Lesson 4: Mass Transfer

Electrochemical Methods and Applications

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Revised and narrated by Tyler Williams

Mass Transfer in Electrochemistry

- **Diffusion** – Movement of a species as a result of a concentration gradient
- **Migration** – Movement of a charged body under an electric field
- **Convection** – Movement of a species due to bulk fluid flow from natural (thermal or density gradients) or forced convection (stirring or pumping)

$$J_i(x) = -D_i \frac{dC_i(x)}{dx} - \frac{z_i F}{RT} D_i C_i \frac{d\varphi(x)}{dx} + C_i v(x)$$

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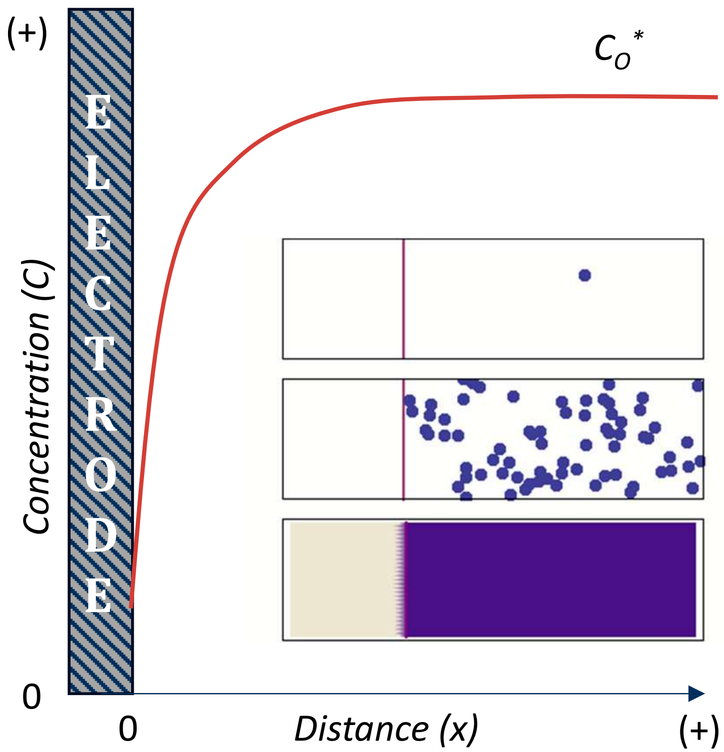
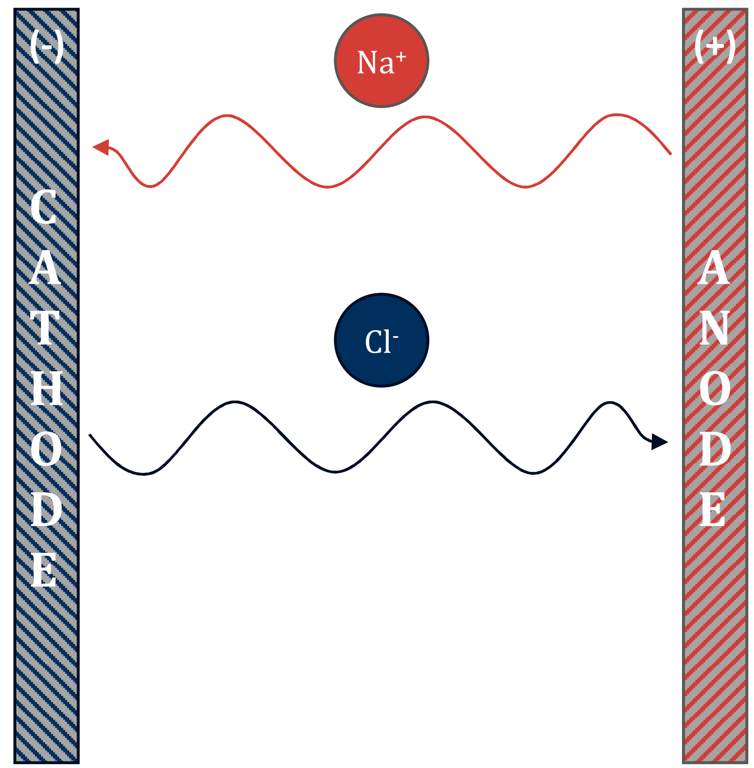
Visual Representations of Mass Transfer

Diffusion



Occurs near electrodes

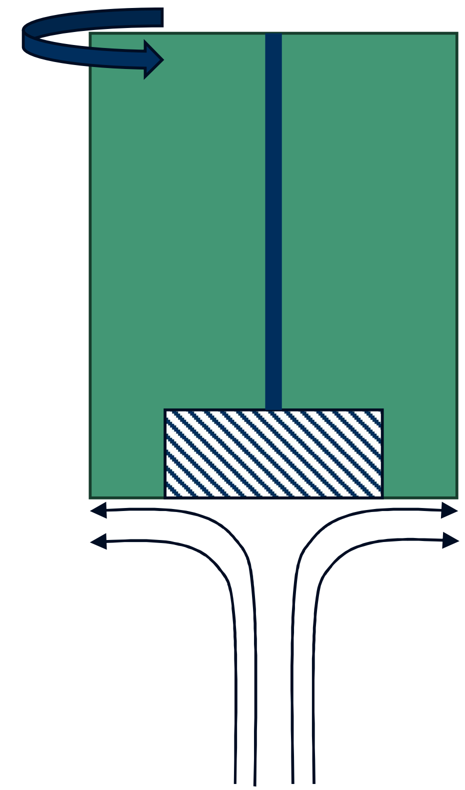
Migration



Occurs in bulk and near electrodes

Carries charge/current through bulk solution

Convection



Occurs in bulk solution

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Forces Driving Mass Transfer

- Diffusion and migration arise from a gradient in electrochemical potential:
  - $J_j(x) = -K\frac{\partial \bar{\mu}_j}{\partial x}$ (1-D)
  - $J_j = -K\nabla\bar{\mu}_j$ (3-D)

Recall:
$\bar{\mu}_j^\alpha = \mu_j^0 + RTln(a_j^\alpha) + z_j F \phi^\alpha$

- Convection arises from local imbalances of mechanical forces within the solution (e.g., stirring, density gradients)
  - $J_j(x) = -K\frac{\partial \bar{\mu}_j}{\partial x} + C_j \upsilon(x)$ (1-D)
  - $J_j = -K\nabla\bar{\mu}_j + C_j\mathbf{v}$ (3-D)

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Assumed Constants:
$\mu_j^0, T, \gamma_j, C_j^0$

