Lecture #8 of 14

(3: TThF, 5: MT*W*Th_F_, 4: MT*W*Th, 2: TW)
{we are halfway through the lectures… tear}

Prof. Shane Ardo

Department of Chemistry

University of California Irvine

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!

Course philosophy (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

... 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*

- One seminal and/or review publication (~70% of the time); 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***

- One recent publication (2015 or later) (~30% of the time); 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!

- 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...

- 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

… 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)

Reaction	$E°/V$	Reaction	$E°/V$
$Fr^+ + e \rightleftharpoons Fr$	−2.9	$La(OH)_3 + 3\,e \rightleftharpoons La + 3\,OH^-$	−2.90
$Ga^{3+} + 3\,e \rightleftharpoons Ga$	−0.549	$Li^+ + e \rightleftharpoons Li$	−3.0401
$Ga^+ + e \rightleftharpoons Ga$	−0.2	$Lr^{3+} + 3\,e \rightleftharpoons Lr$	−1.96
$GaOH^{2+} + H^+ + 3\,e \rightleftharpoons Ga + H_2O$	−0.498	$Lu^{3+} + 3\,e \rightleftharpoons Lu$	−2.28
$H_2GaO_3^- + H_2O + 3\,e \rightleftharpoons Ga + 4\,OH^-$	−1.219	$Md^{3+} + e \rightleftharpoons Md^{2+}$	−0.1
$Gd^{3+} + 3\,e \rightleftharpoons Gd$	−2.279	$Md^{3+} + 3\,e \rightleftharpoons Md$	−1.65
$Ge^{2+} + 2\,e \rightleftharpoons Ge$	0.24	$Md^{2+} + 2\,e \rightleftharpoons Md$	−2.40
$Ge^{4+} + 4\,e \rightleftharpoons Ge$	0.124	$Mg^+ + e \rightleftharpoons Mg$	−2.70
$Ge^{4+} + 2\,e \rightleftharpoons Ge^{2+}$	0.00	$Mg^{2+} + 2\,e \rightleftharpoons Mg$	−2.372
$GeO_2 + 2\,H^+ + 2\,e \rightleftharpoons GeO + H_2O$	−0.118	$Mg(OH)_2 + 2\,e \rightleftharpoons Mg + 2\,OH^-$	−2.690
$H_2GeO_3 + 4\,H^+ + 4\,e \rightleftharpoons Ge + 3\,H_2O$	−0.182	$Mn^{2+} + 2\,e \rightleftharpoons Mn$	−1.185
$2\,H^+ + 2\,e \rightleftharpoons H_2$	0.00000	$Mn^{3+} + e \rightleftharpoons Mn^{2+}$	1.5415
$H_2 + 2\,e \rightleftharpoons 2\,H^-$	−2.23	$MnO_2 + 4\,H^+ + 2\,e \rightleftharpoons Mn^{2+} + 2\,H_2O$	1.224
$HO_2 + H^+ + e \rightleftharpoons H_2O_2$	1.495	$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$	0.558
$2\,H_2O + 2\,e \rightleftharpoons H_2 + 2\,OH^-$	−0.8277	$MnO_4^- + 4\,H^+ + 3\,e \rightleftharpoons MnO_2 + 2\,H_2O$	1.679
$H_2O_2 + 2\,H^+ + 2\,e \rightleftharpoons 2\,H_2O$	1.776	$MnO_4^- + 8\,H^+ + 5\,e \rightleftharpoons Mn^{2+} + 4\,H_2O$	1.507
$Hf^{4+} + 4\,e \rightleftharpoons Hf$	−1.55	$MnO_4^- + 2\,H_2O + 3\,e \rightleftharpoons MnO_2 + 4\,OH^-$	0.595
$HfO^{2+} + 2\,H^+ + 4\,e \rightleftharpoons Hf + H_2O$	−1.724	$MnO_4^{2-} + 2\,H_2O + 2\,e \rightleftharpoons MnO_2 + 4\,OH^-$	0.60
$HfO_2 + 4\,H^+ + 4\,e \rightleftharpoons Hf + 2\,H_2O$	−1.505	$Mn(OH)_2 + 2\,e \rightleftharpoons Mn + 2\,OH^-$	−1.56
$HfO(OH)_2 + H_2O + 4\,e \rightleftharpoons Hf + 4\,OH^-$	−2.50	$Mn(OH)_3 + e \rightleftharpoons Mn(OH)_2 + OH^-$	0.15
$Hg^{2+} + 2\,e \rightleftharpoons Hg$	0.851	$Mn_2O_3 + 6\,H^+ + e \rightleftharpoons 2\,Mn^{2+} + 3\,H_2O$	1.485
$2\,Hg^{2+} + 2\,e \rightleftharpoons Hg_2^{2+}$	0.920	$Mo^{3+} + 3\,e \rightleftharpoons Mo$	−0.200
$Hg_2^{2+} + 2\,e \rightleftharpoons 2\,Hg$	0.7973	$MoO_2 + 4\,H^+ + 4\,e \rightleftharpoons Mo + 4\,H_2O$	−0.152
$Hg_2(ac)_2 + 2\,e \rightleftharpoons 2\,Hg + 2(ac)^-$	0.51163	$H_3Mo_7O_{24}^{3-} + 45\,H^+ + 42\,e \rightleftharpoons 7\,Mo + 24\,H_2O$	0.082
$Hg_2Br_2 + 2\,e \rightleftharpoons 2\,Hg + 2\,Br^-$	0.13923	$MoO_3 + 6\,H^+ + 6\,e \rightleftharpoons Mo + 3\,H_2O$	0.075
$Hg_2Cl_2 + 2\,e \rightleftharpoons 2\,Hg + 2\,Cl^-$	0.26808	$N_2 + 2\,H_2O + 6\,H^+ + 6\,e \rightleftharpoons 2\,NH_4OH$	0.092
$Hg_2HPO_4 + 2\,e \rightleftharpoons 2\,Hg + HPO_4^{2-}$	0.6359	$3\,N_2 + 2\,H^+ + 2\,e \rightleftharpoons 2\,HN_3$	−3.09
$Hg_2I_2 + 2\,e \rightleftharpoons 2\,Hg + 2\,I^-$	−0.0405	$N_5^+ + 3\,H^+ + 2\,e \rightleftharpoons 2\,NH_4^+$	1.275

Reaction	$E°/V$	Reaction	$E°/V$
$Hg_2O + H_2O + 2\,e \rightleftharpoons 2\,Hg + 2\,OH^-$	0.123	$N_2O + 2\,H^+ + 2\,e \rightleftharpoons N_2 + H_2O$	1.766
$HgO + H_2O + 2\,e \rightleftharpoons Hg + 2\,OH^-$	0.0977	$H_2N_2O_2 + 2\,H^+ + 2\,e \rightleftharpoons N_2 + 2\,H_2O$	2.65
$Hg(OH)_2 + 2\,H^+ + 2\,e \rightleftharpoons Hg + 2\,H_2O$	1.034	$N_2O_4 + 2\,e \rightleftharpoons 2\,NO_2^-$	0.867
$Hg_2SO_4 + 2\,e \rightleftharpoons 2\,Hg + SO_4^{2-}$	0.6125	$N_2O_4 + 2\,H^+ + 2\,e \rightleftharpoons 2\,NHO_2$	1.065
$Ho^{2+} + 2\,e \rightleftharpoons Ho$	−2.1	$N_2O_4 + 4\,H^+ + 4\,e \rightleftharpoons 2\,NO + 2\,H_2O$	1.035
$Ho^{3+} + 3\,e \rightleftharpoons Ho$	−2.33	$2\,NH_3OH^+ + H^+ + 2\,e \rightleftharpoons N_2H_5^+ + 2\,H_2O$	1.42
$Ho^{3+} + e \rightleftharpoons Ho^{2+}$	−2.8	$2\,NO + 2\,H^+ + 2\,e \rightleftharpoons N_2O + H_2O$	1.591
$I_2 + 2\,e \rightleftharpoons 2\,I^-$	0.5355	$2\,NO + H_2O + 2\,e \rightleftharpoons N_2O + 2\,OH^-$	0.76
$I_3^- + 2\,e \rightleftharpoons 3\,I^-$	0.536	$HNO_2 + H^+ + e \rightleftharpoons NO + H_2O$	0.983
$H_3IO_6^{2-} + 2\,e \rightleftharpoons IO_3^- + 3\,OH^-$	0.7	$2\,HNO_2 + 4\,H^+ + 4\,e \rightleftharpoons H_2N_2O_2 + 2\,H_2O$	0.86
$H_5IO_6 + H^+ + 2\,e \rightleftharpoons IO_3^- + 3\,H_2O$	1.601	$2\,HNO_2 + 4\,H^+ + 4\,e \rightleftharpoons N_2O + 3\,H_2O$	1.297
$2\,HIO + 2\,H^+ + 2\,e \rightleftharpoons I_2 + 2\,H_2O$	1.439	$NO_2^- + H_2O + e \rightleftharpoons NO + 2\,OH^-$	−0.46
$HIO + H^+ + 2\,e \rightleftharpoons I^- + H_2O$	0.987	$2\,NO_2^- + 2\,H_2O + 4\,e \rightleftharpoons N_2O_2^{2-} + 4\,OH^-$	−0.18
$IO^- + H_2O + 2\,e \rightleftharpoons I^- + 2\,OH^-$	0.485	$2\,NO_2^- + 3\,H_2O + 4\,e \rightleftharpoons N_2O + 6\,OH^-$	0.15
$2\,IO_3^- + 12\,H^+ + 10\,e \rightleftharpoons I_2 + 6\,H_2O$	1.195	$NO_3^- + 3\,H^+ + 2\,e \rightleftharpoons HNO_2 + H_2O$	0.934
$IO_3^- + 6\,H^+ + 6\,e \rightleftharpoons I^- + 3\,H_2O$	1.085	$NO_3^- + 4\,H^+ + 3\,e \rightleftharpoons NO + 2\,H_2O$	0.957
$IO_3^- + 2\,H_2O + 4\,e \rightleftharpoons IO^- + 4\,OH^-$	0.15	$2\,NO_3^- + 4\,H^+ + 2\,e \rightleftharpoons N_2O_4 + 2\,H_2O$	0.803
$IO_3^- + 3\,H_2O + 6\,e \rightleftharpoons IO^- + 6\,OH^-$	0.26	$NO_3^- + H_2O + 2\,e \rightleftharpoons NO_2^- + 2\,OH^-$	0.01
$In^+ + e \rightleftharpoons In$	−0.14	$2\,NO_3^- + 2\,H_2O + 2\,e \rightleftharpoons N_2O_4 + 4\,OH^-$	−0.85
$In^{2+} + e \rightleftharpoons In^+$	−0.40	$Na^+ + e \rightleftharpoons Na$	−2.71
$In^{3+} + e \rightleftharpoons In^{2+}$	−0.49	$Nb^{3+} + 3\,e \rightleftharpoons Nb$	−1.099
$In^{3+} + 2\,e \rightleftharpoons In^+$	−0.443	$NbO_2 + 2\,H^+ + 2\,e \rightleftharpoons NbO + H_2O$	−0.646
$In^{3+} + 3\,e \rightleftharpoons In$	−0.3382	$NbO_2 + 4\,H^+ + 4\,e \rightleftharpoons Nb + 2\,H_2O$	−0.690
$In(OH)_3 + 3\,e \rightleftharpoons In + 3\,OH^-$	−0.99	$NbO + 2\,H^+ + 2\,e \rightleftharpoons Nb + H_2O$	−0.733
$In(OH)_4^- + 3\,e \rightleftharpoons In + 4\,OH^-$	−1.007	$Nb_2O_5 + 10\,H^+ + 10\,e \rightleftharpoons 2\,Nb + 5\,H_2O$	−0.644
$In_2O_3 + 3\,H_2O + 6\,e \rightleftharpoons 2\,In + 6\,OH^-$	−1.034	$Nd^{3+} + 3\,e \rightleftharpoons Nd$	−2.323
$Ir^{3+} + 3\,e \rightleftharpoons Ir$	1.156	$Nd^{2+} + 2\,e \rightleftharpoons Nd$	−2.1
$[IrCl_6]^{2-} + e \rightleftharpoons [IrCl_6]^{3-}$	0.8665	$Nd^{3+} + e \rightleftharpoons Nd^{2+}$	−2.7
$[IrCl_6]^{3-} + 3\,e \rightleftharpoons Ir + 6\,Cl^-$	0.77	$Ni^{2+} + 2\,e \rightleftharpoons Ni$	−0.257
$Ir_2O_3 + 3\,H_2O + 6\,e \rightleftharpoons 2\,Ir + 6\,OH^-$	0.098	$Ni(OH)_2 + 2\,e \rightleftharpoons Ni + 2\,OH^-$	−0.72
$K^+ + e \rightleftharpoons K$	−2.931	$NiO_2 + 4\,H^+ + 2\,e \rightleftharpoons Ni^{2+} + 2\,H_2O$	1.678
$La^{3+} + 3\,e \rightleftharpoons La$	−2.379	$NiO_2 + 2\,H_2O + 2\,e \rightleftharpoons Ni(OH)_2 + 2\,OH^-$	−0.490

… 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)*

Charged Interfaces

Quiz Time!

