Electrochemistry for materials technology

Chapter 4B

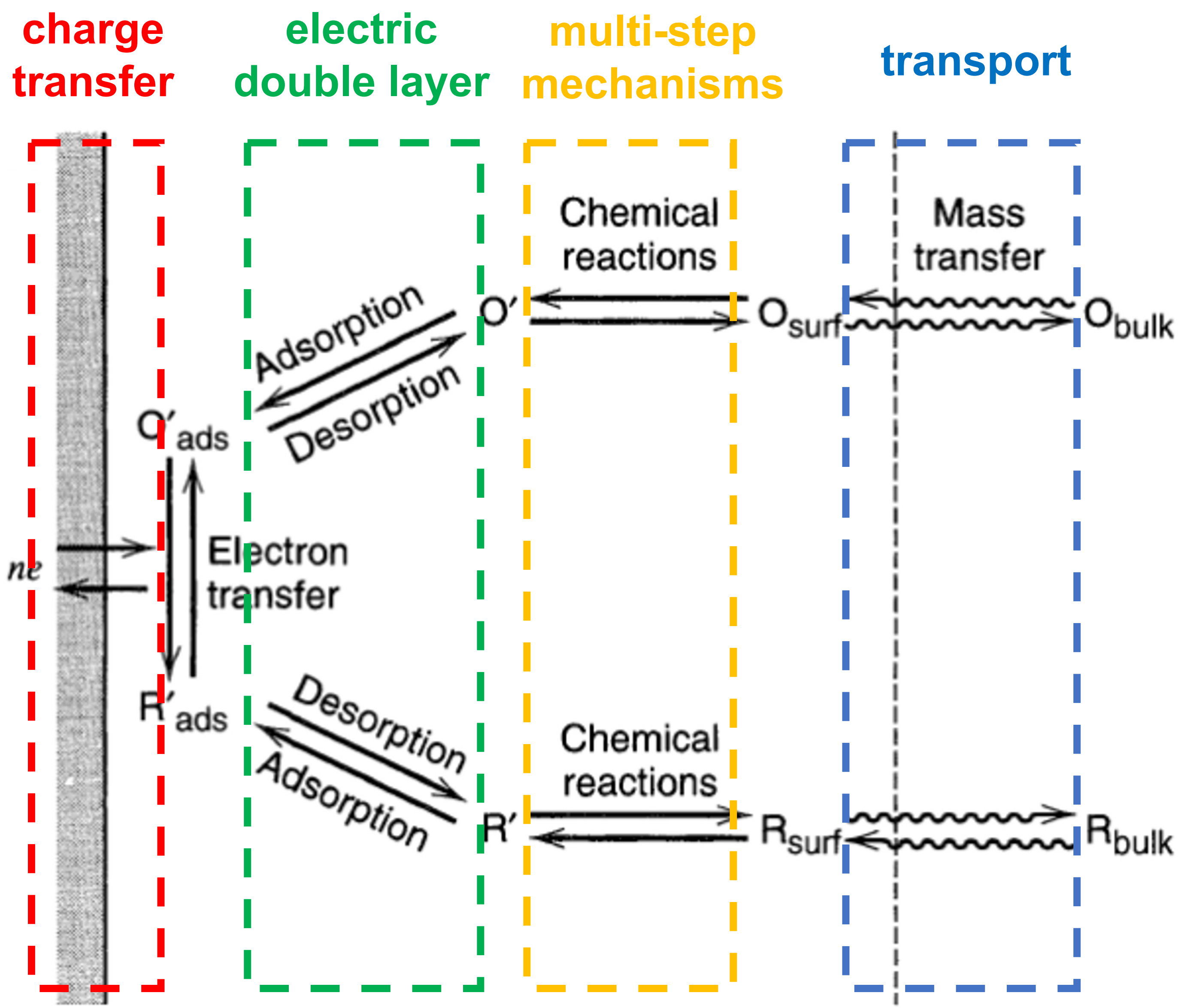
Electrode kinetics

Mass transport phenomena

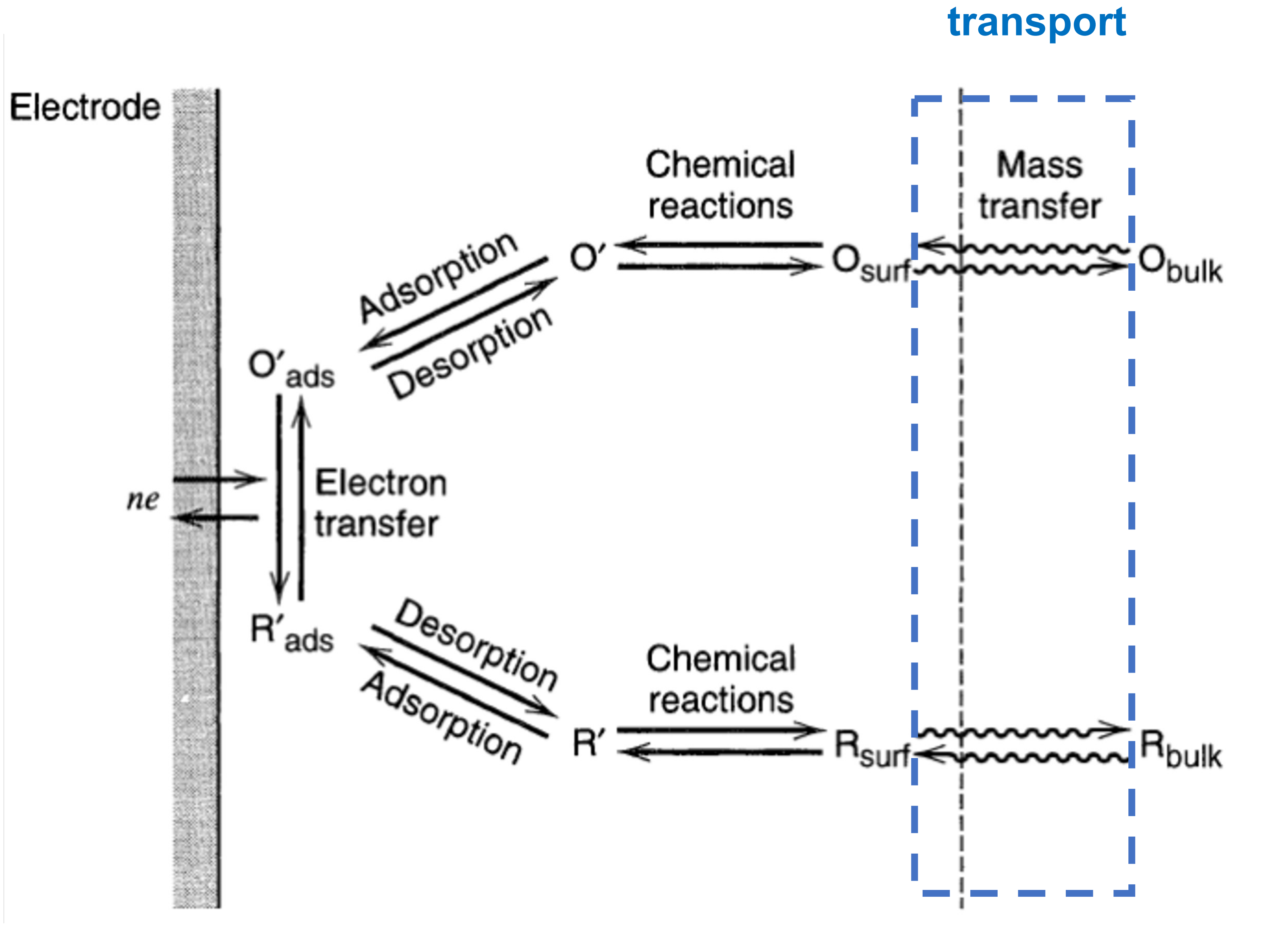
Transport Phenomena

- Diffusion
- Diffusion + Migration
- Convection
- Transient Responses

B-V Model with Mass Transport



B-V Model with Mass Transport



Modes of Mass Transport

Diffusion : movement of a species under the influence of a gradient of chemical potential (i.e. a concentration gradient).

Migration : movement of a charged species under the influence of an electric field (a gradient of electrical potential).

Convection : stirring or hydrodynamic transport (may be characterized by stagnant regions, laminar flow, or turbulent flow).

Modes of Mass Transport

Mass transfer to an electrode is governed by the **Nernst-Planck equation** written for one-dimensional mass transfer along the x-axis as:

$$J_i(x) = -\underbrace{D_i \frac{\partial C_i(x)}{\partial x}}_{\text{diffusion}} - \underbrace{\frac{z_i F}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x}}_{\text{migration}} + \underbrace{C_i v(x)}_{\text{convection}}$$

(C_i: mol/cm^3)

$J_i(x)$: flux of species i at a distance x from the surface [mol s^{-1} cm^{-2}]

$D_i(x)$: diffusion coefficient of species i [cm^2/s]

$\frac{\partial C_i(x)}{\partial x}$: concentration gradient at distance x

$\frac{\partial \Phi(x)}{\partial x}$: potential gradient at distance x *Volt / m*

z_i : charge of species i (not to be confused with z, which is mol e- /mol reactant)

C_i : concentration of species i [mol cm^{-3}]

v(x): velocity with which a volume element in solution moves along the axis [cm s^{-1}]

Modes of Mass Transport

A rigorous solution is not easy when all 3 forms of mass transfer are present; hence electrochemical systems are frequently designed so that one or more of the contributions to mass transfer are negligible.

For example,

Migration can be considered negligible by the addition of inert electrolyte (i.e. a supporting electrolyte) at a concentration much larger than that of the electroactive species. → screens the electric field that is "felt" by the reactive species

Convection can be considered negligible by preventing stirring and vibrations in the ('stagnant') electrochemical cell.

