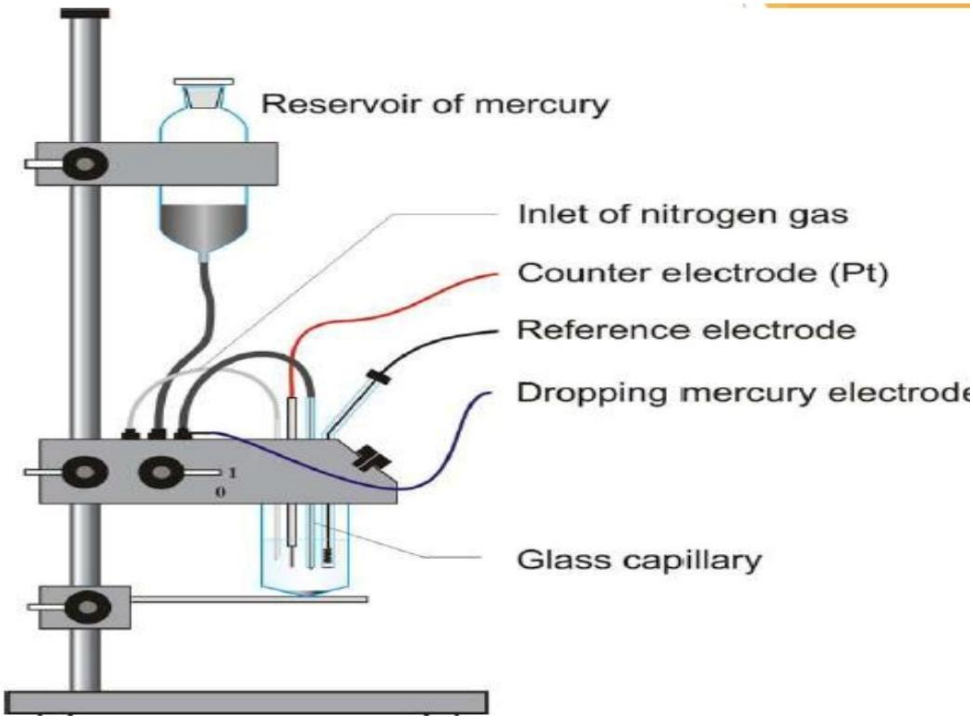
DROPPING MERCURY ELECTRODE

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.

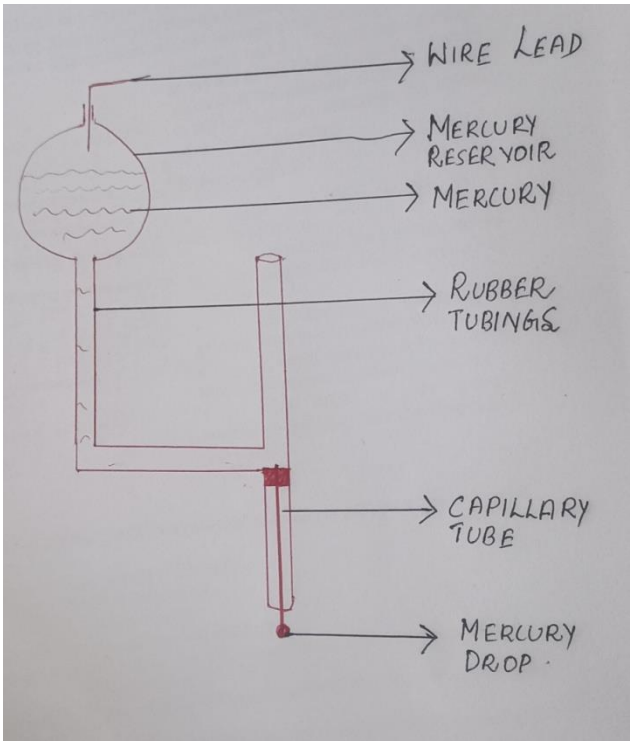


CONSTRUCTION

The whole polarographic setup consists of various parts like ,

1, A MERCURY RESERVOIR

The mercury is placed in a spherical /cylindrical shape container through which the mercury falls drop wise into the sample cell. The reservoir is connected to a rubber tubing, and the mercury enters the glass capillary through which it falls into the sample cell.



2.Glass Capillary

The fine capillaries with bore sizes ranging from 30 to 50 millimetres and lengths ranging from 10-15 centimetres are used. Rubber tubing joins the capillary to the mercury reservoir. The height of the mercury reservoir with glass capillary is arranged in such a way that the drop time will be between 1-5 seconds

3.Nitrogen inlet

A supply of nitrogen gas is given to remove the oxygen present in sample

4. Counter electrode

The drop of mercury falling from the DME will become a pool of mercury and it acts as the counter electrode. It is consider as the non-polarisable electrode.if DME is cathode , Counter electrode will act as an anode(+ve) charged.

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WORKING

Various steps involved in polarography using DME are;

1, Sample solution (analyte) to be determined is collected in the sample cel.

2, Arrange all the electrodes in such a way that it's completly immersed inside the sample solution.

3, Height of glass capillary is arranged as the dropping time will be between 1 – 5 seconds.

4, Pure nitrogen or hydrogen gas is supplied to remove or expel air / oxygen present inside the sample.

5, A supporting electrolyte of KCl is added to the sample in the ratio of 50 – 100 times of sample.

