Chronoamperometry

- Stationary electrode
- Unstirred = mass transport by diffusion
- Constant potential
- Measure current vs time
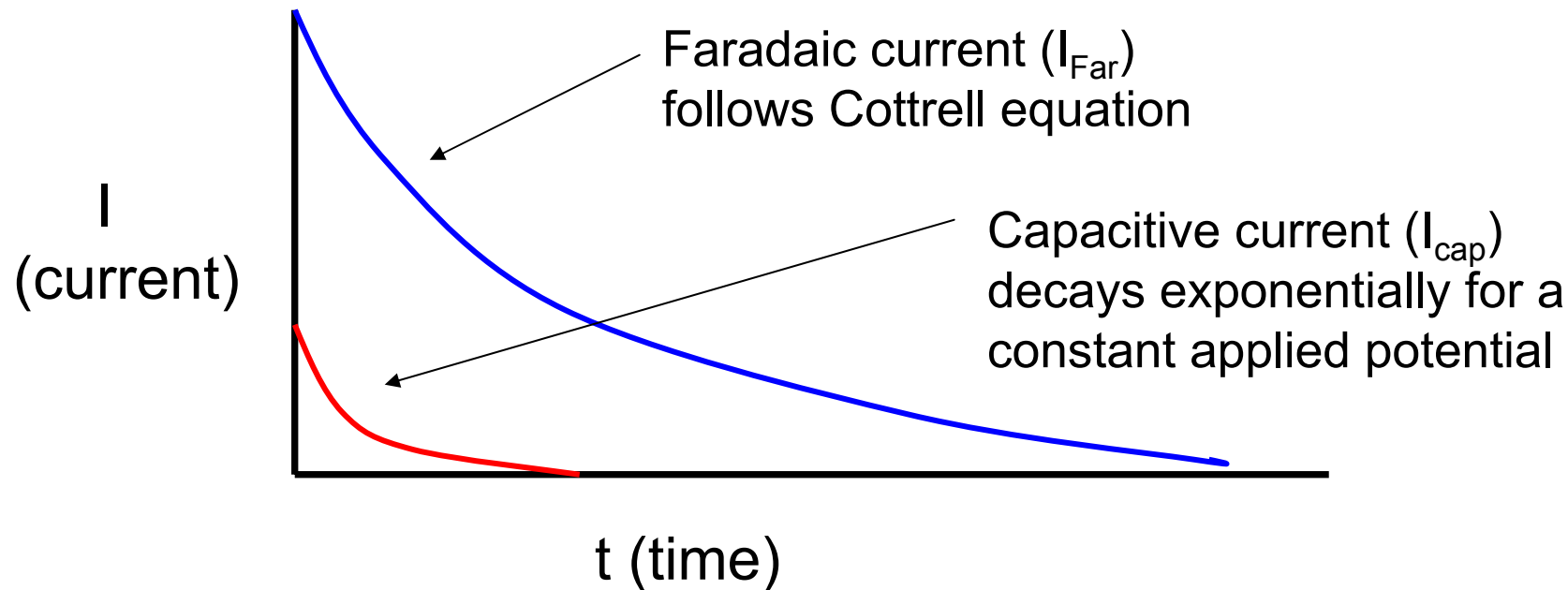
Theory

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

- both Ox and Red are soluble
- reversible reaction (electrochemically)
- potential set so reduction goes to completion at the electrode surface

Components of output signal in Chronoamperometry

I_{Far} decreases because Ox used up at electrode surface and Ox is only replenished by diffusion

Faradaic current (I_{Far}) follows Cottrell equation

Capacitive current (I_{cap}) decays exponentially for a constant applied potential

I (current)

t (time)

I_{cap} is high as electrode capacitive layer charges up, then drops off

Processes perturbing system can cause data to differ from Cottrell Equation

1) Capacitive Current – charging current is exponential as shown

$$I_{cap} = e^{-kt}$$

Note: Capacitive current decreases more rapidly than Faradaic current so at longer times the ratio I_{Far}/I_{cap} is larger

2) Occurrence of coupled chemical reactions e.g. Ox + n e$^-$ → Red

2 Red → A

A + n e$^-$ ←→ B

Affects the shape of the current-time curve

Chronoamperometry Applications

- Can measure concentration by measuring I vs conc. at any fixed time
- Can analyze the shape of the current-time curve in order to study coupled chemical reactions
- There are better ways to do both of these with more modern techniques
- Chronoamperometry is important because it is a fundamental method on which other techniques are based
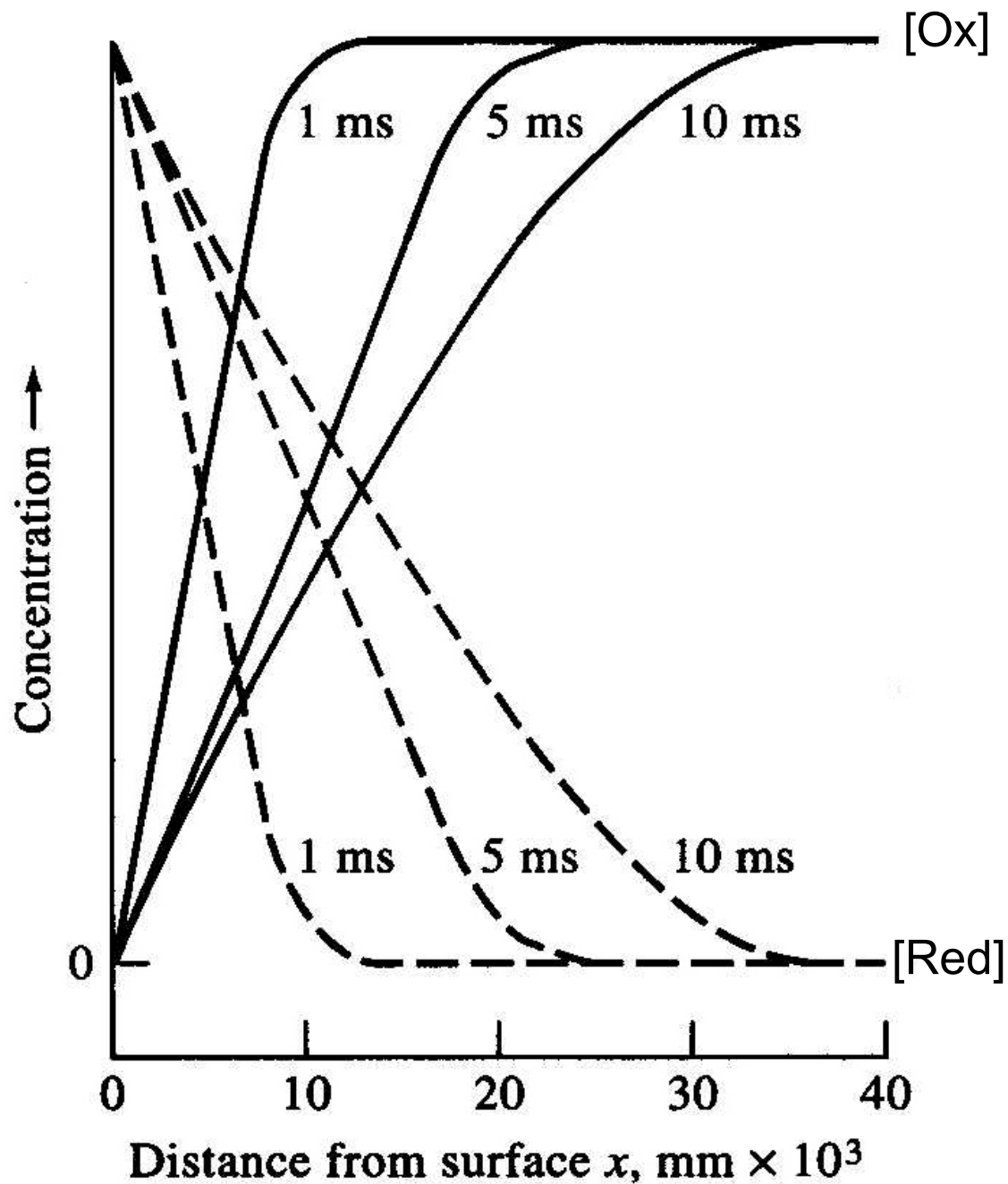
Chronopotentiometry

