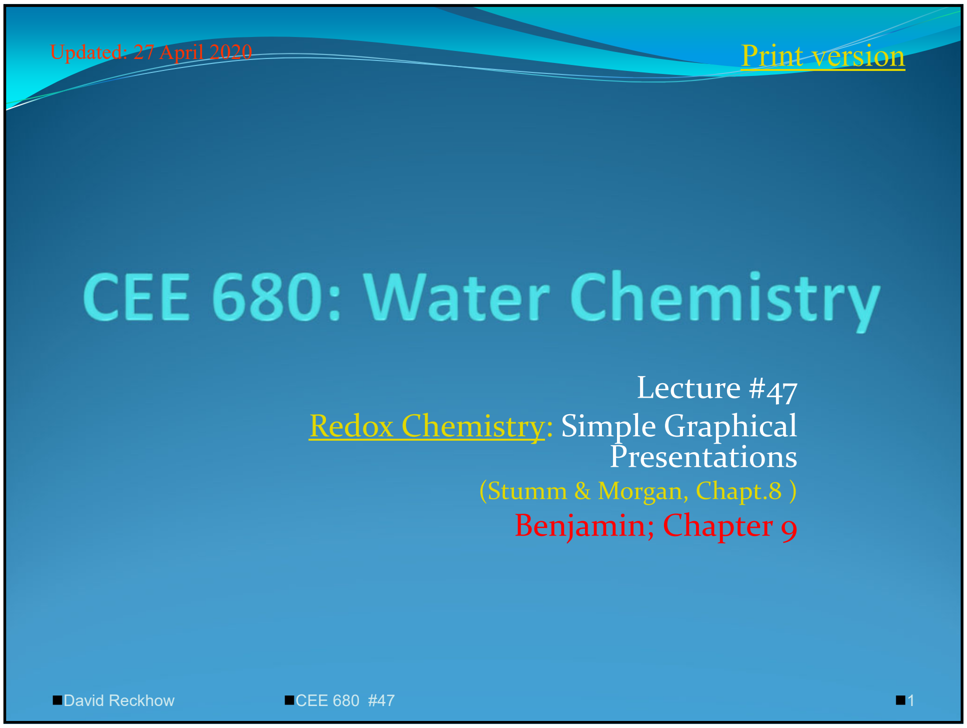


Updated: 27 April 2020

Print version

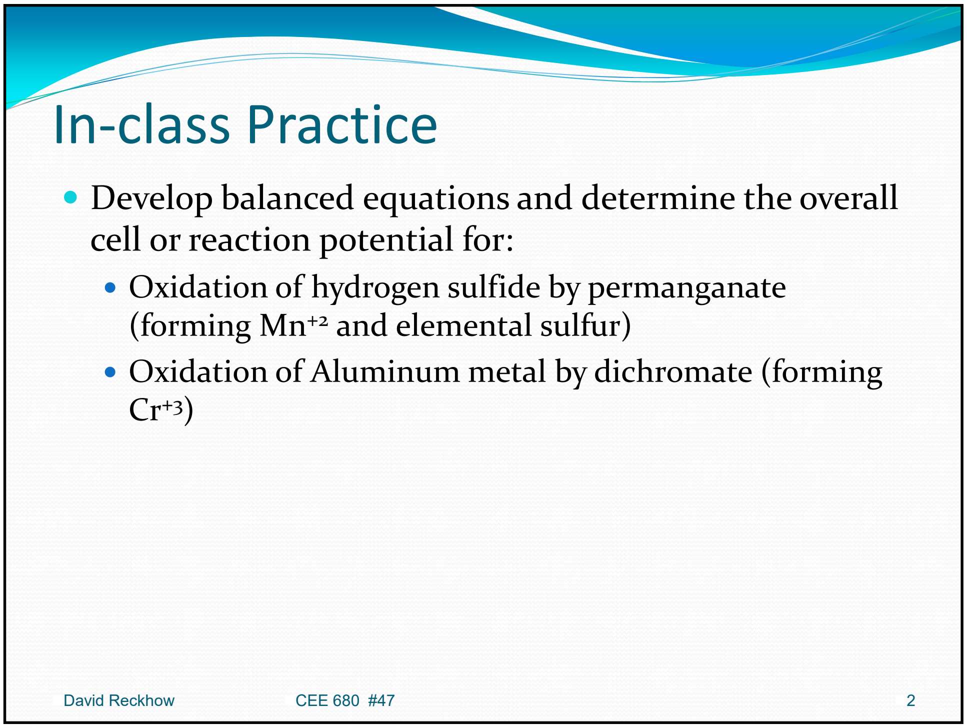
CEE 680: Water Chemistry

Lecture #47

Redox Chemistry: Simple Graphical Presentations

(Stumm & Morgan, Chapt.8)

Benjamin; Chapter 9



In-class Practice

- Develop balanced equations and determine the overall cell or reaction potential for:
  - Oxidation of hydrogen sulfide by permanganate (forming Mn^{+2} and elemental sulfur)
  - Oxidation of Aluminum metal by dichromate (forming Cr^{+3})

pε

- $p\varepsilon = -\log\{e^-\}$
- Low pε means:
  - High $\{e^-\}$
  - Reducing conditions
  - Tend to donate e^-
- $pH = -\log\{H^+\}$
- Low pH means:
  - High $\{H^+\}$
  - Acidic conditions
  - Tend to donate H^+

pε is really a hypothetical construct. There are no free electrons in solution. It is really a measure of the relative tendency to accept or transfer and electron

Equations with pε

$$K = \frac{[Red]}{[Ox]\{e^-\}^n}$$

- Half reactions as equilibria
  - $Ox + ne^- = Red$

$$\{e^-\}^n = \frac{1}{K}\frac{[Red]}{[Ox]}$$

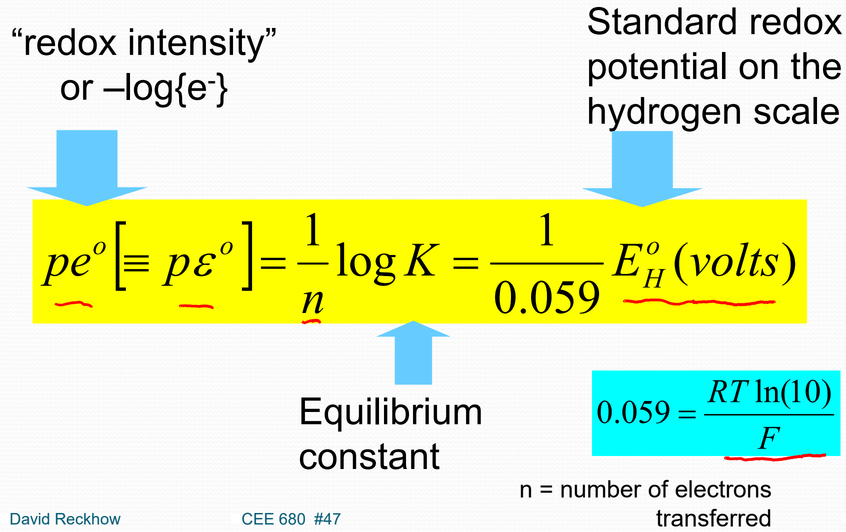
$$n\log\{e^-\} = -\log K + \log\left(\frac{[Red]}{[Ox]}\right)$$

$$p\varepsilon = \frac{1}{n}\log K - \frac{1}{n}\log\left(\frac{[Red]}{[Ox]}\right)$$

The Nernst Equation

$$\boxed{p\varepsilon = p\varepsilon^o - \frac{1}{n}\log\left(\frac{[Red]}{[Ox]}\right)}$$

Conversions



"redox intensity" or –log{e⁻}

Standard redox potential on the hydrogen scale

$$\underline{pe^o}\left[\equiv \underline{p\varepsilon^o}\right]=\frac{1}{\underline{n}}\log K=\frac{1}{0.059}\underline{E_H^o(volts)}$$

