Membrane (Electric) Potentials

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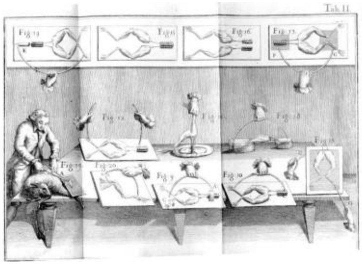
A Short History Lesson…

Electrochemistry is associated with Luigi Galvani who discovered "animal electricity," while trying to Frankenstein frogs' legs (1791)



Physician, Physicist, Philosopher

Luigi Galvani
(1737–1798)
from Wiki

… now how is that electrochemistry?… what the electrons doing?
… well, this is mostly due to the ions…

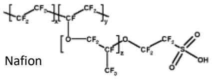
https://en.wikipedia.org/wiki/Luigi_Galvani

Lecture Outline (40 min) – Membrane Electric Potentials

- **Donnan potentials**
- **Liquid-junction potentials**
- **Membrane potentials**
- **pH meter**
- **Ion-selective electrodes**

Donnan potential/exclusion: *A special liquid-junction potential due to* ***fixed charges****…* here are two systems in which they play a prominent role: 5

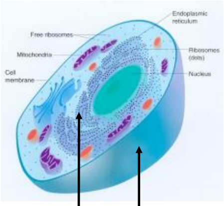
<u>an ionomer film</u>
(used in fuel cells, electrolyzers, etc.)



Nafion

http://www.nafion.mysite.com/

<u>a biological cell</u>



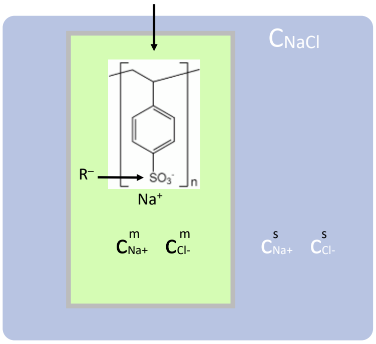
semipermeable membrane

membrane impermeable to charged macromolecules

http://www.williamsclass.com/

… consider this model which applies to both scenarios… 6

a film of poly(styrene sulfonate)… *which is like Nafion*



C_{NaCl}

R^-

SO_3^-

Na^+

C^m_{Na+} C^m_{Cl-}

C^s_{Na+} C^s_{Cl-}

Because differences in electrochemical potential ($\bar{\mu}_i^o$) – *think free energy* – drive net mass transport *(of unstirred solutions)*, mobile Na⁺ and Cl⁻ partition between the membrane and the solution in compliance with their electrochemical potentials: 7

$$\underbrace{\mu_i^{o,m} + RT\ln\gamma_i^m + RT\ln c_i^m + z_iF\phi^m}_{m} = \underbrace{\mu_i^{o,s} + RT\ln\gamma_i^s + RT\ln c_i^s + z_iF\phi^s}_{s}$$

(for ion "i"… its electrochemical potential in the membrane (m)… is the same as in solution (s)… ***this is the definition of something that has equilibrated****)*

Because differences in electrochemical potential ($\bar{\mu}_i^o$) – *think free energy* – drive net mass transport *(of unstirred solutions)*, mobile Na⁺ and Cl⁻ partition between the membrane and the solution in compliance with their electrochemical potentials:

$$\mu_i^{o,m} + RT\ln\gamma_i^m + RT\ln c_i^m + z_iF\phi^m = \mu_i^{o,s} + RT\ln\gamma_i^s + RT\ln c_i^s + z_iF\phi^s$$

… Assuming that standard state chemical potentials (μ_i^{o}) are the same inside and outside of the membrane, we can easily solve for the ("Galvani" / inner) electric potential difference, $\phi^{\mathrm{m}} - \phi^{\mathrm{s}}$

… *which is also exactly what is required to calculate liquid-junction potentials*!

$$\phi^m - \phi^s = \frac{RT}{z_iF}\ln\left(\frac{\gamma_i^s c_i^s}{\gamma_i^m c_i^m}\right) = E_{\mathrm{Donnan}}$$

… so we can express ***E***

$$E_{\mathrm{Donnan}} = \frac{RT}{(1)F}\ln\left(\frac{a_{\mathrm{Na^+}}^s}{a_{\mathrm{Na^+}}^m}\right) = \frac{RT}{(-1)F}\ln\left(\frac{a_{\mathrm{Cl^-}}^s}{a_{\mathrm{Cl^-}}^m}\right)$$

… backing up… **<u>four</u> thermodynamic equations with almost the same derivation.**

Gibbs Free Energy (J)

$$\Delta G^{\beta} = \Delta G^{\mathrm{o}\,\beta} + RT\ln Q^{\beta} = \mu_{\mathrm{C}}^{\beta} - \mu_{\mathrm{A}}^{\beta} - \mu_{\mathrm{B}}^{\beta}$$

(Electro)Chemical Potential (J)

$\mathrm{A}^{aq} + \mathrm{B}^{aq} \rightleftarrows \mathrm{C}^{aq}$

$$\left(\frac{\partial\Delta G^{\beta}}{\partial n_i^{\beta}}\right)_{T_{\mathrm{sys}},p_{\mathrm{sys}},n_{j\neq i}^{\beta}} = \mu_i^{\beta} = \mu_i^{\mathrm{o}\,\beta} + k_{\mathrm{B}}T\ln a_i^{\beta}$$

$$Q = \frac{a_{\mathrm{C}}}{a_{\mathrm{A}}\,a_{\mathrm{B}}} \approx \frac{[\mathrm{C}]}{[\mathrm{A}]\,[\mathrm{B}]}$$