- Stationary electrode
- Unstirred = mass transport by diffusion
- Constant current applied between electrodes
- Measure potential vs time

Galvanostat

Theory

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

- both Ox and Red are soluble
- reversible reaction (electrochemically)
- apply current and use up Ox at electrode
        surface producing Red

Concentration →

[Ox]

1 ms   5 ms   10 ms

$Ox\ +\ n\ e^-\ \longleftrightarrow\ Red$

Apply current & use up
Ox at electrode surface
while producing Red

1 ms   5 ms   10 ms

0

[Red]

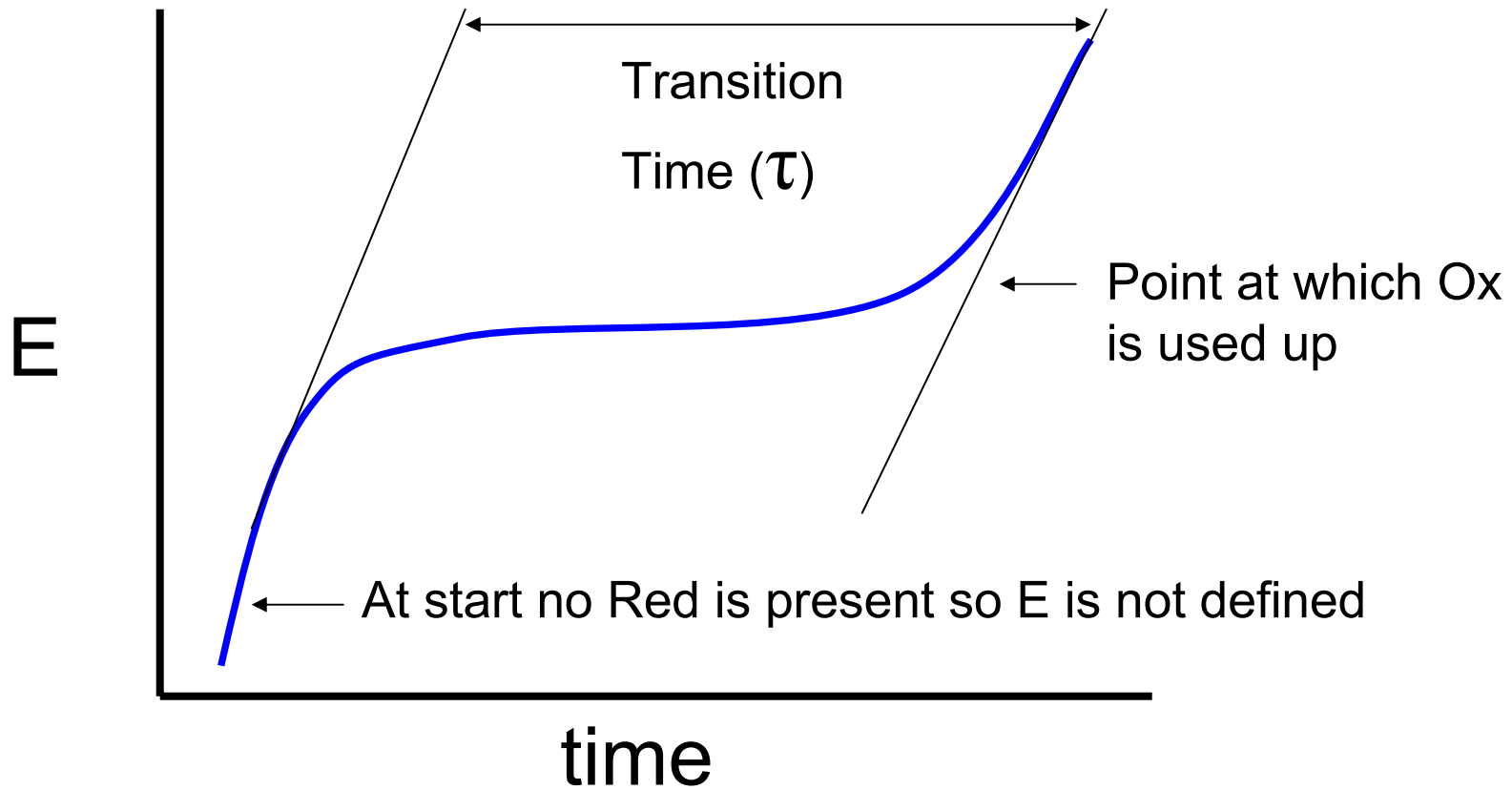0   10   20   30   40

Distance from surface x, mm $\times 10^3$

Theory of Chronopotentiometry

$$E = E^o - \frac{0.059}{n} \log \frac{[Red]}{[Ox]}$$

A gradual change in E occurs as [Red] goes up and [Ox] goes down (transition region)

Ultimately the surface concentration of Ox goes to zero & to sustain the constant current applied, electrode potential makes a rapid change to the value required to make a new process go

Chronopotentiometry Output Wave

E

Transition
Time (τ)