Mass Transport without convection

Mass transfer to an electrode is governed by the **Nernst-Planck equation** written for one-dimensional mass transfer along the x-axis as:

$$J_i(x) = \underbrace{- D_i \frac{\partial C_i(x)}{\partial x}}_{\text{diffusion}} \underbrace{- \frac{z_i F}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x}}_{\text{migration}} + \cancel{C_i v(x)}$$

If the species i is charged, then the flux, J_i, is equivalent to a current density j_i:

$$-J_i = \frac{j_i}{z_i F} = \underbrace{\frac{j_{d,i}}{z_i F}}_{\text{flux due to diffusion}} + \underbrace{\frac{j_{m,i}}{z_i F}}_{\text{flux due to migration}}$$

z_i: charge of species i

$$\frac{j_{d,i}}{z_i F} = D_i \frac{\partial C_i(x)}{\partial x}$$

$$\frac{j_{m,i}}{z_i F} = \frac{z_i F}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x}$$

Mass Transport without convection

At any location in solution, the total current is made up of contributions from all the species i :

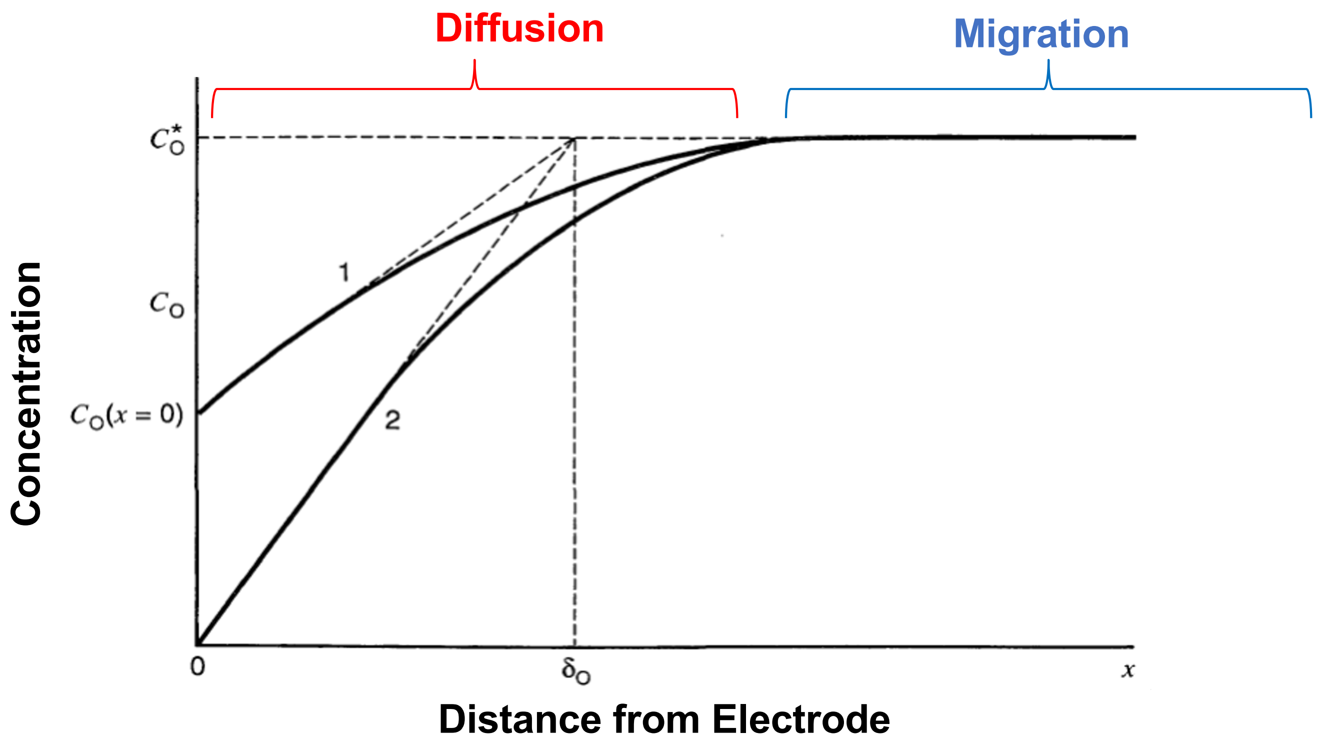
$$j = \sum_i j_i = \sum_i (j_{d,i} + j_{m,i}) = F \sum_i z_j D_i \frac{\partial C_i(x)}{\partial x} + \frac{F^2}{RT} \frac{\partial \Phi(x)}{\partial x} \sum_i z_i^2 D_i C_i$$

where the current for each species at that location is made up of a diffusional component and a migrational component

Mass Transport without convection

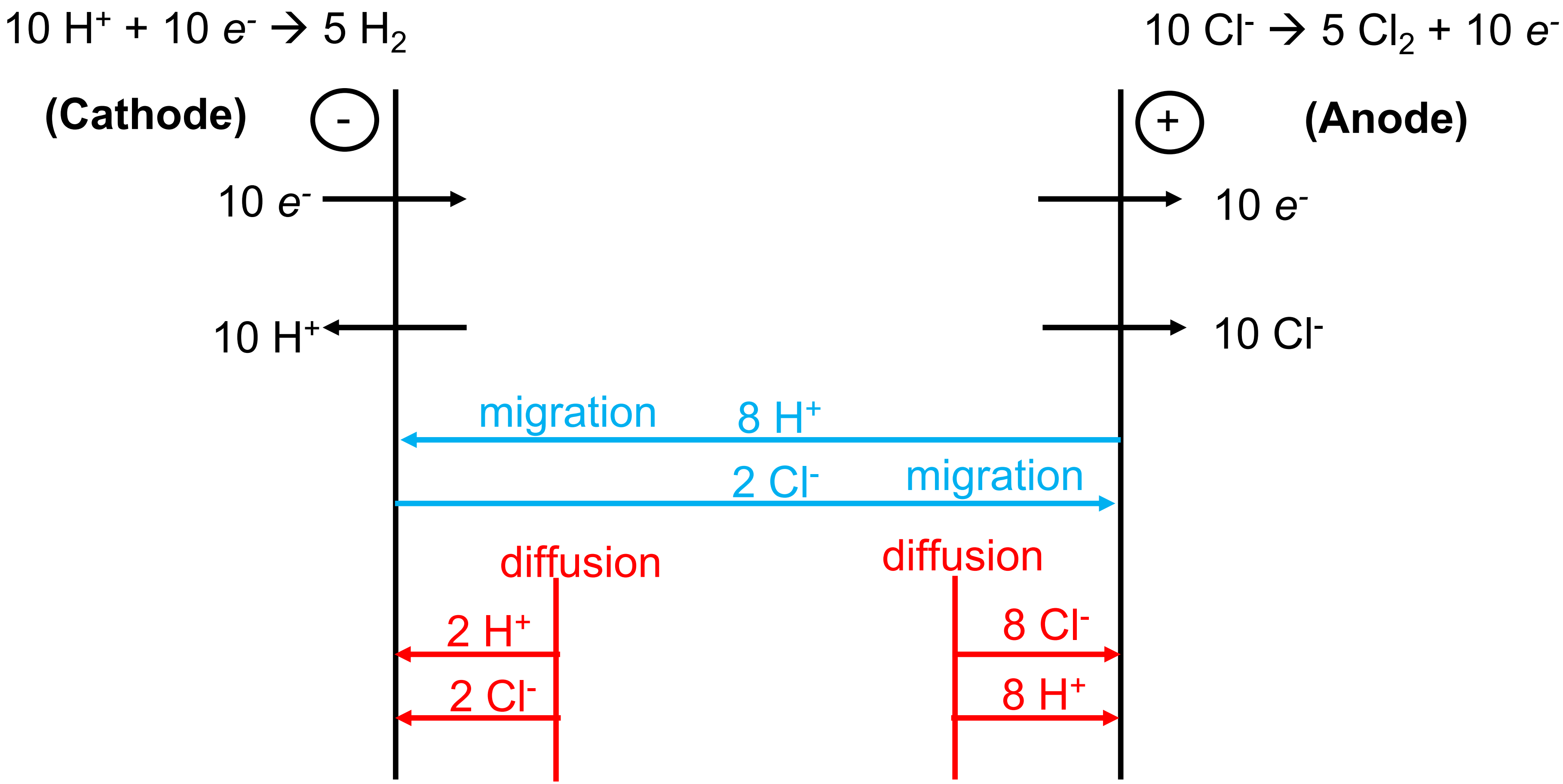
The relative contributions of diffusion and migration to the flux of a species (and the flux of that species to the total current) differ for different locations in solution.

- Far from the electrode, migration can play a dominant role.
- Near an electrode, an electroactive substance is usually transported by both processes.



Mass Transport without convection

$$2\,HCl \Leftrightarrow H_2 + Cl_2$$



Cathode:
80% of H^+ current is migration

Anode:
20% of Cl^- current is migration

Diffusion is independent of an electric field, hence both ions diffuse to both electrodes

Migration

In the bulk solution (away from the electrode), concentration gradients are generally small, and the total current is carried mainly by migration of all charged species.

$$j_i = \cancel{j_{d,i}} + j_{m,i} = \cancel{F z_j D_i \frac{\partial C_i(x)}{\partial x}} + \frac{F^2}{RT} \frac{\partial \Phi(x)}{\partial x} z_i^2 D_i C_i$$

small concentration gradient

$$j_i = \frac{z_i^2 F^2 D_i C_i}{RT} \frac{\partial \Phi(x)}{\partial x}$$

Migration

$$j_{m,i} = \frac{z_i^2 F^2}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x}$$

Mobility of a species i (u_i) is the ability of a charged particle to move through a medium in response to an electric field.

$$u_i = \frac{|z_i| F D_i}{RT}$$

unit: $m^2/V.s$

By substituting for D_i,

assuming linear change in potential (ΔE) over distance L

$$j_{m,i} = |z_i| F u_i C_i \frac{\partial \Phi(x)}{\partial x} \quad \longrightarrow \quad j_{m,i} = \frac{|z_i| F u_i C_i \Delta E}{L}$$

$$\frac{\partial \Phi(x)}{\partial x} \sim \frac{\Delta E}{L}$$

Migration

If multiple species i contribute to current, the total current is the sum of all the individual contributions.

$$j = \sum_i j_i = \frac{F\Delta E}{L} \sum_i |z_i| u_i C_i$$

The **transference number t_i** of species i is the fraction of the total migration current that a given ion i carries.

$$t_i = \frac{j_i}{j} = \frac{|z_i| u_i C_i}{\sum_k |z_k| u_k C_k}$$

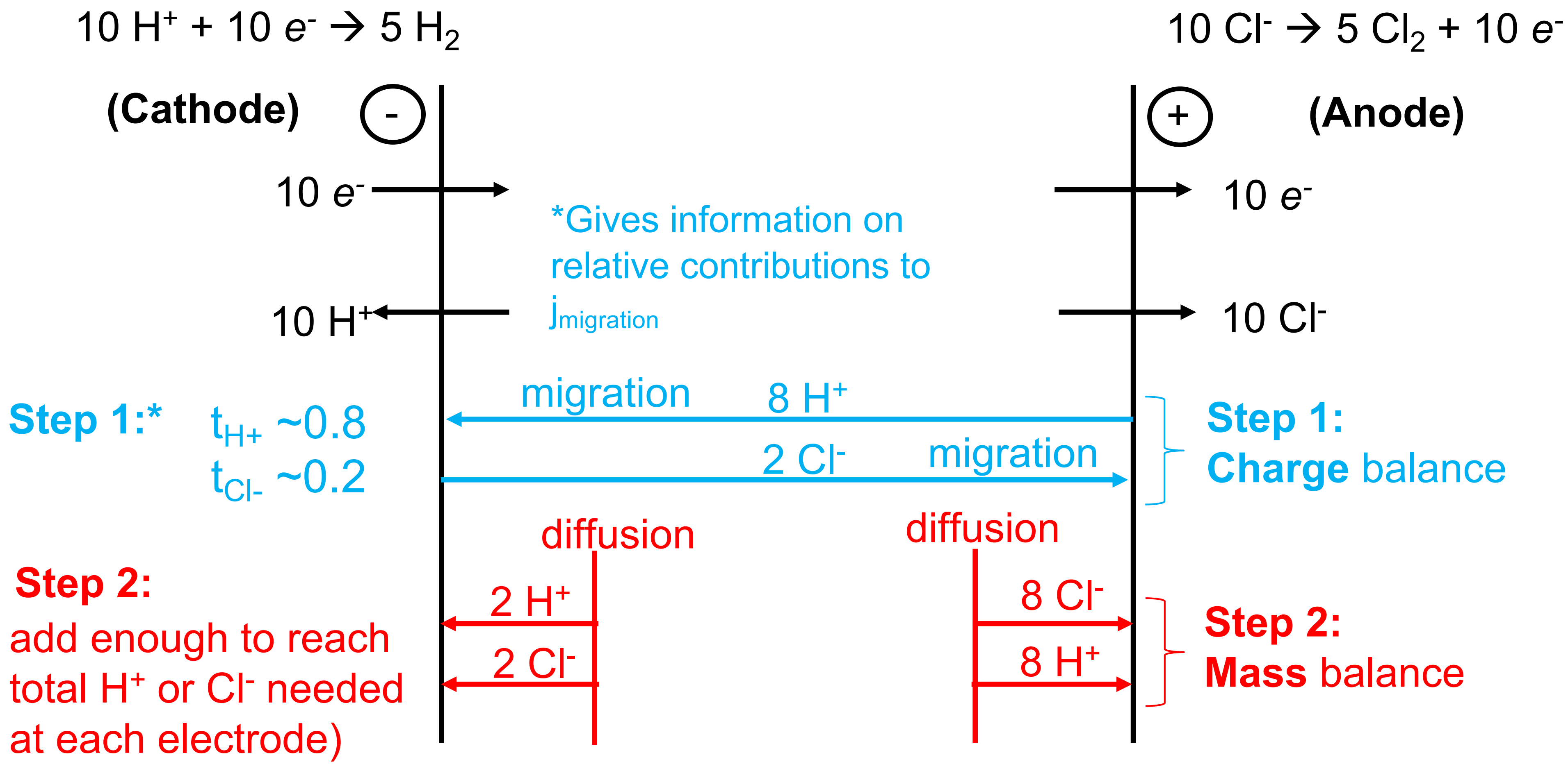
C_i = concentration of i

z_i = charge of i

u_i = mobility of i

Mixed Migration + Diffusion

$2\ HCl \Leftrightarrow H_2 + Cl_2$



Cathode:

