# Introduction, Principle, Advantages & Disadvantages

## Who was Jaroslav Heyrovsky?

Heyrovsky was born in Prague, Checkoslovakia, in the year 1890. He was a good science student and he decided to be a nobel prize winner in the year 1904 when William Ramsay was awarded Nobel prize for the discovery of noble gases.

Though we know the main topic of Heyrovsky's work was on dropping mercury electrode; It was not him who first constructed a dropping mercury electrode. Credit goes to C F Varley and Gabriel Lippmann who made the first DME after getting attracted by the conductivity and large negative electrode potential of the liquid metal. The fact that mercury exists as liquid is very convenient in electrochemistry as we can construct electrodes in any shape; meaning to say any liquid attains the shape of its container. Later the Czech physicist Bohumil Kucera extensively used the electrode for measuring surface tension of polarized mercury. However the method was very cumbersome and also he couldn't explain the results. It was at this time Heyrovsky met Kucera during his PhD defense. Kucera asked some questions to Heyrovsky related to Electrocapillarity and his own experiments. Heyrovsky explained his answer; Kucera was so impressed that he asked Heyrovsky to join him.

He was given the task to measure the changes in surface tension with the applied voltage. For each measurement Heyrovsky had to collect the mercury after 80 measurements; weigh and repeat again. After careful examination he found that he could use the drop time for the calculations instead of weighing Hg. He suspected the passage of electrolytic current was the problem with the inconsistent results and decided to measure the current. In the afternoon of Friday, the 10th of February 1922, he connected a sensitive mirror galvanometer, to the electrolytic circuit with the dropping mercury electrode dipping into 1 M solution of sodium chloride. The instantaneous current oscillated rhythmically according to the regular growing and falling of the drops. After the mean values of the current oscillations were plotted as a function of the voltage applied to the electrodes, the resulting polarization curve showed two equally high steps of current increase, about 0.8 V apart, and a final steep increase of current out of scale, corresponding to the highest value of 2.0 applied volts.

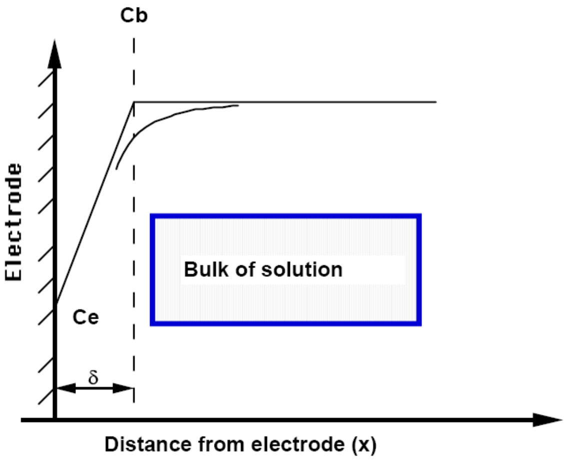
Here you can see the notebook of Heyrovsky in which he recorded the results. After the first experiment he conducted a series of experiments and he found out the diffusion current was directly proportional to the concentration of the analyte. Hearing about the experiment the Japanese scientist, Dr. Masuzo Shikata arrived to work with Heyrovsky. Very soon they made an instrument which will automatically draw the variation of current with applied voltage. Thus, the polarization of dme along with the current was recorded and the polarograph came in to picture. It was in 1933 that Ilkovic the Russian scientist gave the theoretical basis and derived the equation relating direct dependence between the diffusion current and concentration. Heyrovsky also found out that the potential at which the diffusion current was maximum for each analyte was different. This led to the discovery of polarographic wave equation by which we can identify the chemical species present in the solution.

