613

# Lecture #16 of 20+

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# Liquid-Junction Potentials

Chapter 2

615

Q: What's in this set of lectures?
A: B&F Chapter 2 main concepts:

- "Section 2.1":        Salt; Activity; Underpotential deposition

- Section 2.3:        Transference numbers; Liquid-junction potentials

- Sections 2.2 & 2.4: Donnan potentials; Membrane potentials; pH meter; Ion-selective electrodes

we use $t_i$ values, which are based on **kinetic transport** to determine the liquid-junction potential (for derivations, see B&F, pp. 70 – 72)…

# RECALL:

| Type 1 | Type 2 | Type 3 |
|---|---|---|



| 0.01 $M$ HCl \| 0.1 $M$ HCl | 0.1 $M$ HCl \| 0.1 $M$ KCl | 0.1 $M$ HCl \| 0.05 $M$ KNO$_3^-$ |

*(a)* same salt; different concentrations

*(b)* same cation or anion; different counter ion; *same concentration*

*(c)* no common ions, and/or one common ion; different concs

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we use $t_i$ values, which are based on **kinetic transport** to determine the liquid-junction potential (for derivations, see B&F, pp. 70 – 72)…

# RECALL:

**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 $\beta$ vs $\alpha$**

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Last point: clarifying sign conventions in B&F so that this is crystal clear…

**Type 3:**
$$E_j = \frac{\sum_i \frac{|z_i| u_i}{z_i}[C_i(\beta) - C_i(\alpha)]}{\sum_i |z_i| u_i[C_i(\beta) - C_i(\alpha)]}\frac{RT}{F}\ln\frac{\sum_i |z_i| u_i C_i(\alpha)}{\sum_i |z_i| u_i C_i(\beta)}$$
(2.3.39)

where $u_i$ is the mobility of species $i$, and $C_i$ is its molar concentration. For type 2 junctions between 1:1 electrolytes, this equation collapses to the *Lewis–Sargent relation*:

**Type "2":**
$$E_j = \pm\frac{RT}{F}\ln\frac{\Lambda_\beta}{\Lambda_\alpha}$$
(2.3.40)

where $\Lambda$ (the *equivalent conductivity*) is defined as follows: $\Lambda = \frac{\kappa}{C_{eq}}$

… and where $C_{eq}$ is the concentration of positive or negative charges associated with a particular salt in solution, and so rearranging 2.3.40…

$$E_j = \pm\frac{RT}{F}\ln\frac{\kappa_\beta}{\kappa_\alpha}, \text{ where } \kappa = F\sum_i |z_i| u_i C_i$$

… and by comparing this to the form of our Type 2 equation, one sees…

Last point: clarifying sign conventions in B&F so that this is crystal clear… [619]

Type 3:
$$E_j = \frac{\sum_i \frac{|z_i|u_i}{z_i}[C_i(\beta) - C_i(\alpha)]}{\sum_i |z_i|u_i[C_i(\beta) - C_i(\alpha)]} \frac{RT}{F} \ln \frac{\sum_i |z_i|u_i C_i(\alpha)}{\sum_i |z_i|u_i C_i(\beta)}$$ (2.3.39)

where $u_i$ is the mobility of species $i$, and $C_i$ is its molar concentration. For type 2 junctions between 1:1 electrolytes, this equation collapses to the *Lewis–Sargent relation*:

Type "2": $$E_j = \pm \frac{RT}{F} \ln \frac{\Lambda_\beta}{\Lambda_\alpha}$$ (2.3.40)

Type 2: $$E_j = \pm \frac{RT}{F} \ln \frac{\sum_i |z_i|u_i C_i(\alpha)}{\sum_i |z_i|u_i C_i(\beta)}$$ **Note: $\alpha$ and $\beta$ are switched…**

… they are off by a factor of (-1)… *let's look at that pre-factor…*
… *for a specific example:*
0.1M HCl ($\alpha$) | 0.1M KCl ($\beta$)

619

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Last point: clarifying sign conventions in B&F so that this is crystal clear… [620]

Type 3:
$$E_j = \frac{\sum_i \frac{|z_i|u_i}{z_i}[C_i(\beta) - C_i(\alpha)]}{\sum_i |z_i|u_i[C_i(\beta) - C_i(\alpha)]} \frac{RT}{F} \ln \frac{\sum_i |z_i|u_i C_i(\alpha)}{\sum_i |z_i|u_i C_i(\beta)}$$ (2.3.39)

where $u_i$ is the mobility of species $i$, and $C_i$ is its molar concentration. For type 2 junctions between 1:1 electrolytes, this equation collapses to the *Lewis–Sargent relation*:

$$E_j = \frac{\frac{(1)u_{K+}}{1}[0.1-0] + \frac{(1)u_{H+}}{1}[0-0.1]}{(1)u_{K+}[0.1-0] + (1)u_{H+}[0-0.1]} \frac{RT}{F} \ln \frac{\sum_i |z_i|u_i C_i(\alpha)}{\sum_i |z_i|u_i C_i(\beta)}$$

$$E_j = (+1)\frac{RT}{F} \ln \frac{\sum_i |z_i|u_i C_i(\alpha)}{\sum_i |z_i|u_i C_i(\beta)}$$

… so this means that the Lewis–Sargent relation should have a (–) in front of it when net cations diffuse based on our convention… so switch the sign, as $\mp$… or use our equation

… they are off by a factor of (-1)… *let's look at that pre-factor…*
… *for a specific example:*
0.1M HCl ($\alpha$) | 0.1M KCl ($\beta$)

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Last point: clarifying sign conventions in B&F so that this is crystal clear… [621]

Type 3:
$$E_j = \frac{\sum_i \frac{|z_i|u_i}{z_i}[C_i(\beta) - C_i(\alpha)]}{\sum_i |z_i|u_i[C_i(\beta) - C_i(\alpha)]} \frac{RT}{F} \ln \frac{\sum_i |z_i|u_i C_i(\alpha)}{\sum_i |z_i|u_i C_i(\beta)}$$ (2.3.39)

where $u_i$ is the mobility of species $i$, and $C_i$ is its molar concentration. For type 2 junctions between 1:1 electrolytes, this equation collapses to the *Lewis–Sargent relation*:

Type "2": $$E_j = \pm \frac{RT}{F} \ln \frac{\Lambda_\beta}{\Lambda_\alpha}$$ (2.3.40)

… since we know that the $\beta$ side will be (+) in the previous case, this really means the Lewis–Sargent relation should have a (–) sign in front of it when net cations diffuse…

… if we're sticking with our convention that the potential is the $\beta$ (product/reduced phase) versus the $\alpha$ (reactant/oxidized phase)…

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**… anyway…**

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*Donnan potential: A special liquid-junction potential due to **fixed charges*** 623
… here are two systems in which Donnan potentials play a prominent role:

an ionomer film          a cell



Nafion

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

semipermeable
membrane

membrane impermeable to
charged macromolecules

http://www.williamsclass.com/

623

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… consider this model which applies to both scenarios… 624

a film of poly(styrene sulfonate)



$C_{NaCl}$

$R^-$ → $SO_3^-$ ]$_n$
$Na^+$

$C_{Na^+}^m$   $C_{Cl^-}^m$        $C_{Na^+}^s$   $C_{Cl^-}^s$

624

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:

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

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

625

625

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:

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

... Assuming that standard state chemical potentials ($\mu_i^o$) are the same inside and outside of the membrane, we can easily solve for the ("Galvani" / inner) electric potential difference, $\phi^m - \phi^s$
... *which is exactly what was required to calculate liquid-junction potentials*!

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

... so we can express $E_{\text{Donnan}}$, an equilibrium *electric* potential difference, in terms of any ion that has access to both the membrane and the solution:

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

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

Aside #1: Recall Type 1 case of LJ potential... but now with $t_- = 0$...

$$E_j = (\phi^\beta - \phi^\alpha) = (t_+ - t_-)\frac{RT}{F}\ln\frac{a_{1(\alpha)}}{a_{2(\beta)}}$$

$$E_j = \frac{RT}{F}\ln\left(\frac{a_1(\alpha)}{a_1(\beta)}\right) = E_{\text{Donnan}}(\text{Na}^+)$$

... with $\beta$ being the membrane

Aside #2: This is what B&F writes for this (Donnan) potential...