Nernst Potential (V)

$$-\frac{\Delta G^{\beta}}{nF} = E_{\mathrm{cell}} = E_{\mathrm{cell}}^{\mathrm{o}} - \frac{2.303RT}{nF}\log Q = E_{\mathrm{red}} - E_{\mathrm{ox}}$$

$$Q = \frac{Q_{\mathrm{red}}}{Q_{\mathrm{ox}}} \approx \frac{[\mathrm{A}_{\mathrm{red}}^{-}]\,[\mathrm{B}_{\mathrm{ox}}^{+}]}{[\mathrm{A}_{\mathrm{red}}]\,[\mathrm{B}_{\mathrm{ox}}]}$$

Donnan Potential (V)

$$E_{\mathrm{mem}} = -\frac{2.303RT}{z_iF}\log\frac{a_{\mathrm{A^-}}^{\beta}}{a_{\mathrm{A^-}}^{\alpha}} \approx -\frac{59.2\ \mathrm{mV}}{z_i}\log\frac{[\mathrm{A}^{-\,\beta}]}{[\mathrm{A}^{-\,\alpha}]}$$

$$E_{\mathrm{Donnan}} = \frac{RT}{F}\ln\left(\frac{a_{\mathrm{Na^+}}^s}{a_{\mathrm{Na^+}}^m}\right) = \ominus\frac{RT}{F}\ln\left(\frac{a_{\mathrm{Cl^-}}^s}{a_{\mathrm{Cl^-}}^m}\right)$$

But this has additional consequences not relevant to the other thermodynamic relations… divide both sides by *RT*/*F* and invert the argument of the “ln()” on the right to eliminate the negative sign, and we have…

$$\frac{a_{Na^+}^{s}}{a_{Na^+}^{m}} = \frac{a_{Cl^-}^{m}}{a_{Cl^-}^{s}}$$

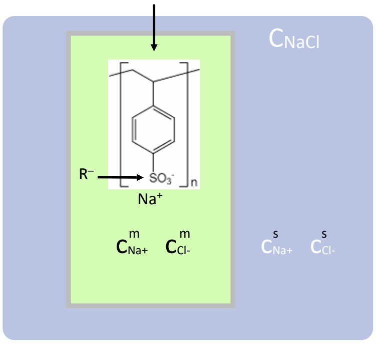
… or…

$$a_{\mathrm{Na^+}}^{\mathrm{s}}a_{\mathrm{Cl^-}}^{\mathrm{s}} = a_{\mathrm{Na^+}}^{\mathrm{m}}a_{\mathrm{Cl^-}}^{\mathrm{m}}$$

… recall the scenario we are analyzing…

… with R⁻ representing the fixed charges…

a film of poly(styrene sulfonate)



$$a^s_{Na^+}a^s_{Cl^-} = a^m_{Na^+}a^m_{Cl^-}$$

… if these are dilute electrolytes, we can neglect activity coefficients…

$$c^s_{Na^+}c^s_{Cl^-} = c^m_{Na^+}c^m_{Cl^-} \quad (1)$$

now, there is an additional constraint: the bulk of the solution and the bulk of the membrane must be *electrically neutral*:

$$c^s_{Na^+} = c^s_{Cl^-} \quad (2) \qquad c^m_{Na^+} = c^m_{Cl^-} + c^m_{R^-} \quad (3)$$

… these ***3 simple equations*** also teach us about ***Donnan exclusion*** as follows…

… ***Donnan exclusion*** is described by an equation that is quadratic in c^m_{Cl-}…

$$(1) \quad \boxed{c^s_{Na^+}c^s_{Cl^-}} = c^m_{Na^+}c^m_{Cl^-}$$

$$(2) \quad c^s_{Na^+} = c^s_{Cl^-}$$

because in solution, $c_{Na+} = c_{Cl-}$, of course!

$$(c^s_{Cl^-})^2$$

… ***Donnan exclusion*** is described by an equation that is quadratic in c^m_{Cl-}…

$$\textbf{(1)}\quad \boxed{c^{s}_{Na^+} c^{s}_{Cl^-}} = \boxed{c^{m}_{Na^+}} c^{m}_{Cl^-}$$

$$\textbf{(2)}\quad c^{s}_{Na^+} = c^{s}_{Cl^-} \qquad\qquad c^{m}_{Na^+} = c^{m}_{Cl^-} + c^{m}_{R^-}\quad \textbf{(3)}$$

$$\left(c^{s}_{Cl^-}\right)^2 = \left(c^{m}_{Cl^-}\right)^2 + c^{m}_{R^-} c^{m}_{Cl^-}$$

$$0 = \underbrace{\left(c^{m}_{Cl^-}\right)^2}_{a\ \ x^2} + \underbrace{c^{m}_{R^-} c^{m}_{Cl^-}}_{b\ \ x} - \underbrace{\left(c^{s}_{Cl^-}\right)^2}_{c}$$