Nernst-Plank Equation (Flux)

$$J_j(x) = -K\frac{\partial \bar{\mu}_j}{\partial x} + C_j \upsilon(x)$$

$$J_j(x) = -K\frac{\partial}{\partial x}\left\{\mu_j^o + RT ln\left(\frac{\gamma_j(x) C_j(x)}{C_j^o}\right) + z_j F\varphi(x)\right\} + C_j \upsilon(x)$$

$$J_j(x) = -K\left[\frac{RT}{C_j(x)}\frac{\partial C_j(x)}{\partial x} + z_j F\frac{\partial \varphi(x)}{\partial x}\right] + C_j \upsilon(x)$$

$$K = D_j C_j(x)/RT$$

$$J_j(x) = -D_j\frac{\partial C_j(x)}{\partial x} - z_j F\frac{D_j C_j(x)}{RT}\frac{\partial \varphi(x)}{\partial x} + C_j(x)\upsilon(x) \text{ (1-D)}$$

$$J_j(x) = -D_j \nabla C_j - z_j F\frac{D_j C_j}{RT}\nabla\varphi(x) + C_j \mathbf{v} \text{ (3-D)}$$

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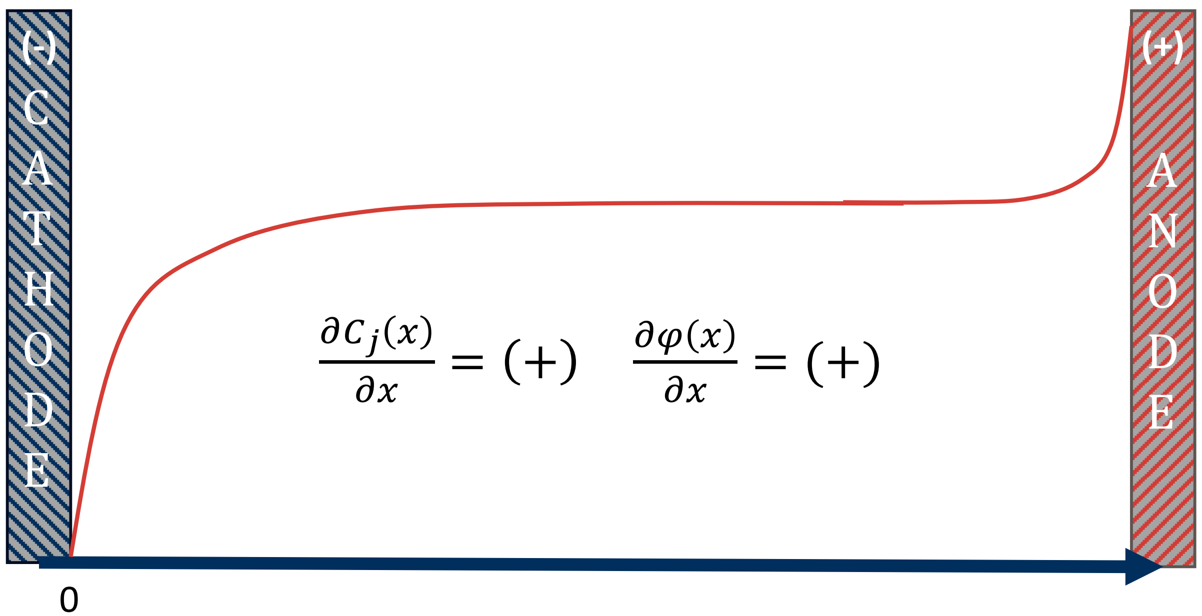
How Does the Flux relate to Current?

- Species Flux → Species Current
  - $I_j = \pm z_j F A J_j$
    - $J_j(x) = -D_j \frac{\partial C_j(x)}{\partial x} - z_j F \frac{D_j C_j(x)}{RT} \frac{\partial \varphi(x)}{\partial x} + C_j(x) \upsilon(x)$

NOTE: In determining the sign on z, careful attention needs to paid to the electrochemical convention being used and sign of the ion being reduced. Here, it is assumed that a positive ion is being reduced, and IUPAC convention is used.



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How Does the Flux relate to Current?

- Species Flux → Species Current
  - $I_j = \pm z_j F A J_j$
  - $I_j = I_{d,j} + I_{m,j} + I_{c,j}$
  - $I_j = -z_j F A D_j \dfrac{\partial C_j(x)}{\partial x} - z_j^2 F^2 A \dfrac{D_j C_j(x)}{RT} \dfrac{\partial \varphi(x)}{\partial x}$

NOTE: A stagnant solution is assumed and $I_{c,j} = 0$

- Total Flux → Total Current
  - $I = \sum I_j = -FA \sum z_j D_j \dfrac{\partial C_j(x)}{\partial x} - \dfrac{F^2 A}{RT} \dfrac{\partial \varphi(x)}{\partial x} \sum z_j^2 D_j C_j(x)$

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Questions

- What are the three forms of mass transport in electrochemical cells?

- Where do each of these forms dominate?

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Questions

- What are the three forms of mass transport in electrochemical cells?

Diffusion, Migration, and Convection

- Where do each of these forms dominate?

Diffusion layer (near electrode)

Bulk

DIFFUSION

Diffusion near Electrode Surface

- Near the electrode with supporting electrolyte (stagnant)
  - $I_j = I_{d,j} = -n_j F A D_j \frac{\partial C_j(x)}{\partial x}$
- What is diffusivity (D_j)?
  - $D = \frac{(\Delta x)^2}{2t} (=) \frac{cm^2}{s}$
  - Stokes-Einstein Equation
    - $D_j = \frac{kT}{6\pi \eta r_j} \approx \frac{\left(10^{-23}\frac{J}{K}\right)(10^2 K)}{(10)(10^{-3}\ Pa*s)(10^{-10} m)} \approx 10^{-9}\frac{m^2}{s}\left(\frac{10^2 cm}{m}\right)^2 \approx 10^{-5}\frac{cm^2}{s}$

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Fick's Laws

- First Law
  - $J_j(x,t) = -D_j \frac{\partial C_j(x,t)}{\partial x}$ (1-D)
  - $J_j(x) = -D_j \nabla C_j$ (3-D)
- Second Law
  - $\frac{\partial C_j(x,t)}{\partial t} = D_j \frac{\partial^2 C_j(x,t)}{\partial x^2}$ (1-D)
  - $\frac{\partial C_j}{\partial t} = D_j \nabla^2 C_j$ (3-D)

