ChE 455/555: Mass Transport

Gerardine G. Botte

Objective/Introduction

- In previous chapters we neglected transport limitations
- In this chapter we will learn how to evaluate the effect of transport limitations
- We will learn how to account for mass transport in electrochemical systems using dilute solution theory.
- Dilute solution theory neglects solute-solute interactions
- The transport mechanisms involved in electrochemical systems include:
  - Diffusion
  - Migration
  - Convection

Outline

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- Fundamental relationships
- Mass transport boundary layer
- Concentration Overpotential
- Limiting Current Density

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Fundamental Relationships

- A general description of an electrochemical system takes into account:
  - Species fluxes
  - Material conservation (material balance)
  - Current flow
  - Electroneutrality
  - Electro-kinetics
  - Global reactions
  - Hydrodynamics

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Species Flux

- Using dilute concentration theory (considers only interactions between solute-solvent), the flux of species is given by:

$$N_i = \underbrace{-z_i u_i F c_i \nabla \phi}_{\text{migration}} \underbrace{- D_i \nabla c_i}_{\text{diffusion}} + \underbrace{c_i v}_{\text{convection}} \quad \text{Eq. 1}$$

Comparing to general chemical engineering systems the difference in the flux is given by the migration term (potential generated due to the ion interactions)

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Species Flux

Where:

N_i: flux of species, mol/cm^2 s

z_i: charge number of species i, eq/mol

u_i: mobility of species i, cm2-mol/Js

c_i: concentration of species i, mol/cm^3

ϕ: electrostatic potential, V

D_i: diffusion coefficient of species i, cm^2/s

v: fluid velocity, cm/s

The flux is perpendicular to the surface area (as usual)

Current Flow

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- Current will arise from the motion of the charges and is given by:

$$i = F\sum_i z_i N_i \qquad \text{Eq. 2}$$

Material Balance

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- The material balance is given by:

$$\frac{\partial c_i}{\partial t} = -\nabla . N_i + R_i \qquad \text{Eq. 3}$$

Where R_i represents a chemical reaction occurring in solution (mol/cm^3).

Eq. 3 assumes constant volume

Electroneutrality Equation

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- Because the electrical forces between charged species are so large, significant charge separation cannot occur. Therefore, in the bulk the electroneutrality assumption is valid:

$$\sum_i z_i c_i = 0 \qquad \text{Eq. 4}$$

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Simulations

- To carry out a simulation of the performance on an electrochemical system, Eqs. 1-4 need to be solved simultaneously
- We need a description of the flow pattern to account for “v” in Eq. 1
- Eqs. 1 to 4 apply at the bulk, the electrode kinetics is used as boundary conditions for the solution of the differential equations

---

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Common simplifications

- If bulk concentrations can be ignored we can demonstrate that the gradient of the current is given by:

$$\nabla . i = 0$$

This Eq. is known as conservation of charge

- When concentration variations can be neglected we obtained ohm’s law instead of Eq. 2:

$$i = -k \nabla \phi$$

Where k (conductivity) is given by:

$$k = F^2 \sum_i z_i^2 u_i c_i$$

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Common simplifications

Another important definition is the transport number:

$$t_j = \frac{z_j^2 u_j c_j}{\sum_i z_i^2 u_i c_i}$$

- When concentration variations are important, ohm’s law becomes modified ohm’s law:

$$\nabla \phi = \frac{-i}{k} - \frac{F}{k} \sum_i z_i D_i \nabla c_i$$

Common Simplifications

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- When migration is negligible (in excess of a supporting electrolyte), the coefficient of the potential gradient in Eq. 1 is large, then the potential gradient must be small
- The material balance can be obtained from substituting simplified Eq. 1 into Eq. 3

Common simplifications (supporting electrolyte)

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- This equation is known as the convective diffusion equation:

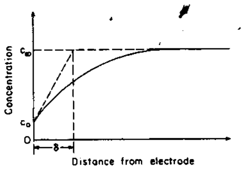
$$\frac{\partial c_i}{\partial t} + v.\nabla c_i = D_i \nabla^2 c_i$$

- The potential distribution can still be obtained by solving the modified ohm’s law equation

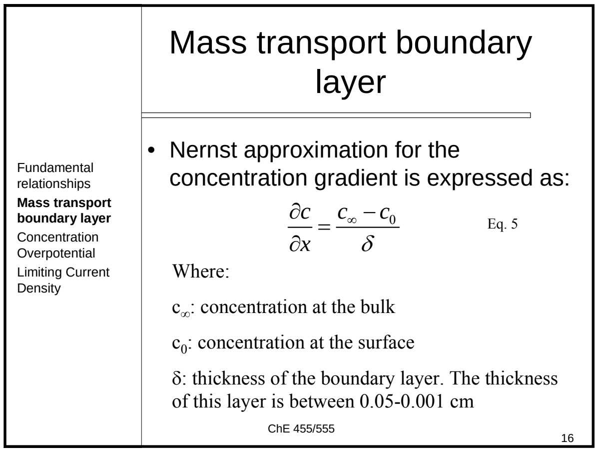
Mass transport boundary layer

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- For systems where the concentration gradient is significant, one common simplification is to treat the boundary layer region as a region with a linear concentration gradient