… use the quadratic formula to solve for c^m_{Cl-} and one gets…

$$c^{m}_{Cl^-} = \frac{\overset{-b}{-c^{m}_{R^-}} + \sqrt{\overset{b^2}{\left(c^{m}_{R^-}\right)^2} + \overset{4ac}{4\left(c^{s}_{Cl^-}\right)^2}}}{\underset{2a}{2}} = \frac{c^{m}_{R^-}}{2}\left(\sqrt{1 + 4\left(\frac{c^{s}_{Cl^-}}{c^{R}_{Cl^-}}\right)^2} - 1\right)$$

$$c^{m}_{Cl^-} = \frac{-c^{m}_{R^-} + \sqrt{\left(c^{m}_{R^-}\right)^2 + 4\left(c^{s}_{Cl^-}\right)^2}}{2} = \frac{c^{m}_{R^-}}{2}\left(\sqrt{1 + 4\left(\frac{c^{s}_{Cl^-}}{c^{m}_{R^-}}\right)^2} - 1\right)$$

if $c^{s}_{Cl^-} \ll c^{m}_{R^-}$ (which is the typical case of interest), then…

$$\sqrt{1 + 4\left(\frac{c^{s}_{Cl^-}}{c^{m}_{R^-}}\right)^2} \approx 1 + 2\left(\frac{c^{s}_{Cl^-}}{c^{m}_{R^-}}\right)^2$$

(Taylor/Maclaurin series expansion to the first 3 (or 4) terms)

$$c^{m}_{Cl^-} = \frac{-c^{m}_{R^-} + \sqrt{\left(c^{m}_{R^-}\right)^2 + 4\left(c^{s}_{Cl^-}\right)^2}}{2} = \frac{c^{m}_{R^-}}{2}\left(\sqrt{1 + 4\left(\frac{c^{s}_{Cl^-}}{c^{m}_{R^-}}\right)^2} - 1\right)$$

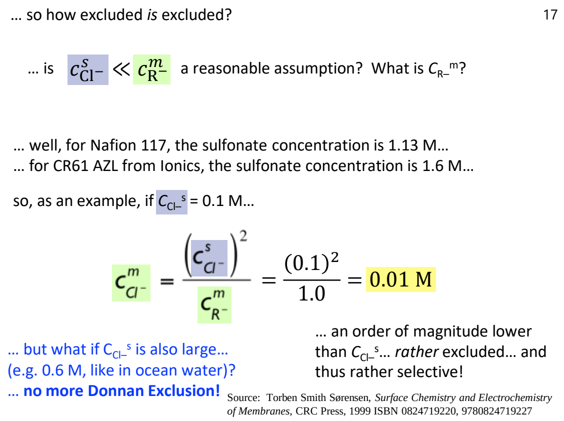
if $c^{s}_{Cl^-} \ll c^{m}_{R^-}$ (which is the typical case of interest), then…

$$\sqrt{1 + 4\left(\frac{c^{s}_{Cl^-}}{c^{m}_{R^-}}\right)^2} \approx 1 + 2\left(\frac{c^{s}_{Cl^-}}{c^{m}_{R^-}}\right)^2$$

$$\boldsymbol{c^{m}_{Cl^-}} = \frac{c^{m}_{R^-}}{2}\left(1 + 2\left(\frac{c^{s}_{Cl^-}}{c^{m}_{R^-}}\right)^2 - 1\right) = \frac{\left(c^{s}_{Cl^-}\right)^2}{c^{m}_{R^-}}$$

… fixed charge sites are responsible for the *electrostatic exclusion* of mobile "like" charges (co-ions) from a membrane, cell, etc. This is ***Donnan Exclusion***.

… the larger is $C_{R-}{}^{m}$, the smaller is $C_{Cl-}{}^{m}$



… so how excluded *is* excluded? 17

… is $c^{s}_{\text{Cl}^-} \ll c^{m}_{\text{R}^-}$ a reasonable assumption? What is $C_{R^-}^{m}$?

… well, for Nafion 117, the sulfonate concentration is 1.13 M…
… for CR61 AZL from Ionics, the sulfonate concentration is 1.6 M…

so, as an example, if $C_{Cl^-}^{s}$ = 0.1 M…

$$c^{m}_{Cl^-} = \frac{\left(c^{s}_{Cl^-}\right)^2}{c^{m}_{R^-}} = \frac{(0.1)^2}{1.0} = 0.01\ \text{M}$$

… but what if $C_{Cl^-}^{s}$ is also large…
(e.g. 0.6 M, like in ocean water)?
… **no more Donnan Exclusion!**

… an order of magnitude lower than $C_{Cl^-}^{s}$… *rather* excluded… and thus rather selective!

Source: Torben Smith Sørensen, *Surface Chemistry and Electrochemistry of Membranes*, CRC Press, 1999 ISBN 0824719220, 9780824719227

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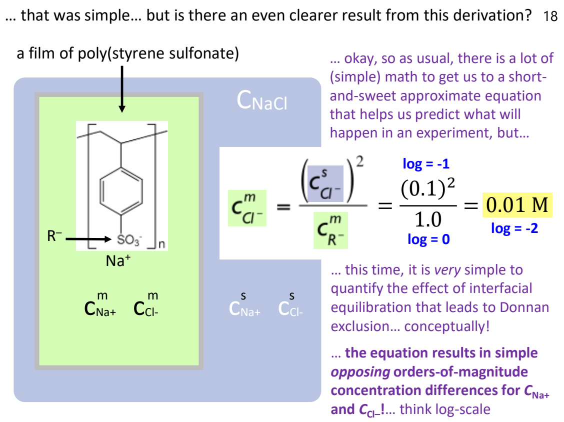


