Lecture #8 of 14

(3: TThF, 5: MT*W*Th<u>F</u>, 4: MT*W*Th, 2: TW)

{we are halfway through the lectures… tear}

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

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so we can already conclude that chemistry…

… is super cool… but you already knew that…

… is quite diverse, and thus requires a wide range of knowledge

… is at the heart of some very interesting, and still unexplained, scientific observations

… opens up many opportunities to innovate on new processes and technologies

… and is consequently an extremely active area of scientific endeavor, of course!

<u>Course philosophy</u> (me *versus* you)

Theory/Experiments *versus* Applications/Processes

I will teach the theory, history, and experimental specifics, and you will teach details of the applications and interesting recent chemical discoveries

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… wow, those were some neat examples of chemistry…

… I wish I could learn more about all of them!

… Lucky you! … Lucky us!

- Synchronous presentation: 12 min max + 3 min for Q&A, as 6 – 8 slides *emailed to me the day before the presentation*
- <u>One seminal and/or review publication (~70% of the time)</u>; include background and the nitty gritty of how it works; **your main goal should be to bridge information presented in the course to your topic, and to teach us something entirely new related to *chemistry***
- <u>One recent publication (2015 or later) (~30% of the time)</u>; include what the paper did, the major discovery, and a critical chemical assessment of their data interpretation, **including at least one graph or plot of useful *chemical* data**!

… this, plus the Assignments, equal 70% of your course grade, so take them seriously, and HAVE FUN!

e-Presentation… *to get a general idea, these are good topic choices in* *<u>photo</u>-chemistry alone*… **(REVIEW)** 149

- silver-halide photography
- photolithography
- vision
- vitamin D synthesis
- ultraviolet-light-driven DNA dimerization
- natural photosynthetic ion pump
- natural photosynthetic light-harvesting complex and coherent energy transfer
- natural photosynthetic Z-scheme electron-transport chain
- nanoparticle solar fuels photocatalysis
- dye-sensitized solar cells
- excitonic solar cells with trap states
- dye lasers
- medical applications
- fluorescence microscopy pH sensing
- fluorescence microscopy electric field sensing
- long-lived phosphorescence by organic molecules
- persistent luminescence by lanthanide-doped phosphors
- chemiluminescence
- photoredox catalysis in organic synthesis
- photolabile organic radicals
- atmospheric chemistry in the ozone layer with refrigerants
- photolabile inorganic coordination compounds
- light-induced excited spin-state trapping (LIESST) spin-crossover effect
- molecular solar thermal energy storage (MOST)
- triplet-triplet annihilation upconversion
- hot/ballistic excited-state electron transfer

… or propose your own to me… which I really do prefer that you do

… you will get one of your top 5 choices… more info coming soon…

e-Presentation… *and these are good topic choices in* *<u>electro</u>-chemistry alone*… **(REVIEW)** 150

- fast electrochemistry
- low conductivity electrochemistry
- rotating (ring) disk electrochemistry
- electro-osmotic flow
- electrochemical impedance spectroscopy
- bulk (water) electrolysis
- thin-layer electrochemistry
- stripping analysis
- coupled reactions / catalysis
- modified electrodes
- electrochemical scanning tunneling microscopy
- scanning electrochemical microscopy
- spectroelectrochemistry
- in situ, operando spectroscopy
- electrochemical quartz crystal microbalance
- electro-generated chemiluminescence
- aluminum extraction and processing
- bipolar electrochemistry
- electrodeposition / electroless deposition
- chlor-alkali process
- polymer-electrolyte fuel cells
- solid-oxide fuel cells / electrolyzers
- batteries (acid/base; intercalation)
- redox flow batteries
- electrochemical supercapacitors
- (bio)sensors
- electrodialysis
- nanopore/nanorod ion conductors

… or propose your own to me… which I really do prefer that you do

… you will get one of your top 5 choices… more info coming soon…

Discussion *(an hour-ish every-other-day-ish)* provides opportunities to discuss applied pchem research 151
… of course, there are way too many topics to cover, but I decided on the following as the **FINAL** list:

