Lecture #10 of 20

{halfway finished… tear}

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

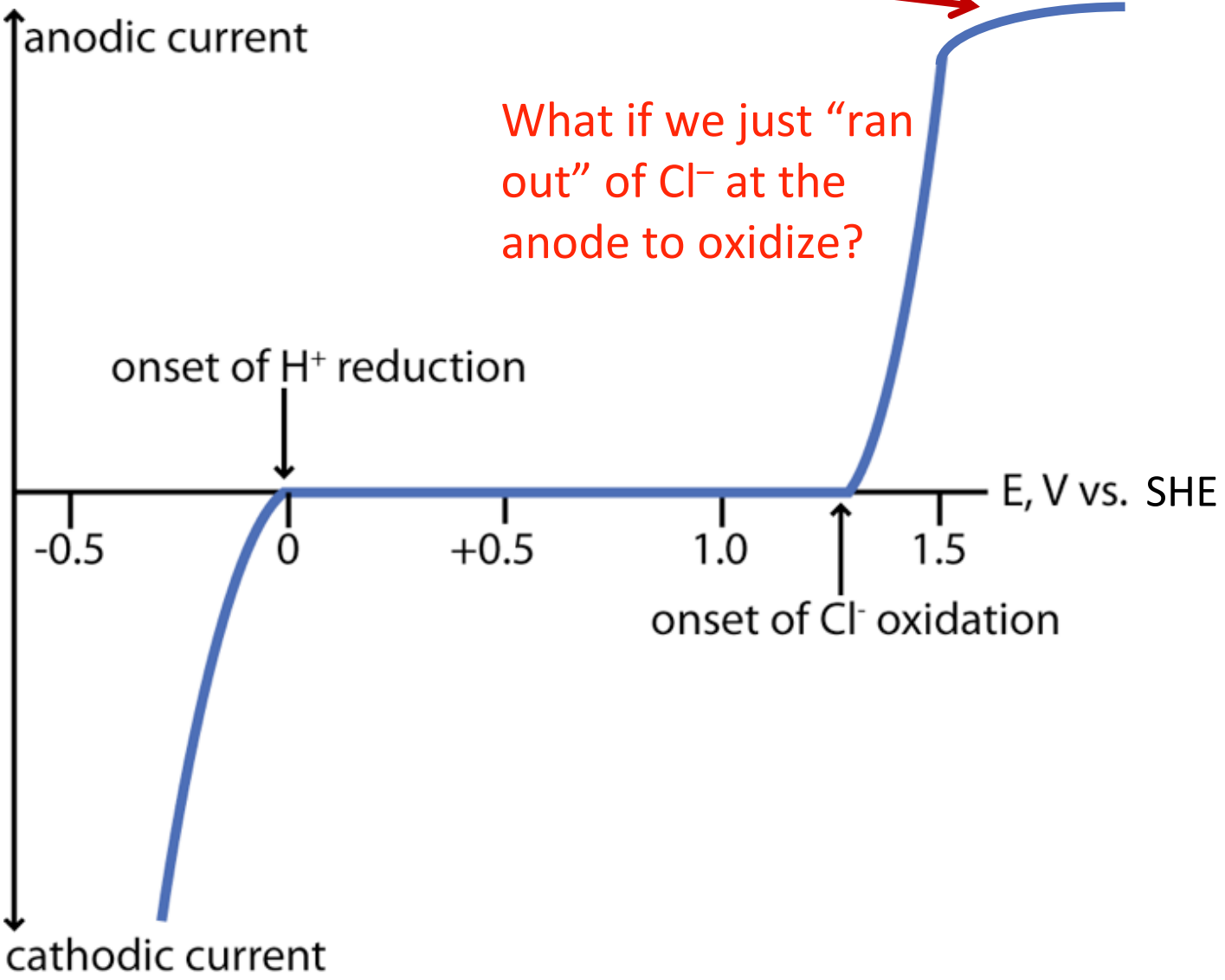
- Chapter 4: Mass transfer

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 spatial dimension x… Enjoy!

$$\frac{\partial c_{\mathrm{A}}}{\partial t} = \sum_i R_{\mathrm{A},i} - \frac{\partial N_{\mathrm{A}}}{\partial x}$$