6, Gradually increse the potential between the electrodes. During this time the supporting electrolyte KCl will dissociate into K^+ & Cl^- ions.

$$KCl \longrightarrow K^+ + Cl^-$$

7, The analyte soln; for example if it contains cadmium ions; then it

will be discharged towards the cathode.

ie $Cd^{2+} + 2e^- \rightarrow Cd(s)$.

↓ move / discharge towards Cathode.

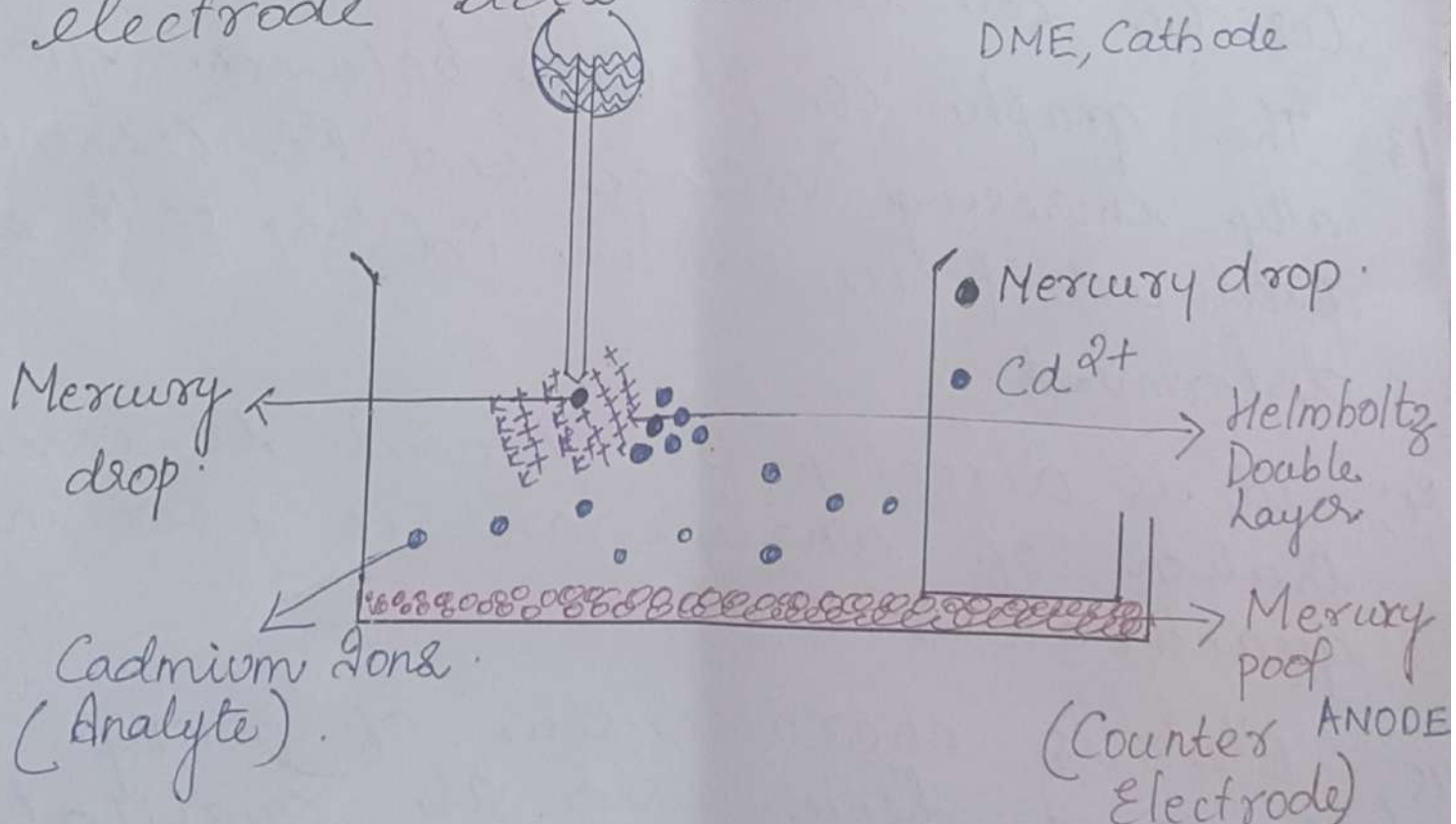
8, The dropping mercury electrode is the polarisable electrode and can act as both cathode and anode.

9, The pool of mercury acts as counter electrode; i.e. a non polarisable electrode.

if DME acts as anode, counter electrode acts as cathode

&

if DME acts as cathode, counter electrode acts as an anode.



10, As DME acts as cathode; (−)ve charged it will attract (+)ve charged ions present in sample cell. As the concentration of KCl taken is high K^+ ions will be in more concentration than Cd^{2+} ions, hence Both Cd^{2+} and K^+ ions will move towards cathode. K^+ ions will form a Helmholtz double layer around the mercury drop as shown in the figure. This results in condensor current.

12, As the Cd^{2+} ions has to diffuse through the Helmholtz double layer to reach the mercury drop; it's called diffusion current 'id'; which is characteristic for each analyte.

13, The graph is plotted between gradually increasing voltage and the current produced from which 'id' & $E^{1/2}$ are determined.

'id' is directly propotional to concentration of analyte and is used in quantitative analysis

'$E^{1/2}$' is characteristic of every compound, hence used as qualitative analysis