Electrogravimetry

- Apply potential to cause a soluble species to reduce or deposit on a solid electrode

  e.g., reduce Cu^{2+} onto Pt cathode

  $Cu^{2+}_{(aq)} + 2\ e^{-} \leftrightarrow$ Cu (metal on Pt)

- Change in weight of dried cathode before & after deposition = amount of Cu in sample
- Assumptions:
  - All Cu is plated out
  - Nothing else plates out

$Cu^{2+}{}_{(aq)} + 2\,e^- \leftarrow\rightarrow Cu$ $\qquad E^o = 0.34\ v$

$\tfrac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \leftarrow\rightarrow H_2O$ $\qquad E^o = 1.23\ v$

$Cu^{2+} + H_2O \leftarrow\rightarrow \tfrac{1}{2}\,O_2 + 2\,H^+ + Cu$

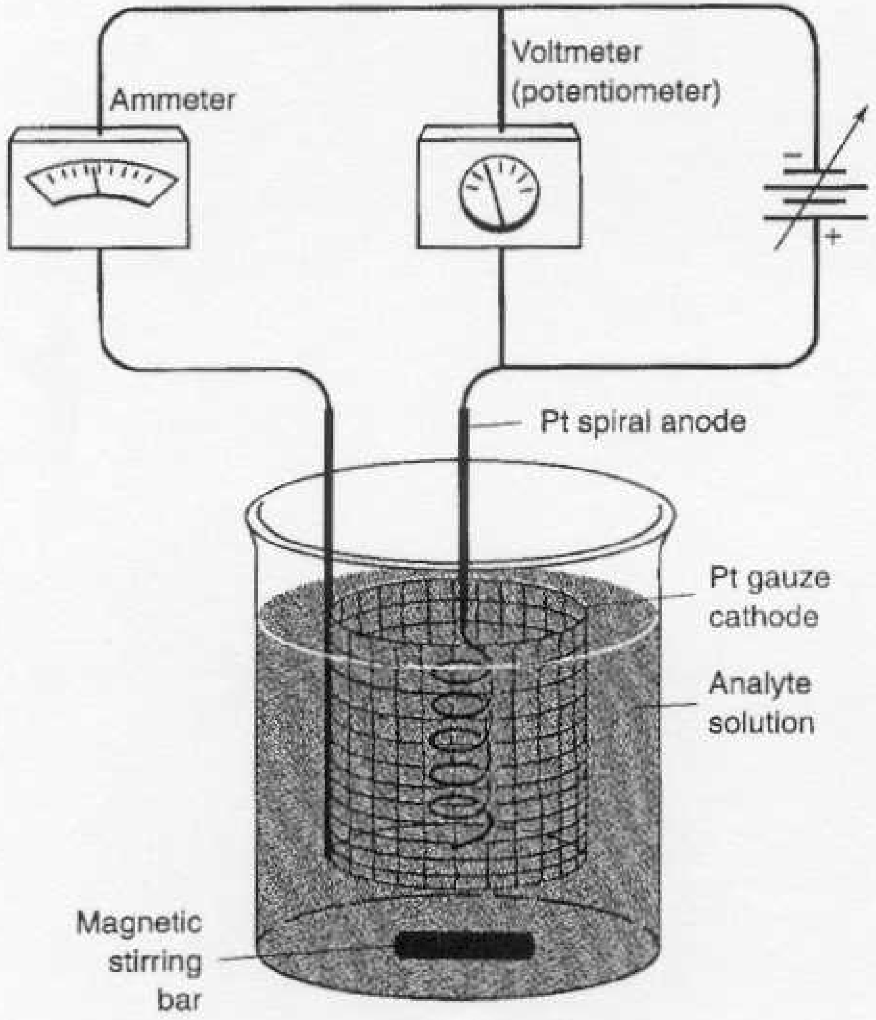
For zero current $\qquad E_{cell} = E_{Cu} - E_{O_2,H_2O}$

Use Nernst Equation with E^o's & concentrations

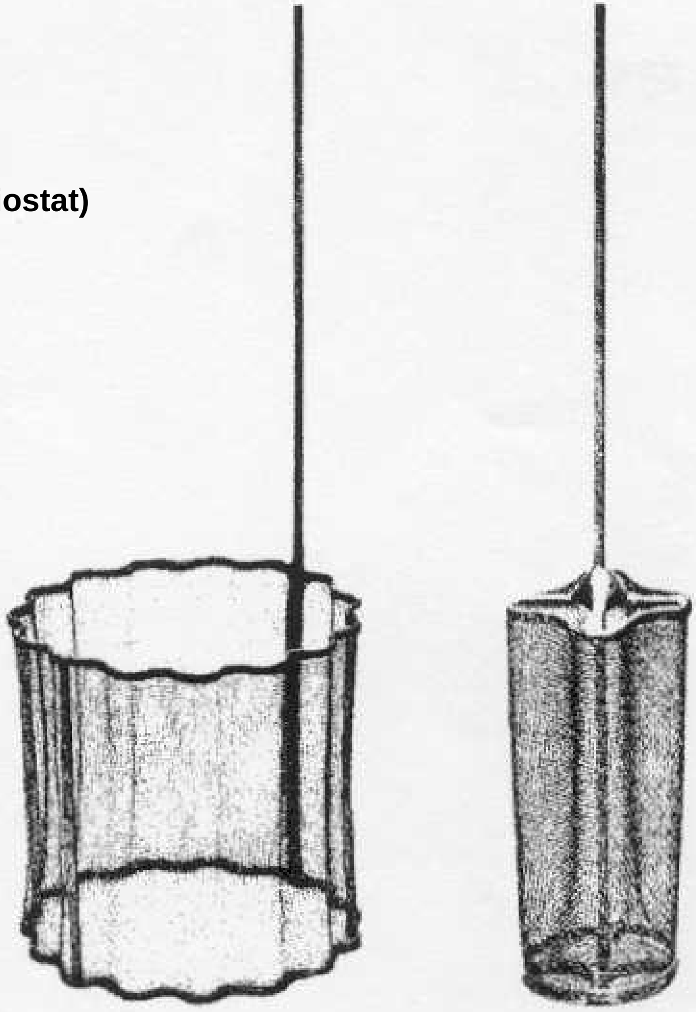
$$E_{cell} = \left(0.34 - \frac{0.059}{2}\log\frac{1}{[Cu^{2+}]}\right) - \left(1.23 - \frac{0.059}{2}\log\frac{1}{(P_{O_2})^{0.5}[H^+]^2}\right) = -\,0.91\ v$$

- Apply potential more negative than – 0.91 v to force system to reach an equilibrium where [Cu^{2+}] is small (like 99.9% lower than the approximate starting concentration)
- Choose cathode potential to reduce equilibrium [Cu^{2+}] to any desired value
- Must be cautious not to set potential too far negative to make sure nothing else is reduced
- Normally set conditions so that reduction is complete in a reasonably short period of time

Cell for Electrogravimetry



Pt Electrodes



Cathode Anode

Problem with simple electrogravimetry system is that the potential of the cathode is not accurately known