... Check!

$$E_m = -\frac{RT}{z_iF}\ln\frac{a_i^\beta}{a_i^\alpha}$$

Eqn. 2.4.2

627

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$$E_{\text{Donnan}} = \frac{RT}{F}\ln\left(\frac{a^s_{\text{Na}^+}}{a^m_{\text{Na}^+}}\right) = \ominus\frac{RT}{F}\ln\left(\frac{a^s_{\text{Cl}^-}}{a^m_{\text{Cl}^-}}\right)$$

**Anyway**… now divide both sides by $RT/F$ and invert the argument of the "ln()" on the right to eliminate the negative sign, and we have…

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

… or…

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

628

… recall the scenario we are analyzing…                    629

… with R⁻ representing the fixed charges…

a film of poly(styrene sulfonate)



629
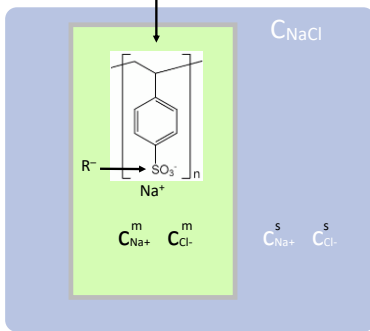
$$a^s_{\text{Na}^+}a^s_{\text{Cl}^-} = a^m_{\text{Na}^+}a^m_{\text{Cl}^-}$$                    630

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

$$c^s_{\text{Na}^+}c^s_{\text{Cl}^-} = c^m_{\text{Na}^+}c^m_{\text{Cl}^-}$$

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

$$c^s_{\text{Na}^+} = c^s_{\text{Cl}^-} \qquad c^m_{\text{Na}^+} = c^m_{\text{Cl}^-} + c^m_{\text{R}^-}$$

… an equation quadratic in $c^m_{\text{Cl}^-}$ is obtained as follows…

630

… an equation quadratic in $c^m_{Cl-}$ is obtained as follows… 631

$$\boxed{c^s_{Na^+} c^s_{Cl^-}} = c^m_{Na^+} c^m_{Cl^-}$$

$$c^s_{Na^+} = c^s_{Cl^-}$$

because in solution, $c_{Na^+} = c_{Cl^-}$ for goodness sakes!

$$\left(c^s_{Cl^-}\right)^2$$

631

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… an equation quadratic in $c^m_{Cl-}$ is obtained as follows… 632

$$\boxed{c^s_{Na^+} c^s_{Cl^-}} = \boxed{c^m_{Na^+}} c^m_{Cl^-}$$

$$c^s_{Na^+} = c^s_{Cl^-} \qquad c^m_{Na^+} = c^m_{Cl^-} + c^m_{R^-}$$

$$\left(c^s_{Cl^-}\right)^2 = \left(c^m_{Cl^-}\right)^2 + c^m_{R^-} c^m_{Cl^-}$$

$$0 = \left(c^m_{Cl^-}\right)^2 + c^m_{R^-} c^m_{Cl^-} - \left(c^s_{Cl^-}\right)^2$$

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

$$c^m_{Cl^-} = \frac{-c^m_R + \sqrt{\left(c^m_R\right)^2 + 4\left(c^s_{Cl^-}\right)^2}}{2} = \frac{c^m_R}{2}\left(\sqrt{1 + 4\left(\frac{c^s_{Cl^-}}{c^R_{Cl^-}}\right)^2} - 1\right)$$

632

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633

$$c^m_{Cl^-} = \frac{-c^m_R + \sqrt{\left(c^m_R\right)^2 + 4\left(c^s_{Cl^-}\right)^2}}{2} = \frac{c^m_R}{2}\left(\boxed{\sqrt{1 + 4\left(\frac{c^s_{Cl^-}}{c^m_{R^-}}\right)^2}} - 1\right)$$

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)

633

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

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

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

$$c_{\text{Cl}^-}^m = \frac{c_{\text{R}^-}^m}{2}\left(1 + 2\left(\frac{c_{\text{Cl}^-}^s}{c_{\text{R}^-}^m}\right)^2 - 1\right) = \frac{\left(c_{\text{Cl}^-}^s\right)^2}{c_{\text{R}^-}^m}$$

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

634

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… so how excluded *is* excluded? 635

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

… 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 $C_{\text{Cl}^-}{}^s$ = 0.1 M…

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

… an order of magnitude lower
than $C_{\text{Cl}^-}{}^s$… *rather* excluded!

… but what if $C_{\text{Cl}^-}{}^s$ is also large…
(e.g. 0.6 M, like in ocean water)?
… **No more Donnan exclusion!** Source: Torben Smith Sørensen, *Surface Chemistry and Electrochemistry of Membranes*, CRC Press, 1999 ISBN 0824719220, 9780824719227

635

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… That was easy… but is there an even clearer result from this derivation? 636

a film of poly(styrene sulfonate)
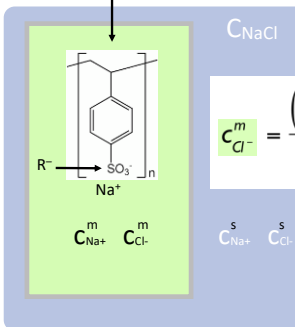


$C_{\text{NaCl}}$

$C_{\text{Na}^+}^m$  $C_{\text{Cl}^-}^m$   $C_{\text{Na}^+}^s$  $C_{\text{Cl}^-}^s$

… 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…

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

log = -1
log = 0
log = -2

… this time, it is *very very 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** $C_{\text{Na}^+}$ **and** $C_{\text{Cl}^-}$**!… think log-scale**

636

… That was easy… but is there an even clearer result from this derivation?    637

a film of poly(styrene sulfonate)
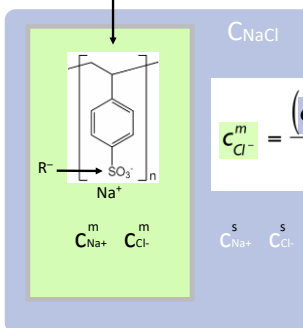
$C_{NaCl}$

$R^-$ — $SO_3^-$ $]_n$

Na$^+$

$C_{Na+}^m$   $C_{Cl-}^m$        $C_{Na+}^s$   $C_{Cl-}^s$

… 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…

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

log = -3

log = -1

log = ?

… what about this?

… this time, it is *very very 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

637

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… That was easy… but is there an even clearer result from this derivation?    638

a film of poly(styrene sulfonate)
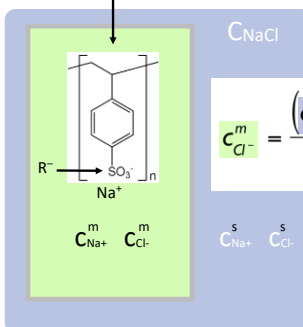
$C_{NaCl}$

$R^-$ — $SO_3^-$ $]_n$

Na$^+$

$C_{Na+}^m$   $C_{Cl-}^m$        $C_{Na+}^s$   $C_{Cl-}^s$

… 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…

$$c_{Cl^-}^m = \frac{\left(c_{Cl^-}^s\right)^2}{c_{R^-}^m} = \frac{(0.001)^2}{0.1} = 10\ \mu M$$

log = -3

log = -1

log = -5

… super simple!

… this time, it is *very very 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

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… but Donnan exclusion is "amplified" in Nafion and other polymers…    639
… How?

$-[CF_2-CF_2]_x-[CF_2-CF]_y-$
$O-CF_2-CF]_z-O-CF_2-CF_2-SO_3H$
$CF_3$
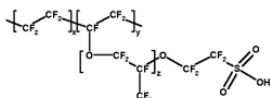
Nafion phase segregates into a hydrophobic phase, concentrated in $-(CF_2)-$ backbone, and hydrophilic clusters of $-SO_3^-$ solvated by water…

$SO_3^-$ clusters: 40 Å, 10 Å, 50 Å
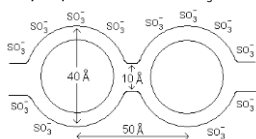
… and $-SO_3^-$ clusters are interconnected by channels that percolate through the membrane, imparting a percolation network for ionic conduction

Mauritz & Moore, *Chem. Rev.*, 2004, *104*, 4535
Kusoglu & Weber, *Chem. Rev.*, 2017, *117*, 987

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… but Donnan exclusion is "amplified" in Nafion and other polymers… 640

… How?

1 nm

640

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641
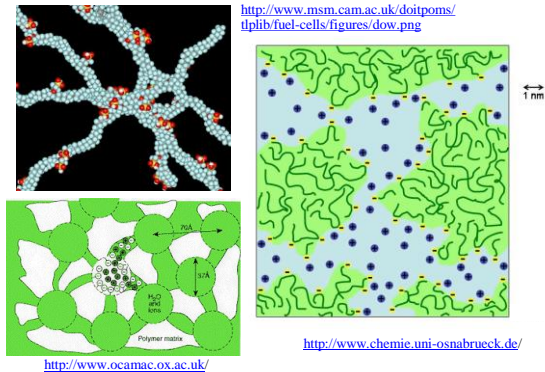
So in Nafion there are two "amplifying" effects that operate in parallel…

1) The aqueous volume accessible to ions of either charge is a small fraction of the polymer's overall volume, and therefore the local concentration of $SO_3^-$ ($C_{R-}{}^m$) is much larger than calculated based on the polymer's density and equivalent weight (i.e. the molecular weight per sulfonic acid moiety), and…

2) The large local concentration of $SO_3^-$ likely results in increases in activity coefficients!

… how can one experimentally measure Donnan potentials?
… in fact, how can one measure liquid-junction potentials?
… the same way with the same set-up for both!

… which can also be used to **measure iR$_u$ drops** across, or in, phases (including solid membranes) and is the **design for pH meters and ion-selective electrodes (ISEs)**… Wow!

P-Chemist

Frederick George Donnan
(1870–1956)
from Wiki

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… the less-frequently discussed *four-electrode* measurement! 642

Waveform generator

WE/CA2 *(P1)*   Galvanostat   CE/CA1 *(S3/P2)*

RE'/ref1 *(S1)*   High impedance DVM   RE/ref2 *(S2)*

$\Delta E_{ref}$

Cation Exchange Membrane

Glass flange

Platinum gauze counter electrode (1.5 cm²)   Luggin capillary   Saturated calomel reference electrode   Silicone-rubber gaskets

20 cm

8 cm

WE/CA2
ref1   $E_{we}$
RE/ref2   $E_{ce}$
ref3
CE/CA1
I

*(EC-Lab diagram, from Bio-Logic)*

… or to simply measure the passive electric potential difference, and not vary it by passing (much) current, measure the potential **between the two reference electrodes** with a voltmeter… like a Keithley 2002 8½ digit multimeter

Slade, …, Walsh, *J. Electrochem. Soc.*, 2002, *149*, A1556

642

**Recall...**  643
## Active I/E Converter versus <mark>Passive I/E Converter</mark>
... meaning "newer"
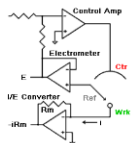


"Many modern potentiostats use the architecture shown here, yet it is rarely discussed at length in textbooks!"

"This scheme has been used by Gamry, PAR, Solartron, and perhaps others [and likely Bio-Logic]."
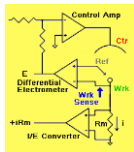
Unlike the active I/E converter design,
- this I/E converter is passive... current only flows through passive circuit elements (e.g. R, C, not op-amp)
- the working electrode is NOT at (virtual) (earth) ground
- the electrometer is differential between the RE and the WE sense (RE #2)

http://www.consultrsr.net/resources/pstats/design2.htm

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**Recall...**  644
## Active I/E Converter versus <mark>Passive I/E Converter</mark>
... meaning "newer"
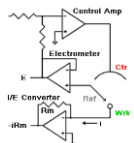


■ **Advantages**

The I/E Converter amplifier must only **report** the iR drop across the current sense resistor. It is is not involved in the control of the working electrode and it does not have to be a high current amplifier. The frequency response of this style of I/E converter can be faster than the "active" design because of this. Its frequency response does not have to be sacrificed for potentiostat stability since the I/E converter is not involved in the "control loop."

Because the electrometer is differential, a potentiostat of this design can be used to control the voltage across a membrane or across the interface between two immiscible liquids. In this application two reference electrodes are used. One is connected to the Reference input, and the other (on the other side of the membrane or interface) is connected to the Working Sense input.

■ **Disadvantages**

The Common Mode Rejection Ratio (CMRR) of the differential electrometer can have a profound influence on the stability of this potentiostat. There are two feedback paths through the differential electrometer. The path through the reference electrode is a net **negative feedback** path if you follow it from the reference electrode to the counter electrode via the electrometer and control amplifier. This path gives stability. The path through the **Wrk Sense** input, however, is a **positive feedback** path and is destabilizing.

The overall 'gain' of the control amplifier is higher with this scheme. This is another way of saying that the control amplifier must work harder to keep the working-reference voltage correct. Not only must it overcome the counter-reference resistance, but the voltage drop across the current measuring resistor as well. In many commercial designs, the voltage drop across this resistor is 100 mV or less, even at 'full scale' current. The differential amplifier often amplifies the voltage level (to a nominal 1V at full scale current) as well as buffering it.

http://www.consultrsr.net/resources/pstats/design2.htm

644

... the less-frequently discussed *four-electrode* measurement!  645
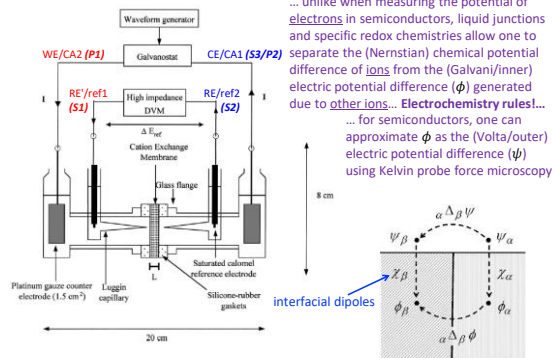


... unlike when measuring the potential of <u>electrons</u> in semiconductors, liquid junctions and specific redox chemistries allow one to separate the (Nernstian) chemical potential difference of <u>ions</u> from the (Galvani/inner) electric potential difference ($\phi$) generated due to <u>other ions</u>... **Electrochemistry rules!...**
... for semiconductors, one can approximate $\phi$ as the (Volta/outer) electric potential difference ($\psi$) using Kelvin probe force microscopy
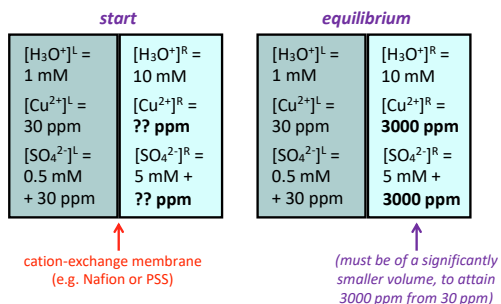
interfacial dipoles

Slade, ..., Walsh, *J. Electrochem. Soc.*, 2002, *149*, A1556    Cheng and Sprik, *PCCP*, 2012, *14*, 11245

645

Donnan potentials can be used to concentrate metal ions... 646

… there are actually **two Donnan potentials**… one at each membrane–solution interface… resulting in a non-equilibrated system

… but that is fine because the Donnan potentials are not equal and opposite… their sum is the net Donnan potential between the two solutions wetting the membrane… we do not need to know each Donnan potential separately, and in fact, it is nearly impossible to measure each individually…

… as long as there is decent Donnan Exclusion, the system will be rather stable and function as desired

