Electroanalytical Techniques-2!

* Potentiometry :- ($\underset{\text{EMF}}{\underline{\text{potential}}}$ of the system)

Direct Potentiometry

→ directly measure the potential

→ activity or concentration of active ion is derived.

Indirect Potentiometry
→ (Potentiometric titration)

→ change in potential on add^n of certain volume of titrant is measured.

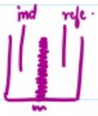
→ cell membrane / sensing surface ⟶ change in activity ⟶ Half cell.
(potential is generated ∝ logarithm of analyte activity)

→ (Potential is measured relative to the inert reference electrode)

→ Potentionmentric measurement ⟶ zero current flow.

* For a complete electrochemical cell, EMF is given by ⟶ 2 electrodes + sol^n.

$$E_{cell} = E_{ind} - E_{ref} + E_j \quad ✓ \qquad — ①$$



E_{cell} = Potential of electrochemical cell.

analyte conc. → E_{ind} = Potential of indicator electrode = senses analyte

usually constant $\begin{cases} E_{ref} = \text{Potential of reference electrode} \\ E_j = \text{Potential of junction.} \end{cases}$

junction = interface b/w two solution.
↳ interferes into the EMF measurement = Should be eliminated.

Acc. to Nernst's eq^n :-

$$E_{ind} = K + \frac{RT}{nF} \ln a_1 \quad — ②$$

$$\ln a_1 = \frac{E_{ind} - K}{RT/nF} \quad — ③ \text{ (using 1 we get)}$$

$$pM = -\log a_1 = \frac{E_{obs} - (E_{ref} + E_j - K)}{RT/nF} \quad — ④$$

At 298K,

$$E_{ind} = K + \frac{0.0591}{n} \ln a_1$$

$$pM = -\log a_1 = \frac{E_{obs} - K'}{RT/nF.} \quad — ⑤$$

where K = constant
K' = constant = experimentally determined.

Ⓘ
* When ion is involved in reaction :-

$$✓ \quad E = E^\circ + \frac{RT}{nF} \ln a_{M^{n+}}$$

* When ion is not involved in reaction :-

Ag wire coated with AgCl.
↳ Ag is involved in reaction
↳ Cl is not involved in reaction.

$$E = E^\circ + \frac{RT}{nF} \ln a_{Ag^+} \quad — ⑥$$

$$K = a_{Ag^+} a_{Cl^-}$$

$$a_{Ag^+} = K. \quad — ⑦$$

$$K = a_{Ag^+} a_{Cl^-}$$

$$a_{Ag^+} = \frac{K}{a_{Cl^-}} \quad — ⑦$$

From 6 and 7,

$$E = E^\circ + \frac{RT}{nF} \ln \frac{K}{a_{Cl^-}}$$

$$E = E^\circ + \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln a_{Cl^-}$$

* How is E_j eliminated ???

1. high concentration of KCl or $NH_4(NO_3)$ where cation & anion have same transport number values.
2. eliminate reference electrode & replace the electrode with solution having same cation as that sol^n.

Boundary	E_j (mV)
0.1 M KCl ‖ 0.1 M NaCl	+6.4
0.01 M KCl ‖ 0.01 M HCl	−2.6
3.5 M KCl ‖ 0.1 M HCl	+3.1

* Electrodes :-

① Indicator electrode :-

potential depends upon activity of particular ion species.
can be in form of gas.
eg. O_2 electrode for ^-OH ions.
Cl_2 electrode for Cl^- ions.

② Reference electrode :-

potential value are known.
Inert, reproducible, reversible, etc.

1. Primary reference electrode — SHE = 0V
2. Secondary reference electrode — calomel electrode = { Hg
   metallic amalgam
   KCl sol^n of fixed conc.

Ⓘⓘ Indirect Potentiometry :- (Potentiometric titration).

→ change in potential as a function of volume of titrant added.
→ end point ⟶ sudden change in potential

● End - Point detection :-

1. Direct method / Graphical method :-

E v/s V
ΔE v/s ΔV } plotted on graph.

⟶ titration curve is symmetrical  max. value is equivalence point

⟶ titration curve is unsymmetrical, max. value depends upon slope.