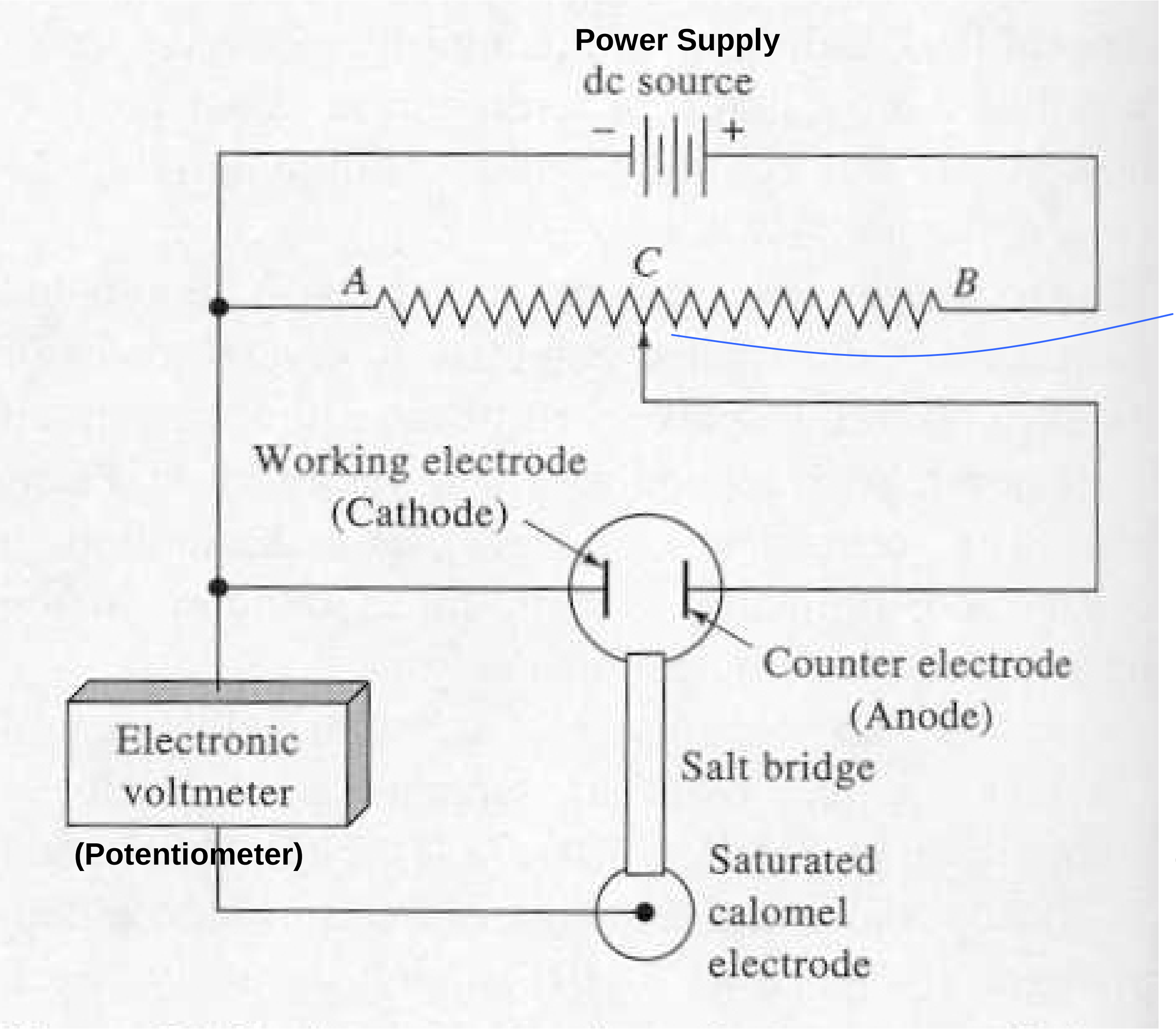
$$E_{applied} = E_{cathode} - E_{anode} - E_{IR} – E_{overvoltage}$$

E_J is insignificant and can be ignored here

Don’t know the magnitude of E_{IR} or $E_{overvoltage}$ & E_{IR} changes throughout experiment

A similar problem exists at the anode since $H_2O \leftrightarrow \frac{1}{2} O_2 + 2 H^+$ and H^+ & O_2 change during electrolysis so anode potential change

Much of this problem can be eliminated by using a three electrode system



Use potentiometer to measure potential of cathode relative to reference electrode then manually adjust slidewire contact to hold $E_{cathode}$ at desired value. This operation must be repeated at intervals during the electrodeposition because the current changes with conc.

Bulk current still flows from cathode to anode, but anode potential is no longer important.

Three Electrode Configuration

1) Reference electrode – maintains fixed potential despite changes in solution comp.

2) Working electrode – electrode of interest which is the cathode in this system

3) Counter electrode (Auxiliary electrode) – third electrode taking most of current flow (acts as current sink)

Advantages of 3 electrode system

1) Changes in concentration at counter electrode are not important, no effect on working electrode potential

2) No current flows through reference → no IR drop (its potential is constant)

Applications of Electrogravimetry

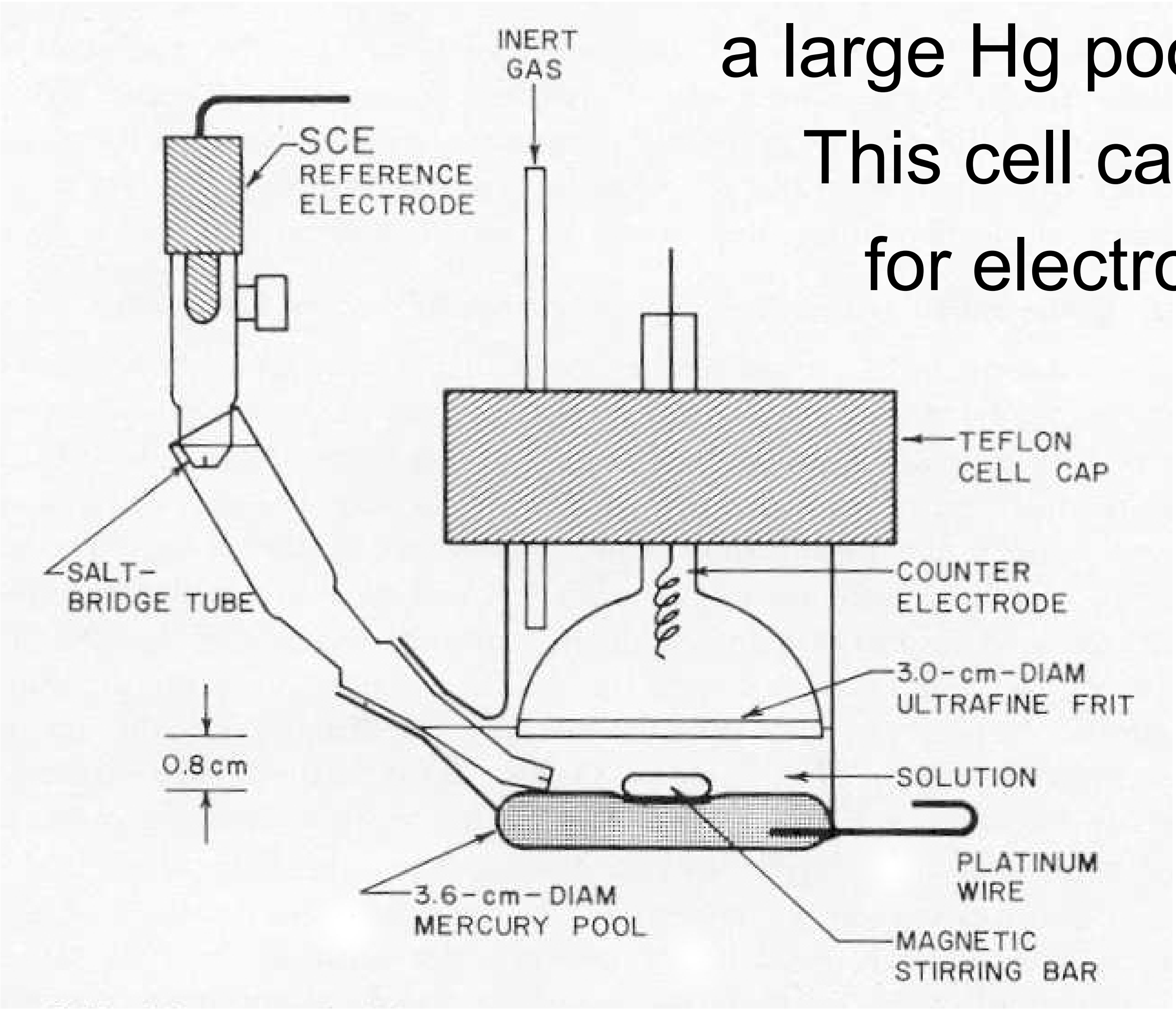
1) Quantitative analysis (electrogravimetry) – very accurate & precise, only measurement operation is weighing, can get deposition reaction to go to any desired degree of completion by proper choice of potential, some degree of selectivity using potential
2) Separations – separate one species from another in solution by selectively plating it out and removing it from solution. This method is used to remove interferences particularly in electrochemical methods

3) Preconcentration – plating out metals from a large volume of solution ($\geq$ 1 L) onto a small electrode effectively increases their concentration. Can also reoxidize metals back into a small volume of solution (e.g., 1 mL) & the ratio of volumes gives preconcentration factor (i.e., 1000). Can also use other methods for analysis of metal on solid electrode surface (e.g., AA, ICP, XRF, XPS).