Conversion between Fick's Laws:

$$Accumulation = Generation + In - Out$$

$$Accumulation + (Out - In) = Generation$$

$$\frac{\partial C_j(x,t)}{\partial t} + \nabla J_j(x,t) = 0$$

$$\frac{\partial C_j(x,t)}{\partial t} = -\nabla J_j(x,t)$$

Electrode	**Variable**	∇^2
Planar	x	$\frac{\partial^2}{\partial x^2}$
Cylindrical	r	$\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}$
Spherical	r	$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)$

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Boundary and Initial Conditions

Boundary Conditions

- Semi-Infinite
  - $\lim_{x \to \infty} C_{Ox}(x,t) = C_{Ox}^*$
  - $\lim_{x \to \infty} C_{Red}(x,t) = C_{Red}^*$
- At Electrode Surface
  - $\frac{C_{Ox}(0,t)}{C_{Red}(0,t)} = e^{\frac{nF}{RT}\left(E - E_{Ox/Red}^{0'}\right)}$
  - $D_{Ox}\frac{\partial^2 C_{Ox}(0,t)}{\partial x^2} + D_{Red}\frac{\partial^2 C_{Red}(x,t)}{\partial x^2} = 0$

Initial Conditions

- Uniform Concentration
  - $C_{Ox}(x,0) = C_{Ox}^*$
  - $C_{Red}(x,0) = C_{Red}^*$

NOTE: These initial and boundary conditions assume a soluble reduced species. Different boundary conditions are needed for an insoluble reduced species.

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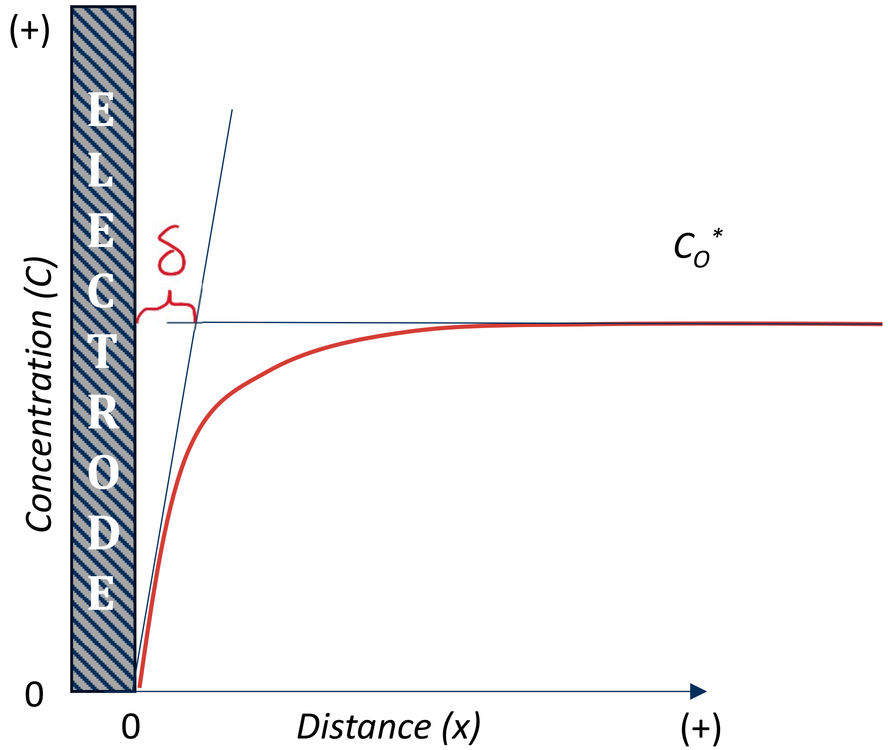
Limiting Current

- The mass-transfer limited current occurs when the surface concentration is practically zero
  - $I_L = nFh_{ox}A(C_{ox} - C^*_{ox})$
  - $I_L = nFh_{red}A(C^*_{red} - C_{red})$
  - $I = -nFAD_{Ox}\frac{\partial C_{Ox}(x,t)}{\partial x} = -nFAD_{Ox}\frac{\Delta C_{Ox}(x,t)}{\Delta x}$
    - $h_j = \frac{D_j}{\Delta x} = \frac{D_j}{\delta}$



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Questions

- For two electrodes with the same area, would you expect to have more current from diffusion with linear diffusion or radial diffusion?

- Why?

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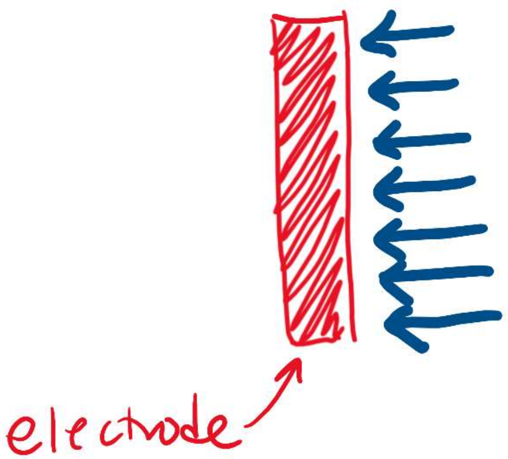
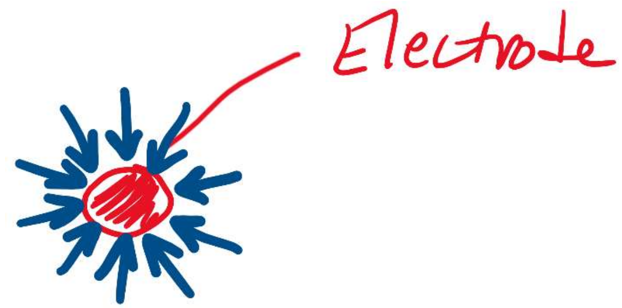
Questions

- For two electrodes with the same area, would you expect to have more current from diffusion with linear diffusion or radial diffusion?