- This is known as Nernst diffusion layer



Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Mass transport boundary layer

- Nernst approximation for the concentration gradient is expressed as:

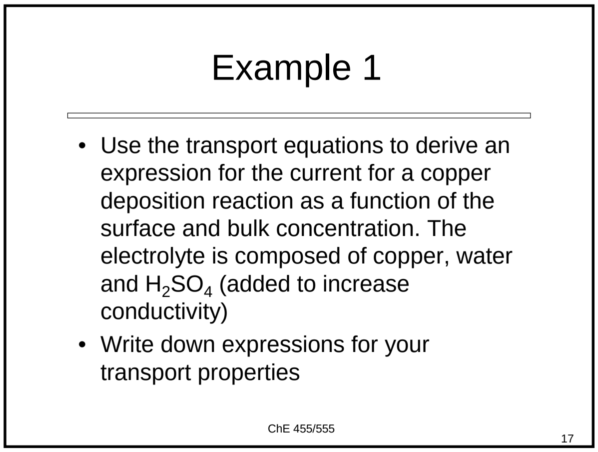
$$\frac{\partial c}{\partial x} = \frac{c_\infty - c_0}{\delta} \qquad \text{Eq. 5}$$

Where:

c_∞: concentration at the bulk

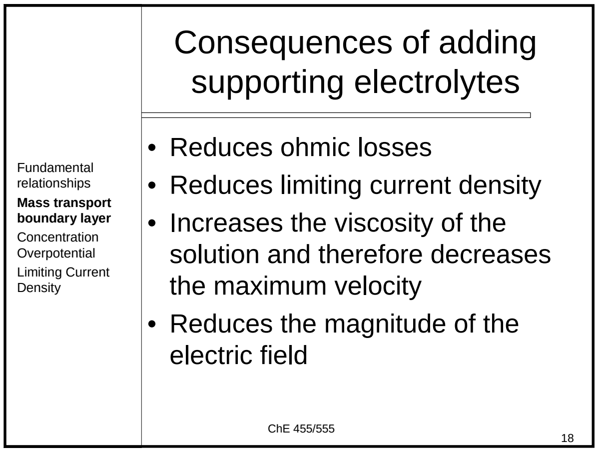
c_0: concentration at the surface

δ: thickness of the boundary layer. The thickness of this layer is between 0.05-0.001 cm



Example 1

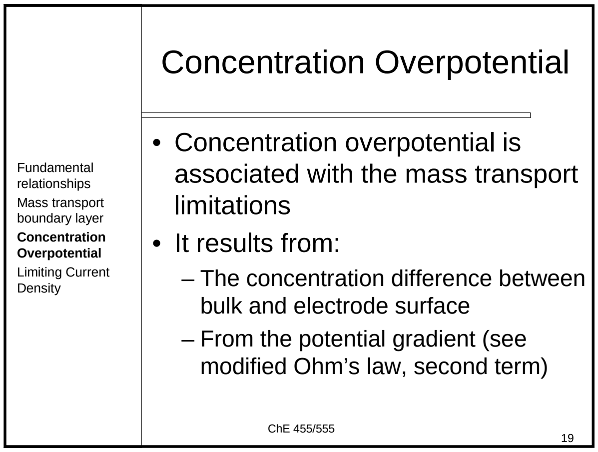
- Use the transport equations to derive an expression for the current for a copper deposition reaction as a function of the surface and bulk concentration. The electrolyte is composed of copper, water and H_2SO_4 (added to increase conductivity)
- Write down expressions for your transport properties



Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Consequences of adding supporting electrolytes

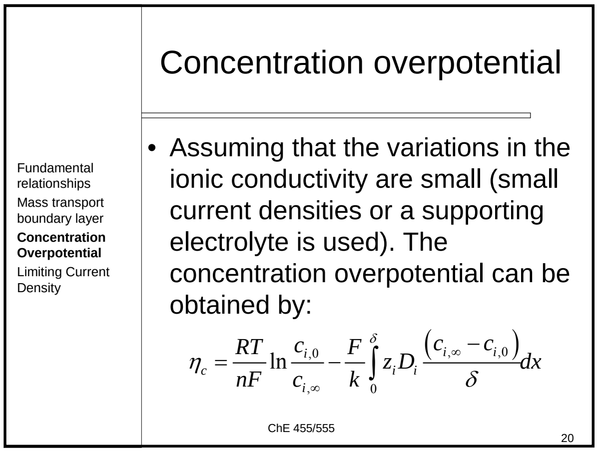
- Reduces ohmic losses
- Reduces limiting current density
- Increases the viscosity of the solution and therefore decreases the maximum velocity
- Reduces the magnitude of the electric field



Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Concentration Overpotential

- Concentration overpotential is associated with the mass transport limitations
- It results from:
  - The concentration difference between bulk and electrode surface
  - From the potential gradient (see modified Ohm's law, second term)

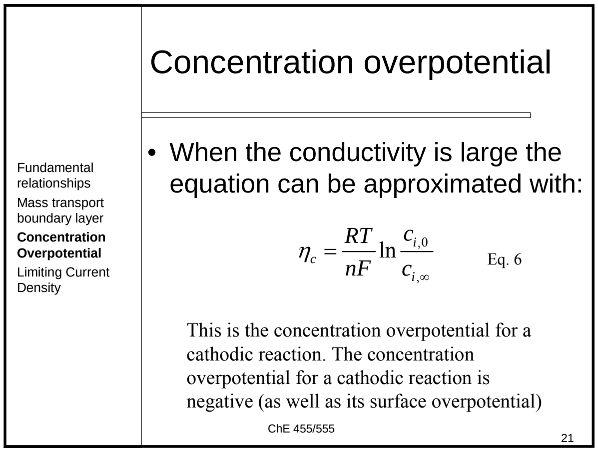


Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Concentration overpotential

- Assuming that the variations in the ionic conductivity are small (small current densities or a supporting electrolyte is used). The concentration overpotential can be obtained by:

$$\eta_c = \frac{RT}{nF}\ln\frac{c_{i,0}}{c_{i,\infty}} - \frac{F}{k}\int_0^{\delta} z_i D_i \frac{\left(c_{i,\infty} - c_{i,0}\right)}{\delta} dx$$



Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Concentration overpotential

- When the conductivity is large the equation can be approximated with:

$$\eta_c = \frac{RT}{nF}\ln\frac{c_{i,0}}{c_{i,\infty}} \qquad \text{Eq. 6}$$

This is the concentration overpotential for a cathodic reaction. The concentration overpotential for a cathodic reaction is negative (as well as its surface overpotential)

Concentration overpotential

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- For an anodic reaction, the concentration overpotential is positive and can be estimated (for large conductivities) by:

$$\eta_c = \frac{RT}{nF}\ln\left(1+\frac{i\delta}{nFDc_\infty}\right) \quad \text{Eq. 7}$$

Limiting current

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- When the current at the surface is equal to zero, the current measured is known as the limiting current
- For the boundary layer assumption, the current is defined as (we demonstrated this in Example 1):

$$i = \frac{-nFD(c_\infty - c_0)}{\delta}$$

Limiting current

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- Then the limiting current for the Nernst diffusion layer is given as:

$$i_l = \frac{-nFDc_\infty}{\delta}$$

The limiting current density is a function of the flow pattern. It is up to 100 order of magnitude larger in stirred solutions

Limiting current

Fundamental relationships

Mass transport boundary layer

Concentration Overpotential

Limiting Current Density

- The overpotential can be expressed as a function of the limiting current, for example for high conductivities the cathodic concentration overpotential is given by Eq. 6, which can be expressed as:

$$\eta_c = \frac{RT}{nF}\ln\left(1-\frac{i}{i_l}\right)$$

Limiting current

Fundamental relationships

Mass transport boundary layer

Concentration Overpotential

Limiting Current Density

- At currents higher than the limiting current additional reactions takes place
- After the limiting current the two reactions take place in parallel with the secondary reaction taking over the primary reaction

Limiting current

Fundamental relationships

Mass transport boundary layer

Concentration Overpotential

Limiting Current Density

- Supporting electrolytes reduce ohmic losses but tend to reduce the limiting current
- Supporting electrolytes increase the viscosity of the solution and decreases the mobility of the ions

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Diffusion coefficient

- The transport equations require the use of the diffusion coefficient.
- The diffusion coefficient for ionic species can be calculate by using the Nernst-Einstein equation:

$$D_i = RTu_i$$

- For a binary electrolyte the diffusion coefficient becomes:

$$D = \frac{D_+ D_- \left(z_+ - z_-\right)}{z_+ D_+ - z_- D_-}$$

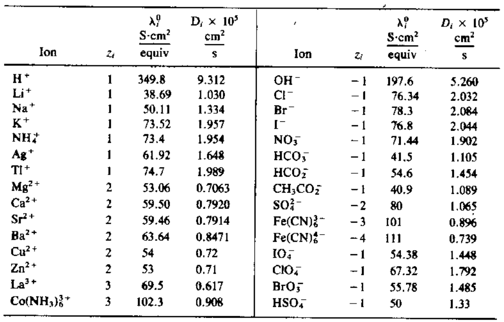
Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Diffusion coefficient