(1) M7/11 (DONE): "Single-Molecule Lysozyme Dynamics Monitored by an Electronic Circuit", Y Choi, IS Moody, PC Sims, SR Hunt, BL Corso, I Perez, GA Weiss & PG Collins, *Science*, **2012**, *335*, 319, DOI: 10.1126/science.1214824

(2) W7/13 (DONE): "Control of hierarchical polymer mechanics with bioinspired metal-coordination dynamics", SC Grindy, R Learsch, D Mozhdehi, J Cheng, DG Barrett, Z Guan, PB Messersmith & N Holten-Andersen, *Nature Materials*, **2015**, *14*, 1210, DOI: 10.1038/nmat4401

(3) Th7/14 (DONE): "Experiments and Simulations of Ion-Enhanced Interfacial Chemistry on Aqueous NaCl Aerosols", EM Knipping, MJ Lakin, KL Foster, P Jungwirth, DJ Tobias, RB Gerber, D Dabdub & BJ Finlayson-Pitts, *Science*, **2000**, *288*, 301, DOI: 10.1126/science.288.5464.301

(4) F7/15 *(today!)*: "Potentially Confusing: Potentials in Electrochemistry", SW Boettcher, SZ Oener, MC Lonergan, Y Surendranath, S Ardo, C Brozek & PA Kempler, *ACS Energy Letters*, **2021**, *6*, 261, DOI: 10.1021/acsenergylett.0c02443

(5) T7/19: "Solid-State Ionic Diodes Demonstrated in Conical Nanopores", TS Plett, W Cai, ML Thai, IV Vlassiouk, RM Penner & ZS Siwy, *Journal of Physical Chemistry C*, **2017**, *121*, 6170, DOI: 10.1021/acs.jpcc.7b00258

(6) Th7/21: "Stable and Efficient Single-Atom Zn Catalyst for CO_2 Reduction to CH_4", L Han, S Song, M Liu, S Yao, Z Liang, H Cheng, Z Ren, W Liu, R Lin, G Qi, X Liu, Q Wu, J Luo & HL Xin, Journal of the American Chemical Society, **2020**, *142*, 12563, DOI: 10.1021/jacs.9b12111

(7) T7/26: "Visualizing vibrational normal modes of a single molecule with atomically confined light", J Lee, KT Crampton, N Tallarida & VA Apkarian, *Nature*, **2019**, *568*, 78, DOI: 10.1038/s41586-019-1059-9

… here is what I converged on… let's stick with these (for now)

152

... the CRC Handbook has a lot of chemical information... including tables of values...
... such as those in the Electrochemical Series...

Can you identify what the reference potential is for this list of standard(-state) reduction potentials? *(it's like the infinite vacuum)*

UCI PHYSICS/CHEM207 – Applied Physical Chemistry, Summer 2022

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Charged Interfaces

Quiz Time!

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

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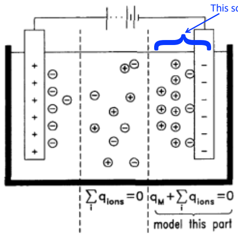
Charged Interfaces

- Vacuum level, Redox half-reactions
- Nernst equation
- History, Conventions
- Electrodes, Potentiostat
- **Electric double layer**
- **Electric potentials, Liquid-junction potentials, Donnan potential, Membrane potential**
- **pH probe, Acidity scale, Titrations, Buffering, Henderson–Hasselbalch equation**
- Latimer diagram, Pourbaix diagram

the electronic and ionic charge on an electrode, q_M, is compensated by the accumulation of oppositely charged ions in solution: $q_M = -q_S$

… we should understand the details of how these electrified interfaces are structured… and metal–solution interfaces are well understood

This sort of looks like a parallel plate capacitor



… the bulk solution is called "quasi-neutral"

What is the potential difference between the two sides of the interface? E_{app}

What is the potential difference between one side and near the middle? $\sim E_{app}/2$

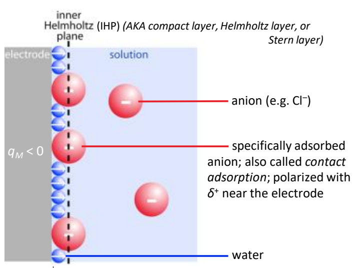
Does a solution reactant located within the double layer "feel" E_{app} or $<E_{app}$?