Prof. Shane Ardo

Department of Chemistry

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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
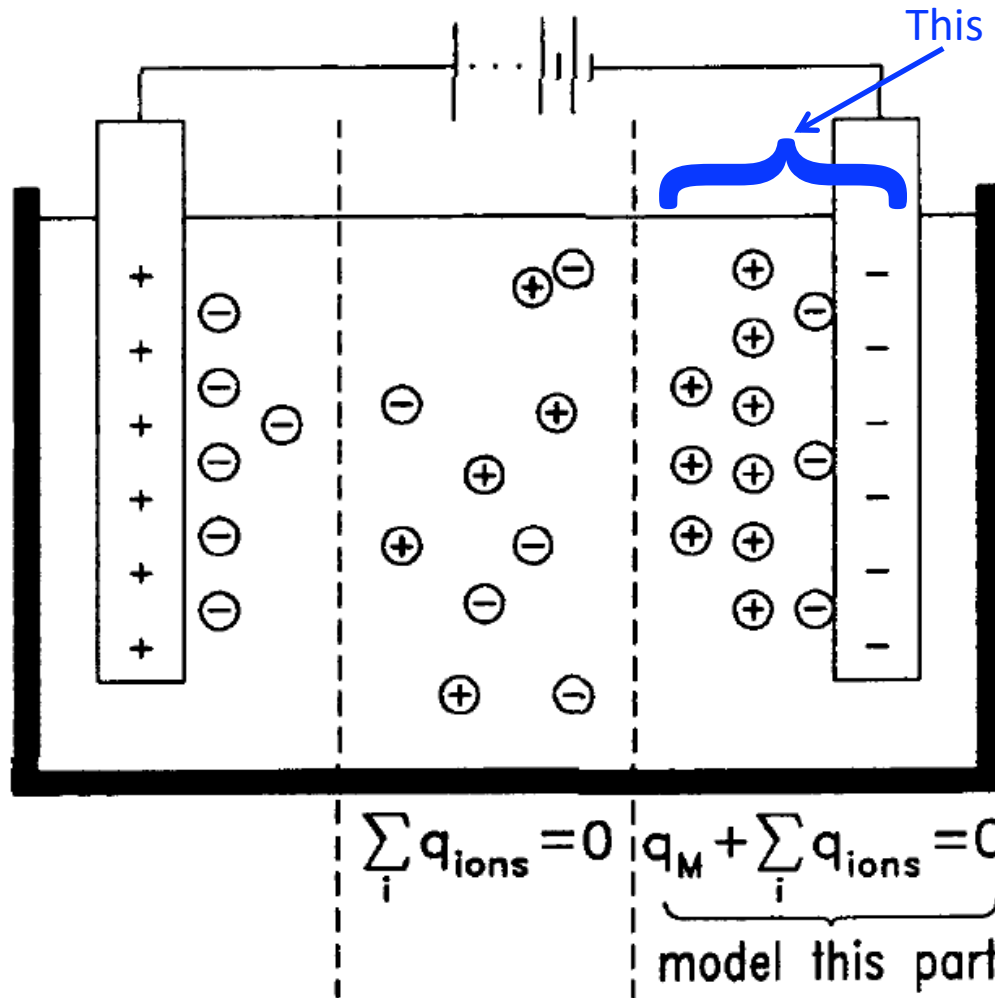
This sort of looks like a parallel plate capacitor

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? $\sim E_{app}/2$

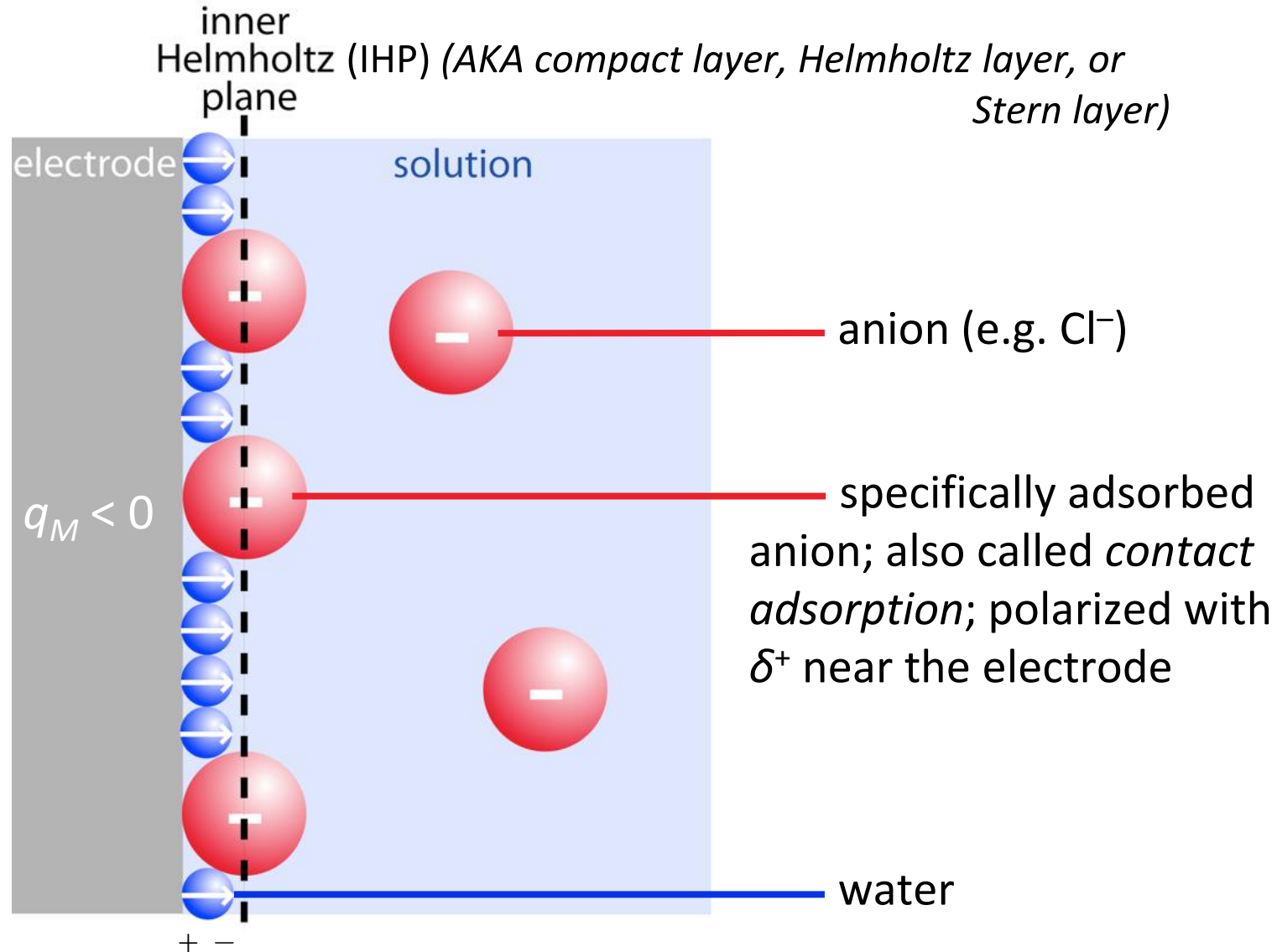Does a solution reactant located within the double layer "feel" E_{app} or $<E_{app}$?

$<E_{app}$… mind = blown!

$$\sum_i q_{ions} = 0 \quad q_M + \sum_i q_{ions} = 0$$

model this part

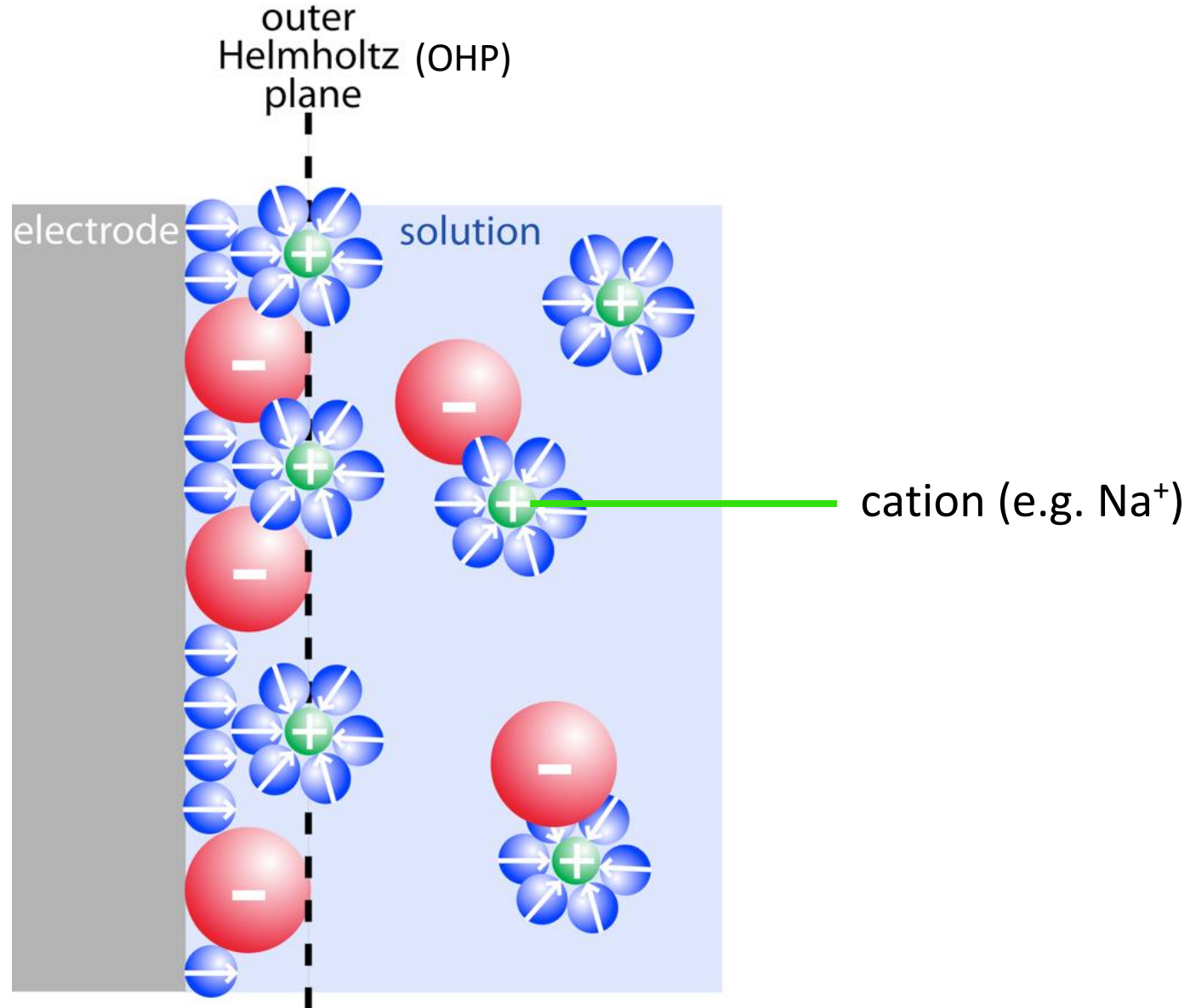… the bulk solution is called "quasi-neutral"

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

inner Helmholtz (IHP) *(AKA compact layer, Helmholtz layer, or Stern layer)*
plane

electrode

solution

$q_M < 0$

anion (e.g. Cl^-)

specifically adsorbed anion; also called *contact adsorption*; polarized with δ^+ near the electrode

water

+ −

... cations have strongly coordinated waters that exchange slowly...

outer Helmholtz (OHP) plane

electrode

solution

cation (e.g. Na$^+$)