80% of H^+ current is migration**

Anode:

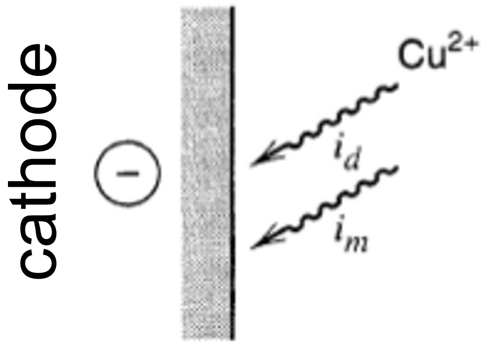
20% of Cl^- current is migration**

**gives information on $j_{migration}$ vs. $j_{diffusion}$ independent of t_{H+}, t_{Cl-} (happens to also be 0.8, 0.2 in this example)

Mixed Migration + Diffusion

Positively charged reactant

$Cu^{2+} + 2e \rightarrow Cu$



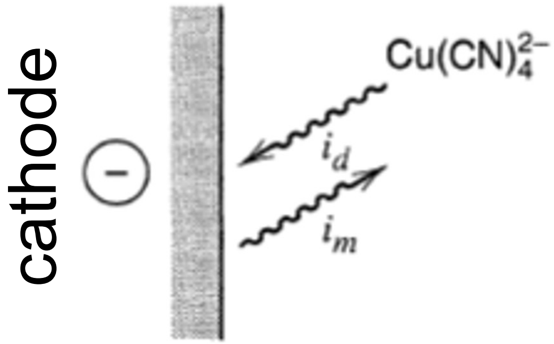
$j = j_d + |j_m|$

Migrational component is same direction as j_d for

- Cations reacting at cathode
- Anions reacting at anode

Negatively charged reactant

$Cu(CN)_4^{2-} + 2e \rightarrow Cu + 4CN^-$



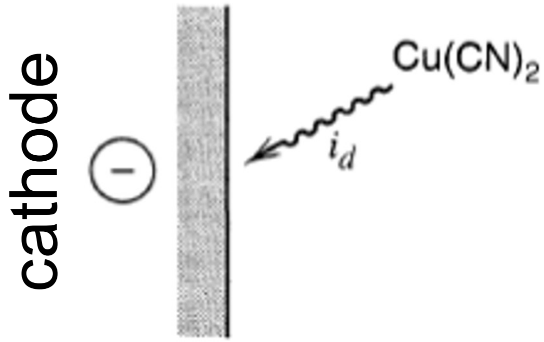
$j = j_d - |j_m|$

Migrational component is different direction from j_d for

- Cations oxidized at anodes
- Anions reduced at cathodes

Uncharged reactant

$Cu(CN)_2 + 2e \rightarrow Cu + 2CN^-$



$j = j_d$

Sign Convention for Diffusion and Migration Currents (see previous slide)

Diffusion current (j_d)

- \+ Oxidized species diffuses to cathode (increases cathodic current at more negative potential)
- \+ Reduced species diffuses to anode (increases anodic current at more positive potential)

Migration current (j_m)

- \+ Cation migrates to cathode (increases cathodic current at more negative potential)
- \+ Anion migrates to anode (increases migration anodic current at more positive potential)
- \- Anion diffuses to cathode (decreases cathodic current at more negative potential)
- \- Cation diffuses to anode (decreases anodic current at more positive potential)

Diffusion-limited case

Consider the reduction reaction

$$O + ze^- \longrightarrow R$$

when the reduction of O begins, $[O]_S << [O]^*$

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \Phi(x)}{\partial x} + C_i v(x)$$

diffusion

assume there is an excess of supporting electrolyte

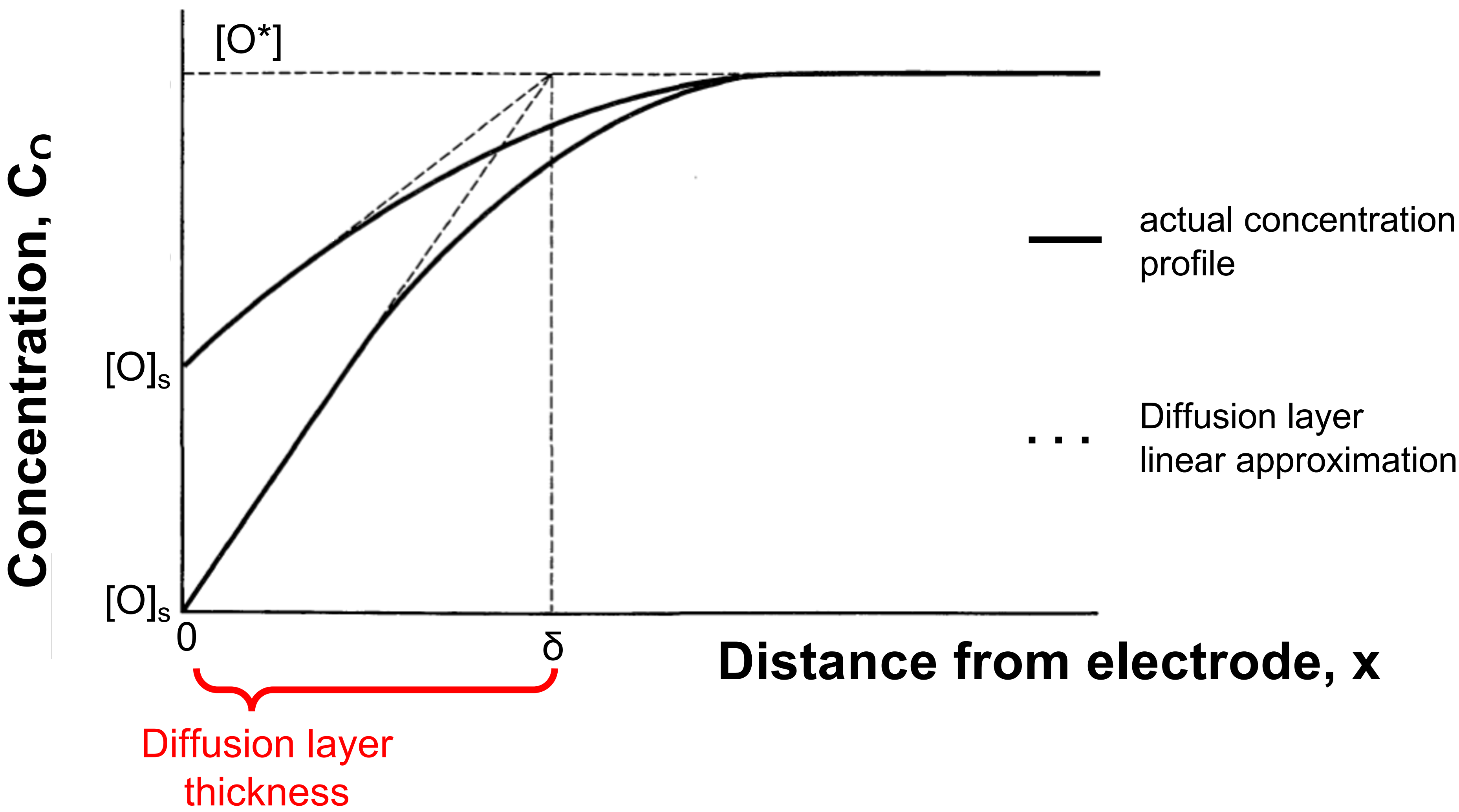
assume stirring is ineffective at the electrode surface

Rate of mass-transfer (v_{mt}) is proportional to the concentration gradient

$$v_{mt} \propto D_O \left.\frac{\partial C_O(x)}{\partial x}\right|_{x=0} \xrightarrow{\text{assuming linear variation}} D_O \frac{[O]^* - [O]_S}{\delta}$$

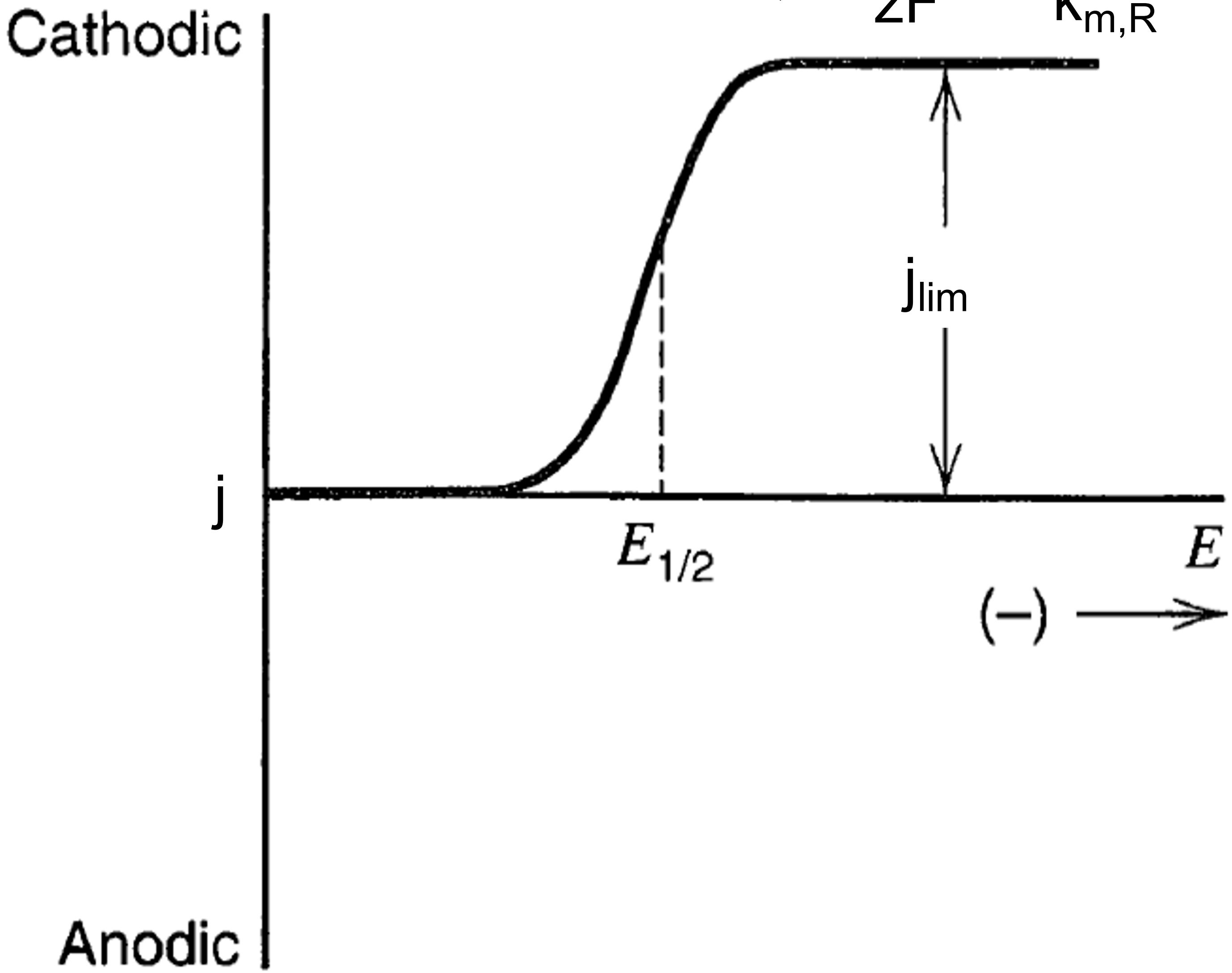
(at the surface)

