POLAROGRAPHY :-

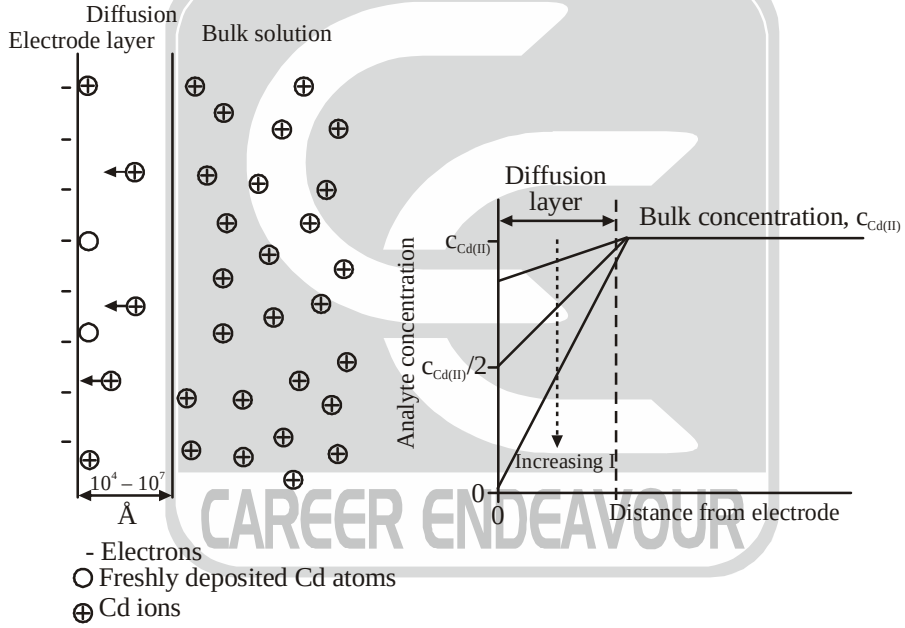
In this, subtance is determined by providing voltage and recording the current during the process.

Component of direct current (DC) polarography :-

(1) Working Electrode :- The electrode at which reduction or oxidation of substance takes place.
In direct current (DC) polarography, working electrode is dropping mercury micro electrode Generally, it is used as cathode.
(2) Counter Electrode :- In DC polarography, counter electrode is generally a pool of mercury or saturated calomel electrode
(3) Supporting Electrolyte :- This is used to eliminate migration current.
(4) Solution of Electroactive Substance :- It is a solution which is under study

Conditions of Working Electrode :-

(1) Working electrode should be concentration polarised so that current which flows through the electrode is propertional to concentration gradient
(2) Working elecrode should have very small surface area to induce polarisation.
(3) Working electrode should not get contaminated as current in polarography is very sensitive to impurity.
(4) Counter Electrode should have a large surface area so that it has a low current density and is non polarised and thus its potential remain constant.



Concentration Polarisation

It occurs due to finite rate of ion transfer from solution (bulk) to electrode surface. Metal ions near to working electrode will get reduced first and there is a fall in concentration of metal ion in the near vicinity of electrode. To maintain the steady current, electrode must be supplied with ions from the bulk of a solution. Concentration polarisation occurs when ions do not arrive at electrode surface fast enough to maintain the desired current. This transportation of ions can be achived by diffusion migration and convection. In dc polarography, we focused only on diffusion process.

(1) Migration Effect : The process of movement of positive ion towards negative electrode due to electrostatic interaction is called migration effect.
This can be reduced to negligible value by adding the salt (KCl), that does not react at working electrode at the potential being used and is called a supporting electrolyte.
The amount of supporting electrolyte added is 100 – 200 times of electroactive ion. On doing so, the ion of supporting electrolyte is present in excess and therefore the current generated due to migration effect is greatly carried by ions of supporting electrolyte.

(2) Convection Effect : The movement of active ions towards electrodes due to stirring or agitation is called convection effect.

This can be eliminated if we take unstirred or undisturbed solution.

(3) Diffusion Effect : The movement of ions towards working electrode due to concentation gradient is called diffusion effect.

The current generated is directly proportional to the difference in concentration of ion at bulk and at electrode surface. Higher the difference, higher will be the current generated.

$I \propto (c^o - c)$ c^o = concentration of ion at bulk

$I = K(c^o - c)$ c = concentration of ion at near vicinity of electrode

where, $K = \frac{DnAF}{\delta}$ D = Diffusion coefficient

n = number of moles of electrons requred for depostion per mole of electroactive species.

A = Surface area of drop

δ = distance of diffusion

$D = \frac{uRT}{zF}$ u = mobility of ion

R = gas constant

T = temperature

z = charge number of ion

F = Faraday

Current will have maximum value when concentration gradient is maximum i.e. c = 0

So, $I_d = Kc^o$

where I_d is diffusion current

Polarography Set up: