Lecture #16 of 20+

Liquid-Junction Potentials

Chapter 2

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

**RECALL:**

<table>
<thead>
<tr>
<th>Type 1</th>
<th>Type 2</th>
<th>Type 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 M HCl</td>
<td>0.1 M HCl</td>
<td>0.1 M HCl</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>H⁺</td>
<td>K⁺</td>
</tr>
<tr>
<td>H⁺</td>
<td>Cl⁻</td>
<td>K⁺</td>
</tr>
<tr>
<td>H⁺</td>
<td>Cl⁻</td>
<td>K⁺</td>
</tr>
</tbody>
</table>

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

**RECALL:**  

<table>
<thead>
<tr>
<th>Type 1</th>
<th>Type 2</th>
<th>Type 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₁ = (φβ – φα) = (μ⁺ – μ⁻)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E₂ = ( \frac{RT}{F} \ln \frac{α}{β} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E₃ = ( \sum \frac{</td>
<td>z</td>
<td>υ_l}{z} [C_l(β) – C_l(α)] )</td>
</tr>
</tbody>
</table>

**Type 1**

\( E₁ = \frac{RT}{F} \ln \frac{α}{β} \) (with a few assumptions, pg. 72) 

**Type 2**

\( E₂ = \frac{RT}{F} \ln \frac{α}{β} \) (with a few assumptions, pg. 72) 

**Type 3**

\( E₃ = \sum \frac{|z|υ_l}{z} [C_l(β) – C_l(α)] \) (with a few assumptions, pg. 72) 

---

---

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

**Type 3:**

\[ E₃ = \sum \frac{|z|υ_l}{z} [C_l(β) – C_l(α)] \]

where \( α \) is the mobility of species \( i \), and \( C_l \) is its molar concentration. For type 2 junctions between 1:1 electrolytes, this equation collapses to the Lewis-Dragendt relation:

\[ E₂ = \frac{RT}{F} \ln \frac{α}{β} \] (2.3.40)

where \( J \) (the equivalent conductivity) is defined as follows: \( \Lambda = \frac{K}{C_{eq}} \)

---

---

... 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...

\[ E₃ = \frac{RT}{F} \ln \frac{α}{β}, \text{ where } K = \frac{f}{C_{eq}} \]

---

---

... 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...

Type 3: \[
E_i = \frac{\sum \left| \frac{n_i}{z_i} \right| (C_i(B) - C_i(\alpha))}{\sum |n_i| C_i(B) - C_i(\alpha)} \text{RT} \ln \frac{\sum |n_i| C_i(B)}{\sum |n_i| C_i(\alpha)}
\] (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*”: \[
E_i = \frac{RT}{F} \lambda \frac{\sum |n_i| C_i(\alpha)}{\sum |n_i| C_i(B)}
\] (2.3.40)

... 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 (\( \beta \))

... 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)...

Note: \( \alpha \) and \( \beta \) are switched...
... anyway...

Donnan potential: A special liquid-junction potential due to fixed charges

... here are two systems in which Donnan potentials play a prominent role:

- an ionomer film
- a cell

... consider this model which applies to both scenarios...

a film of poly(styrene sulfonate)
Because differences in electrochemical potential ($\mu_i^m$) – 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:

$$\mu_i^m + RT \ln y_i^m + RT \ln z_i^m + z_i F \phi^m = \mu_i^s + RT \ln y_i^s + RT \ln z_i^s + z_i F \phi^s$$

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

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

... or...

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

... recall the scenario we are analyzing...

... with $R^-$ representing the fixed charges...

a film of poly(styrene sulfonate)

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

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

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

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

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

... an equation quadratic in $c^m_{Cl^-}$ is obtained as follows...
because in solution, $c_{Na^+} = c_{Cl^-}$ for goodness sakes!