Diffusion-limited case



Linear diffusion approximation: 1) R initially absent

$$E_{1/2} = E°_{cell,T} - \frac{RT}{zF} \ln \frac{k_{m,O}}{k_{m,R}}$$



Linear diffusion approximation: 1) R initially absent

If the kinetics are fast, the concentrations of O and R at the electrode surface can be assumed to be at equilibrium:

Nernst Equation

substitution

$$E_{cell} = E^\circ_{cell,T} - \frac{RT}{zF}\ln\frac{[R]_S}{[O]_S} = E^\circ_{cell,T} - \frac{RT}{zF}\ln\left(\frac{-j}{k_{m,R}\cdot z\cdot F}\cdot\frac{k_{m,O}\cdot z\cdot F}{j - j_{lim,c}}\right)$$

$$E_{cell} = E^\circ_{cell,T} - \frac{RT}{zF}\ln\frac{k_{m,O}}{k_{m,R}} + \frac{RT}{zF}\ln\frac{j - j_{lim,c}}{-j}$$

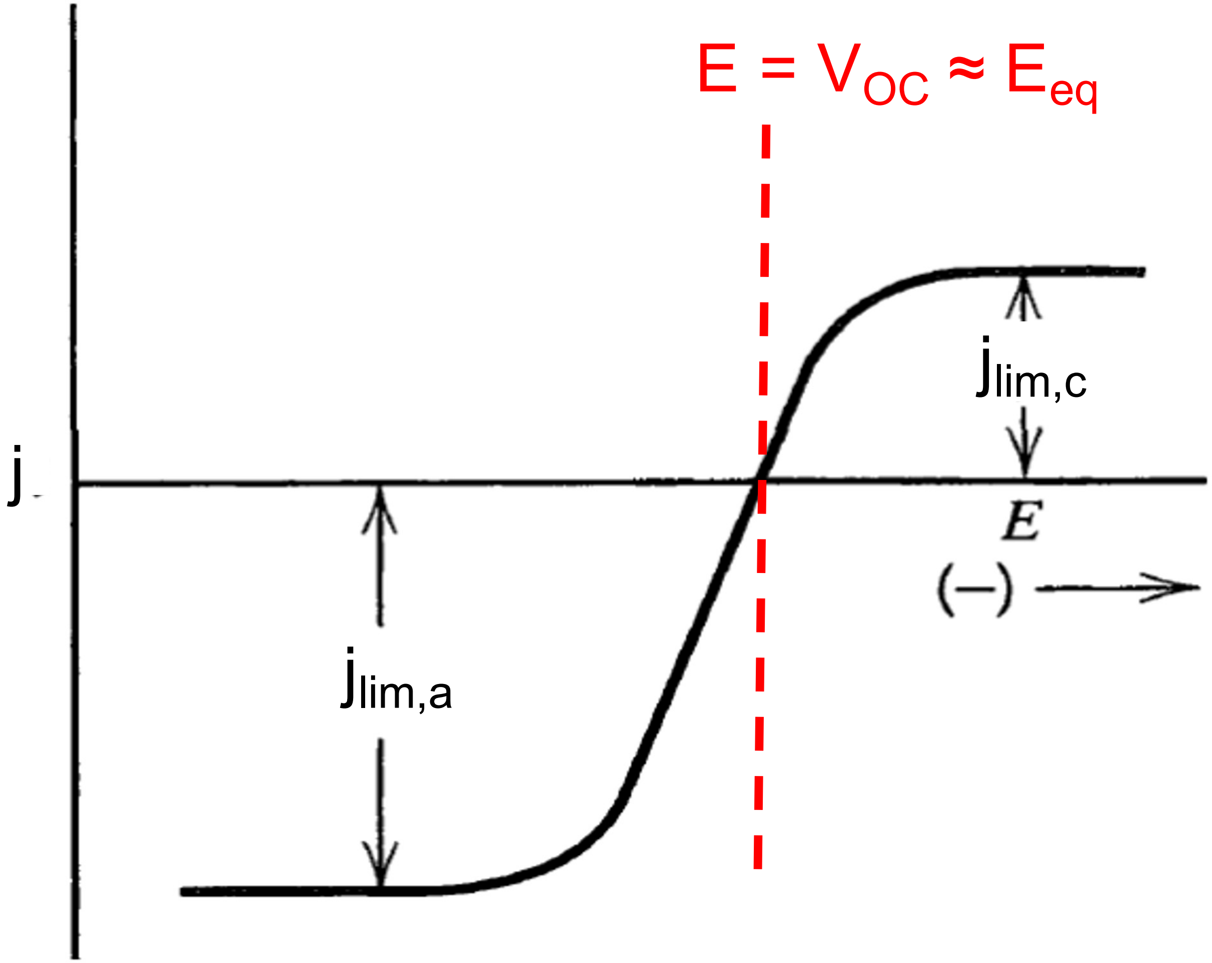
when $j = j_{lim,c}/2$ **$E_{1/2}$ is a characteristic of the system**

$$E_{1/2} = E^\circ_{cell,T} - \frac{RT}{zF}\ln\frac{k_{m,O}}{k_{m,R}}$$

$$\Rightarrow \quad E_{cell} = E_{1/2} + \frac{RT}{zF}\ln\frac{j - j_{lim,c}}{-j}$$

Linear diffusion approximation: 2) O and R initially present

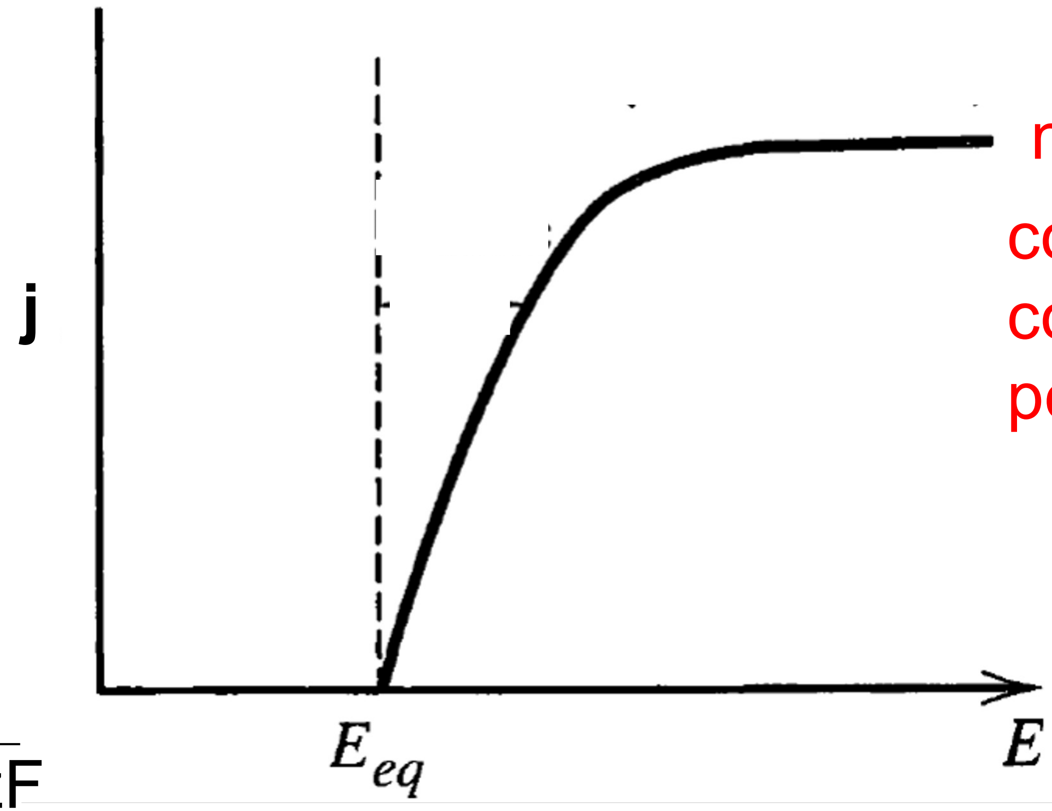
When $j = 0$, $E = E_{eq}$ and the system is at equilibrium. When current flows, the potential deviates from E_{eq}, and the extent of this deviation is the concentration overpotential.



