Voltammetry

- Methods based on an electrolytic cell
- Apply potential or current to electrochemical cell & concentrations change at electrode surface due to oxidation & reduction reactions
- Can have 2 or 3 electrodes
- Stirred or unstirred solution
- Measure current or voltage

In all electrochemical methods, the rate of oxidation & reduction depend on:

1) rate & means by which soluble species reach electrode surface (mass transport)

2) kinetics of the electron transfer process at electrode surface (electrode kinetics), which depend on:

   a) nature of the reaction

   b) nature of electrode surface

   c) temperature

(we don't have much control over #2)

Mass Transport or Mass Transfer

1) Migration – movement of a charged particle in a potential field – generally bad (important for conductance & electrophoresis)

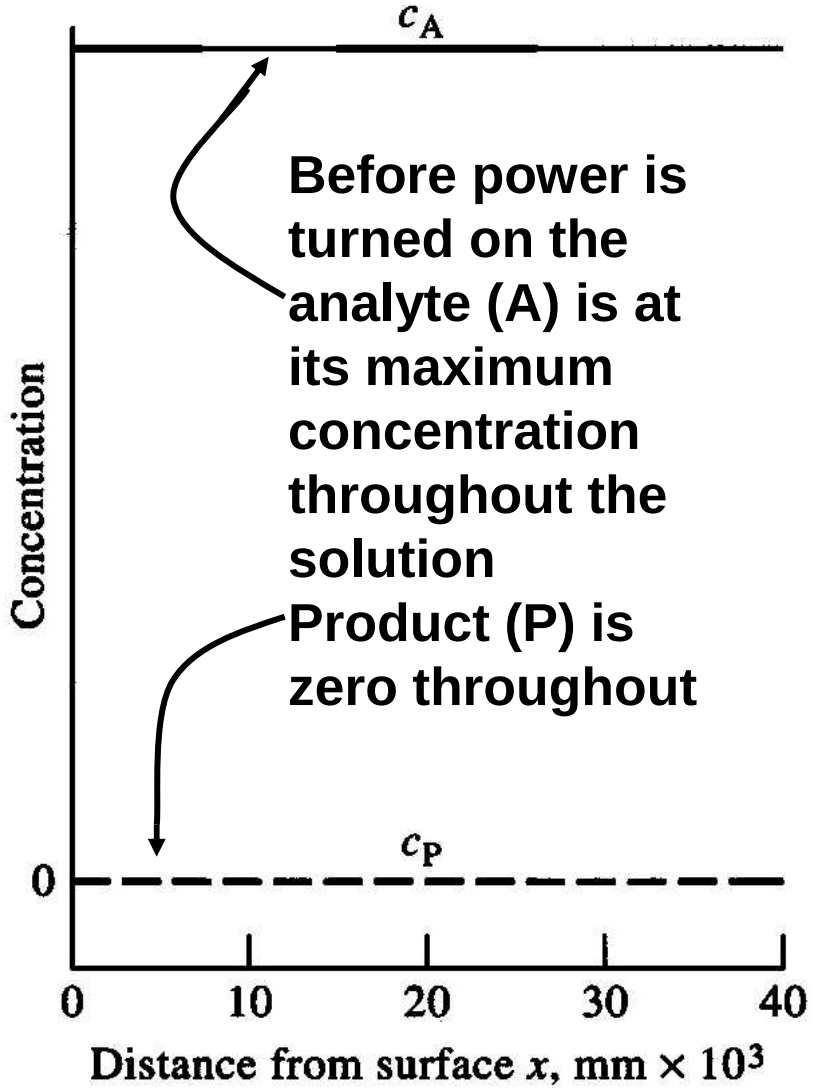
In most cases migration is undesirable and can be eliminated by adding a 100 fold excess of an inert electrolyte (i.e., electrochemically inert – not oxidized or reduced) Inert electrolyte does the migrating, not the analyte