... an equation quadratic in $c_{Cl^-}$ is obtained as follows...

\[ c_{Na^+}^S + c_{Cl^-}^S = c_{Na^+}^m + c_{Cl^-}^m \]

\[ c_{Na^+}^S = c_{Cl^-}^S \]

\[ (c_{Cl^-}^S)^2 = (c_{Cl^-}^m)^2 + c_{Cl^-}^m c_{Cl^-}^R \]

\[ 0 = (c_{Cl^-}^m)^2 + c_{Cl^-}^m c_{Cl^-}^R - (c_{Cl^-}^S)^2 \]

... use the quadratic formula to solve for $c_{Cl^-}^m$ and one gets...

\[ c_{Cl^-}^m = \frac{-c_{Cl^-}^R + \sqrt{(c_{Cl^-}^R)^2 + 4(c_{Cl^-}^S)^2}}{2} = \frac{c_{Cl^-}^m}{2} \left( \sqrt{1 + \frac{4}{c_{Cl^-}^R}} - 1 \right) \]

632

\[ c_{Cl^-}^m = \frac{-c_{Cl^-}^R + \sqrt{(c_{Cl^-}^R)^2 + 4(c_{Cl^-}^S)^2}}{2} = \frac{c_{Cl^-}^m}{2} \left( \sqrt{1 + \frac{4}{c_{Cl^-}^R}} - 1 \right) \]

if $c_{Cl^-}^S \ll c_{Cl^-}^R$ (which is the typical case of interest), then...

\[ \sqrt{1 + \frac{4}{c_{Cl^-}^R}} = 1 + 2 \left( \frac{c_{Cl^-}^S}{c_{Cl^-}^R} \right)^2 \]

(Taylor/Maclaurin series expansion to the first 3 (or 4) terms)
... 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 \( C_{R-} \), the smaller is \( C_{Cl^-} \)

... so how excluded is excluded?

... is \( C_{Cl^-} < C_{R-} \) a reasonable assumption? What is \( C_{R-} \)?

... 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 \( C_{Cl^-} = 0.1 \) M...

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

... but what if \( C_{Cl^-} \) is also large... (e.g. 0.6 M, like in ocean water)?

... No more Donnan exclusion!

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

\[ \text{log} = -3 \]

\[ \text{log} = -1 \]

\[ \text{log} = -3 \]

\[ \text{log} = -5 \]

... 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...

... 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 \( \text{C}_{\text{Na}^+} \) and \( \text{C}_{\text{Cl}^-} \)!

... think log-scale

a film of poly(styrene sulfonate)

... but Donnan exclusion is “amplified” in Nafion and other polymers...  

How?

Nafion phase segregates into a hydrophobic phase, concentrated in \(-(\text{CF}_2)\)- backbone, and hydrophilic clusters of \(-\text{SO}_3^-\) solvated by water...

... and \(-\text{SO}_3^-\) clusters are interconnected by channels that percolate through the membrane, imparting a percolation network for ionic conduction

... but Donnan exclusion is “amplified” in Nafion and other polymers...

How?

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 \( \text{SO}_3^- \left( C_{s_{m}} \right) \) 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 \( \text{SO}_3^- \) 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 drops across, or in, phases (including solid membranes) and is the design for pH meters and ion-selective electrodes (ISEs). Wow!

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

... 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

http://www.chemie.uni-osnabrueck.de/
Active I/E Converter versus Passive I/E Converter

... 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)

Recall...
Active I/E Converter versus Passive I/E Converter
... meaning “newer”

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

... unlike when measuring the potential of electrons in semiconductors, liquid junctions and specific redox chemistries allow one to separate the (Nernstian) chemical potential difference of ions from the (Galvani/inner) electric potential difference \( \phi \) generated due to other ions. Electrochemistry rules...

... for semiconductors, one can approximate \( \phi \) as the (Volta/outer) electric potential difference \( \phi \) using Kelvin probe force microscopy

Cheung and Sprak, PCCP, 2012, 14, 11245
Donnan potentials can be used to concentrate metal ions...

... 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


from Wiki

Frederick George Donnan (1870–1956)

\[
\begin{align*}
[H_3O^+]_R &= 10 \text{ mM} \\
[Cu^{2+}]_R &= 30 \text{ ppm} \\
[SO_4^{2-}]_R &= 0.5 \text{ mM} + 30 \text{ ppm} \\

[H_3O^+]_L &= 1 \text{ mM} \\
[Cu^{2+}]_L &= 30 \text{ ppm} \\
[SO_4^{2-}]_L &= 0.5 \text{ mM} + 30 \text{ ppm} \\
\end{align*}
\]

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

\[
E_{\text{Donnan}} = \frac{-RT}{zF} \ln \left( \frac{a_{R^{+}}}{a_{L^{+}}} \right) = \frac{0.05916}{1} \log \frac{10}{1} = 0.059V
\]

\[
E_{\text{Donnan}} = 0.059V = \frac{-RT}{(2)F} \ln \left( \frac{a_{G_{\text{Cu}^{2+}}}}{a_{G_{L^{+}}}} \right)
\]

\[
\frac{a_{G_{\text{Cu}^{2+}}}}{a_{G_{L^{+}}}} = \left( \frac{a_{G_{\text{Cu}^{2+}}}}{30 \text{ ppm}} \right)^R = 10^{\frac{0.05916}{0.05916}} = 100
\]

\[
\left( a_{G_{\text{Cu}^{2+}}} \right)^R = 3000 \text{ ppm}
\]
Donnan potentials can be used to concentrate metal ions...