4) Electrosynthesis (controlled potential electrolysis) – used by organic chemists to perform oxidation or reduction reactions at bench scale. Take advantage of ability to control potential & produce any oxidizing or reducing strength desired.

3)Purification – to remove trace metals from reagents by plating them out of solution onto a large Hg pool electrode.

This cell can also be used for electrosynthesis, etc.



Coulometry

Methods based on counting coulombs (C), the basic unit of electrical charge (Q)

Faraday's Law

$$\boxed{W = \frac{Q\ M}{n\ F}}$$

Where: M = molecular weight (g/mole)

W = weight (g)

n = number of electrons (unitless)

F = Faraday's constant (96,500 C/mol)

Fundamental assumption is that reaction is 100 % current efficient i.e, all coulombs go to oxidizing or reducing species of interest

Kinds of coulometry

1) Controlled Potential Coulometry

$$\boxed{Q = \int_0^t i\,dt}$$

Nothing more than integrating area under the curve in chronoamperometry

Can be referred to as chronocoulometry

2) Constant Current Coulometry

$$\boxed{Q = i\,t}$$

Care must be taken so that there is enough stuff to carry the current at electrode surface

Rarely used anymore

Major application is coulometric titrations where titrant is prepared electrochemically and standardized by counting coulombs e.g. bromine Br_2 as titrant

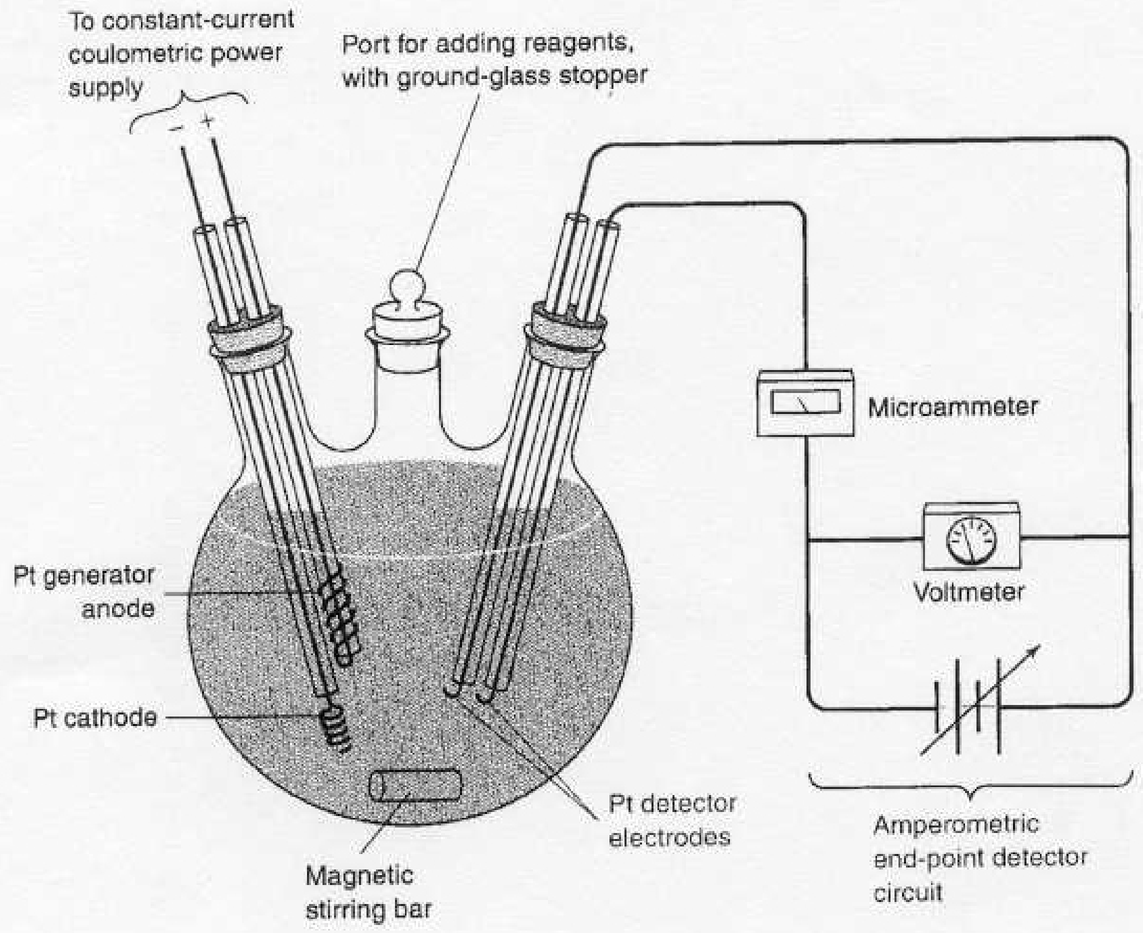
$$2\,Br^- \rightarrow Br_2 + 2\,e^-$$

1) Useful for titrants that can't be stored as stable solutions
2) Small currents can be measured accurately so even very dilute titrants can be used
3) In theory can count coulombs for any method where current is measured by integrating

Coulometric cell

$2\ Br^- \rightarrow Br_2 + 2\ e^-$

$Br_2 + C_6H_{10} \rightarrow C_6H_{10}Br_2$



Apparatus for coulometric titration of cyclohexene with Br_2. The solution contains cyclohexene, 0.15 M KBr, and 3 mM mercuric acetate in a mixed solvent of acetic acid, methanol, and water. Mercuric acetate catalyzes the addition of Br_2 to the olefin. [Adapted from D. H. Evans, *J. Chem. Ed.* **1968**, *45*, 88.]

Examples of Coulometric Titrations

Assayed Substance	Reagent Generated	Precursor	Titration Type
Br^-	Ag^+	Ag° anode	Precipitation
Fe^{++}	Cl_2	HCl	Redox
H_2O	I_2, I_3^-	KI ($pH < 9$)	Karl Fisher reagent
Organic acids	OH^-	H_2O	Neutralization
Bases	H^+	H_2O	Neutralization
Ca^{++}, Zn^{++}	$Hedta^{3-*}$	$HgNH_3edta^{=}$	Complexometric
Olefins	Br_2	KBr ($pH < 5$)	Olefin addition (redox)

* edta = ethylenediaminetetraacetate. See Table 10.4 for the structure.

Further references: Stock, J. T. biennial reviews in *Anal. Chem.* 1986, 1984, 1982, 1980, etc. Farrington, P. S. In "Handbook of Analytical Chemistry" Meites, L., Ed. McGraw-Hill: New York, 1963, Table 5.55.

Voltammetry

- Stationary electrode
- Stirred = mass transport by convection
- Vary potential linearly with time
- Measure current vs time

Theory

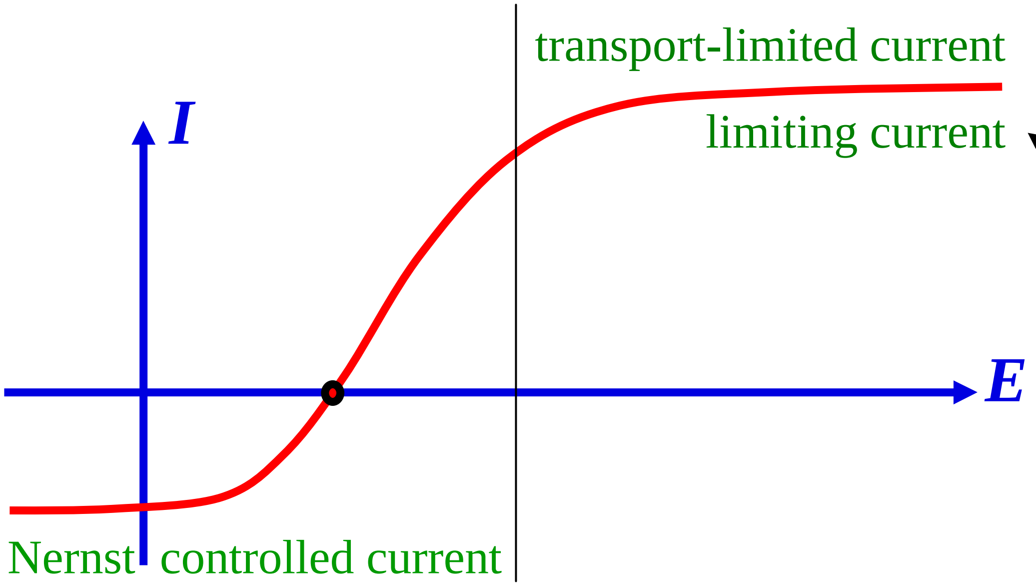
assume Ox + n e^- ←→ Red

- both Ox and Red are soluble

- reversible reaction (electrochemically)