$<E_{app}$… *mind = blown!*

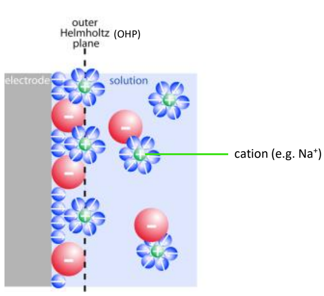
Michael R. Philpott and James N. Glosli†

IBM Almaden Research Center
650 Harry Road, San Jose CA 95120-6099
†Lawrence Livermore National Laboratory
Livermore CA 94550

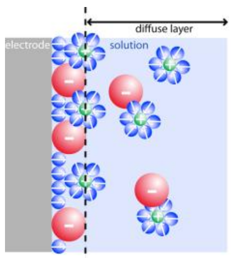
… anyway… in polar solvents, all charged electrode surfaces possess a common structure…

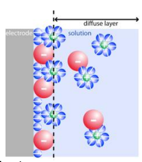


… cations have strongly coordinated waters that exchange slowly…



… the (second) layer of solution extending from the OHP that has a composition perturbed from bulk is called the diffuse layer

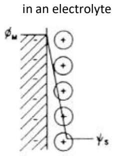




Notice particularly the following:

1) A layer of *oriented waters* covers the surface…
   … water orientation (O or H) is dictated by the surface charge
2) Anions shed their primary hydration layers and directly adsorb onto the surface. This is called "specific adsorption"…
   … with F^- being an exception
3) In general, cations do not specifically adsorb; their primary hydration layers are too strongly attached (by the ion–dipole interaction) to be shed at room temperature. This is an example of "nonspecific adsorption"…
   … with $(CH_3)_4N^+$ being an exception

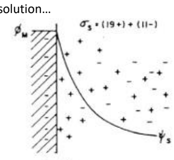
… three models for the potential distribution near a charged electrode immersed in an electrolyte solution…



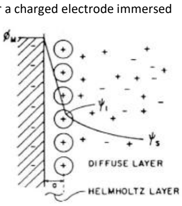
Helmholtz (H)

$\varepsilon_r \approx 6$

$$C_d = \frac{\varepsilon\varepsilon_0}{d}$$



Gouy–Chapman (GC)



Gouy–Chapman–Stern (GCS)

$$\frac{d\phi}{dx} = -\left(\frac{8kTn^0}{\varepsilon\varepsilon_0}\right)^{1/2} \sinh\left(\frac{ze\phi}{2kT}\right)$$ … Poisson–Boltzmann Equation for a 1:1 electrolyte

$\phi \approx \phi^0 \exp(-\kappa x)$… when we assume ϕ^0 is small

$$\kappa = \left(\frac{2n^0 z^2 e^2}{\varepsilon\varepsilon_0 kT}\right)^{1/2}$$ … Debye screening length… a characteristic length

http://electrochem.cwru.edu/

… History…

Physician & Physicist

Hermann Ludwig Ferdinand von Helmholtz
(1821–1894)

Physicist

Otto Stern
(1888–1926)
Nobel Prize (Physics, 1943)

Physicist

Louis Georges Gouy
(1854–1926)

P-Chemist

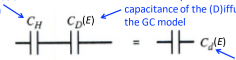
David Leonard Chapman
(1869–1958)

from Wiki

The Gouy–Chapman–Stern Model: basically, the idea is to use both the Helmholtz Model and the Gouy–Chapman Model in series:

Parallel plate capacitance of the compact layer from the (H)elmholtz model

Potential-dependent non-parallel-plate capacitance of the (D)iffuse layer from the GC model



Potential-dependent non-parallel-plate capacitance of the (d)ouble layer from the GCS model

$$\frac{1}{C_{\mathrm{d}}} = \frac{1}{C_{\mathrm{H}}} + \frac{1}{C_{\mathrm{D}}}$$

But, wait a minute! This is modeling just one interface with two sides, but there are two capacitors (and thus in total seemingly four sides)… what gives?