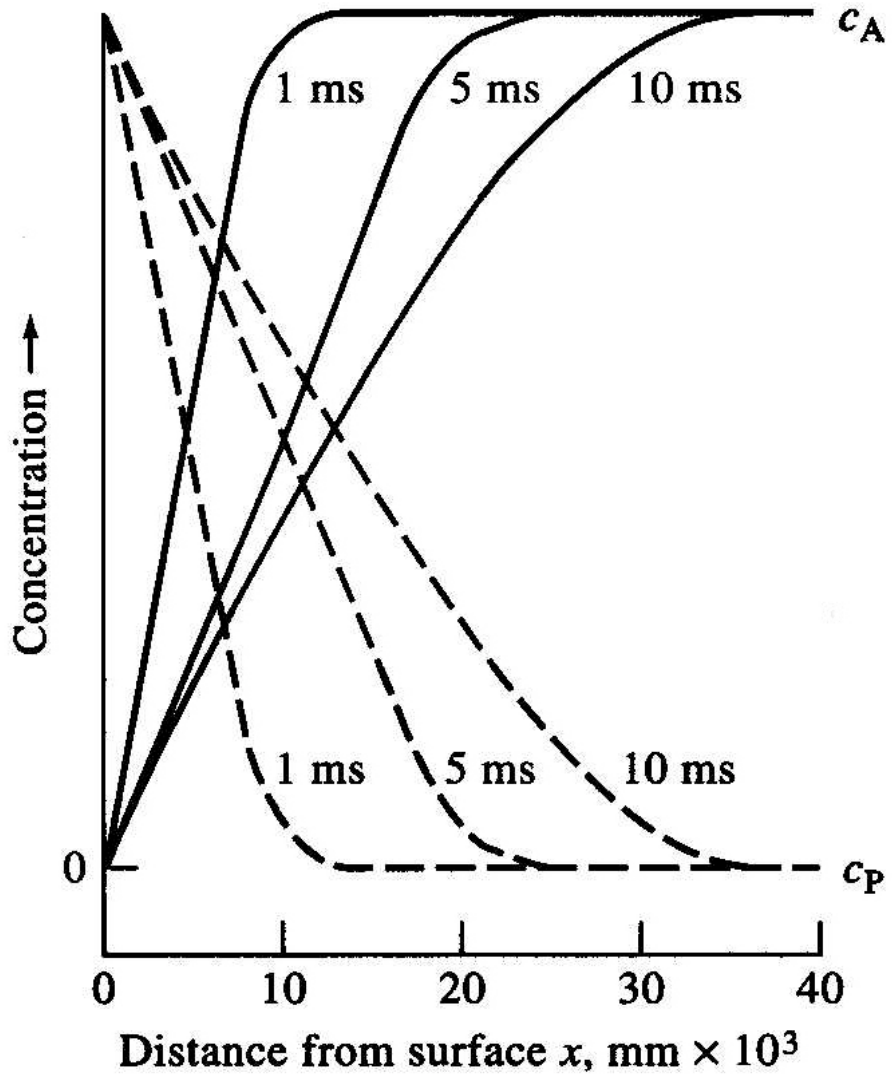
Mass Transport or Mass Transfer

2) Diffusion – movement due to a concentration gradient. If electrochemical reaction depletes (or produces) some species at the electrode surface, then a concentration gradient develops and the electroactive species will tend to diffuse from the bulk solution to the electrode (or from the electrode out into the bulk solution)

Concentration polarization

Reaction is $A + e^- \rightarrow P$





Fick's Laws describe diffusion

1st Law

$$J = -D \frac{\partial C(x,t)}{\partial x}$$

Where

J = flux of material i.e., moles passing a 1 cm^2 plane at point x & time t ($mol/cm^2/sec$)

D = diffusion coefficient (cm^2/sec)

C = concentration

t = time (sec) from when power is turned on

x = distance from electrode surface (cm)

Using an expression for Conservation of Mass

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$$

And combining with Fick's First law gives Fick's Second Law

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Solving Fick's Laws for particular applications like electrochemistry involves establishing Initial Conditions and Boundary Conditions