Radial

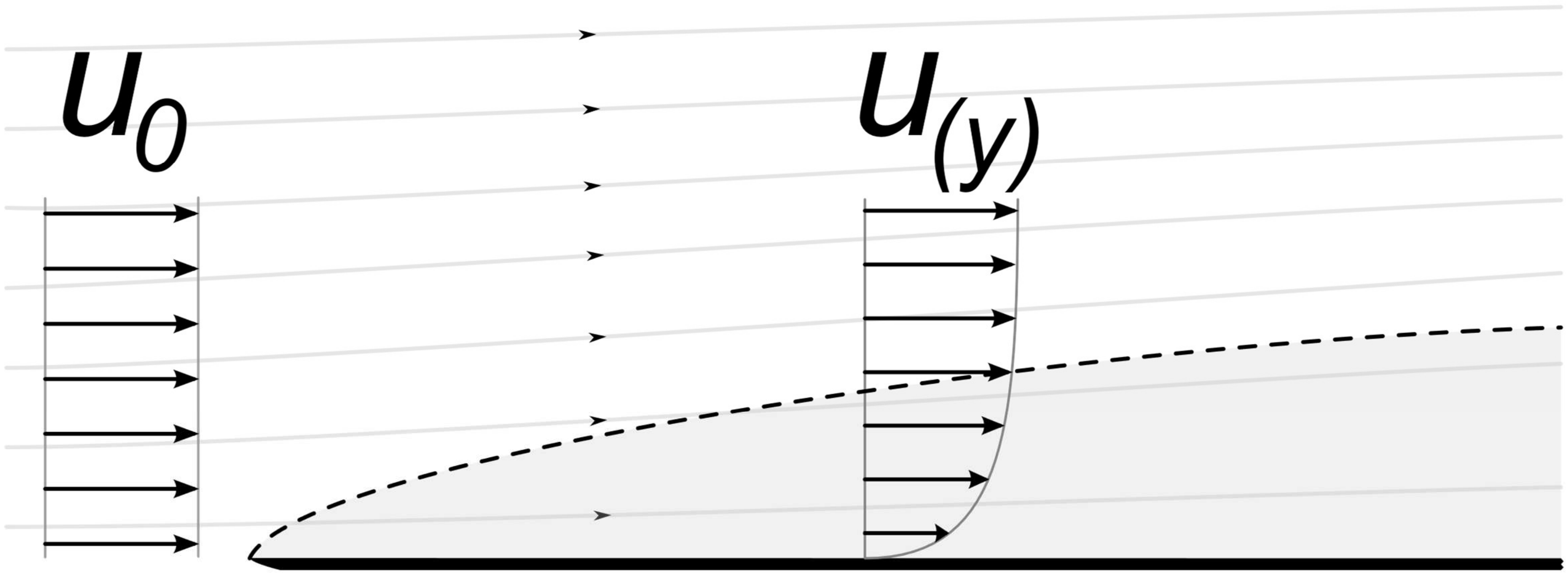
- Why?





Convection

Boundary Layers + the No-Slip Condition



https://commons.wikimedia.org/wiki/File:Laminar_boundary_layer_scheme.svg

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Rotating Electrodes

$$i_{l,c} = 0.62nFAD_{Ox}^{2/3}\omega^{1/2}\nu^{-1/6}C_{Ox}^{*}$$

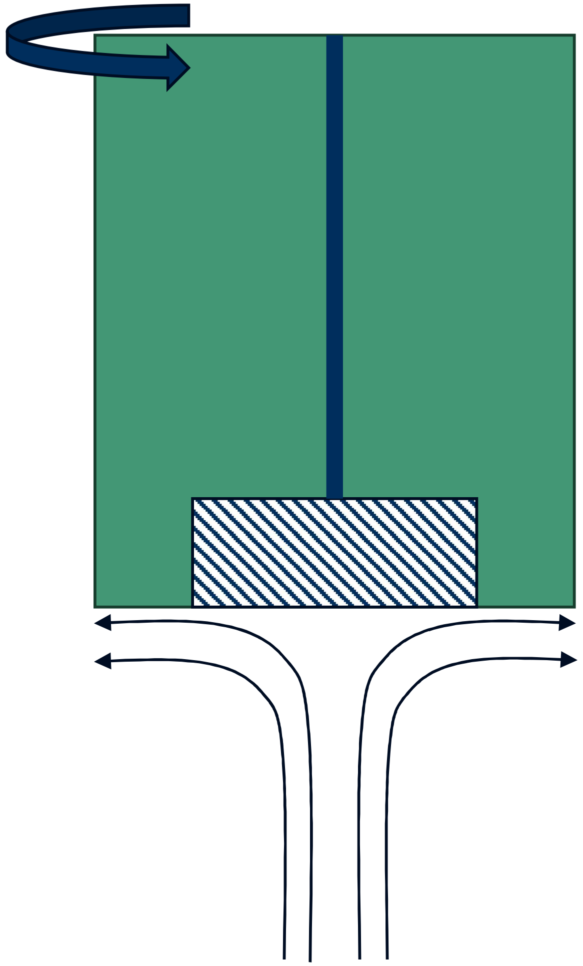
$$i_{l,c} = nFAh_{Ox}C_{Ox}^{*}$$

$$\downarrow$$

$$h_{Ox,rotating-disk} = \frac{D_{Ox}}{\delta_{Ox}} = 0.62D_{Ox}^{2/3}\omega^{1/2}\nu^{-1/6}$$

$$\downarrow$$

$$\delta_{Ox} = 1.61\,D_{Ox}^{1/3}\omega^{-1/2}\nu^{1/6}$$



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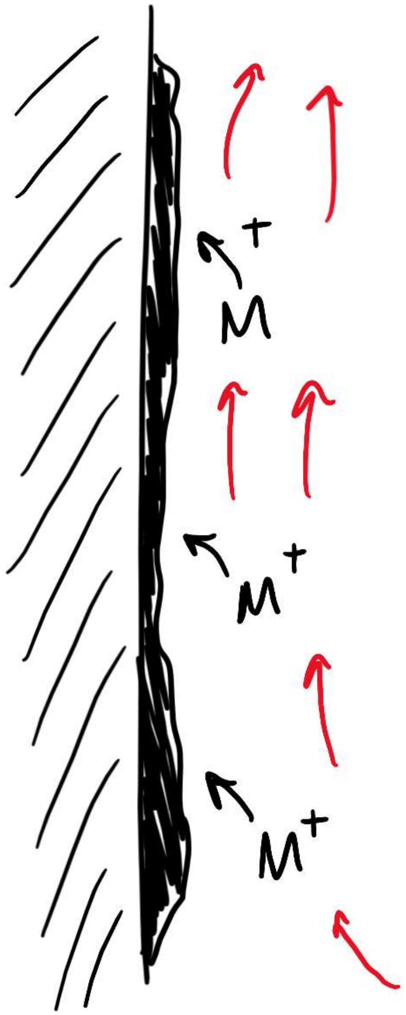
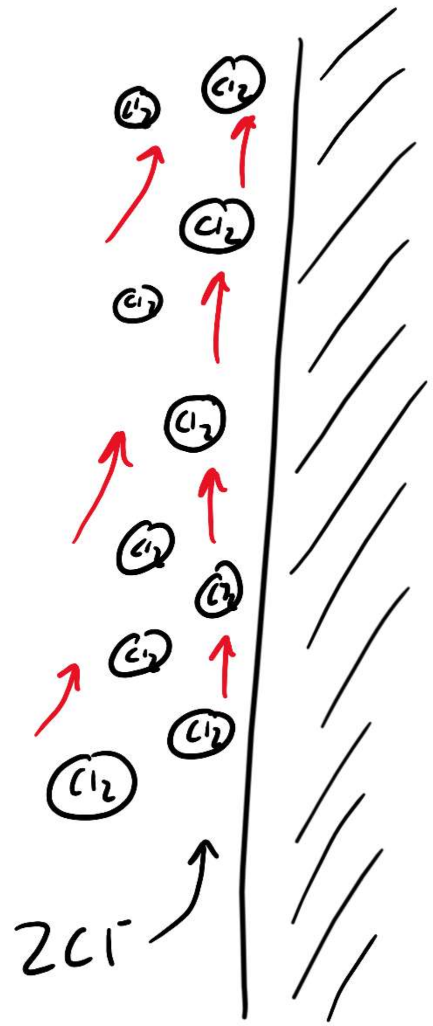
Bubble-Driven Flow and Its Inverse