If it barks like a dog, and it smells like a dog, then maybe we should model it as being a dog… **What are the units?**

This means that the electric potential drop across the Helmholtz Layer (inside of the OHP) will be linear, and a quasi-exponential potential drop will extend from this point and into the bulk solution…

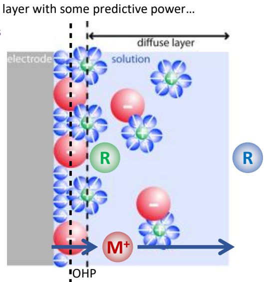
In summary, the Guoy–Chapman–Stern Model provides a semi-quantitative understanding of this electric double layer with some predictive power…

…. but don't forget my questions from the start of these slides on the double layer…

… What is the potential difference between the two sides of the interface? E_{app}

What is the potential difference between one side and near the middle? $\sim E_{\mathrm{app}}/2$

NEW QUESTION: **Can anyone explain how a corrosion reaction can be potential dependent when the electron never transfers across the metal|solution interface?**

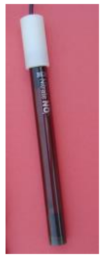


An ion transfers across the double layer… *mind = blown, again!*

Liquid-junction potentials are important in two types of electrodes / sensors…

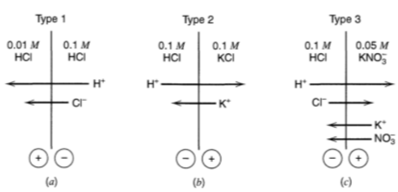
a Ag/AgCl RE

an ISE (for nitrate ions)



… liquid-junction (electric) potentials:

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

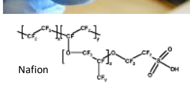


same salt; different conc. | one ion in common; same conc. | everything else

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

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

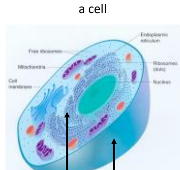
an ionomer film



Nafion

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

a cell



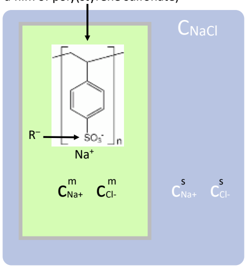
semipermeable membrane

membrane impermeable to charged macromolecules

http://www.williamsclass.com/

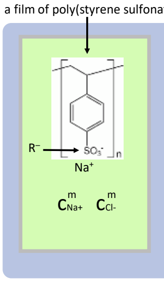
… consider this model which applies to both scenarios…

a film of poly(styrene sulfonate)



… and then there is a lot of (simple) math to get us to a simple approximate equation that helps us predict what will happen in an experiment, where…

a film of poly(styrene sulfonate)



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

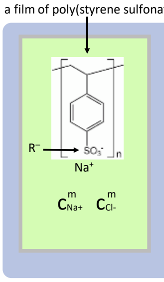
$$C^m_{Cl^-} = \frac{\left(C^s_{Cl^-}\right)^2}{C^m_{R^-}} = \frac{(0.1)^2}{1.0} = 0.01\ \mathrm{M}$$

log = -1; log = 0; log = -2

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

… and then there is a lot of (simple) math to get us to a simple approximate equation that helps us predict what will happen in an experiment, where…

a film of poly(styrene sulfonate)



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

$$C^m_{Cl^-} = \frac{\left(C^s_{Cl^-}\right)^2}{C^m_{R^-}} = \frac{(0.001)^2}{0.1} = ???\ \mathrm{M}$$

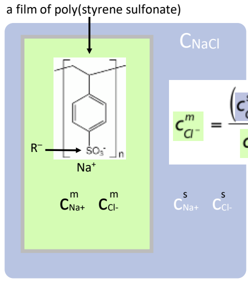
log = -3; log = -1; log = ?

… what about this?

