeter

In each type of assembly Voltage source along with Digital voltmeter is provided which is utilized to apply controlled potential across the drop of mercury.

## Recorder

With the application of this potential either oxidation or reduction of electrochemical species occurs as a result diffusion current is observed. To measure this diffusion current recorder is provided.

## Working of DME based Polarographic instrument

### Working of DME:

- 1) Liquid mercury is passed from Hg reservoir via the fine capillary tubing at a steady and fixed rate. Here Hg drop is allowed to form at tip of capillary tubing, when sufficiently large drop is formed, it detaches from capillary tubing and falls into media. Immediately after it new drop is formed at the process is repeated.
- 2) **Hg Drop (before detachment) acting as cathode, reduction of analyte occurs and Hg Pool acting as anode.** Now with the help of this analyte is get reduced if it is cathode or analyte gets oxidized if it anode.
- 3) When the drop if formed at tip of capillary tubing, potential is applied. Due to smaller surface area, it is easily get polarized.

- 4) In the solution where this this tubing is immersed, one more electrolyte species is present which is known as supporting electrolyte, here KCl used (NaCl can also be used).
- 5) After application of potential, as soon as drop is polarized the electrical double layer of supporting electrolyte is formed around it.
- 6) After formation of electrical double layer, analyte species diffuses toward the drop through this double layer, and gets reduced at electrode surface.
- 7) Due to this diffusion the current is generated which is of interest and termed as diffusing current, and it is directly proportional to concentration of analyte.

### **Polarographic Current :**

The total current that flow in consists of the following components:

- a) Residual Current,
- b) Migration Current and
- c) Diffusion Current.

#### **a) Residual Current**

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

Here, mercury pool is not formed at bottom but voltage is applied. However, this voltage is not sufficient to cause either oxidation/reduction of analyte. With the continued application of voltage to mercury drops forming, polarization occurs which is known as **Activation Polarization**.

#### **b) Migration Current**

When cathode (Hg Drop at tip of capillary tubing) and Anode (Hg Pool at bottom) is formed electrostatic attraction for respectively charged ions is established and with the migration of these electrolytes under electrostatic attraction influence current observed is known as Migration Current.

It is the current due to migration of ions caused by the electrostatic field between the two polarographic electrodes.

The contribution of this component is minimized under experimental conditions by taking large concentrations of the supporting electrolyte.

Under these conditions, only ions of the supporting electrolyte migrate in electrostatic field. The ions of the depolarizer do not take part in migration. They reach the surface of the electrode by the process of diffusion.

### c) Diffusion Current

At this stage: Potential value is reached to value which is sufficient for either oxidation or reduction of analyte species and it is known as **Decomposition Potential**.

Diffusion current is due to analyte ions. When the potential of the d.m.e is in the plateau region the analyte ion are reduced or oxidized as soon as they reach the electrode surface. As a result they are consumed and their concentration in a thin layer of solution in contact with the electrode becomes zero.

Now, there is a concentration gradient of the analyte ion in the solution and these ions or molecules diffuse towards the drop from electrical double layers. The current observed due to flow of this ions is known as Diffusion current.

**Half Wave Potential:** The potential Value at which concentration of reducible species is equal to oxidizable species is called as Half wave Potential.

### d) Limiting Current

With continued application of voltage one stage comes where no proportionate increase in diffusion current observed, while it remains in steady state, this steady state current known as Limiting Current. This limiting current is combination of Diffusion Current and Migration Current.

**The basis for the quantitative polarographic analysis is the existence of the linear proportionality between the diffusion current and the concentration of the depolarizer as given by Ilkovic equation.**

$$i_d = 607 n D^{1/2} C m^{2/3} t^{1/6} \quad \dots(1)$$

where,

$i_d$  = Average diffusion current,  $\mu\text{A}$  ( $10^{-6}$  amps)

$n$  = Number of Faradays per mol involved in the electrode reaction

$D$  = Diffusion coefficient of the electroactive material, ( $\text{cm}^2/\text{sec}$ )

$C$  = Concentration of the electroactive material, (millimoles/litre).

$m$  = rate of flow of mercury through the capillary, (mg/sec).

$t$  = time between successive drops of mercury, (in seconds).

**The terms  $m^{2/3}$  and  $t^{1/6}$  are dependent on the character and size of the capillary, the terms,  $n$ ,  $C$  and  $D^{1/2}$  are determined by the properties of the solute and solution.**