Initial $C(x,0) = C$

At t=0 i.e., before experiment starts, concentration is C & is same throughout the solution

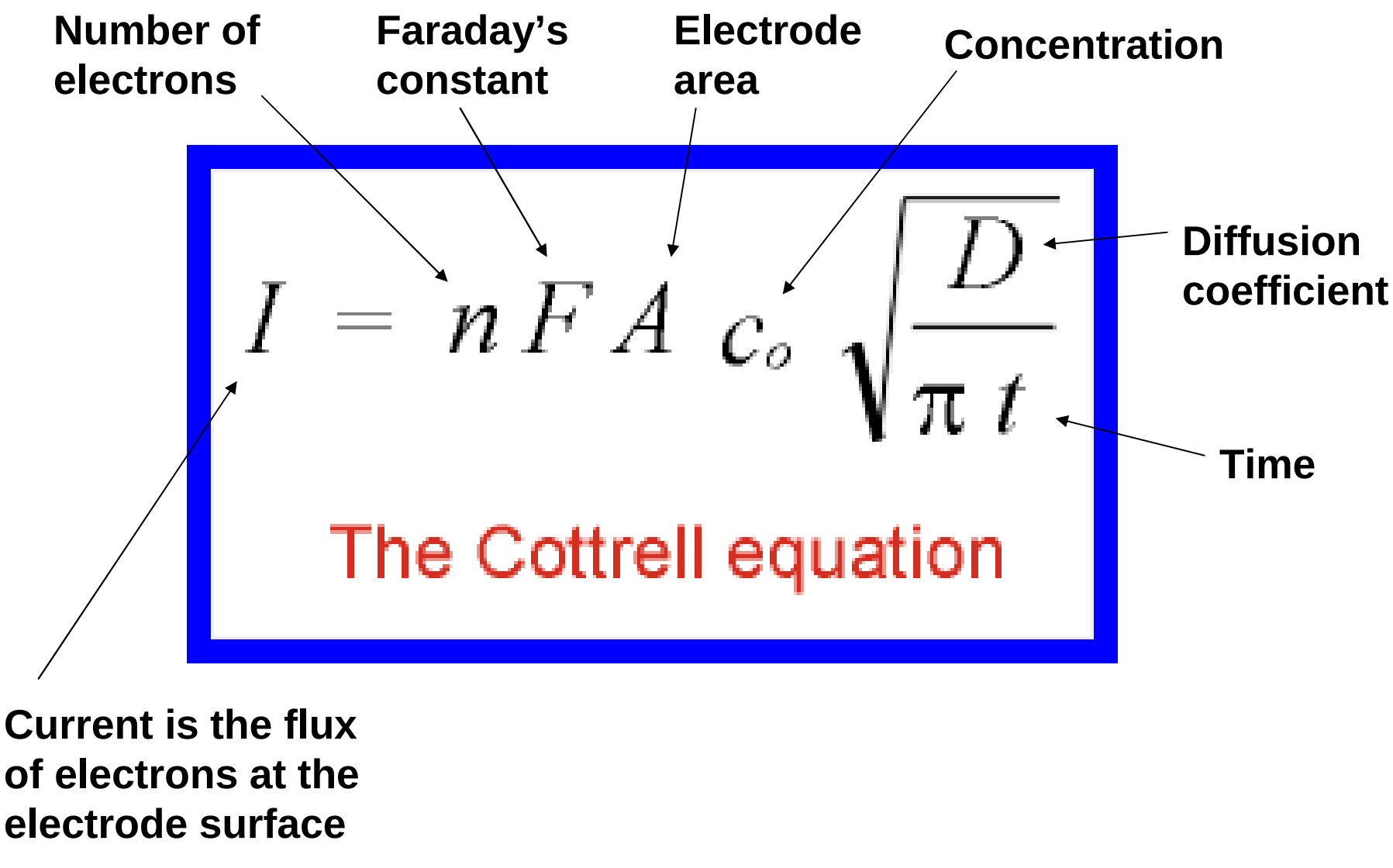
Boundary 1 $C(0,t) = 0$

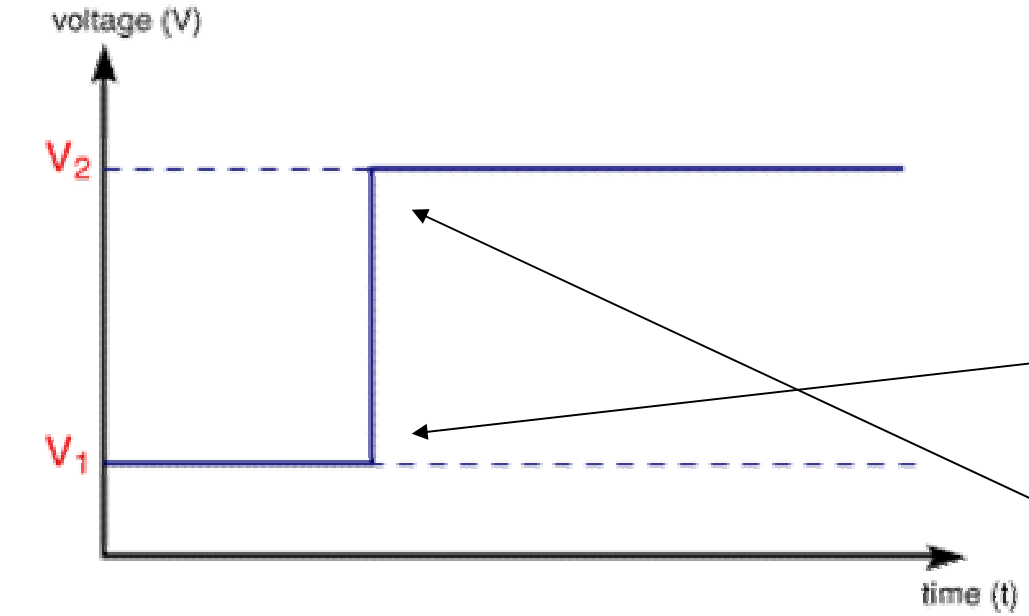
At t>0 the concentration at the electrode surface