DENSITY INDUCED



BUBBLE-DRIVEN

Bubble induced recirculatory flow in a tank

Jason Duguay
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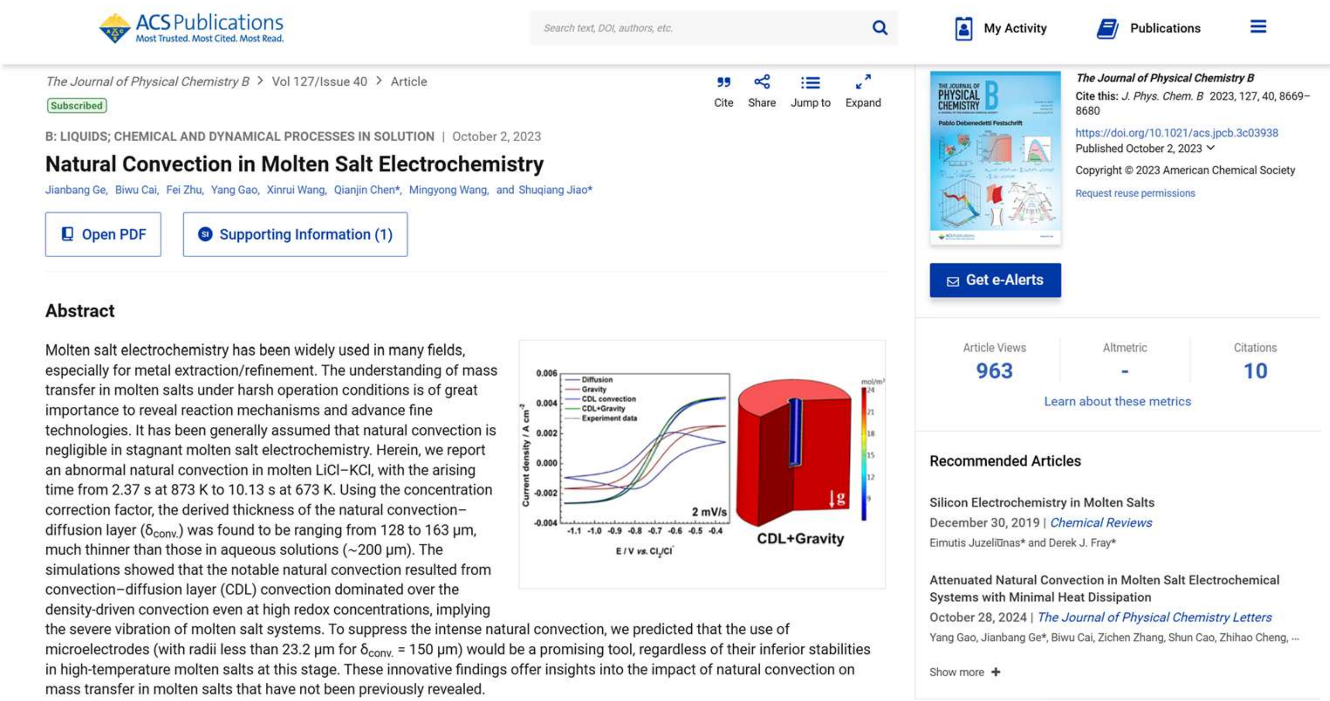
Natural Convection in Molten Salts

$$h_{Ox} = \frac{D_{Ox}}{\delta_{Ox}} \approx \frac{10^{-10}\,\frac{m^2}{s}}{10^{-4}\,m} \approx \frac{1\mu m}{s}$$

equivalent to 1 rpm rotation
(~4 cm $ID_{crucible}$ *@ ~ 500 °C)*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Natural Convection in Molten Salt Electrochemistry

Jianbang Ge, Biwu Cai, Fei Zhu, Yang Gao, Xinrui Wang, Qianjin Chen*, Mingyong Wang, and Shuqiang Jiao*

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Abstract

Molten salt electrochemistry has been widely used in many fields, especially for metal extraction/refinement. The understanding of mass transfer in molten salts under harsh operation conditions is of great importance to reveal reaction mechanisms and advance fine technologies. It has been generally assumed that natural convection is negligible in stagnant molten salt electrochemistry. Herein, we report an abnormal natural convection in molten LiCl–KCl, with the arising time from 2.37 s at 873 K to 10.13 s at 673 K. Using the concentration correction factor, the derived thickness of the natural convection–diffusion layer ($\delta_{conv.}$) was found to be ranging from 128 to 163 μm, much thinner than those in aqueous solutions (~200 μm). The simulations showed that the notable natural convection resulted from convection–diffusion layer (CDL) convection dominated over the density-driven convection even at high redox concentrations, implying the severe vibration of molten salt systems. To suppress the intense natural convection, we predicted that the use of microelectrodes (with radii less than 23.2 μm for $\delta_{conv.}$ = 150 μm) would be a promising tool, regardless of their inferior stabilities in high-temperature molten salts at this stage. These innovative findings offer insights into the impact of natural convection on mass transfer in molten salts that have not been previously revealed.

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Note: This is specific to soluble-soluble reactions. Natural convection can be more intense for soluble-insoluble reactions due to greater density gradients.

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Questions?

- When should you consider convection as being significant?