## Principle and basic instrumentation of POLAROGRAPHY

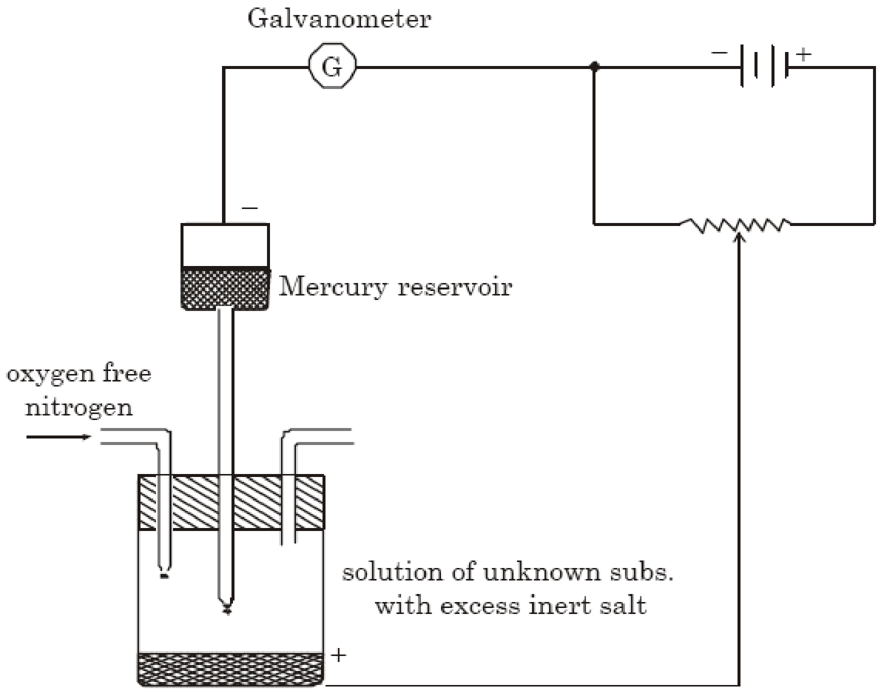
### Concentration polarization:-

At anode the dissolution of metal will result in an increase in the number of ions in contact with it in the solution. If rate of diffusion is slow, the concentration of cations in the immediate vicinity of anode will be greater than in the bulk of the solution. This creates an increase in potential.

Opposite situation arises at the cathode. As cations gets discharged at cathode, there will be decrease in concentration of cations around the electrode. Thus there will be a concentration difference compared to the bulk of the solution. The potential of the electrode thus increase in the cathodic direction and rate of discharge of cations becomes greater.



Polarography is the study of the electrolysis of solutions of electrooxidizable and or electroreducible substances between a **dropping mercury electrode (DME)** and some reference electrode (RE) . The potential between these electrodes is varied and the consequent changes in the flow of current is measured Fig. 1. On plotting the changes in current flow versus the potential variation, one obtains an **i - E** curve known as **polarogram**. The first scientist who discovered the use of the DME in electrolysis is Jaroslaw Heyrovsky in 1922 and received the Nobel Prize in Chemistry in 1959.



From the measurements of the current - potential curves resulting from electron transfer processes at the surface of a **DME**, the identity and concentration of the reactant substance can be determined. One of the virtues of polarography is that solutions as dilute as **$10^{-8}$ M** can be analyzed and sample volumes as small as **0.05 ml** can be manipulated. Thus, the position of a wave in a polarogram along the potential axis gives the identity of the substance while the magnitude of the limiting current gives picture of the concentration variation of this material. A very pure mercury patch can be obtained through distillation under vacuum (99.99 % pure ) . Each drop represents a fresh electrode with a new exposed surface. The reproducibility of geometry of each drop with the laps of time is another advantage of the DME over other electrodes. The large **activation overpotential** for hydrogen gas evolution makes this electrode valuable for the study of cathodic processes.

One of the most important drawbacks of the Hg as electrode is its **ease of oxidation**. Thus, Hg undergoes **anodic dissolution at +0.25 V vs. SCE** and is oxidized to insoluble Hg2Cl2 in presence of chloride ions at zero V vs. SCE so it cannot be used for anodic oxidation above +0.25 V vs. SCE. Also it is important to mention that **Mercury vapors are very poisonous** besides Hg itself is considered to be one of the major **pollutants of the environment.**

A **polarogram** or better a polarographic wave has the S shape illustrated in Fig. 2

