Lecture #9 of 14

(3: TThF, 5: MT*W*ThF, 4: MT*W*Th, 2: TW)

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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!

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!

e-Presentation… *to get a general idea, these are good topic choices in photo-chemistry alone…* **(REVIEW)** 197

- 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 electro-chemistry alone…* 198

- 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**…

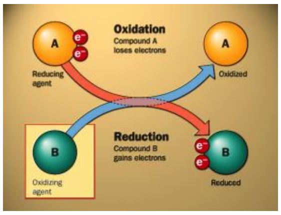
Discussion *(an hour-ish every-other-day-ish)* provides opportunities to discuss applied pchem research. 199
… of course, there are way too many topics to cover, but I decided on the following as the **FINAL** list:

(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.


A
e⁻
e⁻
Reducing agent
Oxidation
Compound A loses electrons
A
Oxidized
B
Oxidizing agent
Reduction
Compound B gains electrons
e⁻
e⁻
B
Reduced

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.

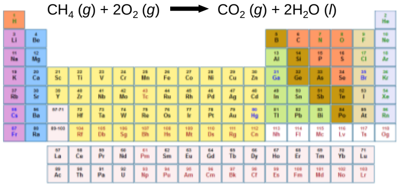
N_2H_4 (H_2NNH_2)	N:-2, H:+1

Closed (filled) orbital shells are most stable…

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

$$\overset{0}{Zn}\ (s) + 2\overset{+1}{H}\overset{-1}{Cl}\ (aq) \longrightarrow \overset{+2}{Zn}(\overset{-1}{Cl})_2\ (aq) + \overset{0}{H_2}\ (g)$$

$$CH_4\ (g) + 2\overset{0}{O_2}\ (g) \longrightarrow C\overset{-2}{O_2}\ (g) + 2H_2\overset{-2}{O}\ (l)$$



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

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Oxidation and Reduction

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

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

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⁻

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

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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**

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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.

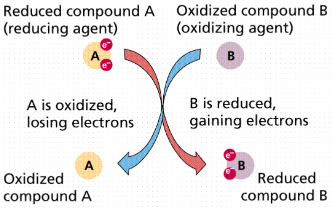
4. Use the changes in oxidation state for each atom to determine what is being oxidized and reduced.

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

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?*


Reduced compound A
(reducing agent)
Oxidized compound B
(oxidizing agent)
A
e⁻
e⁻
B
A is oxidized,
losing electrons
B is reduced,
gaining electrons
A
Oxidized
compound A
e⁻
e⁻
B
Reduced
compound B

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.

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

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

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

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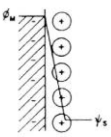
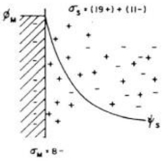
Charged Interfaces

- 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**

… three models for the potential distribution near a charged electrode immersed in an electrolyte solution… **(REVIEW)** 215

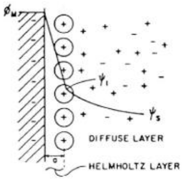


Helmholtz (H)



ϕ_M
σ_s = (19+) + (11−)
ψ_s
σ_M = 8−

Gouy–Chapman (GC)



ϕ_M
ψ_1
ψ_s
DIFFUSE LAYER
a
HELMHOLTZ LAYER

Gouy–Chapman–Stern (GCS)

$\varepsilon_r \approx 6$

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

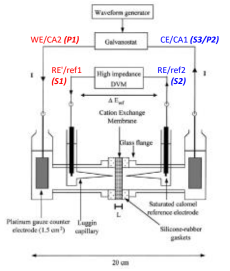
$$\frac{d\phi}{dx} = -\left(\frac{8kTn^0}{\varepsilon\varepsilon_0}\right)^{1/2}\sinh\left(\frac{ze\phi}{2kT}\right)$$ … Poisson–Boltzmann Equation for a 1:1 electrolyte