goes to zero the moment power is turned on

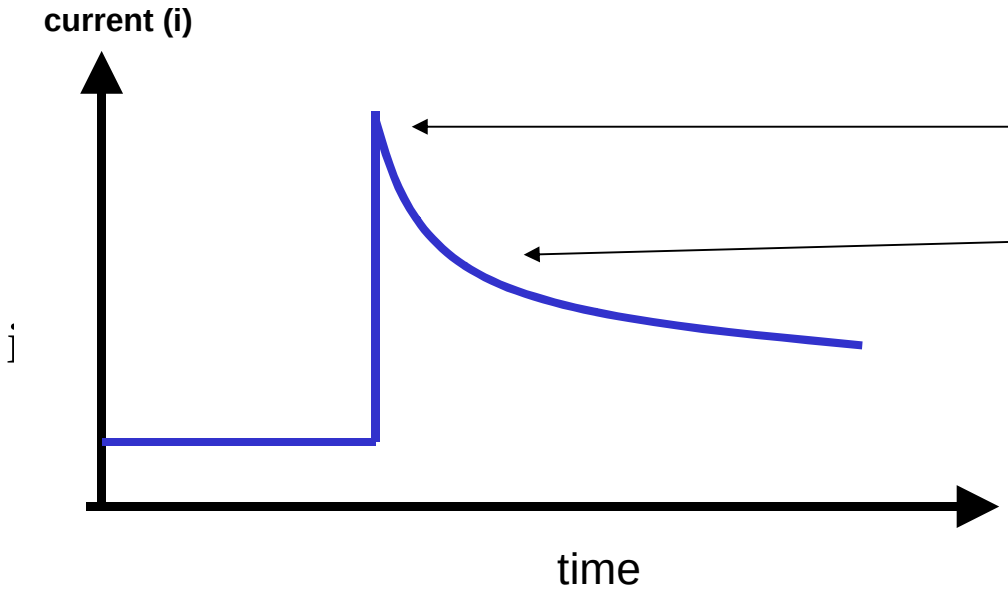
Boundary 2 $C(\infty,t) = C$

Some distance away from the electrode surface at anytime t>0 the concentration is still C in the "bulk solution" unaffected by the electrode process