...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!

\[
\begin{align*}
\text{start} & \quad \text{equilibrium} \\
[\text{H}_3\text{O}^+] = 1 \text{ mM} & \quad [\text{H}_3\text{O}^+] = 10 \text{ mM} \\
[\text{Cu}^{2+}] = 30 \text{ ppm} & \quad [\text{Cu}^{2+}] = ?? \text{ ppm} \\
[\text{SO}_4^{2-}] = 0.5 \text{ mM} + + 30 \text{ ppm} & \quad [\text{SO}_4^{2-}] = 5 \text{ mM} + + 30 \text{ ppm} \\
\end{align*}
\]

\text{cation-exchange membrane (e.g. Nafion or PSS)}

...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)...
example: Given the following two RHE REs, calculate $E_{\text{cell}}$ and $E_j$?

\[ E_{\text{cell}} = E_{\text{Nernst}} + E_j = E^0 - \frac{RT}{F} \ln \left( \frac{a_\alpha^{\text{H}_2} a_\beta^{\text{HCl}}}{a_\text{cell}^{\text{H}_2} a_\text{cell}^{\text{HCl}}} \right) + (t_+ - t_-) \frac{RT}{F} \ln \left( \frac{a_\alpha^{\text{HCl}}}{a_\beta^{\text{HCl}}} \right) \]

Nernst potential  Li potential

\[ E_{\text{cell}} = -\frac{RT}{F} \ln \left( \frac{a_\alpha^{\text{H}_2}}{a_\alpha^{\text{H}_2}} \right) + (t_+ - t_-) \frac{RT}{F} \ln \left( \frac{a_\text{cell}^{\text{HCl}}}{a_\text{cell}^{\text{HCl}}} \right) \]

\[ E_{\text{cell}} = 0.05916 \log \left( \frac{a_\text{cell}^{\text{H}_2}}{a_\text{cell}^{\text{H}_2}} \right) (-1 + (0.83 - 0.17)) \]

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

... so what is $E_{\text{Nernst}}$, and what is $E_j$? $E_{\text{Nernst}} = -60 \text{ mV}; E_j = +40 \text{ mV}$

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

\[ E_{\text{cell}} = E_{\text{Nernst}} + E_j = E^0 - \frac{RT}{F} \ln \left( \frac{a_\alpha^{\text{H}_2} a_\beta^{\text{HCl}}}{a_\text{cell}^{\text{H}_2} a_\text{cell}^{\text{HCl}}} \right) + (t_+ - t_-) \frac{RT}{F} \ln \left( \frac{a_\alpha^{\text{HCl}}}{a_\beta^{\text{HCl}}} \right) \]

Nernst potential  Li potential

\[ E_{\text{cell}} = -\frac{RT}{F} \ln \left( \frac{a_\alpha^{\text{H}_2}}{a_\alpha^{\text{H}_2}} \right) + (t_+ - t_-) \frac{RT}{F} \ln \left( \frac{a_\text{cell}^{\text{HCl}}}{a_\text{cell}^{\text{HCl}}} \right) \]

\[ E_{\text{cell}} = 0.05916 \log \left( \frac{a_\text{cell}^{\text{H}_2}}{a_\text{cell}^{\text{H}_2}} \right) (-1 + (0.83 - 0.17)) \]

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

... neither term dominates $E_{\text{cell}}$... but what can we do to isolate $E_j$ in the cell?