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

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

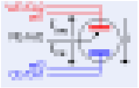
http://electrochem.cwru.edu/

… the less-frequently discussed *four-electrode* measurement! **(REVIEW)** 216



Waveform generator
WE/CA2 (P1)
Galvanostat
CE/CA1 (S3/P2)
I
RE'/ref1
(S1)
High impedance DVM
RE/ref2
(S2)
I
ΔE_ref
Cation Exchange Membrane
Glass flange
8 cm
Saturated calomel reference electrode
Platinum gauze counter electrode (1.5 cm²)
Luggin capillary
L
Silicone-rubber gaskets
20 cm

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/

… and this leads us nicely to: ~110 years of Ion-Selective Electrodes (ISEs)… 217

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

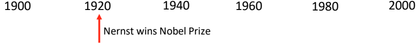
1920's – Duncan MacInnes & Malcolm Dole discover a glass suitable for glass pH electrodes…

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

the Beckman G

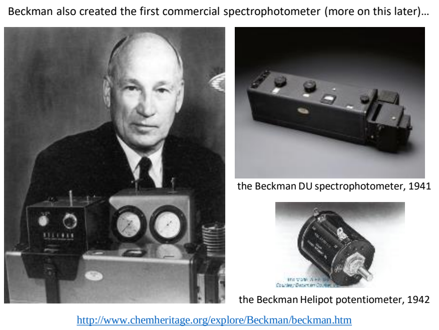
NTI's second home
Courtesy Beckman Coulter, Inc.

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

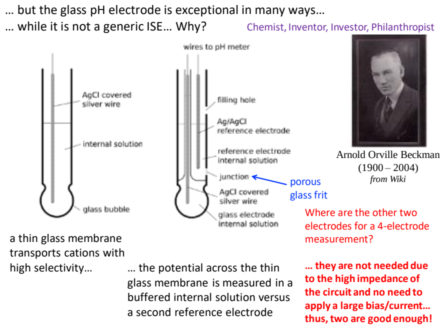


Beckman also created the first commercial spectrophotometer (more on this later)…

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

AgCl covered silver wire
internal solution
glass bubble
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

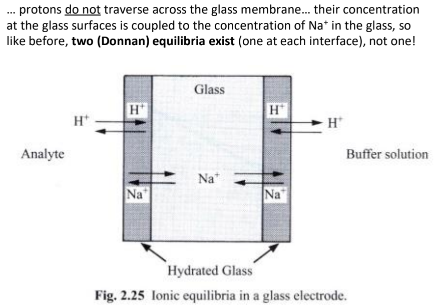
Arnold Orville Beckman
(1900 – 2004)
from Wiki

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 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!

Glass
H^+
H^+
H^+
H^+
Analyte
Buffer solution
Na^+
Na^+
Na^+
Hydrated Glass

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!

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

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

What type of LJ is this?

Type 2!

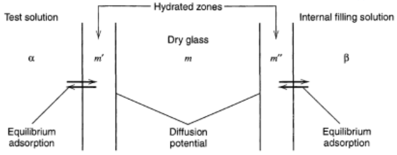


Figure 2.4.3 Model for treating the membrane potential across a glass barrier.

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

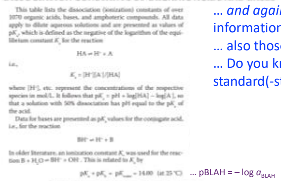
… just like when speciation within the diffuse layer is calculated using the Poisson–Boltzmann equation…

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

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

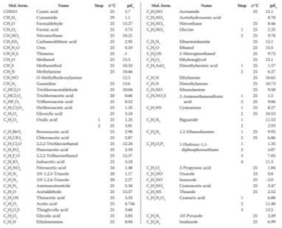
Can you identify what the reference potential is for this list of standard(-state) reduction potentials? *(it's like the infinite vacuum)*

DISSOCIATION CONSTANTS OF ORGANIC ACIDS AND BASES



… pBLAH = – log a_{BLAH}

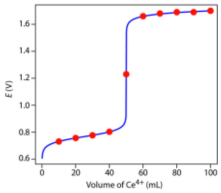
… *and again*, the CRC Handbook has a lot of chemical information… including tables of values…
… also those in the **Acidity/Basicity Series**…
… Do you know what the reference acidity is for this list of standard(-state) equilibrium acid dissociation constants?