Skipping to the Electrochemical Solution







Experiment showing how Cottrell equation describes current as a function of time

Voltage applied to cell begins at V_1 where no reaction occurs and is stepped up to V_2 causing electrode process to begin and a current spike results.

Current drops off with time according to the Cottrell equation since material must diffuse to the electrode surface in order to react.

Quantity		Unit	
Q	charge	C	coulomb
I	current	A	ampere
i	current density	A m^{-2}	ampere per square metre
ϕ, E	electrical potential	V	volt
$\Delta\phi$, ΔE	potential difference; voltage	V	volt
κ	conductivity	S m^{-1}	siemens per metre
R	resistance	Ω	ohm
u	mobility	m^2 s^{-1} V^{-1}	square metre per second volt
z	charge number	(none)	
ε	permittivity	F m^{-1}	farad per metre
C	capacitance	F	farad
j	flux density	mol m^{-2} s^{-1}	mole per square metre second

note that
- Ω F = s second
- V C = J joule

Mass Transport or Mass Transfer

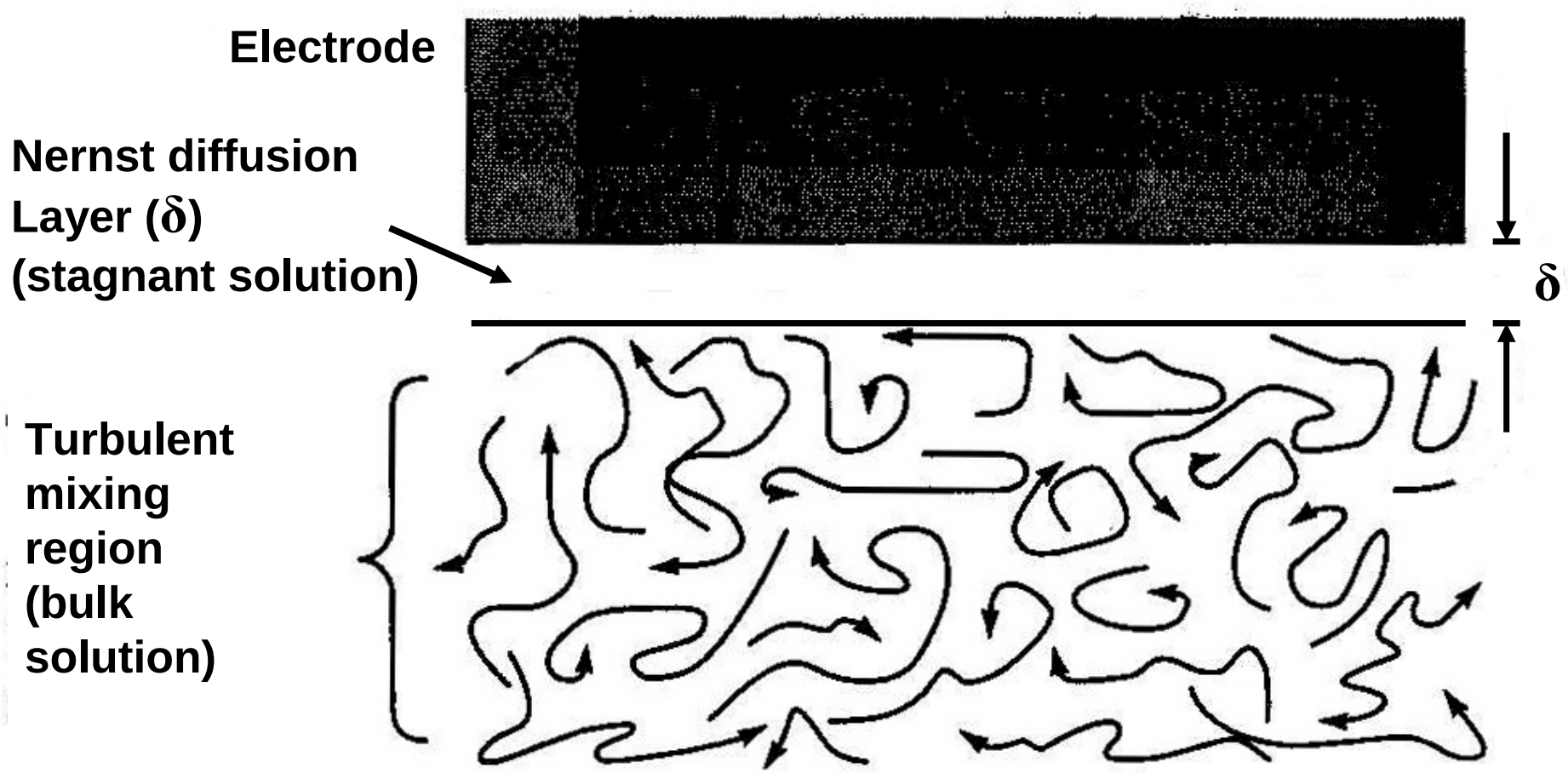
3) Convection – mass transfer due to stirring. Achieved by some form of mechanical movement of the solution or the electrode i.e., stir solution, rotate or vibrate electrode

