Lecture #9 of 14

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

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*

- <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)**

- 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*…

- 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 **NOW**…

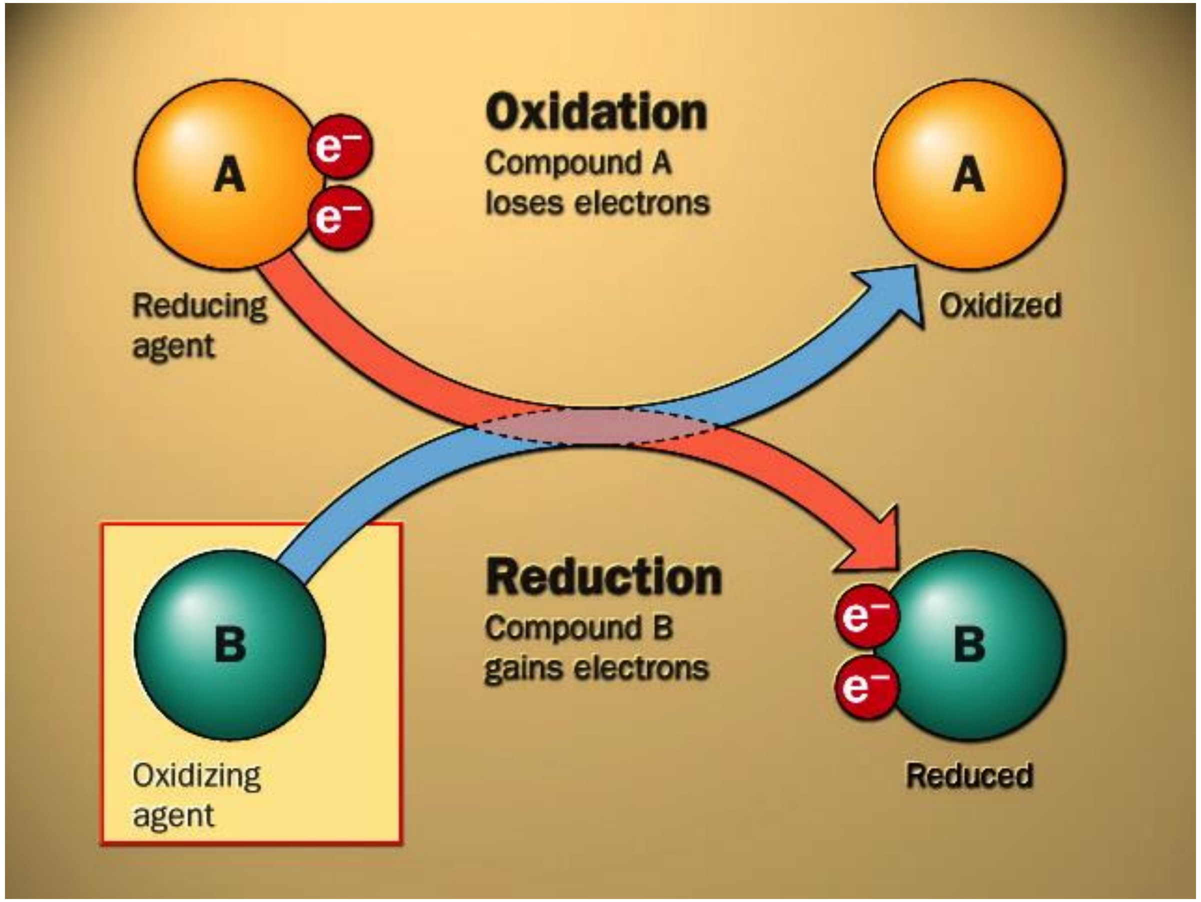
Discussion *(an hour-ish every-other-day-ish)* provides opportunities to discuss applied pchem research…
… of course, there are way too many topics to cover, but I decided on the following as the **FINAL** list:

(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) **F7/15 (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) **M7/18** *(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)

Oxidation and reduction

An oxidation-reduction, or “redox” reaction is one in which one or more electrons are transferred.



Oxidation states

Ionic compound: the oxidation state of an atom is equal to its charge.

KCl — K:+1, Cl:-1

Covalent compound, different types of atoms: the oxidation state equals the charge that would result if the electrons were given to the most electronegative atom.

NH_3 — N:-3, H:+1

Covalent compound, same type of atoms: the oxidation state equals the charge that would result if the electrons were divided evenly among atoms of the same type.

N_2H_4 (H_2NNH_2) — N:-2, H:+1

Closed (filled) orbital shells are most stable…

… in general H (+1), O (-2), halides (-1), etc.

0 +1 -1 → +2 -1 0

$Zn\ (s) + 2HCl\ (aq) \longrightarrow Zn(Cl)_2\ (aq) + H_2\ (g)$

0 → -2 -2

$CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l)$

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

… let’s not worry about the oxidation state of C or H for now… more on this soon…

Oxidation and Reduction

Oxidizing agent (oxidant) ⇒ molecule that ***gains*** electrons
Reducing agent (reductant) ⇒ molecule that ***loses*** electrons

$$\overset{0}{2Mg}\,(s) + \overset{0}{O_2}\,(g) \longrightarrow 2\overset{2+}{Mg}\overset{2-}{O}\,(s)$$

This reaction can be split into two ***half-reactions***

Oxidation half-reaction
reactant (= reducing agent) ***loses*** e^-

$$2\,Mg \rightarrow 2\,Mg^{2+} + 4\,e^-$$

Reduction half-reaction
Reactant (= oxidizing agent) ***gains*** e^-

$$O_2 + 4\,e^- \rightarrow 2\,O^{2-}$$

Redox reactions

Zinc metal reacts with aqueous hydrochloric acid to form zinc chloride in solution and hydrogen gas. Is this a redox reaction? If yes, identify the oxidizing agent, the reducing agent, and the substances being oxidized and reduced.

1. Write a balanced chemical equation *(not always easy)*.

$$\overset{0}{Zn}\,(s) + 2\overset{+1}{H}\overset{-1}{Cl}\,(aq) \longrightarrow \overset{+2}{Zn}\overset{-1}{Cl_2}\,(aq) + \overset{0}{H_2}\,(g)$$

2. Assign oxidation states.

3. Determine whether atomic oxidation states change. **Yes**

Redox reactions

Zinc metal reacts with aqueous hydrochloric acid to form zinc chloride in solution and hydrogen gas. Is this a redox reaction? If yes, identify the oxidizing agent, the reducing agent, and the substances being oxidized and reduced.

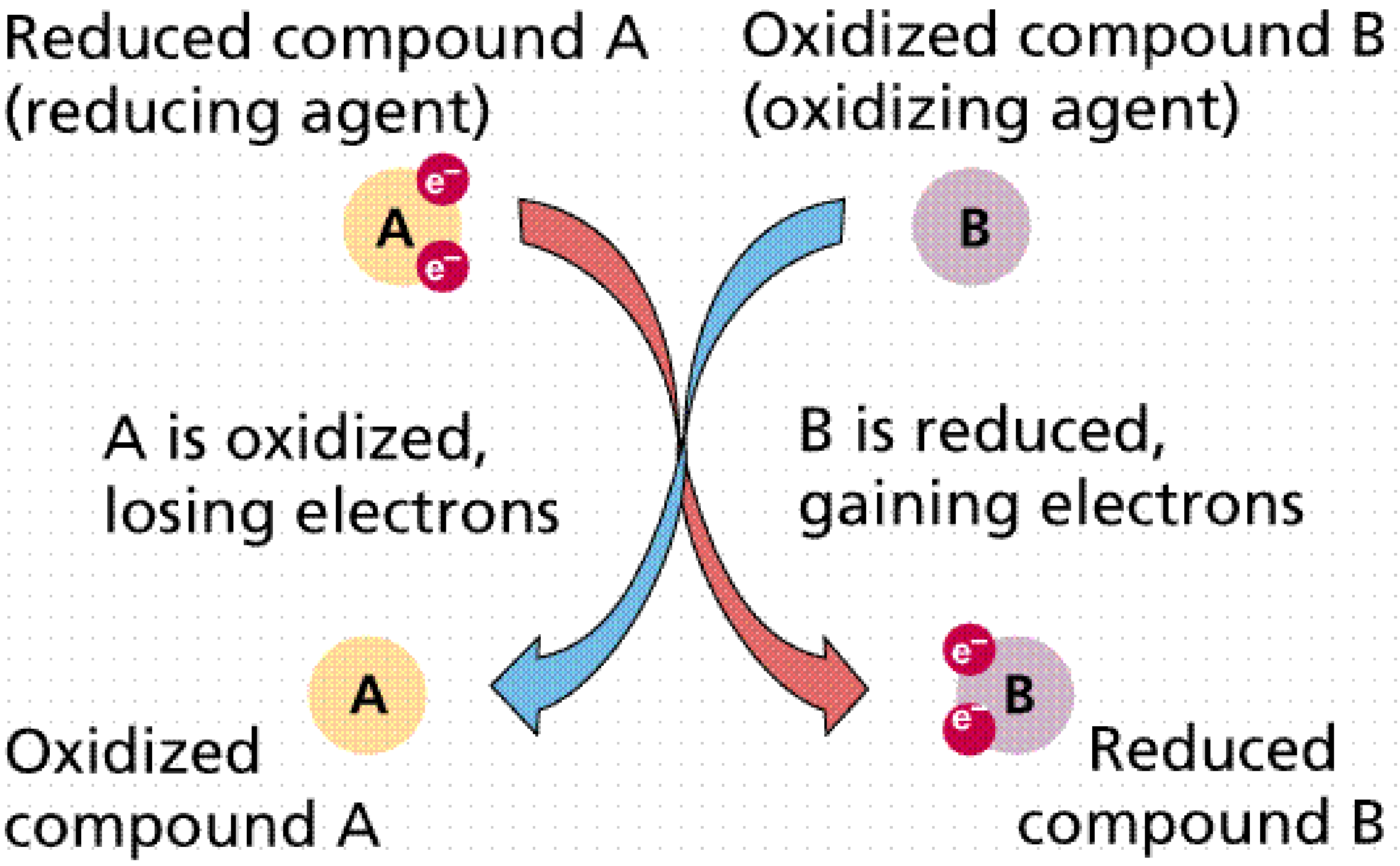
4. Use the changes in oxidation state for each atom to determine what is being oxidized and reduced.

$$\overset{0}{Zn}\,(s) + 2\overset{+1}{H}\overset{-1}{Cl}\,(aq) \longrightarrow \overset{+2}{Zn}\overset{-1}{Cl_2}\,(aq) + \overset{0}{H_2}\,(g)$$

Zn: 0	⟶	+2	oxidized, reducing agent
H: +1	⟶	0	reduced, oxidizing agent
Cl: -1	⟶	-1	spectator ion

Half-reactions

Redox reactions are often difficult to balance by inspection. Instead, we can use the method of half-reactions. *Half-reactions don't actually exist all that often… infinite vacuum anyone?*



Writing half-reactions

1. Assign oxidation states for each element in the reactants and products.

2. Determine what is being oxidized, what is being reduced, and how many electrons are transferred.

3. Write balanced half-reactions, using electrons as reactants or products, as appropriate.

Method of half-reactions

Each redox reaction can be separated into two half-reactions, one for oxidation and one for reduction.

$$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(g)$$

oxidation half-reaction

$$\overset{-4}{C}H_4 \longrightarrow \overset{+4}{C}O_2 + 8e^-$$

reduction half-reaction

$$2\overset{0}{O}_2 + 8e^- \longrightarrow C\overset{-2}{O}_2 + 2H_2\overset{-2}{O}$$

In half-reactions, electrons are written as reactants or products depending on whether they are gained or lost.

Balancing redox equations

The oxidation of Fe^{2+} to Fe^{3+} by $Cr_2O_7^{2-}$ (becomes Cr^{3+}) in aqueous acid solution?