Equilibrium constant

$$0.059=\frac{RT\ln(10)}{\underline{F}}$$

n = number of electrons transferred

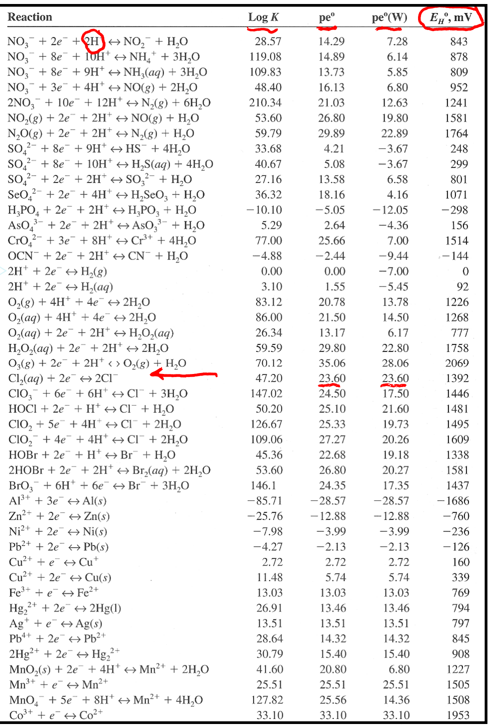
Constants

- Reference reaction

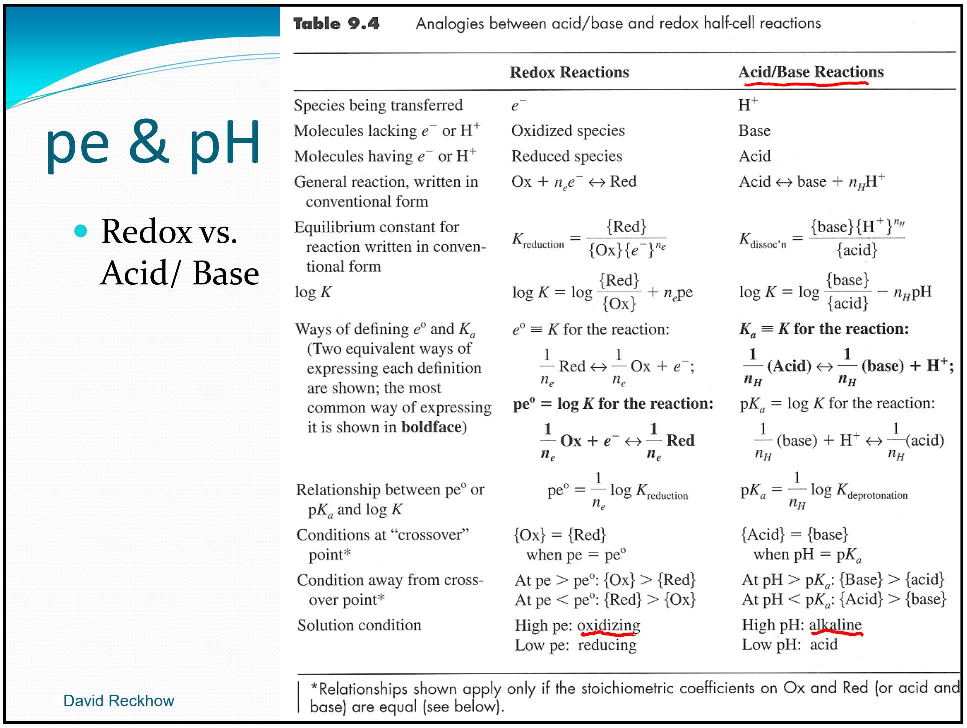
$$H^+ + e^- \leftrightarrow \tfrac{1}{2}H_2(g)$$

  - Where {e⁻}=1, if all chemical species activities are also unity

$$K=\frac{\{H_2(g)\}^{0.5}}{\{H^+\}\{e^-\}}=1.0$$



Reaction	Log K	pe°	pe°(W)	E_H°, mV
$NO_3^- + 2e^- + 2H^+ \leftrightarrow NO_2^- + H_2O$	28.57	14.29	7.28	843
$NO_3^- + 8e^- + 10H^+ \leftrightarrow NH_4^+ + 3H_2O$	119.08	14.89	6.14	878
$NO_3^- + 8e^- + 9H^+ \leftrightarrow NH_3(aq) + 3H_2O$	109.83	13.73	5.85	809
$NO_3^- + 3e^- + 4H^+ \leftrightarrow NO(g) + 2H_2O$	48.40	16.13	6.80	952
$2NO_3^- + 10e^- + 12H^+ \leftrightarrow N_2(g) + 6H_2O$	210.34	21.03	12.63	1241
$NO_2(g) + 2e^- + 2H^+ \leftrightarrow NO(g) + H_2O$	53.60	26.80	19.80	1581
$N_2O(g) + 2e^- + 2H^+ \leftrightarrow N_2(g) + H_2O$	59.79	29.89	22.89	1764
$SO_4^{2-} + 8e^- + 9H^+ \leftrightarrow HS^- + 4H_2O$	33.68	4.21	−3.67	248
$SO_4^{2-} + 8e^- + 10H^+ \leftrightarrow H_2S(aq) + 4H_2O$	40.67	5.08	−3.67	299
$SO_4^{2-} + 2e^- + 2H^+ \leftrightarrow SO_3^{2-} + H_2O$	27.16	13.58	6.58	801
$SeO_4^{2-} + 2e^- + 4H^+ \leftrightarrow H_2SeO_3 + H_2O$	36.32	18.16	4.16	1071
$H_3PO_4 + 2e^- + 2H^+ \leftrightarrow H_3PO_3 + H_2O$	−10.10	−5.05	−12.05	−298
$AsO_4^{3-} + 2e^- + 2H^+ \leftrightarrow AsO_3^{3-} + H_2O$	5.29	2.64	−4.36	156
$CrO_4^{2-} + 3e^- + 8H^+ \leftrightarrow Cr^{3+} + 4H_2O$	77.00	25.66	7.00	1514
$OCN^- + 2e^- + 2H^+ \leftrightarrow CN^- + H_2O$	−4.88	−2.44	−9.44	−144
$2H^+ + 2e^- \leftrightarrow H_2(g)$	0.00	0.00	−7.00	0
$2H^+ + 2e^- \leftrightarrow H_2(aq)$	3.10	1.55	−5.45	92
$O_2(g) + 4H^+ + 4e^- \leftrightarrow 2H_2O$	83.12	20.78	13.78	1226
$O_2(aq) + 4H^+ + 4e^- \leftrightarrow 2H_2O$	86.00	21.50	14.50	1268
$O_2(aq) + 2e^- + 2H^+ \leftrightarrow H_2O_2(aq)$	26.34	13.17	6.17	777
$H_2O_2(aq) + 2e^- + 2H^+ \leftrightarrow 2H_2O$	59.59	29.80	22.80	1758
$O_3(g) + 2e^- + 2H^+ \leftrightarrow O_2(g) + H_2O$	70.12	35.06	28.06	2069
$Cl_2(aq) + 2e^- \leftrightarrow 2Cl^-$ $\longleftarrow$	47.20	$\underline{23.60}$	$\underline{23.60}$	1392
$ClO_3^- + 6e^- + 6H^+ \leftrightarrow Cl^- + 3H_2O$	147.02	24.50	17.50	1446
$HOCl + 2e^- + H^+ \leftrightarrow Cl^- + H_2O$	50.20	25.10	21.60	1481
$ClO_2 + 5e^- + 4H^+ \leftrightarrow Cl^- + 2H_2O$	126.67	25.33	19.73	1495
$ClO_2^- + 4e^- + 4H^+ \leftrightarrow Cl^- + 2H_2O$	109.06	27.27	20.26	1609
$HOBr + 2e^- + H^+ \leftrightarrow Br^- + H_2O$	45.36	22.68	19.18	1338
$2HOBr + 2e^- + 2H^+ \leftrightarrow Br_2(aq) + 2H_2O$	53.60	26.80	20.27	1581
$BrO_3^- + 6H^+ + 6e^- \leftrightarrow Br^- + 3H_2O$	146.1	24.35	17.35	1437
$Al^{3+} + 3e^- \leftrightarrow Al(s)$	−85.71	−28.57	−28.57	−1686
$Zn^{2+} + 2e^- \leftrightarrow Zn(s)$	−25.76	−12.88	−12.88	−760
$Ni^{2+} + 2e^- \leftrightarrow Ni(s)$	−7.98	−3.99	−3.99	−236
$Pb^{2+} + 2e^- \leftrightarrow Pb(s)$	−4.27	−2.13	−2.13	−126
$Cu^{2+} + e^- \leftrightarrow Cu^+$	2.72	2.72	2.72	160
$Cu^{2+} + 2e^- \leftrightarrow Cu(s)$	11.48	5.74	5.74	339
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	13.03	13.03	13.03	769
$Hg_2^{2+} + 2e^- \leftrightarrow 2Hg(l)$	26.91	13.46	13.46	794
$Ag^+ + e^- \leftrightarrow Ag(s)$	13.51	13.51	13.51	797
$Pb^{4+} + 2e^- \leftrightarrow Pb^{2+}$	28.64	14.32	14.32	845
$2Hg^{2+} + 2e^- \leftrightarrow Hg_2^{2+}$	30.79	15.40	15.40	908
$MnO_2(s) + 2e^- + 4H^+ \leftrightarrow Mn^{2+} + 2H_2O$	41.60	20.80	6.80	1227
$Mn^{3+} + e^- \leftrightarrow Mn^{2+}$	25.51	25.51	25.51	1505
$MnO_4^- + 5e^- + 8H^+ \leftrightarrow Mn^{2+} + 4H_2O$	127.82	25.56	14.36	1508
$Co^{3+} + e^- \leftrightarrow Co^{2+}$	33.10	33.10	33.10	1953