Difficult to get perfect reproducibility with stirring, better to move the electrode

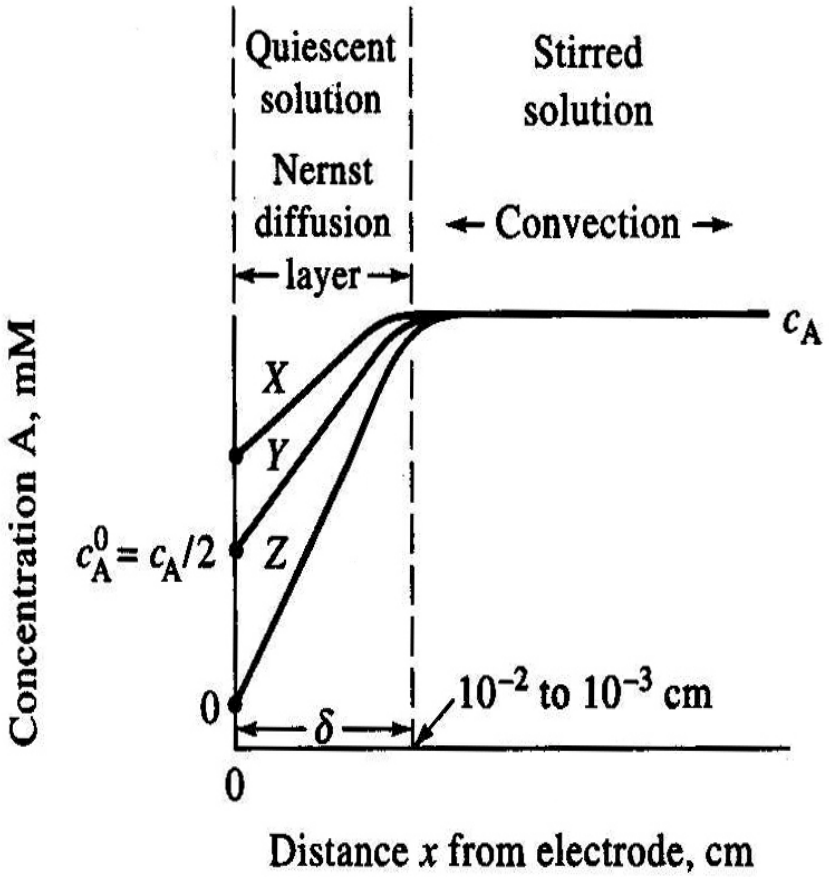
Convection is considerably more efficient than diffusion or migration = higher currents for a given concentration = greater analytical sensitivity