… the (second) layer of solution extending from the OHP that has a composition perturbed from bulk is called the diffuse layer
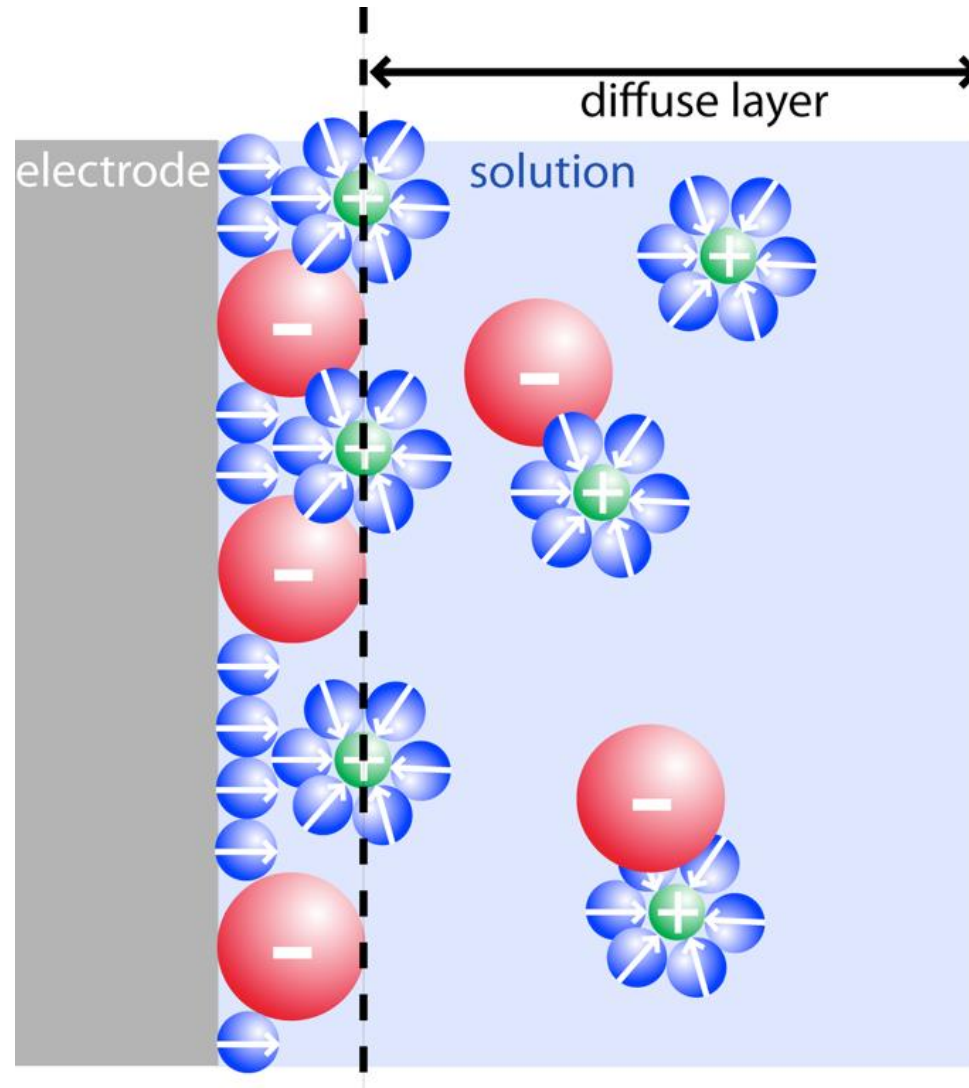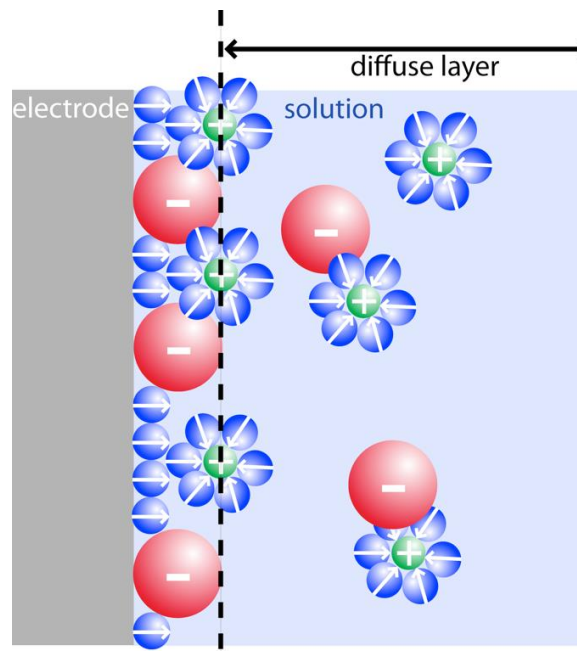
Notice particularly the following:
  1) A layer of *oriented waters* covers the surface…
   … water orientation (O or H) is dictated by the surface charge
  2) Anions shed their primary hydration layers and directly adsorb onto the surface. This is called "specific adsorption"…
                              … 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"…

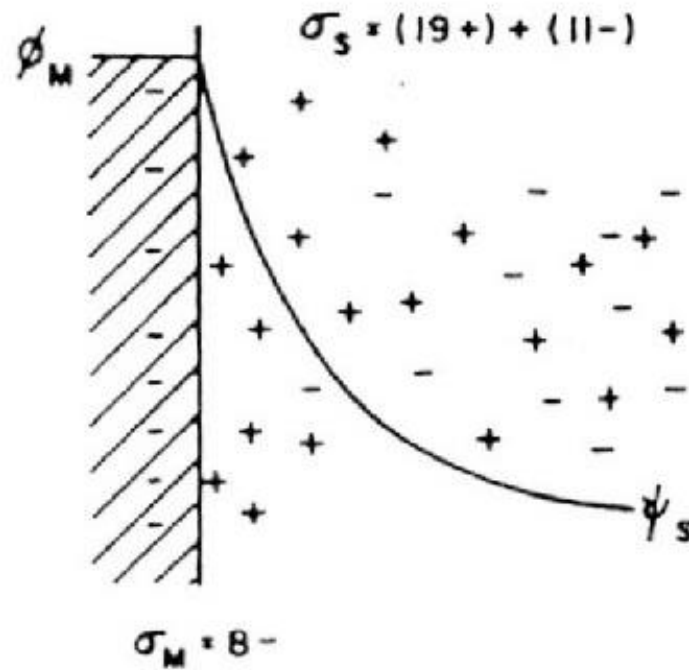   … with $(CH_3)_4N^+$ being an exception

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

Helmholtz (H)

$\varepsilon_r \approx 6$
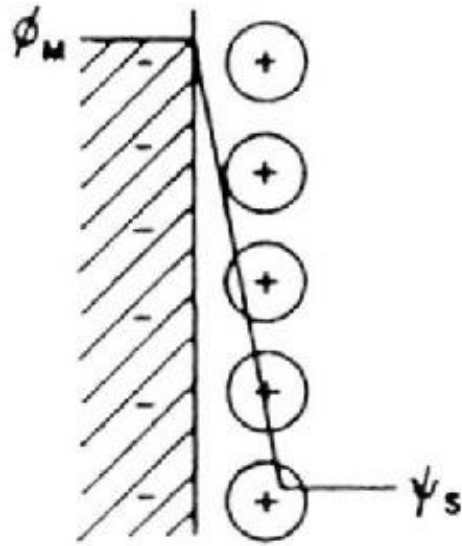
$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$
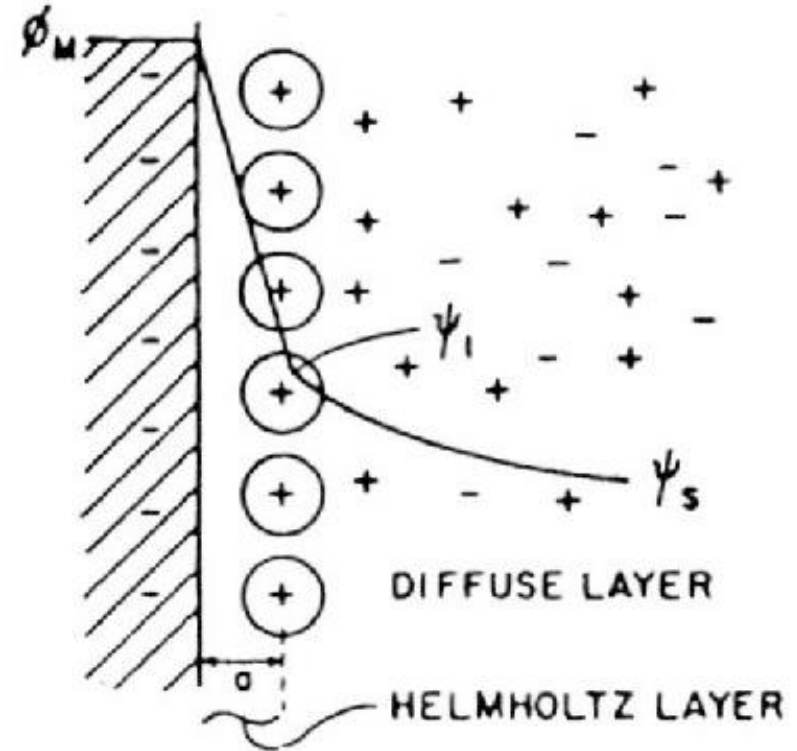
Gouy–Chapman (GC)

Gouy–Chapman–Stern (GCS)

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

$$\phi \approx \phi^0 \exp(-\kappa x)... \text{ when we assume } \phi^0 \text{ is small}$$

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

http://electrochem.cwru.edu/

... History...

Physician & Physicist

Hermann Ludwig Ferdinand von Helmholtz
(1821–1894)

Physicist

Louis Georges Gouy
(1854–1926)

P-Chemist

David Leonard Chapman
(1869–1958)

Physicist

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

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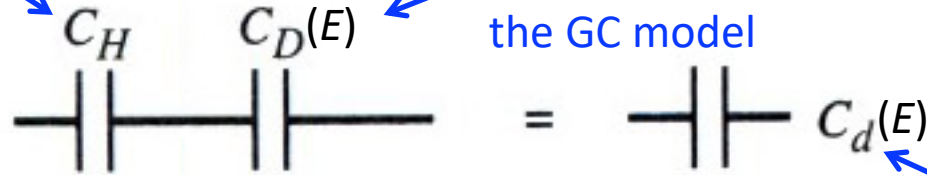
The Gouy–Chapman–Stern Model: basically, the idea is to use both the Helmholtz Model and the Gouy–Chapman Model in series:

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

$$C_H \quad C_D(E) \qquad = \qquad C_d(E)$$

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

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}$$

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? $\sim E_{app}/2$

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

diffuse layer

electrode

solution

R

R

M⁺

OHP

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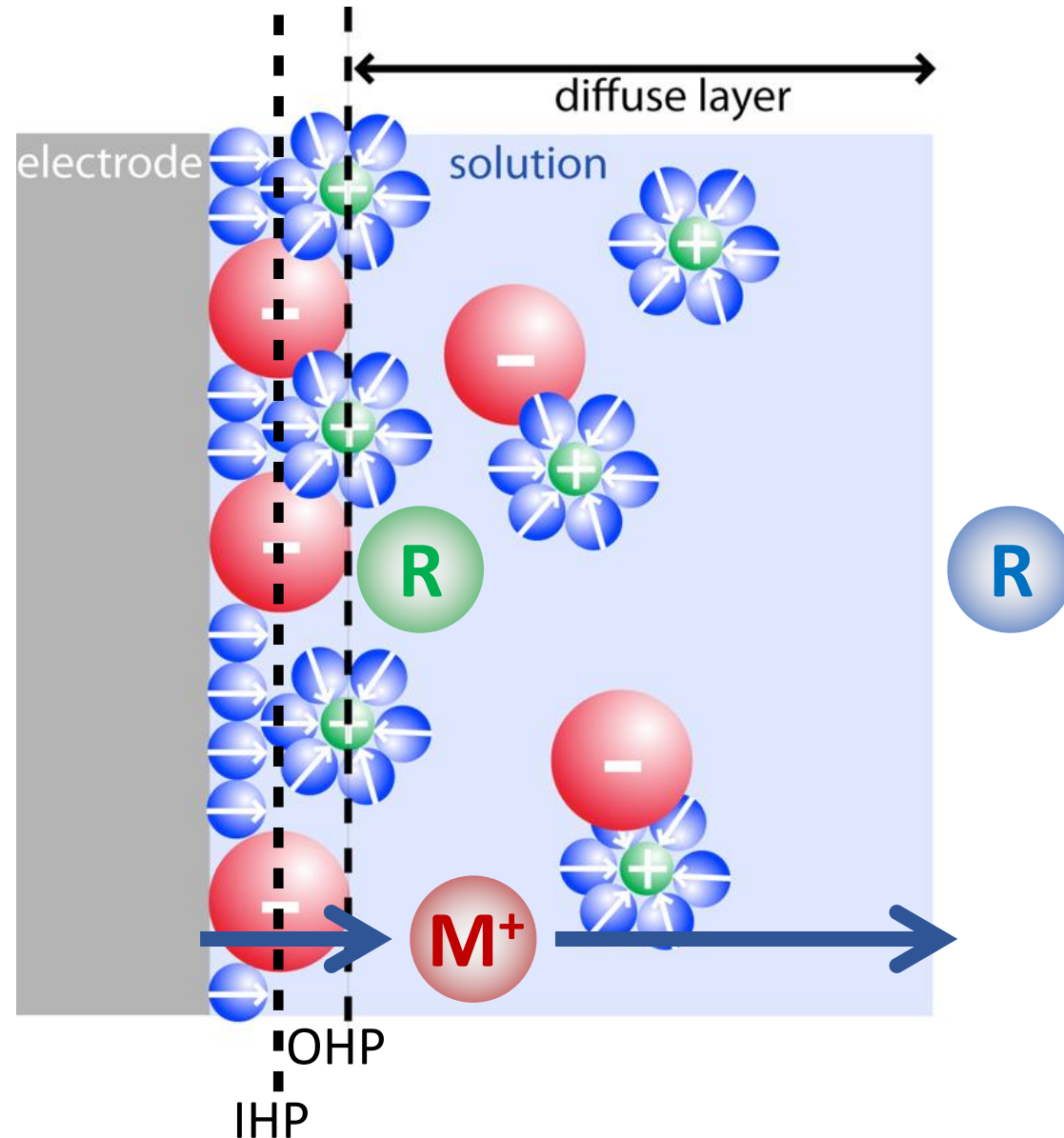
An ion transfers across the double layer… *mind = blown, again!*