pe & pH

- Redox vs. Acid/ Base

Table 9.4 Analogies between acid/base and redox half-cell reactions

	Redox Reactions	Acid/Base Reactions
Species being transferred	e^-	H^+
Molecules lacking e^- or H^+	Oxidized species	Base
Molecules having e^- or H^+	Reduced species	Acid
General reaction, written in conventional form	$Ox + n_e e^- \leftrightarrow Red$	$Acid \leftrightarrow base + n_H H^+$
Equilibrium constant for reaction written in conventional form	$K_{reduction} = \frac{\{Red\}}{\{Ox\}\{e^-\}^{n_e}}$	$K_{dissoc'n} = \frac{\{base\}\{H^+\}^{n_H}}{\{acid\}}$
log K	$\log K = \log \frac{\{Red\}}{\{Ox\}} + n_e pe$	$\log K = \log \frac{\{base\}}{\{acid\}} - n_H pH$
Ways of defining e^o and K_a (Two equivalent ways of expressing each definition are shown; the most common way of expressing it is shown in **boldface**)	$e^o \equiv K$ for the reaction: $\frac{1}{n_e} Red \leftrightarrow \frac{1}{n_e} Ox + e^-$; **$pe^o = \log K$ for the reaction:** $\frac{1}{n_e} Ox + e^- \leftrightarrow \frac{1}{n_e} Red$	**$K_a \equiv K$ for the reaction:** $\frac{1}{n_H}(Acid) \leftrightarrow \frac{1}{n_H}(base) + H^+$; $pK_a = \log K$ for the reaction: $\frac{1}{n_H}(base) + H^+ \leftrightarrow \frac{1}{n_H}(acid)$
Relationship between pe^o or pK_a and log K	$pe^o = \frac{1}{n_e} \log K_{reduction}$	$pK_a = \frac{1}{n_H} \log K_{deprotonation}$
Conditions at "crossover" point*	$\{Ox\} = \{Red\}$ when $pe = pe^o$	$\{Acid\} = \{base\}$ when $pH = pK_a$
Condition away from crossover point*	At $pe > pe^o$: $\{Ox\} > \{Red\}$ At $pe < pe^o$: $\{Red\} > \{Ox\}$	At $pH > pK_a$: $\{Base\} > \{acid\}$ At $pH < pK_a$: $\{Acid\} > \{base\}$
Solution condition	High pe: oxidizing Low pe: reducing	High pH: alkaline Low pH: acid

*Relationships shown apply only if the stoichiometric coefficients on Ox and Red (or acid and base) are equal (see below).