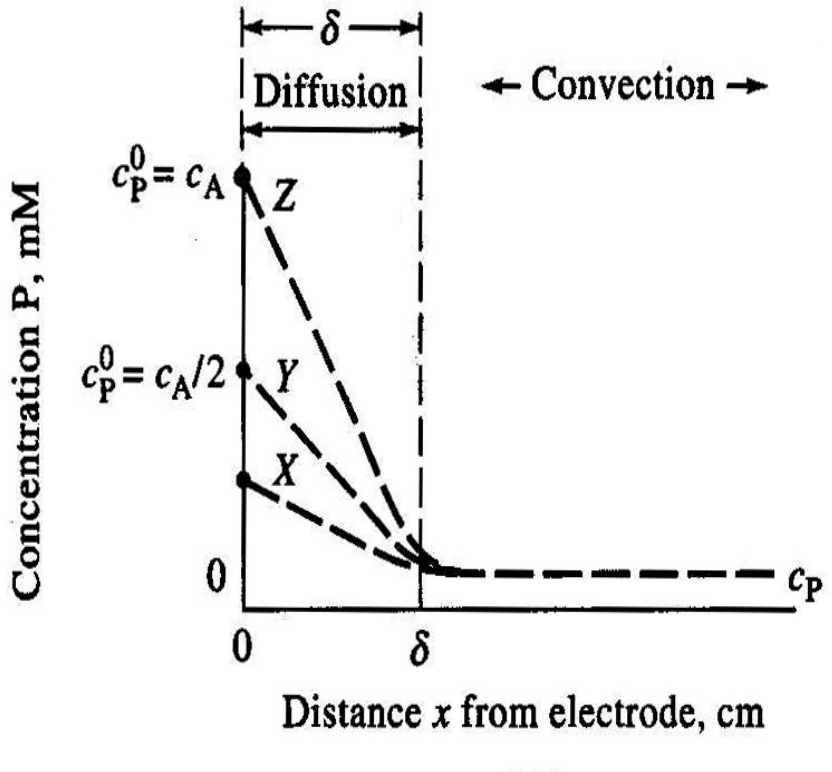
Nernst Diffusion Layer Concept

for stirred solution & stationary electrode



Convective Mass Transport
Electrode converts A + e^- → P at surface





Fick's first law applied to stagnant layer

$$\frac{\partial C(x,t)}{\partial x} = \frac{C_{bulk} - C_{surface}}{\delta}$$

$$i = nFAD \frac{C_{bulk} - C_{surface}}{\delta}$$

For stirred solutions

$$i = nFAD \frac{C_{bulk}}{\delta}$$

Mass Transport vs Electrode Kinetics

Experimentally rate of electron transfer is fast for many processes so can assume:

- current depends only on mass transfer

- surface concentrations are in equilibrium with applied potential as expressed by the Nernst equation

Processes which satisfy these assumptions are known as electrochemically **reversible**