… that was simple… but is there an even clearer result from this derivation? 18

a film of poly(styrene sulfonate)

… okay, so as usual, there is a lot of (simple) math to get us to a short-and-sweet approximate equation that helps us predict what will happen in an experiment, but…

$$c^{m}_{Cl^-} = \frac{\left(c^{s}_{Cl^-}\right)^2}{c^{m}_{R^-}} = \frac{(0.1)^2}{1.0} = 0.01\ \text{M}$$

log = -1

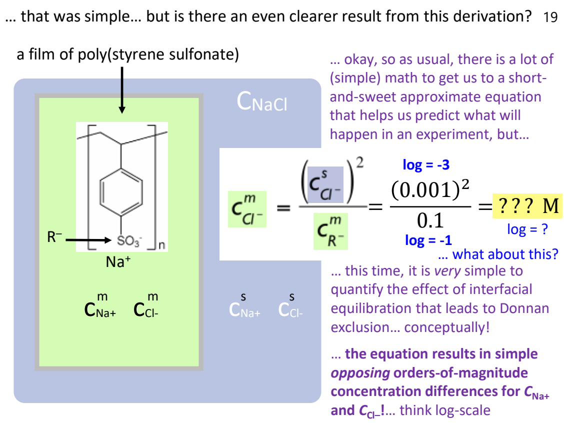
log = 0

log = -2

… this time, it is *very* simple to quantify the effect of interfacial equilibration that leads to Donnan exclusion… conceptually!

… **the equation results in simple *opposing* orders-of-magnitude concentration differences for C_{Na+} and C_{Cl-}!**… think log-scale

18



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a film of poly(styrene sulfonate)

… okay, so as usual, there is a lot of (simple) math to get us to a short-and-sweet approximate equation that helps us predict what will happen in an experiment, but…

$$c^{m}_{Cl^-} = \frac{\left(c^{s}_{Cl^-}\right)^2}{c^{m}_{R^-}} = \frac{(0.001)^2}{0.1} = ???\ \text{M}$$

log = -3

log = -1

log = ?

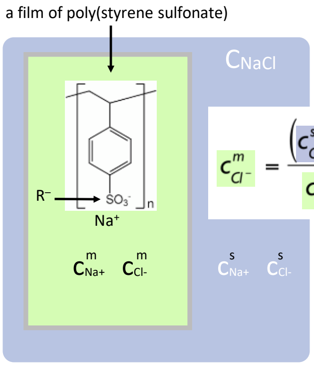
… what about this?

… this time, it is *very* simple to quantify the effect of interfacial equilibration that leads to Donnan exclusion… conceptually!

… **the equation results in simple *opposing* orders-of-magnitude concentration differences for C_{Na+} and C_{Cl-}!**… think log-scale

19

… that was simple… but is there an even clearer result from this derivation? 20



… okay, so as usual, there is a lot of (simple) math to get us to a short-and-sweet approximate equation that helps us predict what will happen in an experiment, but…

$$C^{m}_{Cl^-} = \frac{\left(C^{s}_{Cl^-}\right)^2}{C^{m}_{R^-}} = \frac{\overset{\text{log = -3}}{(0.001)^2}}{\underset{\text{log = -1}}{0.1}} = \underset{\text{log = -5}}{10\ \mu\text{M}}$$

… super simple!

… this time, it is *very* simple to quantify the effect of interfacial equilibration that leads to Donnan exclusion… conceptually!

… **the equation results in simple *opposing* orders-of-magnitude concentration differences for C_{Na+} and C_{Cl-}!**… think log-scale

20

example: Given the following two RHE REs, calculate E_{cell} and E_{mem}? 21

$$\text{Pt }(s)\ |\ \text{H}_2\ (g,\ 1\text{ bar})\ |\ \overset{\alpha}{\text{HCl }(aq,\ 0.1\text{ M})}\ ||\ \overset{\beta}{\text{HCl }(aq,\ 0.01\text{ M})}\ |\ \text{H}_2\ (g,\ 1\text{ bar})\ |\ \text{Pt }(s)$$

… does this have a liquid junction or a Donnan potential?

… it depends on what the middle lines are…
… assume they represent a poly(styrene sulfonate) (PSS) film…

21

example: Given the following two RHE REs, calculate E_{cell} and E_{mem}? 22

$$\text{Pt }(s)\ |\ \text{H}_2\ (g,\ 1\text{ bar})\ |\ \overset{\alpha}{\text{HCl }(aq,\ 0.1\text{ M})}\ |\ \overset{\beta}{\text{HCl }(aq,\ 0.01\text{ M})}\ |\ \text{H}_2\ (g,\ 1\text{ bar})\ |\ \text{Pt }(s)$$

… does this have a liquid junction or a Donnan potential? **Donnan!**

22

example: Given the following two RHE REs, calculate E_{cell} and E_{mem}?