Liquid-junction potentials are important in two types of electrodes / sensors...
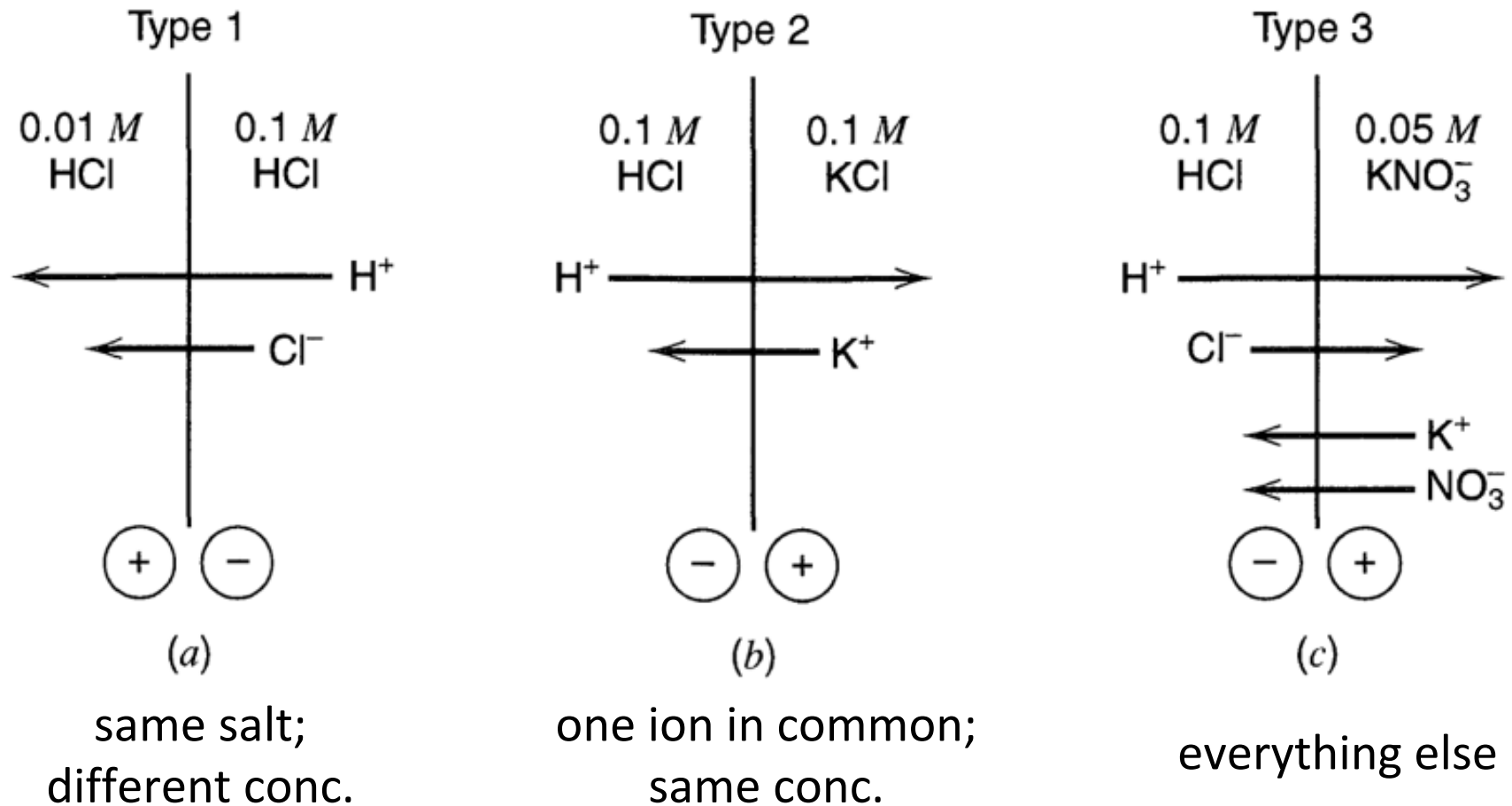
a Ag/AgCl RE   an ISE (for nitrate ions)

... 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*.

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$_3^-$ |

H^+ Cl^-

H^+ K^+

H^+ Cl^- K^+ NO_3^-

(+) (−)   (−) (+)   (−) (+)

(*a*)   (*b*)   (*c*)

same salt; different conc.

one ion in common; same conc.

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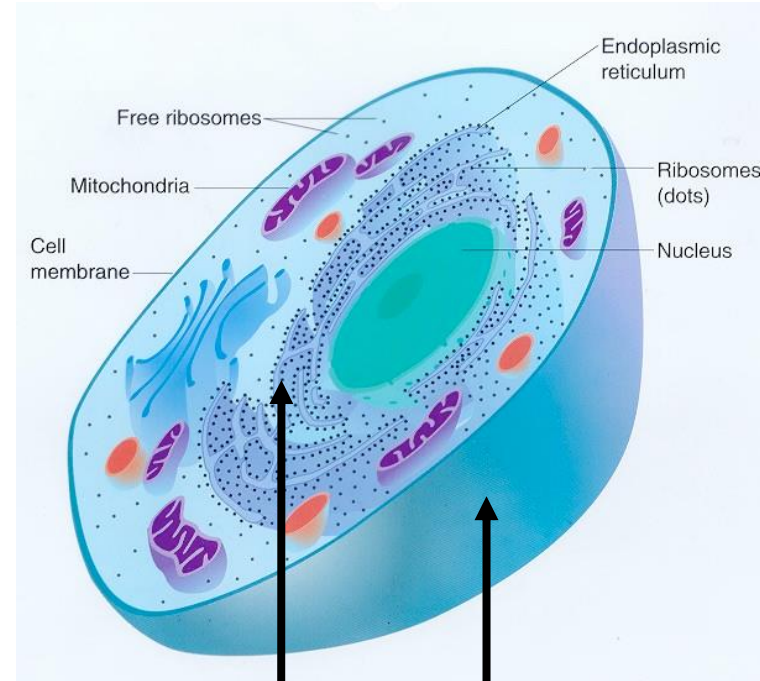
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 2.3.2

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

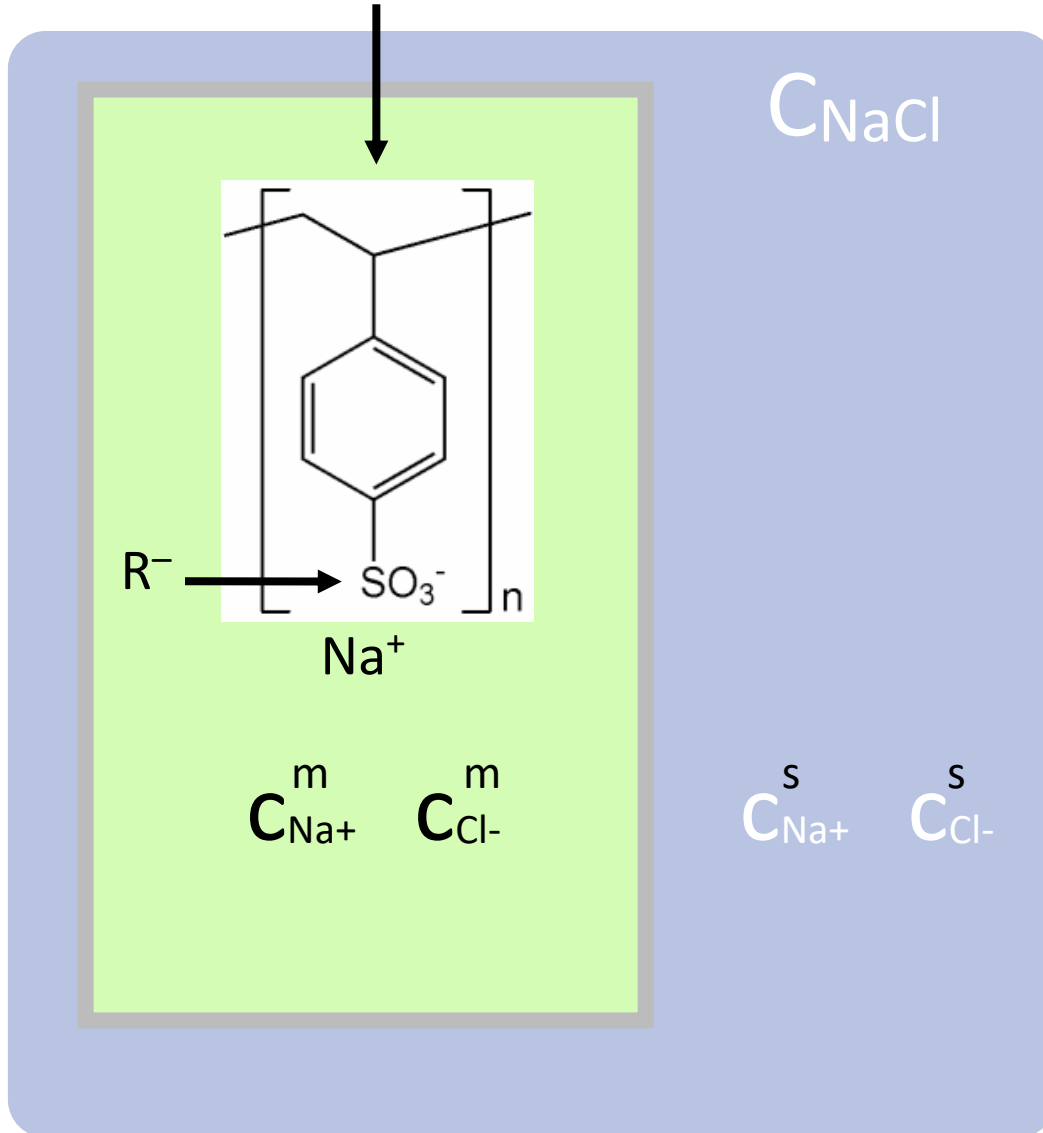an ionomer film   a cell

Nafion
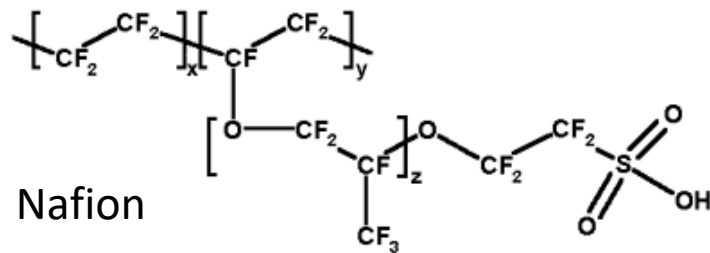
semipermeable
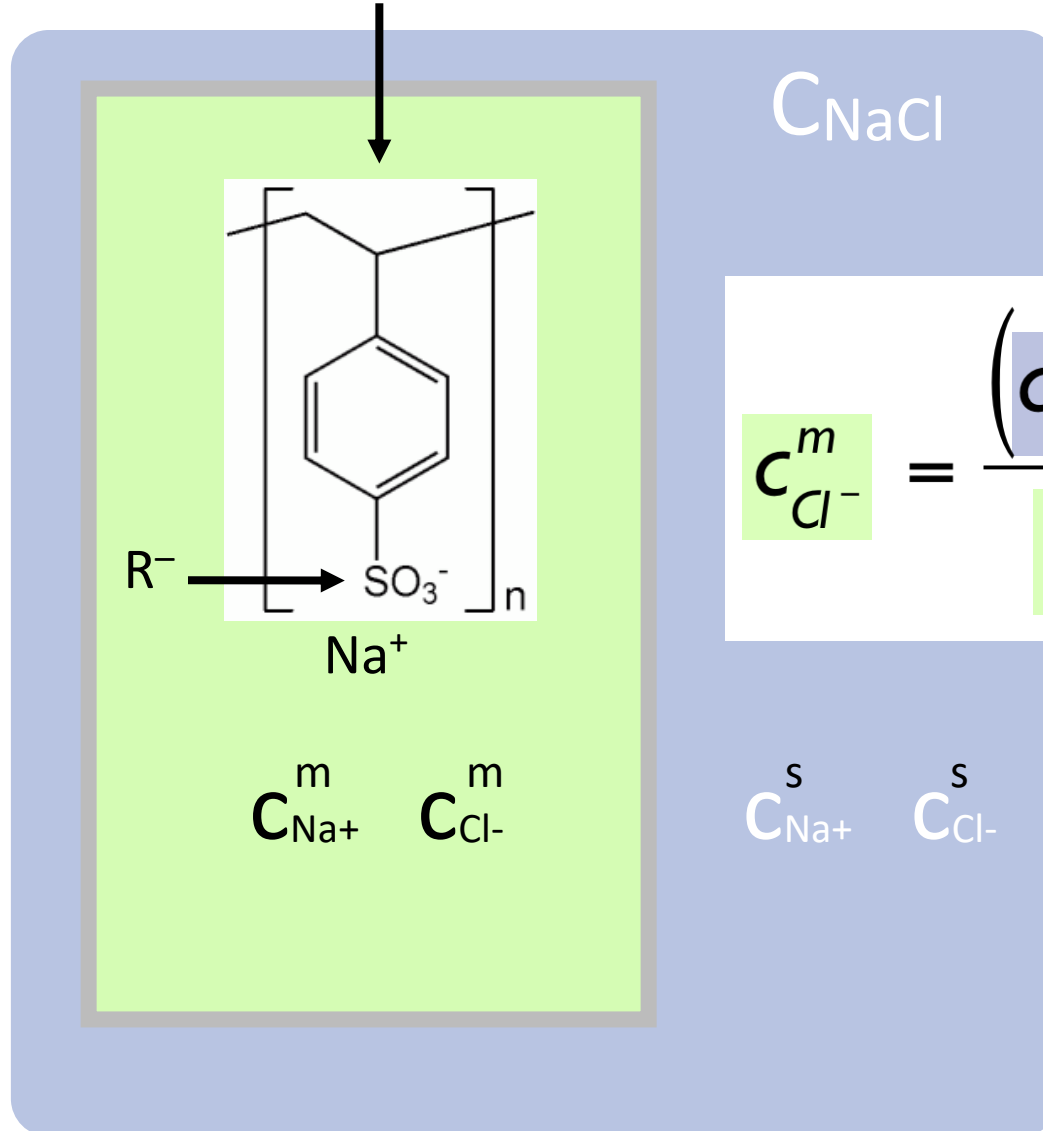membrane

membrane impermeable to
charged macromolecules

… consider this model which applies to both scenarios…

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

... 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)