**start**

| | |
|---|---|
| $[H_3O^+]^L$ = 1 mM | $[H_3O^+]^R$ = 10 mM |
| $[Cu^{2+}]^L$ = 30 ppm | $[Cu^{2+}]^R$ = **?? ppm** |
| $[SO_4^{2-}]^L$ = 0.5 mM + 30 ppm | $[SO_4^{2-}]^R$ = 5 mM + **?? ppm** |

cation-exchange membrane
(e.g. Nafion or PSS)

Wallace, *I&EC Process Design Development*, 1967, 6, 423

P-Chemist

Frederick George Donnan
(1870–1956)
from Wiki

646

---

Donnan potentials can be used to concentrate metal ions... 647

$$E_{Donnan} = \frac{-RT}{zF} \ln \frac{(a_{H^+})^R}{(a_{H^+})^L} = \frac{-0.05916}{(1)} \log \frac{10}{1} = 0.059V$$

**start**

| | |
|---|---|
| $[H_3O^+]^L$ = 1 mM | $[H_3O^+]^R$ = 10 mM |
| $[Cu^{2+}]^L$ = 30 ppm | $[Cu^{2+}]^R$ = **?? ppm** |
| $[SO_4^{2-}]^L$ = 0.5 mM + 30 ppm | $[SO_4^{2-}]^R$ = 5 mM + **?? ppm** |

cation-exchange membrane
(e.g. Nafion or PSS)

Wallace, *I&EC Process Design Development*, 1967, 6, 423

P-Chemist

Frederick George Donnan
(1870–1956)
from Wiki

647

---

Donnan potentials can be used to concentrate metal ions... 648

$$E_{Donnan} = \frac{-RT}{zF} \ln \frac{(a_{H^+})^R}{(a_{H^+})^L} = \frac{-0.05916}{(1)} \log \frac{10}{1} = 0.059V$$

$$E_{Donnan} = 0.059V = \frac{-RT}{(2)F} \ln \frac{(a_{Cu^{2+}})^R}{(a_{Cu^{2+}})^L}$$

$$\frac{(a_{Cu^{2+}})^R}{(a_{Cu^{2+}})^L} = \frac{(a_{Cu^{2+}})^R}{(30ppm)^L} = 10^{2(.05916)/0.05916} = 100$$

$$(a_{Cu^{2+}})^R = 3000 \text{ ppm}$$

648

Donnan potentials can be used to concentrate metal ions... 649

… one net Donnan potential for the entire system that satisfies **equilibrium for each ion at each interface**, but is **at steady-state overall** due to net flux of all the ions… Cool!

|  | start |  | equilibrium |  |
|---|---|---|---|---|
| $[H_3O^+]^L = $ 1 mM | $[H_3O^+]^R = $ 10 mM | $[H_3O^+]^L = $ 1 mM | $[H_3O^+]^R = $ 10 mM |
| $[Cu^{2+}]^L = $ 30 ppm | $[Cu^{2+}]^R = $ **?? ppm** | $[Cu^{2+}]^L = $ 30 ppm | $[Cu^{2+}]^R = $ **3000 ppm** |
| $[SO_4^{2-}]^L = $ 0.5 mM + 30 ppm | $[SO_4^{2-}]^R = $ 5 mM + **?? ppm** | $[SO_4^{2-}]^L = $ 0.5 mM + 30 ppm | $[SO_4^{2-}]^R = $ 5 mM + **3000 ppm** |

cation-exchange membrane
(e.g. Nafion or PSS)

*(must be of a significantly smaller volume, to attain 3000 ppm from 30 ppm)*

649

---

*example*: Given the following two RHE REs, calculate $E_{cell}$ and $E_j$? 650

$\alpha$ $\beta$

Pt | H₂ (1 bar) | HCl (*aq*, 0.1 M) **||** HCl (*aq*, 0.01 M) | H₂ (1 bar) | Pt
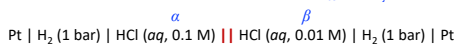
… does this have a liquid junction or a Donnan potential?

… it depends on what the middle lines are…
… assume they represent a single porous glass frit (not Nafion)…

650

---

*example*: Given the following two RHE REs, calculate $E_{cell}$ and $E_j$? 651

$\alpha$ $\beta$

Pt | H₂ (1 bar) | HCl (*aq*, 0.1 M) **|** HCl (*aq*, 0.01 M) | H₂ (1 bar) | Pt

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

651

*example*: Given the following two RHE REs, calculate $E_{cell}$ and $E_j$? 652

$$\overset{\alpha}{\phantom{x}} \qquad \overset{\beta}{\phantom{x}}$$
Pt | H$_2$ (1 bar) | HCl (*aq*, 0.1 M) **|** HCl (*aq*, 0.01 M) | H$_2$ (1 bar) | Pt

$$E_{cell} = E_{Nernst} + E_j = E^0 - \frac{RT}{2F}\ln\left(\frac{a_{H_2}^{\beta} a_{H^+}^{\alpha\,2}}{a_{H^+}^{\beta\,2} a_{H_2}^{\alpha}}\right) + (t_+ - t_-)\frac{RT}{F}\ln\left(\frac{a_{HCl}^{\alpha}}{a_{HCl}^{\beta}}\right)$$

$$\underbrace{\phantom{E^0 - \frac{RT}{2F}}}_{\text{Nernst potential}} \quad \underbrace{\phantom{(t_+ - t_-)}}_{\text{LJ potential}}$$

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

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

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

*… so what is $E_{Nernst}$, and what is $E_j$?* **$E_{Nernst}$ ≈ −60 mV; $E_j$ ≈ +40 mV**

652

*example*: Given the following two RHE REs, calculate $E_{cell}$ and $E_j$? 653

$$\overset{\alpha}{\phantom{x}} \qquad \overset{\beta}{\phantom{x}}$$
Pt | H$_2$ (1 bar) | HCl (*aq*, 0.1 M) **|** HCl (*aq*, 0.01 M) | H$_2$ (1 bar) | Pt

$$E_{cell} = E_{Nernst} + E_j = E^0 - \frac{RT}{2F}\ln\left(\frac{a_{H_2}^{\beta} a_{H^+}^{\alpha\,2}}{a_{H^+}^{\beta\,2} a_{H_2}^{\alpha}}\right) + (t_+ - t_-)\frac{RT}{F}\ln\left(\frac{a_{HCl}^{\alpha}}{a_{HCl}^{\beta}}\right)$$

$$\underbrace{\phantom{E^0 - \frac{RT}{2F}}}_{\text{Nernst potential}} \quad \underbrace{\phantom{(t_+ - t_-)}}_{\text{LJ potential}}$$

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

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

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

*… neither term dominates $E_{cell}$… but what can we do to isolate $E_j$ in the cell?*

653

*example*: Given the following two RHE REs, calculate $E_{cell}$ and $E_j$? 654
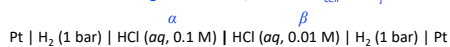
$$\overset{\alpha}{\phantom{x}} \qquad \overset{\beta}{\phantom{x}}$$
Pt | H$_2$ (1 bar) | HCl (*aq*, 0.1 M) **|** HCl (*aq*, 0.01 M) | H$_2$ (1 bar) | Pt

*… use two of the same electrodes, (i) whose potential does not depend on the
concentration of salt… which is often difficult… or (ii) with salt bridges…
… let's examine the second case…*

SCE | HCl (*aq*, 0.1 M) **||** HCl (*aq*, 0.01 M) | SCE

**Two salty reference electrodes**…
*… where $E_{cell} = E_{Nernst}(a_i) + iR_u + E_{j1} + E_{j2\text{-}net} + E_{j3}$*

*… and only $E_{j2\text{-}net}$ is not zero-ish because…*

*… neither term dominates $E_{cell}$… but what can we do to isolate $E_j$ in the cell?*

654

14

*example*: Given the following two RHE REs, calculate $E_{cell}$ and $E_j$? 655
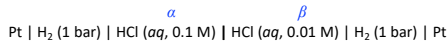
$$\alpha \qquad\qquad \beta$$

