

Lecture #9 of 17

RECALL:

(1) For working electrodes benefitting from convergent transport, worthwhile compensation is impossible unless a midget RE 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

Q: What's in this set of lectures?

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

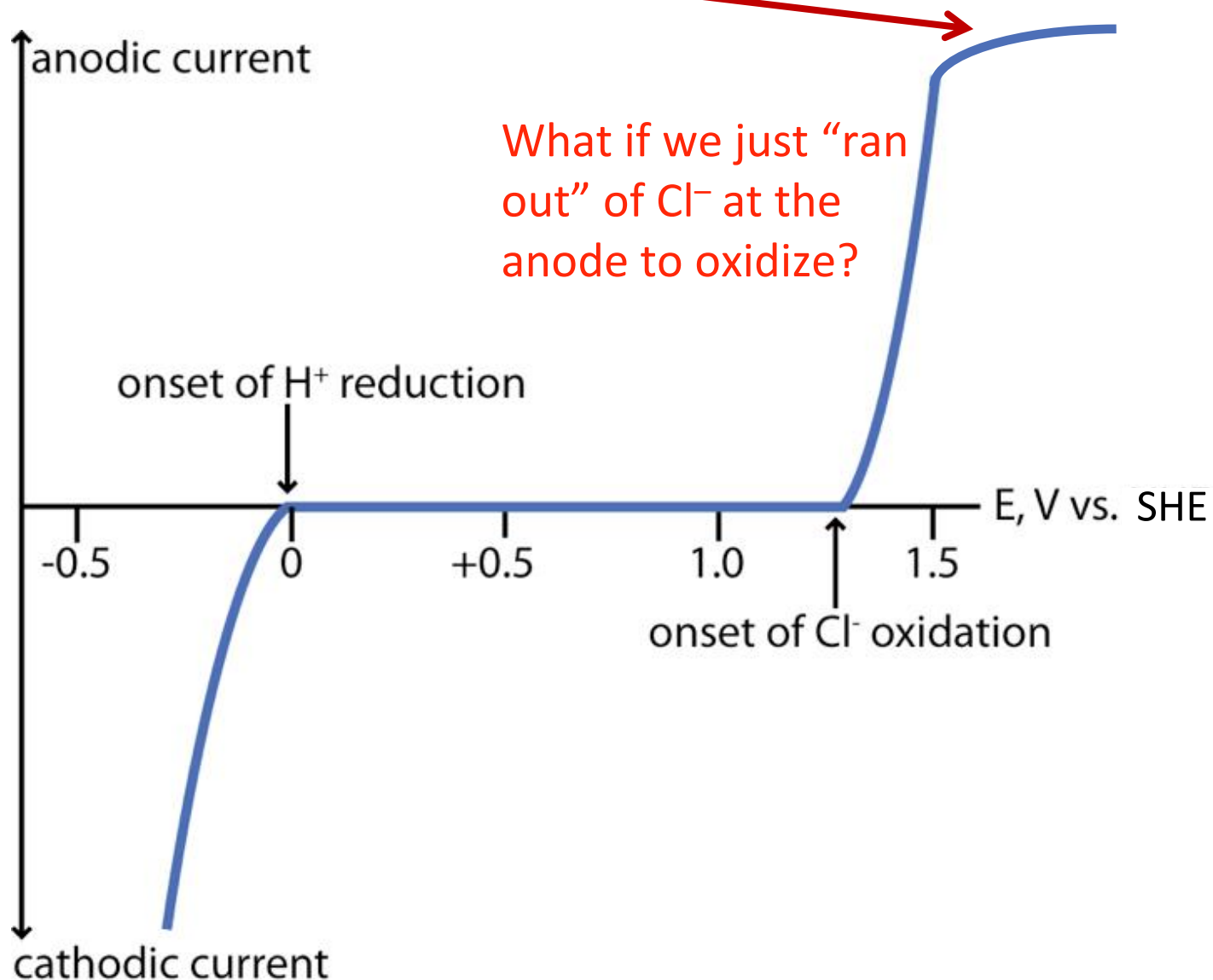
- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations
- Chapter 4: Mass transfer

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?



... 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!