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

… and then there is a lot of (simple) math to get us to a simple approximate equation that helps us predict what will happen in an experiment, where…

a film of poly(styrene sulfonate)



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

$$c^m_{Cl^-} = \frac{\left(c^s_{Cl^-}\right)^2}{c^m_{R^-}} = \frac{(0.001)^2}{0.1} = 10\ \mu\text{M}$$

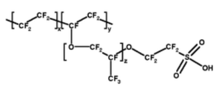
log = -3; log = -1; log = -5

… super simple!

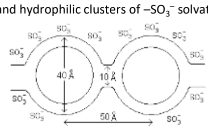
… the equation results in simple *opposing* orders-of-magnitude concentration differences for C_{Na+} and C_{Cl-}!… think log-scale

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

… How?



Nafion phase segregates into a hydrophobic phase, concentrated in –(CF_2)– backbone, and hydrophilic clusters of –SO_3^- solvated by water…

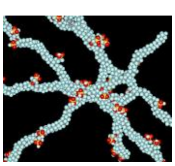


… and –SO_3^- clusters are interconnected by channels that percolate through the membrane, imparting a percolation network for ionic conduction

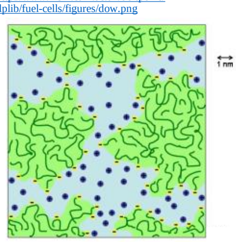
Mauritz & Moore, *Chem. Rev.*, 2004, *104*, 4535
Kusoglu & Weber, *Chem. Rev.*, 2017, *117*, 987

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

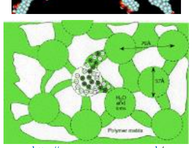
… How?



http://www.msm.cam.ac.uk/doitpoms/tlplib/fuel-cells/figures/dow.png



http://www.chemie.uni-osnabrueck.de/



http://www.ocamac.ox.ac.uk/

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!

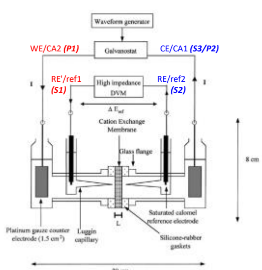
… how can one experimentally measure Donnan potentials?
… in fact, how can one measure liquid-junction potentials?
… the same way with the same set-up for both!

… 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!

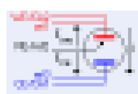
P-Chemist

Frederick George Donnan (1870–1956)
from Wiki

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



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



(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

http://www.keithley.com/products/

So, in summary, five equations for junction potentials…

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

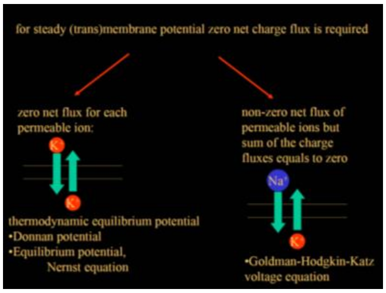
LJ, Type 1 $$E_j = (\phi^\beta - \phi^\alpha) = (t_+ - t_-)\frac{RT}{F}\ln\frac{a(\alpha)}{a(\beta)}$$

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

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

Donnan $$E_m = \frac{RT}{z_i F}\ln\frac{a_1(\alpha)}{a_2(\beta)}$$ ← the only model that, with one salt and one interface, definitely equilibrates

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

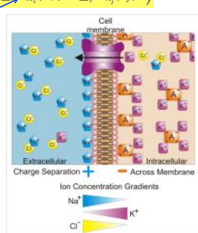


http://biophys.med.unideb.hu/old/pharmacy/Donnan%20angol2009.pdf

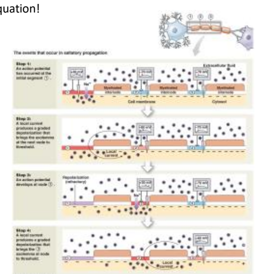
… but first, what about "the fifth" equation?
… the Goldman–(Hodgkin–(Huxley)–Katz)) equation!