Pt | H₂ (1 bar) | HCl (*aq*, 0.1 M) **|** HCl (*aq*, 0.01 M) | H₂ (1 bar) | Pt

*… use two of the same electrodes, (i) whose potential does not depend on the concentration of salt… which is often difficult… or (ii) with salt bridges…*
*… let's examine the second case…*

SCE | HCl (*aq*, 0.1 M) **|** HCl (*aq*, 0.01 M) | SCE
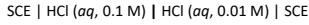
*… by looking at a somewhat related case that B&F did for us…*

Hg | Hg₂Cl₂ | HCl (*aq*, 0.1 M) | KCl (*conc*) | KCl (*aq*, 0.01 M) | Hg₂Cl₂ | Hg
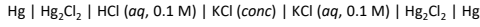
**TABLE 2.3.3  Effect of a Salt Bridge on Measured Junction Potentials**[a]

| Concentration of KCl, $C(M)$ | $E_j$, mV |
|---|---|
| 0.1 | 27 |
| 0.2 | 20 |
| 0.5 | 13 |
| 1.0 | 8.4 |
| 2.5 | 3.4 |
| 3.5 | 1.1 |
| 4.2 (saturated) | <1 |

[a] See J. J. Lingane, "Electroanalytical Chemistry," Wiley-Interscience, New York, 1958, p. 65. Original data from H. A. Fales and W. C. Vosburgh, *J. Am. Chem. Soc.*, **40**, 1291 (1918); E. A. Guggenheim, *ibid.*, **52**, 1315 (1930); and A. L. Ferguson, K. Van Lente, and R. Hitchens, *ibid.*, **54**, 1285 (1932).

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

**Recall**, the Henderson Equation…
… summations are dominated by large values ($C_i$)
… so $E_j \approx 0$ at interfaces with (conc)entrated salt
… so other $E_j$ values in the cell can be isolated

655

---

**So, in summary, <u>five</u> equations for junction potentials…** 656

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

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

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

Donnan  $E_m = \dfrac{RT}{z_i F}\ln\dfrac{a_1(\alpha)}{a_2(\beta)}$ ⟵ the only model that, with one salt and one interface, <u>definitely</u> equilibrates

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

656

---

657



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

657

15

... but first, what about "the fifth" equation?　　　　658

... the Goldman–(Hodgkin–(Huxley)–Katz)) equation!
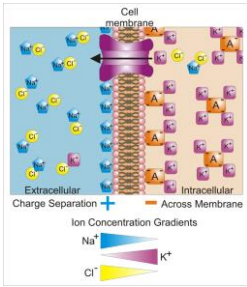
$$E_m = \frac{RT}{F} \ln \left( \frac{\sum_i^N P_{M_i^+} [M_i^+]_{\text{out}} + \sum_j^M P_{A_j^-} [A_j^-]_{\text{in}}}{\sum_i^N P_{M_i^+} [M_i^+]_{\text{in}} + \sum_j^M P_{A_j^-} [A_j^-]_{\text{out}}} \right)$$

permeabilities

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

658

... no need for a squid giant axon (H & H)　　　　659
(diameter ≈ 0.5 mm)...
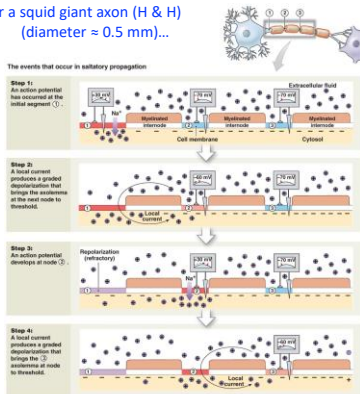
www.highlands.edu/academics/divisions/scipe/biology/faculty/harnden/2121/notes/nervous.htm

659

**~110 years of Ion-Selective Electrodes (ISEs)...**　　　　660

1906 – Max Cremer discovers that a thin glass membrane separating two solutions develops a potential related to the difference in pH between them

1920's – Duncan MacInnes & Malcolm Dole discover a glass suitable for glass pH electrodes...

1933 – Arnold Beckman markets first pH electrode in Fullerton, CA for measuring acidity of lemon juice...

*the Beckman G*

NTU's second home
*Courtesy Beckman Coulter, Inc.*

1905 Walter Nernst proposes 3rd Law of Thermodynamics; In Bern, Einstein describes PE effect, Brownian motion, and Special Rel.

1900　1920　1940　1960　1980　2000

Nernst wins Nobel Prize

660

16
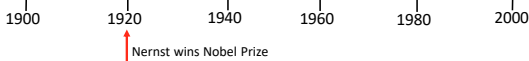
Beckman also created the first commercial spectrophotometer… 661



the Beckman DU spectrophotometer, 1941



the Beckman Helipot potentiometer, 1942

http://www.chemheritage.org/explore/Beckman/beckman.htm

661

---

… but the glass pH electrode is exceptional in many ways… 662
… while it is not a generic ISE… Why?  Chemist, Inventor, Investor, Philanthropist
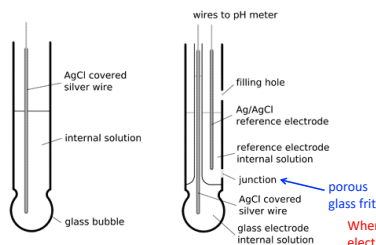


Arnold Orville Beckman
(1900 – 2004)
*from Wiki*

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

Where are the other two electrodes for a 4-electrode measurement?

**… they are not needed due to the high impedance of the circuit and no need to apply a large bias/current… thus, two are good enough!**

662

---

… protons <u>do not</u> traverse across the glass membrane… their concentration[663] 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!
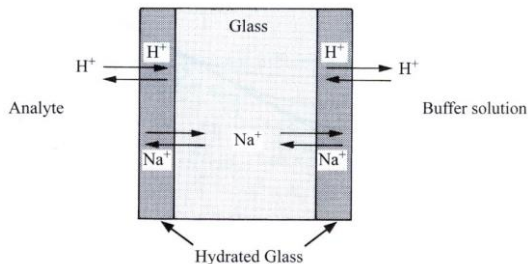


**Fig. 2.25** Ionic equilibria in a glass electrode.

663

17

… protons <u>do not</u> traverse across the glass membrane… their concentration[664] 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!

$$E_m = \frac{RT}{F} \ln \frac{a_{H^+}^\alpha + a_{H^+}^{m'}}{a_{H^+}^\beta + a_{H^+}^{m'}}$$ (Donnan Term)

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

What type of LJ is this?
**Type 2!**
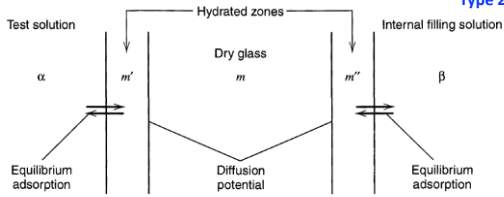


**Figure 2.4.3** Model for treating the membrane potential across a glass barrier.

664

---

**~110 years of Ion-Selective Electrodes (ISEs)…** 665

1906 – Max Cremer discovers that a thin glass membrane separating two solutions develops a potential related to the difference in pH between them

1920's – Duncan MacInnes & Malcolm Dole discover a glass suitable for glass pH electrodes…

1933 – Arnold Beckman markets first pH electrode in Fullerton, CA for measuring acidity of lemon juice…

*the Beckman G*

1961 – Pungor & Hallos-Rokosinyi invent the solid membrane ISE

1905 Walter Nernst proposes 3$^{rd}$ Law of Thermodynamics; In Bern, Einstein describes PE effect, Brownian motion, and Special Rel.