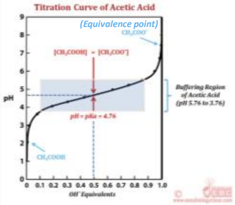
… why does this state that $pK_a + pK_b = pK_w$?
… because $K_aK_b = K_w$… **okaaaayyyy**… but why?
… because $\exp(-(\Delta G_a^{o} + \Delta G_b^{o})) = \exp(-\Delta G_w^{o})$…
… **Ahhhhh!**… enough with the algebra already!
… but wait!… for B, BH^+ this looks like Hess's law!
… so, let's add up these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

Titrations and Buffering

Recall: $\Delta G = \Delta G^{o} + RT\ln Q = \Delta G^{o} + RT\ln\left(\frac{a_{\text{product}}}{a_{\text{reactant}}}\right)$ 224



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…

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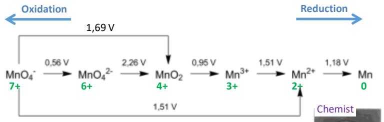
A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



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…

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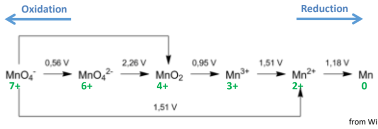
A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur



from Wiki

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

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

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

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

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

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

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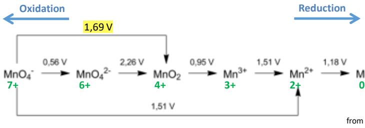

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$\Delta G^o = -nFE^o = -3FE^o$

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

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

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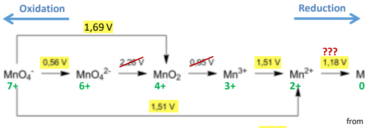

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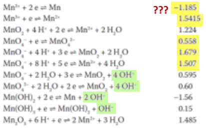
Recall from before…

???



$Mn^{2+} + 2e \rightleftharpoons Mn$	−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^-!

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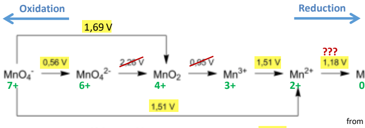

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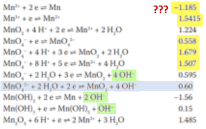

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What would this E^o value be when at acidic standard state?

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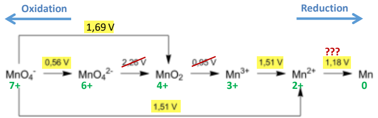
Oxidation
Reduction
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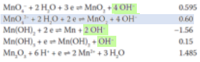
0,56 V
~~2,26 V~~
~~0,95 V~~
1,51 V
???
1,18 V
MnO_4^-
7+
MnO_4^{2-}
6+
MnO_2
4+
Mn^{3+}
3+
Mn^{2+}
2+
Mn
0
1,51 V

from Wiki

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

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

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



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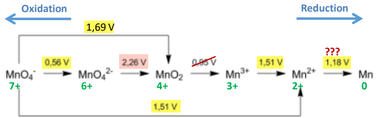
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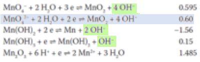
What would this E^0 value be when at acidic standard state?



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$$E^o_{\text{SHE}} = 2{,}25648\text{ V}$$

SWEET!

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

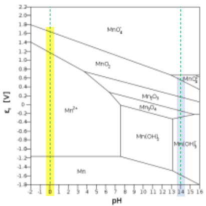
… a second diagram of (not truly) empirical standard potentials…

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



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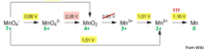
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7+
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6+
MnO_2
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Mn^{3+}
3+
Mn^{2+}
2+
Mn
0
1,51 V
from Wiki

… because in acid, the reaction does not occur!

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974

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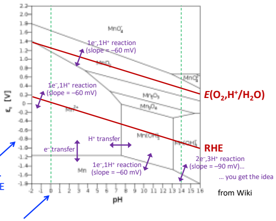

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Why don't I like this? …
Even though EVERYONE
plots it this way

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)

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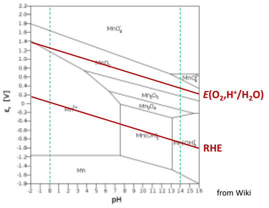

from Wiki

(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!