1. Write the unbalanced equation for the reaction in ionic form.

$$Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + Cr^{3+}$$

2. Separate the equation into two half-reactions.

Oxidation: $\overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}}$

Reduction: $\overset{+6}{Cr_2O_7^{2-}} \longrightarrow \overset{+3}{Cr^{3+}}$

3. Balance the atoms other than O and H in each half-reaction.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

$$Fe^{2+} \longrightarrow Fe^{3+}$$

Balancing redox equations

4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$$

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$$

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

Balancing redox equations

7. Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**

Oxidation: $6Fe^{2+} \longrightarrow 6Fe^{3+} + \cancel{6e^-}$

Reduction: $\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

$$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

8. Verify that the number of atoms and the charges are balanced.

$$(14 \times 1) – (1 \times 2) + (6 \times 2) = \mathbf{24} = (6 \times 3) + (2 \times 3) + (7 \times 0)$$

9. *For reactions in basic solutions, add $OH^–$ to **both sides** of the equation for every H^+ that appears in the final equation…*

Method of half-reactions
(under basic/alkaline conditions)

1. Use the half reaction method for acidic solution to balance the equation as if excess H^+ ions were present.

2. To both sides of the equation, add the number of $OH^–$ ions needed to balance the H^+ ions added in the last step.

3. Form H_2O on the side containing both H^+ and $OH^–$ ions, and cancel out the number of H_2O molecules appearing on both sides of the equation.

4. Check to make sure that the equation is balanced.

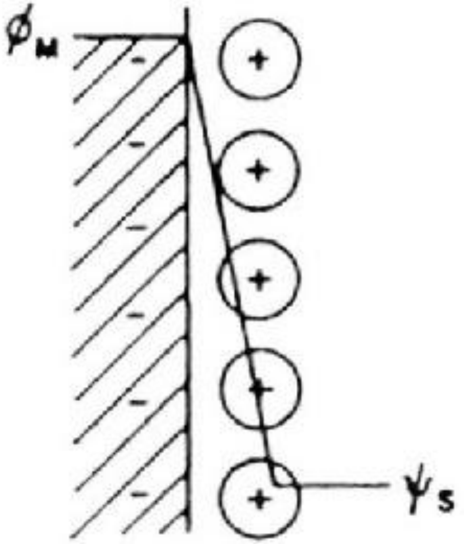
Charged Interfaces

Prof. Shane Ardo
Department of Chemistry
University of California Irvine

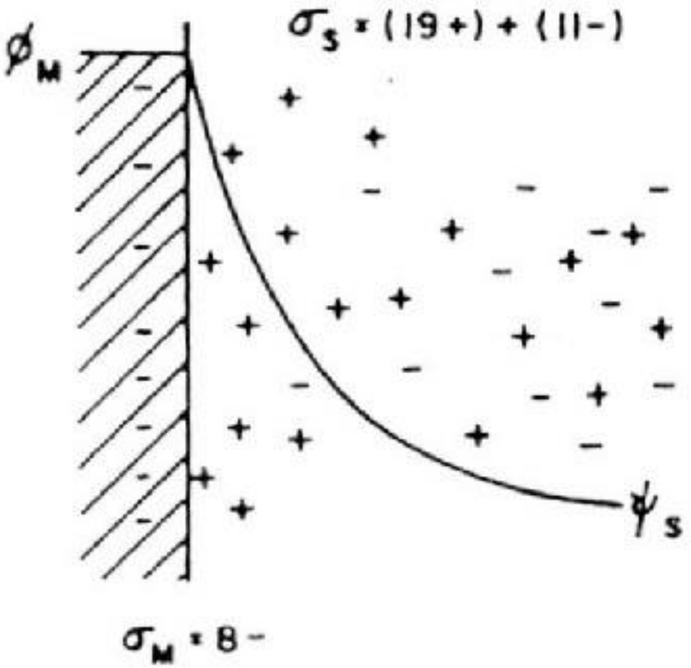
Charged Interfaces

- 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**

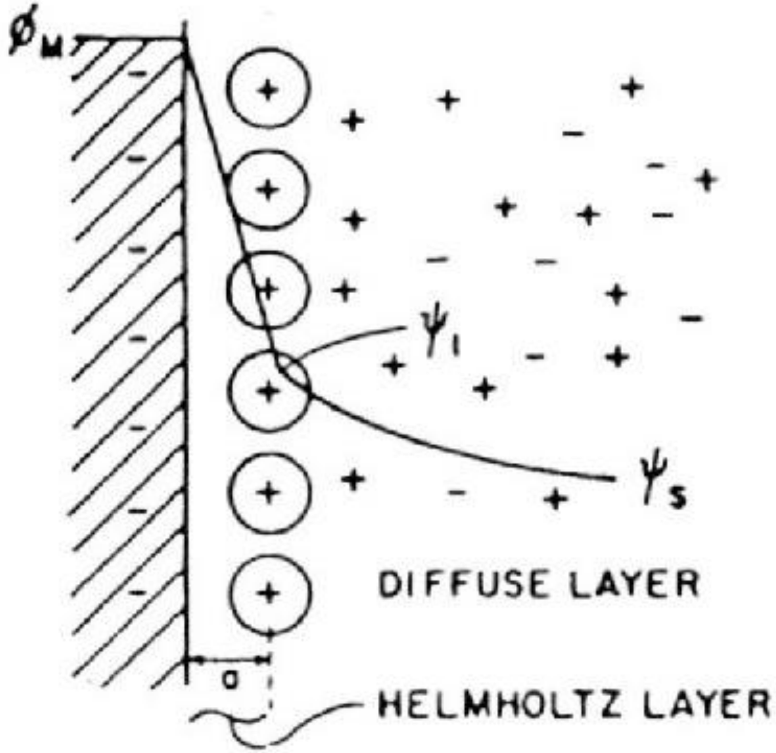
… three models for the potential distribution near a charged electrode immersed in an electrolyte solution…



Helmholtz (H)



Gouy–Chapman (GC)



Gouy–Chapman–Stern (GCS)

$\varepsilon_r \approx 6$

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

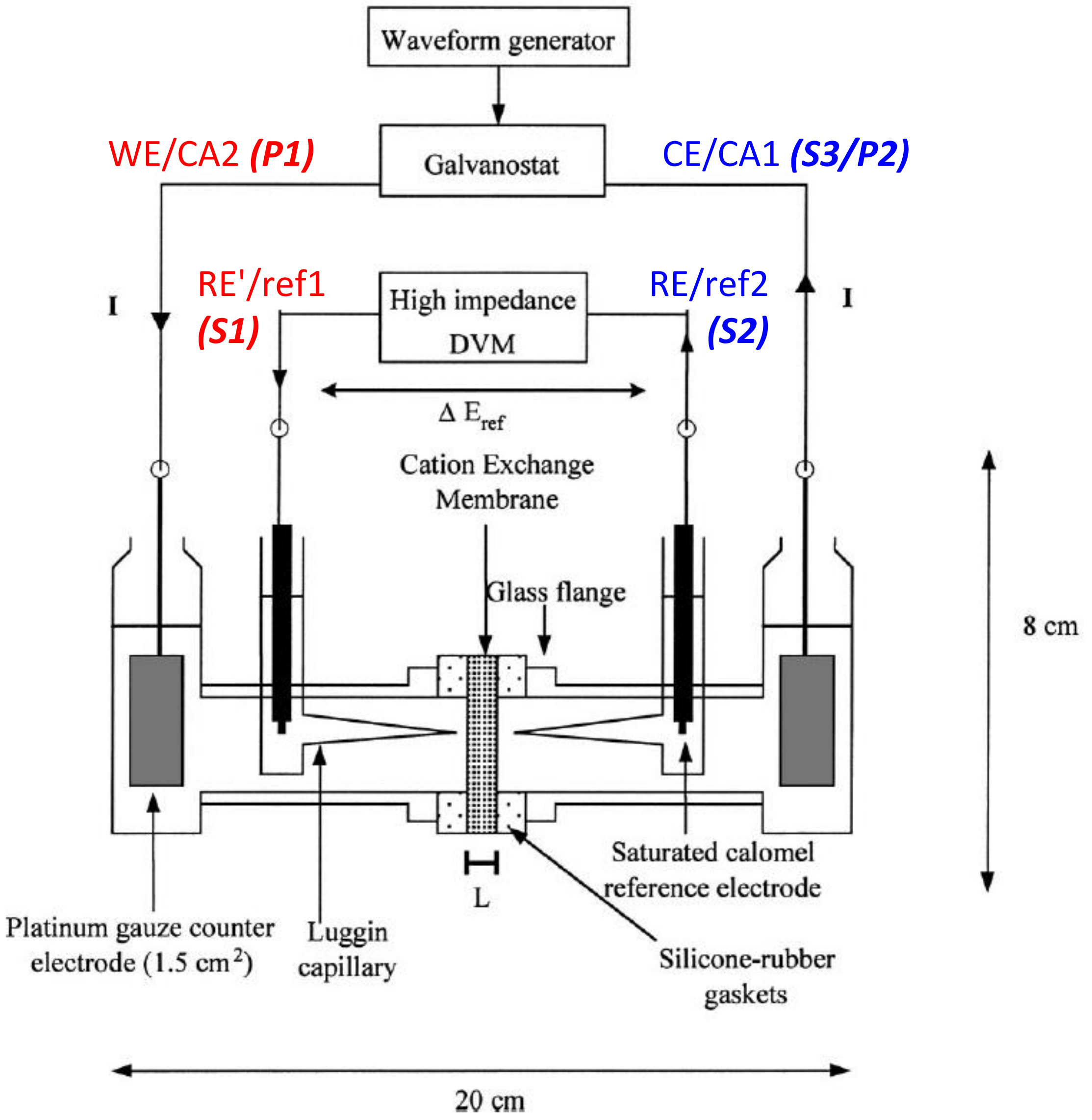
$$\frac{d\phi}{dx} = -\left(\frac{8kTn^0}{\varepsilon\varepsilon_0}\right)^{1/2} \sinh\left(\frac{ze\phi}{2kT}\right)$$ … Poisson–Boltzmann Equation for a 1:1 electrolyte

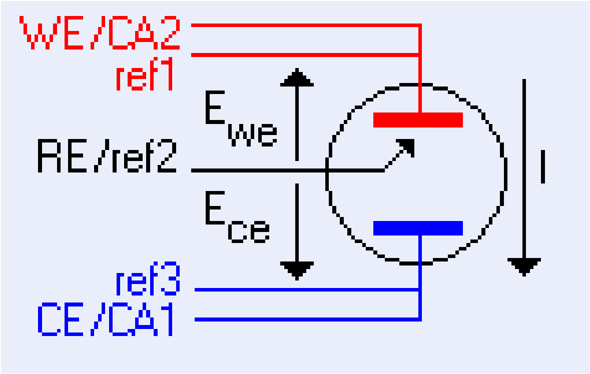
$\phi \approx \phi^0 \exp(-\kappa x)$… when we assume ϕ^0 is small

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

http://electrochem.cwru.edu/

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





(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/

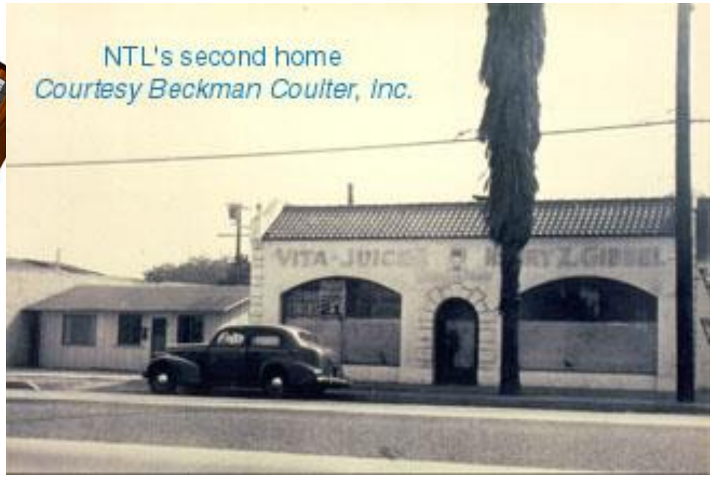
… and this leads us nicely to: ~110 years of Ion-Selective Electrodes (ISEs)…