Nernst dies

Nernst wins Nobel Prize

665

---

… like the pH probe, the elements of an ISE are: (1) an internal reference electrode, (2) a filling solution, (3) an ion transporting element (i.e. membrane), and (4) an external reference electrode… 666



Why use a double-junction reference electrode?
… **To slow KCl salt leakage**
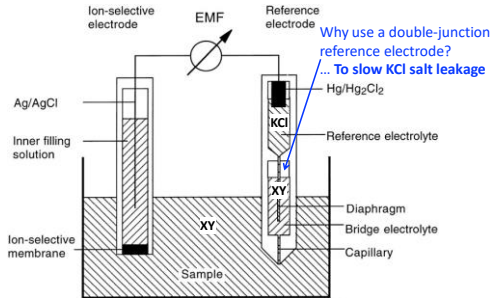
Bakker, Bühlmann, & Pretsch, *Chem. Rev.*, 1997, *97*, 3083, and *Chem. Rev.*, 1998, *98*, 1593

666

… "#3: ion transporting element" is the key… it must be engineered to transport one ion selectively… in other words, its transport number is one  667

*(SKIPPED)*

Type 1 LJ $\quad E_j = (\phi^\beta - \phi^\alpha) = (t_+ - t_-)\dfrac{RT}{F}\ln\dfrac{a(\alpha)}{a(\beta)}$

*activity of detected ion outside the electrode*

ideal ISE $\quad E_m = \dfrac{RT}{z_iF}\ln\dfrac{a(\alpha)}{a(\beta)}$

*charge on the ion that is detected*

*activity of detected ion inside the electrode (i.e. filling solution)*

667

---

… "#3: ion transporting element" is the key… it must be engineered to transport one ion selectively… in other words, its transport number is one  668

*(SKIPPED)*

Type 1 LJ $\quad E_j = (\phi^\beta - \phi^\alpha) = (t_+ - t_-)\dfrac{RT}{F}\ln\dfrac{a(\alpha)}{a(\beta)}$

*this is the concentration outside the ISE, in α…*

ideal ISE $\quad E_m = \dfrac{RT}{z_iF}\ln\dfrac{a(\alpha)}{a(\beta)} \quad$ or $\quad E = \text{constant} + \dfrac{RT}{z_iF}\ln a_i^{soln}$

*… and this offset is determined by the concentration of the ion inside the ISE*

668

---

… "#3: ion transporting element" is the key… it must be engineered to transport one ion selectively… in other words, its transport number is one  669

*(SKIPPED)*

Type 1 LJ $\quad E_j = (\phi^\beta - \phi^\alpha) = (t_+ - t_-)\dfrac{RT}{F}\ln\dfrac{a(\alpha)}{a(\beta)}$

ideal ISE $\quad E_m = \dfrac{RT}{z_iF}\ln\dfrac{a(\alpha)}{a(\beta)} \quad$ or $\quad E = \text{constant} + \dfrac{RT}{z_iF}\ln a_i^{soln}$

real ISE $\quad E_i = \text{constant} + \dfrac{RT}{z_iF}\ln\left( a_i + \sum_j K_j a_j^{\left(\frac{z_i}{z_j}\right)} \right)$

*selectivity coefficient*

*activity of interfering ion, j*

669

… a generic ISE calibration curve…

670

$$E_i = \text{constant} + \frac{RT}{z_iF}\ln\left(a_i + \sum_j K_j a_i^{\left(\frac{z_i}{z_j}\right)}\right) \text{ (SKIPPED)}$$

$$\frac{RT}{z_iF}\ln\left(\sum_j K_j a_j^{\left(\frac{z_i}{z_j}\right)}\right)$$

slope = $RT/(z_iF)$

UPPER DETECTION LIMIT

EMF

LOWER DETECTION LIMIT

log a
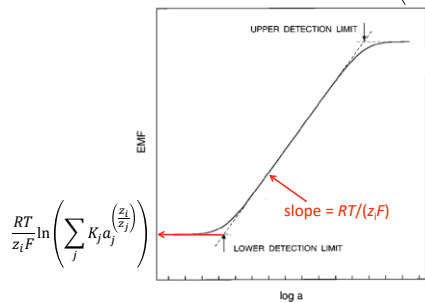
**Figure 19.** Definition of the upper and lower detection limits of an ion-selective electrode according to the IUPAC recommendations.[89]

670

… the magnitude of the selectivity terms dictate the detection limit…    671
**(SKIPPED)**

$\Delta\phi/V$

$K_{ij}^{\text{pot}} a_j = 10^{-2}$
$K_{ij}^{\text{pot}} a_j = 10^{-3}$
$K_{ij}^{\text{pot}} a_j = 10^{-4}$
$K_{ij}^{\text{pot}} a_j = 10^{-5}$

log $a_i$
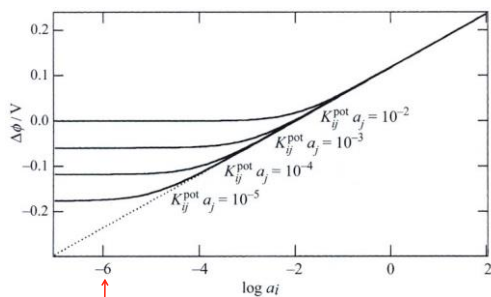
for reasons that were not clear (until 1997),
the very best ISEs had detection limits of only ~$10^{-6}$ M

671

**~110 years of Ion-Selective Electrodes (ISEs)…**    672

1906 – Max Cremer discovers that a thin glass membrane separating two solutions develops a potential related to the difference in pH between them

1920's – Duncan MacInnes & Malcolm Dole discover a glass suitable for glass pH electrodes…

1933 – Arnold Beckman markets first pH electrode in Fullerton, CA for measuring acidity of lemon juice…

the Beckman G

1961 – Pungor & Hallos-Rokosinyi invent the solid membrane ISE

1966 – Frant and Ross describe the F⁻ selective electrode

1905 Walter Nernst proposes 3rd Law of Thermodynamics;
In Bern, Einstein describes PE effect, Brownian motion, and Special Rel.

1900    1920    1940    1960    1980    2000

Nernst dies

Nernst wins Nobel Prize

672

## Electrode for Sensing Fluoride Ion Activity in Solution

MARTIN S. FRANT
JAMES W. ROSS, JR.
Orion Research Incorporated,
Cambridge, Massachusetts 02139
SCIENCE, VOL. 154

We report the development of an electrode-type of sensor, which will give a Nernstian response over a wide range of fluoride ion activity and which is highly selective for fluoride in the presence of many ions commonly found in public water supplies and biological systems.

Construction of the electrode is similar in principle to that of a conventional glass $p$H electrode, except that the membrane material is a disk-shaped section of single-crystal rare earth fluoride, such as $LaF_3$, $NdF_3$, or $PrF_3$. The section, typically 1 cm in diameter and 1 to 2 mm in thickness, is sealed to the end of a rigid polyvinyl chloride tube with epoxy cement. The only critical step is assembling the electrode so that the seal is watertight. The tube

Frant & Ross, *Science*, 1966, *154*, 1553

673

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The Champion of ISEs: The F⁻ selective electrode…     674

## Lanthanum Fluoride Electrode Response in Water and in Sodium Chloride

Theodore B. Warner
*Naval Research Laboratory, Washington, D.C. 20390*

… however, as one might guess, OH⁻ is a strongly interfering ion for this ISE membrane

Figure 1. Cell potential *vs.* NaF activity in water (○), *vs.* NaF activity in 1*M* NaCl (□), and predicted by Nernst equation (line with slope of 59.16 mV/decade)
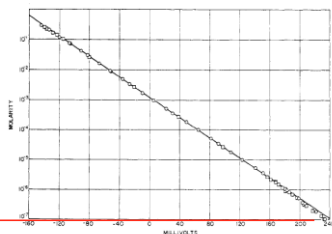


LOD [F⁻] ≈ $10^{-7}$ M…
no other ISE can achieve this small of a LOD…
the F⁻ selective electrode is a singularity!

VOL. 41, NO. 3, MARCH 1969 • 527

Warner, *Anal. Chem.*, 1969, *41*, 527

674

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**~110 years of Ion-Selective Electrodes (ISEs)…**     675

1906 – Max Cremer discovers that a thin glass membrane separating two solutions develops a potential related to the difference in pH between them

1920's – Duncan MacInnes & Malcolm Dole discover a glass suitable for glass pH electrodes…

1933 – Arnold Beckman markets first pH electrode in Fullerton, CA for measuring acidity of lemon juice…

*the Beckman G*

1961 – Pungor & Hallos-Rokosinyi invent the solid membrane ISE

1966 – Frant and Ross describe the F⁻ selective electrode

1967 – Ross demonstrates the first liquid membrane ISE

1905 Walter Nernst proposes 3rd Law of Thermodynamics; In Bern, Einstein describes PE effect, Brownian motion, and Special Rel.