Point at which Ox
is used up

At start no Red is present so E is not defined

time

$$\tau^{1/2} = \frac{\pi^{1/2} n F A D^{1/2} C_{Ox}}{2\, i}$$

Sand Equation

Summary of Chronopotentiometry

- In principle quantitative analysis can be done by relating $\tau^{½}$ to C_{ox}
- In reality it is better done by other methods
- Chronopotentiometry illustrates constant current situation in electrochemistry
- Chronopotentiometry is very poor at handling capacitive current

Coulometry

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

Faraday's Law

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

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

$$Q = \int_0^t i\, dt$$

Nothing more than integrating area under the curve in chronoamperometry

Can be referred to as chronocoulometry

2) Constant Current Coulometry

$$Q = it$$

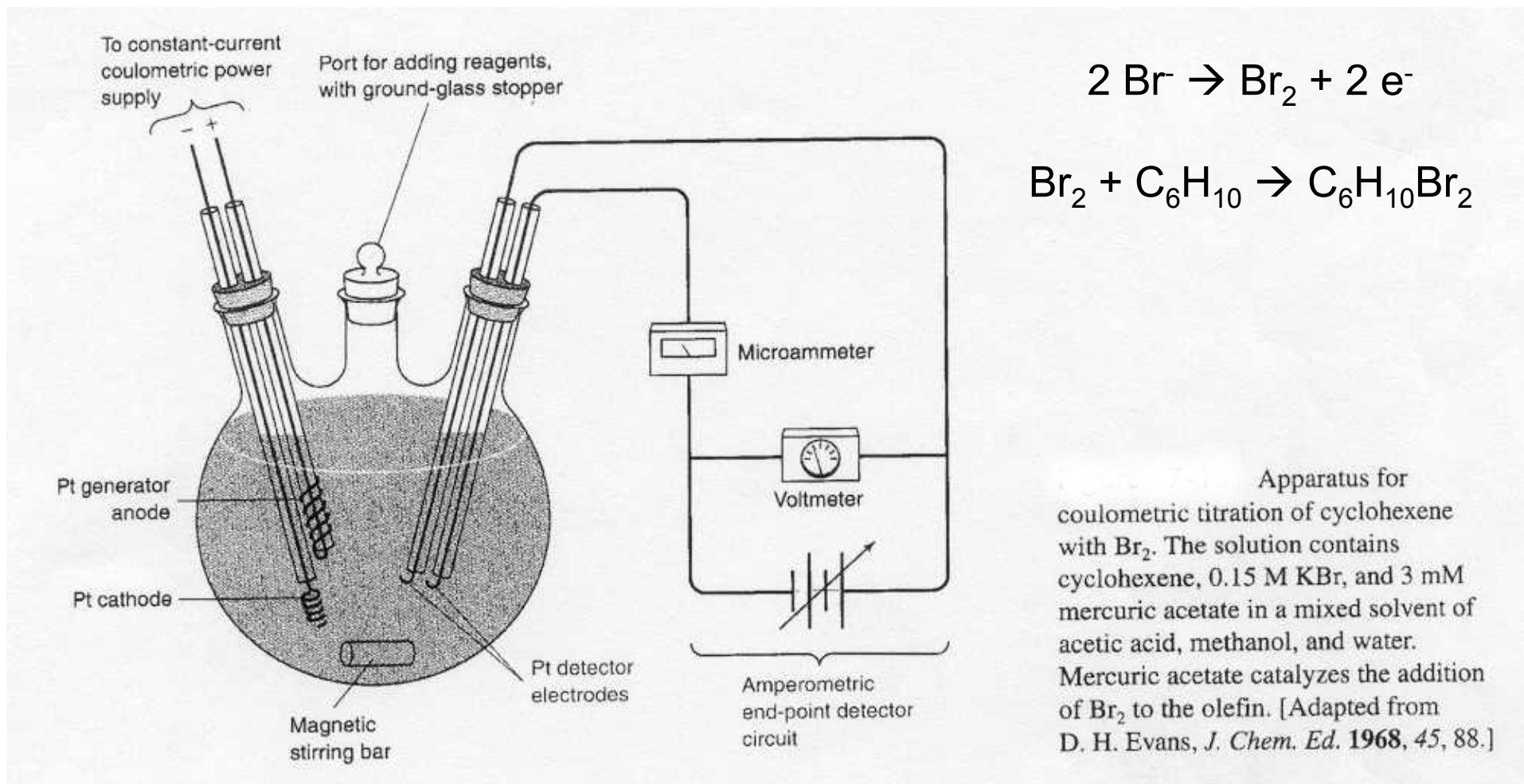Care must be taken so that there is enough stuff to carry the current at electrode surface
Rarely used anymore

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

To constant-current coulometric power supply

Port for adding reagents, with ground-glass stopper

Pt generator anode

Pt cathode

Magnetic stirring bar

Pt detector electrodes

Microammeter

Voltmeter

Amperometric end-point detector circuit

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

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

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.
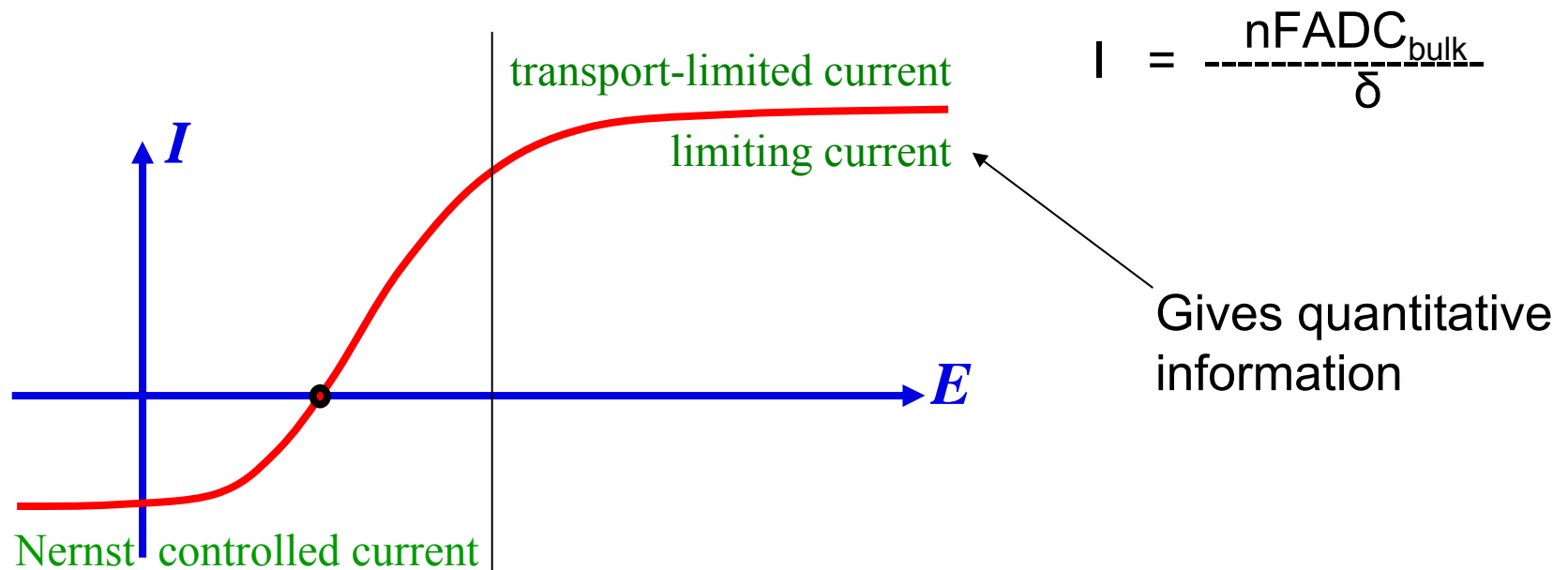
Voltammetry (stirred)