Linear diffusion approximation: 3) R is insoluble

$$E_{cell} = E^\circ_{cell,T} + \frac{RT}{zF}\ln[O^*] + \frac{RT}{zF}\ln\frac{j_{lim,c} - j}{j_{lim,c}}$$

η_{conc}



$\eta_{conc} \rightarrow \infty$

complete concentration polarization

Recall Chapter 4A (slide 28+)

mass transfer resistance

$$R_{mt,c} = \frac{RT}{|j_{lim,c}|zF}$$

Summary: linear diffusion approximation

O and R initially present:

$$E_{cell} = E^{\circ}_{cell,T} - \frac{RT}{zF} \ln \frac{k_{m,O}}{k_{m,R}} + \frac{RT}{zF} \ln \frac{j - j_{lim,c}}{j_{lim,a} - j}$$

R initially absent: ($j_{lim,a} = 0$)

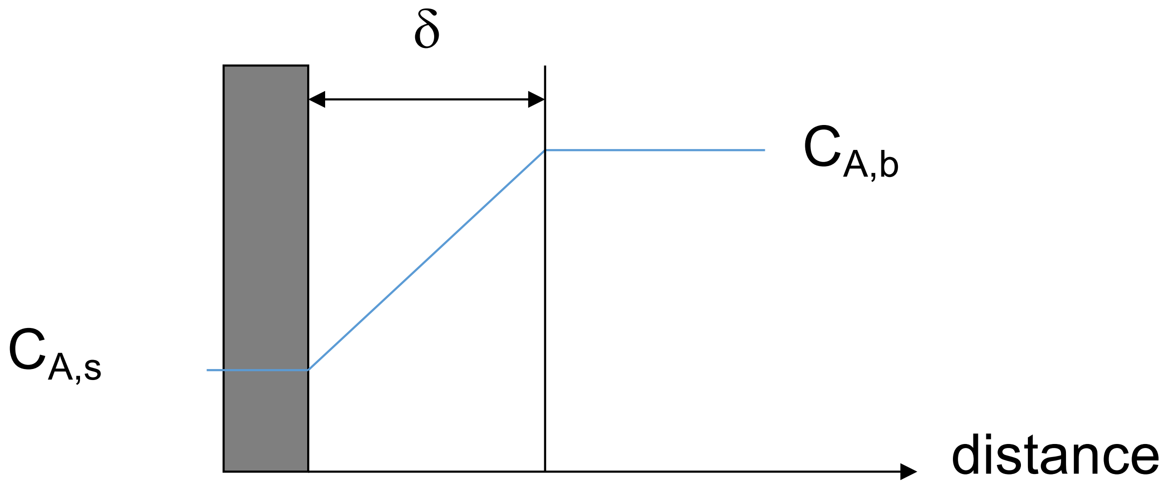
$$E_{cell} = E^{\circ}_{cell,T} - \frac{RT}{zF} \ln \frac{k_{m,O}}{k_{m,R}} + \frac{RT}{zF} \ln \frac{j - j_{lim,c}}{-j}$$

O initially absent: ($j_{lim,c} = 0$)

$$E_{cell} = E^{\circ}_{cell,T} - \frac{RT}{zF} \ln \frac{k_{m,O}}{k_{m,R}} + \frac{RT}{zF} \ln \frac{j}{j_{lim,a} - j}$$

Recall: k_{mO}, $k_{m,R}$ α $\delta(t)^{-1}$, so they are actually **functions of time**

Flux N_A of species A normal to the electrode surface



$$N_A = -D_A \frac{C_{A,b} - C_{A,s}}{\delta} \qquad (mol/m^2\ s)$$

D_A : coefficient of diffusion (m^2/s)

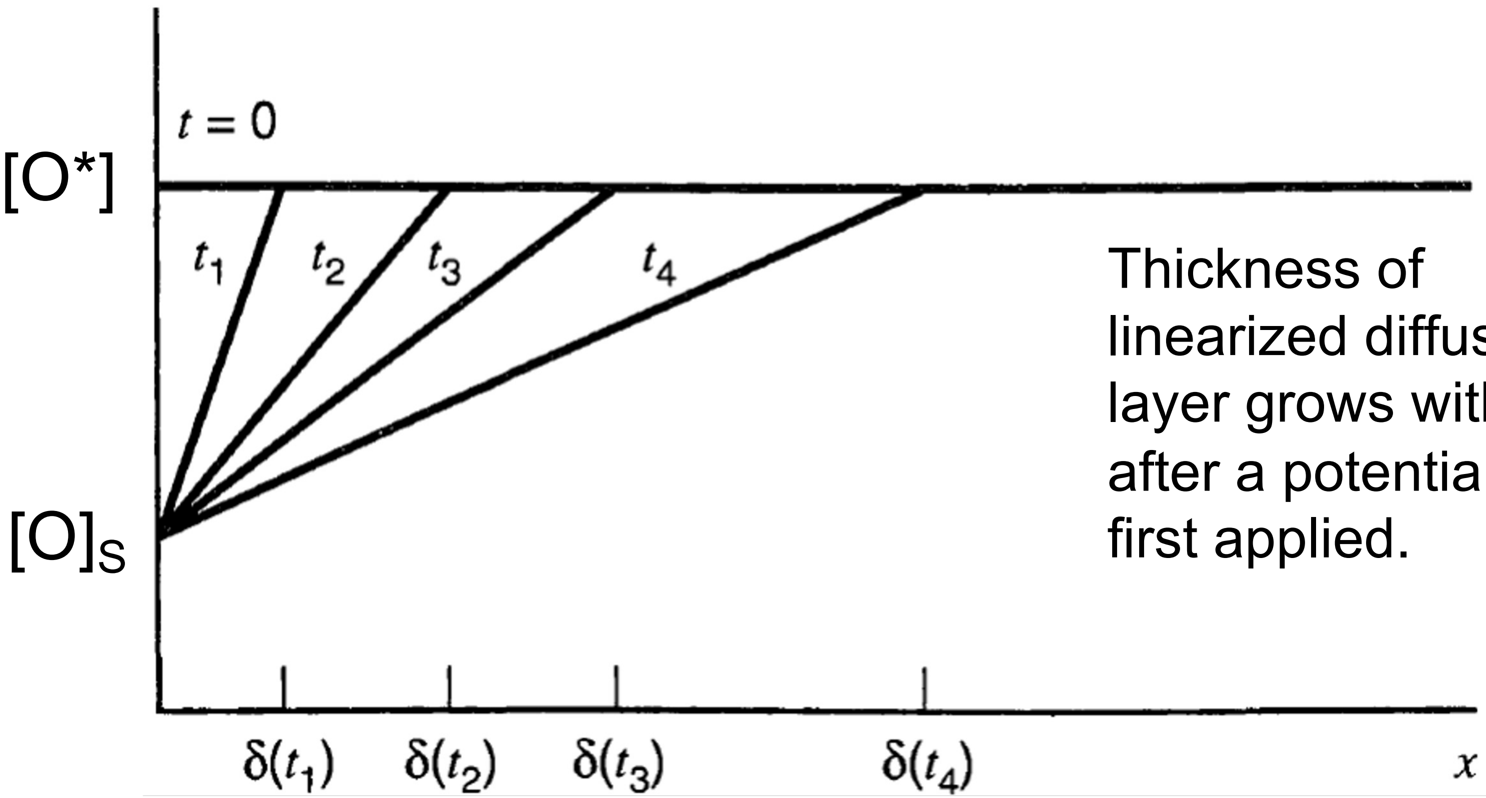
δ : thickness of Nernst diffusion layer (m)

$i_{lim} = +/- z F D_A c_{A,b} / \delta$

Linear diffusion approximation: transient response

Now consider the diffusion layer thickness to be a time-dependent response:

mol/m²·s rate of mass transfer (v_{mt}) = rate of reaction (v_{rxn}) = $\frac{j}{zF}$ = $\frac{D([O]^* - [O]_S)}{\delta(t)}$



Thickness of linearized diffusion layer grows with time after a potential E is first applied.

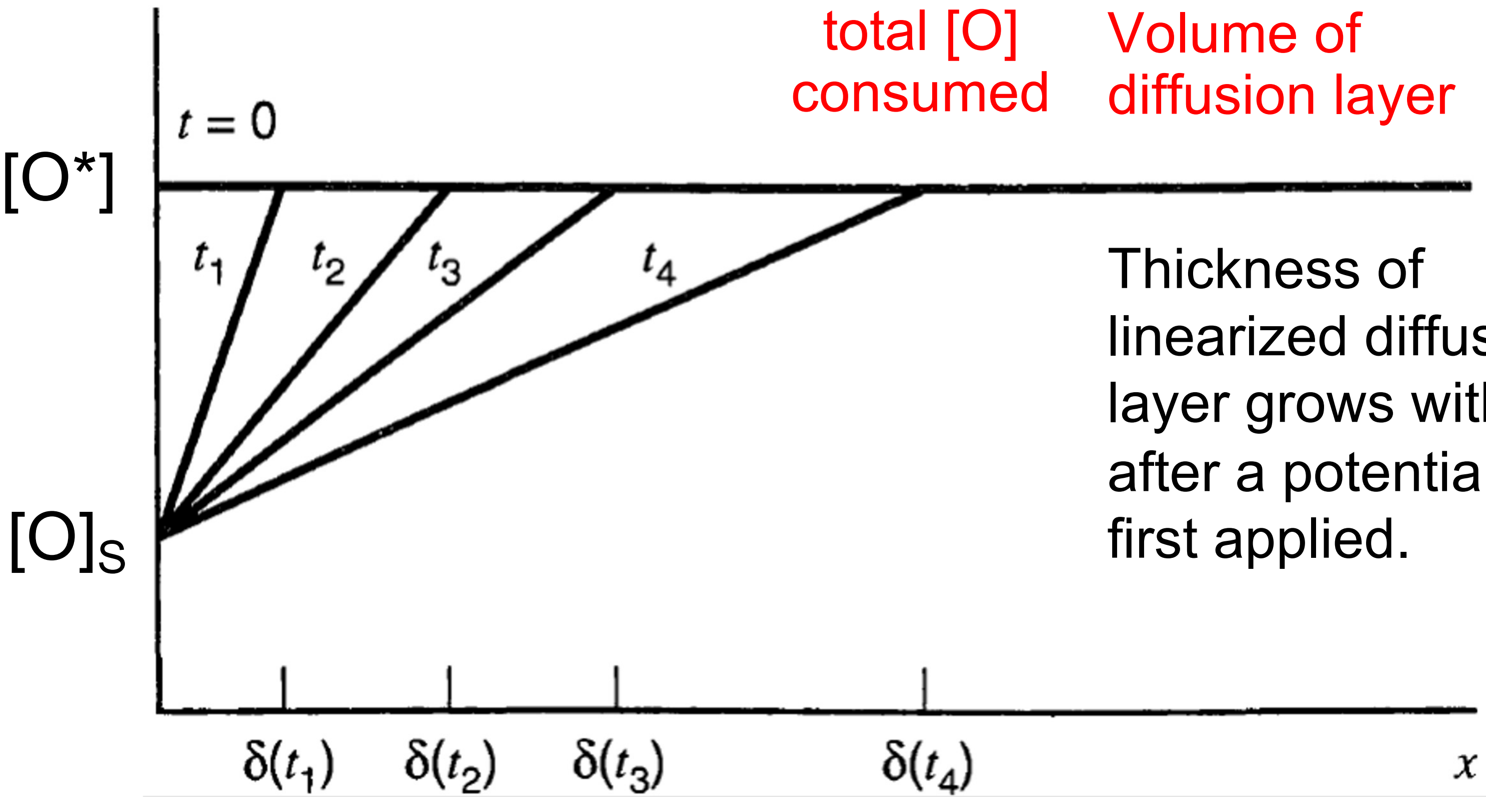
Linear diffusion approximation: transient response

The current flow causes a depletion of O, where the amount of O reacted is given by

$$\text{Moles of O reacted in diffusion layer} = \left([O]^* - [O]_S\right)\frac{A\cdot\delta(t)}{2} = \int_0^t \frac{i}{zF}\,dt$$

total [O] consumed

Volume of diffusion layer



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$$\text{Moles of O reacted in diffusion layer} = ([O]^* - [O]_S)\frac{A\cdot\delta(t)}{2} = \int_0^t \frac{i}{zF}\,dt$$

$$\cancel{([O]^* - [O]_S)}\frac{\cancel{A}}{2}\frac{d\delta(t)}{dt} = \frac{i}{zF} = \frac{D_O}{\delta(t)}\cancel{A}\cdot\cancel{([O^*]-[O]_S)}$$