C_{NaCl}

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

R^- → SO_3^-

Na^+

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

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

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

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_{NaCl}

R^- $\longrightarrow$ SO_3^-]ₙ

Na^+

c_{Na+}^m c_{Cl-}^m

c_{Na+}^s c_{Cl-}^s

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

log = -3

log = -1

log = ?
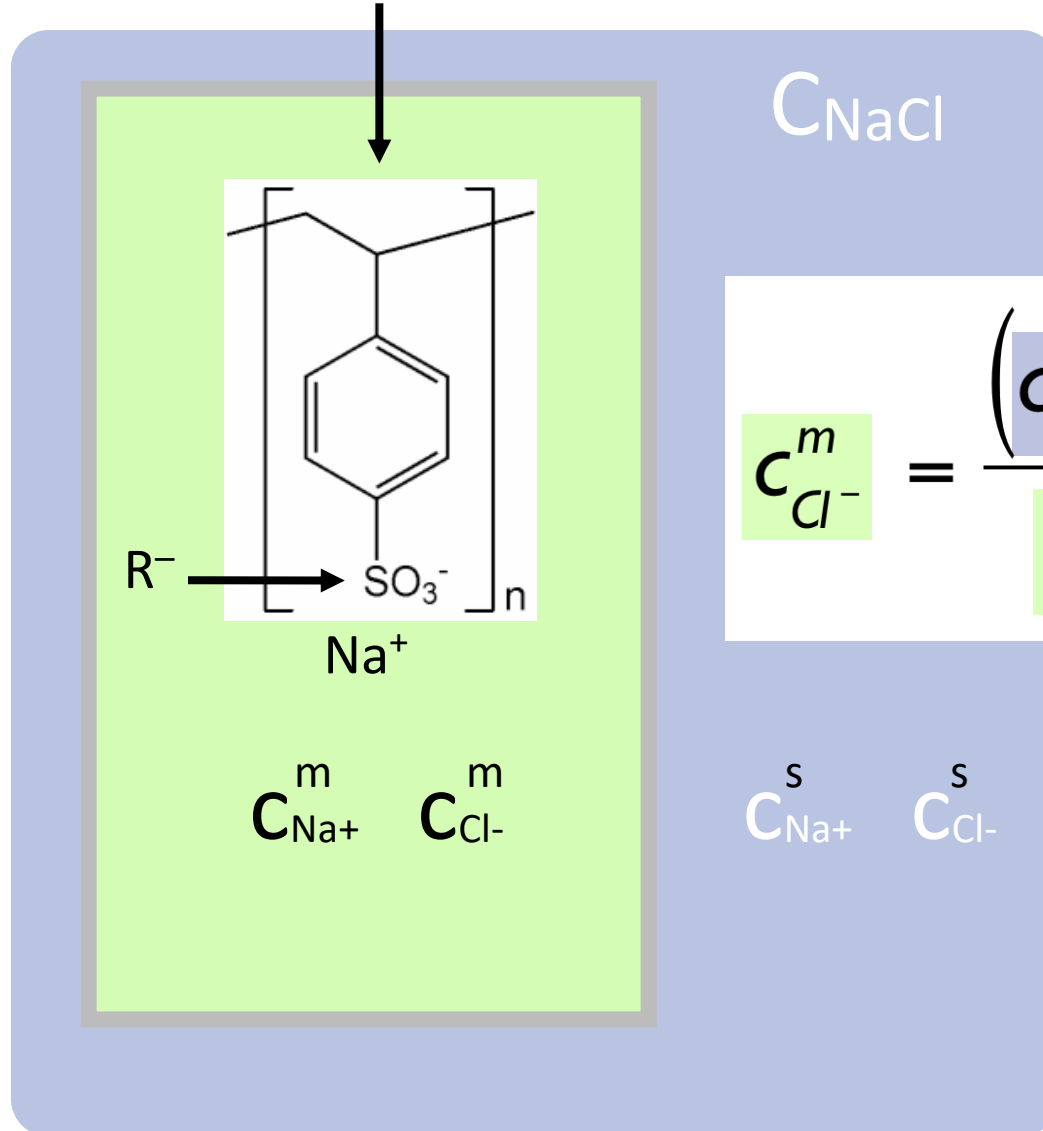
… what about this?

… 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)

C_{NaCl}

R^- → SO_3^- $]_n$

Na^+

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

C_{Na+}^s C_{Cl-}^s
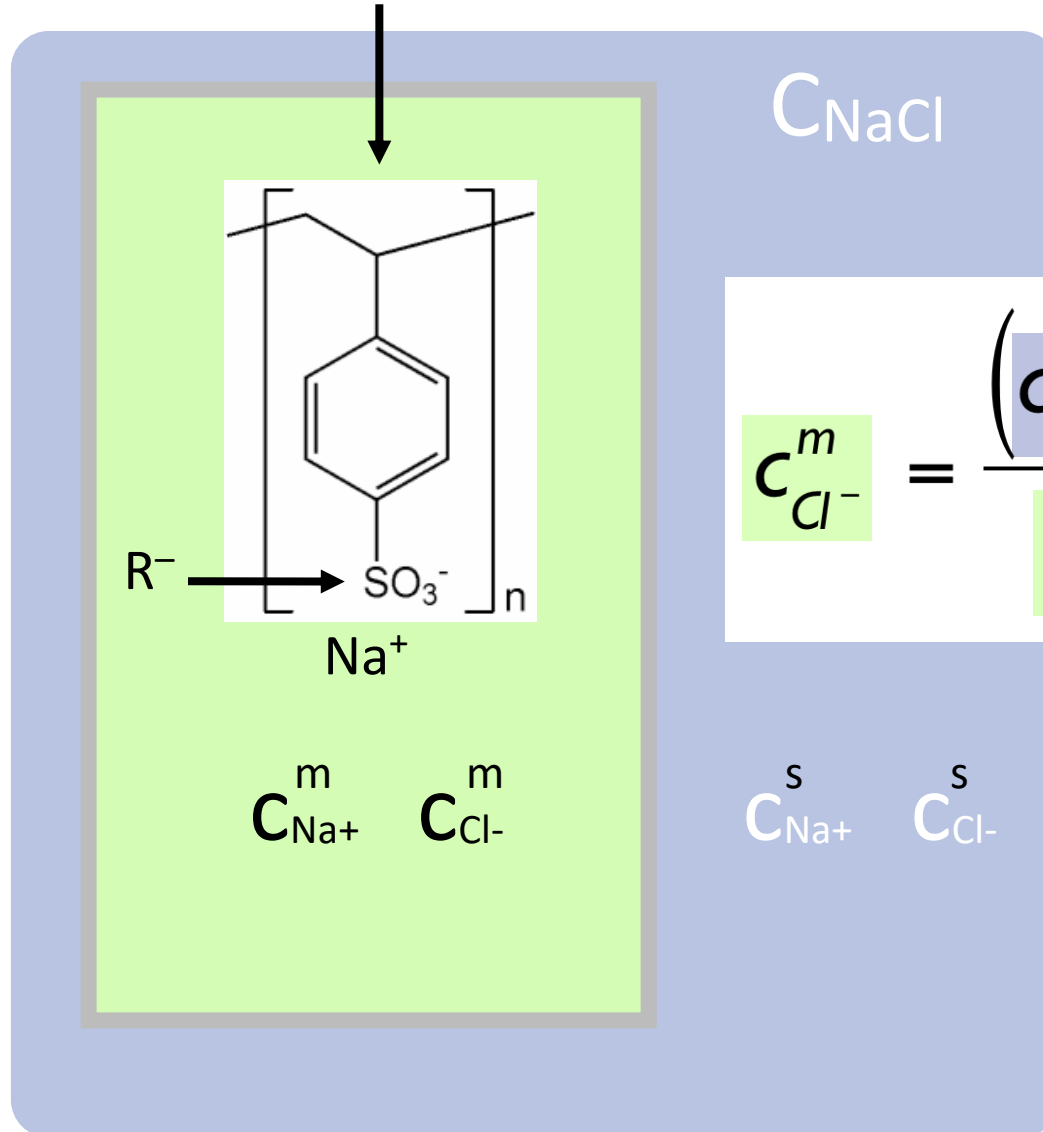
… it is *very very very* simple to quantify the effect of interfacial equilibration that leads to Donnan exclusion… conceptually!
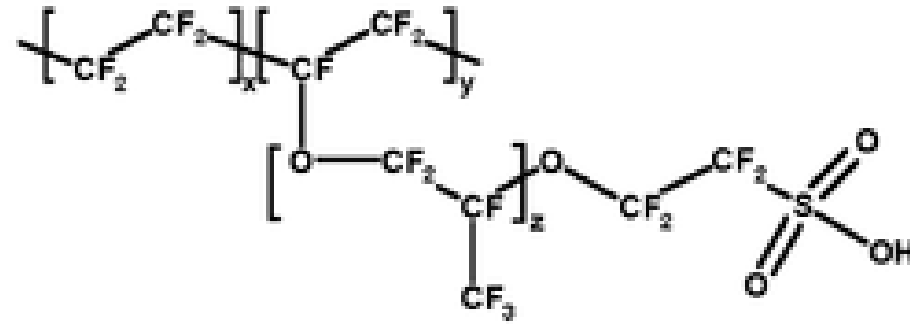
$$c_{Cl^-}^m = \frac{\left(c_{Cl^-}^s\right)^2}{c_{R^-}^m} = \frac{(0.001)^2}{0.1} = 10\ \mu M$$
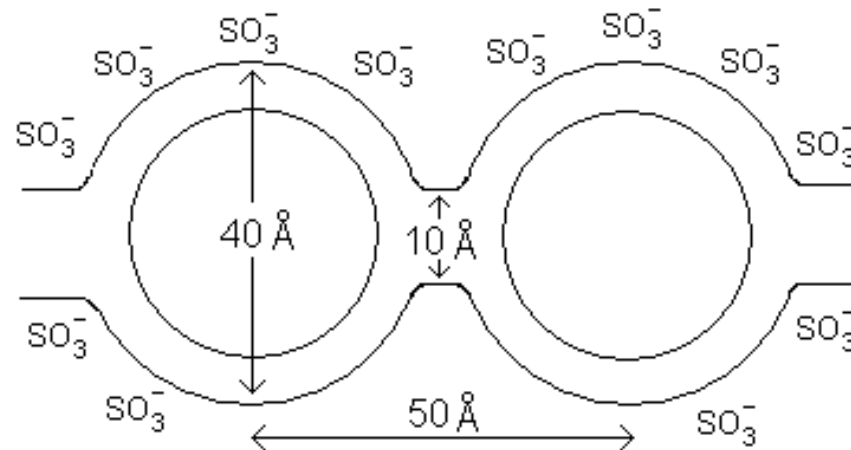
log = -3

log = -1

log = -5

… super simple!

… **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?
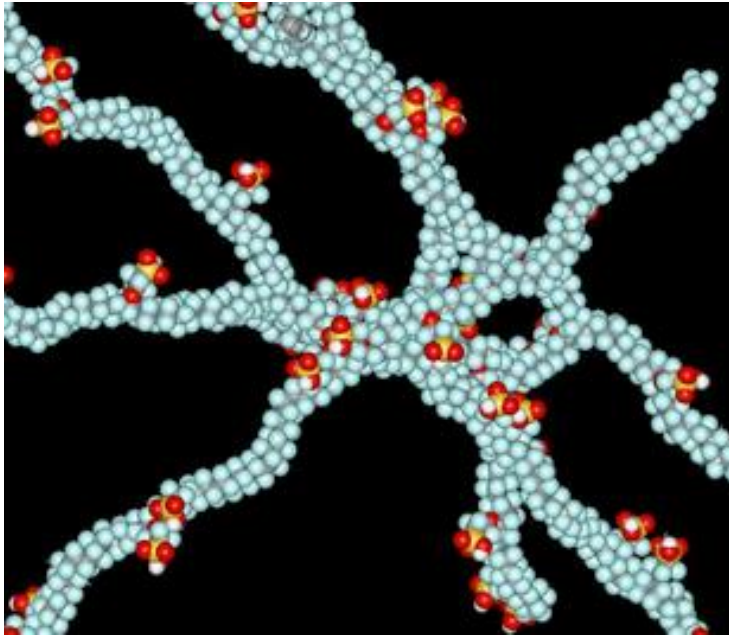