- potential varies

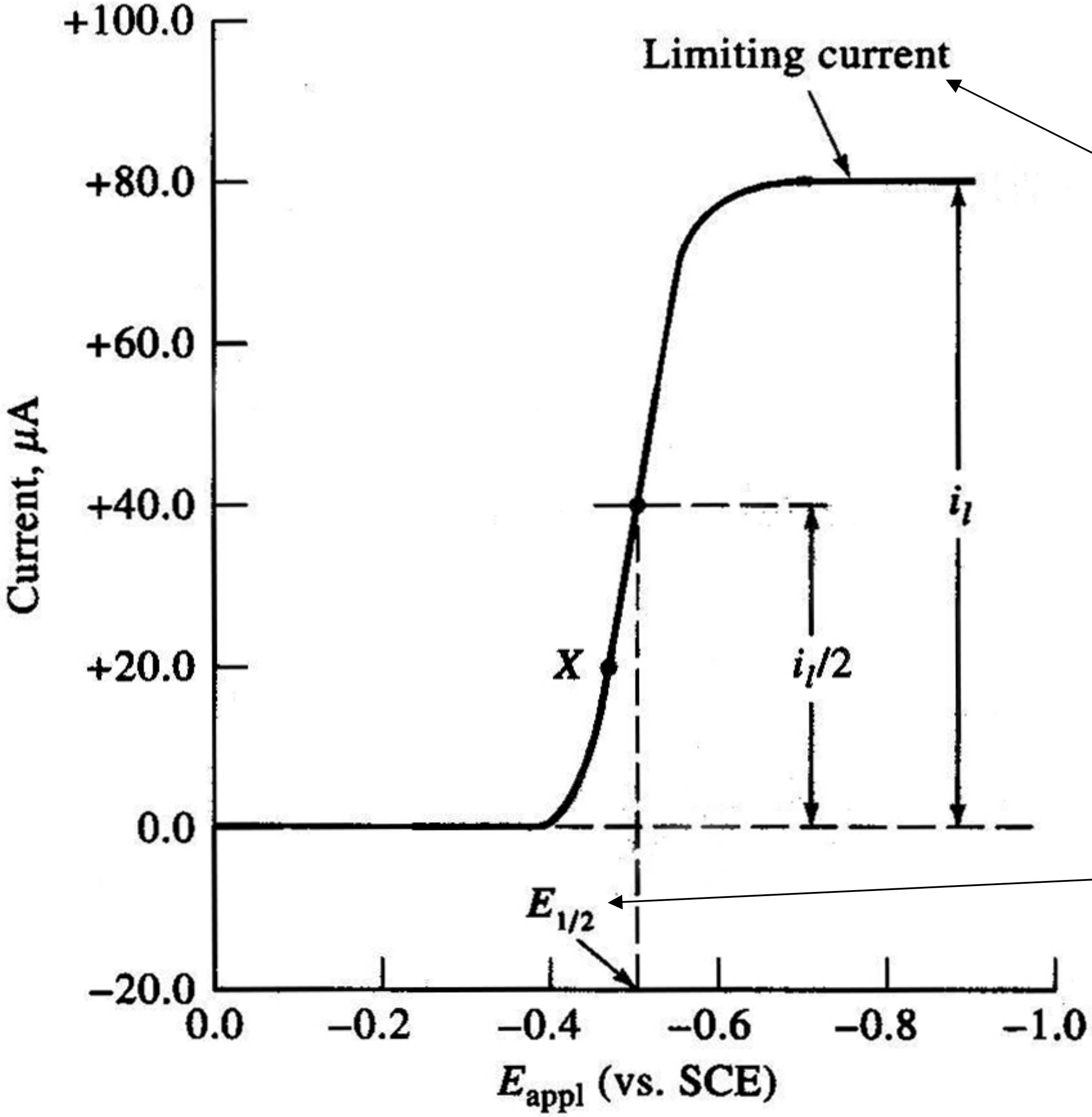
Define - Limiting Current as steady state current when [Ox] = 0 at electrode surface i.e., applied potential is sufficiently cathodic such that all Ox is reduced at electrode