Recall: Chapter 4A (linearization of Fick's Law)

$$j = k_{m,O}([O^*]-[O]_S)\cdot z\cdot F$$

$$\frac{d\delta(t)}{dt} = \frac{2D_O}{\delta(t)}$$

Since $\delta(t) = 0$ at $t = 0$,

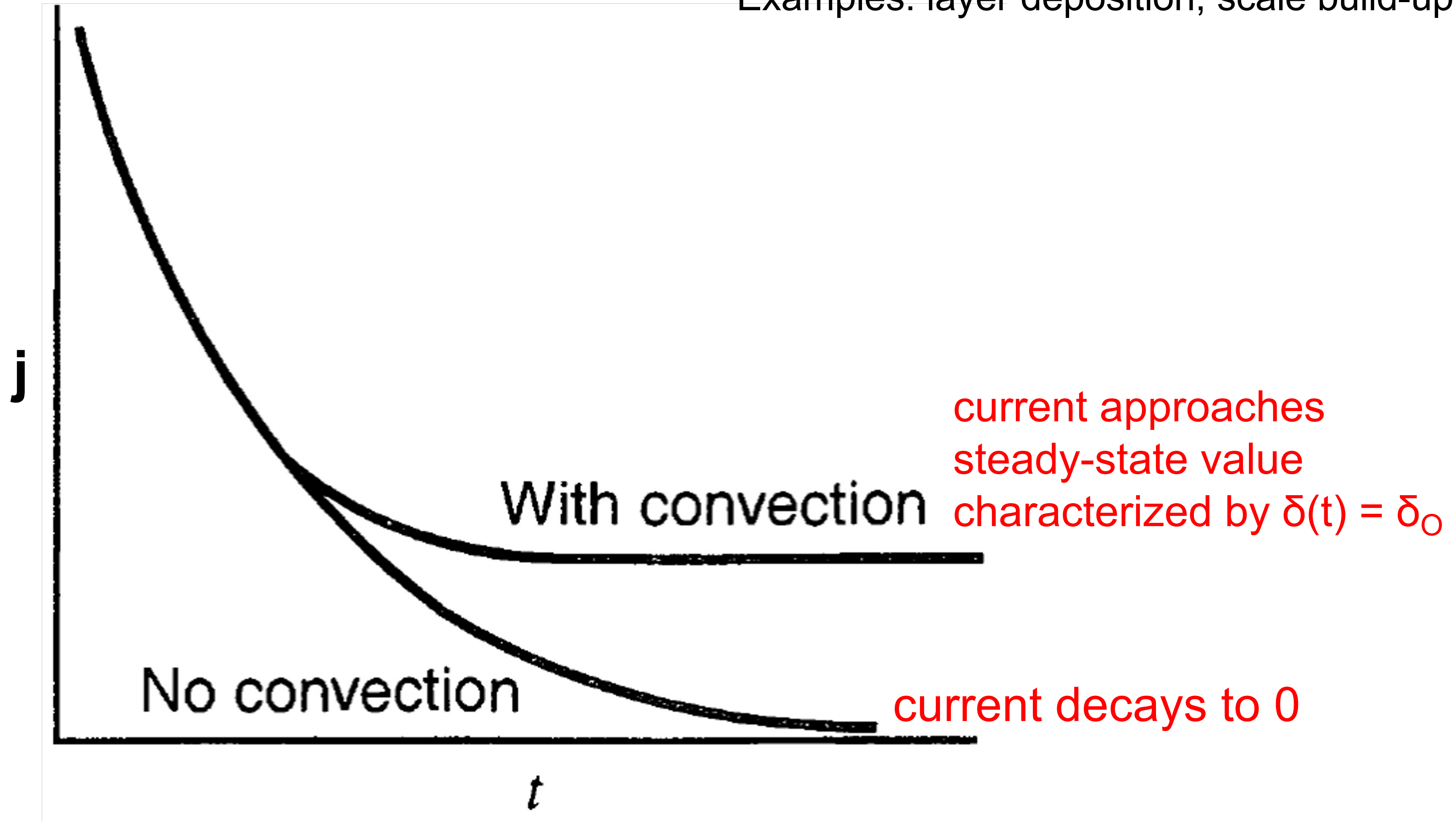
$$\delta(t) = 2(D_O t)^{0.5}$$

$$\frac{j}{zF} = \frac{D_O^{0.5}}{2t^{0.5}}([O^*]-[O]_S)$$

Linear diffusion approximation: transient response

- δ(t) increases with $t^{0.5}$
- j decays with $t^{-0.5}$

Examples: layer deposition, scale build-up,…



Diffusion-limited case: rigorous approach

Semi-empirical approach used thus far

<u>Assumptions</u>

- Nernstian behavior
- $j = k_{m,O}([O]_S-[O^*])\cdot z \cdot F$
- $j = k_{m,R}([R^*]-[R]_S)\cdot z \cdot F$

Simple math →

i-E Curve

Can we justify these assumptions?

Diffusion-limited case

Fick's First Law

$$J_i(x) = - D_i \frac{\partial C_i(x)}{\partial x}$$

Fick's Second Law

$$\frac{\partial C_i(x,t)}{\partial t} = D_i \frac{\partial^2 C_i(x,t)}{\partial x^2}$$

More generally,

Fick's First Law

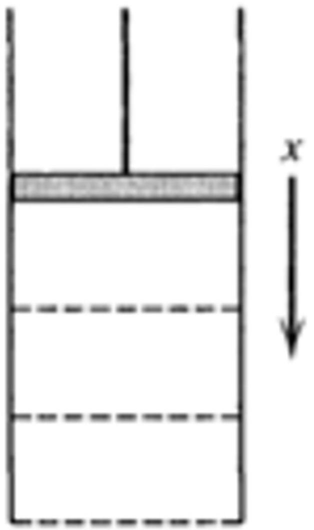
$$J_i = - D_i \nabla C_i$$

Fick's Second Law

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i$$

Linear diffusion-limited case

Consider the first case where we apply a step potential to go from a non-faradaic process to a mass-transport limited process



$$O + ze^- \longrightarrow R$$

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2}$$

1. Initial conditions (t = 0) → $C_O(x,0) = [O^*]$
2. Conditions at far distances (x >> 0) → $\lim_{x \to \infty} C_O(x,t) = [O^*]$
3. Conditions at the surface (x = 0) → $C_O(0,t) = 0 \quad (t > 0)$

Diffusion-limited case: rigorous approach

Semi-empirical approach used thus far

Assumptions

- Nernstian behavior
- Linear profile
- $j = k_{m,O}([O]_S - [O^*]) \cdot z \cdot F$
- $j = k_{m,R}([R^*] - [R]_S) \cdot z \cdot F$

Simple math →

$$\frac{j}{zF} = \frac{D_O^{0.5}}{2t^{0.5}}([O^*] - [O]_S)$$

Assumptions

- Nernstian behavior
- Diffusion equations
- Boundary conditions

More complex math →

$$j = \left[\frac{D_O}{\pi \cdot t}\right]^{0.5}([O^*] - [O]_S) \cdot z \cdot F$$

Current density for non-steady state concentration profiles

Case of the cathodic reduction of a species at the electrode:

$$i_c = -nF \left.\frac{dc}{dx}\right|_{x=0}$$

mass transport controlled kinetics, Fick's 1st Law
(current is proportional to the **concentration gradient**)

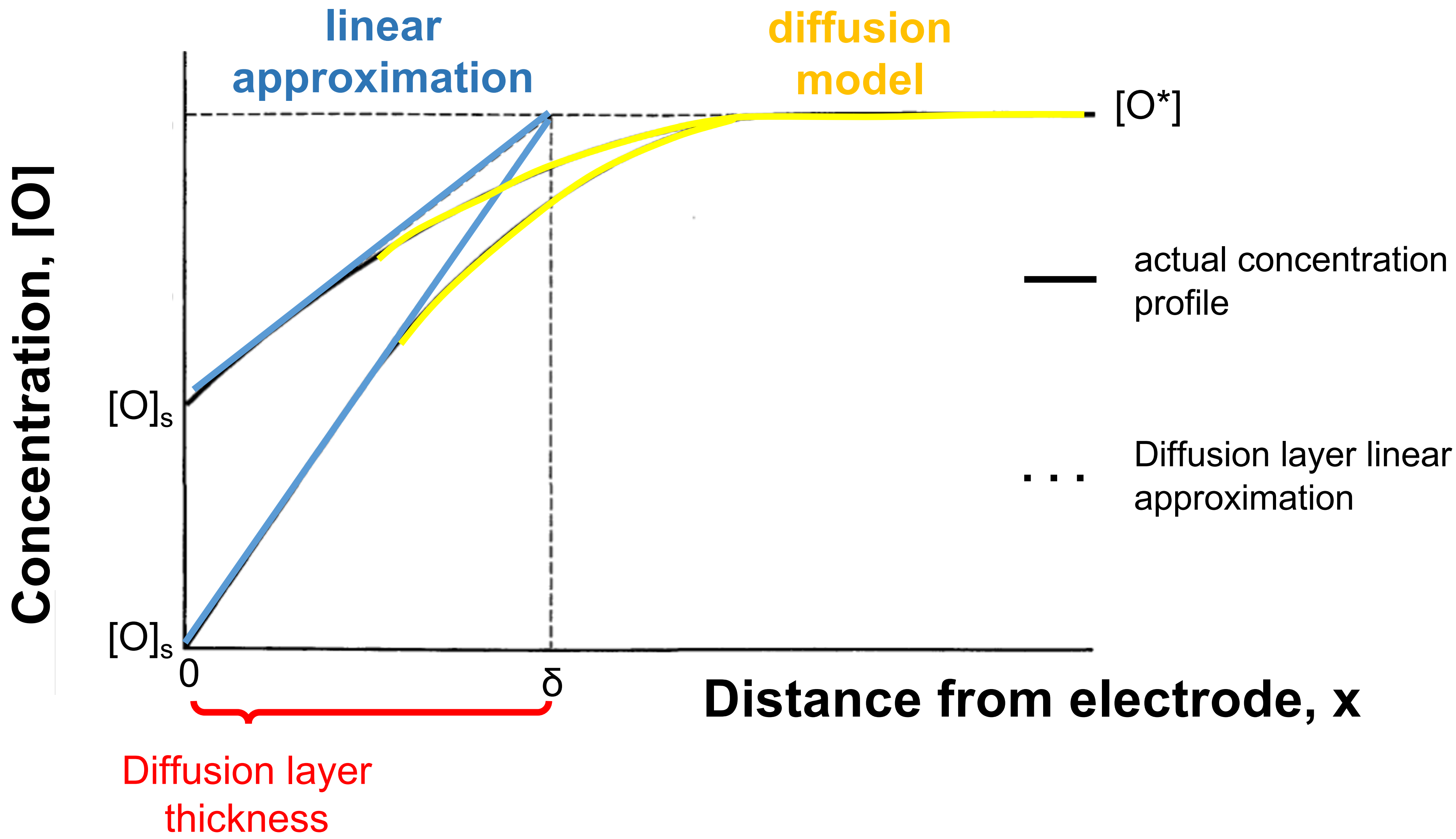
$$\left.\frac{dc}{dt}\right|_x = D\frac{d^2c}{dx^2}$$

concentration evolution with time, Fick's 2nd Law
(conc. change with t, at position x, changes with the **current gradient** di/dx at that position)