David Reckhow

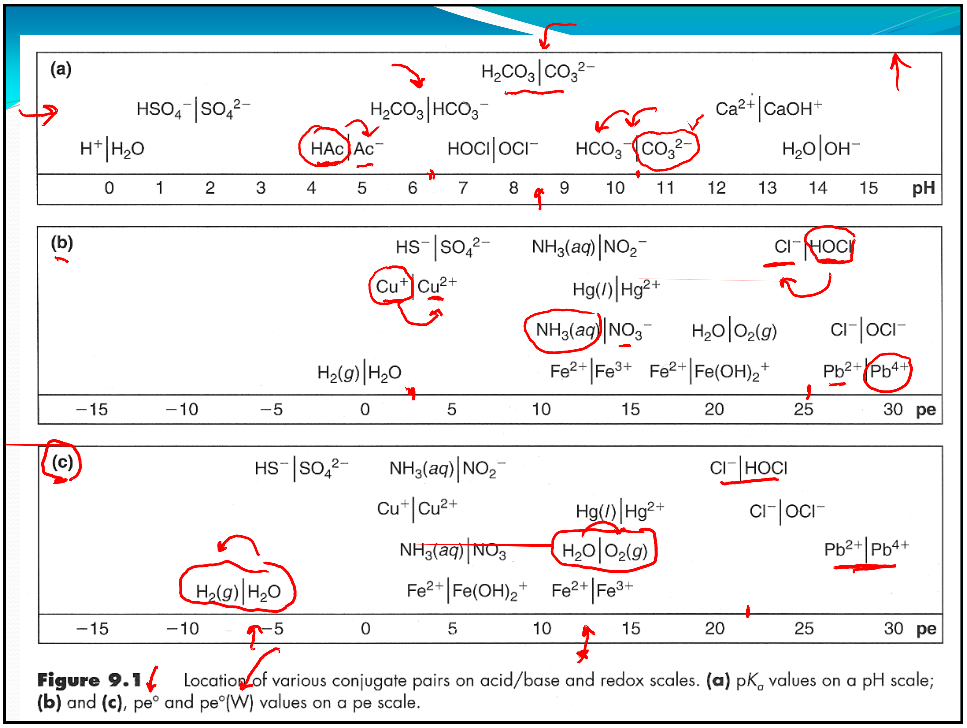


Figure 9.1 Location of various conjugate pairs on acid/base and redox scales. **(a)** pK_a values on a pH scale; **(b)** and **(c)**, pe° and pe°(W) values on a pe scale.

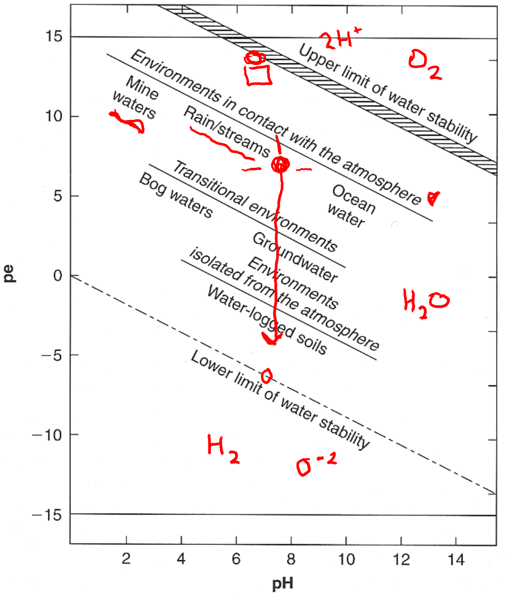


Figure 9.2 Typical pe and pH values in natural aquatic systems.

Adapted from R. Garrels and C. Christ. SOLUTIONS, MINERALS, AND EQUILIBRIA. Harper-Row (1965).