$$I = \frac{nFADC_{bulk}}{\delta}$$

Gives quantitative information

$$E = E^{o} - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$

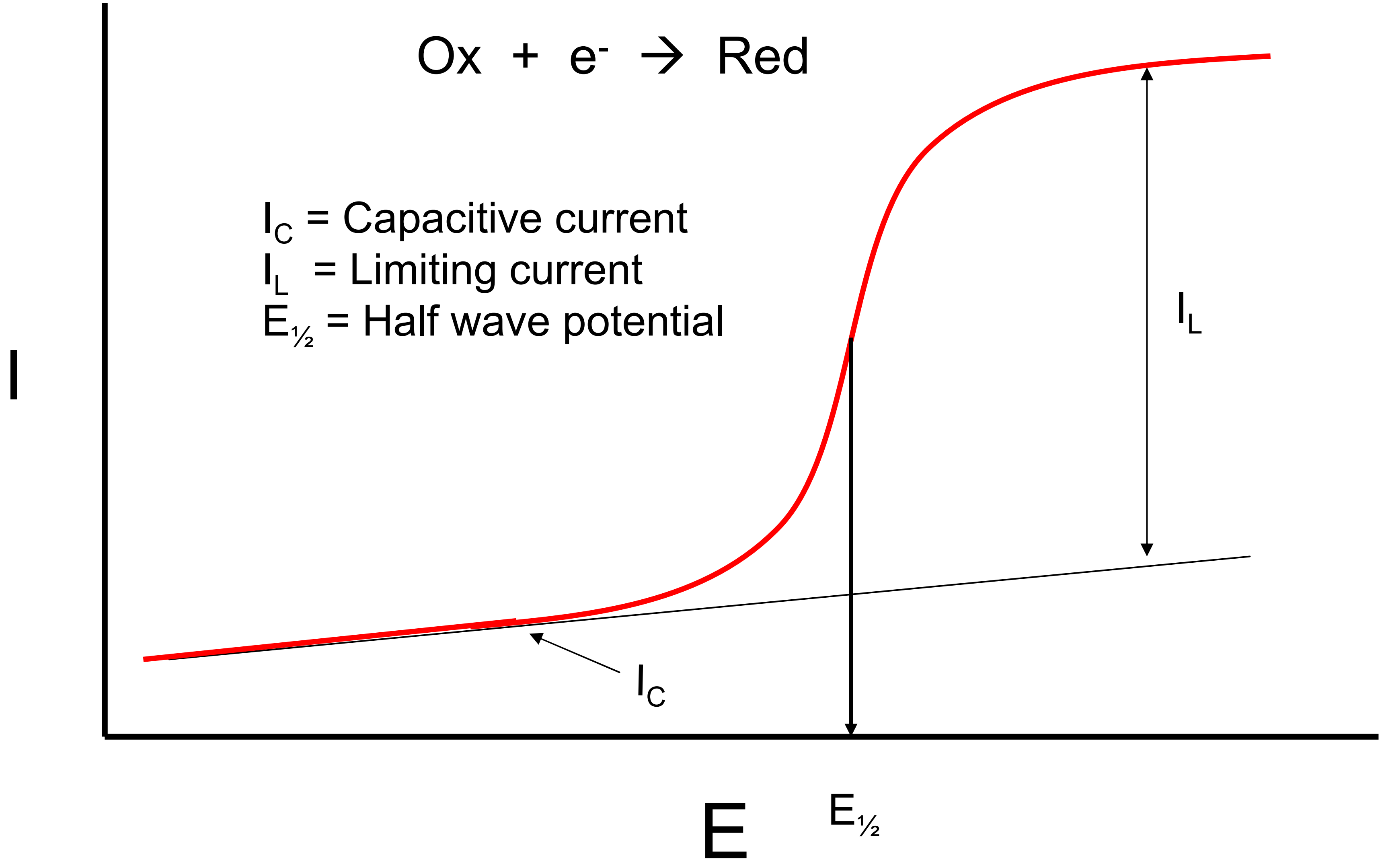


quantitative information

qualitative information

Linear-scan voltammogram → for stirred solution

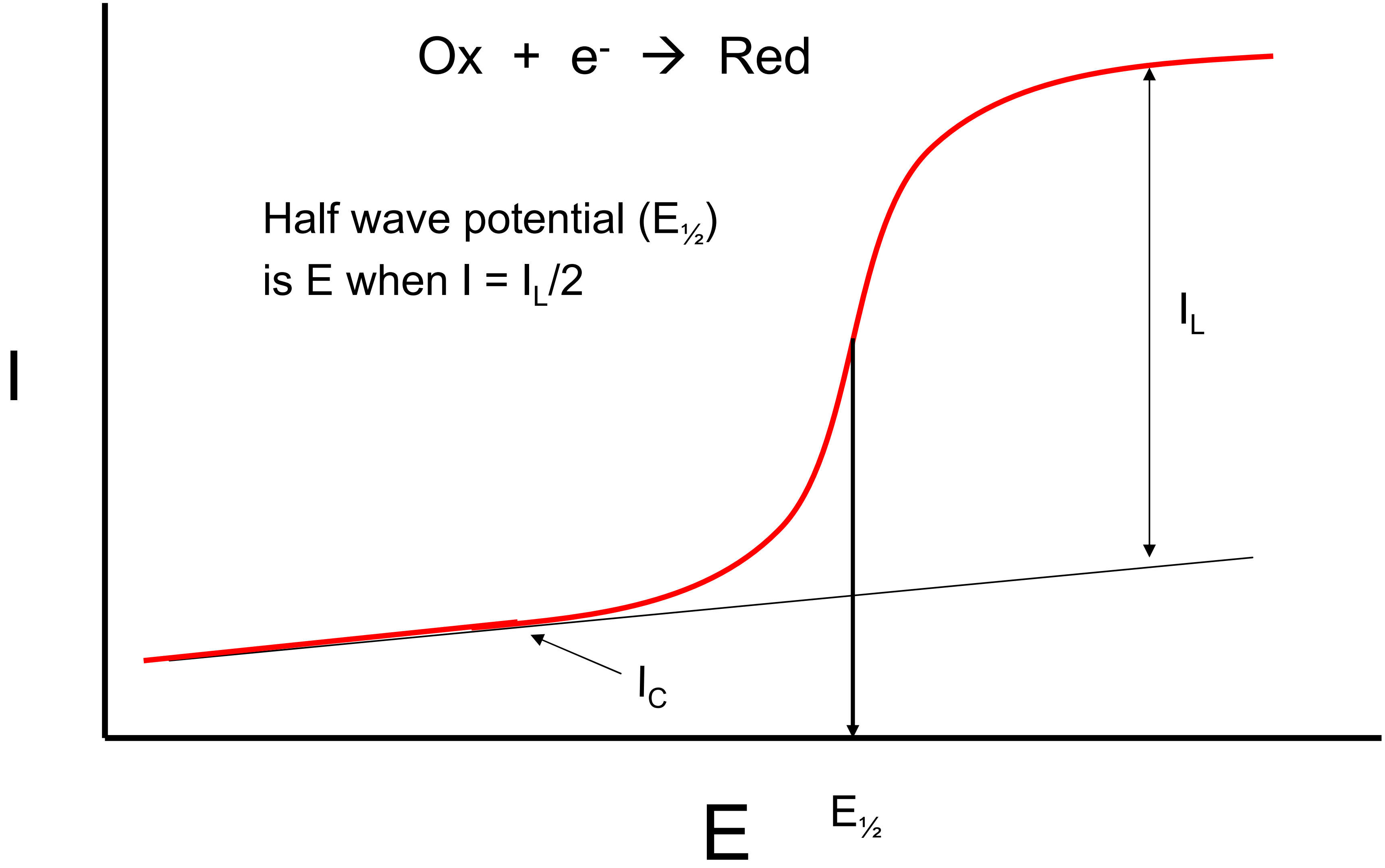
Linear Scan Voltammetry (stirred)



$Ox + e^- \rightarrow Red$

I_C = Capacitive current
I_L = Limiting current
$E_{½}$ = Half wave potential

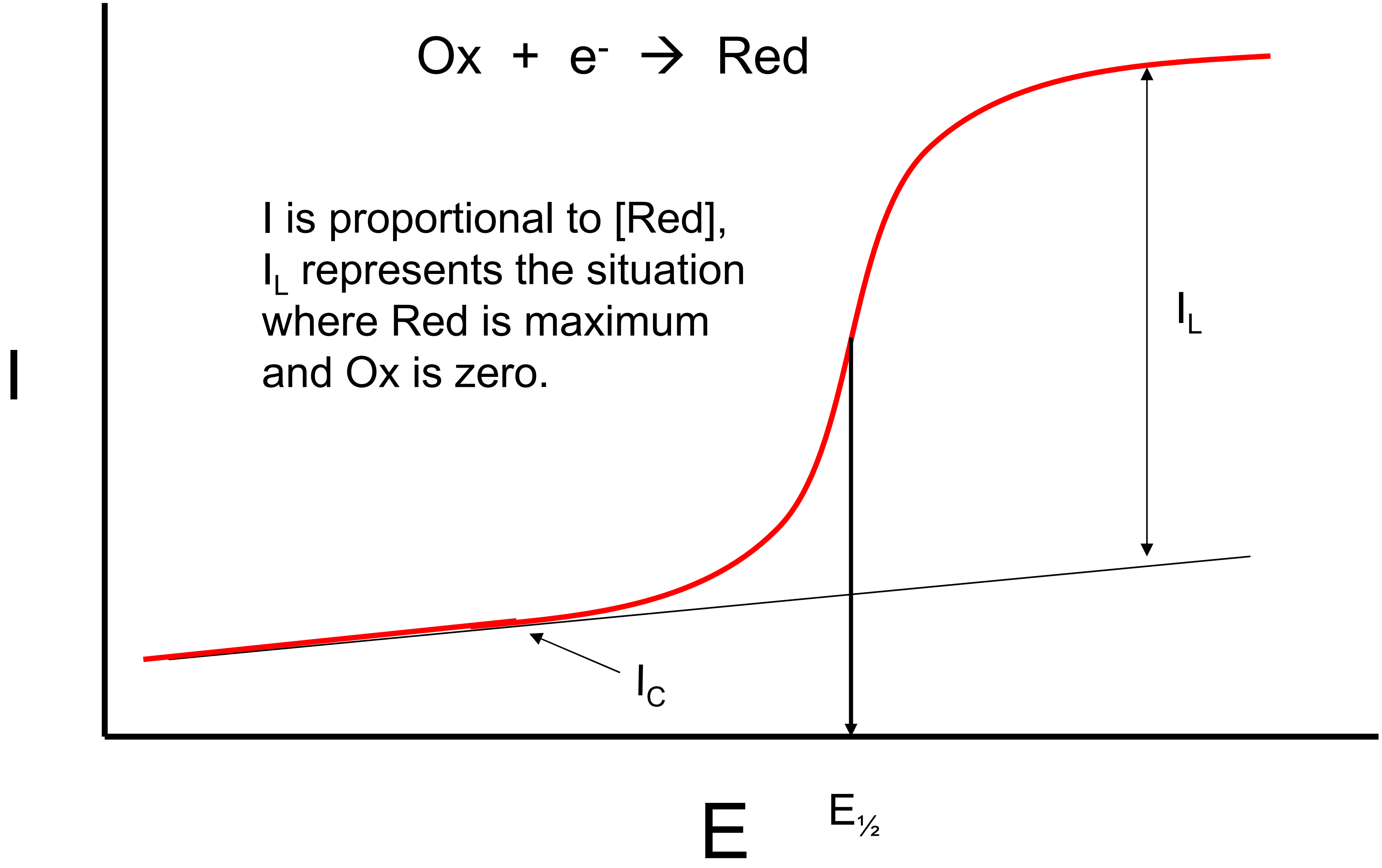
Linear Scan Voltammetry (stirred)