Nafion phase segregates into a hydrophobic phase, concentrated in $-(CF_2)-$ backbone, and hydrophilic clusters of $-SO_3^-$ solvated by water...
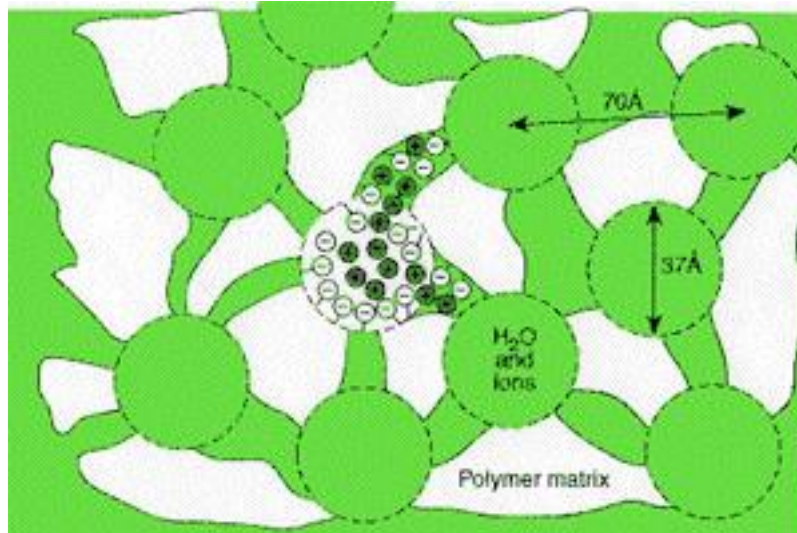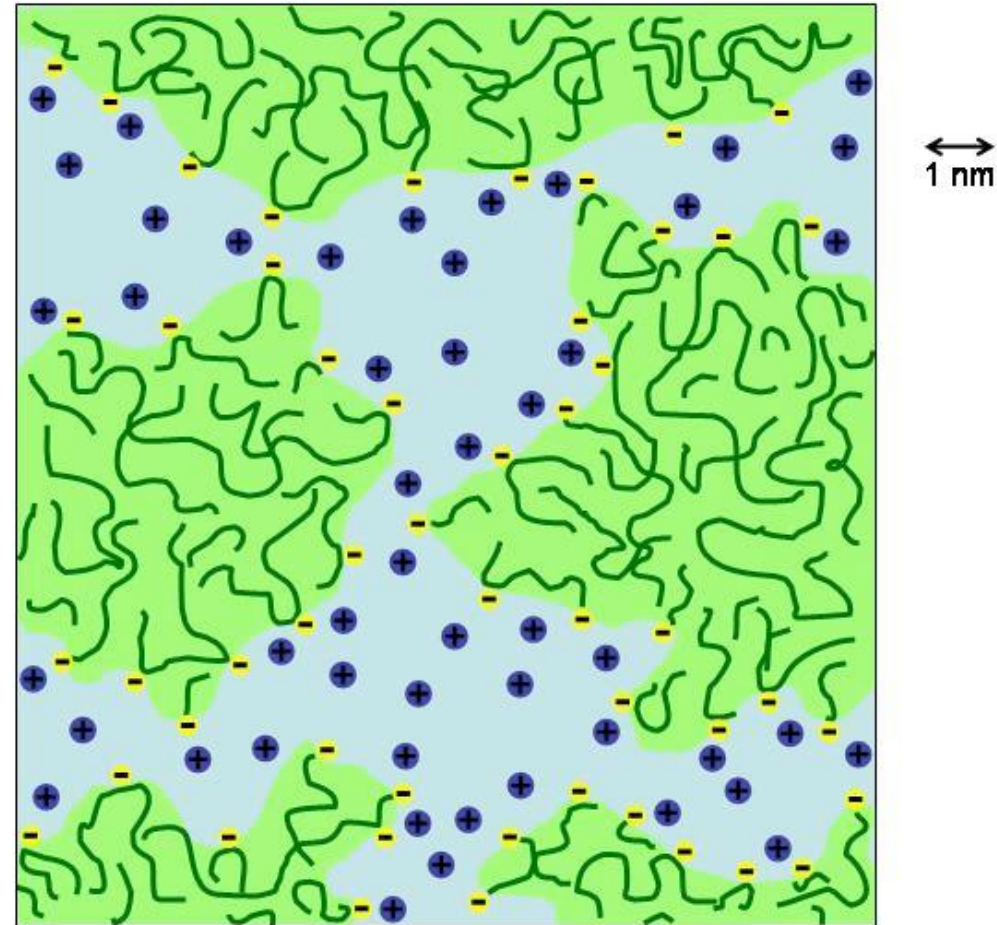

... and $-SO_3^-$ clusters are interconnected by channels that percolate through the membrane, imparting a percolation network for ionic conduction

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?

13

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?
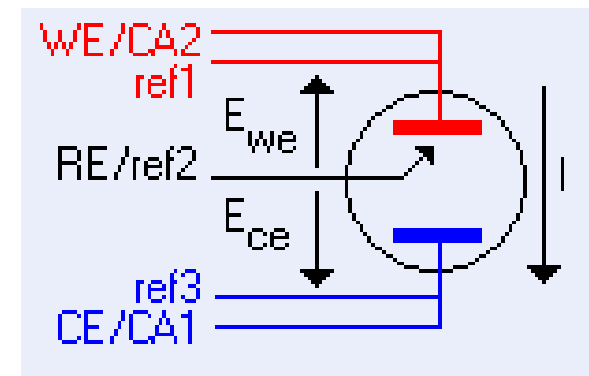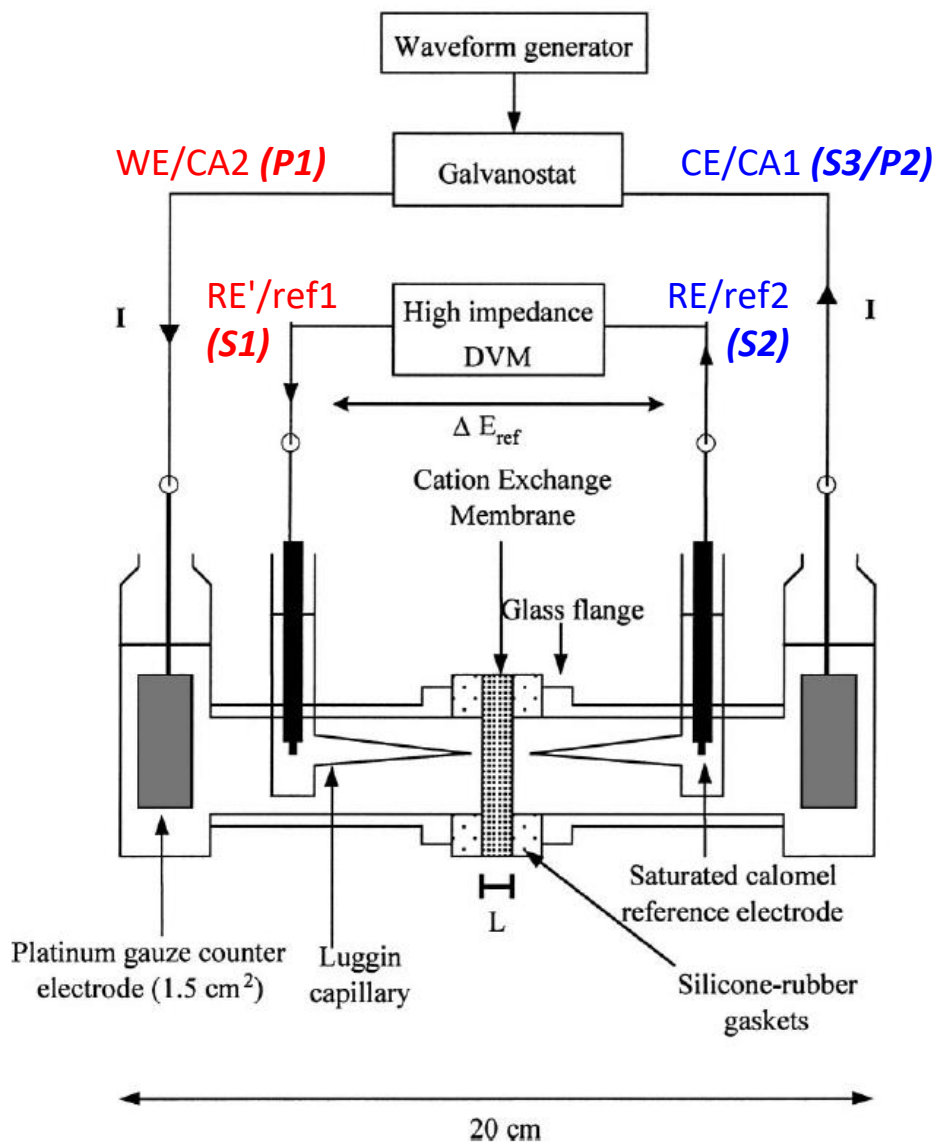... the same way with the same set-up for both!

... 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!

WE/CA2 *(P1)*

CE/CA1 *(S3/P2)*

RE'/ref1 *(S1)*

RE/ref2 *(S2)*

ΔE_{ref}

Waveform generator

Galvanostat

High impedance DVM

Cation Exchange Membrane

Glass flange

8 cm

L

Platinum gauze counter electrode (1.5 cm²)

Luggin capillary

Saturated calomel reference electrode

Silicone-rubber gaskets

20 cm

WE/CA2
ref1

RE/ref2

E_{we}

E_{ce}

ref3
CE/CA1

(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

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

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

… 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 $E_j = \pm\dfrac{RT}{F}\ln\dfrac{\sum\limits_i |z_i|u_i C_i(\alpha)}{\sum\limits_i |z_i|u_i C_i(\beta)}$
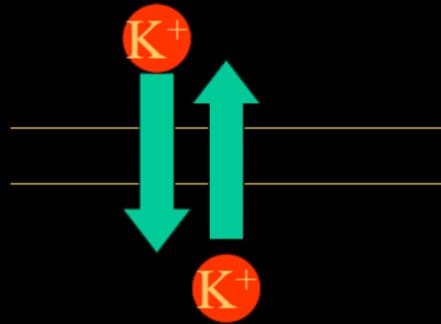
LJ, Type 3
(Henderson) $E_j = \dfrac{\sum\limits_i \dfrac{|z_i|u_i}{z_i}[C_i(\beta) - C_i(\alpha)]}{\sum\limits_i |z_i|u_i[C_i(\beta) - C_i(\alpha)]}\dfrac{RT}{F}\ln\dfrac{\sum\limits_i |z_i|u_i C_i(\alpha)}{\sum\limits_i |z_i|u_i C_i(\beta)}$

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

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

for steady (trans)membrane potential zero net charge flux is required
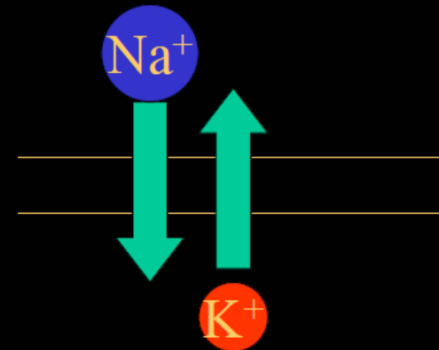
zero net flux for each permeable ion:

K⁺ ⇅ K⁺

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

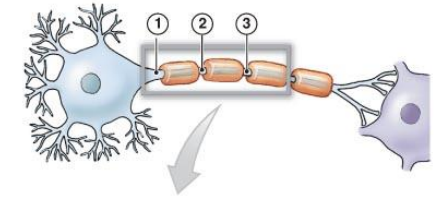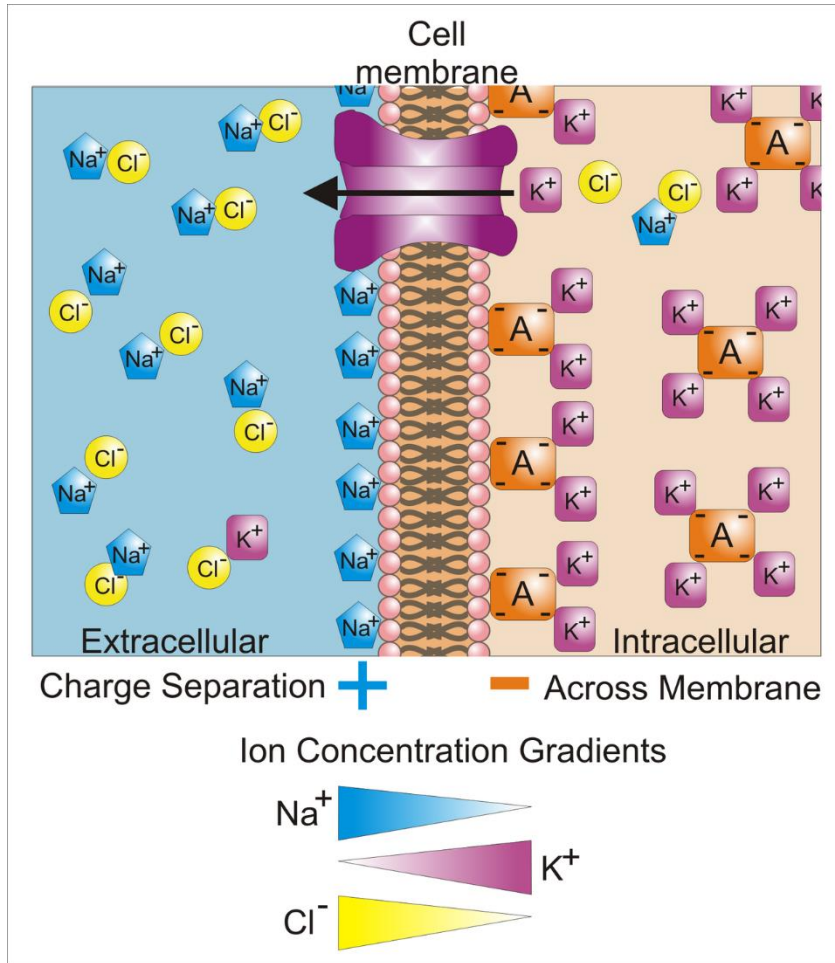non-zero net flux of permeable ions but sum of the charge fluxes equals to zero
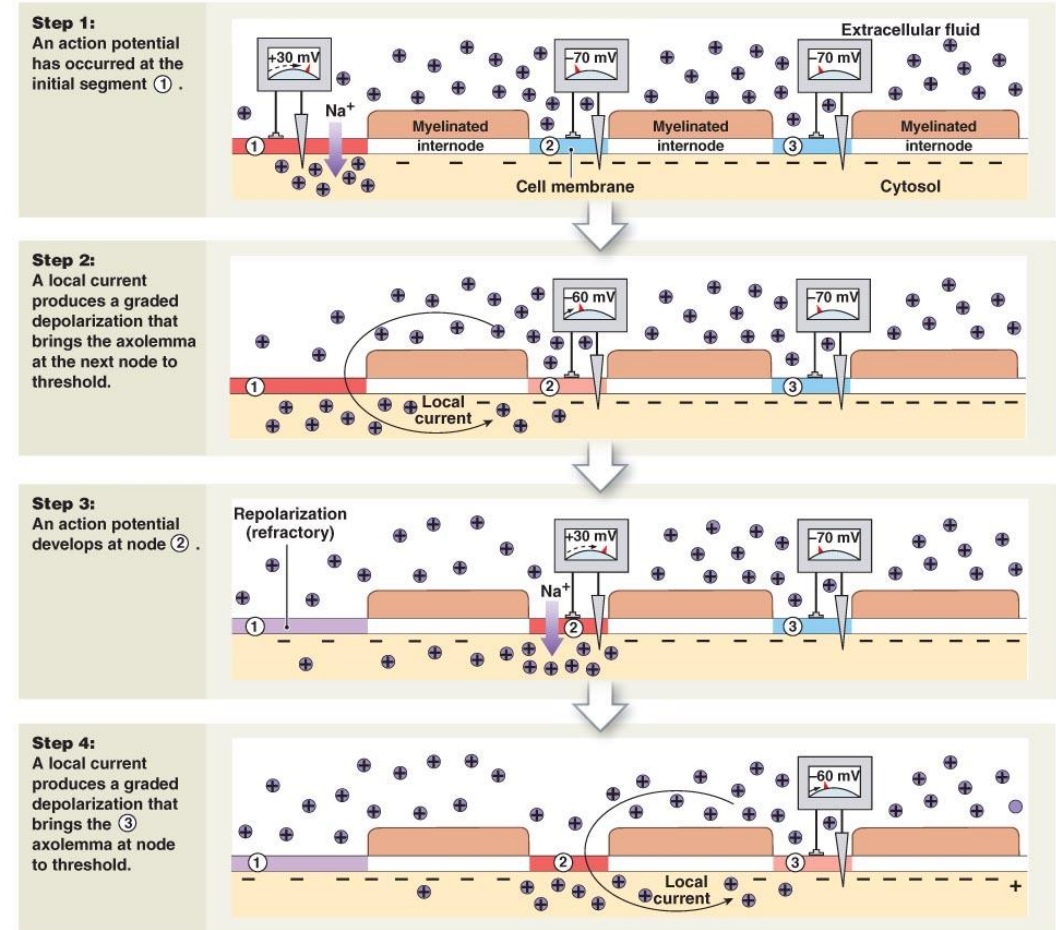
Na⁺ ⇅ K⁺