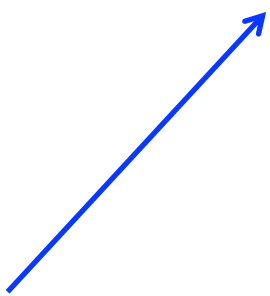
$$\frac{\partial c_A}{\partial t} = \sum_i R_{A,i} - \frac{\partial N_A}{\partial x}$$

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rate of change of the
(c)oncentration of species A
with respect to (t)ime

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$$\frac{\partial c_A}{\partial t} = \sum_i R_{A,i}$$

rate of change of the (c)oncentration of species A with respect to (t)ime

mass action (R)ate 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 (R)eactions are driven by differences in chemical potential, μ , of various species, including A

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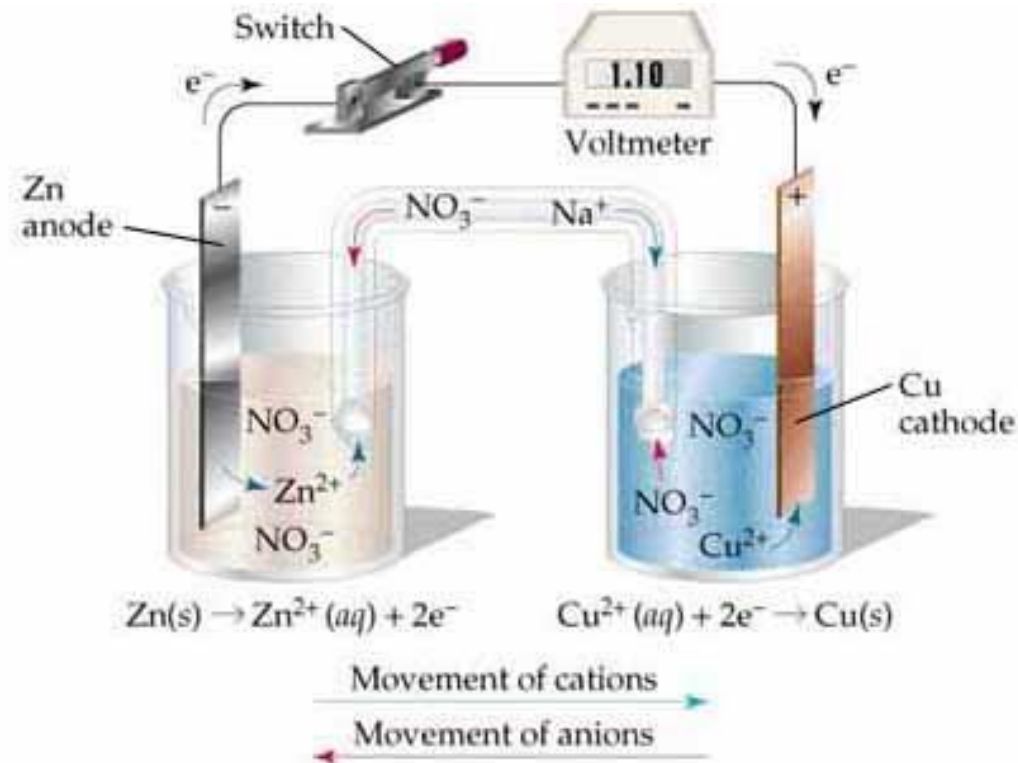
rate of change of the flux (N) of species A with respect to position (x)

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

... what is mass flux?
... **it's simple too...**

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

Flux ($\text{mol cm}^{-2} \text{s}^{-1}$) 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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Net flux of *species* due to a spatial gradient in their concentration and random thermal motion (no real “force”)



Diffusion

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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

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anions



charged
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and

(2) Diffusi
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Convection here, too!

<http://en.wikipedia.org/wiki/Diffusion>

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

How is current density (\mathbf{J} , A cm⁻²) related to flux (\mathbf{N} , mol cm⁻² s⁻¹)?

... well, current density has units of A cm⁻² = 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*...

$$\mathbf{J}_x = z F \mathbf{N}_x \dots \text{the Faraday constant... and } z$$

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

$$J_x = z F N_x = F \sum_i z_i \left(-\frac{D_{i,x} c_i}{RT} \cdot \frac{d\bar{\mu}_i}{dx} + c_i v_x \right), \text{ and in 3D...}$$

$$\mathbf{J} = z F \mathbf{N} = F \sum_i z_i \left(-\frac{D_i c_i}{RT} \cdot \nabla \bar{\mu}_i + c_i \mathbf{v} \right), \text{ where } \nabla \text{ is "del" (nabla)}$$

... where D_i is the diffusion coefficient of species i (in units of cm² s⁻¹), c_i is the concentration (in units of mol cm⁻³), $\bar{\mu}_i$ is the electrochemical potential (in units of J mol⁻¹), and \mathbf{v} is the velocity of the solution (in units of cm s⁻¹)

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For derivation, see Bockris & Reddy, Modern EChem, Vol. 1, 2002, Section 4.4.15

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As we will see, besides the sign, this equals conductivity (σ_i) divided by $z_i F$...