$Ox + e^- \rightarrow Red$

Half wave potential ($E_{½}$)
is E when I = $I_L/2$

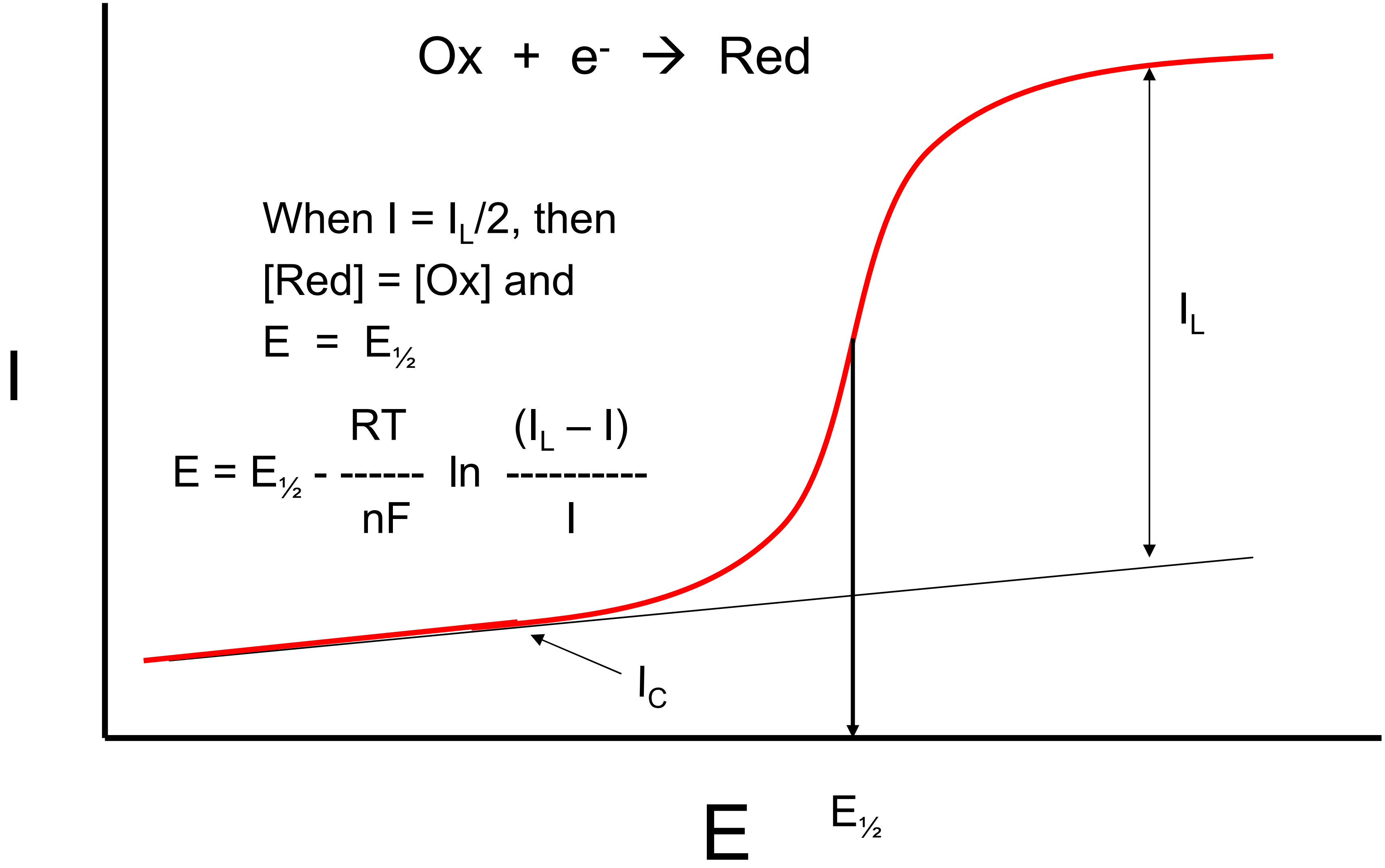
Linear Scan Voltammetry (stirred)



Ox + e^- → Red

I is proportional to [Red], I_L represents the situation where Red is maximum and Ox is zero.

Linear Scan Voltammetry (stirred)