Iron Redox Calculations

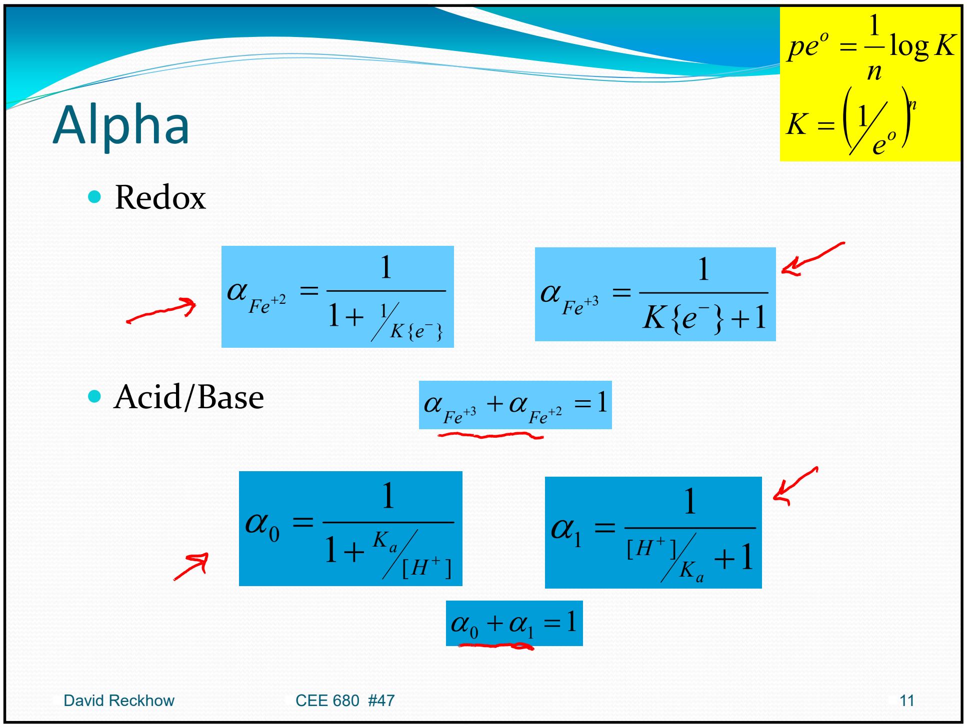
- Half cell reaction $Fe^{+3} + e^{-} = Fe^{+2}$ $\quad {}^{\Delta}\varepsilon^{o} = +0.769$

$$K = \frac{[Fe^{+2}]}{[Fe^{+3}]\{e^{-}\}} = 10^{\left({}^{\Delta}\varepsilon^{o}/_{0.059}\right)} = 10^{+13.03}$$

$$K\{e^{-}\} = \frac{[Fe^{+2}]}{[Fe^{+3}]} \checkmark$$

$$\alpha_{Fe^{+3}} \equiv \frac{[Fe^{+3}]}{[Fe^{+3}]+[Fe^{+2}]} = \frac{1}{1+([Fe^{+2}]/[Fe^{+3}])}$$

$$\boxed{= \frac{1}{1+K\{e^{-}\}}}$$



$$pe^o = \frac{1}{n}\log K$$

$$K = \left(\frac{1}{e^o}\right)^n$$

Alpha

- Redox

$$\alpha_{Fe^{+2}} = \frac{1}{1+\frac{1}{K\{e^-\}}}$$

$$\alpha_{Fe^{+3}} = \frac{1}{K\{e^-\}+1}$$

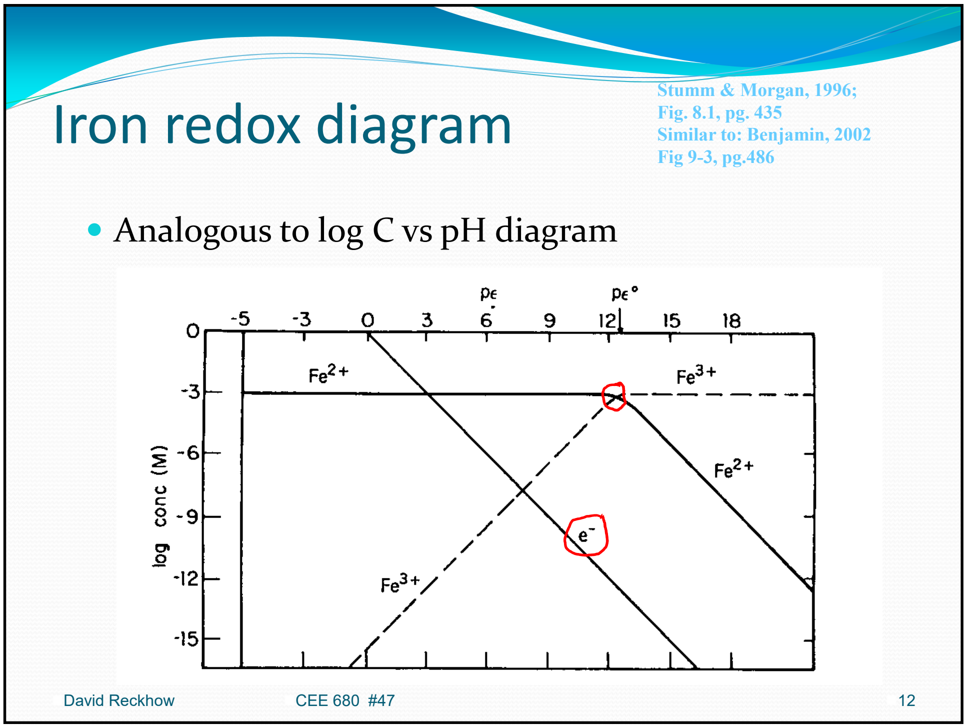
$$\underline{\alpha_{Fe^{+3}} + \alpha_{Fe^{+2}}} = 1$$