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)…

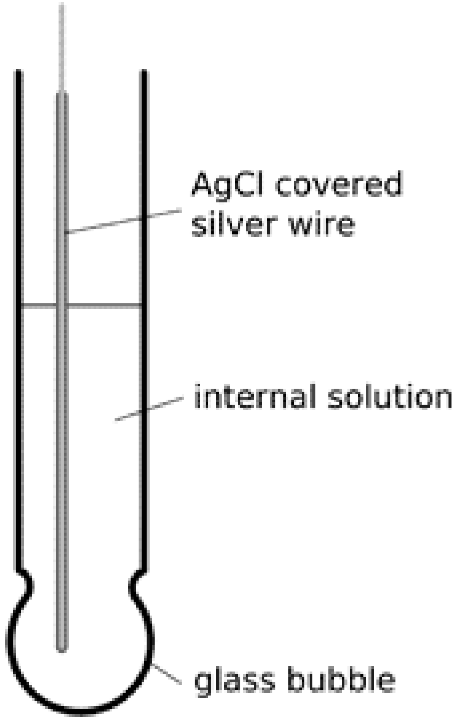
the Beckman DU spectrophotometer, 1941

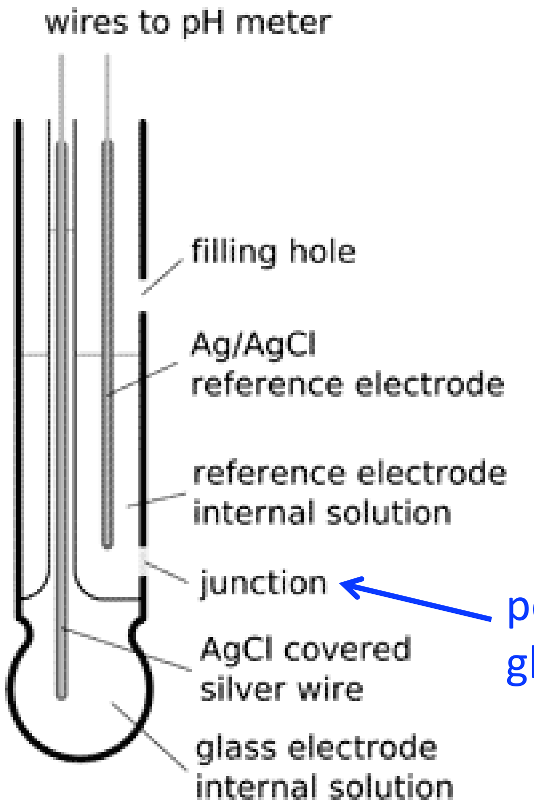
the Beckman Helipot potentiometer, 1942

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?





porous glass frit

Chemist, Inventor, Investor, Philanthropist

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!

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 <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!

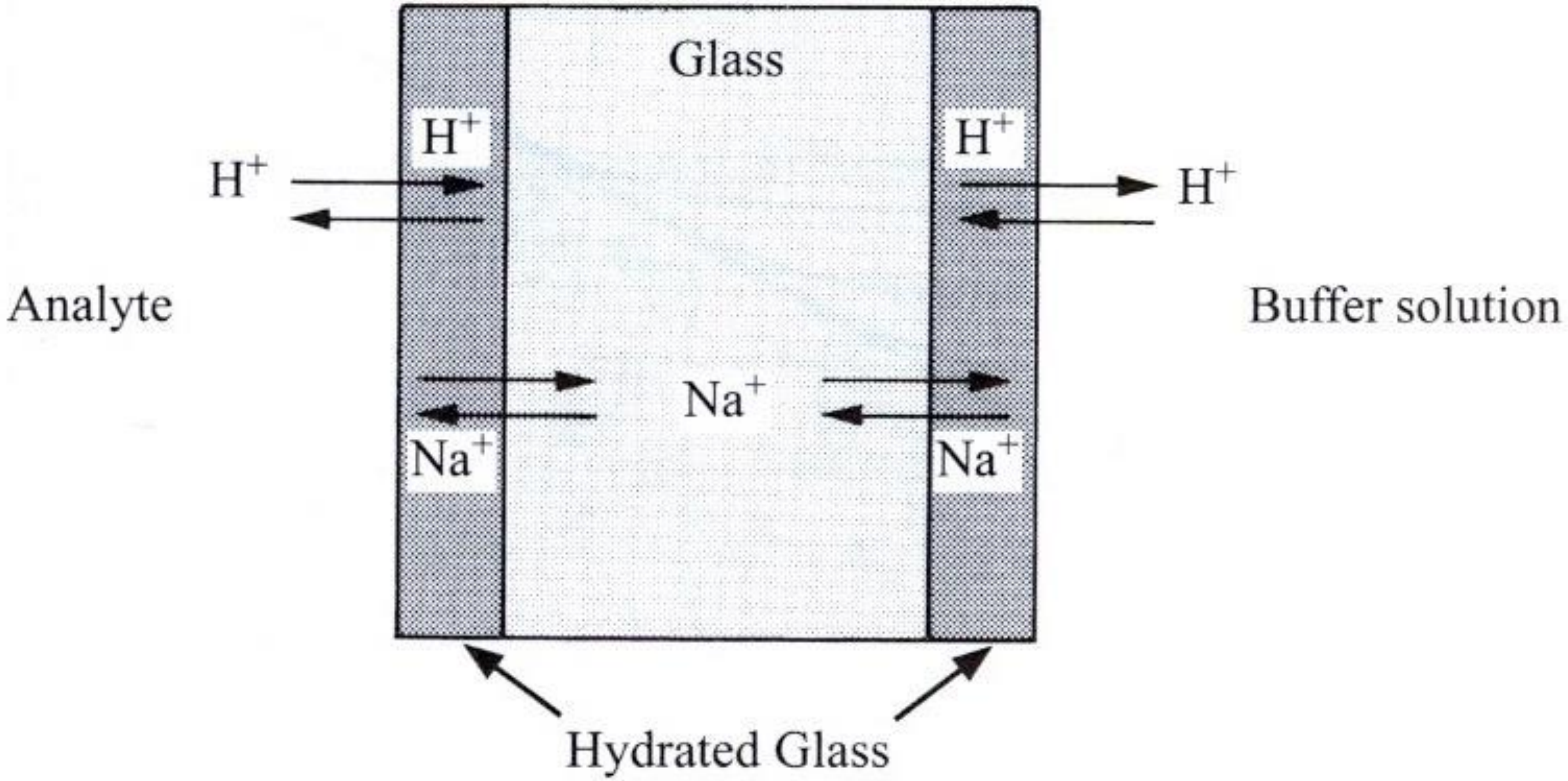


Fig. 2.25 Ionic equilibria in a glass electrode.

… 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!

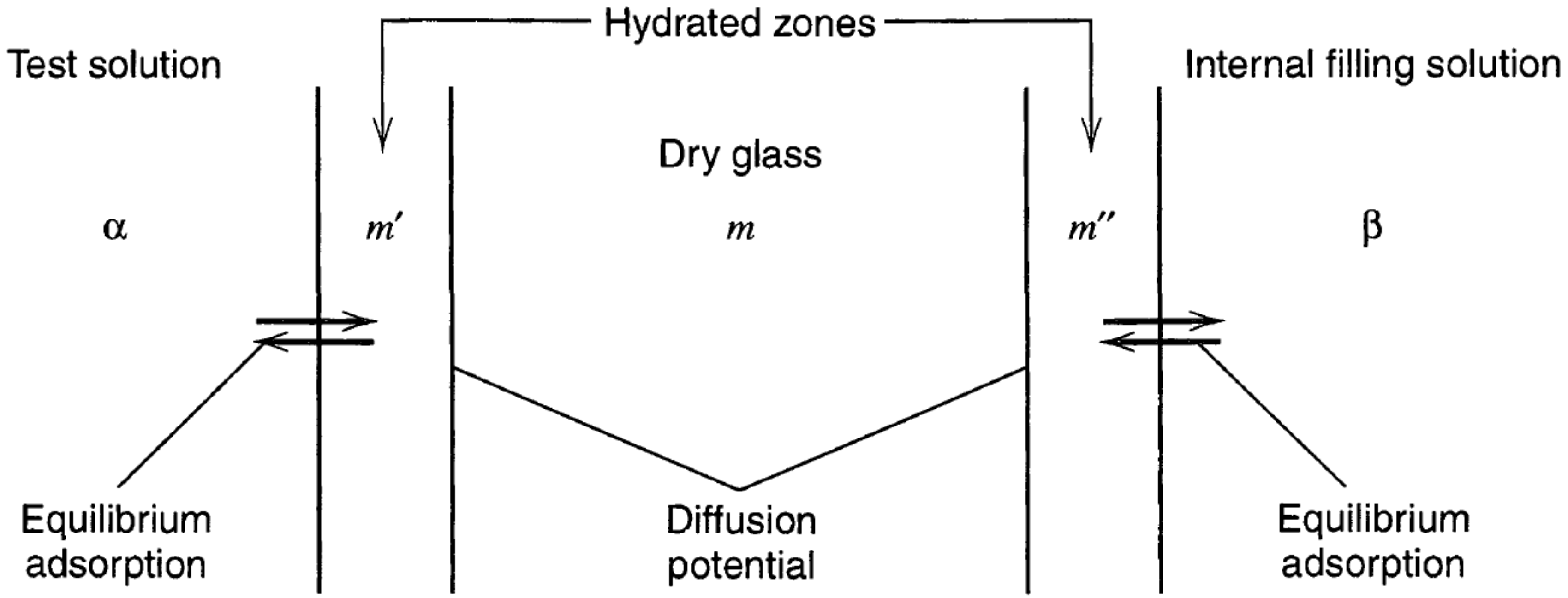


Figure 2.4.3 Model for treating the membrane potential across a glass barrier.