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

\[ E_{\text{cell}} = E_{\text{Nernst}} + E_j = E^0 - \frac{RT}{F} \ln \left( \frac{a_\alpha^{\text{H}_2} a_\beta^{\text{HCl}}}{a_\text{cell}^{\text{H}_2} a_\text{cell}^{\text{HCl}}} \right) + (t_+ - t_-) \frac{RT}{F} \ln \left( \frac{a_\alpha^{\text{HCl}}}{a_\beta^{\text{HCl}}} \right) \]

Nernst potential  Li potential

\[ E_{\text{cell}} = -\frac{RT}{F} \ln \left( \frac{a_\alpha^{\text{H}_2}}{a_\alpha^{\text{H}_2}} \right) + (t_+ - t_-) \frac{RT}{F} \ln \left( \frac{a_\text{cell}^{\text{HCl}}}{a_\text{cell}^{\text{HCl}}} \right) \]

\[ E_{\text{cell}} = 0.05916 \log \left( \frac{a_\text{cell}^{\text{H}_2}}{a_\text{cell}^{\text{H}_2}} \right) (-1 + (0.83 - 0.17)) \]

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

... neither term dominates $E_{\text{cell}}$... but what can we do to isolate $E_j$ in the cell?

... 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 $E_{\text{cell}} = E_{\text{Nernst}}(\alpha) + R_i + E_j + E_{\text{salt}} + E_j$

... and only $E_{\text{salt}}$ is non-zero because...

... neither term dominates $E_{\text{cell}}$... but what can we do to isolate $E_j$ in the cell?
example: Given the following two RHE REs, calculate $E_{\text{cell}}$ and $E_j$?

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

... by looking at a somewhat related case that B&F did for us...

Hg | HgCl$_2$ | HCl (aq, 0.1 M) | KCl (conc) | KCl (aq, 0.1 M) | Hg

Recall, the Henderson Equation...

... summations are dominated by large values ($C_i$)

... so $E_j \approx 0$ at interfaces with (concentrated salt)

... so other $E_j$ values in the cell can be isolated

---

So, in summary, five equations for junction potentials...

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

\[ E_j = (\phi^a - \phi^b) = (r_a - r_b) \frac{RT}{F} \ln \frac{a^\alpha}{a^\beta} \]

\[ E_j = a \frac{RT}{F} \ln \frac{\sum C_i^\alpha}{\sum C_i^\beta} \]

\[ E_j = \frac{RT}{F} \ln \frac{\sum C_i^\alpha}{\sum C_i^\beta} \]

\[ E_n = \frac{RT}{F} \ln \frac{\sum P_{\alpha \beta} [M_i^\alpha] [\alpha^\beta]}{\sum P_{\alpha \beta} [M_i^\alpha] + \sum P_{\alpha \beta} [\alpha^\beta]} \]

---

... but first, what about “the fifth” equation?

... the Goldman–(Hodgkin–Huxley)–Katz) equation!

\[ E_m = \frac{RT}{F} \ln \left( \frac{\sum P_{\text{Na}} [\text{Na}^+]_{\text{in}} + \sum P_{\text{K}} [\text{K}^+]_{\text{in}}}{\sum P_{\text{Na}} [\text{Na}^+]_{\text{out}} + \sum P_{\text{K}} [\text{K}^+]_{\text{out}}} \right) \]

permeabilities

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

... no need for a squid giant axon (H & H)
(diameter = 0.5 mm)...

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

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

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...

1905 Walter Nernst proposes 3rd Law of Thermodynamics; In Bern, Einstein describes Brownian motion, and special

Nernst wins Nobel Prize
Beckman also created the first commercial spectrophotometer...

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

... but the glass pH electrode is exceptional in many ways...
... while it is not a generic ISE... Why?

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 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!

\[
E = \frac{RT}{F} \ln \left( \frac{a_{Na^+}}{a_{H^+}} \right) + \frac{RT}{F} \ln \left( \frac{a_{H^+} + a_{Na^+}}{a_{H^+} + a_{H_2O}} \right)
\]

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

---

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

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

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

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

1937 – Duncan Mastrines & Malcolm Dole discover a glass suitable for glass pH electrodes...

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

1961 – Max Cremer discovers that a thin glass membrane separating two solutions develops a potential related to the difference in pH between them

1906 - Arnold Beckman markets first pH electrode in Fullerton, CA for measuring acidity of lemon juice...

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...

