Lecture #9 of 17

RECALL: Geometry and... uncompensated resistance models

1. For working electrodes benefiting from convergent transport, worldwide compensation is impossible unless a wafer NE is positioned extremely close to WE.

2. Uncompensated resistance declines dramatically as RE approaches WE, however, the angle of approach may be important.

3. A large CE is effectively remote when its distance from the working electrode is at least 5 times the radius of WE.

4. When the CE is of a size comparable to that of WE, it is effectively remote when the interelectrode distance is at least 10 times the radius of WE.

5. The resistance is effectively that of a cell in an infinitely large vessel, if the vessel's radius exceeds that of the electrodes 5-fold.

6. An electrode must be covered by at least 10 times its own radius of solution, before it is immersed in an effectively infinite volume.


Mass Transfer Processes

Chapters 1 and 4
What's in this set of lectures?

A: B&F Chapters 1 & 4 main concepts:

- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations
- Chapter 4: Mass transfer

Looking forward... Section 1.4 and Chapter 4

- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical diffusive models
- Conductivity
- Transport (Transference) number
- Balance sheets
- Ohmic drop/loss

We can all label the faradaic and non-faradaic processes... but what is this new feature?

What if we just “ran out” of Cl⁻ at the anode to oxidize?
mass transfer in electrochemistry is concerned with the movement of material = mass (even species as small as electrons) from one location (in solution) to another, and arises from spatial differences in electric potential, chemical potential, or from volume movement (of solution)...

We need to understand mass transfer! ...

but first, because it relates directly to mass transfer, I need to introduce the governing equation for the continuity of mass, which is even more stringent than the law of the conservation of mass!

since the continuity of mass equation is "better than" the conservation of mass law, and it is highly relevant to electrochemistry and in fact all science and engineering fields, we better know it...

it is introduced to most undergraduate students studying chemical engineering, materials science, and physics, but only partially to chemists (first half) and mechanical engineers (second half)...

anyway, here it is for species A along dimension x... Enjoy!

\[
\frac{\partial c_A}{\partial t} = \sum_i R_{A,i} - \frac{\partial N_A}{\partial x}
\]

https://en.wikipedia.org/wiki/Continuity_equation
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rate of change of the (concentration of species A with respect to (time) mass action (rate laws that effect species A, e.g. \( R_A = k[A][B] \)) rate of change of the (flux (of species A with respect to position (x))... what is mass flux?

... it's simple too...

https://en.wikipedia.org/wiki/Continuity_equation

Mass transfer... which is similar to heat transfer... and momentum transfer

(1) Migration / Drift (no analogous term for heat, as heat is not charged)

Flux (mol cm\(^{-2}\) s\(^{-1}\)) of charged species due to an electric field (electric potential)... in general, stirring does not affect this as cations and anions move in opposite directions

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(2) **Diffusion (analogous heat transport is down a temperature gradient)**
Net flux of species due to a spatial gradient in their concentration and random thermal motion (no real "force")

![Diffusion](http://en.wikipedia.org/wiki/Diffusion)

(3) **Convection (analogous heat transport is fluid/gas motion)**
Hydrodynamic movement (e.g. forced convection (stirring)) of species, where charged species still remain near each other (Coulombic attraction)

... FYI: even without intentional forced convection, unintentional forced convection (e.g. vibrations) influences an electrochemical experiment after ~30 seconds
Mass transfer is driven (mostly) by gradients in electrochemical potential...

Mass transfer, for a charged species, seems like a current!

How is current density \( J \, A \, \text{cm}^{-2} \) related to flux \( (N, \ \text{mol \ cm}^{-2} \cdot \text{s}^{-1})? \)
... well, current density has units of \( A \ \text{cm}^{-2} = C \ \text{cm}^{-2} \cdot \text{s}^{-1} \)
... and flux has units of \( \text{mol cm}^{-2} \cdot \text{s}^{-1} \)
... So what do we need to equate these? ...
... something with units of \( C \ \text{mol}^{-2} \)...
\[ J = z F N \] \( z \) the Faraday constant... and \( z \)

The total current density, in one-dimension, due to all charged species is,
\[ J_x = z F N = F \sum_i z_i \left( -\frac{\partial c_i}{\partial x} + c_i \mu_i \right), \text{ and in 3D...} \]
\[ J = z F N = F \sum_i z_i \left( -\frac{\partial c_i}{\partial x} \nabla \mu_i + c_i \mu_i \right), \text{ where } \nabla \text{ is "del" (nabla)} \]
... where \( D_i \) is the diffusion coefficient of species \( i \) (in units of cm^2 s^-1), \( c_i \) is the concentration (in units of mol cm^-3), \( \mu_i \) is the electrochemical potential (in units of J mol^-1), and \( v \) is the velocity of the solution (in units of cm s^-1)

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mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration/drift, and convection.

The Nernst–Planck Equation:

\[
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)
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\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x) \]

the flux due to convection of reactant \( i \) where \( \nu(x) \) is the velocity profile of the solution.

... so, because we are adding up three contributions to the flux – which is proportional to the current (density) – if we drew a circuit to represent these terms, would these contributions be in series or in parallel?

... in parallel... \( J_i(x) = J_1 + J_2 + J_3 \)

... so, if \( J_{\text{migration/drift}} \) is huge and \( J_{\text{diffusion}} \) is small, what process dominates \( J_i \)?