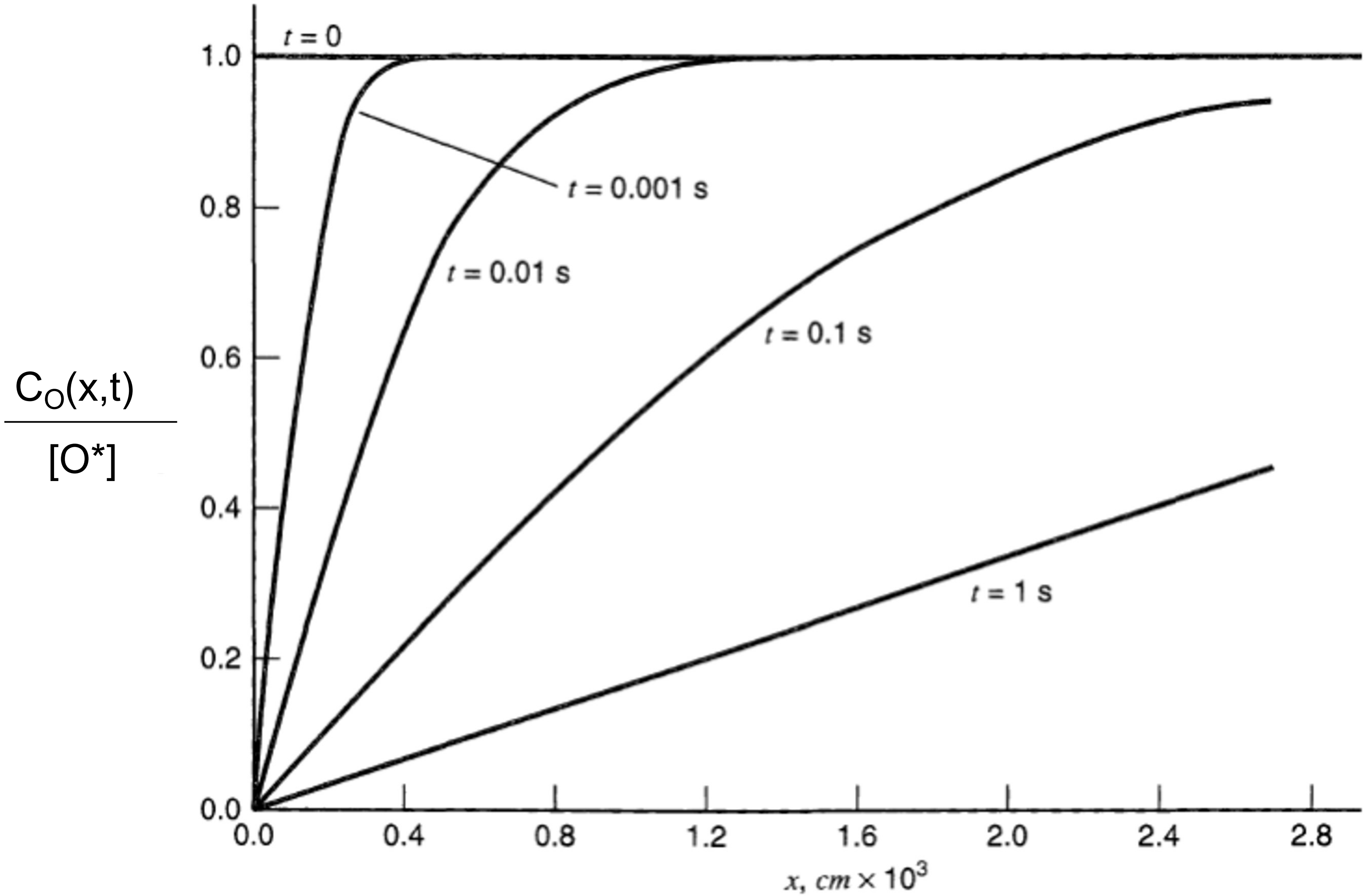
Solving the above equation system yields the **Cottrell equation**:
$\mathbf{i_c = - n F (c_b - c_s) (D/(\pi t))^{0.5}}$

in practice : plot i vs $1/\sqrt{t}$; (see chapter 5 'Experimental techniques')
when the result is linear, the reaction is diffusion-controlled, and from the slope a diffusion coefficient D can be extracted

Diffusion-limited case



Potential Step methods under diffusion control: planar diffusion



Modes of Mass Transfer

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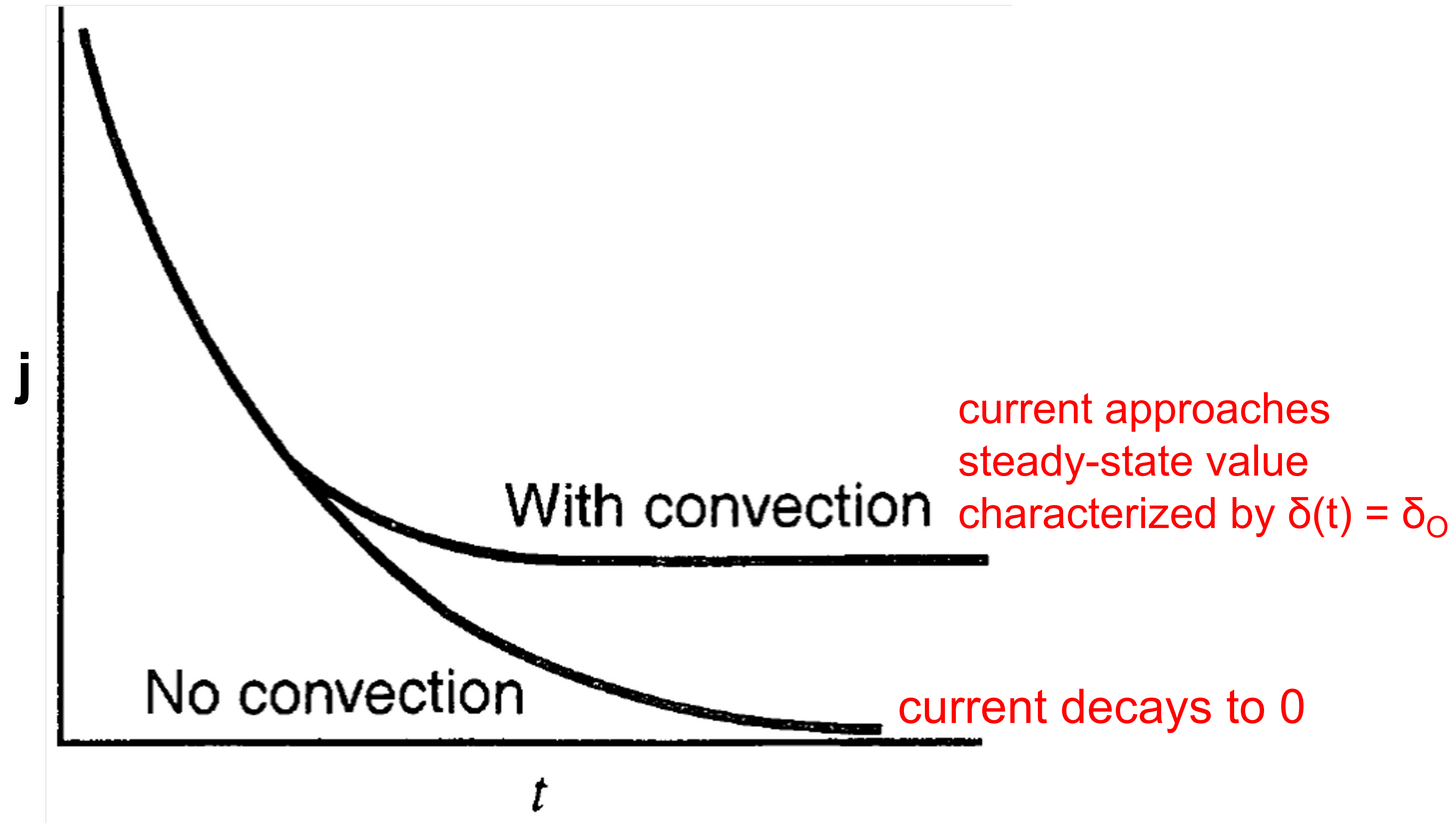
Migration : Movement of a charged body under the influence of an electric field (a gradient of electrical potential).

Convection : Stirring or hydrodynamic transport (may be characterized by stagnant regions, laminar flow, or turbulent flow).

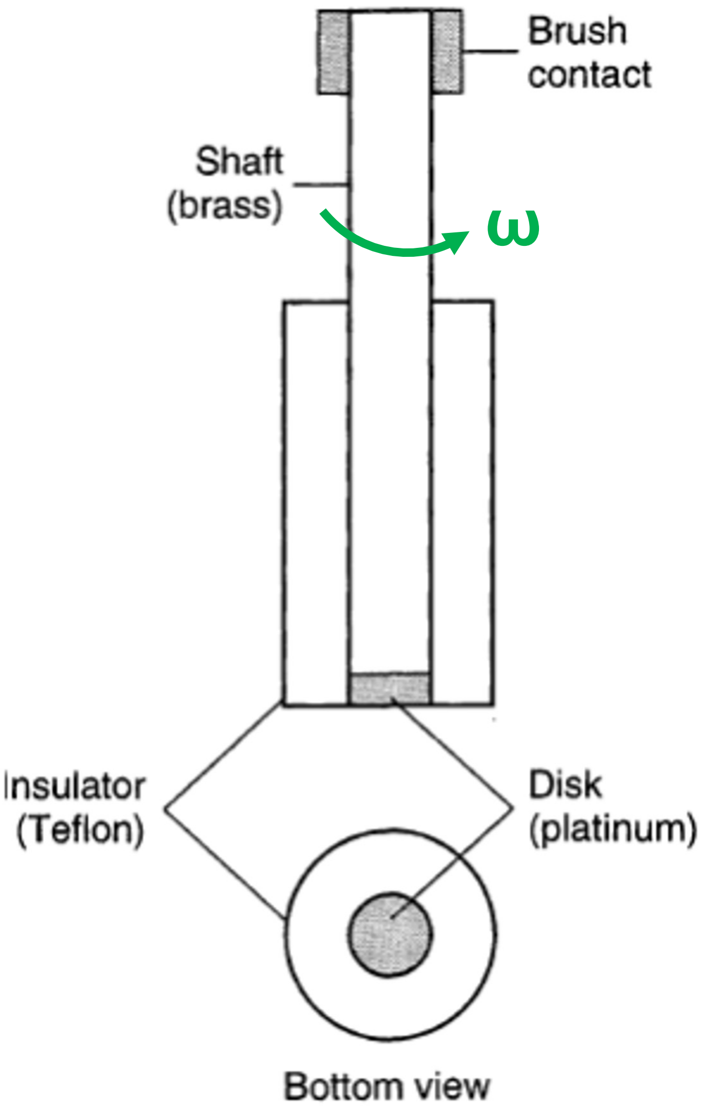
→ Rotating disc electrode (RDE)