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

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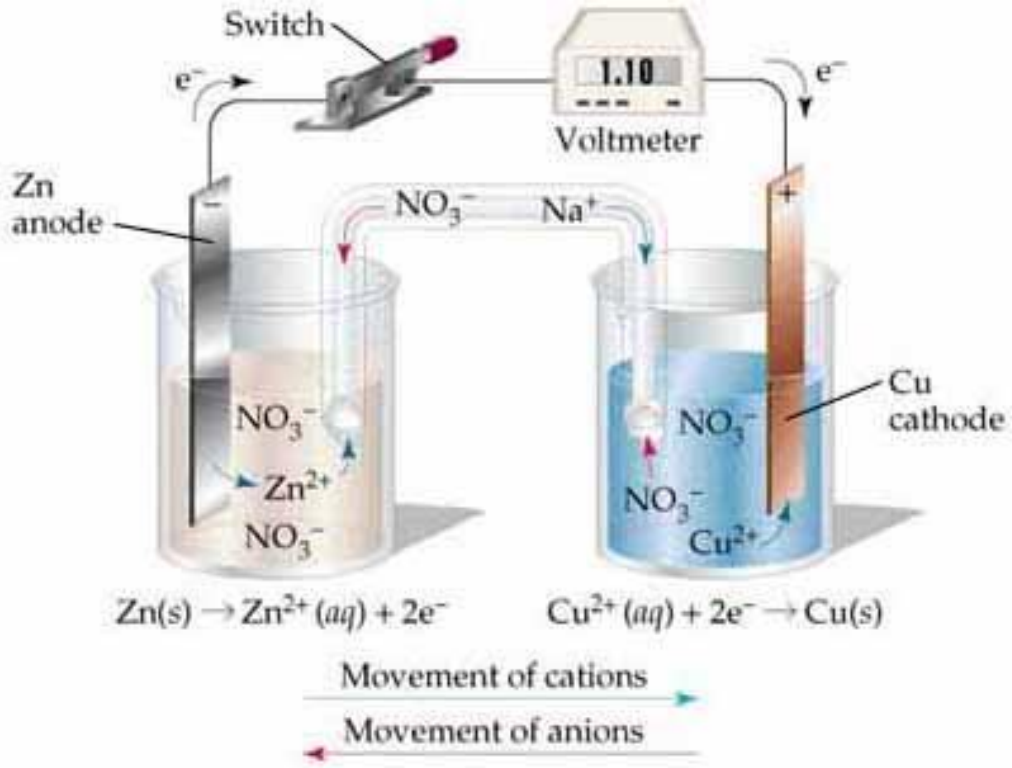
rate of change of the flux (*N*) of species A with respect to position (*x*)

… what is mass flux?
… **it’s simple too**…

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

(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



http://wps.prenhall.com/wps/media/objects/3313/3392587/blb2003.html

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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

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… FYI: even without intentional forced convection, unintentional forced convection (e.g. vibrations) influences an electrochemical experiment after ~30 seconds

(1) **Migrat** *charged)*
Flux (m (electric
potent and
anions



(2) **Diffusi** *radient)*
Net flu ation and
randor

Convection here, too!

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

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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^{-2}) related to flux (***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}*…

$\boldsymbol{J_x = z\,F\,N_x}$ … the Faraday constant… and *z*

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

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

$$\boldsymbol{J} = zF\boldsymbol{N} = F\sum_i z_i\left(-\frac{D_i c_i}{RT}\cdot\boldsymbol{\nabla}\bar{\mu}_i + c_i\boldsymbol{v}\right)$$, where ∇ 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}), $\bar{\mu}_i$ is the electrochemical potential (in units of J mol^{-1}), and $\boldsymbol{v}$ 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… and think *mass action*

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$\boldsymbol{J_x = z\,F\,N_x}$ … the Faraday constant… and z

As we will see, besides the sign, this equals conductivity (σ_i) divided by z_iF…
… and thus in the absence of convection…

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

… where D_i is the diffusion coefficient of species i (in units of cm^2 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 $\boldsymbol{v}$ is the velocity of the solution (in units of cm s^{-1})

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

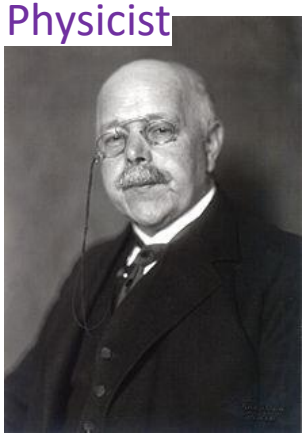
the *Nernst–Planck Equation:*

B&F, 1.4.2 & 4.1.8

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

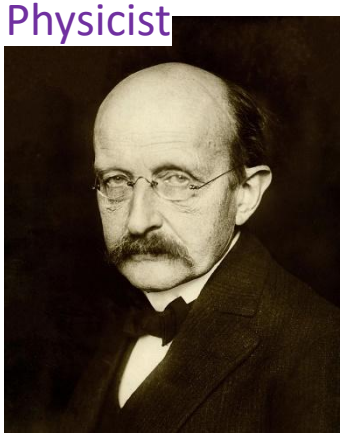
the total **flux** of reactant *i* to a flat electrode (this is $N_i(x)$ in many textbooks – not ours! – especially engineering ones; it has units of mol cm^{-2} s^{-1})