• Goldman-Hodgkin-Katz voltage equation

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

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

permeabilities

The events that occur in saltatory propagation

Step 1:
An action potential has occurred at the initial segment ① .

Step 2:
A local current produces a graded depolarization that brings the axolemma at the next node to threshold.

Step 3:
An action potential develops at node ② .

Step 4:
A local current produces a graded depolarization that brings the ③ axolemma at node to threshold.

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Cell membrane

Extracellular   Intracellular
Charge Separation ✚   ▬ Across Membrane

Ion Concentration Gradients

Na⁺
K⁺
Cl⁻

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

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

… 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

NTL'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.
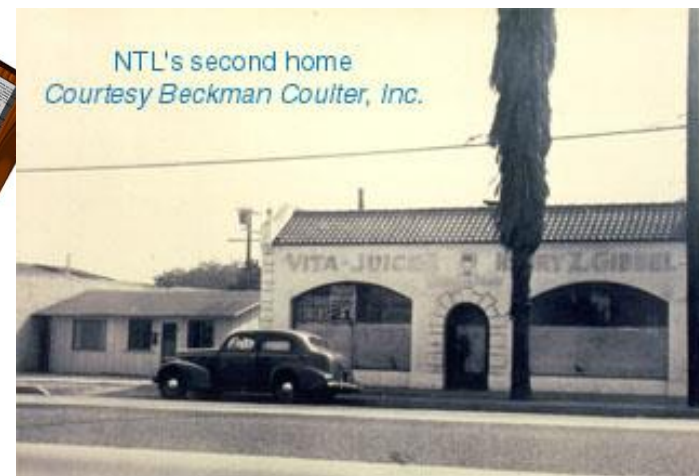
1900   1920   1940   1960   1980   2000

Nernst wins Nobel Prize

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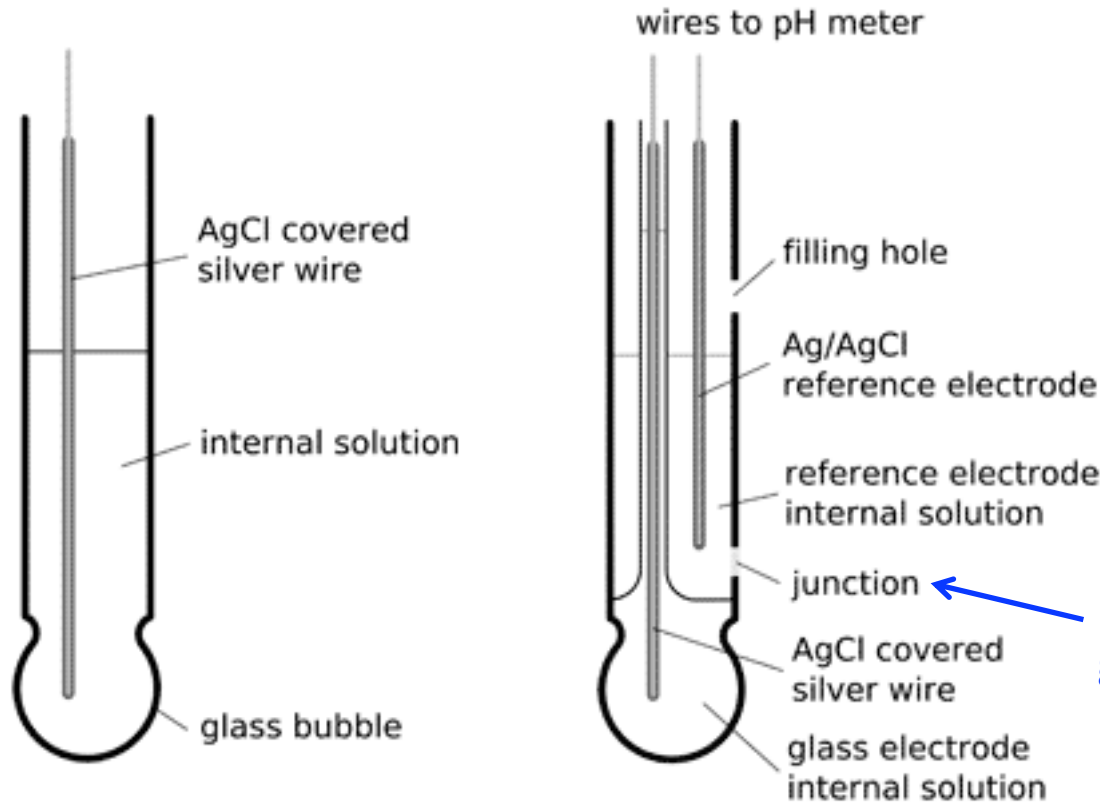

the Beckman DU spectrophotometer, 1941

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

wires to pH meter

filling hole

Ag/AgCl reference electrode

reference electrode internal solution

junction ← porous glass frit

AgCl covered silver wire

glass electrode internal solution

AgCl covered silver wire

internal solution

glass bubble

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!

... 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!
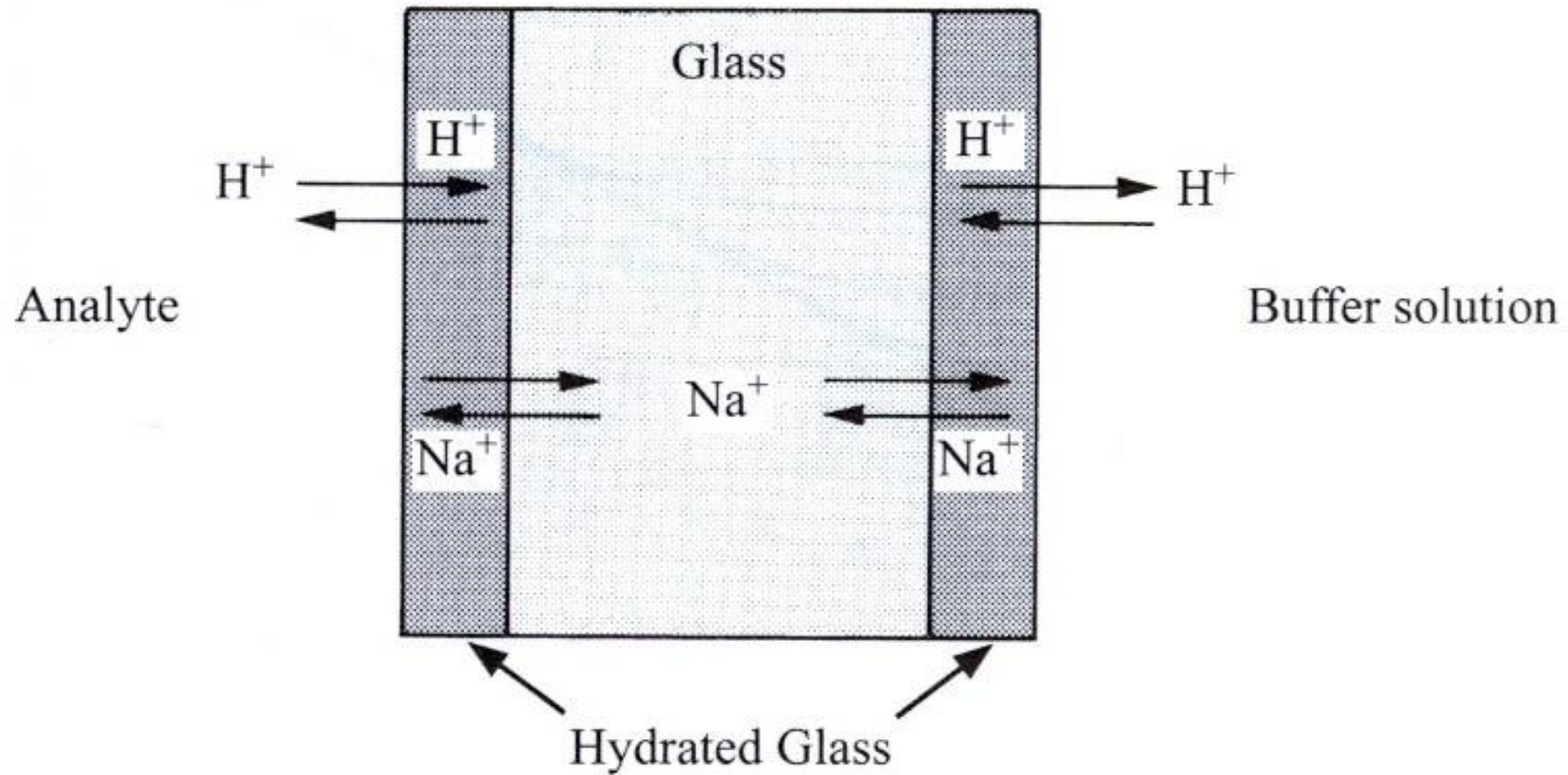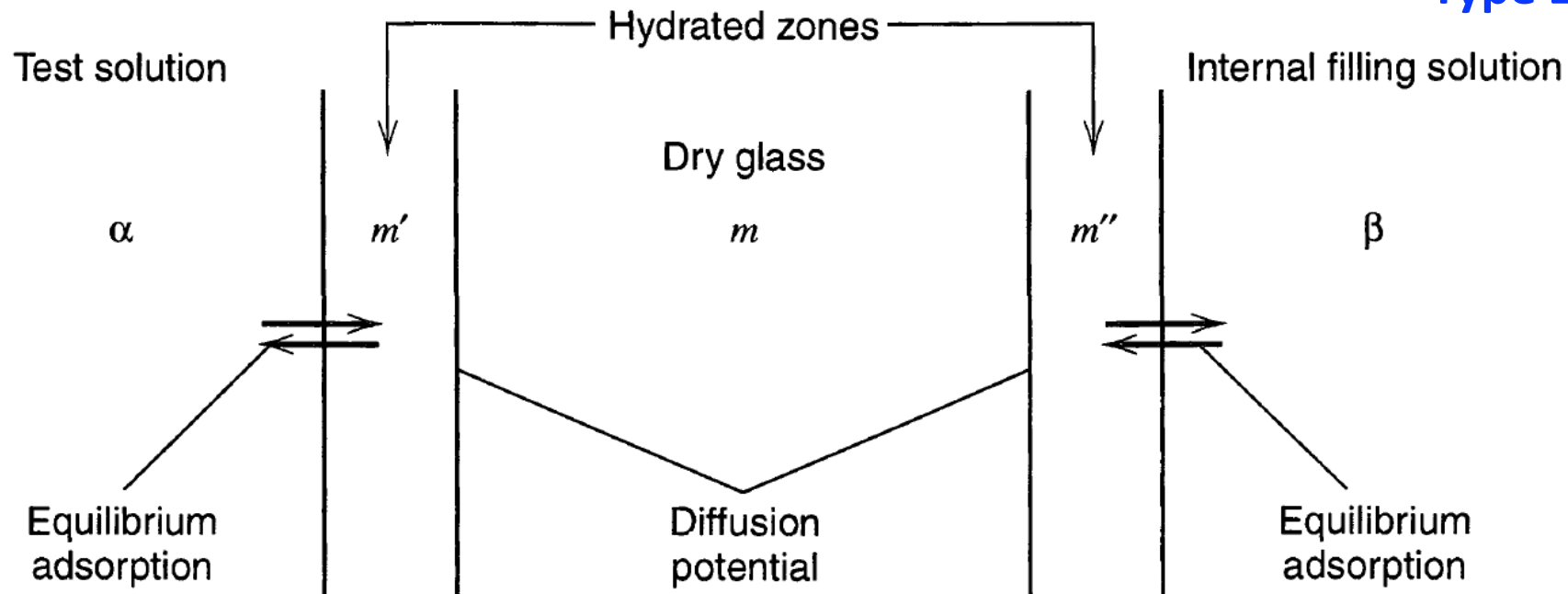

Fig. 2.25 Ionic equilibria in a glass electrode.