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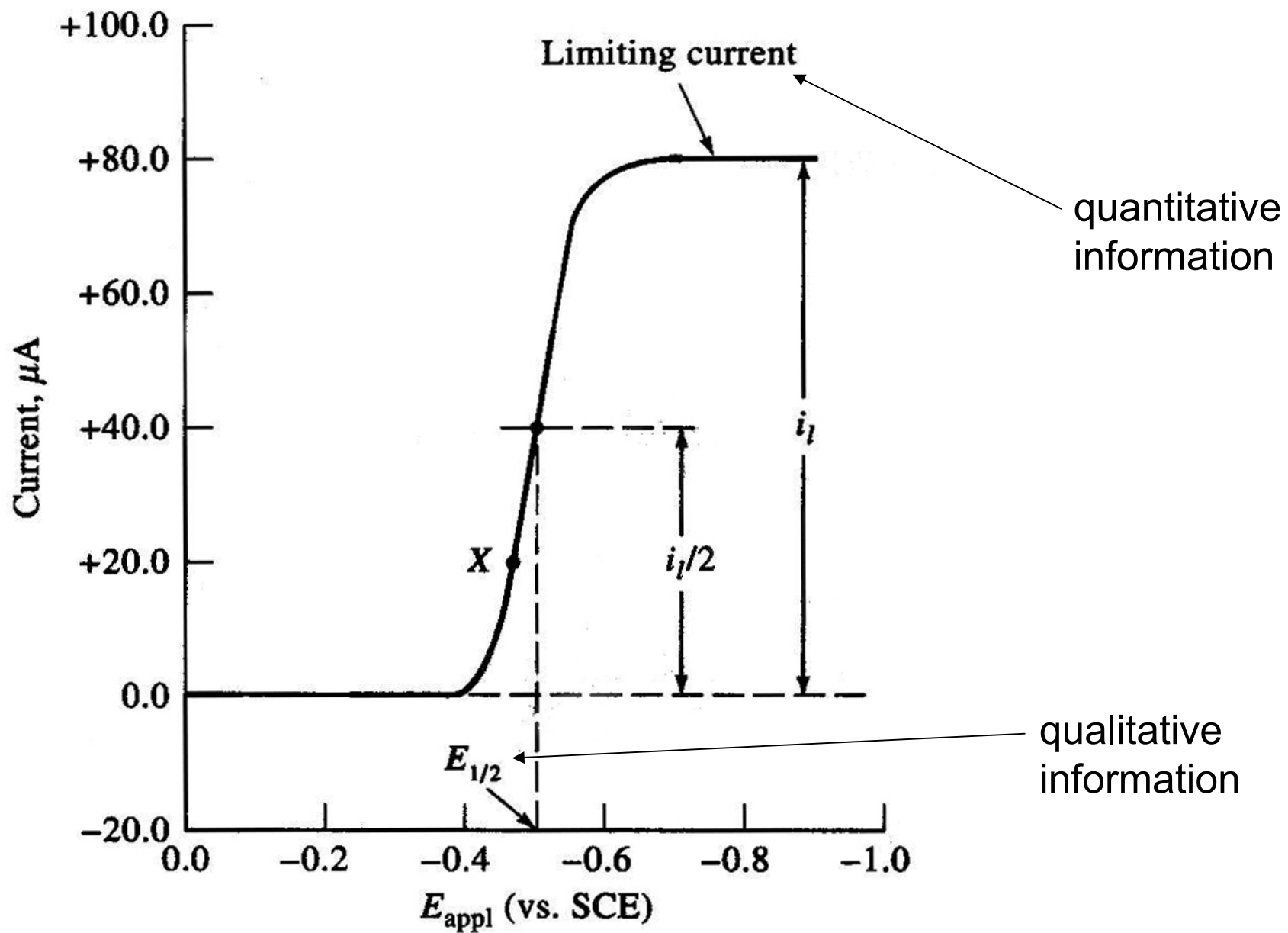- Measure current vs time

Theory

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

- both Ox and Red are soluble

- reversible reaction (electrochemically)