1900     1920     1940     1960     1980     2000

Nernst dies

Nernst wins Nobel Prize

675

What is a liquid membrane ISE?



- internal filling solution *(aqueous)*
- organic solvent immiscible with water *(non-aqueous)*
- porous hydrophobic membrane material (e.g., Goretex)

*(aqueous)*
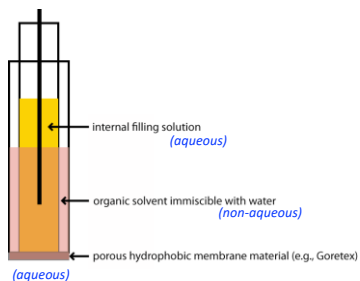
676

What is Gore-Tex?   **(BRIEFLY)**



an expanded, porous PTFE

*Discovered in New Zealand in 1966 by John Cropper, and again in 1969 by Wilbert and Robert Gore*

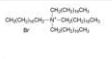http://openjurist.org/721/f2d/1540/wl-gore-associates-inc-v-garlock-inc

677



678

… dissolved in the organic solvent is a transporting agent that (ideally) complexes the metal of interest reversibly, and with high selectivity

678

Thermo Scientific, ISE Manuals

… Nitrate selective electrode…    **(BRIEFLY)** 680



$$E = E_o + S * log\ (A)$$

E = measured electrode potential
$E_o$ = reference potential (a constant)
A = nitrate ion activity level in solution
S = electrode slope (about -57 mV per decade)
$S = (2.3\ R\ T)\ /\ nF$
R and F are constants, T = temperature in degrees K and
n = ionic charge

Thermo Scientific, ISE Manuals

… Interfering ions (and concentrations) for the nitrate selective electrode… 681

| Interferences Moles/Liter | $10^{-4}$ M Nitrate | $10^{-3}$ M Nitrate | $10^{-2}$ M Nitrate |
|---|---|---|---|
| (d) $ClO_4^-$ | $1 \times 10^{-8}$ | $1 \times 10^{-7}$ | $1 \times 10^{-6}$ |
| (b) $I^-$ | $5 \times 10^{-7}$ | $5 \times 10^{-6}$ | $5 \times 10^{-5}$ |
| (d) $ClO_3^-$ | $5 \times 10^{-6}$ | $5 \times 10^{-5}$ | $5 \times 10^{-4}$ |
| (b) $CN^-$ | $1 \times 10^{-5}$ | $1 \times 10^{-4}$ | $1 \times 10^{-3}$ |
| (b) $Br^-$ | $7 \times 10^{-5}$ | $7 \times 10^{-4}$ | $7 \times 10^{-3}$ |
| (c) $NO_2^-$ | $7 \times 10^{-5}$ | $7 \times 10^{-4}$ | $7 \times 10^{-3}$ |
| (b) $HS^-$ | $1 \times 10^{-4}$ | $1 \times 10^{-3}$ | $1 \times 10^{-2}$ |
| (a) $HCO_3^-$ | $1 \times 10^{-3}$ | $1 \times 10^{-2}$ | 0.1 |
| (a) $CO_3^{-2}$ | $2 \times 10^{-3}$ | $2 \times 10^{-2}$ | 0.2 |
| (b) $Cl^-$ | $3 \times 10^{-3}$ | $3 \times 10^{-2}$ | 0.3 |
| (b) $H_2PO_4^-$ | $5 \times 10^{-3}$ | $5 \times 10^{-2}$ | 0.5 |
| (b) $HPO_4^{-2}$ | $5 \times 10^{-3}$ | $5 \times 10^{-2}$ | 0.5 |
| (b) $PO_4^{-3}$ | $5 \times 10^{-3}$ | $5 \times 10^{-2}$ | 0.5 |
| (e) $OAc^-$ | $2 \times 10^{-2}$ | 0.2 | 2 |
| $F^-$ | $6 \times 10^{-2}$ | 0.6 | 6 |
| $SO_4^{-2}$ | 0.1 | 1.0 | 10 |

Thermo Scientific, ISE Manuals

… Calcium selective electrode…  **(BRIEFLY)** 682



$$E = E_o + S * \log (A)$$

E = measured electrode potential
$E_o$ = reference potential (a constant)
A = calcium ion activity level in solution
S = electrode slope (about 28 mV per decade)
S = (2.3 R T) / nF
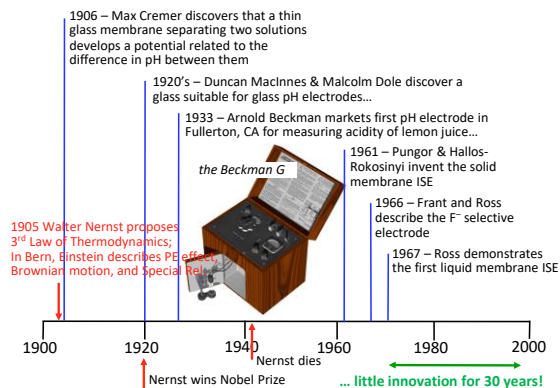R and F are constants, T = temperature in degrees K and
n = ionic charge

Thermo Scientific, ISE Manuals

… you get the idea…

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**~110 years of Ion-Selective Electrodes (ISEs)…**  **(SKIPPED)** 683

1906 – Max Cremer discovers that a thin glass membrane separating two solutions develops a potential related to the difference in pH between them

1920's – Duncan MacInnes & Malcolm Dole discover a glass suitable for glass pH electrodes…

1933 – Arnold Beckman markets first pH electrode in Fullerton, CA for measuring acidity of lemon juice…

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1905 Walter Nernst proposes 3rd Law of Thermodynamics;
In Bern, Einstein describes PE effect, Brownian motion, and Special Rel…

1967 – Ross demonstrates the first liquid membrane ISE

1900    1920    1940    1960    1980    2000

Nernst dies

Nernst wins Nobel Prize

**… little innovation for 30 years!**

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a breakthrough discovery by Ernö Pretsch (ETH Zürich)…  **(SKIPPED)** 684

**Large Improvement of the Lower Detection Limit of Ion-Selective Polymer Membrane Electrodes**

Tomasz Sokalski, Alan Ceresa, Titus Zwickl, and Ernö Pretsch

Department of Organic Chemistry
Swiss Federal Institute of Technology (ETH)
CH-8092 Zürich, Switzerland

Received August 20, 1997
Revised Manuscript Received October 8, 1997
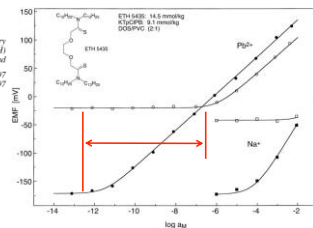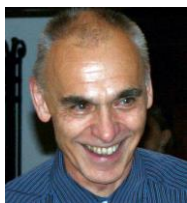


*6+ orders of magnitude more?!?!?!?! …*
*It's real, general, and new… after 91 years!*
*… How did he do it?*

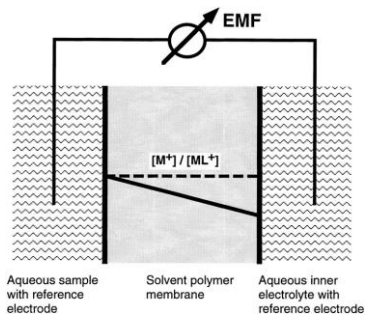684

What did Ernö Petsch do? **(SKIPPED)** 685
… a "simple" idea…
**… replace the inner filling solution of the ISE with a metal ion buffer!**



**EMF**

$[M^+] / [ML^+]$

Aqueous sample with reference electrode

Solvent polymer membrane
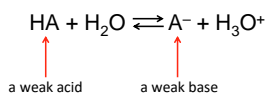
Aqueous inner electrolyte with reference electrode

Sokalski, …, Pretsch, *J. Am. Chem. Soc.*, 1997, *119*, 11347

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What's a metal ion buffer? **(SKIPPED)** 686
… Well, first of all, what's a H⁺ (pH) buffer?