This forms and is measurable due to a balance of entropic diffusion and classical electrostatic drift…

… just like when speciation within the diffuse layer is calculated using the Poisson–Boltzmann equation…

… and for the space–charge region of a pn-junction diode *(which we will cover in much more detail soon)*

Reaction	E°/V
$\mathrm{Fr^{+} + e \rightleftharpoons Fr}$	–2.9
$\mathrm{Ga^{3+} + 3\,e \rightleftharpoons Ga}$	–0.549
$\mathrm{Ga^{+} + e \rightleftharpoons Ga}$	–0.2
$\mathrm{GaOH^{2+} + H^{+} + 3\,e \rightleftharpoons Ga + H_2O}$	–0.498
$\mathrm{H_2GaO_3^{-} + H_2O + 3\,e \rightleftharpoons Ga + 4\,OH^{-}}$	–1.219
$\mathrm{Gd^{3+} + 3\,e \rightleftharpoons Gd}$	–2.279
$\mathrm{Ge^{2+} + 2\,e \rightleftharpoons Ge}$	0.24
$\mathrm{Ge^{4+} + 4\,e \rightleftharpoons Ge}$	0.124
$\mathrm{Ge^{4+} + 2\,e \rightleftharpoons Ge^{2+}}$	0.00
$\mathrm{GeO_2 + 2\,H^{+} + 2\,e \rightleftharpoons GeO + H_2O}$	–0.118
$\mathrm{H_2GeO_3 + 4\,H^{+} + 4\,e \rightleftharpoons Ge + 3\,H_2O}$	–0.182
$\mathrm{2\,H^{+} + 2\,e \rightleftharpoons H_2}$	0.00000
$\mathrm{H_2 + 2\,e \rightleftharpoons 2\,H^{-}}$	–2.23
$\mathrm{HO_2 + H^{+} + e \rightleftharpoons H_2O_2}$	1.495
$\mathrm{2\,H_2O + 2\,e \rightleftharpoons H_2 + 2\,OH^{-}}$	–0.8277
$\mathrm{H_2O_2 + 2\,H^{+} + 2\,e \rightleftharpoons 2\,H_2O}$	1.776
$\mathrm{Hf^{4+} + 4\,e \rightleftharpoons Hf}$	–1.55
$\mathrm{HfO^{2+} + 2\,H^{+} + 4\,e \rightleftharpoons Hf + H_2O}$	–1.724
$\mathrm{HfO_2 + 4\,H^{+} + 4\,e \rightleftharpoons Hf + 2\,H_2O}$	–1.505
$\mathrm{HfO(OH)_2 + H_2O + 4\,e \rightleftharpoons Hf + 4\,OH^{-}}$	–2.50
$\mathrm{Hg^{2+} + 2\,e \rightleftharpoons Hg}$	0.851
$\mathrm{2\,Hg^{2+} + 2\,e \rightleftharpoons Hg_2^{2+}}$	0.920
$\mathrm{Hg_2^{2+} + 2\,e \rightleftharpoons 2\,Hg}$	0.7973
$\mathrm{Hg_2(ac)_2 + 2\,e \rightleftharpoons 2\,Hg + 2(ac)^{-}}$	0.51163
$\mathrm{Hg_2Br_2 + 2\,e \rightleftharpoons 2\,Hg + 2\,Br^{-}}$	0.13923
$\mathrm{Hg_2Cl_2 + 2\,e \rightleftharpoons 2\,Hg + 2\,Cl^{-}}$	0.26808
$\mathrm{Hg_2HPO_4 + 2\,e \rightleftharpoons 2\,Hg + HPO_4^{2-}}$	0.6359
$\mathrm{Hg_2I_2 + 2\,e \rightleftharpoons 2\,Hg + 2\,I^{-}}$	–0.0405

Reaction	E°/V
$\mathrm{La(OH)_3 + 3\,e \rightleftharpoons La + 3\,OH^{-}}$	–2.90
$\mathrm{Li^{+} + e \rightleftharpoons Li}$	–3.0401
$\mathrm{Lr^{3+} + 3\,e \rightleftharpoons Lr}$	–1.96
$\mathrm{Lu^{3+} + 3\,e \rightleftharpoons Lu}$	–2.28
$\mathrm{Md^{3+} + e \rightleftharpoons Md^{2+}}$	–0.1
$\mathrm{Md^{3+} + 3\,e \rightleftharpoons Md}$	–1.65
$\mathrm{Md^{2+} + 2\,e \rightleftharpoons Md}$	–2.40
$\mathrm{Mg^{+} + e \rightleftharpoons Mg}$	–2.70
$\mathrm{Mg^{2+} + 2\,e \rightleftharpoons Mg}$	–2.372
$\mathrm{Mg(OH)_2 + 2\,e \rightleftharpoons Mg + 2\,OH^{-}}$	–2.690
$\mathrm{Mn^{2+} + 2\,e \rightleftharpoons Mn}$	–1.185
$\mathrm{Mn^{3+} + e \rightleftharpoons Mn^{2+}}$	1.5415
$\mathrm{MnO_2 + 4\,H^{+} + 2\,e \rightleftharpoons Mn^{2+} + 2\,H_2O}$	1.224
$\mathrm{MnO_4^{-} + e \rightleftharpoons MnO_4^{2-}}$	0.558
$\mathrm{MnO_4^{-} + 4\,H^{+} + 3\,e \rightleftharpoons MnO_2 + 2\,H_2O}$	1.679
$\mathrm{MnO_4^{-} + 8\,H^{+} + 5\,e \rightleftharpoons Mn^{2+} + 4\,H_2O}$	1.507
$\mathrm{MnO_4^{-} + 2\,H_2O + 3\,e \rightleftharpoons MnO_2 + 4\,OH^{-}}$	0.595
$\mathrm{MnO_4^{2-} + 2\,H_2O + 2\,e \rightleftharpoons MnO_2 + 4\,OH^{-}}$	0.60
$\mathrm{Mn(OH)_2 + 2\,e \rightleftharpoons Mn + 2\,OH^{-}}$	–1.56
$\mathrm{Mn(OH)_3 + e \rightleftharpoons Mn(OH)_2 + OH^{-}}$	0.15
$\mathrm{Mn_2O_3 + 6\,H^{+} + e \rightleftharpoons 2\,Mn^{2+} + 3\,H_2O}$	1.485
$\mathrm{Mo^{3+} + 3\,e \rightleftharpoons Mo}$	–0.200
$\mathrm{MoO_2 + 4\,H^{+} + 4\,e \rightleftharpoons Mo + 4\,H_2O}$	–0.152
$\mathrm{H_3Mo_7O_{24}^{3-} + 45\,H^{+} + 42\,e \rightleftharpoons 7\,Mo + 24\,H_2O}$	0.082
$\mathrm{MoO_3 + 6\,H^{+} + 6\,e \rightleftharpoons Mo + 3\,H_2O}$	0.075
$\mathrm{N_2 + 2\,H_2O + 6\,H^{+} + 6\,e \rightleftharpoons 2\,NH_4OH}$	0.092
$\mathrm{3\,N_2 + 2\,H^{+} + 2\,e \rightleftharpoons 2\,HN_3}$	–3.09
$\mathrm{N_5^{+} + 3\,H^{+} + 2\,e \rightleftharpoons 2\,NH_4^{+}}$	1.275

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

$\mathrm{Hg_2O + H_2O + 2\,e \rightleftharpoons 2\,Hg + 2\,OH^{-}}$	0.123
$\mathrm{HgO + H_2O + 2\,e \rightleftharpoons Hg + 2\,OH^{-}}$	0.0977
$\mathrm{Hg(OH)_2 + 2\,H^{+} + 2\,e \rightleftharpoons Hg + 2\,H_2O}$	1.034
$\mathrm{Hg_2SO_4 + 2\,e \rightleftharpoons 2\,Hg + SO_4^{2-}}$	0.6125
$\mathrm{Ho^{2+} + 2\,e \rightleftharpoons Ho}$	–2.1
$\mathrm{Ho^{3+} + 3\,e \rightleftharpoons Ho}$	–2.33
$\mathrm{Ho^{3+} + e \rightleftharpoons Ho^{2+}}$	–2.8
$\mathrm{I_2 + 2\,e \rightleftharpoons 2\,I^{-}}$	0.5355
$\mathrm{I_3^{-} + 2\,e \rightleftharpoons 3\,I^{-}}$	0.536
$\mathrm{H_3IO_6^{2-} + 2\,e \rightleftharpoons IO_3^{-} + 3\,OH^{-}}$	0.7
$\mathrm{H_5IO_6 + H^{+} + 2\,e \rightleftharpoons IO_3^{-} + 3\,H_2O}$	1.601
$\mathrm{2\,HIO + 2\,H^{+} + 2\,e \rightleftharpoons I_2 + 2\,H_2O}$	1.439
$\mathrm{HIO + H^{+} + 2\,e \rightleftharpoons I^{-} + H_2O}$	0.987
$\mathrm{IO^{-} + H_2O + 2\,e \rightleftharpoons I^{-} + 2\,OH^{-}}$	0.485
$\mathrm{2\,IO_3^{-} + 12\,H^{+} + 10\,e \rightleftharpoons I_2 + 6\,H_2O}$	1.195
$\mathrm{IO_3^{-} + 6\,H^{+} + 6\,e \rightleftharpoons I^{-} + 3\,H_2O}$	1.085
$\mathrm{IO_3^{-} + 2\,H_2O + 4\,e \rightleftharpoons IO^{-} + 4\,OH^{-}}$	0.15
$\mathrm{IO_3^{-} + 3\,H_2O + 6\,e \rightleftharpoons I^{-} + 6\,OH^{-}}$	0.26
$\mathrm{In^{+} + e \rightleftharpoons In}$	–0.14
$\mathrm{In^{2+} + e \rightleftharpoons In^{+}}$	–0.40
$\mathrm{In^{3+} + e \rightleftharpoons In^{2+}}$	–0.49
$\mathrm{In^{3+} + 2\,e \rightleftharpoons In^{+}}$	–0.443
$\mathrm{In^{3+} + 3\,e \rightleftharpoons In}$	–0.3382
$\mathrm{In(OH)_3 + 3\,e \rightleftharpoons In + 3\,OH^{-}}$	–0.99
$\mathrm{In(OH)_4^{-} + 3\,e \rightleftharpoons In + 4\,OH^{-}}$	–1.007
$\mathrm{In_2O_3 + 3\,H_2O + 6\,e \rightleftharpoons 2\,In + 6\,OH^{-}}$	–1.034
$\mathrm{Ir^{3+} + 3\,e \rightleftharpoons Ir}$	1.156
$\mathrm{[IrCl_6]^{2-} + e \rightleftharpoons [IrCl_6]^{3-}}$	0.8665
$\mathrm{[IrCl_6]^{3-} + 3\,e \rightleftharpoons Ir + 6\,Cl^{-}}$	0.77
$\mathrm{Ir_2O_3 + 3\,H_2O + 6\,e \rightleftharpoons 2\,Ir + 6\,OH^{-}}$	0.098
$\mathrm{K^{+} + e \rightleftharpoons K}$	–2.931
$\mathrm{La^{3+} + 3\,e \rightleftharpoons La}$	–2.379

$\mathrm{N_2O + 2\,H^{+} + 2\,e \rightleftharpoons N_2 + H_2O}$	1.766
$\mathrm{H_2N_2O_2 + 2\,H^{+} + 2\,e \rightleftharpoons N_2 + 2\,H_2O}$	2.65
$\mathrm{N_2O_4 + 2\,e \rightleftharpoons 2\,NO_2^{-}}$	0.867
$\mathrm{N_2O_4 + 2\,H^{+} + 2\,e \rightleftharpoons 2\,NHO_2}$	1.065
$\mathrm{N_2O_4 + 4\,H^{+} + 4\,e \rightleftharpoons 2\,NO + 2\,H_2O}$	1.035
$\mathrm{2\,NH_3OH^{+} + H^{+} + 2\,e \rightleftharpoons N_2H_5^{+} + 2\,H_2O}$	1.42
$\mathrm{2\,NO + 2\,H^{+} + 2\,e \rightleftharpoons N_2O + H_2O}$	1.591
$\mathrm{2\,NO + H_2O + 2\,e \rightleftharpoons N_2O + 2\,OH^{-}}$	0.76
$\mathrm{HNO_2 + H^{+} + e \rightleftharpoons NO + H_2O}$	0.983
$\mathrm{2\,HNO_2 + 4\,H^{+} + 4\,e \rightleftharpoons H_2N_2O_2 + 2\,H_2O}$	0.86
$\mathrm{2\,HNO_2 + 4\,H^{+} + 4\,e \rightleftharpoons N_2O + 3\,H_2O}$	1.297
$\mathrm{NO_2^{-} + H_2O + e \rightleftharpoons NO + 2\,OH^{-}}$	–0.46
$\mathrm{2\,NO_2^{-} + 2\,H_2O + 4\,e \rightleftharpoons N_2O_2^{2-} + 4\,OH^{-}}$	–0.18
$\mathrm{2\,NO_2^{-} + 3\,H_2O + 4\,e \rightleftharpoons N_2O + 6\,OH^{-}}$	0.15
$\mathrm{NO_3^{-} + 3\,H^{+} + 2\,e \rightleftharpoons HNO_2 + H_2O}$	0.934
$\mathrm{NO_3^{-} + 4\,H^{+} + 3\,e \rightleftharpoons NO + 2\,H_2O}$	0.957
$\mathrm{2\,NO_3^{-} + 4\,H^{+} + 2\,e \rightleftharpoons N_2O_4 + 2\,H_2O}$	0.803
$\mathrm{NO_3^{-} + H_2O + 2\,e \rightleftharpoons NO_2^{-} + 2\,OH^{-}}$	0.01
$\mathrm{2\,NO_3^{-} + 2\,H_2O + 2\,e \rightleftharpoons N_2O_4 + 4\,OH^{-}}$	–0.85
$\mathrm{Na^{+} + e \rightleftharpoons Na}$	–2.71
$\mathrm{Nb^{3+} + 3\,e \rightleftharpoons Nb}$	–1.099
$\mathrm{NbO_2 + 2\,H^{+} + 2\,e \rightleftharpoons NbO + H_2O}$	–0.646
$\mathrm{NbO_2 + 4\,H^{+} + 4\,e \rightleftharpoons Nb + 2\,H_2O}$	–0.690
$\mathrm{NbO + 2\,H^{+} + 2\,e \rightleftharpoons Nb + H_2O}$	–0.733
$\mathrm{Nb_2O_5 + 10\,H^{+} + 10\,e \rightleftharpoons 2\,Nb + 5\,H_2O}$	–0.644
$\mathrm{Nd^{3+} + 3\,e \rightleftharpoons Nd}$	–2.323
$\mathrm{Nd^{2+} + 2\,e \rightleftharpoons Nd}$	–2.1
$\mathrm{Nd^{3+} + e \rightleftharpoons Nd^{2+}}$	–2.7
$\mathrm{Ni^{2+} + 2\,e \rightleftharpoons Ni}$	–0.257
$\mathrm{Ni(OH)_2 + 2\,e \rightleftharpoons Ni + 2\,OH^{-}}$	–0.72
$\mathrm{NiO_2 + 4\,H^{+} + 2\,e \rightleftharpoons Ni^{2+} + 2\,H_2O}$	1.678
$\mathrm{NiO_2 + 2\,H_2O + 2\,e \rightleftharpoons Ni(OH)_2 + 2\,OH^{-}}$	–0.490