$Ox + e^- \rightarrow Red$

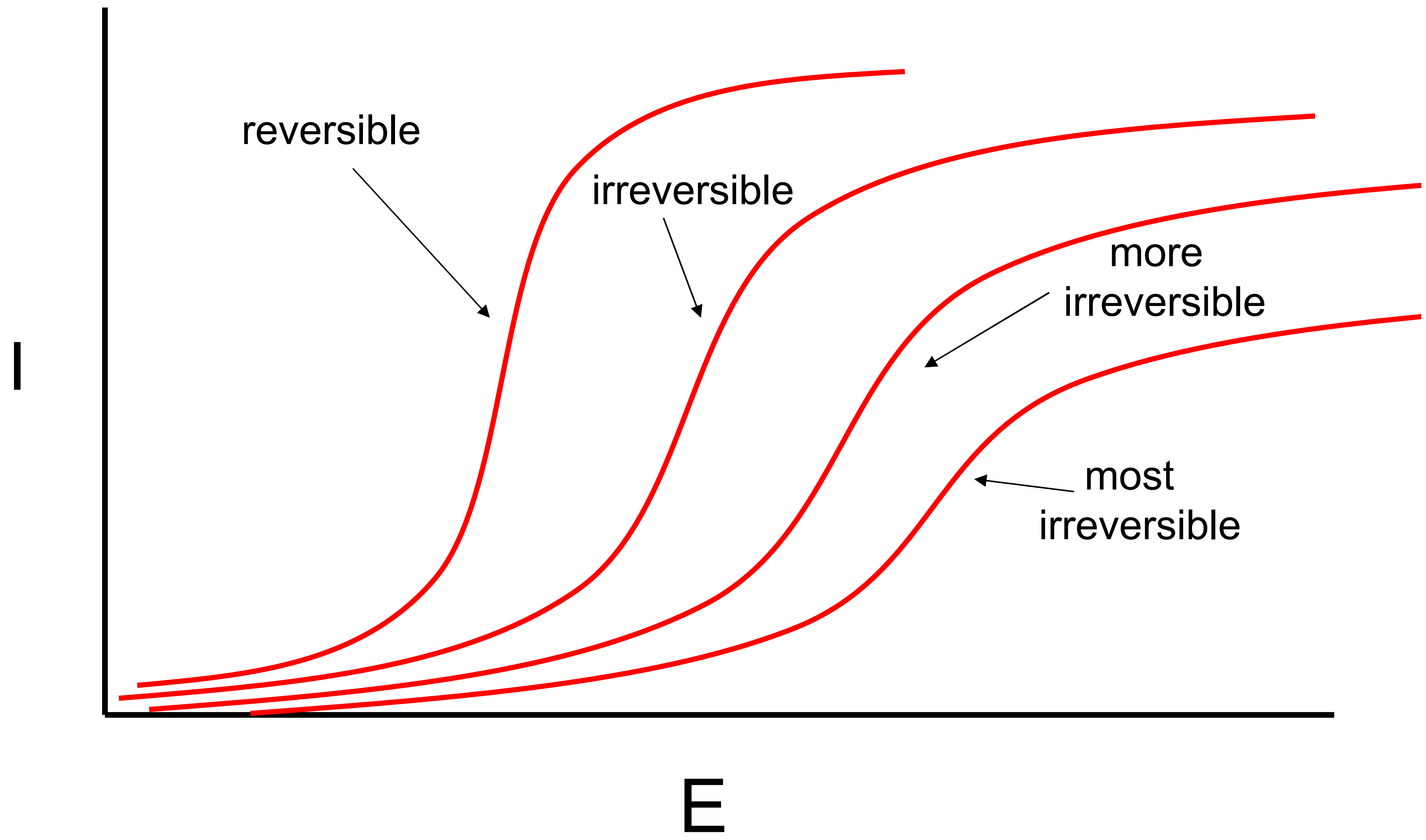
When $I = I_L/2$, then

$[Red] = [Ox]$ and

$E = E_{1/2}$

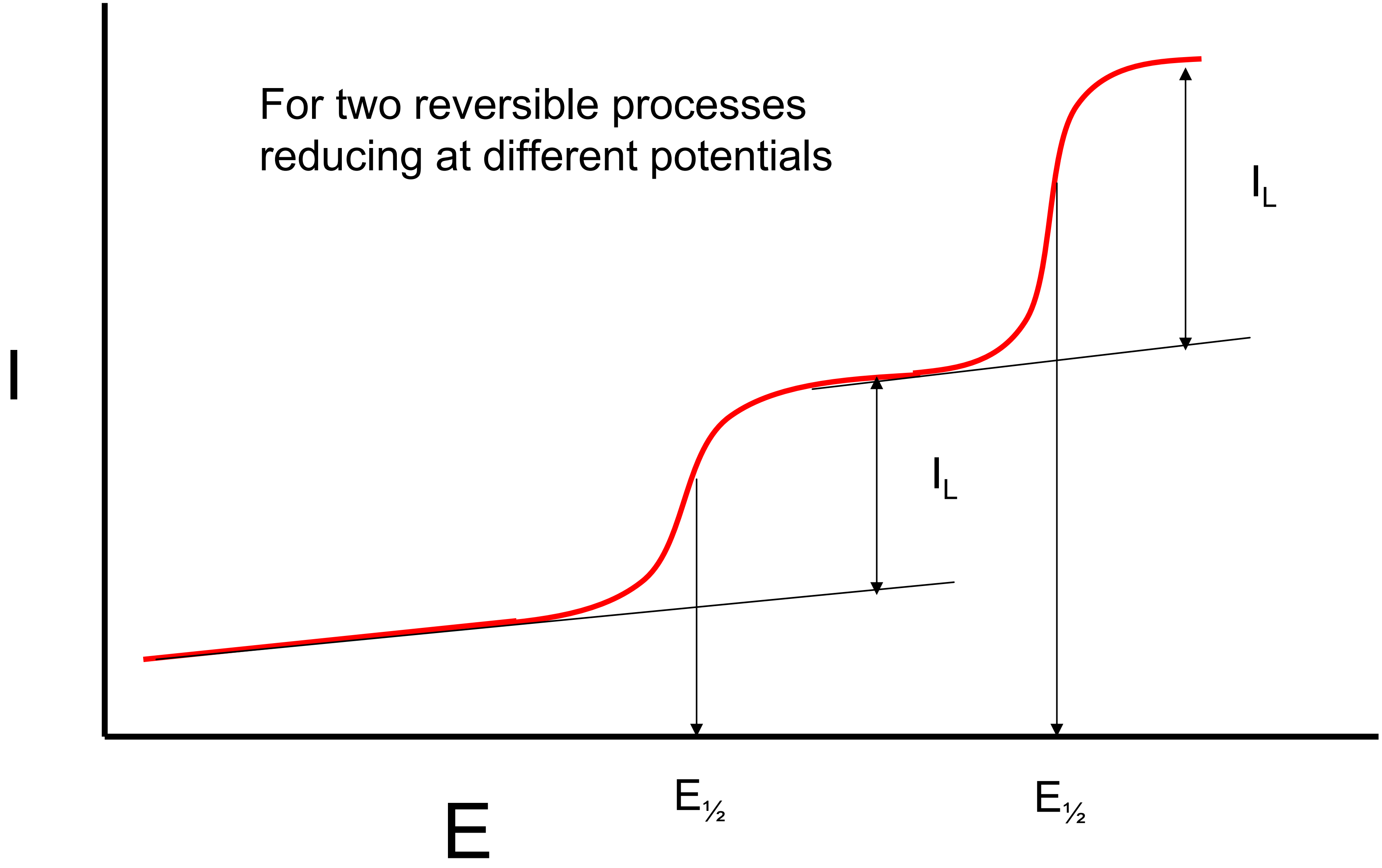
$$E = E_{1/2} - \frac{RT}{nF} \ln \frac{(I_L - I)}{I}$$

Linear Scan Voltammetry (stirred)



Can assign rate constants (k) for irreversible processes

Linear Scan Voltammetry (stirred)

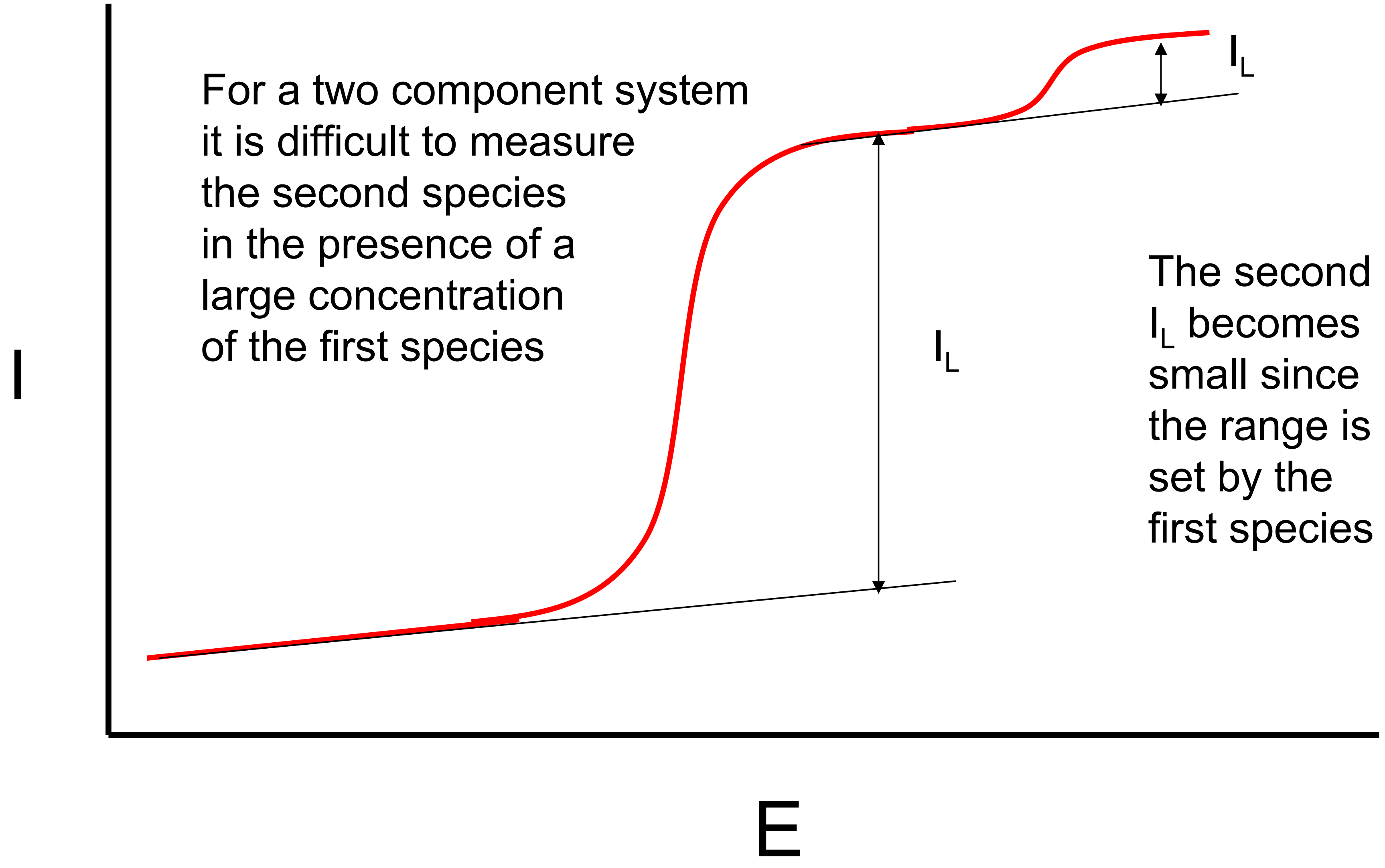


For two reversible processes reducing at different potentials

Linear Scan Voltammetry (stirred)

- Normally use Pt or C (graphite) electrodes
- Better to use rotating electrode than stir bar
- LSV can be used for quantitative analysis
- Can measure many metal ions & organics
- Fairly sensitive due to convective mass transport, i.e., I_F is large
- The output signal in the form of a wave is considered a drawback
  - can be difficult to perform data analysis
  - multiple components gives stacked waves

Linear Scan Voltammetry (stirred)



For a two component system it is difficult to measure the second species in the presence of a large concentration of the first species

The second I_L becomes small since the range is set by the first species

This problem is inherent for techniques that produce waves

Voltammetry (unstirred)