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

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

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

What type of LJ is this?

Type 2!

Hydrated zones

Test solution   Internal filling solution

Dry glass

α m' m m'' β

Equilibrium adsorption   Diffusion potential   Equilibrium adsorption

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

DISSOCIATION CONSTANTS OF ORGANIC ACIDS AND BASES

This table lists the dissociation (ionization) constants of over 1070 organic acids, bases, and amphoteric compounds. All data apply to dilute aqueous solutions and are presented as values of pK_a, which is defined as the negative of the logarithm of the equilibrium constant K_a for the reaction
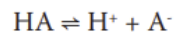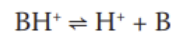
$$HA \rightleftharpoons H^+ + A^-$$

i.e.,

$$K_a = [H^+][A^-]/[HA]$$

where $[H^+]$, etc. represent the concentrations of the respective species in mol/L. It follows that $pK_a = pH + \log[HA] - \log[A^-]$, so that a solution with 50% dissociation has pH equal to the pK_a of the acid.

Data for bases are presented as pK_a values for the conjugate acid, i.e., for the reaction

$$BH^+ \rightleftharpoons H^+ + B$$

In older literature, an ionization constant K_b was used for the reaction $B + H_2O \rightleftharpoons BH^+ + OH^-$. This is related to K_a by

$$pK_a + pK_b = pK_{water} = 14.00 \quad (\text{at } 25\,°C)$$

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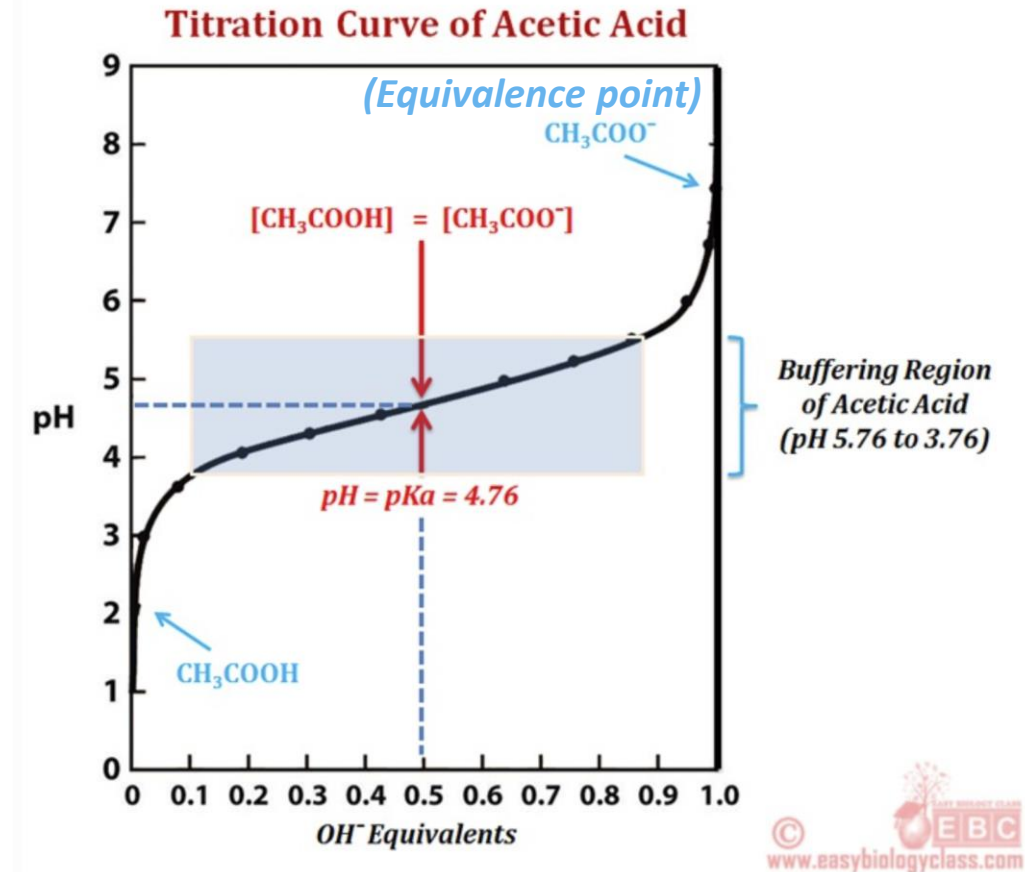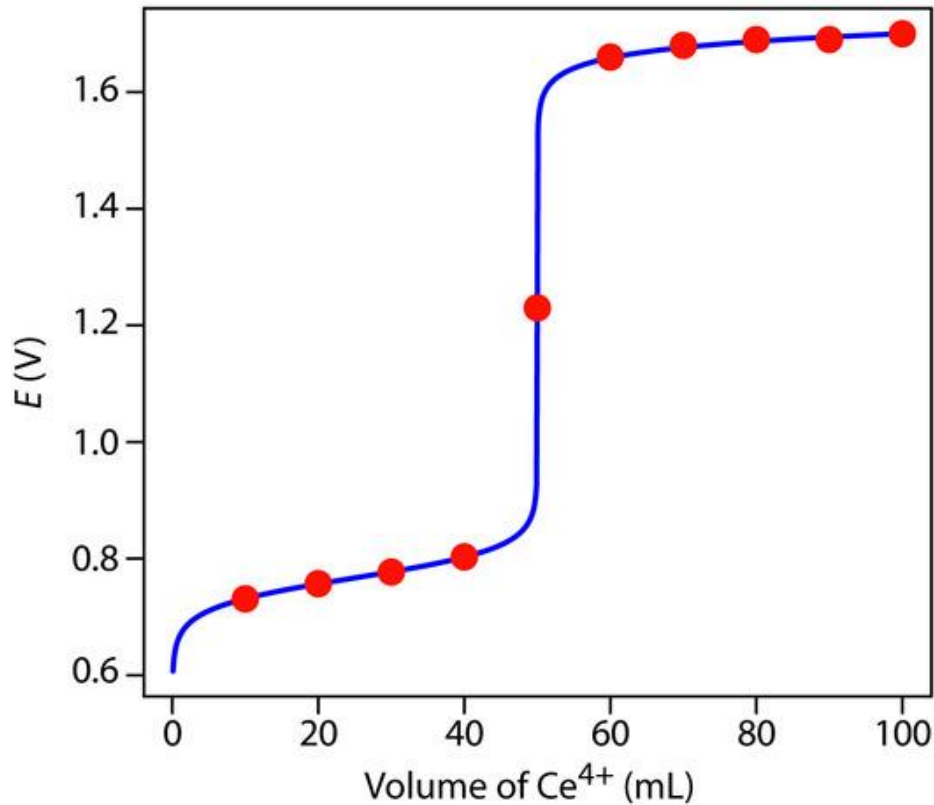... such as those in Acidity/Basicity Series...
... Again, can you identify what the reference acidity is for this list of standard(-state) equilibrium acid dissociation constants?

... pBLAH = − log a_{BLAH}

... why does this state that pK_a + pK_b = pK_w?
... because $K_a K_b = K_w$... **okaaaayyyy**... but why?
... because exp(−(Δ$G_a°$ + Δ$G_b°$)) = exp(−Δ$G_w°$)...
... **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!

Mol. form.	Name	Step	t/°C	pK$_a$
CHNO	Cyanic acid		25	3.7
CH$_2$N$_2$	Cyanamide		29	1.1
CH$_2$O	Formaldehyde		25	13.27
CH$_2$O$_2$	Formic acid		25	3.75
CH$_3$NO$_2$	Nitromethane		25	10.21
CH$_3$NS$_2$	Carbamodithioic acid		25	2.95
CH$_4$N$_2$O	Urea		25	0.10
CH$_4$N$_2$S	Thiourea		25	-1
CH$_4$O	Methanol		25	15.5
CH$_4$S	Methanethiol		25	10.33
CH$_5$N	Methylamine		25	10.66
CH$_5$NO	O-Methylhydroxylamine		25	12.5
CH$_5$N$_3$	Guanidine		25	13.6
C$_2$HCl$_3$O	Trichloroacetaldehyde		25	10.04
C$_2$HCl$_3$O$_2$	Trichloroacetic acid		20	0.66
C$_2$HF$_3$O$_2$	Trifluoroacetic acid		25	0.52
C$_2$H$_2$Cl$_2$O$_2$	Dichloroacetic acid		25	1.35
C$_2$H$_2$O$_3$	Glyoxylic acid		25	3.18
C$_2$H$_2$O$_4$	Oxalic acid	1	25	1.25
		2	25	3.81
C$_2$H$_3$BrO$_2$	Bromoacetic acid		25	2.90
C$_2$H$_3$ClO$_2$	Chloroacetic acid		25	2.87
C$_2$H$_3$Cl$_3$O	2,2,2-Trichloroethanol		25	12.24
C$_2$H$_3$FO$_2$	Fluoroacetic acid		25	2.59
C$_2$H$_3$F$_3$O	2,2,2-Trifluoroethanol		25	12.37
C$_2$H$_3$IO$_2$	Iodoacetic acid		25	3.18
C$_2$H$_3$NO$_4$	Nitroacetic acid		24	1.48
C$_2$H$_3$N$_3$	1H-1,2,3-Triazole		20	1.17
C$_2$H$_3$N$_3$	1H-1,2,4-Triazole		20	2.27
C$_2$H$_4$N$_2$	Aminoacetonitrile		25	5.34
C$_2$H$_4$O	Acetaldehyde		25	13.57
C$_2$H$_4$OS	Thioacetic acid		25	3.33
C$_2$H$_4$O$_2$	Acetic acid		25	4.756
C$_2$H$_4$O$_2$S	Thioglycolic acid		25	3.68
C$_2$H$_4$O$_3$	Glycolic acid		25	3.83
C$_2$H$_5$N	Ethyleneimine		25	8.04

Mol. form.	Name	Step	t/°C	pK$_a$
C$_2$H$_5$NO	Acetamide		25	15.1
C$_2$H$_5$NO$_2$	Acetohydroxamic acid			8.70
C$_2$H$_5$NO$_2$	Nitroethane		25	8.46
C$_2$H$_5$NO$_2$	Glycine	1	25	2.35
		2	25	9.78
C$_2$H$_6$N$_2$	Ethanimidamide		25	12.1
C$_2$H$_6$O	Ethanol		25	15.5
C$_2$H$_6$OS	2-Mercaptoethanol		25	9.72
C$_2$H$_6$O$_2$	Ethyleneglycol		25	15.1
C$_2$H$_7$AsO$_2$	Dimethylarsinic acid	1	25	1.57
		2	25	6.27
C$_2$H$_7$N	Ethylamine		25	10.65
C$_2$H$_7$N	Dimethylamine		25	10.73
C$_2$H$_7$NO	Ethanolamine		25	9.50
C$_2$H$_7$NO$_3$S	2-Aminoethanesulfonic	1	25	1.5
	acid	2	25	9.06
C$_2$H$_7$NS	Cysteamine	1	25	8.27
		2	25	10.53
C$_2$H$_7$N$_5$	Biguanide	1		11.52
		2		2.93
C$_2$H$_8$N$_2$	1,2-Ethanediamine	1	25	9.92
		2	25	6.86
C$_2$H$_8$O$_7$P$_2$	1-Hydroxy-1,1-	1		1.35
	diphosphonoethane	2		2.87
		3		7.03
		4		11.3
C$_3$H$_2$O$_2$	2-Propynoic acid		25	1.84
C$_3$H$_3$NO	Oxazole		33	0.8
C$_3$H$_3$NO	Isoxazole		25	-2.0
C$_3$H$_3$NO$_2$	Cyanoacetic acid		25	2.47
C$_3$H$_3$NS	Thiazole		25	2.52
C$_3$H$_3$N$_3$O$_3$	Cyanuric acid	1		6.88
		2		11.40
		3		13.5
C$_3$H$_4$N$_2$	1H-Pyrazole		25	2.49
C$_3$H$_4$N$_2$	Imidazole		25	6.99

Titrations and Buffering

Titration Curve of Acetic Acid

(Equivalence point)
CH$_3$COO$^-$

[CH$_3$COOH] = [CH$_3$COO$^-$]

Buffering Region of Acetic Acid (pH 5.76 to 3.76)

pH = pKa = 4.76

CH$_3$COOH

© www.easybiologyclass.com

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

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

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

Henderson–Hasselbalch equation

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

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

Charged Interfaces *(summary for today)*

- **Vacuum level, Redox half-reactions**

- **Nernst equation**

- **History, Conventions**

- **Electrodes, Potentiostat**

- <u>**Electric double layer**</u>

- <u>**Electric potentials, Liquid-junction potentials, Donnan potential, Membrane potential**</u>

- <u>**pH probe, Acidity scale, Titrations, Buffering, Henderson–Hasselbalch equation**</u>

- Latimer diagram, Pourbaix diagram

Paper Time!