Linear diffusion approximation: transient response

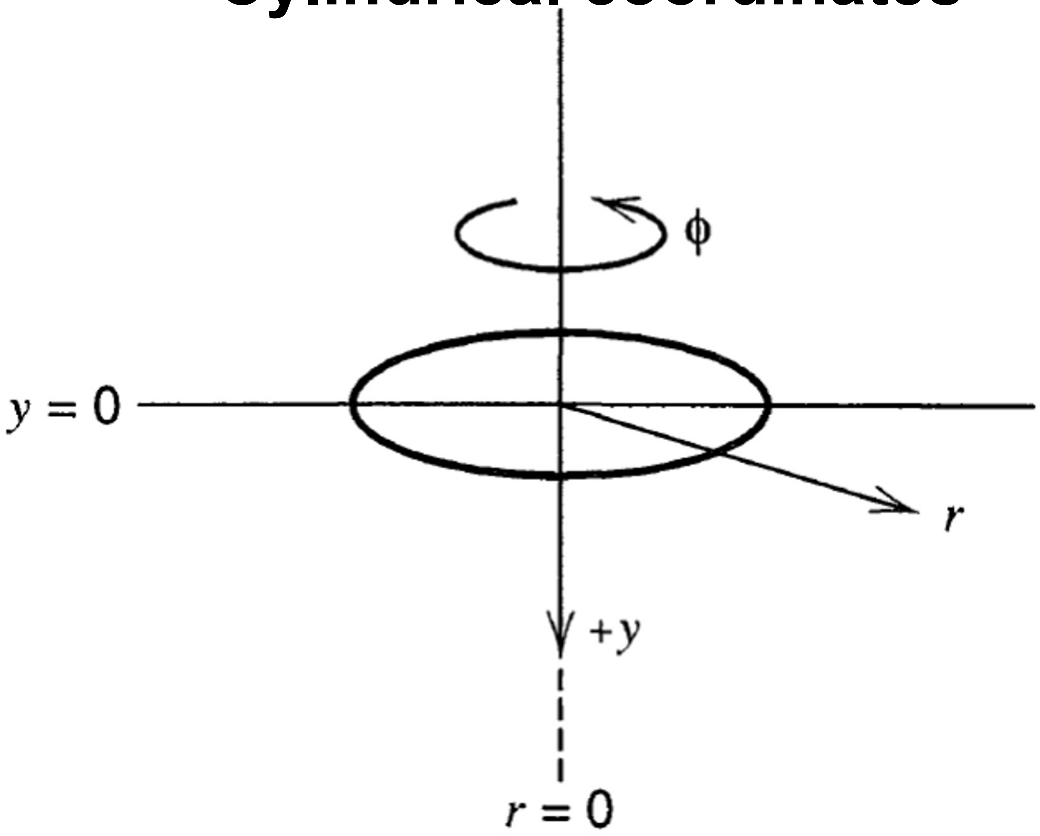
- $\delta(t)$ increases with $t^{0.5}$
- j decays with $t^{-0.5}$



Rotating Disk Electrode (RDE)



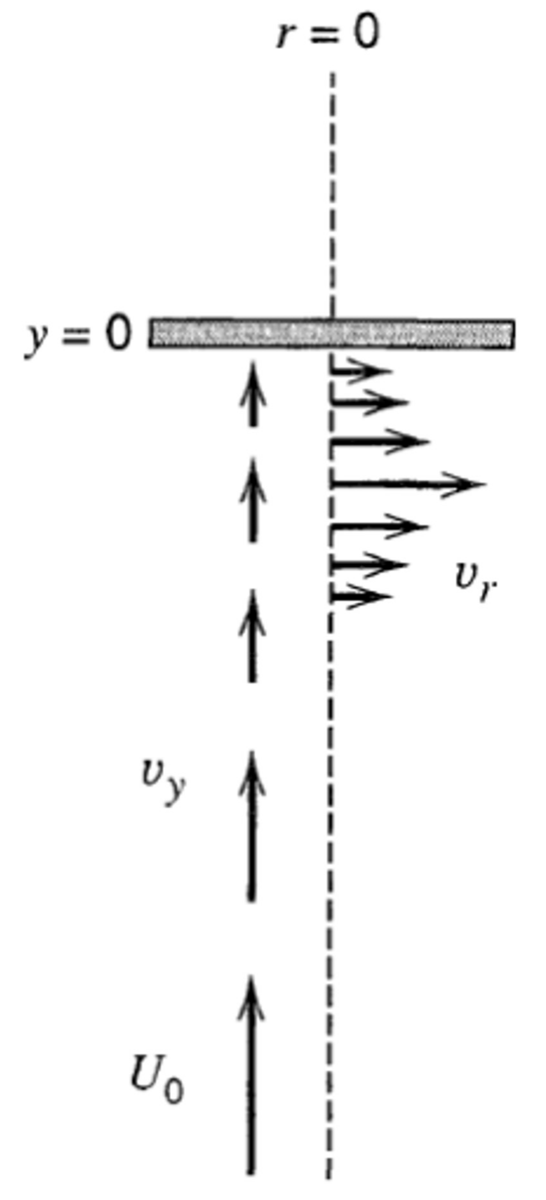
Cylindrical coordinates

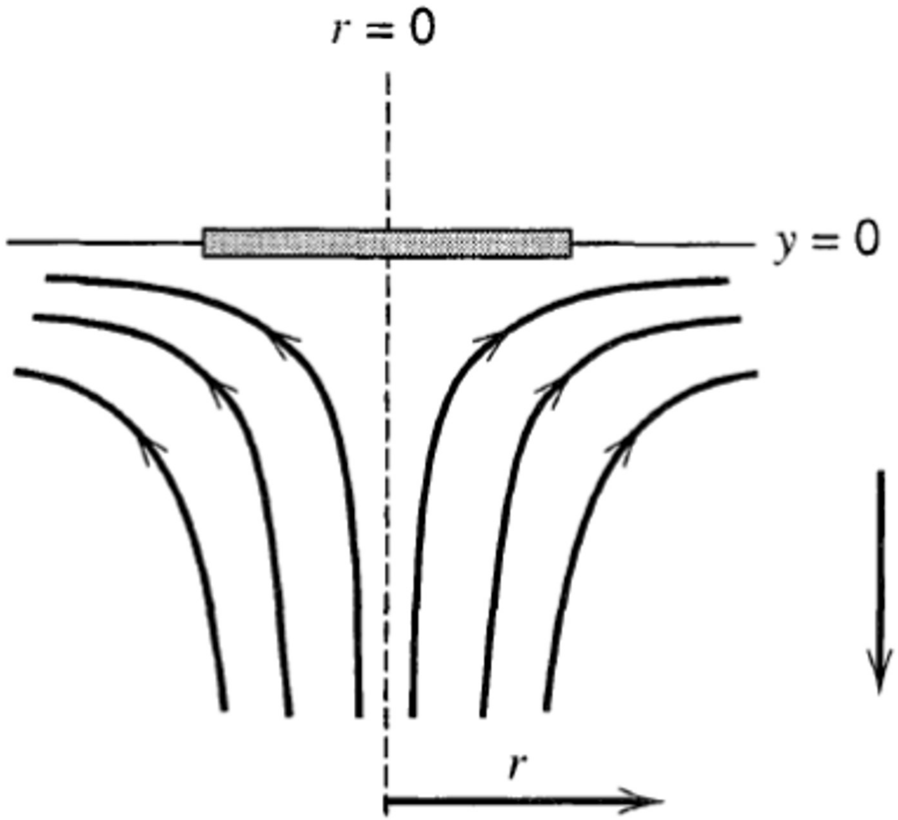


ω = angular velocity (s^{-1})

= 2πN — **rotation frequency [revolutions/s]**

Solving for RDE velocity profile



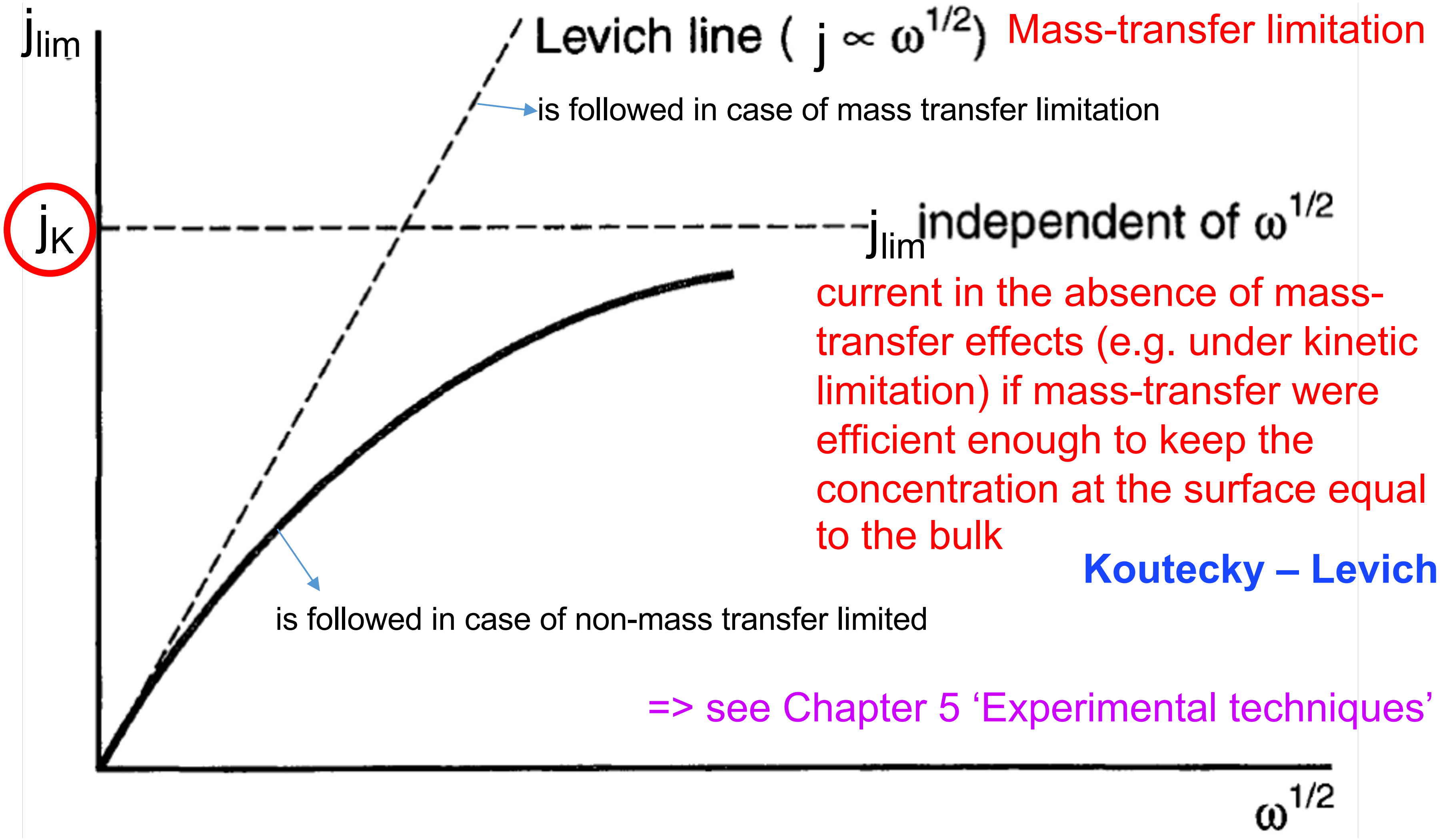


Rotating Disk Electrode (RDE)

$$j_{lim,c} = 0.62\, zFD_O^{2/3}\omega^{1/2}\nu^{-1/6}[O^*]$$

Levich Equation

(ν = viscosity)



=> see Chapter 5 ‘Experimental techniques’