\( J_{\text{migration/drift}} \)

... and now what if there was rapid stirring?

\( J_{\text{convection}} \)
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\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]

... again... but where did this equation for flux come from?

... who's comfortable with me just giving you this equation?

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Electrochemical potential of species \( i \) in phase \( \beta \) is an energy (J/mol),

\[ \bar{\mu}_i^\beta = \left( \frac{G_i}{n_i} \right)_{\rho_0, n_{i0}} = \mu_i^\beta + z_i F \phi^\beta, \]

where

- \( G \) (Gibbs free energy (J))
- \( n_i \) (amount of species \( i \) (mol))
- \( \mu_i = \mu_i^\beta + RT \ln a_i \) (chemical potential (J/mol))
- \( z_i \) (valency of species \( i \))
- \( F \approx 10^5 \) (Faraday constant (C/mol))
- \( \phi^\beta \) (Galvani/inner electric potential (V))
- \( a_i \) (activity of species \( i \))

For an uncharged species \( \bar{\mu}_i^\beta = \mu_i^\beta \).

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... don't worry... there aren't too many steps...

From before, for one species the total flux in one-dimension is

\[ N = -\frac{DC_i}{RT} \cdot \frac{\partial \mu_i}{\partial x} + C_i v, \]

where again \( D \) is diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( c \) is concentration (mol cm\(^{-3}\)), \( \mu \) is the electrochemical potential (J mol\(^{-1}\)), \( v \) is velocity (cm s\(^{-1}\))

Recall that \( \bar{\mu}_i^\beta = \mu_i^\beta + z_i F \phi^\beta \) and so,

\[ N = -\frac{DC_i}{RT} \cdot \frac{d(\mu_i + z_i F \phi)}{dx} + C_i v \]

and recall that \( \mu_i = \mu_i^\beta + RT \ln a_i \) and so,

\[ N = -\frac{DC_i}{RT} \cdot \frac{d(\mu_i^\beta + RT \ln a_i + z_i F \phi)}{dx} + C_i v \]

---

From above, the flux

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]
From before, for one species the total flux in one-dimension is

\[ N = -\frac{Dc}{RT} \cdot \frac{d\mu}{dx} + cv, \]

where again \( D \) is diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( c \) is concentration (mol cm\(^{-3}\)), \( \mu \) is the electrochemical potential (J mol\(^{-1}\)), \( v \) is velocity (cm s\(^{-1}\)).

Recall that \( \mu_0 = \mu_i + z_i F \phi \) and so,

\[ N = -\frac{Dc}{RT} \cdot \frac{d\mu}{dx} + z_i F \phi \]

... and assuming \( a \approx c \),

\[ N = -Dc \cdot \frac{d(a(x))}{dx} - \frac{\alpha F}{RT} c \cdot \frac{d\phi}{dx} + cv \]

and finally...

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \]
Steady-state?...

... Initial states equilibrate using ICE, ICE Baby!

A ⇌ B + C

Vanilla Ice wants to know, “As the initial state progresses, what happens if you keep supplying A and pulling B and C away?” ...

... Le Chatelier’s Principle keeps the reaction going...

A ⇌ B + C →

... but for how long? ...

M₁ → A ⇌ B + C → M₂

... as long as the rate of supply in and the rate of exit out are constant...

... and in electrochemical systems, as long as a constant potential bias is applied!

In an ideal world, i.e. under certain rare conditions,

\[
\frac{\partial \text{A}}{\partial t} = \frac{\partial \text{B}}{\partial t} = \frac{\partial \text{C}}{\partial t} = 0,
\]

and the system is in a steady-state where there is a net flux of species (generation of A, from the left, and loss of B & C, to the right) but the species concentrations in the cell do not change with time.

Who cares? ...

... when the current is at a steady-state, the current is constant, and there is no new capacitive charging!

M₁ → A ⇌ B + C → M₂

... for steady-state current, KCL applies... no, not KC... no, KC!

**Kirchhoff's Current Law (KCL)**

\[
\sum_{k=1}^{n} I_k = 0
\]

But KCL applies to the *entire circuit*, including in the potentiostat!

(when current flows, i.e. due motion of charges, it is the same everywhere in the circuit)

![Electrical Circuit Diagram](image)

... hey, what are those minus signs at the bottom? ...

**Migrating/Drifting Ions!**

... we’ll get to this shortly

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Back to the first flux term... Diffusion...

**Diffusion coefficient** \( (D, \text{cm}^2 \text{s}^{-1}) \) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient...” [IUPAC Gold Book]

**Fick’s first law of steady-state Diffusion**: \( N_x = -D \frac{dc}{dz} \) in 1D

\[ \Delta G < 0 \]

**Do the units of D make sense?**

\[ N_x \text{ (mol cm}^{-2} \text{s}^{-1}) , \text{ as } xy = D_x \text{ (cm}^{-2} \text{s}^{-1}) \]

\[ \text{ (mol cm}^{-2} \text{s}^{-1}) , \text{ as } xy = D_x \text{ (mol cm}^{-2} \text{s}^{-1}) \]

Therefore, \( D_x \) is has units of cm\(^2\) s\(^{-1}\)... but as \( z \)... Huh? \( z z \)?! What?! That was unexpected... Is it right?...

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Physician & Physiologist

**Adolf Eugen Fick** (1829-1901)

From Wiki