Why use a double-junction reference electrode? 
To slow KCl salt leakage

... “#3: ion transporting element” is the key... it must be engineered to transport one ion selectively... in other words, its transport number is one

Type 1 LJ \[ E_i = (\phi^0 - \phi^*) = (z_i - 1) \frac{RT}{z_iF} \ln \frac{a_i}{a_i^0} \]

ideal ISE \[ E_m = \frac{RT}{z_iF} \ln \frac{a_i}{a_i^0} \]

charge on the ion that is detected

activity of detected ion outside the electrode

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

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

real ISE \[ E_i = \text{constant} + \frac{RT}{z_iF} \ln \left( a_i + \sum_j K_j a_j \right) \]

selectivity coefficient

activity of interfering ion, j
... a generic ISE calibration curve...

\[ E_i = \text{constant} + \frac{RT}{z_i F} \ln \left( \sum_{j} K_{ij} a_j \right) \]

**IGram 19** Definition of the upper and lower detection limits of an ion-selective electrode according to the EUPAC recommendations.\(^{38}\)

\[ \frac{RT}{z_i F} \ln \left( \sum_{j} K_{ij} a_j \right) \]

slope = \( \frac{RT}{z_i F} \)

... the magnitude of the selectivity terms dictate the detection limit...

(SKIPPED)

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

---

**110 years of Ion-Selective Electrodes (ISEs)**

1900 – Max Cremer discovers a thin glass membrane separating two solutions develops a potential related to the difference in pH between them

1905 – Walter Nernst proposes 3rd Law of Thermodynamics

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

1908 – Duncan MacInnes & Malcolm Dole discover a glass suitable for glass pH-electrodes...

1913 – Arnold Beckman markets first pH electrode in Fullerton, CA for measuring acidity of lemon juice...

1916 – Pungor & Hallos-Rokosini invent the solid membrane ISE

1930 – Arnold Beckman markets first pH electrode in Fullerton, CA for measuring acidity of lemon juice...

1961 – Frant & Ross describe the F selectivity electrode

1966 – Frant and Ross describe the F-selective electrode

1980 – Pungor & Hallos-Rokosini invent the solid membrane ISE
Electrode for Sensing Fluoride
Ion Activity in Solution

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 pH 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, 1555

The Champion of ISEs: The F$^-$ selective electrode...

... however, as one might guess, OH$^-$ is a strongly interfering ion for this ISE membrane

![Figure 1. Cell potential vs. NaF activity in water (left) vs. NaF activity in 1 M NaF (right), showing selectivity of F$^-$-selective membrane filmed with film of Fig. 1, bottom.)](image)

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

The Beckman G

Nernst wins Nobel Prize

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

1920s – Duncan Mastines & 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...

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

1966 – Frant and Ross describe the F$^-$ selective electrode

1967 – Ross demonstrates the first liquid membrane ISE

1967 – Ross demonstrates the first liquid membrane ISE
What is a liquid membrane ISE?

(aqueous)

organic solvent immiscible with water (non-aqueous)

porous hydrophobic membrane material (e.g., Goretex)

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

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

**BRIEFLY**

Interfering ions (and concentrations) for the nitrate selective electrode...

<table>
<thead>
<tr>
<th>Interferences</th>
<th>Molar/Liter</th>
<th>10^-4 M Nitrate</th>
<th>10^-3 M Nitrate</th>
<th>10^-2 M Nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ClO₂⁻</td>
<td>5 x 10⁻²</td>
<td>5 x 10⁻²</td>
<td>5 x 10⁻²</td>
<td></td>
</tr>
<tr>
<td>(b) NO₂⁻</td>
<td>5 x 10⁻²</td>
<td>5 x 10⁻²</td>
<td>5 x 10⁻²</td>
<td></td>
</tr>
<tr>
<td>(c) Cl⁻</td>
<td>1 x 10⁻³</td>
<td>1 x 10⁻³</td>
<td>1 x 10⁻³</td>
<td></td>
</tr>
<tr>
<td>(d) Br⁻</td>
<td>1 x 10⁻³</td>
<td>1 x 10⁻³</td>
<td>1 x 10⁻³</td>
<td></td>
</tr>
<tr>
<td>(e) H₂PO₄⁻</td>
<td>1 x 10⁻³</td>
<td>1 x 10⁻³</td>
<td>1 x 10⁻³</td>
<td></td>
</tr>
<tr>
<td>(f) HPO₄²⁻</td>
<td>5 x 10⁻³</td>
<td>5 x 10⁻³</td>
<td>5 x 10⁻³</td>
<td></td>
</tr>
<tr>
<td>(g) PO₄³⁻</td>
<td>5 x 10⁻³</td>
<td>5 x 10⁻³</td>
<td>5 x 10⁻³</td>
<td></td>
</tr>
<tr>
<td>(h) OAc</td>
<td>2 x 10⁻¹</td>
<td>0.2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>(i) F⁻</td>
<td>6 x 10⁻⁴</td>
<td>0.6</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>(j) SO₄²⁻</td>
<td>6.1</td>
<td>16.0</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>
... Calcium selective electrode...

\[ E = E_r + S \cdot \log (A) \]

Thermo Scientific, ISE Manuals

... you get the idea...