$$\overset{}{\text{Pt }(s)\mid \text{H}_2\ (g,\ 1\ \text{bar})\mid \overset{\alpha}{\text{HCl }(aq,\ 0.1\ \text{M})}\ \mathbf{|}\ \overset{\beta}{\text{HCl }(aq,\ 0.01\ \text{M})}\mid \text{H}_2\ (g,\ 1\ \text{bar})\mid \text{Pt (s)}}$$

$$E_{\text{cell}} = E_{\text{Nernst}} + E_{\text{mem}} = E^{\text{o}} \underbrace{- \frac{RT}{2F}\ln\left(\frac{a^{\beta}_{H_2}a^{\alpha}_{H^+}{}^{2}}{a^{\beta}_{H^+}{}^{2}\ a^{\alpha}_{H_2}}\right)}_{\text{Nernst potential}} + \underbrace{\frac{RT}{F}\ln\left(\frac{a^{\alpha}_{HCl}}{a^{\beta}_{HCl}}\right)}_{\text{Donnan potential}}$$

$$E_{\text{cell}} = -\frac{RT}{F}\ln\left(\frac{a^{\alpha}_{H^+}}{a^{\beta}_{H^+}}\right) + \frac{RT}{F}\ln\left(\frac{a^{\alpha}_{HCl}}{a^{\beta}_{HCl}}\right) = \mathbf{0\ mV}$$

… so what is E_{Nernst}, and what is E_{mem}? $\mathbf{E_{Nernst} \approx -60\ mV;\ E_{mem} \approx +60\ mV}$

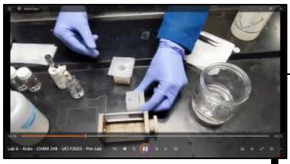
$$\text{Ag }(s)\mid \text{AgCl }(s)\mid \overset{\alpha}{\text{HCl }(aq,\ 0.1\ \text{M})}\ \mathbf{|}\ \overset{\beta}{\text{HCl }(aq,\ 0.01\ \text{M})}\mid \text{AgCl }(s)\mid \text{Ag}(s)$$

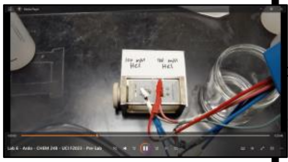
… this is your lab!

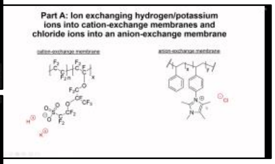
$$E_{\text{cell}} = -\frac{RT}{F}\ln\left(\frac{a^{\beta}_{Cl^-}}{a^{\alpha}_{Cl^-}}\right) + \frac{RT}{F}\ln\left(\frac{a^{\alpha}_{HCl}}{a^{\beta}_{HCl}}\right) = \mathbf{120\ mV!}$$

… so what is E_{Nernst}, and what is E_{mem}? $\mathbf{E_{Nernst} \approx +60\ mV;\ E_{mem} \approx +60\ mV}$

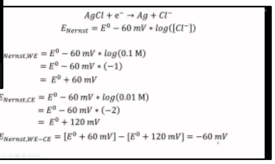
Images from this amazing pre-lab video for your next lab… thanks, Leanna!







Part A: Ion exchanging hydrogen/potassium ions into cation-exchange membranes and chloride ions into an anion-exchange membrane



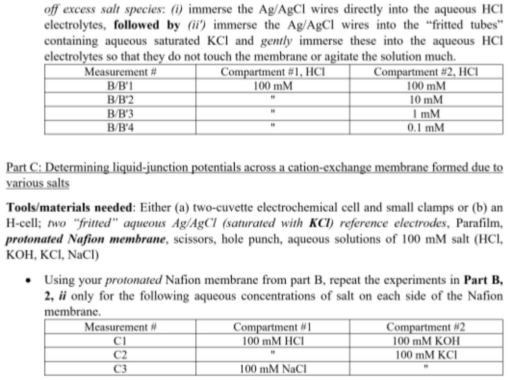
$$AgCl + e^- \rightarrow Ag + Cl^-$$
$$E_{Nernst} = E^0 - 60\ mV * log([Cl^-])$$

$$\begin{aligned} E_{Nernst,WE} &= E^0 - 60\ mV * log(0.1\ \text{M}) \\ &= E^0 - 60\ mV * (-1) \\ &= E^0 + 60\ mV \end{aligned}$$

$$\begin{aligned} E_{Nernst,CE} &= E^0 - 60\ mV * log(0.01\ \text{M}) \\ &= E^0 - 60\ mV * (-2) \\ &= E^0 + 120\ mV \end{aligned}$$

$$E_{Nernst,WE-CE} = [E^0 + 60\ mV] - [E^0 + 120\ mV] = -60\ mV$$

And a screenshot of the lab document… makes sense, right?



off excess salt species: *(i)* immerse the Ag/AgCl wires directly into the aqueous HCl electrolytes, **followed by** *(ii')* immerse the Ag/AgCl wires into the "fritted tubes" containing aqueous saturated KCl and *gently* immerse these into the aqueous HCl electrolytes so that they do not touch the membrane or agitate the solution much.

Measurement #	Compartment #1, HCl	Compartment #2, HCl
B/B'1	100 mM	100 mM
B/B'2	"	10 mM
B/B'3	"	1 mM
B/B'4	"	0.1 mM

Part C: Determining liquid-junction potentials across a cation-exchange membrane formed due to various salts

Tools/materials needed: Either (a) two-cuvette electrochemical cell and small clamps or (b) an H-cell; *two "fritted" aqueous Ag/AgCl (saturated with* ***KCl****) reference electrodes*, Parafilm, ***protonated Nafion membrane***, scissors, hole punch, aqueous solutions of 100 mM salt (HCl, KOH, KCl, NaCl)

- Using your *protonated* Nafion membrane from part B, repeat the experiments in **Part B, 2, *ii*** only for the following aqueous concentrations of salt on each side of the Nafion membrane.