$J_x = z F N_x$... the Faraday constant... and z

... and thus in the absence of convection...

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

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... $J_{x,i} = \frac{\sigma_i}{z_i F} \frac{d\bar{\mu}_i}{dx}$... how elegant... and rather easy to memorize!

... where D_i is the diffusion coefficient of species i (in units of cm² s⁻¹), c_i is the concentration (in units of mol cm⁻³), $\bar{\mu}_i$ is the electrochemical potential (in units of J mol⁻¹), and \mathbf{v} is the velocity of the solution (in units of cm s⁻¹)

mass transport/transfer of molecules to the WE in an electrochemical cell 323
has three contributions: *diffusion, migration/drift, and convection*

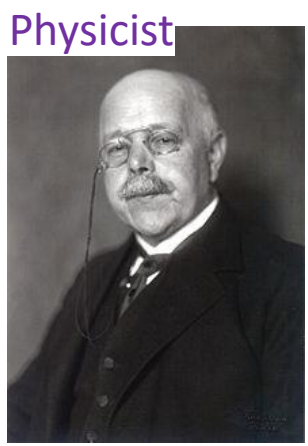
the *Nernst–Planck Equation*:

B&F, 1.4.2
& 4.1.8

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

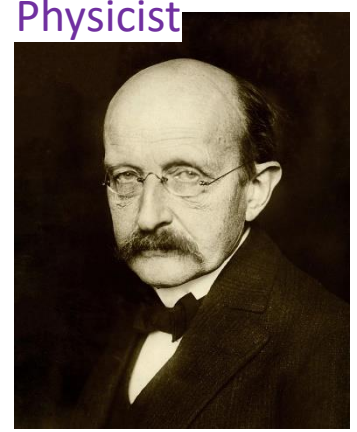


the total **flux** of reactant *i* to a flat electrode (this is $N_i(x)$ in many textbooks – not ours! – especially engineering ones; it has units of mol cm⁻² s⁻¹)



Physicist

Walther Hermann Nernst
(1864–1941)
Nobel Prize (Chemistry, 1920)



Physicist

Max Karl Ernst Ludwig Planck
(1858–1947)
Nobel Prize (Physics, 1918)

from Wiki

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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 has units of $\text{cm}^2 \text{s}^{-1}$)

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↑
the flux due to migration/drift of reactant i
where z_i is the charge on species i ,
and $\partial\phi/\partial x$ 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 326
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B&F, 1.4.2
& 4.1.8

↑
the flux due to convection of
reactant *i* where $v(x)$ 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*:

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

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

mass transport/transfer of molecules to the WE in an electrochemical cell 328
has three contributions: *diffusion*, *migration/drift*, and *convection*

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

$J_{\text{migration/drift}}$

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

$J_{\text{convection}}$

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

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... 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 β is an energy (J/mol),

$$\bar{\mu}_i^\beta = \left(\frac{\partial G}{\partial n_i^\beta} \right)_{T,p,n_{j \neq i}} = \mu_i^\beta + z_i F \phi^\beta, \text{ where}$$

G (Gibbs free energy (J))

n_i (amount of species i (mol))

$\mu_i = \mu_i^0 + RT \ln a_i$ (chemical potential (J/mol))

z_i (valency of species i)

$F \approx 10^5$ (Faraday constant (C/mol))

ϕ^β (Galvani/inner electric potential (V))

a_i (activity of species i)

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

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

$$N = -\frac{Dc}{RT} \cdot \frac{d\bar{\mu}}{dx} + c\nu, \text{ where again } D \text{ is diffusion coefficient (cm}^2 \text{ s}^{-1}\text{), } c \text{ is}$$


concentration (mol cm⁻³), $\bar{\mu}$ is the electrochemical potential (J mol⁻¹), ν is velocity (cm s⁻¹)