2. Analytical method / Derivative method :-

This is obtained by first derivative or second derivative of the potential & volume

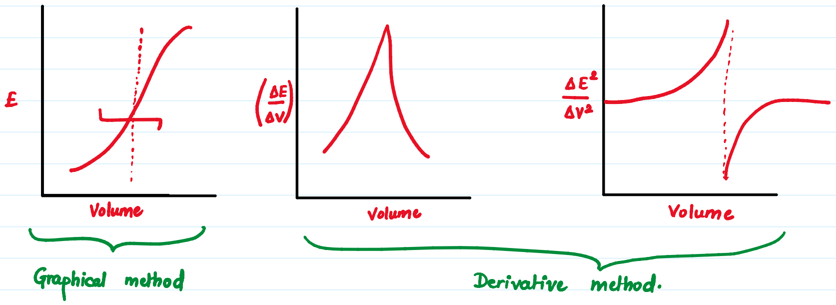
$\downarrow$ $(\Delta E/\Delta V)$ v/s V

$\downarrow$ $(\Delta E^2/\Delta V^2)$ v/s V

2. Analytical method / Derivative method :-

This is obtained by <u>first derivative</u> or <u>second derivative</u> of the potential & volume

$(\Delta E/\Delta V)$ v/s V $(\Delta E^2/\Delta V^2)$ v/s V



* Advantages :-

1) applicable for all type of titration
2) no need external indicator
3) applicable for dilute solⁿ, non-aqueous solⁿ
4) better accuracy
5) other equivalence point, we can get an idea of other thermodynamic property.

(II) Conductometry :-

→ electrical conductance.

→ 2 inert electrode & conductance is measured with Wheatstone bridge.

1. $G = \frac{1}{R}$ G = conductance = reciprocal of resistance
   R = resistance

2. $R = \frac{E}{i}$ E = Potential
   i = current } Ohm's law.

* Conductance depends upon.

1. Temperature :- increases with increase in temp.

2. Nature of ions :- (velocity with which ions move) depends the nature of ions.

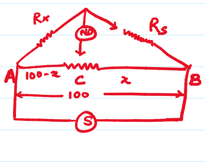
3. Concentration :- no. of ions increases ; conductance increases.

4. Size of electrode :- conductance $\propto \frac{\text{area of electrode}}{\text{length of electrode}}$

$$R = \rho\frac{l}{A} \longrightarrow \underline{\underline{G}} = k\frac{A}{l} \implies G \propto \frac{A}{l}.$$

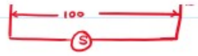
* Measurement of conductance :-

↳ measure the resistance ⟶ conductance
?
↳ using Wheatstone's bridge.



$$\frac{R_s}{R_{CB}} = \frac{R_x}{R_{AC}}.$$ (Null detector; Wheatstone bridge)

$$R_x = R_s \cdot \frac{R_{AC}}{R_{CB}}$$



$$R_x = R_s \cdot \frac{R_{AC}}{R_{CB}}$$

$$R_x = R_s \cdot \left(\frac{100-x}{x}\right)$$

$$G = \frac{1}{R_x} = \frac{1}{R_s} \cdot \left(\frac{x}{100-x}\right)$$

*** Application :-**

→ applicatⁿ in ion chromatography
→ analysis of natural water & brine
→ analysis of ammonia in biological sample
→ analysis of HNO_3 ⟶ NO_2 : H_2O content.

*** Advantages of conductometry.**

→ can be used for turbid solⁿ
→ can be used for coloured solⁿ
→ can be used for dilute solⁿ
→ Rxn is not complete.

Direct Conductometry

Indirect conductometry
(Conductometric Titration)

→ change in the magnitude of conductance } doesn't depend upon the conc.

→ conductance is not useful if accompanied by precipitation or complexation.

Best suit { conductometric titration ⟶ Acid / Base
potentiometric titration ⟶ Redox.

Ⅲ Coulometry :- (Uses Faraday's law)

→ pass current with both electrode polarized ; Electrolysis of solⁿ
→ most common type of electrolysis ⟶ constant current & Indirect method
↓
One electrode
=
generator electrode
=
Titrant generated insitu.

eg. As(III) determination using.

$$\left.\begin{array}{l} 2Br^- \longrightarrow \underline{\underline{Br_2}} + 2e^- \\ AsO_3^{3-} + Br_2 + H_2O \longrightarrow AsO_4^{3-} + 2Br^- + 2H^+ \end{array}\right\} \underline{\underline{\text{used in-situ}}}$$

→ End point is obtained using some indicator electrode.