- Acid/Base

$$\alpha_0 = \frac{1}{1+\frac{K_a}{[H^+]}}$$

$$\alpha_1 = \frac{1}{\frac{[H^+]}{K_a}+1}$$

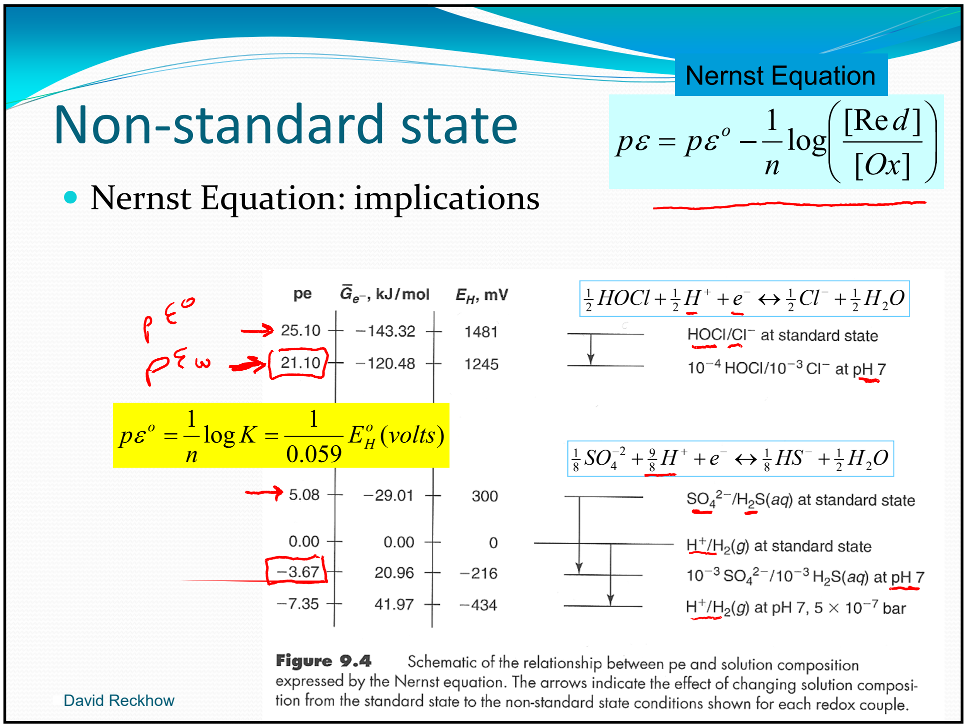
$$\underline{\alpha_0 + \alpha_1} = 1$$



Iron redox diagram

Stumm & Morgan, 1996; Fig. 8.1, pg. 435
Similar to: Benjamin, 2002 Fig 9-3, pg.486

- Analogous to log C vs pH diagram



Non-standard state

Nernst Equation

$$p\varepsilon = p\varepsilon^o - \frac{1}{n}\log\left(\frac{[\mathrm{Re}d]}{[Ox]}\right)$$

- Nernst Equation: implications

$$p\varepsilon^o = \frac{1}{n}\log K = \frac{1}{0.059}E_H^o(volts)$$

	pe	$\bar{G}_{e^-}$, kJ/mol	E_H, mV
$p\varepsilon^o$	25.10	−143.32	1481
$p\varepsilon_w$	$\boxed{21.10}$	−120.48	1245
	5.08	−29.01	300
	0.00	0.00	0
	$\boxed{-3.67}$	20.96	−216
	−7.35	41.97	−434

$\frac{1}{2}HOCl + \frac{1}{2}H^+ + e^- \leftrightarrow \frac{1}{2}Cl^- + \frac{1}{2}H_2O$

HOCl/Cl⁻ at standard state

10^{-4} HOCl/10^{-3} Cl⁻ at pH 7

$\frac{1}{8}SO_4^{-2} + \frac{9}{8}H^+ + e^- \leftrightarrow \frac{1}{8}HS^- + \frac{1}{2}H_2O$