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

$$N = -\frac{Dc}{RT} \cdot \frac{d(\mu + zF\phi)}{dx} + c\nu \dots \text{ and recall that } \mu_i = \mu_i^0 + RT \ln a_i \text{ and so,}$$

$$N = -\frac{Dc}{RT} \cdot \frac{d(\mu^0 + RT \ln a + zF\phi)}{dx} + c\nu$$

flux



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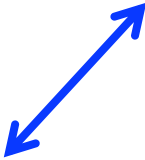
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$$N = -\frac{Dc}{RT} \cdot \frac{d(\cancel{\mu^0} + RT \ln a + zF\phi)}{dx} + c\mathcal{V} \dots \text{ and assuming } a \approx c,$$

$$N = -Dc \cdot \frac{d(\ln c)}{dx} - \frac{zFD}{RT} c \cdot \frac{d\phi}{dx} + c\mathcal{V} \dots \text{ and finally...}$$



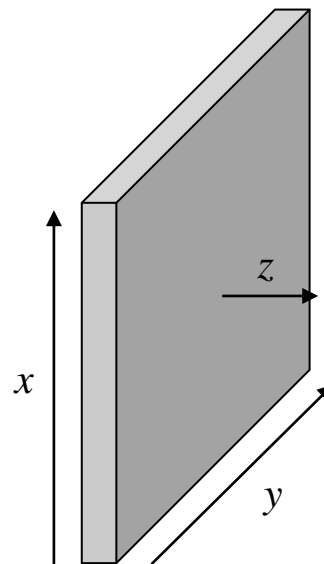
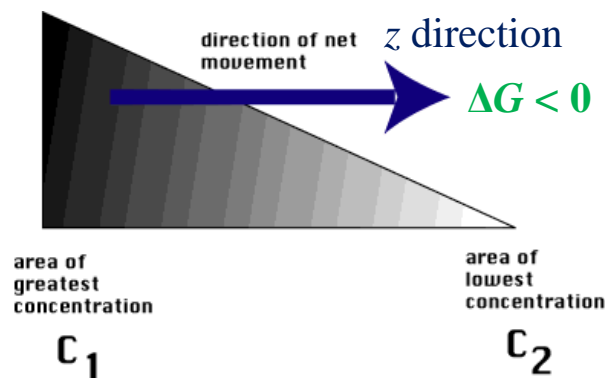
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Some very important background “first”... okay, second!

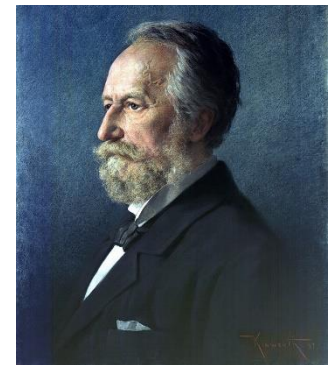
Diffusion coefficient (D , $\text{cm}^2 \text{s}^{-1}$) – “proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient...” (IUPAC Gold Book)

Fick’s first law of steady-state Diffusion: $N_z = -D_z \frac{dc}{dz}$ in 1D

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



Physician & Physiologist



Adolf Eugen Fick
(1829–1901)

from Wiki

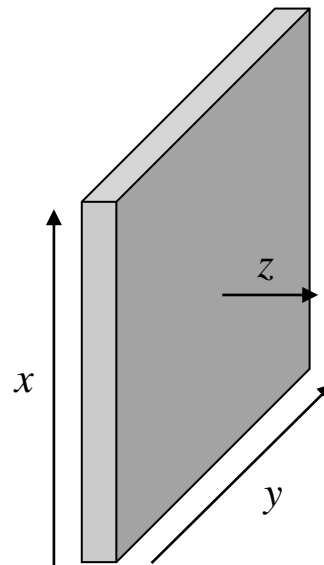
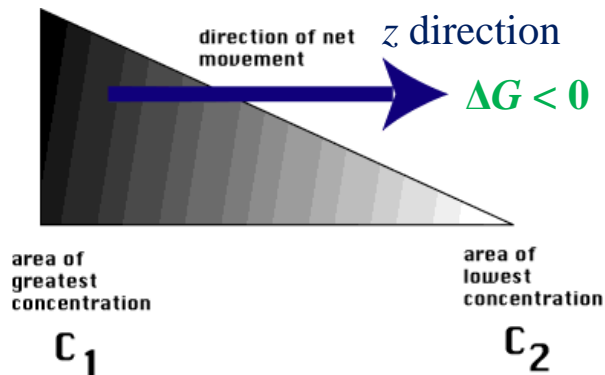
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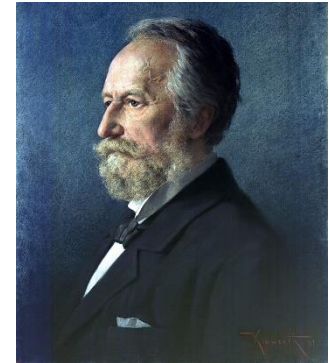
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D also exhibits Arrhenius behavior: $D = D_0 e^{-\frac{E_a}{RT}}$

where D_0 is the maximum D (at infinite T)



Physician & Physiologist



Adolf Eugen Fick
 (1829–1901)

from Wiki

Steady-state? ...