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 $cm^2\ s^{-1}$)

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

the *Nernst–Planck Equation:*

… this C_i should also be $C_i(x)$…

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 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,* $\boldsymbol{E}$)

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

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… and here too…

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*

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… 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 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))
$\mu_i = \mu_i^{o} + RT \ln a_i$ **(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 $\bar{\mu}_i^{\beta} = \mu_i^{\beta}$.

Parsons, *Pure & Appl. Chem.*, 1973, *37*, 501
IUPAC Gold (http://goldbook.iupac.org)

From before, <u>for one species</u> the total flux <u>in one-dimension</u> is

$N = -\frac{Dc}{RT} \cdot \frac{d\bar{\mu}}{dx} + cv$, where again *D* is diffusion coefficient ($cm^2\ s^{-1}$), *c* is concentration ($mol\ cm^{-3}$), $\bar{\mu}$ 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,

$N = -\frac{Dc}{RT} \cdot \frac{d(\mu + zF\phi)}{dx} + cv$… and recall that $\mu_i = \mu_i{}^{o} + RT \ln a_i$ and so,

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

flux

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

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$N = -\frac{Dc}{RT} \cdot \frac{d(\mu^{o} + RT \ln a + zF\phi)}{dx} + cv$… and assuming $a \approx c$,

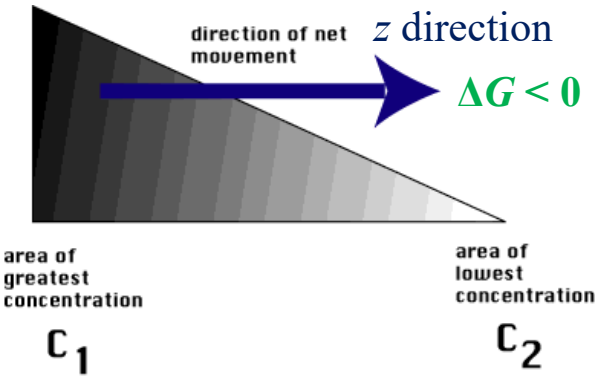
$N = -Dc \cdot \frac{d(\ln c)}{dx} - \frac{zFD}{RT} c \cdot \frac{d\phi}{dx} + cv$… and finally…

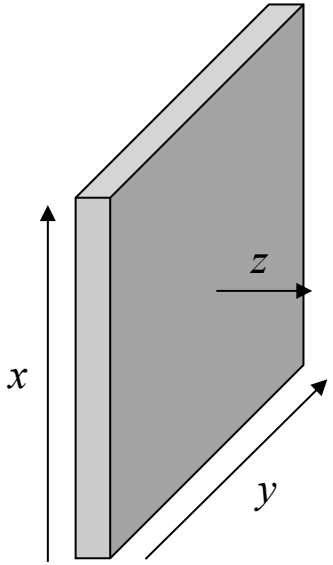
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Diffusion coefficient (*D*, cm^2 s^{-1}) – "proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…" (IUPAC Gold Book)

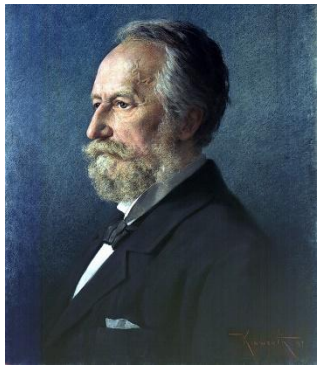
Fick's first law of <u>steady-state</u> Diffusion: $N_z = -D_z \frac{dc}{dz}$ in 1D

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





Physician & Physiologist



Adolf Eugen Fick
(1829–1901)