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

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

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

… pBLAH = – log a_{BLAH}

… *and again*, the CRC Handbook has a lot of chemical information… including tables of values…

… also those in the **Acidity/Basicity Series**…

… Do you know what the reference acidity is for this list of standard(-state) equilibrium acid dissociation constants?

Mol. form.	Name	Step	t/°C	pK_a
$CHNO$	Cyanic acid		25	3.7
CH_2N_2	Cyanamide		29	1.1
CH_2O	Formaldehyde		25	13.27
CH_2O_2	Formic acid		25	3.75
CH_3NO_2	Nitromethane		25	10.21
CH_3NS_2	Carbamodithioic acid		25	2.95
CH_4N_2O	Urea		25	0.10
CH_4N_2S	Thiourea		25	-1
CH_4O	Methanol		25	15.5
CH_4S	Methanethiol		25	10.33
CH_5N	Methylamine		25	10.66
CH_5NO	*O*-Methylhydroxylamine			12.5
CH_5N_3	Guanidine		25	13.6
C_2HCl_3O	Trichloroacetaldehyde		25	10.04
$C_2HCl_3O_2$	Trichloroacetic acid		20	0.66
$C_2HF_3O_2$	Trifluoroacetic acid		25	0.52
$C_2H_2Cl_2O_2$	Dichloroacetic acid		25	1.35
$C_2H_2O_3$	Glyoxylic acid		25	3.18
$C_2H_2O_4$	Oxalic acid	1	25	1.25
		2	25	3.81
$C_2H_3BrO_2$	Bromoacetic acid		25	2.90
$C_2H_3ClO_2$	Chloroacetic acid		25	2.87
$C_2H_3Cl_3O$	2,2,2-Trichloroethanol		25	12.24
$C_2H_3FO_2$	Fluoroacetic acid		25	2.59
$C_2H_3F_3O$	2,2,2-Trifluoroethanol		25	12.37
$C_2H_3IO_2$	Iodoacetic acid		25	3.18
$C_2H_3NO_4$	Nitroacetic acid		24	1.48
$C_2H_3N_3$	1H-1,2,3-Triazole		20	1.17
$C_2H_3N_3$	1H-1,2,4-Triazole		20	2.27
$C_2H_4N_2$	Aminoacetonitrile		25	5.34
C_2H_4O	Acetaldehyde		25	13.57
C_2H_4OS	Thioacetic acid		25	3.33
$C_2H_4O_2$	Acetic acid		25	4.756
$C_2H_4O_2S$	Thioglycolic acid		25	3.68
$C_2H_4O_3$	Glycolic acid		25	3.83
C_2H_5N	Ethyleneimine		25	8.04

Mol. form.	Name	Step	t/°C	pK_a
C_2H_5NO	Acetamide		25	15.1
$C_2H_5NO_2$	Acetohydroxamic acid			8.70
$C_2H_5NO_2$	Nitroethane		25	8.46
$C_2H_5NO_2$	Glycine	1	25	2.35
		2	25	9.78
$C_2H_6N_2$	Ethanimidamide		25	12.1
C_2H_6O	Ethanol		25	15.5
C_2H_6OS	2-Mercaptoethanol		25	9.72
$C_2H_6O_2$	Ethyleneglycol		25	15.1
$C_2H_7AsO_2$	Dimethylarsinic acid	1	25	1.57
		2	25	6.27
C_2H_7N	Ethylamine		25	10.65
C_2H_7N	Dimethylamine		25	10.73
C_2H_7NO	Ethanolamine		25	9.50
$C_2H_7NO_3S$	2-Aminoethanesulfonic acid	1	25	1.5
		2	25	9.06
C_2H_7NS	Cysteamine	1	25	8.27
		2	25	10.53
$C_2H_7N_5$	Biguanide	1		11.52
		2		2.93
$C_2H_8N_2$	1,2-Ethanediamine	1	25	9.92
		2	25	6.86
$C_2H_8O_7P_2$	1-Hydroxy-1,1-diphosphonoethane	1		1.35
		2		2.87
		3		7.03
		4		11.3
$C_3H_2O_2$	2-Propynoic acid		25	1.84
C_3H_3NO	Oxazole		33	0.8
C_3H_3NO	Isoxazole		25	-2.0
$C_3H_3NO_2$	Cyanoacetic acid		25	2.47
C_3H_3NS	Thiazole		25	2.52
$C_3H_3N_3O_3$	Cyanuric acid	1		6.88
		2		11.40
		3		13.5
$C_3H_4N_2$	1*H*-Pyrazole		25	2.49
$C_3H_4N_2$	Imidazole		25	6.99

… 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!

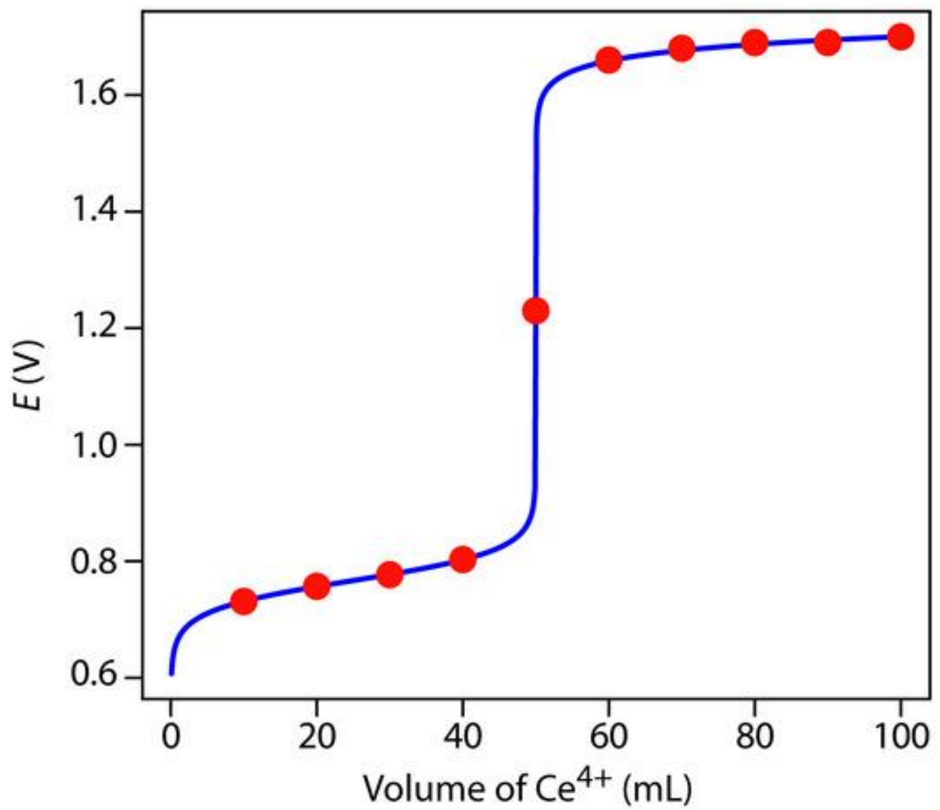
… but wait!… for B, BH^+ this looks like Hess's law!

… so, let's add up these chemical reactions!

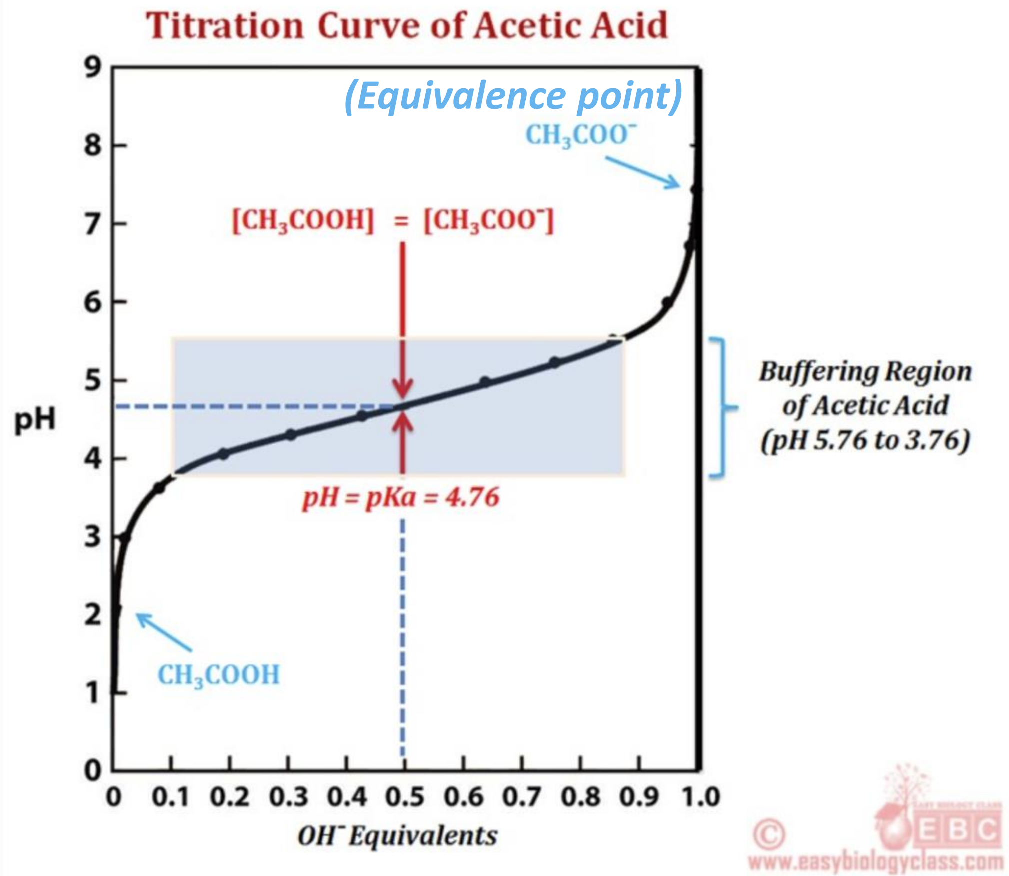
… and that gives us water dissociation… Nice!