- potential varies

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

transport-limited current

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

limiting current

Gives quantitative
information

Nernst controlled current

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

Linear-scan voltammogram ⟶ for stirred solution
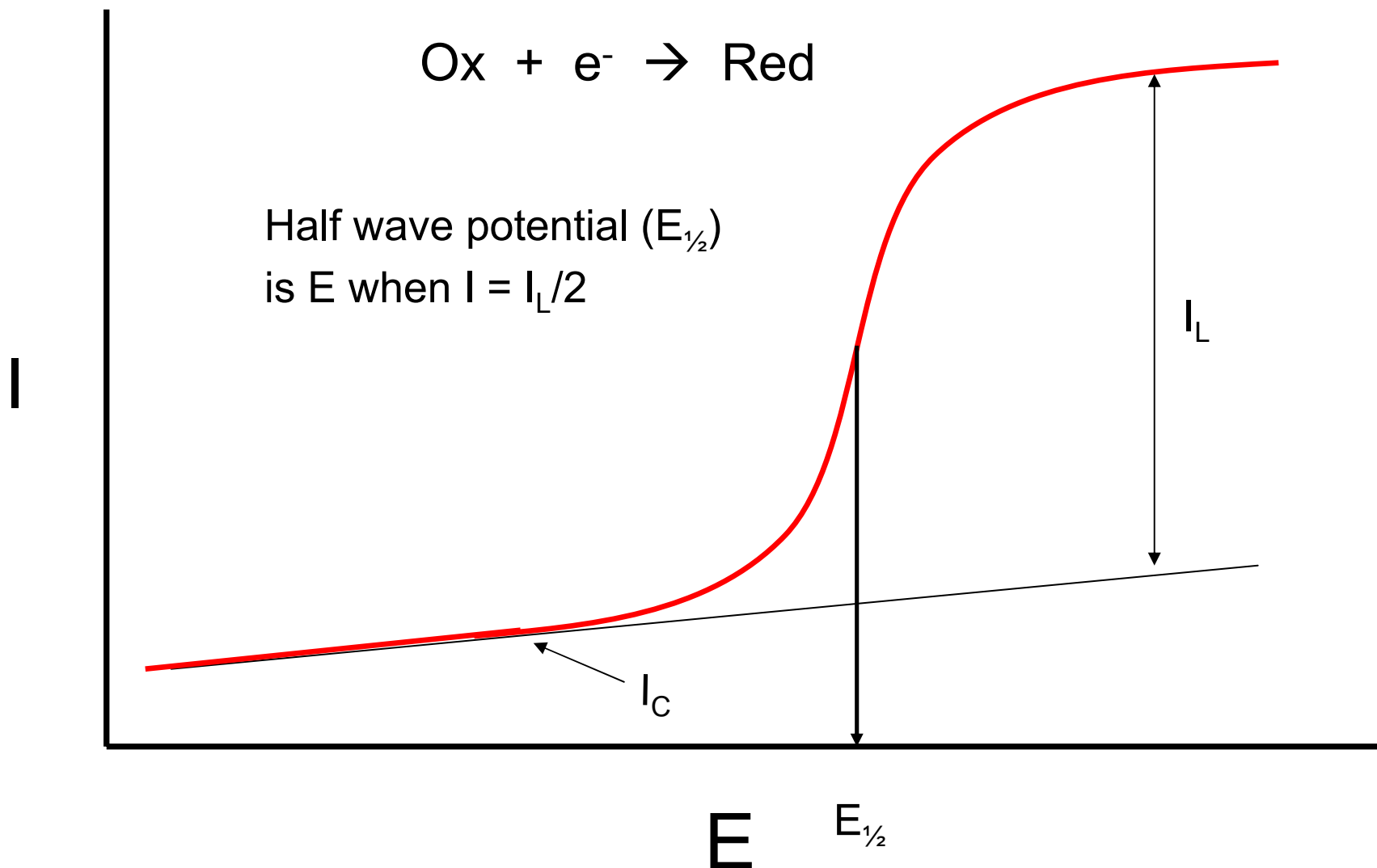
Linear Scan Voltammetry (stirred)

$$Ox + e^- \rightarrow Red$$

I_C = Capacitive current
I_L = Limiting current
$E_{1/2}$ = Half wave potential

I_L

I_C

I

E $E_{1/2}$
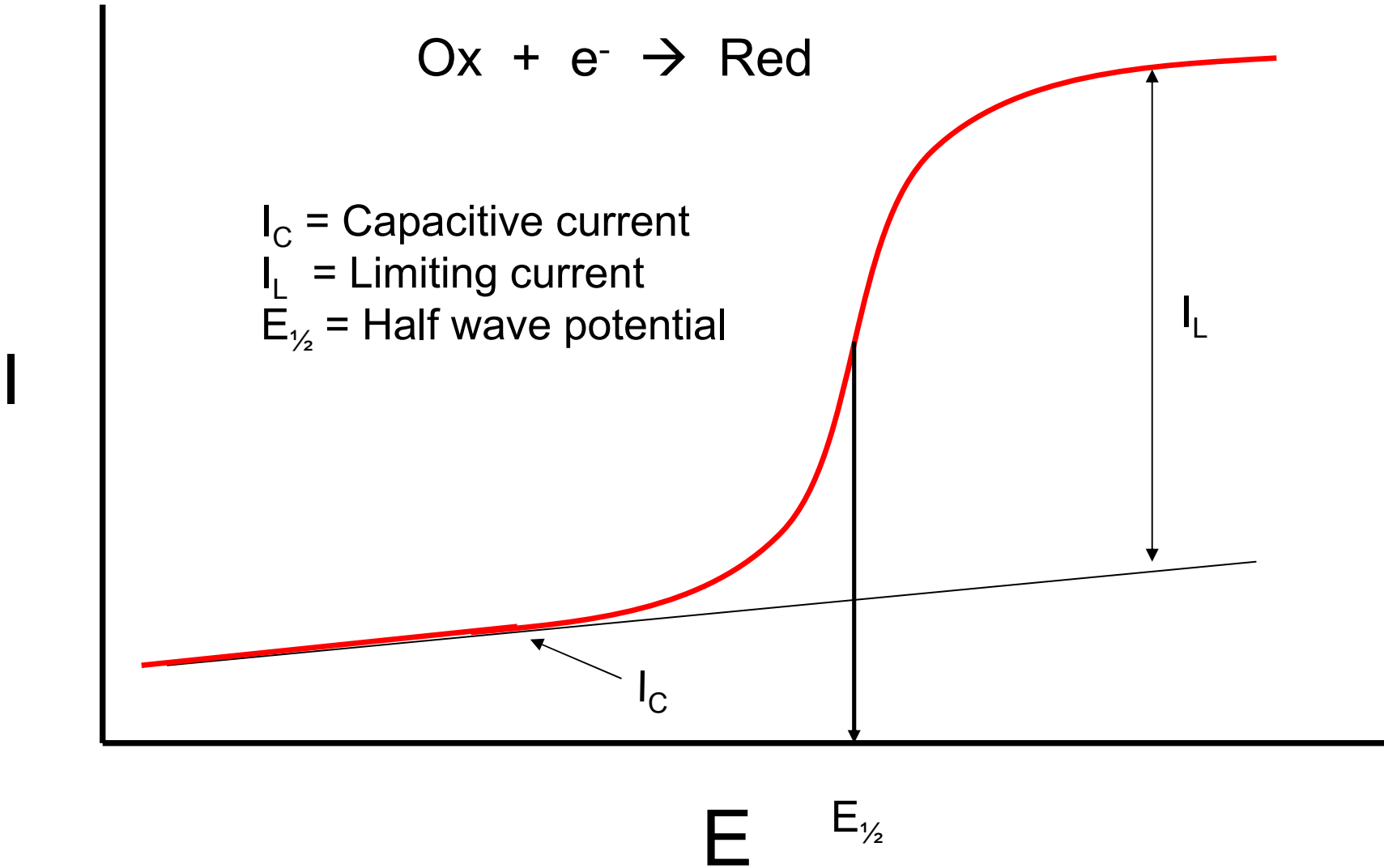
Linear Scan Voltammetry (stirred)

$$Ox + e^- \rightarrow Red$$

Half wave potential ($E_{1/2}$)
is E when $I = I_L/2$

I_L

I_C

I

E $E_{1/2}$

Linear Scan Voltammetry (stirred)