- Because the ionic diffusion coefficient is related to the mobility, it can be calculated using the equivalent conductances:

$$D_i = \frac{RT\lambda_i}{\left|z_i\right| F^2}$$

Values of diffusion coefficients of selected ions at infinite dilution in water at 25^{o}C



Ion	z_i	λ_i^0 $\frac{S\cdot cm^2}{equiv}$	$D_i \times 10^5$ $\frac{cm^2}{s}$	Ion	z_i	λ_i^0 $\frac{S\cdot cm^2}{equiv}$	$D_i \times 10^5$ $\frac{cm^2}{s}$
H^+	1	349.8	9.312	OH^-	−1	197.6	5.260
Li^+	1	38.69	1.030	Cl^-	−1	76.34	2.032
Na^+	1	50.11	1.334	Br^-	−1	78.3	2.084
K^+	1	73.52	1.957	I^-	−1	76.8	2.044
NH_4^+	1	73.4	1.954	NO_3^-	−1	71.44	1.902
Ag^+	1	61.92	1.648	HCO_3^-	−1	41.5	1.105
Tl^+	1	74.7	1.989	HCO_2^-	−1	54.6	1.454
Mg^{2+}	2	53.06	0.7063	$CH_3CO_2^-$	−1	40.9	1.089
Ca^{2+}	2	59.50	0.7920	SO_4^{2-}	−2	80	1.065
Sr^{2+}	2	59.46	0.7914	$Fe(CN)_6^{3-}$	−3	101	0.896
Ba^{2+}	2	63.64	0.8471	$Fe(CN)_6^{4-}$	−4	111	0.739
Cu^{2+}	2	54	0.72	IO_4^-	−1	54.38	1.448
Zn^{2+}	2	53	0.71	ClO_4^-	−1	67.32	1.792
La^{3+}	3	69.5	0.617	BrO_3^-	−1	55.78	1.485
$Co(NH_3)_6^{3+}$	3	102.3	0.908	HSO_4^-	−1	50	1.33

Newman J. S., Electrochemical Systems, Second edition, 1991

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Estimation of limiting current

- The limiting current can be estimated from the mass transfer correlations
- Usually mass transfer limitations are expressed as:

$$N_i = k_m\left(c_\infty - c_0\right)$$

Where k_m is the mass transfer coefficient (cm/s)

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Estimation of limiting current

- At the limiting current the surface concentration is zero, therefore, the limiting current is related to the mass transfer coefficient:

$$i_l = nFk_m c_\infty$$

- The mass transfer coefficient is related to the Sherwood number (Sh) which is a function of the Reynolds (Re) and the Schmidt (Sc) numbers

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

Estimation of limiting current

- The following correlations are used

$$Sh = \frac{k_m L}{D}$$

$$\mathrm{Re} = \frac{L\mathrm{v}}{\nu}$$

$$Sc = \frac{\nu}{D}$$

Where L is the characteristic length, v is the velocity of the fluid, and ν is the kinematic viscosity (cm^2/s) ($\nu = \mu/\rho$)

Estimation of limiting current

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- Some correlations require the use of the Grashof number (Gr).
- This number is used when the mass transport is affected by density differences

$$Gr = \frac{g\left(\rho_\infty - \rho_0\right)L^3}{\rho_\infty v^2}$$

$$\Delta\rho = \rho_\infty - \rho_0$$

Where:

g: acceleration due to gravity

ρ_∞: bulk density

ρ_0: surface density, equal to the solvent density

Estimation of limiting current

Fundamental relationships
Mass transport boundary layer
Concentration Overpotential
Limiting Current Density

- Correlations for the Sherwood number has been determine for specific geometries where the flow pattern is well known
- The correlations are summarized in appendix E of the book

Example 2

- For the cathodic deposition of copper from 0.5 M $CuSO_4$ and 0.5 M H_2SO_4 electrolyte, the kinetic parameters are α_c=0.5 and i_0=1 mA/cm^2. If the applied potential is 100 mV respect to a SCE. Calculate:
  - A. The current density for copper deposition expected if only kinetics limitations are involved
  - B. The limiting current density if two plane parallel copper electrodes, 2 cm long are used in a beaker of unstirred electrolyte
  - C. Estimate the thickness of the Nernst diffusion layer

Summary

- At the end of this chapter you should be able to:
  - Calculate diffusion coefficients for ionic species
  - Determine limiting current for different geometries
  - Calculate currents when kinetics and mass transport limitations are involved
  - Write down the fundamental equations to model an electrochemical system assuming dilute solution theory