682

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

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

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

1905 – Duncan Mastinnes & Malcolm Dole discover a glass suitable for glass pH electrodes...

1913 – Arnold Beckman markets first pH electrode in Fullerton, CA for measuring acidity of lemon juice.

1920 – Arnold Beckman in Fullerton, CA...

1920’s – Duncan Mastinnes & Malcolm Dole discover a glass suitable for glass pH electrodes...

1920’s – Duncan Mastinnes & 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.

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

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

1940 – Walter Nernst wins Nobel Prize.

1950 – Arnold Beckman in Fullerton, CA...

1961 – Pungor & Hallos-Rokosinij invent the solid membrane ISE.

1961 – Pungor & Hallos-Rokosinij invent the solid membrane ISE.

1961 – Pungor & Hallos-Rokosinij invent the solid membrane ISE.

1967 – Ross demonstrates the first liquid membrane ISE.

1967 – Ross demonstrates the first liquid membrane ISE.

1967 – Ross demonstrates the first liquid membrane ISE.

1967 – Ross demonstrates the first liquid membrane ISE.

1967 – Ross demonstrates the first liquid membrane ISE.

1966 – Frant and Ross describe the F- selective electrode.

1966 – Frant and Ross describe the F- selective electrode.

1966 – Frant and Ross describe the F- selective electrode.

1966 – Frant and Ross describe the F- selective electrode.

1966 – Frant and Ross describe the F- selective electrode.

1966 – Frant and Ross describe the F- selective electrode.

1966 – Frant and Ross describe the F- selective electrode.

683

a breakthrough discovery by Ernö Pretsch (ETH Zürich)...

6+ orders of magnitude more?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!?!!!
What did Ernö Petsch do?

... a "simple" idea...
... replace the inner filling solution of the ISE with a metal ion buffer!

![Diagram of an ion selective electrode](https://example.com/diagram.png)


What’s a metal ion buffer?

... Well, first of all, what’s a $\text{H}^+$ (pH) buffer?

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$$

$a$ weak acid $a$ weak base

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

make these large...
... which fixes $[\text{H}_3\text{O}^+]$
... even at a small value

$$[\text{H}_3\text{O}^+] = K_a[\text{HA}]$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = pK_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

... Henderson–Hasselbalch equation

Case in point: Phosphate = three equilibria, three $\text{H}^+$ buffers

![Phosphate Titration](https://example.com/graph.png)

$pK_{a1} = 2.1$

$pK_{a2} = 7.2$

$pK_{a3} = 12.4$

$pH_{\text{end point 1}}$

$pH_{\text{end point 2}}$

$pH_{\text{end point 3}}$

Equivalents $\text{OH}^-$ (to remove $\text{H}^+$)

... by adding $\text{OH}^-$ buffer
What's a metal ion buffer? Just like it sounds...

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

EDTA

**EDTA-metal chelate**

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

... which fixes \([M^{n+}]\) ... even at a small value

\[ pM = -\log[M^{n+}] = -pK_{MY} + \log \left( \frac{[Y^{4-}]}{[MY]^{(n-4)+}} \right) \]
... buffering of $M^{n+}$ occurs after (SKIPPED)

$pM = -\log[M^{n+}] = -pK_{M^{n+}} + \log \left( \frac{[Y^{4-}]_0}{[Y^{4-}]_t} \right)$ ... by adding EDTA buffer

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

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

conventional ISE

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

leaked $M^{n+}$, $[M^{n+}] = 10^6 \text{ M}$

... so you can't detect anything lower than this!
... so, what does a metal ion buffer have to do with an ISE?

**Conventional ISE**

- Filling solution: \([M^{n+}]_{\text{free}} = 10^{-10} \text{ M}\)
- Leaked \(M^{n+}\): \([M^{n+}] = 10^{-12} \text{ M}\)

... and so \(\approx 10^{-12} \text{ M}\) can be detected!

---

A breakthrough discovery by Ernő Pretsch (ETH Zürich)...

![Graph](image)

**Thank you, Ernő!**

http://www.pretsch.ethz.ch/EP/Pretsch.html


---

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