Titrations and Buffering

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



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



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

Nernst equation

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

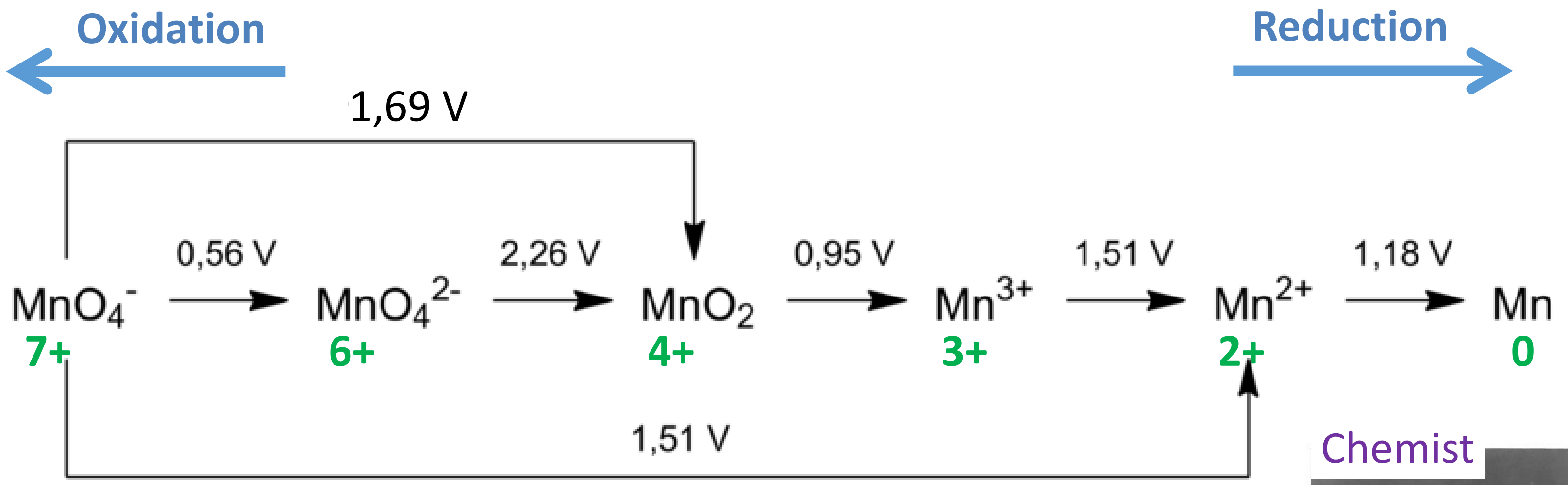
Henderson–Hasselbalch equation

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

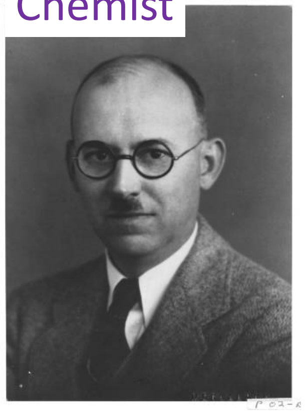
… Oh chemists!… make up your minds already!… and I thought physicists were bad with *q* being positive!

Two diagrams of empirical standard potentials…

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



Chemist



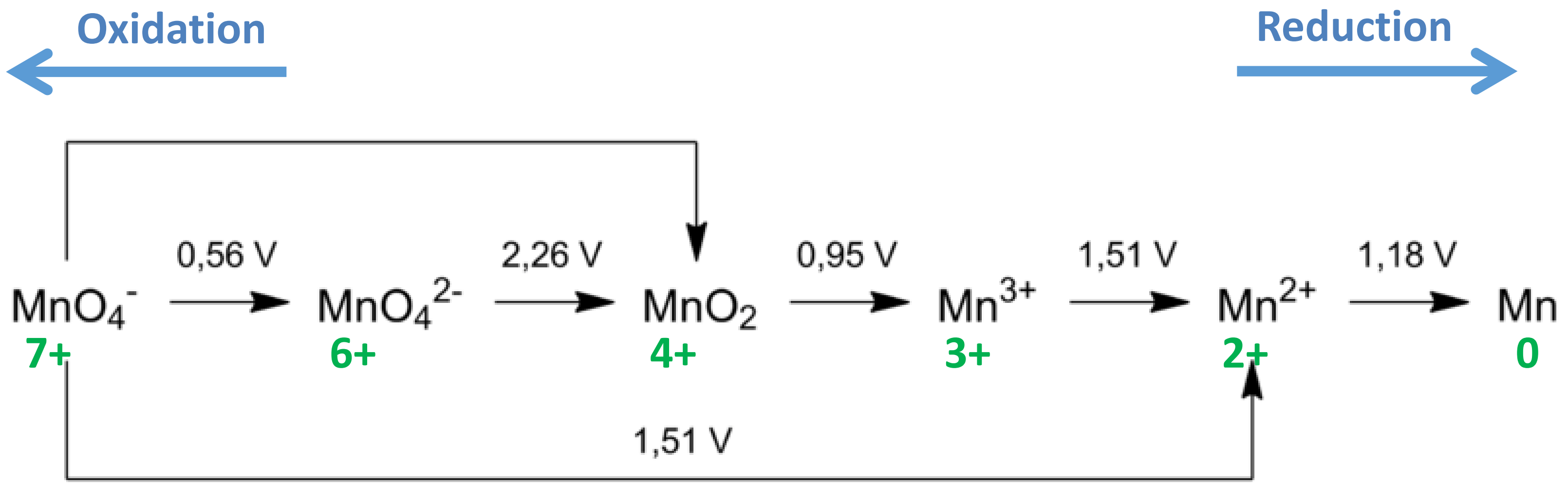
Wendell Mitchell Latimer (1893–1955)

http://academictree.org/chemistry/peopleinfo.php?pid=24644

Latimer, The oxidation states of the elements and their potentials in aqueous solution, 1938

Two diagrams of empirical standard potentials…

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



from Wiki

Disproportionation – spontaneous and simultaneous reduction and oxidation of a molecule *(the opposite is comproportionation (AKA: symproportionation))*

(1) Does Mn^{2+} disproportionate? NO. $E^o = E_{red} - E_{ox} = 1.18 - 1.51 = -0.33$ V

(2) What is the standard reduction potential of MnO_4^- to MnO_2?

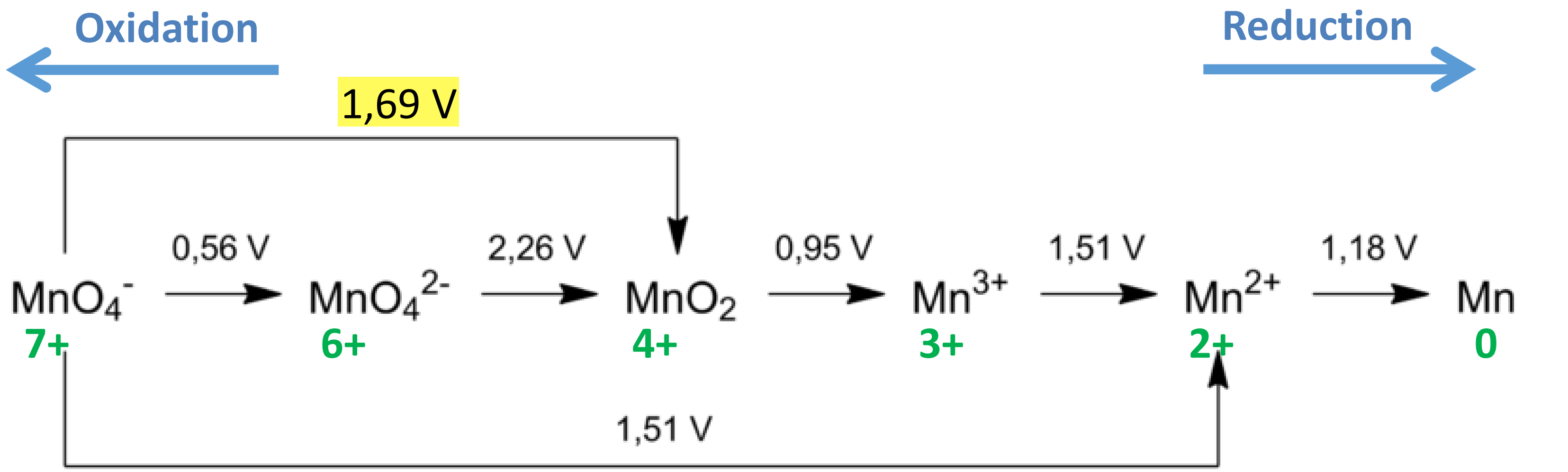
Total Reaction: $3Mn^{2+} \rightleftharpoons Mn^o + 2Mn^{3+}$ E^o_{total} = ?

Reduction: $Mn^{2+} \rightleftharpoons Mn^o$ $E^o = +1.18$ V

Oxidation: $Mn^{2+} \rightleftharpoons Mn^{3+}$ $E^o = +1.51$ V

Two diagrams of empirical standard potentials…

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



from Wiki

Disproportionation – spontaneous and simultaneous reduction and oxidation of a molecule *(the opposite is comproportionation (AKA: symproportionation))*

(1) Does Mn^{2+} disproportionate? **NO.** $E^o = E_{red} - E_{ox} = 1.18 - 1.51 = -0.33$ V

(2) What is the standard reduction potential of MnO_4^- to MnO_2?

$\Delta G^o = -nFE^o = -3FE^o$

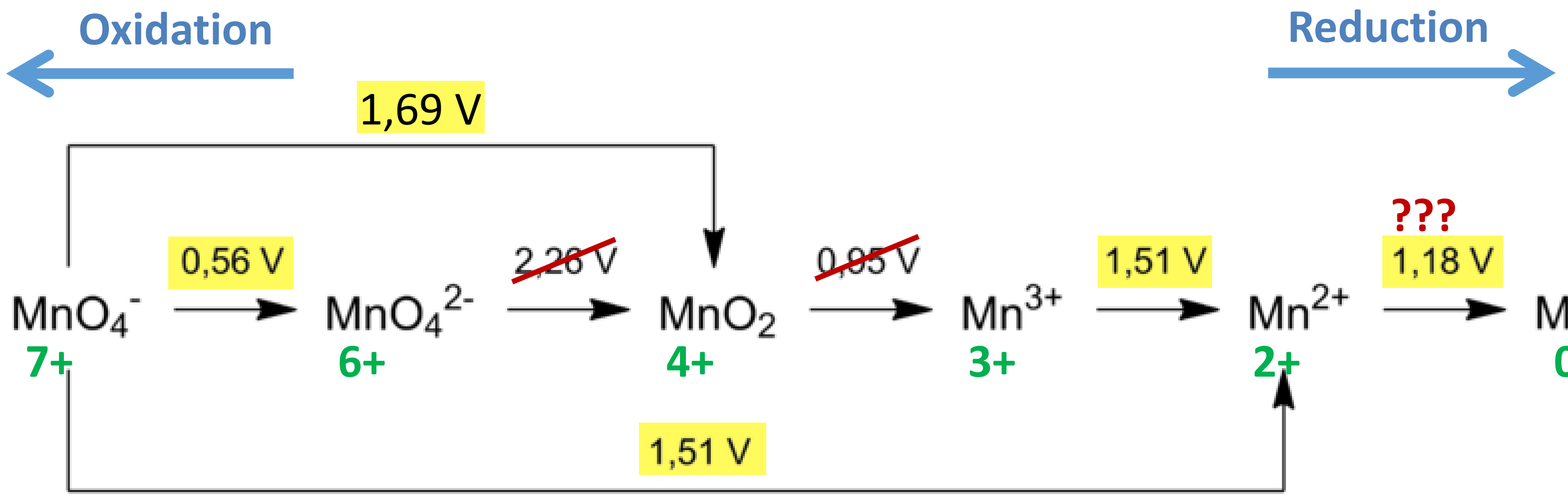
$\Delta G^o = -nFE^o_1 + -nFE^o_2 = -F((1 \times 0.56\ V) + (2 \times 2.26\ V)) = -F(5.08\ V)$