$$Ox\ +\ e^-\ \rightarrow\ Red$$

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

I_L
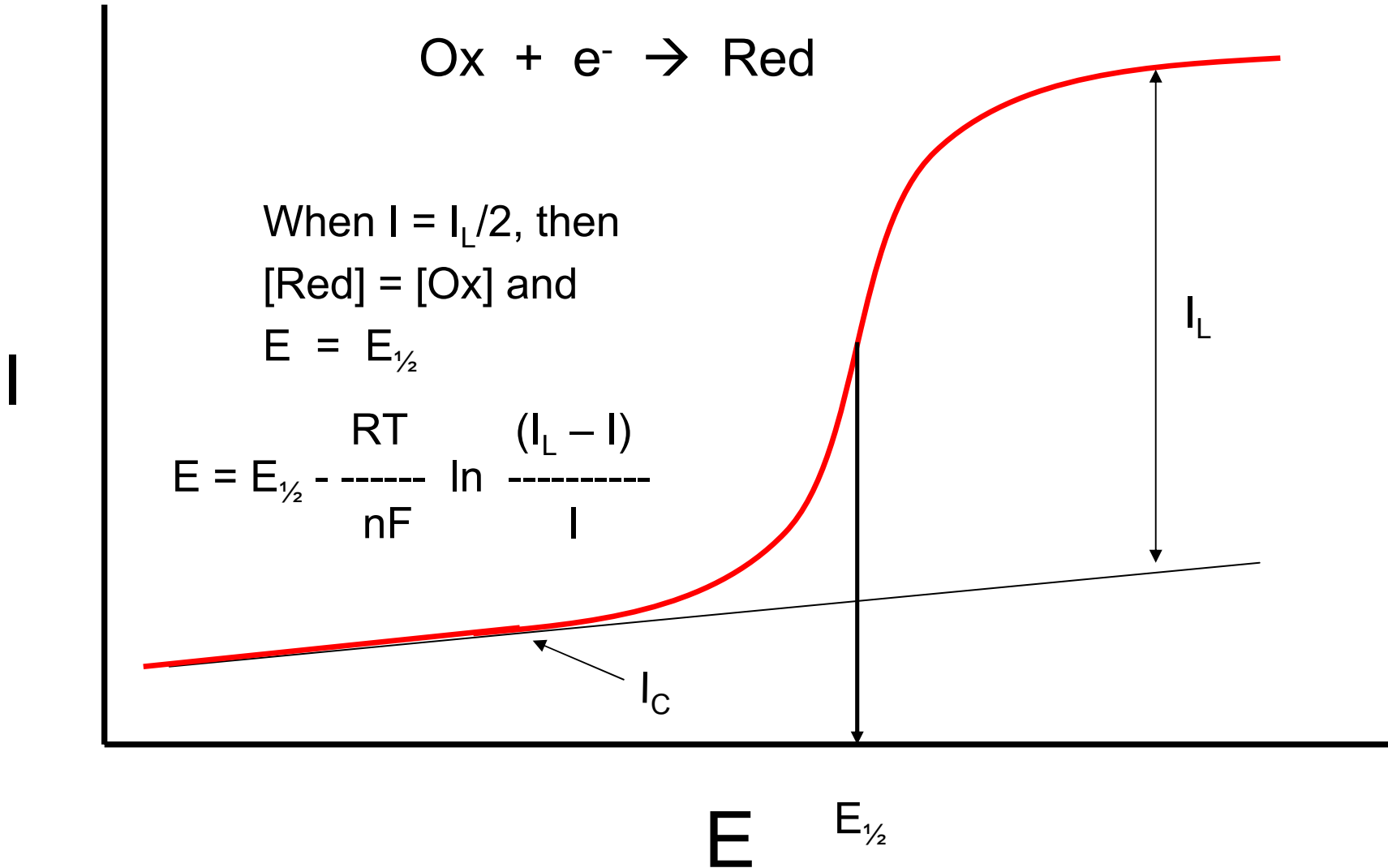