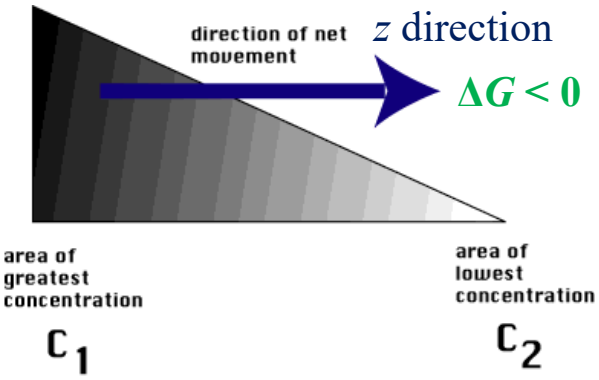
from Wiki

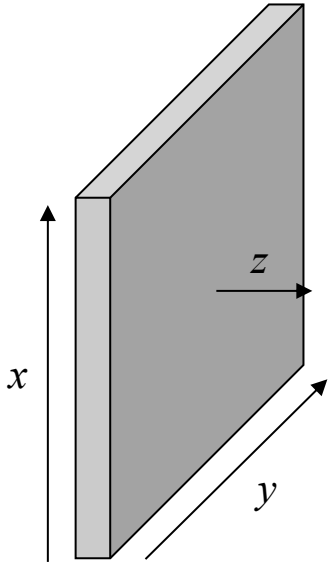
Diffusion coefficient (*D*, cm^2 s^{-1}) – "proportionality constant relating the flux of [the] amount of [an entity to its] concentration gradient…" (IUPAC Gold Book)

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

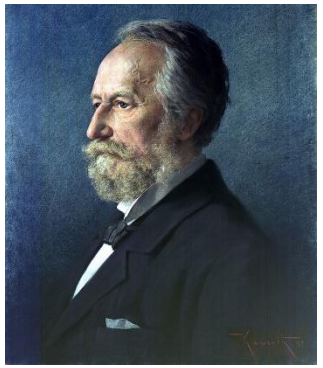
D for solution species exhibits Arrhenius behavior: $D = D_0 e^{-\frac{E_a}{RT}}$

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!

$$A \rightleftharpoons B + C$$

Reaction:	HA	A^-	H_3O^+
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



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

$$A \rightleftharpoons B + C$$

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…

$$\longrightarrow A \rightleftharpoons B + C \longrightarrow$$

… but for how long? …

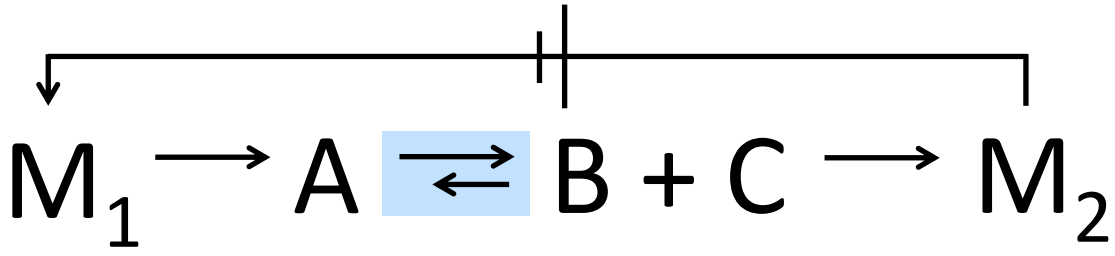
$$M_1 \longrightarrow A \rightleftharpoons B + C \longrightarrow M_2$$

… as long as the rate of supply in and the rate of exit out are the same…
… 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

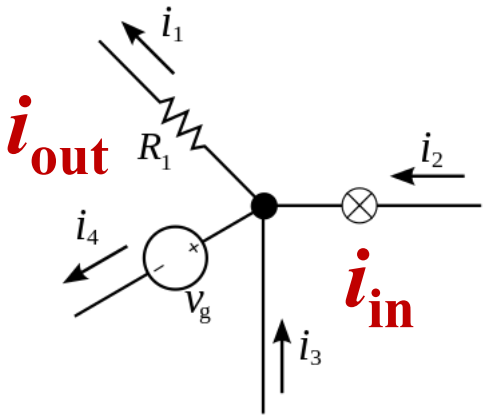
… when the current is at a steady-state, *the current is constant*, and there is no new capacitive charging!



… for steady-state current, KCL applies… no, not KC**l**… but KC**L**!

