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 electrode 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!

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

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. \( R_A = k_2[A][B] \)

... this is what chemists were taught... it's simple!

... and recall that these reactions are driven by differences in chemical potential, \( \mu \), of various species, including A

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

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

rate of change of the (concentration of species A with respect to (t)ime
mass action (rate laws that effect species A, e.g. \( R_A = k_2[A][B] \))
rate of change of the (flux (N) of species A with respect to position (x))

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

What is mass flux? It's simple too...

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

1. **Migration**
   Flux (in mol cm$^{-2}$ s$^{-1}$) of charged species due to an electric field (electric potential and anions).

2. **Convection** *(analogous heat transport is fluid/gas motion)*
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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 cm$^{-1}$) related to flux ($N$, mol cm$^{-2}$ s$^{-1}$)?
   ... well, current density has units of A cm$^{-1}$ = C cm$^{-2}$ s$^{-1}$...
   ... and flux has units of mol cm$^{-2}$ s$^{-1}$...
   ... So what do we need to equate these? ...
   ... something with units of C mol$^{-1}$...

The total current density, in one-dimension, due to all charged species is,

$$J_{x} = zF \sum_{i} N_{i} \left( \frac{\partial c_{i}}{\partial x} + \frac{\partial \phi_{i}}{\partial x} + c_{i} v_{x} \right),$$

and in 3D...

$$J = zF \sum N_{i} \left( \frac{\partial c_{i}}{\partial x} \nabla \phi_{i} + c_{i} v_{x} \right),$$

where $\nabla$ 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$^{-3}$), $\phi_{i}$ is the electrochemical potential (in units of V mol$^{-1}$), and $v_{x}$ is the velocity of the solution (in units of cm s$^{-1}$).
Mass transfer is driven (mostly) by gradients in electrochemical potential... 293

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... something with units of \( \text{C mol}^{-1} \cdot \text{cm}^2 \)

\[ \mathbf{J}_i = z_i F N_i \text{ ... the Faraday constant... and } z \]

The total current density, in one-dimension, due to all charged species is,

\[ \mathbf{J} = zF \mathbf{N} = F \sum_i z_i \left( \frac{\partial C_i}{\partial x} + \frac{\partial_d C_i}{\partial x} \right), \]

... where \( D_i \) is the diffusion coefficient of species \( i \) (in units of \( \text{cm}^2 \text{s}^{-1} \)), \( c_i \) is the concentration (in units of \( \text{mol cm}^{-3} \)), \( j_i \) is the electrochemical potential (in units of \( \text{J mol}^{-1} \)), and \( v \) is the velocity of the solution (in units of \( \text{cm s}^{-1} \))

Mass transfer is driven (mostly) by gradients in electrochemical potential... 294

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As we will see, besides the sign, this equals conductivity \( \sigma \) divided by \( F \), and in 3D...

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mass transport/transfer of molecules to the WE in an electrochemical cell 295

has three contributions: diffusion, migration/drift, and convection

the Nernst–Planck Equation:

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

the total flux of reactant \( i \) to a flat electrode (this is \( \mathbf{J}(x) \)) in many textbooks — not ours! — especially engineering ones; it has units of \( \text{mol cm}^{-2} \text{s}^{-1} \)

Walter Hermann Nernst (1864–1941)
Nobel Prize (Chemistry, 1920)
from Wiki

Max Karl Ernst Ludwig Planck (1858–1947)
Nobel Prize (Physics, 1918)
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mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration/drift, and convection

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the diffusive flux of reactant \( i \) to a flat electrode where, again, \( D_i \) is the diffusion coefficient for species \( i \) (\( D_i \) has units of \( \text{cm}^2 \text{s}^{-1} \)).

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

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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 migration/drift of reactant \( i \) where \( z_i \) is the charge on species \( i \), and \( \phi(x) \) is the gradient in electric potential (which is equal to the negative of the electric field, \( E \)).