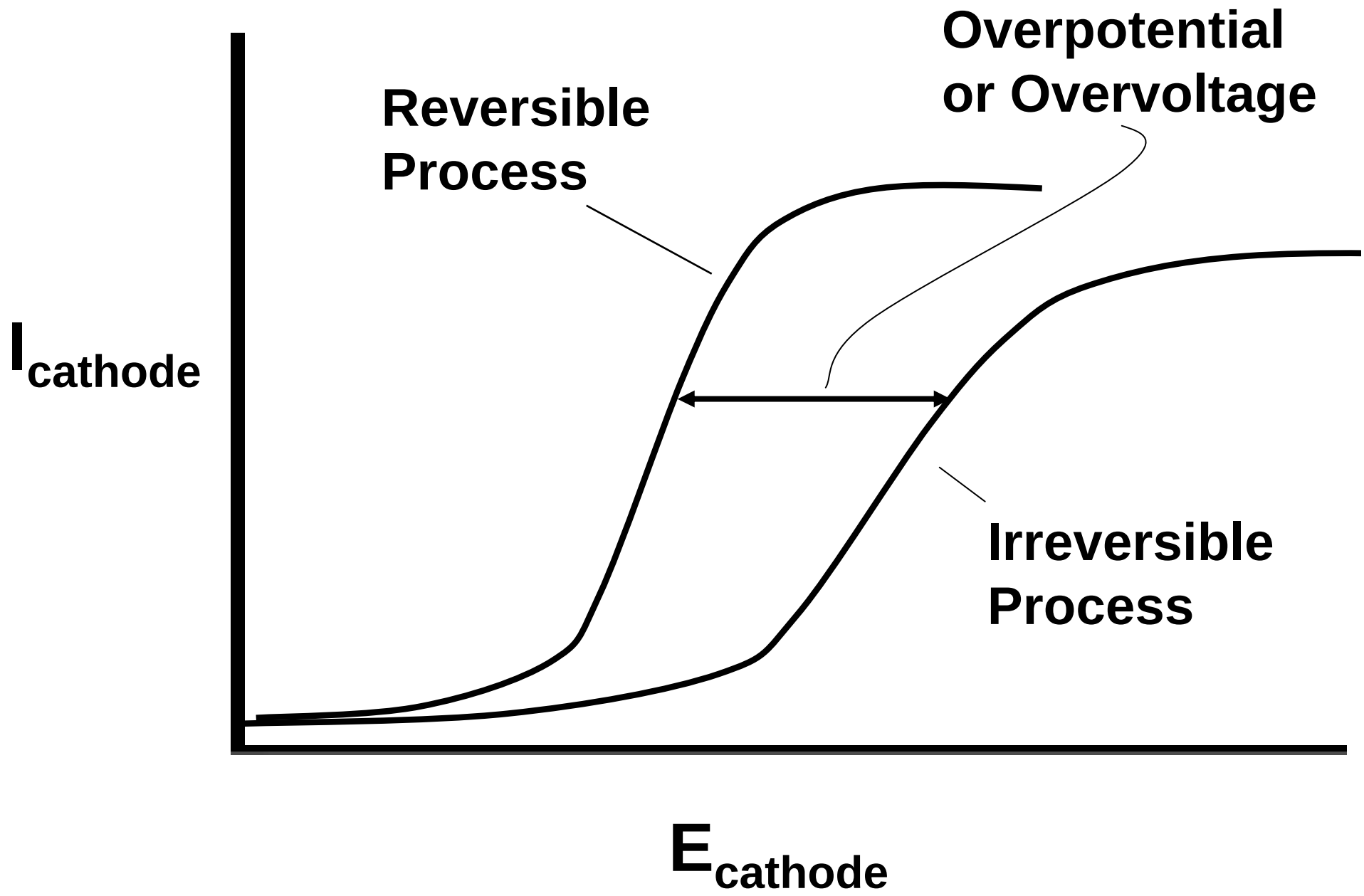
- A process may be reversible under one set of conditions and irreversible under other conditions
- Process is more likely to be irreversible if

  - it involves a high current

  - employs a rapid potential scan
- If a process is irreversible, then the rate of reaction at the electrode surface (i.e., current) will be slower than predicted from mass transfer considerations alone
- Varying potential (E) linearly at a stationary electrode in a stirred solution for

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

$Ox + e^- \rightarrow Red$



- Overpotential (overvoltage) = potential to achieve the same current as if process was reversible
- Large overvoltage → process more irreversible
- For reversible processes $E_{overpotential} = 0$
- Overvoltage characteristics:

  1) increases with current density (current/area)
  2) decreases with increasing temp
  3) high for reactions producing gases
  4) depends on electrode composition
  5) difficult to specify exactly – electrode surface