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



Reaction:	HA	A ⁻	H ₃ O ⁺
I	0.150 M	0.000 M	0.000 M
C	-x M	+x M	+x M
E	0.150 - x M	x M	x M

http://chemwiki.ucdavis.edu/Physical_Chemistry/Equilibria/Le_Chatelier%27s_Principle/Ice_Tables



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



<http://buzzworthy.mtv.com/2012/11/14/justin-bieber-vanilla-ice-photo/>



... but for how long? ...



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

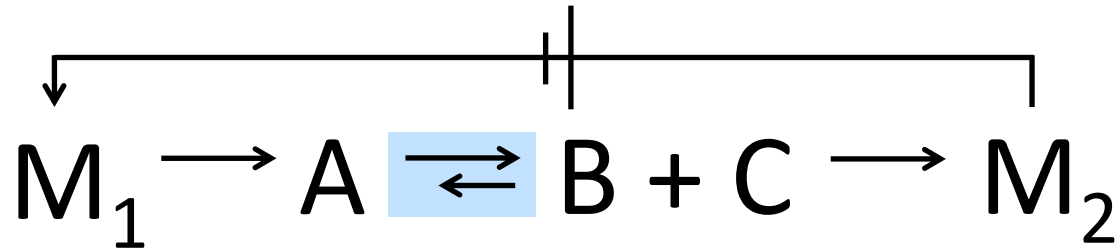
... and in electrochemical systems, as long as a constant potential bias is applied!

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

$\frac{\partial c_A}{\partial t} = \frac{\partial c_B}{\partial t} = \frac{\partial c_C}{\partial t} = 0$, 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? ...

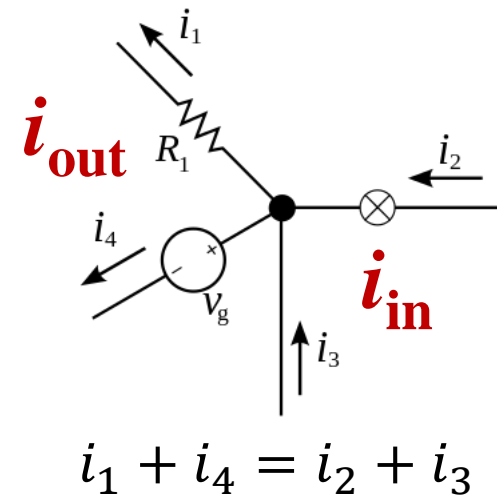
... when the current is at a steady-state, *the current is constant*, and there is no new capacitive charging!



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

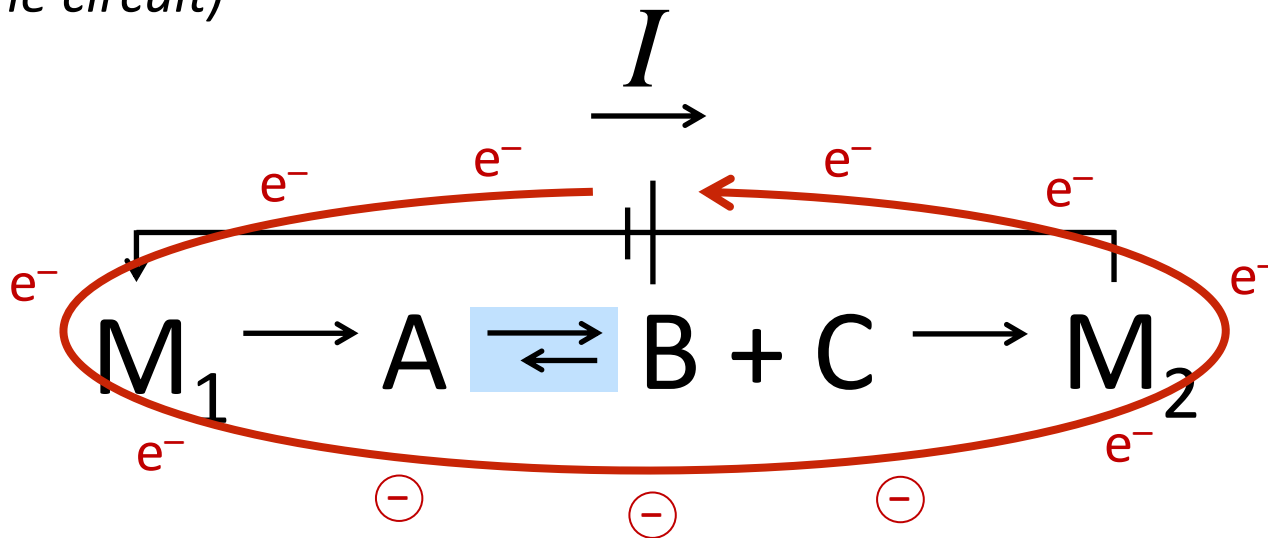
Kirchhoff's Current Law (KCL)