Set them equal to each other, and thus, $3E^o = 5.08$ and $E^o = 1.69$ V

… for #1, you can work with E^o only (do not need ΔG^o), because the reaction is always balanced/equal in the number of electrons

Two diagrams of empirical standard potentials…

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



from Wiki

Recall from before…

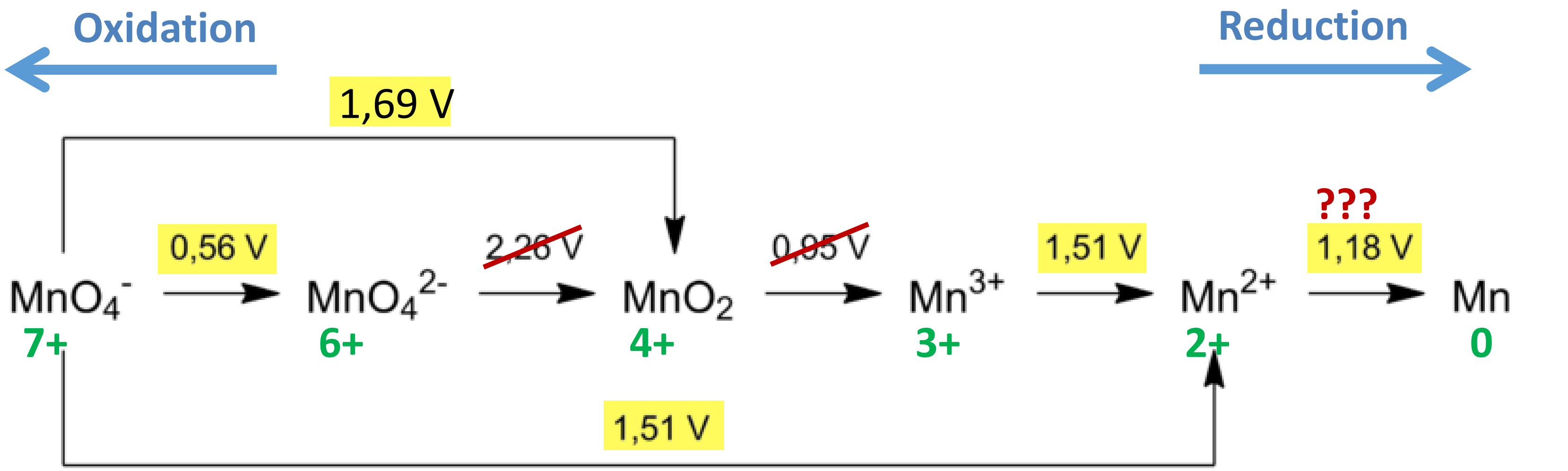
$Mn^{2+} + 2e \rightleftharpoons Mn$	???	−1.185
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$		1.5415
$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$		1.224
$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$		0.558
$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$		1.679
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$		1.507
$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^-$		0.595
$MnO_4^{2-} + 2H_2O + 2e \rightleftharpoons MnO_2 + 4OH^-$		0.60
$Mn(OH)_2 + 2e \rightleftharpoons Mn + 2OH^-$		−1.56
$Mn(OH)_3 + e \rightleftharpoons Mn(OH)_2 + OH^-$		0.15
$Mn_2O_3 + 6H^+ + e \rightleftharpoons 2Mn^{2+} + 3H_2O$		1.485

… anyway, why are these bottom E^o values not on the Latimer diagram?

… because they are at basic/alkaline standard state with ~1 M OH^-!

Two diagrams of empirical standard potentials…

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



from Wiki

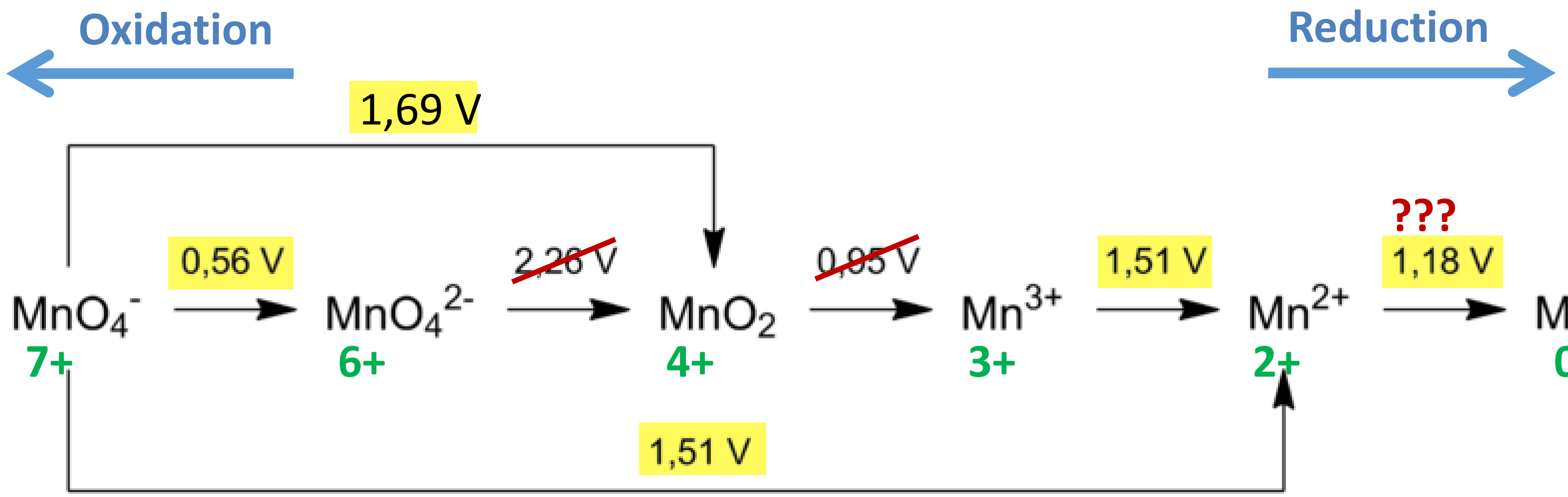
Recall from before…

$Mn^{2+} + 2e \rightleftharpoons Mn$	???	−1.185
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$		1.5415
$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$		1.224
$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$		0.558
$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$		1.679
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$		1.507
$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^-$		0.595
$MnO_4^{2-} + 2H_2O + 2e \rightleftharpoons MnO_2 + 4OH^-$		0.60
$Mn(OH)_2 + 2e \rightleftharpoons Mn + 2OH^-$		−1.56
$Mn(OH)_3 + e \rightleftharpoons Mn(OH)_2 + OH^-$		0.15
$Mn_2O_3 + 6H^+ + e \rightleftharpoons 2Mn^{2+} + 3H_2O$		1.485

What would this E^o value be when at acidic standard state?

Two diagrams of empirical standard potentials…

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



from Wiki

$$E = E^o_{acid} - \frac{0.05916\ V}{n}\log\left(\frac{[MnO_2]^1[H_2O]^2}{[MnO_4{}^{2-}]^1[H^+]^4}\right) = E^o_{acid} - \frac{0.05916\ V}{2}\log\left(\frac{(1)^1}{(1)^1(10^{-14})^4}\right) = E^o_{acid} - 0.02958\ V(56)$$

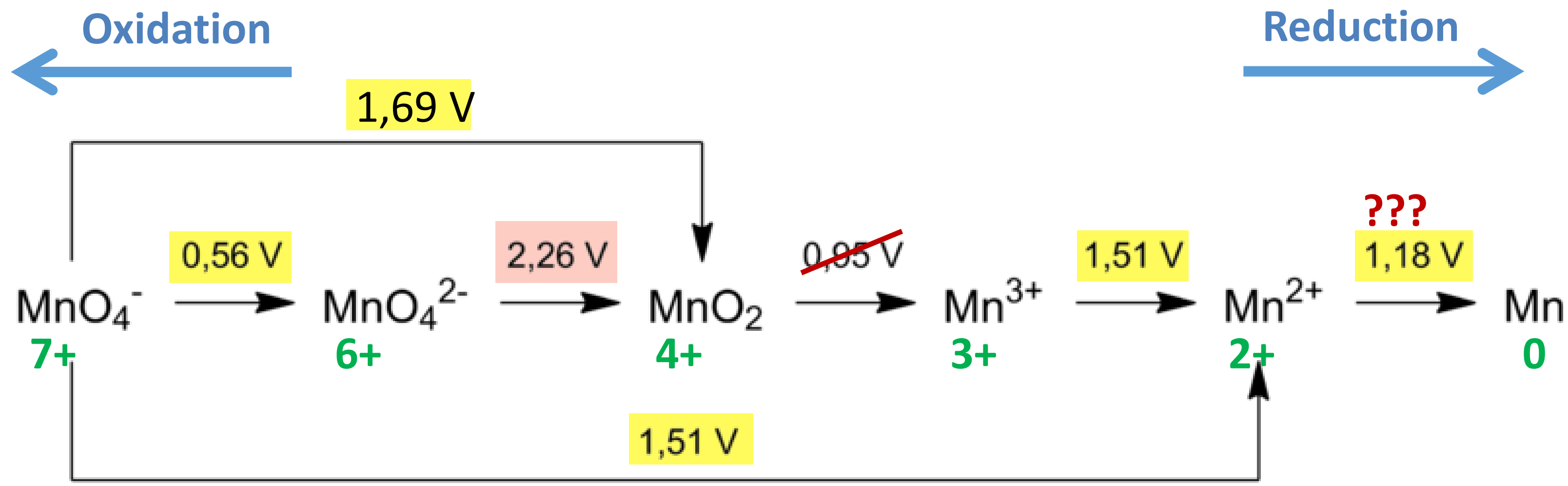
$$E = E^o_{acid} - 1.65648\ V = 0.60\ V$$

What would this E^o value be when at acidic standard state?

$MnO_4^- + 2\,H_2O + 3\,e \rightleftharpoons MnO_2 + 4\,OH^-$	0.595
$MnO_4^{2-} + 2\,H_2O + 2\,e \rightleftharpoons MnO_2 + 4\,OH^-$	0.60
$Mn(OH)_2 + 2\,e \rightleftharpoons Mn + 2\,OH^-$	−1.56
$Mn(OH)_3 + e \rightleftharpoons Mn(OH)_2 + OH^-$	0.15
$Mn_2O_3 + 6\,H^+ + e \rightleftharpoons 2\,Mn^{2+} + 3\,H_2O$	1.485

Two diagrams of empirical standard potentials…

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



from Wiki

$$E = E^{o}_{acid} - \frac{0.05916\ \mathrm{V}}{n}\log\left(\frac{[\mathrm{MnO_2}]^1[\mathrm{H_2O}]^2}{[\mathrm{MnO_4}^{2-}]^1[\mathrm{H^+}]^4}\right) = E^{o}_{acid} - \frac{0.05916\ \mathrm{V}}{2}\log\left(\frac{(1)^1}{(1)^1(10^{-14})^4}\right) = E^{o}_{acid} - 0.02958\ \mathrm{V}(56)$$

$$E = E^{o}_{acid} - 1.65648\ \mathrm{V} = 0.60\ \mathrm{V}$$

What would this E^0 value be when at acidic standard state?