Ⅳ Polarography :-

→ current voltage curves are constructed
↓
called Polarogram

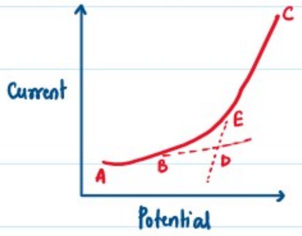
called Polarogram

→ measurement of current at diff. potential.

→ sample is electrolyzed btw two electrodes

Small & Polarizable	large & non-polarizable
→ called as micro	→ called as macro
→ small in size	→ large in size
→ can take up any potential applied to it.	→ has its fixed potential → can't take any potential
→ small surface	→ large surface area

1. Situation 1 :- Electrolysis of metal with appreciable conc. & stirred. ($CdCl_2$)

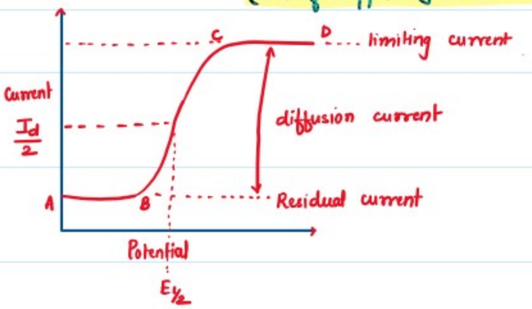


AB → small current
→ acc. Ohm's law
→ no electrode process.

B → deposition of Cd^{2+} reached.
→ cathodic red^n of Cd^{2+} will take place & current increases.
→ Since sol^n is stirred, Cd goes in sol^n & new Cd^{2+} arrives at electrode surface
→ Thus current increases continuously.

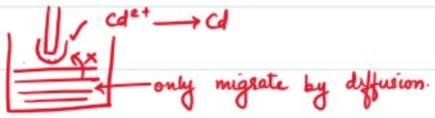
2. Situation 2 :- Electrolysis of metal ion (Cd^{2+}) with small conc. & large conc. of supporting electrolyte and not stirred.

(conc. of supporting electrode = 1000 times more)



AB → Non-faradic / Ohm's law.
→ supporting electrolyte migrat^n
→ Residual current
→ no electrode process

BC → K^+ conc. is more than Cd^{2+}
→ But K^+ doesn't undergo electrode rxn
→ Cd^{2+} start deposition.
→ Red^n of Cd^{2+} takes place.
→ Faradic current increases
→ continues till Cd^{2+} are deposited



C → conc. of Cd^{2+} around electrode = 0
→ sol^n is not stirred.
→ Cd^{2+} migrat^n is prevented
→ Cd^{2+} can only be obtained by diffusion.

Limiting current = $\left[\text{Residual Current}\right] + \left[\text{Diffusion current}\right]$

LC = RC + DC

CD → limiting current
→ current is because of K^+ & Cl^-

(DME = Dropping mercury electrode ⟶ Polarizable) ⟹ used in Polarography.

① Capillary → mercury flows
→ tip, mercury drop is formed, grows in size & detaches

① Capillary
- → mercury flows
- → tip, mercury drop is formed, grows in size & detaches (surface tension can't be balance against weight of the drop)
- → fine & uniform size
- → outer dia = 0.3 to 0.5 cm
  inner dia = 0.03 to 0.05 mm.

② Mercury reservior
- → glass reservior containing Hg.
- → Pt wire through which electrode can be connected to outer circuit.
- → height of mercury reservior = fixed =(30 to 80 cms)
  - ↳ managed such that drop time = 3-6 seconds
    ↓
    time btw two successive fall of Hg drop.
- → Hg is triple distilled.

③ Latex / Rubber tubing ⟶ capillary is connected with reservior.

* advantages :-

1. DME can run from +0.4 V to 2 V V/s SCE.
   beyond +0.4 V ⟶ Hg starts dissolving
   beyond -2.0 V ⟶ Hg starts evolving → Evolution of Hg takes place.
2. most of metals can be scanned btw this range.
3. Electrode area is reproducible, current is reproducible.
4. Electrode surface is continuously renewed, free from product
5. Most metal form amalgam on reduction
6. Electrode area is small, current is in order of few mA. Several measurement is possible.
7. Since electrode surface is renewed, simultaneous determination of metal is possible.

* Disadvantages :-
1. Hg is costly
2. Hg is hazardous
3. Hg purification is necessary.
4. only metal that can form amalgam can be student.
5. Oxidizing agent cant be used.
6. DME acts as anode & can't function at positive potential.

