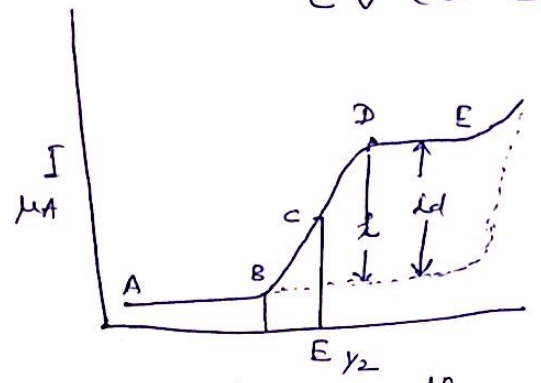
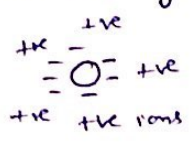


Factors affecting Limiting current:

CV curve

Residual I:

growing Hg drop, ions from supporting electrolyte gather around it.
 Drop is -ve & ions are +ve
 eg: KCl soln; \bar{c} K⁺ ions.
 K⁺ → attracted to drop.
 K⁺ → not reduced to K atom until -ve potⁿ is too ↑



K⁺ remain close to Hg surface → electrical double layer
 It is like charging of a condenser.
 When one drop falls another forms & new condenser is charged up.
 ∴ Continuous flow of electric I that goes as Potent^l of Drop is ↑.
 Charging I is zero, when surface tension is max.
 Happens at about 0.52 V more -ve than sat. Calomel electrode.
 If electrolyte contains impurities; small faradic current is superimposed on condenser current.
 ∴ $I_x = I_f + I_c$

Migration I:

Electroactive material reaches surface of electrode by:-
 ① Migration of charged particles in electrical field caused by potential difference existing b/w electrode surface & the soln.
 ② By diffusion of particles.

I req. for above 2 processes is Migration I.
 Migration current can almost be eliminated if an indifferent electrolyte is added to soln in a conc. so large that its ions carry almost all the I.

eg: 0.1 M KCl & 0.01 M Cd ions. → soln.
 ∴ I is carried by all the ions present in soln.
 Fraction of I carried by each type of ion will depend on its relative concⁿ compared to other ions + transport no.
 Here, about 90% of I will be transported to cathode by K⁺.
 If conc. of K⁺ is ↑ to more than 99% of total cations present, relative I carried by other cations are reduced to zero. ∴ All I thru cell will be transported by K⁺ ion.

Hittorf's no or Transport no: or Transference no.
 by an ion is known as transport no.
 t_+ t_-
 How much charge is carried by an ion is its transport no.
 $t_+ = u_+$ $t_- = u_-$ ②

Fraction of total I carried
 Ionic mobility of cation u_+
 among u_-
 Charge or $\frac{\lambda_+}{F}$ $\frac{\lambda_-}{F}$
 carried by ion. Faraday const. 96500 C

Divide eq. -1 by eq. 2

$$\frac{t_+}{t_-} = \frac{u_+}{u_-} \quad \text{if add } +1 \text{ to both sides } \therefore \frac{t_+}{t_-} + 1 = \frac{u_+}{u_-} + 1$$

$$\frac{t_+ + t_-}{t_-} = \frac{u_+ + u_-}{u_-} \quad \text{interchange } \frac{t_-}{t_+ - t_-} = \frac{u_-}{u_+ - u_-} \quad \text{--- (3)}$$

Both ions carry same charge $\therefore t_+ + t_- = 1$

$$t_- = \frac{u_-}{u_+ + u_-} \quad t_- = \frac{\lambda_-^0}{\lambda_m^0} \quad \text{from Kohlrausch law.}$$

$$t_+ = \frac{\lambda_+^0}{\lambda_m^0}$$

depends on speed of ions.

Diffusion I :- I_d :

It is Max. current. I_1 & I_2

$I_d \propto$ Conc. of subs. being reduced or oxidised at DME

I_d is given by Ilkovic eq.

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

i_d = diff. current in μA averaged over lifetime of drop.

n = no. of e^- transferred/ion. C = Conc. in mmol/lit.

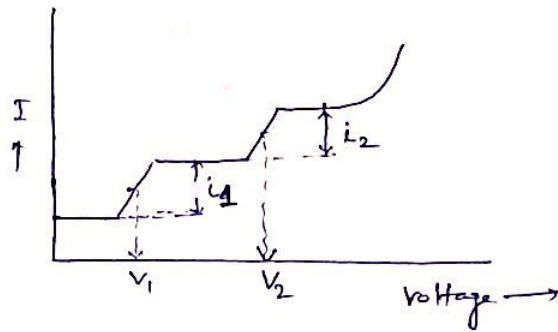
D = Diff. coeff. of reducible ion in cm^2/sec

m = mass of Hg flowing per second in mg.

t = drop time in seconds.

observed $I_d \propto$ Conc. of electroactive material.

Limiting I $\left\{ \begin{array}{l} \text{Kinetic I} \\ \text{Adsorption I} \\ \text{Catalytic I} \end{array} \right.$



Kinetic current:

(Hr. of polarographic wave) Limiting current may be affected by rate of non-electrode reaction \rightarrow Kinetic I.

if rate of chemical reactn. governs Ht. of polarographic wave or limiting current \rightarrow Kinetic I.

$$I_k = 493 n D^{1/2} C_y m^{2/3} t^{2/3} \left(\frac{k_b}{k_r v_c} \right)$$

I_k = Av. kinetic current during life of drop, D = Diff. coeff. of Y or O

C_y = Conc. of Y in mmol/lit. n = no. of e^- transferred m = mass of drop in mg

t = droptime in second.

I_k is direct function of ~~flow~~ size of Hg drop but independent of velocity of flow of Hg from capillary

I_k is formed when oxidized or reduced form of electrosp. are involved in chem. eq. \bar{e} other subst.