Questions?

- When should you consider convection as being significant?
  - Measurements with long time scales
  - Significant bubble production or metal plating
  - Stirring or flowing or rotating
  - Density gradients (perhaps from thermal gradients)

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Migration

Migration in Bulk Solution

- In Bulk Solution (stagnant, no convection)
  - $I_j = I_{m,j} = -z_j^2 F^2 A \frac{D_j C_j(x)}{RT} \frac{\partial \varphi(x)}{\partial x}$
  - Ionic Mobility (u) and Equivalent Ionic Conductivities (λ)
    - $u_j = D_j \frac{|z_j| F}{RT} \qquad \lambda_j = F u_j$
  - Transference (t)
    - $t_j = \frac{I_j}{I} = \frac{-|z_j| F A \quad {}_j C_j(x) \frac{\partial \varphi(x)}{\partial x}}{-FA \frac{\partial \varphi(x)}{\partial x} \sum |z_j| u_j C_j(x)} = \frac{|z_j| u_j C_j(x)}{\sum |z_j| u_j C_j(x)} = \frac{|z_j| \lambda_j C_j(x)}{\sum |z_j| \lambda_j C_j(x)}$

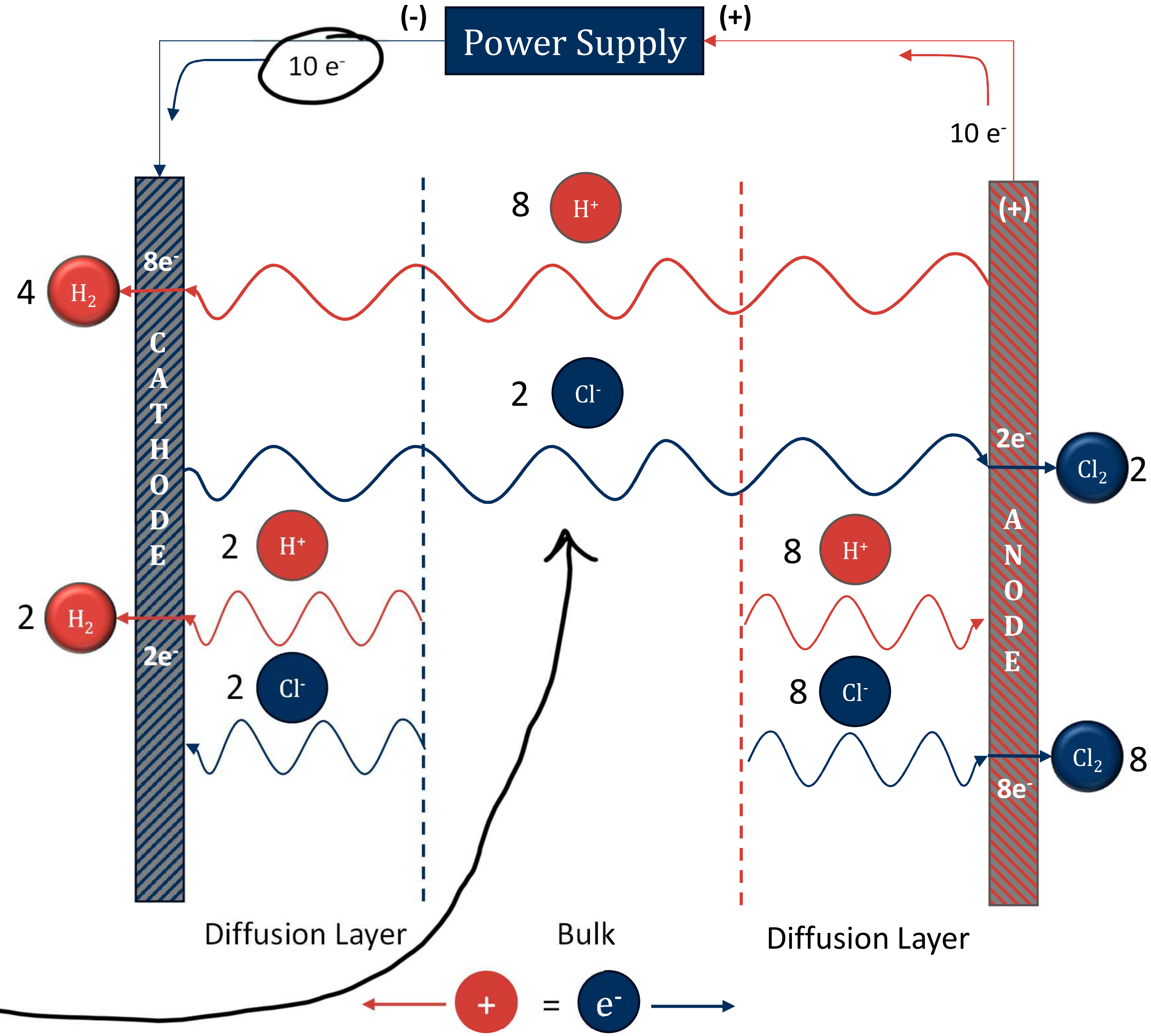
Balance Sheets

- Flow of 10e⁻ per unit time

$$2H^+ + 2e^- \leftrightarrow H_2 \text{ (cathode)}$$

$$Cl_2 + 2e^- \leftrightarrow 2Cl^- \text{ (anode)}$$

  - Equivalent Ionic Conductivity
    - $\lambda_{H^+} \approx 350\ \mathrm{cm}^2\,\Omega^{-1}$
    - $\lambda_{Cl^-} \approx 75\ \mathrm{cm}^2\,\Omega^{-1}$
  - Transference
    - $t_j = \frac{|z_j|\lambda_j C_j(x)}{\sum |z_j|\lambda_j C_j(x)}$
      - $|z_{H^+}| = |z_{Cl^-}|, C_{H^+} = C_{Cl^-}$
    - $t_{H^+} \approx 0.8$
    - $t_{Cl^-} \approx 0.2$