Kirchhoff's Current Law (KCL)

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

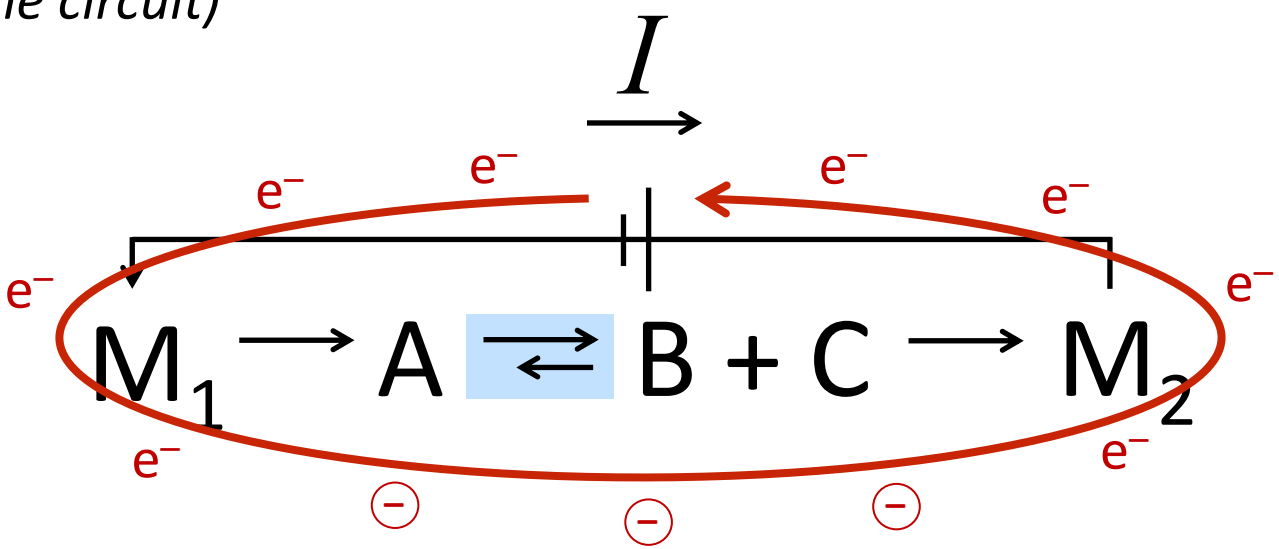


$$i_1 + i_4 = i_2 + i_3$$

http://en.wikipedia.org/wiki/Kirchhoff%27s_circuit_laws

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)



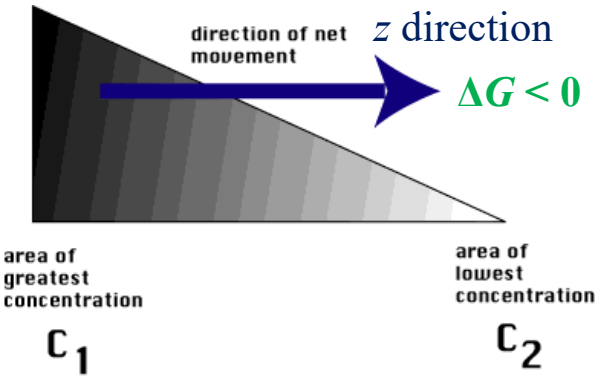
… hey, what are those minus signs at the bottom? …

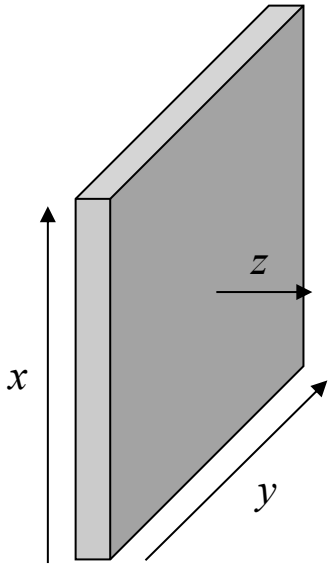
Migrating/Drifting Ions!

… we'll get to this shortly

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 <u>steady-state</u> Diffusion: $N_z = -D_z \frac{dc}{dz}$ in 1D





Do the units of *D* make sense?

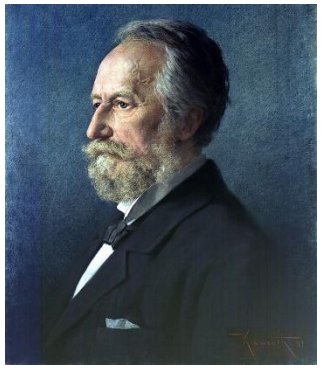
N_z (mol **cm^{-2}** s^{-1}, as ***xy***) = D_z · d*c*/d*z* ((mol **cm^{-3}**) **cm^{-1}**, as ***xyz z***)

(mol **cm^{-2}** s^{-1}, as ***xy***) = D_z · (mol **cm^{-4}**, as ***xyzz***)

Therefore, D_z is has units of **cm^2** s^{-1}… but as ***zz***…

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

Physician & Physiologist



Adolf Eugen Fick
(1829–1901)

from Wiki