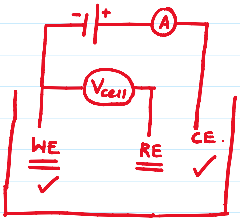
→ we use three electrode system.
Reference electrode

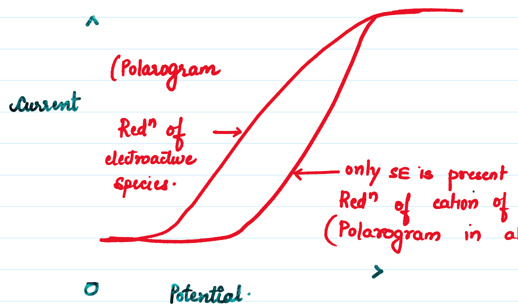
→ we use three electrode system.

Reference electrode

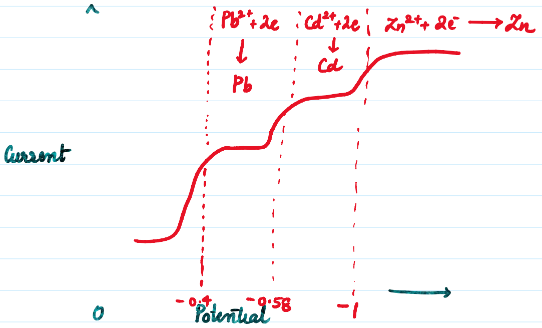
Working electrode → Potential relative to RE } Current passes b/w them.

Auxiliary /Counter electrode





1) Electroactive species is absent
→ only supporting electrolyte is present.
→ current will increase till deposit^n potential of SE reaches.



(Polarogram for more than one electroactive species.)

* Half wave potential → Potential at which current flowing is half the diffusion current

$E = E_{1/2}$ when $i_d = \frac{i_d}{2}$

- indep. of conc.
- depends upon SE.
- helps identify the species.

$$Ox + ne^- \rightleftharpoons Red.$$

$$E_{sys} = E^{\circ}_{sys} - 2.303 \frac{RT}{nF} \log \frac{[Red]}{[Ox]} \quad \text{—①}$$

① (Current is diffusion controlled)

Rate of diffusion ∝ Current ∝ conc. gradient at electrode surface & bulk sol^n.

$$I = \text{Rate of diffusion} = k_1 [Ox_{bulk} - Ox_{electrode}]$$

$$I = k_1 [Ox_{bulk} - Ox_{elec}] \quad \text{—②}$$

When conc. at electrode = 0 ; then current = diffusion current

$$I_d = K_1 [Ox_{bulk} - 0]$$

$$\therefore \quad Ox_{bulk} = \frac{I_d}{K_1} \quad — ③$$

Subs. 3 in 2,

$$\therefore I = K_1 \left[\frac{I_d}{K_1} - Ox_{ele} \right]$$

$$I = I_d - K_1 Ox_{elec}.$$

$$\therefore [Ox]_{ele} = \frac{I_d - I}{K_1} \quad — ④$$

② Amt of substance reduced will depend upon current passed ⇒ Faraday's law.

$$I \propto [Red]_{ele}.$$

$$I = K_2 [Red]_{ele}.$$

$$[Red]_{elec} = \frac{I}{K_2} \quad — ⑤$$

Subs. 4 & 5 in 1.

$$\therefore E_{sys} = E^\circ_{sys} - 2.303 \frac{RT}{nF} \log \frac{[Red]}{[Ox]}$$

$$E_{sys} = E^\circ_{sys} - 2.303 \frac{RT}{nF} \log \left[\frac{I}{K_2} \cdot \frac{K_1}{I_d - I} \right]$$

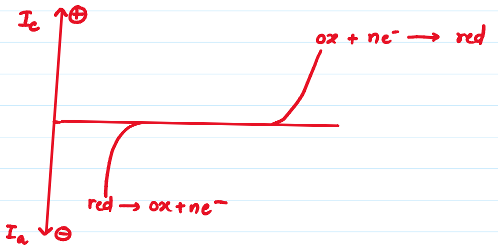
$$E_{sys} = E^\circ_{sys} - 2.303 \frac{RT}{nF} \log \left(\frac{K_1}{K_2} \right) - 2.303 \frac{RT}{nF} \log \left(\frac{I}{I_d - I} \right)$$