I_C

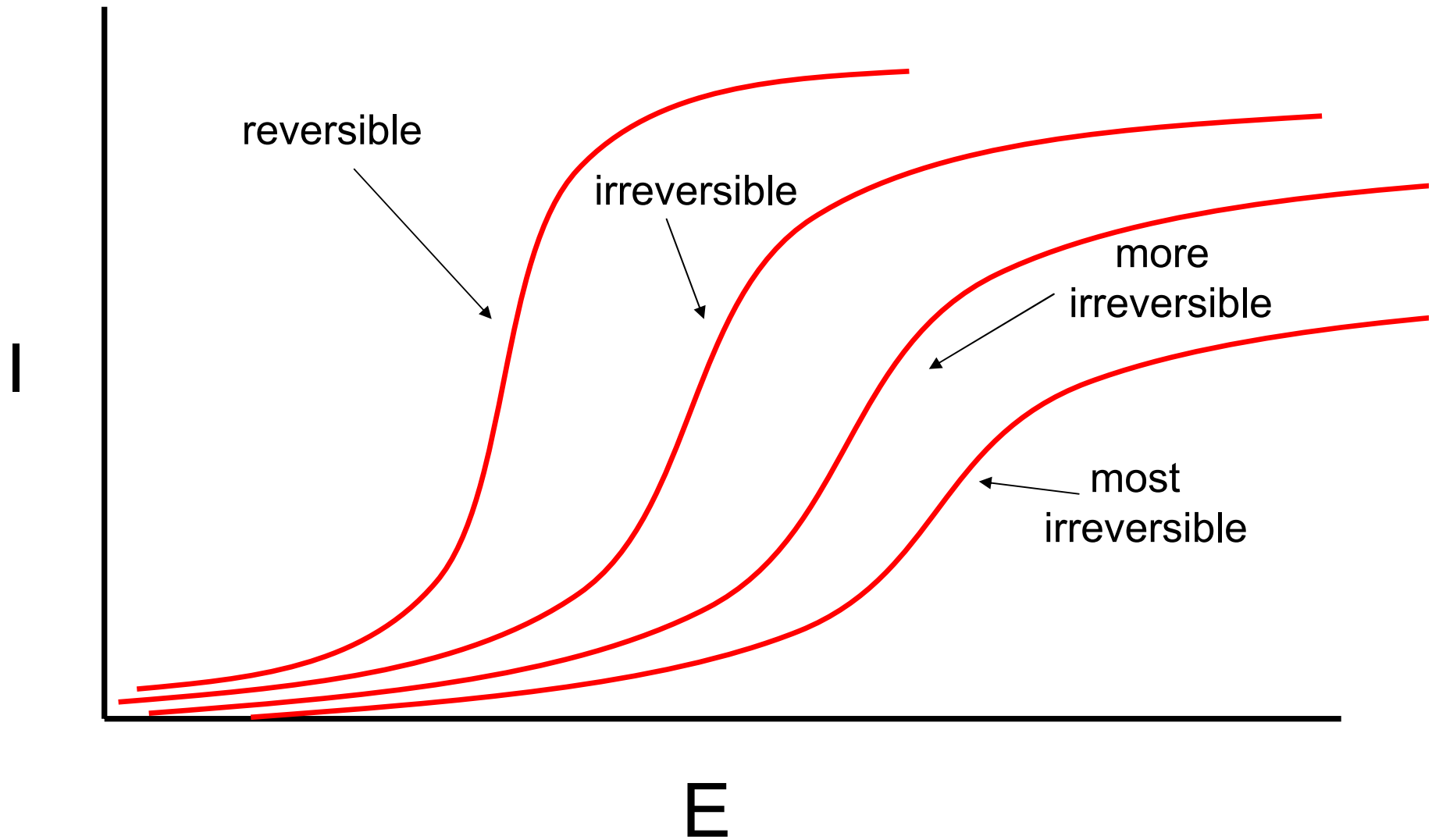I
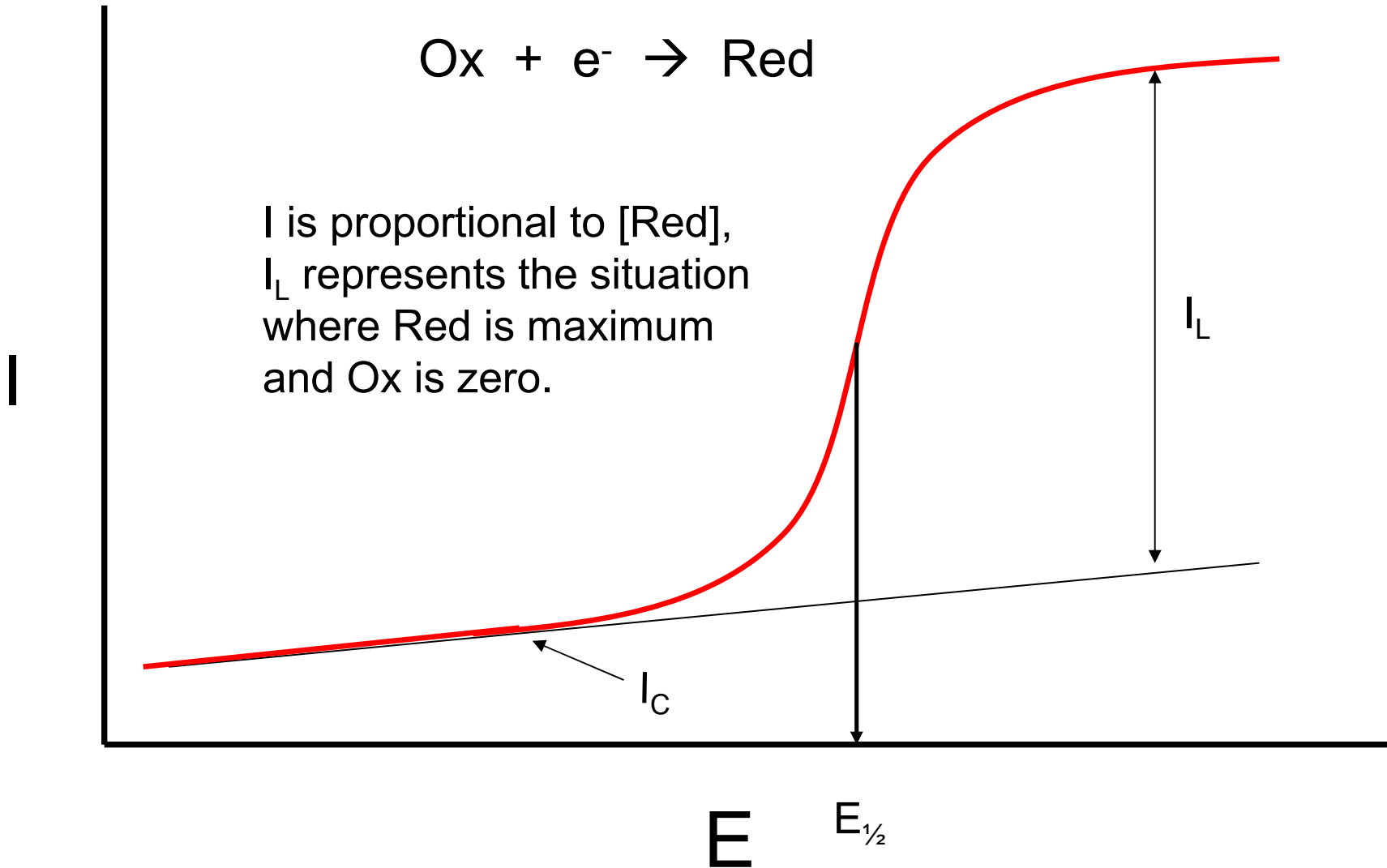
E $E_{1/2}$

Linear Scan Voltammetry (stirred)