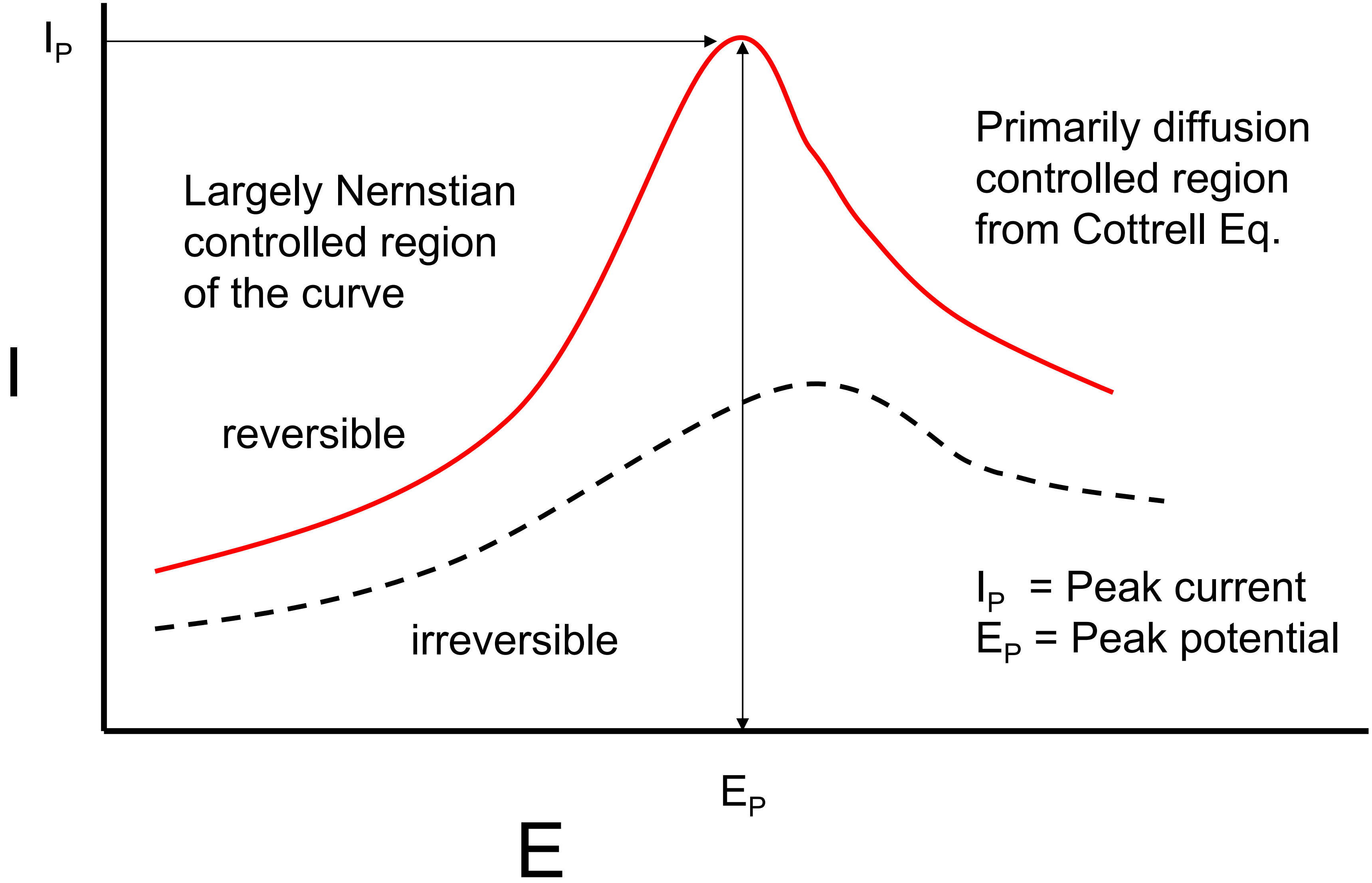
- Stationary electrode
- Unstirred solution = mass transfer by diffusion
- Vary potential linearly with time
- Measure current vs time

Theory

assume $Ox + n e^- \leftrightarrow Red$

- both Ox and Red are soluble
- reversible reaction (electrochemically)
- potential varies

Linear Scan Voltammetry (unstirred)



I_P = Peak current
E_P = Peak potential

Voltammetry (unstirred) - Theory

$$I_P = 0.452 \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} A D^{1/2} C_{bulk} \nu^{1/2}$$

New term ν = scan rate

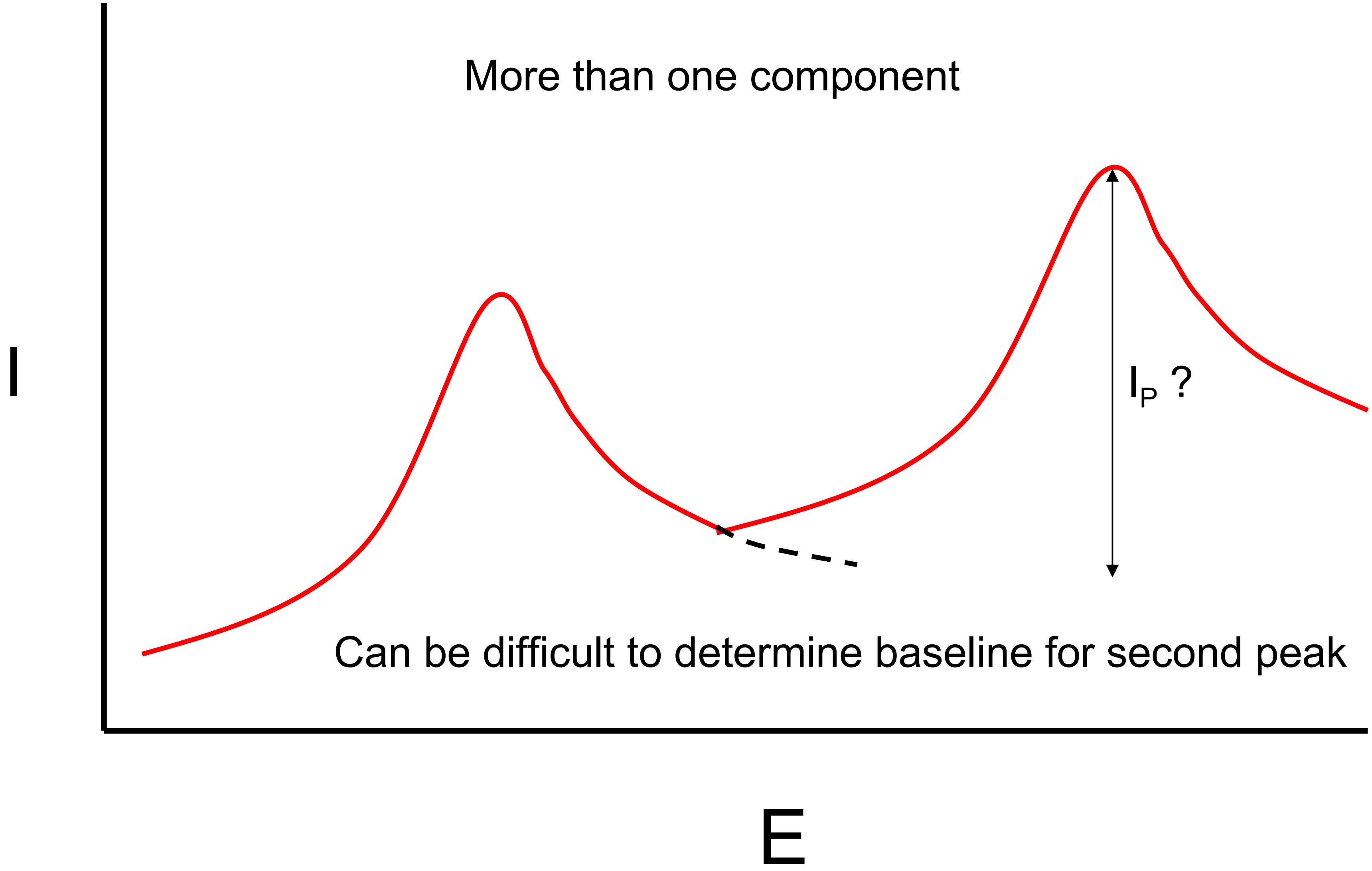
Increase scan rate & I_P increases, however,

I_C is directly proportional to ν

Ratio I_F/I_C is greatest at slow scan rates

$$E_P = E_{1/2} - 1.1 \frac{R T}{n F}$$

Linear Scan Voltammetry (unstirred)



More than one component

Can be difficult to determine baseline for second peak