Measurement #	Compartment #1	Compartment #2
C1	100 mM HCl	100 mM KOH
C2	"	100 mM KCl
C3	100 mM NaCl	"

Lecture Outline (30 min) – Membrane Electric Potentials

- Donnan potentials
- **Liquid-junction potentials**
- **Membrane potentials**
- **pH meter**
- **Ion-selective electrodes**

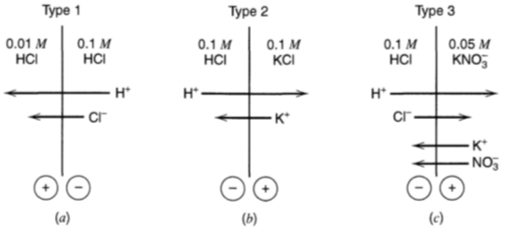
Two general ***liquid junctions*** that electrochemists care about (the most)…

an SCE

an ISE (for nitrate ions)

… ***liquid junctions***:

when two ionic solutions are separated across an interface that prevents bulk mixing of the ions, but has ionic permeability, a potential (drop) develops called the *liquid junction potential*.



same salt;
different conc.

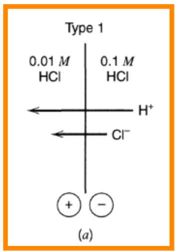
one ion in common;
same conc.

everything else

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 2.3.2

… example “1”:

- starting at the side with larger ion concentration
- the ion the with larger mobility will impart its charge to the opposite side of the junction



same salt;
different conc.

… conceptually, let’s think about a condition in the limit where H^+ transports much faster than Cl^-…

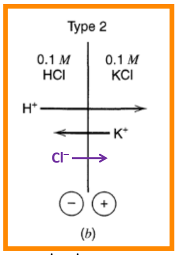
… as H^+ *diffuses* down its concentration gradient, an electrostatic force is exerted on Cl^- to pull it along by *migration/drift* (at a larger flux) while at the same time slowing down transport of H^+

… this happens until both H^+ and Cl^- have the same flux for transport and at which time the system has attained steady state and *has generated a maximum liquid-junction potential*.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 2.3.2

… example “2”:

- compare dissimilar ions (cations or anions)
- the ion with the larger mobility will impart its charge to the opposite side of the junction



one ion in common;
same conc.

… let’s walk through how this one works too…

… the sign of the liquid-junction potential is obvious for Types 1 and 2 (but not Type 3) based on the mobilities of the individual ions…

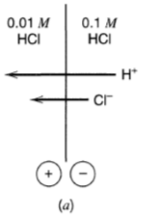
… and so, when in doubt, think logically about the sign of the potential to verify answers…

… and yes, Cl^- will *migrate/drift* based on the electric potential formed by cation transport

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 2.3.2

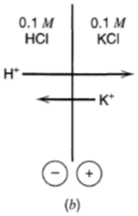
we use *transport/transference numbers*, which describe ***transport kinetics***, to determine the liquid-junction potential… using mobilities/diffusion coefficients found in lookup tables (for derivations, see B&F, pp. 70 – 72)…

Type 1



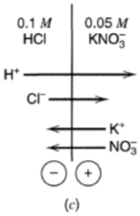
same salt;
different concentrations

Type 2



same cation or anion;
different counter ion;
same concentration

Type 3



no common ions,
and/or one common
ion; different concs

we use *transport/transference numbers*, which describe ***transport kinetics***, to determine the liquid-junction potential… using mobilities/diffusion coefficients found in lookup tables (for derivations, see B&F, pp. 70 – 72)…

Type 1
$$E_j = (\phi^\beta - \phi^\alpha) = (t_+ - t_-)\frac{RT}{F}\ln\frac{a(\alpha)}{a(\beta)}$$
… use the activity of the entire salt

Type 2
$$E_j = \pm\frac{RT}{F}\ln\frac{\sum_i |z_i| u_i C_i(\alpha)}{\sum_i |z_i| u_i C_i(\beta)}$$
… use the conductivity due to all ions, even the common one

(with a few assumptions, pg. 72)

… sign depends on the charge of the dissimilar ion:
(+) when cations are dissimilar, and (–) when anions are dissimilar

Type 3
$$E_j = \frac{\sum_i \frac{|z_i| u_i}{z_i}[C_i(\beta) - C_i(\alpha)]}{\sum_i |z_i| u_i [C_i(\beta) - C_i(\alpha)]}\frac{RT}{F}\ln\frac{\sum_i |z_i| u_i C_i(\alpha)}{\sum_i |z_i| u_i C_i(\beta)}$$

the *Henderson Eq.*

(with a few assumptions, pg. 72)

… as written, these equations calculate E_j at β *vs* α

Example, AGAIN: Given the following two RHE REs, calculate E_{cell} and E_{mem}?

Pt (*s*) | H_2 (*g*, 1 bar) | HCl (*aq*, 0.1 M) $\overset{\alpha}{}$ || $\overset{\beta}{}$ HCl (*aq*, 0.01 M) | H_2 (*g*, 1 bar) | Pt (s)

… does this have a liquid junction or a Donnan potential?

… it depends on what the middle lines are…

… assume they represent a single porous glass frit (not PSS)…

Example, AGAIN: Given the following two RHE REs, calculate E_{cell} and E_{mem}?