$$Ox + e^- \rightarrow Red$$

When $I = I_L/2$, then
[Red] = [Ox] and
$E = E_{1/2}$

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

I_L

I_C

I

E $E_{1/2}$

Linear Scan Voltammetry (stirred)
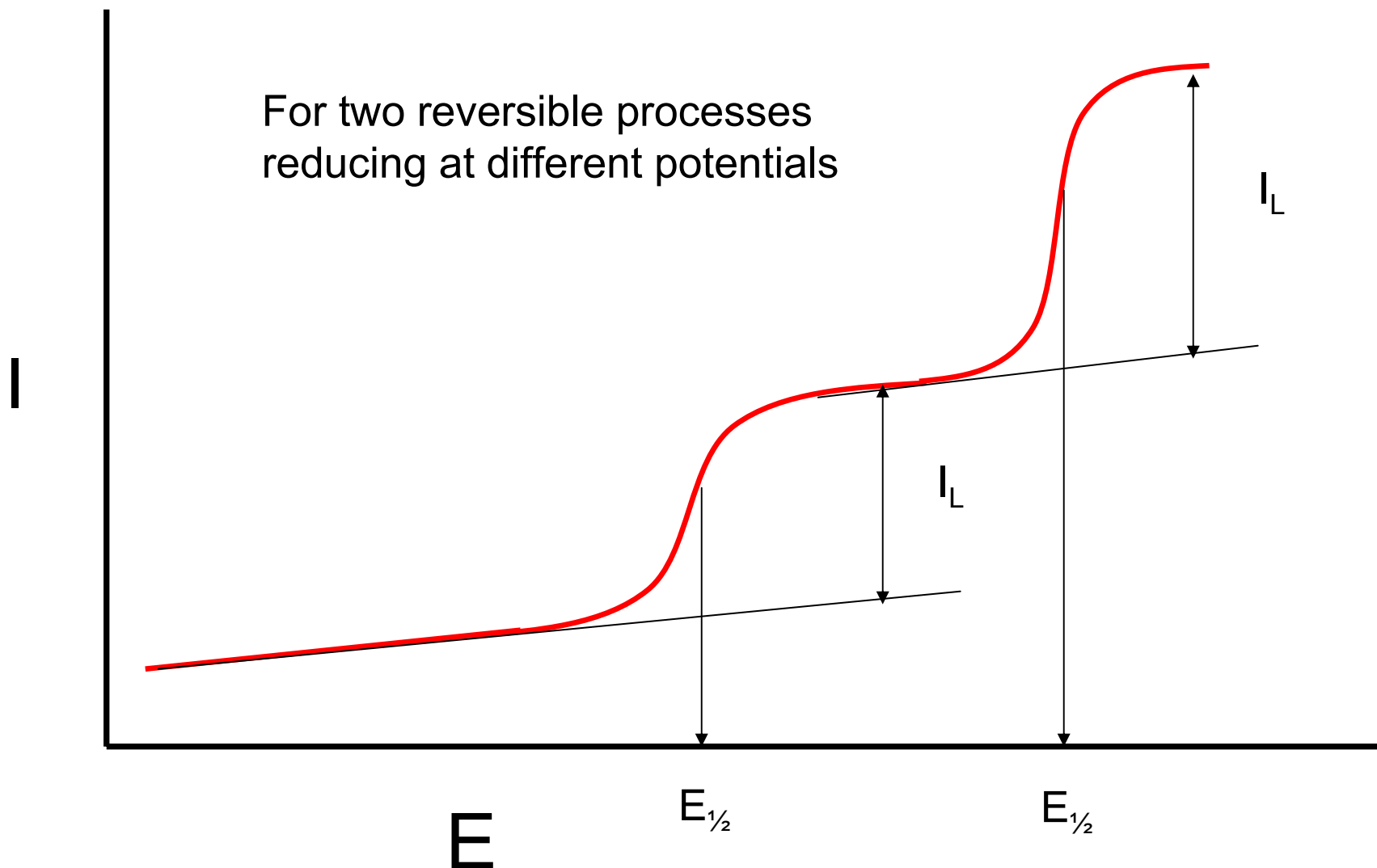

reversible

irreversible

more
irreversible

most
irreversible

I

E

Can assign rate constants (k) for irreversible processes

Linear Scan Voltammetry (stirred)

For two reversible processes
reducing at different potentials

I_L

I_L

I

E

$E_{1/2}$ $E_{1/2}$

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)

I

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

I_L

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

I_L

E
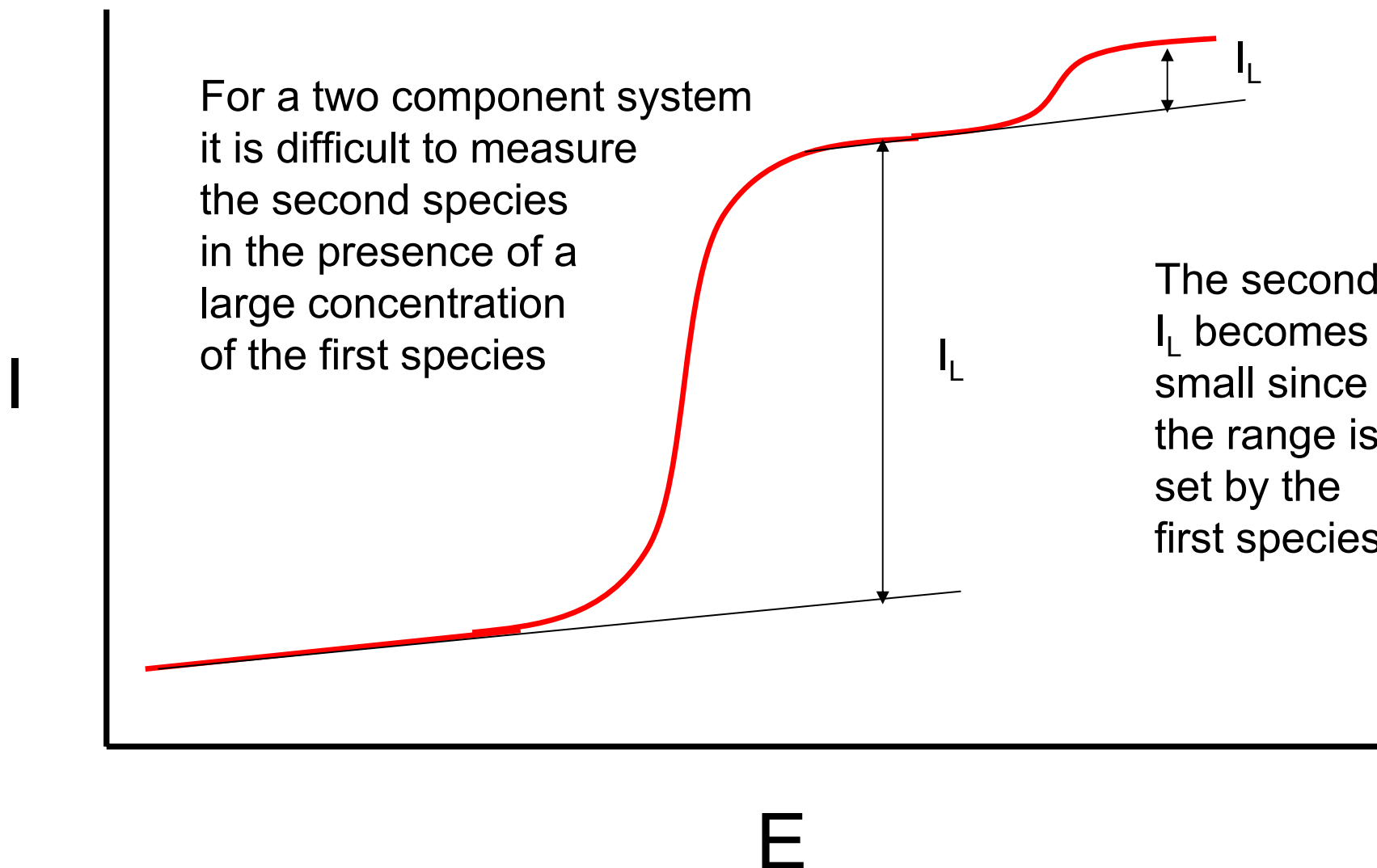
This problem is inherent for techniques that produce waves