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

permeabilities



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



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

… and this leads us nicely to: ~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…

the Beckman G

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

Beckman also created the first commercial spectrophotometer (more on this later)…

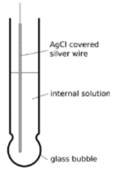
the Beckman DU spectrophotometer, 1941

the Beckman Helipot potentiometer, 1942

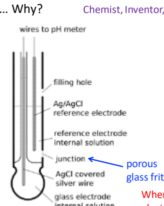
http://www.chemheritage.org/explore/Beckman/beckman.htm

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

Chemist, Inventor, Investor, Philanthropist



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

Arnold Orville Beckman
(1900 – 2004)
from Wiki

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!

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

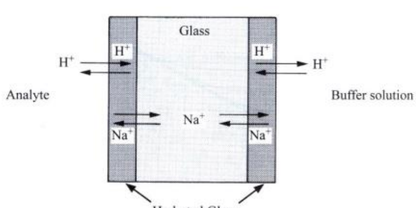


Fig. 2.25 Ionic equilibria in a glass electrode.

… 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!

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

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

What type of LJ is this?

Type 2!

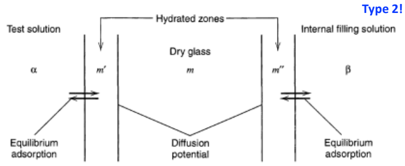


Figure 2.4.3 Model for treating the membrane potential across a glass barrier.

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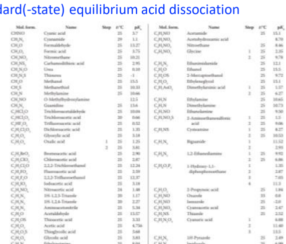
DISSOCIATION CONSTANTS OF ORGANIC ACIDS AND BASES

… *as before*, the CRC Handbook has a lot of chemical information… including tables of values… … such as those in Acidity/Basicity Series… … Again, can you identify what the reference acidity is for this list of standard(-state) equilibrium acid dissociation constants?



… pBLAH = – log a_{BLAH}

… why does this state that $pK_a + pK_b = pK_w$?
… because $K_aK_b = K_w$… **okaaaayyyy**… but why?
… because $\exp(-(\Delta G_a^o + \Delta G_b^o)) = \exp(-\Delta G_w^o)$…
… **Ahhhhh!**… enough with the algebra already!
… but wait!… this looks like Hess's law, yet again!
… so, let's add up these chemical reactions!
… Nice!

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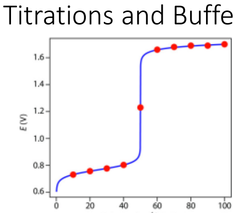
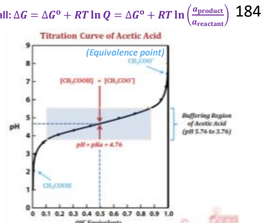
Titrations and Buffering

Recall: $\Delta G = \Delta G^o + RT\ln Q = \Delta G^o + RT\ln\left(\frac{a_{product}}{a_{reactant}}\right)$



https://chem.libretexts.org/Courses/Northeastern_University/09%3A_Titrimetric_Methods/9.4%3A_Redox_Titrations

$$E = E^o - \frac{2.303RT}{n}\log Q = E^o - \frac{0.05916\text{ V}}{n}\log\left(\frac{a_{red}}{a_{ox}}\right)$$



https://www.easybiologyclass.com/titration-curve-of-a-weak-acid-and-its-pka-biochemistry-notes/

Henderson–Hasselbalch equation

$$pH = pK_a + \log Q = pK_a + \log\left(\frac{a_{A^-}}{a_{HA}}\right)$$

… Oh chemists!… make up your minds already!… and I thought physicists were bad with q being positive!

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Charged Interfaces *(summary for today)*

- Vacuum level, Redox half-reactions
- Nernst equation
- History, Conventions
- Electrodes, Potentiostat
- **Electric double layer**
- **Electric potentials, Liquid-junction potentials, Donnan potential, Membrane potential**
- **pH probe, Acidity scale, Titrations, Buffering, Henderson–Hasselbalch equation**
- Latimer diagram, Pourbaix diagram

Paper Time!