GG325 -- GEOCHEMISTRY
Fall 2014
Homework set #2 (Due Friday, 4 Oct)

1. Plot the pE and pH changes associated with each of the five steps (e.g., O_2 reduction is the first step, nitrate reduction is the next step, etc..) in the model calculations in of Fig 11.12 of lecture 9-10 notes (page 21) on a pE=PH diagram. Be sure to label your axes and to also include the two lines for the upper and lower water stability limits.

2. Upon what *half reaction* is the rigorous definition of pE based?

3. The acid-base reaction for the dissociation of acetic acid is

$$CH_3COOH + H_2O : H_3O^+ + CH_3COO^-$$

a) Break the reaction above into two half-reactions involving hydrogen ions, H^+

b) Next, break the redox reaction for iron and hydrogen (below) into two redox half-reactions.

$$Fe^{2+} + H^+ \leftrightarrow Fe^{3+} + 2H_2$$

Compare the acid- base reaction to the redox reaction by drawing an analogy between the roles of H^+ and e^- in the two reactions.

4. What determines the oxidizing and reducing limits for the thermodynamic stability of water (and thus, the exogenic hydrosphere)? *Hint:* Write chemical equations for the two reactions that are involved in the decomposition of water outside of its stability limit (the oxidation of water and reduction of water).

5. a) Calculate $[Fe^{3+}]$, pE and pH at the point in the figure where Fe^{2+}, $Fe(OH)_2$ and $Fe(OH)_3$ are in equilibrium, for maximum Fe concentration in solution of 10^{-5} M

b) Calculate the pE at the point on the Fe^{2+} - $Fe(OH)_3$ boundary line where pH =5 in a solution with a soluble iron concentration of 10^{-4} M? note, the diagram is for 10^{-5} M so you can just read off of it.

K_{sp} for the reaction $Fe(OH)_3$ (s) + $3H^+ \leftrightarrow Fe^{3+} + 3H_2O$ is $9.1x10^3$ pE = 13.2 + log $[Fe^{3+}]/[Fe^{2+}]$ for the reaction $Fe^{2+} \equiv Fe^{3+} + 1e^-$

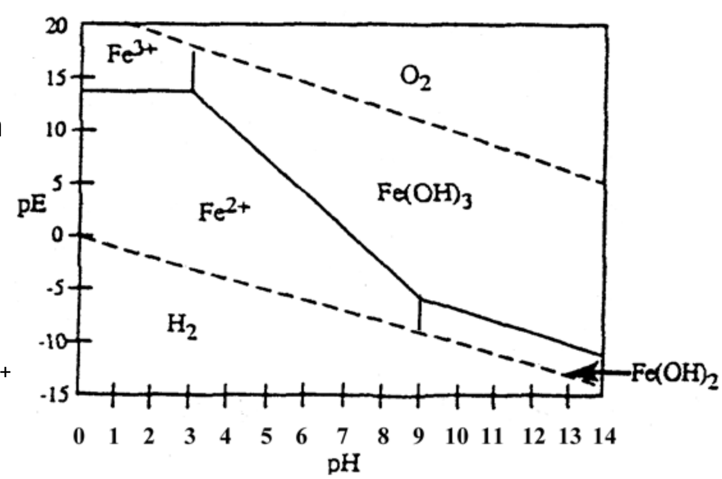

Figure 4.4 Simplified pE-pH diagram for iron in water. The maximum soluble iron concentration is 1.00 x 10^{-5} M.

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6. a) What is the chemical role of SO_4^{2-} in the following reaction?

$$SO_4^{2-} (aq) + [CH_2O]_n \leftrightarrow HS^- (aq) + CO_2 + H_2O$$

b) How are microorganisms involved in this reaction?

7. Thermodynamics of Redox reactions
a. Find ΔG for the reaction:
$Pb^{2+} + Mn \leftrightarrow Pb + Mn^{2+}$

b. Which side of the reaction is favored? (HINT: use the data in Table 3.3 from White, reproduced on the next page of this assignment)

8. More thermodynamics of Redox reactions
a. Find $\Delta G°$ for the reaction:
$Cu^{2+} + e^- \rightarrow Cu^+$

b. What is the pe° for this reaction?

9. Why is sulfate reduction further down in diagrams of the "redox ladder" than nitrate reduction?

10. (White Chapter 14 digital problem 2)
Write the chemical formula and sketch the structure of 2-hydroxy-propanoic acid (lactic acid).

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Table 3.3. $E_H°$ and pε° for some Half-cell Reactions

Half Cell Reaction	$E_H°$ (V)	pε°
$Li^+ + e^- \rightleftarrows Li$	-3.05	–51.58
$Ca^{2+} + 2e- \rightleftarrows Ca$	-2.93	–49.55
$Th^{4+} + 4e- \rightleftarrows Th$	-1.83	–30.95
$U^{+4} + 4e^- \rightleftarrows U$	-1.38	–23.34
$Mn^{2+} + 2e^- \rightleftarrows Mn$	-1.18	–19.95
$Zn^{2+} + 2e^- \rightleftarrows Zn$	-0.76	–12.85
$Cr^{3+} + 3e- \rightleftarrows Cr$	-0.74	–12.51
$Fe^{2+} + 2e^- \rightleftarrows Fe$	-0.44	–7.44
$Eu^{3+} + e^- \rightleftarrows Eu^{2+}$	-0.36	-6.08
$Pb^{2+} + 2e^- \rightleftarrows Pb$	-0.13	–2.2
$CO_{2(g)} + 4H^+ + 4e^- \rightleftarrows CH_2O^* + 2H_2O$	-0.71	–1.2
$2H^+ + 2e^- \rightleftarrows H_{2(g)}$	0	0
$N_{2(g)} + 6H^+ + 6e^- \rightleftarrows 2NH_3$	0.093	1.58
$Cu^{2+} + 2e^- \rightleftarrows Cu$	0.34	5.75
$UO_2^{2+} + 2e^- \rightleftarrows UO_2$	0.41	6.85
$S + 2e^- \rightleftarrows S^{2-}$	0.44	7.44
$Cu^+ + e^- \rightleftarrows Cu$	0.52	8.79
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	0.77	13.02
$NO_3^- + 2H^+ + e^- \rightleftarrows NO_2 + H_2O$	0.80	13.53
$Ag^+ + e^- \rightleftarrows Ag$	0.80	13.53
$Hg^{2+} + 2e^- \rightleftarrows Hg$	0.85	14.37
$MnO_{2(s)} + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$	1.23	20.8
$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$	1.23	20.8
$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O$	1.51	25.53
$Au^+ + e^- \rightleftarrows Au$	1.69	28.58
$Ce^{4+} + e^- \rightleftarrows Ce^{3+}$	1.72	29.05
$Pt^+ + e^- \rightleftarrows Pt$	2.64	44.64

*CH_2O refers to carbohyrate, the basic product of photosynthesis.

Table is from Chapter 3 of White