Effects of Migration on Measurements

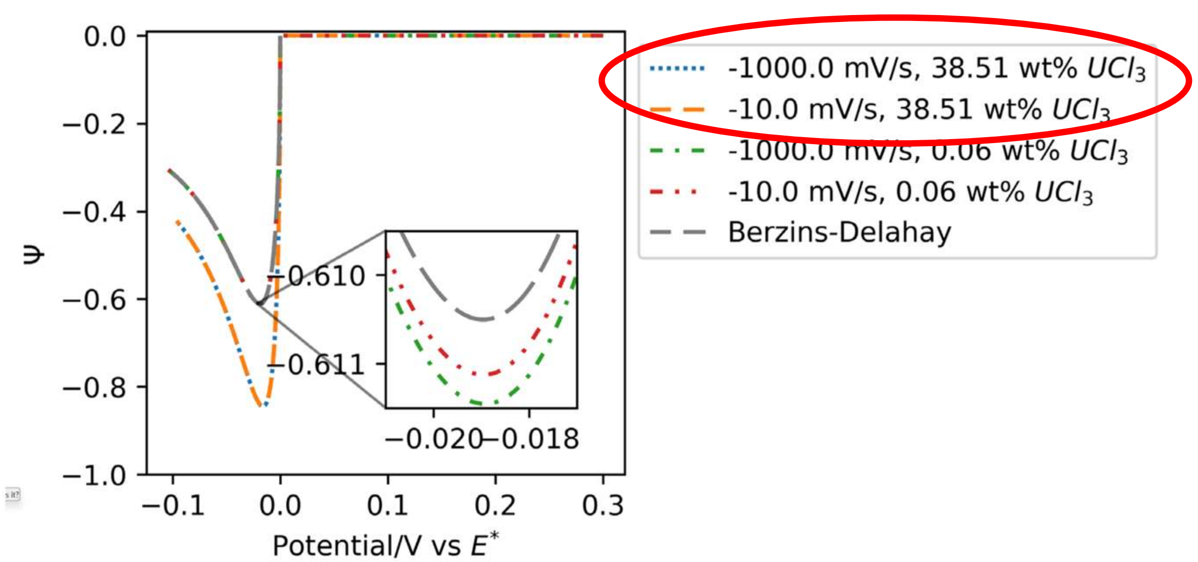


Figure 4.16 Simulations of migration without complexation (i.e., U^{3+}) at the extremes of scan rate and concentration evaluated.

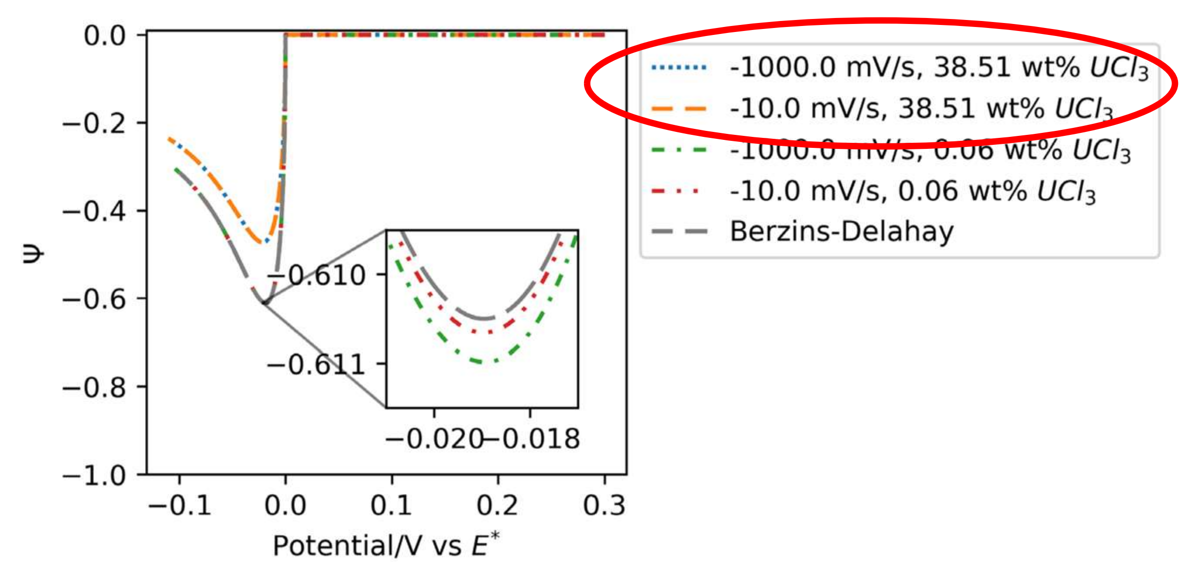


Figure 4.17 Simulations of migration with complexation (i.e., $[UCl_6]^{3-}$) at the extremes of scan rate and concentration evaluated.

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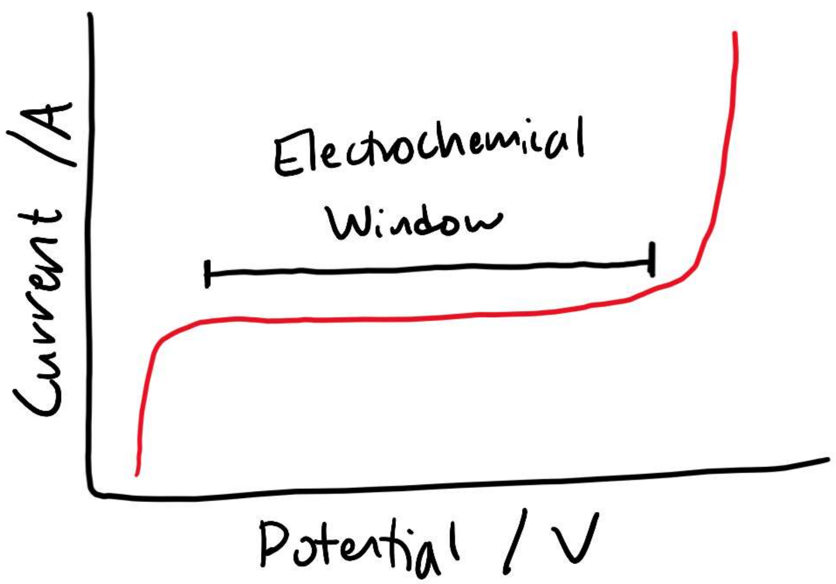
Supporting Electrolyte (SE)

- High solubility
  - SE carries almost all the migration current
  - Mass transfer of electroactive species occurs almost exclusively by diffusion
- Electrochemically inactive at electrode surface
  - No reduction or oxidations
- Examples
  - LiCl, NaCl, $CaCl_2$
    - High solubility, inactive



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Supporting Electrolyte (SE)

Advantages

- Decrease ohmic resistance
- Simplification of cell and analysis (i.e., diffusion only)
- Reduce double layer thickness

Disadvantages

- Impurities can interfere
  - Adsorption/desorption
  - Redox reaction
- Properties of medium differ from pure state

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Questions

- When do you need to consider migration?
- If your analyte is positively charged and you're reducing it, would you expect enhanced or diminished currents?