$$\sum_{k=1}^n I_k = 0$$



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)



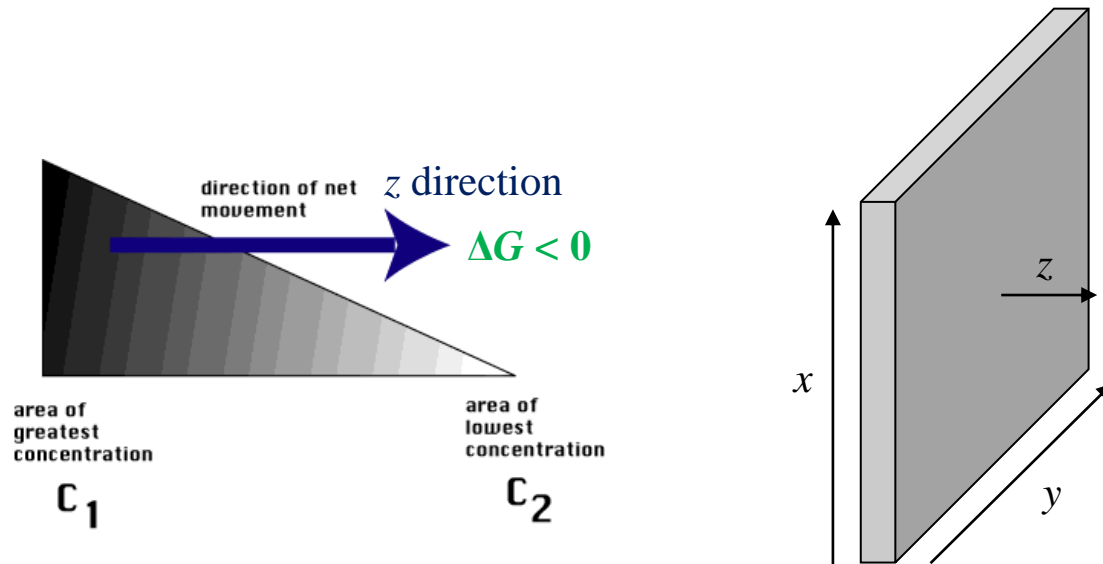
... hey, what are those minus signs at the bottom? ...

Migrating/Drifting Ions!

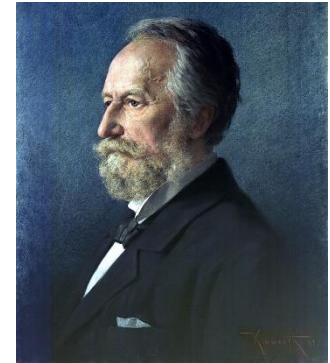
... we'll get to this shortly

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Physician & Physiologist



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Do the units of D make sense?

$$N_z \text{ (mol cm}^{-2} \text{ s}^{-1}, \text{ as } xy) = D_z \cdot dc/dz \text{ ((mol cm}^{-3}) \text{ cm}^{-1}, \text{ as } xyz \text{ z)}$$

$$\text{(mol cm}^{-2} \text{ s}^{-1}, \text{ as } xy) = D_z \cdot \text{(mol cm}^{-4}, \text{ as } xyzz)$$

Therefore, D_z has units of $\text{cm}^2 \text{s}^{-1}$... but as zz ...

Huh? zz ? z^2 ? What?... That was unexpected!... Is it right?...