Pt (*s*) | H_2 (*g*, 1 bar) | HCl (*aq*, 0.1 M) $\overset{\alpha}{}$ | $\overset{\beta}{}$ HCl (*aq*, 0.01 M) | H_2 (*g*, 1 bar) | Pt (s)

… does this have a liquid junction or a Donnan potential? **LJ!**

*Example, **AGAIN***: Given the following two RHE REs, calculate E_{cell} and E_{mem}?

$$\text{Pt }(s) \mid \text{H}_2\ (g,\ 1\text{ bar}) \mid \overset{\alpha}{\text{HCl }(aq,\ 0.1\text{ M})}\ \Vert\ \overset{\beta}{\text{HCl }(aq,\ 0.01\text{ M})} \mid \text{H}_2\ (g,\ 1\text{ bar}) \mid \text{Pt }(s)$$

$$E_{\text{cell}} = E_{\text{Nernst}} + E_{\text{mem}} = E^{\text{o}} \underbrace{- \frac{RT}{2F}\ln\left(\frac{a^{\beta}_{H_2} {a^{\alpha}_{H^+}}^2}{{a^{\beta}_{H^+}}^2\ a^{\alpha}_{H_2}}\right)}_{\text{Nernst potential}} \underbrace{+ (t_+ - t_-)\frac{RT}{F}\ln\left(\frac{a^{\alpha}_{HCl}}{a^{\beta}_{HCl}}\right)}_{\text{Liquid-Junction potential}}$$

$$E_{\text{cell}} = -\frac{RT}{F}\ln\left(\frac{a^{\alpha}_{H^+}}{a^{\beta}_{H^+}}\right) + (t_+ - t_-)\frac{RT}{F}\ln\left(\frac{a^{\alpha}_{HCl}}{a^{\beta}_{HCl}}\right)$$

… $t_{\pm}$ are transport/transference numbers…
… the fraction of the current carried by each ion

$$E_{\text{cell}} = 0.05916\log\left(\frac{a^{\alpha}_{H^+}}{a^{\beta}_{H^+}}\right)\big(-1 + (0.83 - 0.17)\big)$$

$$E_{\text{cell}} = 0.05916\log\left(\frac{0.1}{0.01}\right)(-1 + 0.66) = -0.0201 \approx \mathbf{-20\ mV}$$

… so what is E_{Nernst}, and what is E_{mem}? **E_{Nernst} ≈ –60 mV; E_{mem} ≈ +40 mV**

Lecture Outline (40 min) – Membrane Electric Potentials

- Donnan potentials
- Liquid-junction potentials
- **Membrane potentials**
- **pH meter**
- **Ion-selective electrodes**

So, in summary, we've learned five equations for junction potentials…

… why do they all include "kinetic" transport properties?

Donnan $E_{\text{m}} = \dfrac{RT}{z_{\text{i}}F}\ln\dfrac{a_1(\alpha)}{a_2(\beta)}$ ← the only model that, with one salt and one interface, definitely equilibrates

LJ, Type 1 $E_{\text{j}} = (\phi^{\beta} - \phi^{\alpha}) = (t_+ - t_-)\dfrac{RT}{F}\ln\dfrac{a(\alpha)}{a(\beta)}$

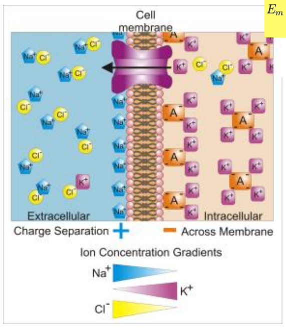
LJ, Type 2 $E_j = \pm\dfrac{RT}{F}\ln\dfrac{\sum_i |z_i| u_i C_i(\alpha)}{\sum_i |z_i| u_i C_i(\beta)}$

LJ, Type 3 (Henderson) $E_{\text{j}} = \dfrac{\sum_{\text{i}} \frac{|z_{\text{i}}| u_{\text{i}}}{z_{\text{i}}}[C_{\text{i}}(\beta) - C_{\text{i}}(\alpha)]}{\sum_{\text{i}} |z_{\text{i}}| u_{\text{i}}[C_{\text{i}}(\beta) - C_{\text{i}}(\alpha)]}\dfrac{RT}{F}\ln\dfrac{\sum_{\text{i}} |z_{\text{i}}| u_{\text{i}} C_{\text{i}}(\alpha)}{\sum_{\text{i}} |z_{\text{i}}| u_{\text{i}} C_{\text{i}}(\beta)}$

Goldman (GHHK) $E_m = \dfrac{RT}{F}\ln\left(\dfrac{\sum_i^N P_{M_i^+}[M_i^+]_{\text{out}} + \sum_j^M P_{A_j^-}[A_j^-]_{\text{in}}}{\sum_i^N P_{M_i^+}[M_i^+]_{\text{in}} + \sum_j^M P_{A_j^-}[A_j^-]_{\text{out}}}\right)$

… that math looks ugly… what is that last equation?… who is a Biology major?

… what about "the fifth" equation?
… it's the Goldman–(Hodgkin–(Huxley)–Katz)) equation…
… and describes nonequilibrium membrane potentials, like in cells and neurons!