$SO_4^{2-}/H_2S(aq)$ at standard state

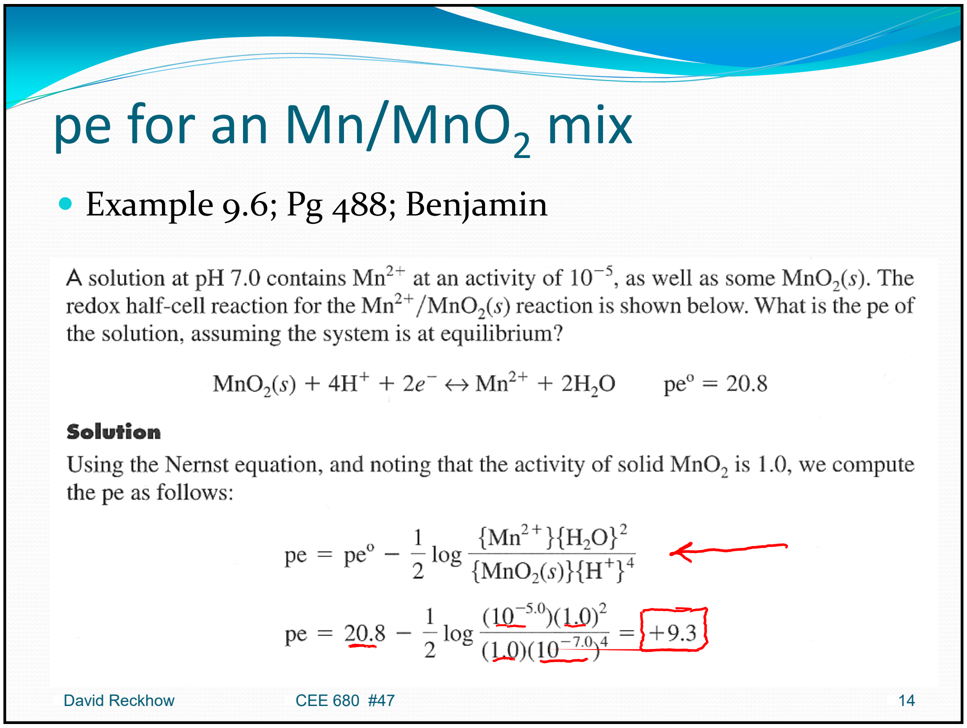
$H^+/H_2(g)$ at standard state

10^{-3} $SO_4^{2-}/10^{-3}$ $H_2S(aq)$ at pH 7

$H^+/H_2(g)$ at pH 7, 5×10^{-7} bar

Figure 9.4 Schematic of the relationship between pe and solution composition expressed by the Nernst equation. The arrows indicate the effect of changing solution composition from the standard state to the non-standard state conditions shown for each redox couple.

David Reckhow



pe for an Mn/MnO$_2$ mix

- Example 9.6; Pg 488; Benjamin

A solution at pH 7.0 contains Mn^{2+} at an activity of 10^{-5}, as well as some $MnO_2(s)$. The redox half-cell reaction for the $Mn^{2+}/MnO_2(s)$ reaction is shown below. What is the pe of the solution, assuming the system is at equilibrium?

$$MnO_2(s) + 4H^+ + 2e^- \leftrightarrow Mn^{2+} + 2H_2O \qquad pe^o = 20.8$$

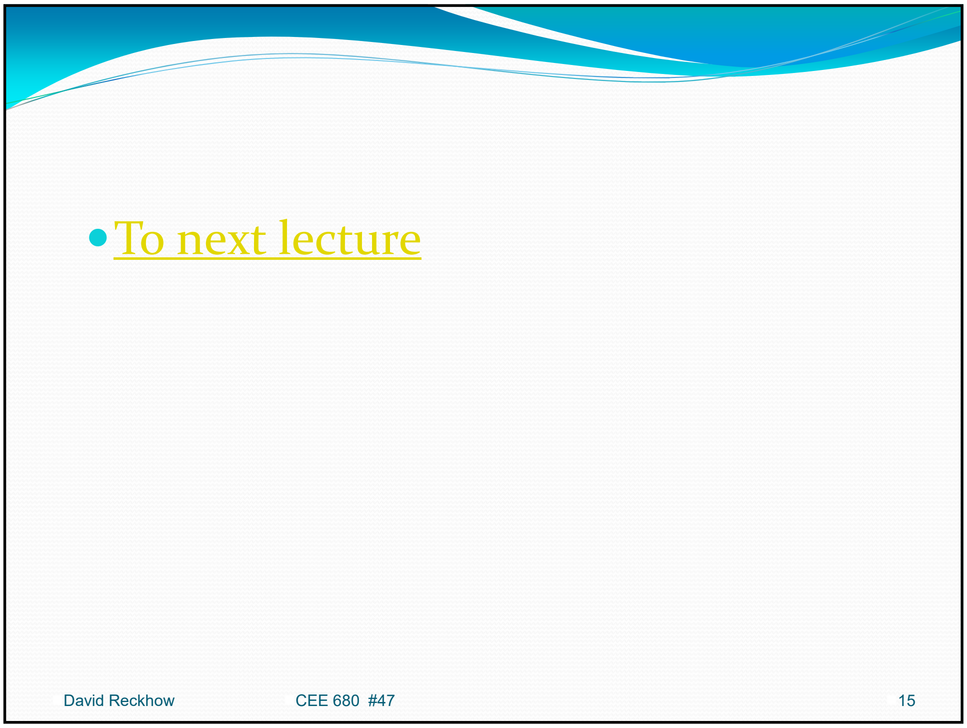
Solution

Using the Nernst equation, and noting that the activity of solid MnO_2 is 1.0, we compute the pe as follows:

$$pe = pe^o - \frac{1}{2}\log\frac{\{Mn^{2+}\}\{H_2O\}^2}{\{MnO_2(s)\}\{H^+\}^4} \longleftarrow$$

$$pe = 20.8 - \frac{1}{2}\log\frac{(10^{-5.0})(1.0)^2}{(1.0)(10^{-7.0})^4} = \boxed{+9.3}$$

David Reckhow CEE 680 #47 14



- To next lecture