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

the Nernst–Planck Equation:

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

the flux due to convection of reactant \( i \) where \( \nu(x) \) is the velocity profile of the solution.
mass transport/transfer of molecules to the WE in an electrochemical cell has three contributions: diffusion, migration/drift, and convection

The Nernst–Planck Equation:

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

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

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

... who's comfortable with me just giving you this equation?
Electrochemical potential of species $i$ in phase $\beta$ is an energy (J/mol),

$$\mu_i^\beta = \left( \frac{\partial G}{\partial n_i} \right)_{T, \rho, n_{\rho i}} = \mu_i^0 + z_i F \phi^\beta,$$

where $G$ (Gibbs free energy (J)), $n_i$ (amount of species $i$ (mol)), $\mu_i^0$ (chemical potential (J/mol)), $z_i$ (valency of species $i$), $F$ (Faraday constant (C/mol)), $\phi^\beta$ (Galvani/inner electric potential (V)), $a_i$ (activity of species $i$).

For an uncharged species $\mu_i^\beta = \mu_i^0$.

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

$$N = -D \frac{dc}{dx} + c \nu,$$

where again $D$ is diffusion coefficient (cm$^2$/s), $c$ is concentration (mol cm$^{-3}$), $\nu$ is velocity (cm s$^{-1}$).

Recall that $\mu_i^\beta = \mu_i^0 + z_i F \phi^\beta$ and so,

$$N = -\frac{D c^0}{RT} \frac{d(\mu_i^0 + z_i F \phi^\beta)}{dx} + c \nu...$$

and assuming $a = c$,

$$N = -D \frac{dc}{dx} \frac{d(\mu_i^0 + z_i F \phi^\beta)}{dx} + c \nu...$$

and finally...

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \nu(x)$$
Diffusion coefficient (D, cm$^2$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:** $N_z = -D_z \frac{dc}{dz}$ in 1D

(His second law is for non-steady-state conditions, where time is another independent variable.)

Some very important background “first”... okay, second!

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$D$ also exhibits Arrhenius behavior: $D = D_0 e^{-\frac{E_a}{RT}}$

where $D_0$ is the maximum $D$ (at infinite $T$)

Some very important background “first”... okay, second!

**Steady-state? ...**

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

$\text{A} \rightleftharpoons \text{B} + \text{C}$

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...

\[ \text{M_1} \xrightarrow{\text{A}} \text{B + C} \xrightarrow{\text{M_2}} \]

... but for how long? ...

\[ \frac{\partial c_A}{\partial t} = \frac{\partial c_B}{\partial t} = \frac{\partial c_C}{\partial t} = 0 \]

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

Who cares? ...

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

\[ \text{M_1} \xrightarrow{\text{A}} \text{B + C} \xrightarrow{\text{M_2}} \]

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

**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)

... why are those minus signs at the bottom? ...

**Migrating/Drifting Ions!**

... we’ll get to this shortly
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

Do the units of \(D\) make sense?

\[N_x (\text{mol cm}^{-1} \text{s}^{-1}, \text{as } xy) = D_x \frac{d c}{dz} \quad (\text{mol cm}^{-1} \text{s}^{-1}, \text{as } xy z)\]

Therefore, \(D_x\) is has units of \(\text{cm}^2 \text{s}^{-1}\), but as \(xyz\)...

Huh? z? z? What?… That was unexpected!… Is it right?…

... well, that must have been incorrect (it’s not!)... anyway, let’s try this again... Grab a beverage and let’s go on a (random) walk!

From B&F

\[\Delta = \sqrt{(2D\Delta t)}(\Delta \text{ displacement (variance)})\]

\(\Delta:\) is the dimension
\(\Delta t:\) is just the number
\(\Delta:\) is step time
\(\Delta:\) is step length

\(\Delta = \sqrt{(2D\Delta t)}\), where \(d\) is the dimension

… and the “2” is for positive and negative directions
... so how far do species diffuse in electrochemistry?

<table>
<thead>
<tr>
<th>Dimension</th>
<th>$\bar{\Delta}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>$\sqrt{2Dt}$</td>
</tr>
<tr>
<td>2D</td>
<td>$\sqrt{4Dt}$</td>
</tr>
<tr>
<td>3D</td>
<td>$\sqrt{6Dt}$</td>
</tr>
</tbody>
</table>

$\bar{\Delta} = \sqrt{(2d)Dt}$, where $d$ is the dimension … and the “2” is for positive and negative directions

... plane

... wire, line, tube

... point, sphere, disk

$\bar{\Delta} = \sqrt{(2d)Dt}$, where $d$ is the dimension

(root mean square (rms) displacement)

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(root mean square (rms) displacement)