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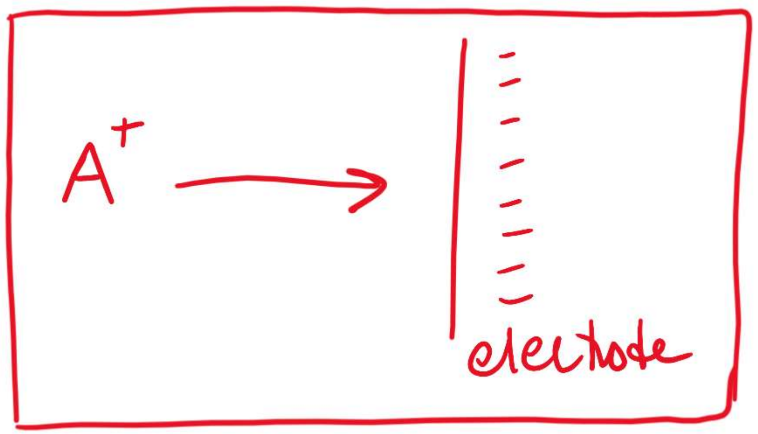
Questions

- When do you need to consider migration?

When your analyte is concentrated with respect to your electrolyte. (> 1:30)

- If your analyte is positively charged and you're reducing it, would you expect enhanced or diminished currents?

Enhanced



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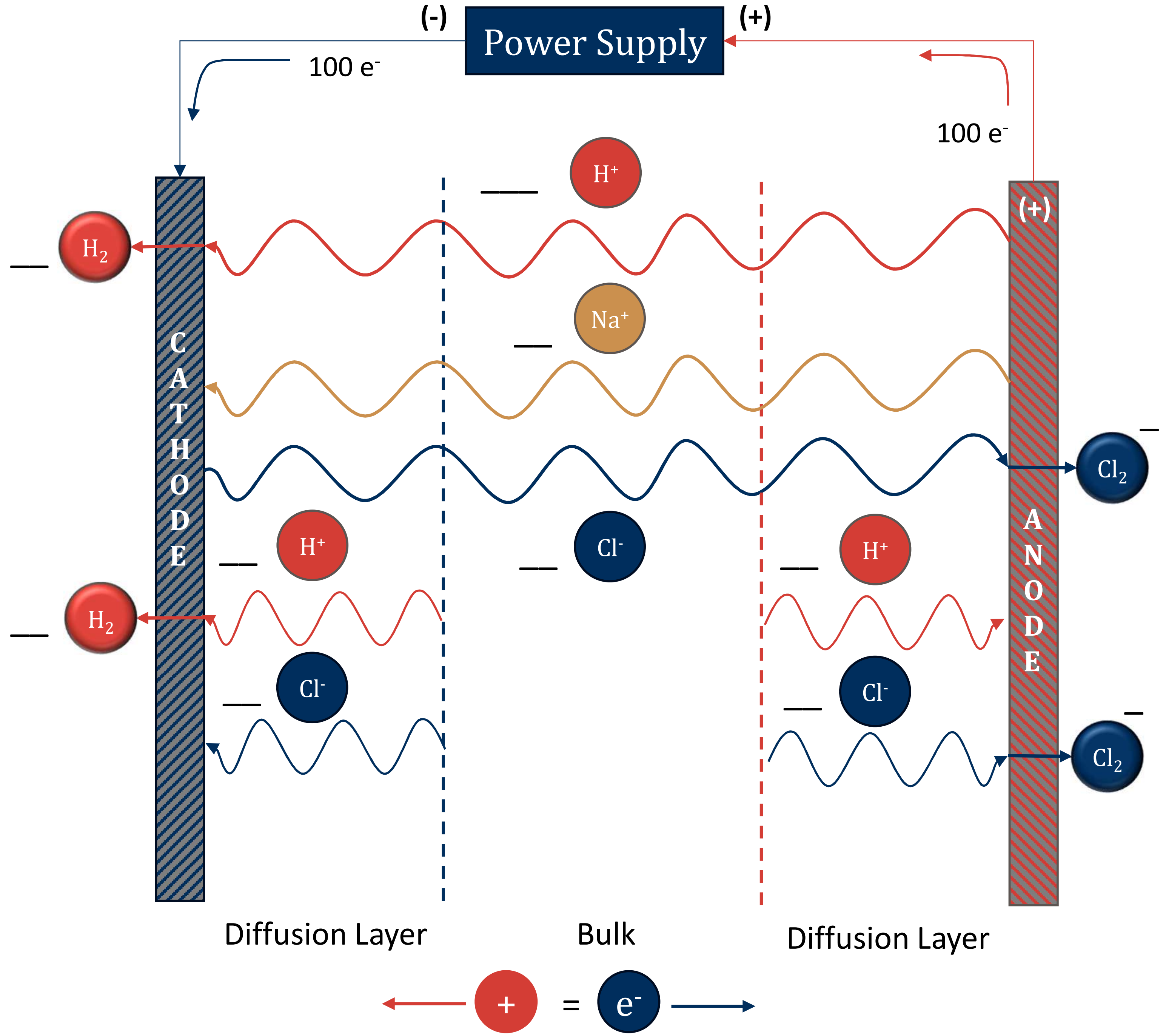
Fill-in Blanks

- 1 M NaCl and 0.015 M HCl with 100 e^-

$$2H^+ + 2e^- \leftrightarrow H_2 \text{ (cathode)}$$

$$Cl_2 + 2e^- \leftrightarrow 2Cl^- \text{ (anode)}$$

  - Ionic Conductivity
    - $\lambda_{Na^+} \approx 50$ cm^2 Ω^{-1}
    - $\lambda_{H^+} \approx 350$ cm^2 Ω^{-1}
    - $\lambda_{Cl^-} \approx 75$ cm^2 Ω^{-1}
  - Transference
    - $t_j = \frac{|z_j|\lambda_j C_j(x)}{\sum|z_j|\lambda_j C_j(x)}$
    - $t_{H^+} \approx$_____
    - $t_{Cl^-} \approx$_____
    - $t_{Na^+} \approx$_____



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    - $\lambda_{Cl^-} \approx 75 \text{ cm}^2\,\Omega^{-1}$
  - Transference
    - $t_j = \frac{|z_j|\lambda_j C_j(x)}{\sum |z_j|\lambda_j C_j(x)}$
    - $t_{H^+} \approx$ 0.04
    - $t_{Cl^-} \approx$ 0.58
    - $t_{Na^+} \approx$ 0.38