$MnO_4^- + 2\,H_2O + 3\,e \rightleftharpoons MnO_2 + 4\,OH^-$	0.595
$MnO_4^{2-} + 2\,H_2O + 2\,e \rightleftharpoons MnO_2 + 4\,OH^-$	0.60
$Mn(OH)_2 + 2\,e \rightleftharpoons Mn + 2\,OH^-$	−1.56
$Mn(OH)_3 + e \rightleftharpoons Mn(OH)_2 + OH^-$	0.15
$Mn_2O_3 + 6\,H^+ + e \rightleftharpoons 2\,Mn^{2+} + 3\,H_2O$	1.485

$E^{o}_{SHE} = 2{,}25648\ \mathrm{V}$

SWEET!

… but then why didn't the CRC Handbook list this? …

… a second diagram of (not truly) empirical standard potentials…

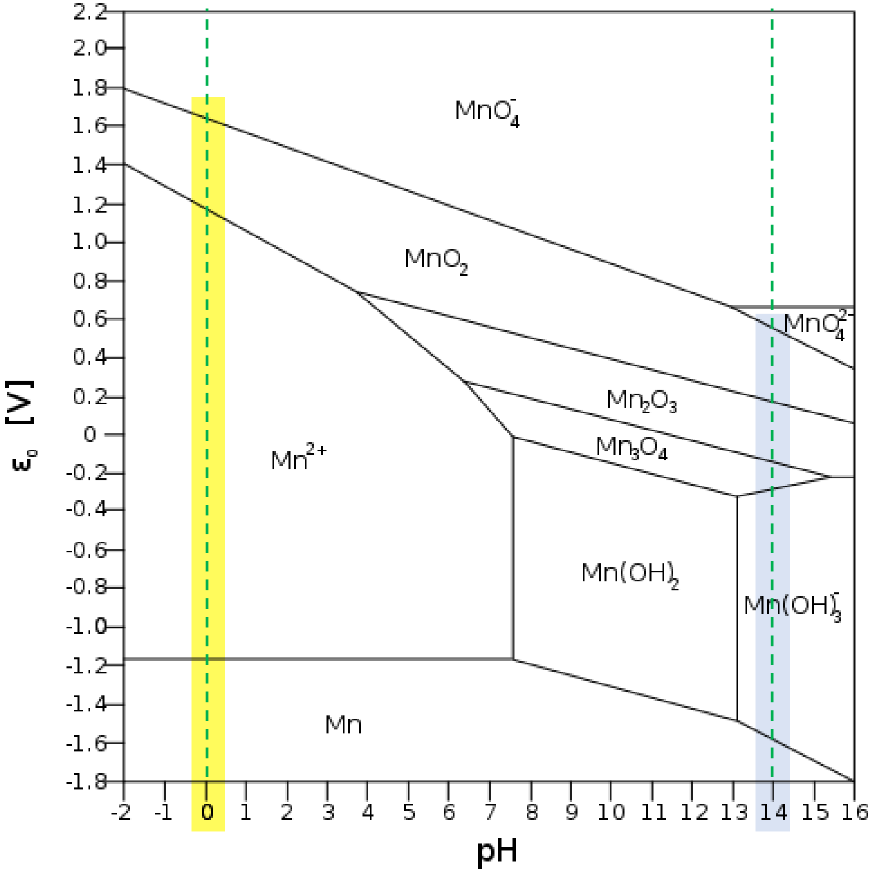
A **Pourbaix diagram** is a map of the predominant *equilibrium* species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable

… mostly based on thermochemical data

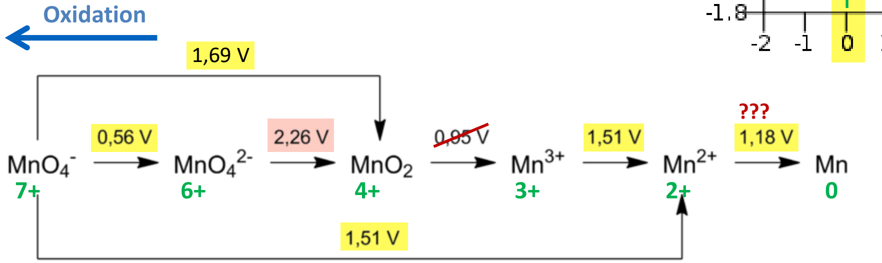
Chemist

Marcel Pourbaix
(1904–1998)

http://corrosion-doctors.org/Biographies/PourbaixBio.htm



from Wiki



from Wiki

… because in acid, the reaction does not occur!

… but then why didn't the CRC Handbook list this? …

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974

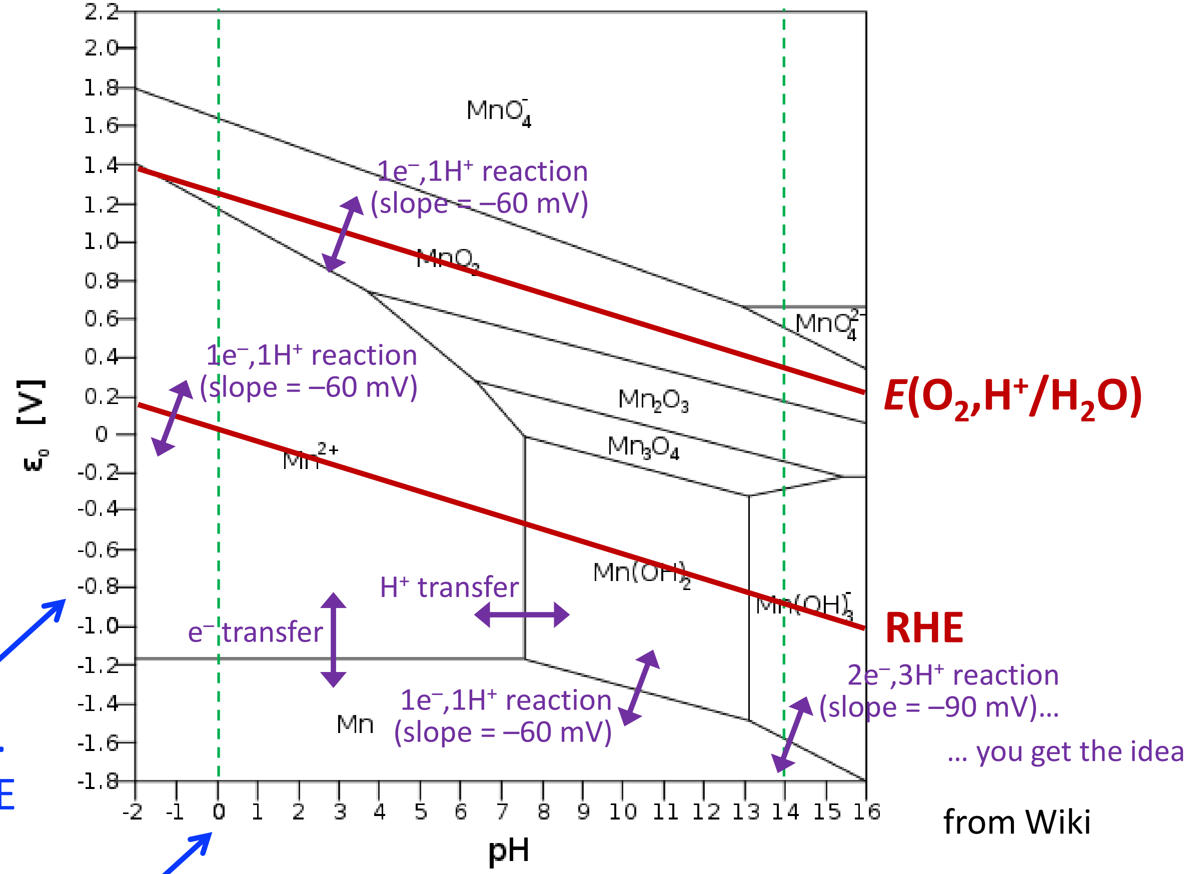
… a second diagram of (not truly) empirical standard potentials…

A **Pourbaix diagram** is a map of the predominant *equilibrium* species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable

… mostly based on thermochemical data

Chemist

Marcel Pourbaix
(1904–1998)
http://corrosion-doctors.org/Biographies/PourbaixBio.htm



from Wiki

Why don't I like this? …
Even though EVERYONE plots it this way

Anyway, … standard state is here, at ~1 M H^+ (pH = 0) → SHE
… but if written under alkaline conditions, ~1 M OH^- is standard state (pH 14)

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974

… a second diagram of (not truly) empirical standard potentials…

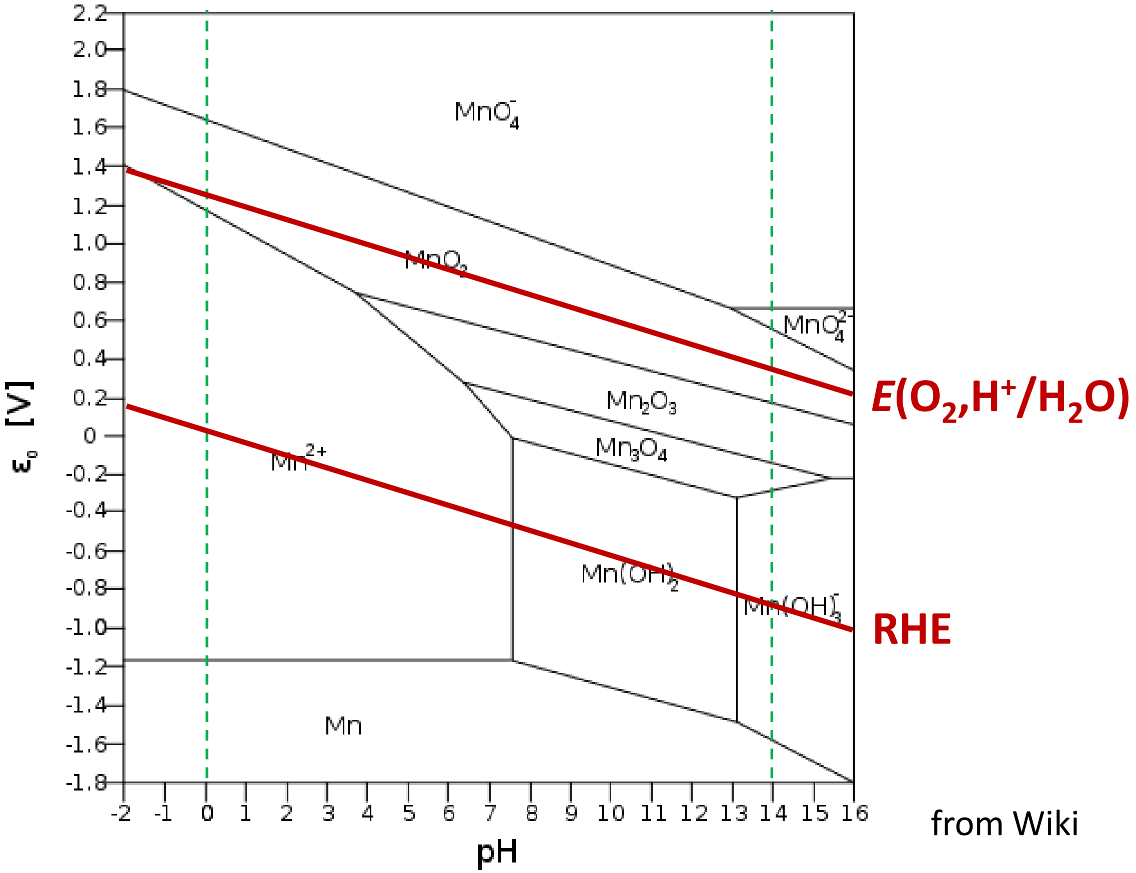
A **Pourbaix diagram** is a map of the predominant *equilibrium* species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable

… mostly based on thermochemical data

Chemist

Marcel Pourbaix
(1904–1998)

http://corrosion-doctors.org/Biographies/PourbaixBio.htm



from Wiki

(1) What is the electrocatalyst for O_2 evolution through water oxidation? **MnO_2**

(2) At what pH values is a solid electrocatalyst for H_2 evolution stable? **pH 7.5 – 13**

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974

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!