$\therefore$ when $I = \frac{I_d}{2}$; $E = E_{1/2}$.

$$E_{sys} = E^\circ_{sys} - 2.303 \frac{RT}{nF} \log \frac{K_1}{K_2} - 2.303 \frac{RT}{nF} \log \left(\frac{I_d/2}{I_d - I_d/2} \right)$$

$$E_{1/2} = E^\circ_{sys} - 2.303 \frac{RT}{nF} \log \frac{K_1}{K_2}$$

$$\therefore E_{sys} = E_{1/2} - 2.303 \frac{RT}{nF} \log \left(\frac{I}{I_d - I} \right)$$



Plotting $E_{1/2}$ v/s $\log \left(\frac{I}{I_d - I} \right)$

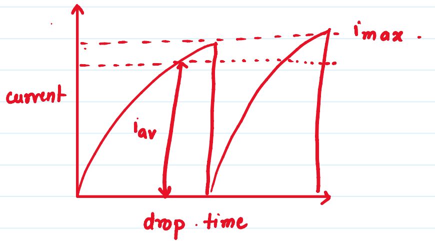
↓

slope = 'n'.

calculate 'n' using this graph.

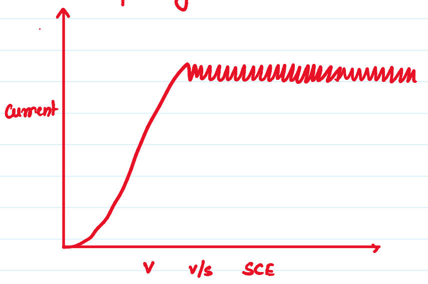
* Ilkovic Eq^n

* Ilkovic Eqⁿ



Hg drop grows → current increases
Hg drop detaches → current becomes zero.

→ Actual polarogram is not smooth



$$(i_d)_{max} = \underbrace{706}_{I}\ \underbrace{nD^{1/2}}_{II}\ \underbrace{m^{2/3}t^{1/6}}_{III}\ \underbrace{C_{bulk} - C_{electrode}}_{IV}$$

I → constant
II → related to medium & electroactive species → n = reactⁿ of electroactive species ; D = diffusion
III → capillary characteristics → depends upon drop time, diameter, etc
IV → conc. of electroactive species.

$$(i_d)_{av} = \frac{6}{7}(i_d)_{max} = \underbrace{607}_{I}\ \underbrace{nD^{1/2}}_{II}\ \underbrace{m^{2/3}t^{1/6}}_{III}\ \underbrace{(C_{bulk} - C_{electrode})}_{IV}$$

n = no. of e⁻ transferred
D = Diffusion coefficient = amt of substance that diffuses per unit area per unit time and unit conc. gradient (cm²/sec)

t = drop lifetime (sec)
c = conc. of species (mmoles dm⁻³)

→ diffusion is directly proportⁿ to conc. of electroactive species.

→ variatⁿ in diffusion current may be 3% to 5% of dependence of diffusion coefficient

* Limitation:-

→ If t is less than 3 sec, drop falls rapidly. Thus solⁿ gets stirred & eqⁿ becomes invalid

→ Eqⁿ is invalid if supporting electrolyte conc. is less than 50 times.

→ This eqⁿ shows diffusion current is independent of temp. Diffusion coefficient depends upon temperature. Increase in D is by 1.5% to 2% per degree rise in increase.

* Oxygen Interference

O_2 ⟶ depolarizer ⟶ subs. gets reduced in presence of electroactive species.

Red^n of O_2 takes place in 2 stages

①
$$\left.\begin{aligned} O_2 + 2H^+ + 2e^- &\rightleftharpoons H_2O_2 \\ 2H_2O + O_2 + 2e^- &\rightleftharpoons 2\bar{O}H + H_2O_2 \end{aligned}\right\} \text{ 0 to } -0.3\text{ V v/s SCE}$$

②
$$\left.\begin{aligned} H_2O_2 + 2H^+ + 2e^- &\rightleftharpoons 2H_2O \\ H_2O_2 + 2e^- &\rightleftharpoons 2\bar{O}H \end{aligned}\right\} -0.6 \text{ to } -1.4\text{ V v/s SCE.}$$

→ Inert Gas is purge 30 mins ⟶ 200 cm³ per minute
↳ Nitrogen gas.

→ Suppresors ⟶ surface active agent
eg. Gelatin
Triton-X.

— min. amt of suppressor.

Thank-You!!!