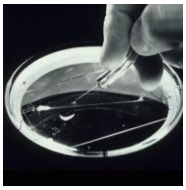


$$E_m = \frac{RT}{F}\ln\left(\frac{\sum_i^N P_{M_i^+}[M_i^+]_{\mathrm{out}} + \sum_j^M P_{A_j^-}[A_j^-]_{\mathrm{in}}}{\sum_i^N P_{M_i^+}[M_i^+]_{\mathrm{in}} + \sum_j^M P_{A_j^-}[A_j^-]_{\mathrm{out}}}\right)$$

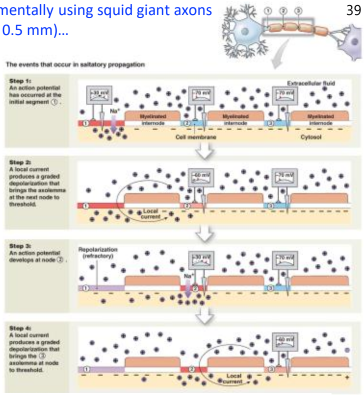
permeabilities

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

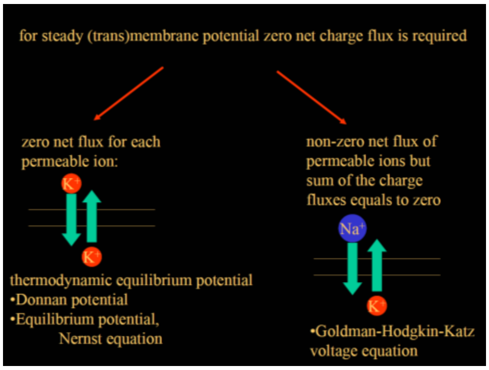
… initially discovered experimentally using squid giant axons (diameter ≈ 0.5 mm)…



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



www.highlands.edu/academics/divisions/scipe/biology/faculty/harnden/2121/notes/nervous.htm



for steady (trans)membrane potential zero net charge flux is required

zero net flux for each permeable ion:

thermodynamic equilibrium potential
- Donnan potential
- Equilibrium potential, Nernst equation

non-zero net flux of permeable ions but sum of the charge fluxes equals to zero

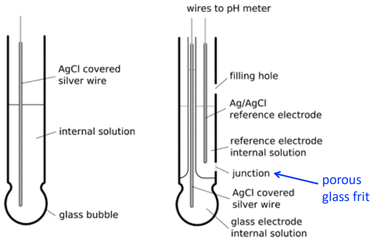
- Goldman-Hodgkin-Katz voltage equation

http://biophys.med.unideb.hu/old/pharmacy/Donnan%20angol2009.pdf

Lecture Outline (40 min) – Membrane Electric Potentials

- Donnan potentials
- Liquid-junction potentials
- Membrane potentials
- **pH meter**
- **Ion-selective electrodes**

… the ***glass pH electrode*** is exceptional in many ways…



Chemist, Inventor, Investor, Philanthropist

Arnold Orville Beckman
(1900 – 2004)
from Wiki

a thin glass membrane transports cations with high selectivity…

… the potential across the thin glass membrane is measured in a buffered internal solution versus a second reference electrode

… protons do not traverse across the glass membrane… their concentration at the glass surfaces is coupled to the concentration of Na^+ in the glass, so like before, **two (Donnan) equilibria exist** (one at each interface), not one!

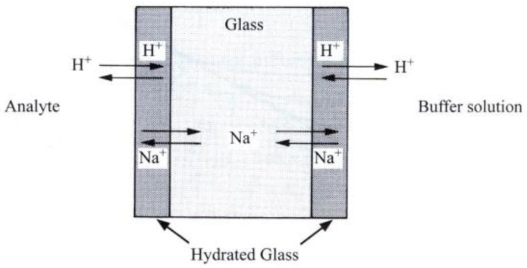


Fig. 2.25 Ionic equilibria in a glass electrode.

… protons <u>do not</u> traverse across the glass membrane… their concentration at the glass surfaces is coupled to the concentration of Na⁺ in the glass, so like before, **two (Donnan) equilibria exist** (one at each interface), not one!

$$E_m = \frac{RT}{F}\ln\frac{a^{\alpha}_{H^+}\,a^{m''}_{H^+}}{a^{\beta}_{H^+}a^{m'}_{H^+}} \qquad \text{(Donnan Term)}$$

$$+\frac{RT}{F}\ln\frac{(u_{Na^+}/u_{H^+})a^{m'}_{Na^+} + a^{m'}_{H^+}}{(u_{Na^+}/u_{H^+})a^{m''}_{Na^+} + a^{m''}_{H^+}} \qquad \text{(Diffusion term)}$$

What type of LJ is this?

Type 2!

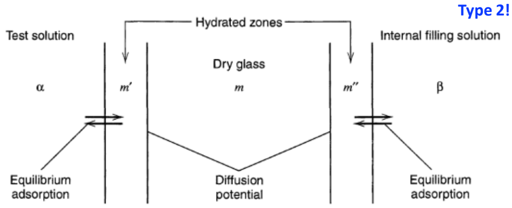


Figure 2.4.3 Model for treating the membrane potential across a glass barrier.

Lecture Outline (40 min) – Membrane Electric Potentials

- <u>Donnan potentials</u>
- <u>Liquid-junction potentials</u>
- <u>Membrane potentials</u>
- <u>pH meter</u>
- <u>Ion-selective electrodes</u>

… Prof. Ardo, those potentiometric data were neat… how did you learn it all?