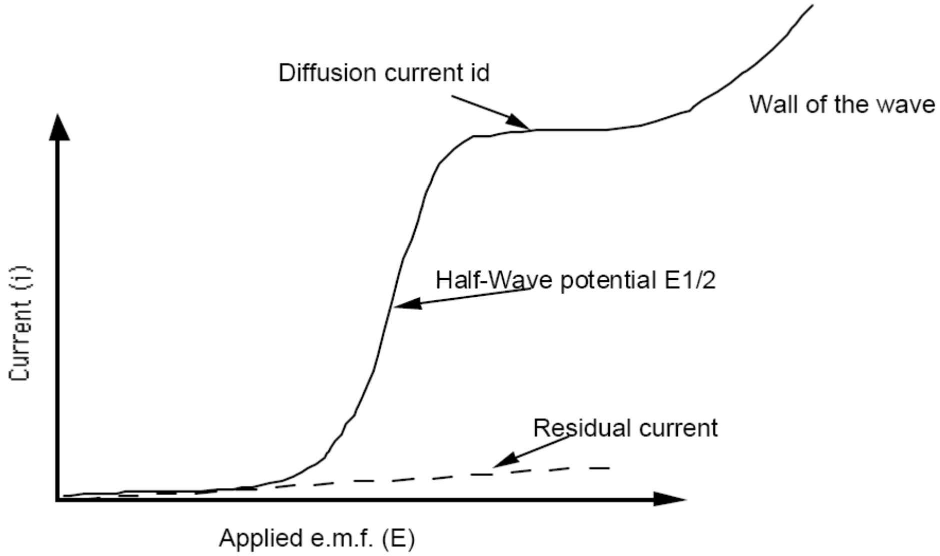


**Fig.2 The i - E Curve ( Polarogram )**

The slowly increasing current at the foot of the wave is known as the residual current. This current is non faradaic in nature. The diffusion current id is, as shown, the distance between the limiting diffusion plateau and the residual current. The potential at the midpoint of the wave, where the current is exactly half its limiting value, is known as the half-wave potential $E_{1/2}$ and its quantity is characteristic of a particular species under fixed experimental conditions. Thus $E_{1/2}$ value serves as finger-print for the species undergoing redox. Furthermore, the limiting current is usually proportional to concentration of the species being reduced or oxidized and thus serves for quantitative analyses.

*Over the diffusion current plateau region the DME is behaving as a completely polarized electrode since it adopts any applied potential to it with no change in current flow. It is interesting to notify that polarization always results from slow stage in the overall electrode process. The slow stage here is the diffusion process which occurs very much slower than the electron transfer. This type of polarization is known as concentration polarization and the DME is said to be concentration polarized.*

At potentials corresponding to the rising part of the wave the electrode is depolarized since here the current flow is strongly dependent on the applied potential. At this stage it is important to emphasize that in any electrolysis two types of processes are encountered.

**i-** Mass transfer process which brings the electroactive material to the electrode surface

**ii-** Electrochemical process which involves the act of electron transfer between the

surface of electrode and the electroactive species.

The mass transfer is usually achieved through **a-** migration, **b-** diffusion and **d** convection.

**Migration** is an electric field effect and depends upon the charge on the species, concentration and mobility in a field of force. **Diffusion** depends upon differences in concentration between species at the surface of the electrode and in the bulk of solution. Finally **convection** arises from any mechanical or thermal disturbance in the solution. For a redox process to occur it is essential that electrons pass between the electrode and the species in solution.

However, by no means electron transfer in its crude definition acts alone, thus adsorption, rearrangement of electronic configuration within the species to give a suitable form for the electron exchange is a normal observable sequence. After the electron exchange a primary product is formed which undergoes an electronic rearrangement, desorption and may suffer further side reactions to form the final product. These electrolytic processes may be reversible or irreversible in nature depending on the activation energy values.

## Role of supporting electrolyte in polarographic analysis:-

In polarographic analysis excess of supporting electrolyte is added to the electrolytic solution. The concentration of supporting electrolyte is 10 times higher than the electrolytic solution. The role of supporting electrolyte is to support to the ions of the electrolyte for the migration from solution to DME. Migration of charged particles caused due to potential difference existing between the electrode and solutions. The diffusion of particles from the solution to the surface of DME is due to difference in concentration. Another advantage of the supporting electrolyte is ionic strength of the solution is maintained.

Role of supporting electrolytes

1. To make the solution sufficiently conducting by ensuring a low electrical resistance. This is very important during the use of non aqueous solvents.
2. The highly conducting ions of supporting electrolyte carries much of the migration current while the analyte ions can carry the diffusion current.

## Advantages of Dropping mercury electrode:-

1) Surface is reproducible, smooth and continuously renewed.

2) Hg forms soluble amalgam with many metals hence lowers their reduction potentials.

3) High over voltage of hydrogen on mercury makes possible the deposition of ions difficult to reduce in aqueous solution eg.alkali metal ions.

4) The surface area can be calculated from the weight of the drops.

5) Diffusion current assumes steady value

## Limitations of Dropping mercury electrode:-

1) Hg is costly and poisons.

2) Current passing through the cell increases as drop grows and decreases as drops breaks.

3) DME electrode generates some current like Residual current, migration current, kinetic current which add error in current measurement.

4) Hg is oxidized ,it restricts the use of electrode as anode.

## Applications of polarography:-

1) Estimation of inorgainc and organic substances
2) Analysis of mixtures
3) Determination of diffusion coefficients