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

a weak acid      a weak base

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

make these large…
… which fixes $[H_3O^+]$
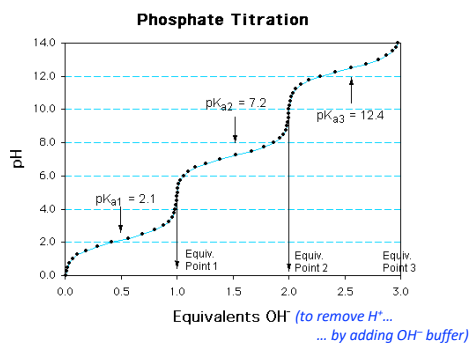… even at a small value

$$[H_3O^+] = \frac{K_a[HA]}{[A^-]}$$

$$pH = -\log[H_3O^+] = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

… Henderson–Hasselbalch equation

686

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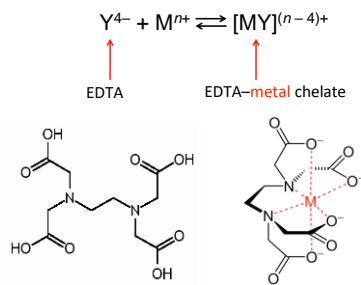Case in point: Phosphate = three equilibria, three H⁺ buffers **(SKIPPED)** 687



**Phosphate Titration**

$pK_{a2} = 7.2$

$pK_{a3} = 12.4$

$pK_{a1} = 2.1$

pH

Equiv. Point 1

Equiv. Point 2

Equiv. Point 3

Equivalents OH⁻ *(to remove H⁺…*
*… by adding OH⁻ buffer)*

687

What's a metal ion buffer?  Just like it sounds…          **(SKIPPED)** 688

$$Y^{4-} + M^{n+} \rightleftharpoons [MY]^{(n-4)+}$$

EDTA          EDTA–metal chelate



688

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What's a metal ion buffer?  Just like it sounds…          **(SKIPPED)** 689

$$Y^{4-} + M^{n+} \rightleftharpoons [MY]^{(n-4)+}$$

EDTA          EDTA–metal chelate

$$K_{MY} = \frac{\left[MY^{(n-4)+}\right]}{[Y^{4-}][M^{n+}]}$$

make these large…
… which fixes $[M^{n+}]$
… even at a small value

689

---

What's a metal ion buffer?  Just like it sounds…          **(SKIPPED)** 690

$$Y^{4-} + M^{n+} \rightleftharpoons [MY]^{(n-4)+}$$

EDTA          EDTA–metal chelate

$$K_{MY} = \frac{\left[MY^{(n-4)+}\right]}{[Y^{4-}][M^{n+}]}$$

make these large…
… which fixes $[M^{n+}]$
… even at a small value

$$[M^{n+}] = \frac{\left[MY^{(n-4)+}\right]}{[Y^{4-}]K_{MY}}$$

$$pM = -\log[M^{n+}] = -pK_{MY} + \log\left(\frac{[Y^{4-}]}{[MY^{(n-4)+}]}\right)$$

690

... buffering of $M^{n+}$ occurs after **(SKIPPED)** 691
the equivalence point... *Why?*



$K_{FeY^-} = 1.3 \times 10^{25}$

$K_{HgY^{2-}} = 6.3 \times 10^{21}$

$K_{ZnY^{2-}} = 3.2 \times 10^{16}$

$K_{FeY^{2-}} = 2.1 \times 10^{14}$

$K_{CaY^{2-}} = 5.0 \times 10^{10}$

no buffering here...
(started with $M^{n+}$ in solution)

Volume of 0.0100–F EDTA, ml *(to remove $M^{n+}$...*

$$pM = -\log[M^{n+}] = -pK_{MY} + \log\left(\frac{[Y^{4-}]}{[MY^{(n-4)+}]}\right)$$

*... by adding EDTA buffer)*

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$K_{MY}$ is adjustable based on pH... here is data for $Ca^{2+}$ **(SKIPPED)** 692
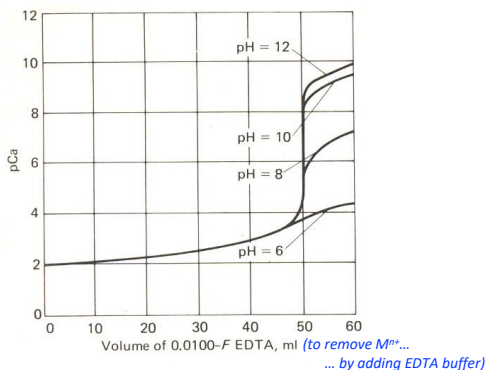


pH = 12

pH = 10

pH = 8

pH = 6

Volume of 0.0100–F EDTA, ml *(to remove $M^{n+}$...*
*... by adding EDTA buffer)*

692

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... so, what does a metal ion buffer have to do with an ISE? **(SKIPPED)** 693

conventional ISE



filling solution, $[M^{n+}] = 10^{-4}$ M

leaked $M^{n+}$, $[M^{n+}] \approx 10^{-6}$ M

... so you can't detect anything
lower than this!

693

… so, what does a metal ion buffer have to do with an ISE?  *(SKIPPED)* 694

conventional ISE     with metal ion buffer

filling solution,
$[M^{n+}]_{free} = 10^{-10}$ M

leaked $M^{n+}$,
$[M^{n+}] \approx 10^{-12}$ M
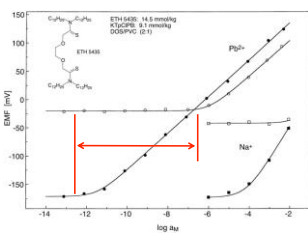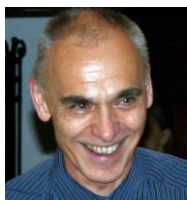… and so $\sim 10^{-12}$ M
can be detected!
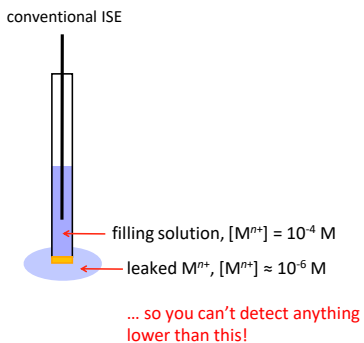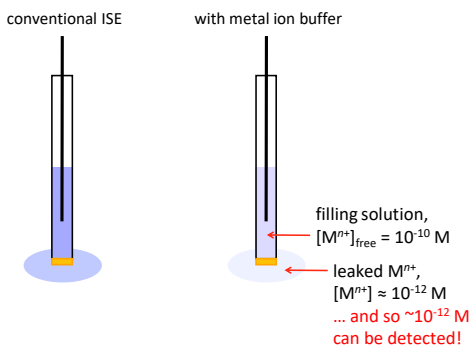
694

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a breakthrough discovery by Ernö Pretsch (ETH Zürich)…  *(SKIPPED)* 695

Large Improvement of the Lower Detection Limit of Ion-Selective Polymer Membrane Electrodes

Tomasz Sokalski,† Alan Ceresa,‡ Tims Zwickl,‡ and Ernö Pretsch*,‡

Department of Organic Chemistry
Swiss Federal Institute of Technology (ETH)
CH-8092 Zürich, Switzerland

Received August 20, 1997
Revised Manuscript Received October 8, 1997

**THANK YOU, Ernö!**

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Q: What *was* in this set of lectures?
A: B&F Chapter 2 main concepts:

- "Section 2.1":     Salt; Activity; Underpotential deposition

- Section 2.3:       Transference numbers; Liquid-junction potentials

- Sections 2.2 & 2.4: Donnan potentials; Membrane potentials; pH meter; Ion-selective electrodes

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