

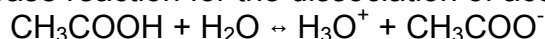
GG325 -- GEOCHEMISTRY
Fall 2009

Homework set #2 (Due next week 25 Sep)

1. Plot the pE and pH changes associated with each step in the model calculations in of Fig 11.12 of lecture 11 notes (page 13) 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.

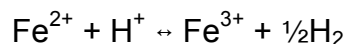
2. Upon what *half reaction* is the rigorous definition of pE based?

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



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.



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

b) Calculate the pE at the point on the Fe^{2+} - $\text{Fe}(\text{OH})_3$ boundary line where $\text{pH} = 5$ in a solution with a soluble iron concentration of 10^{-5} M?

c) Calculate the pE for a soluble iron concentration of 10^{-4} M?

K_{sp} for the reaction $\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ \leftrightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O}$ is 9.1×10^{-38} pE = $13.2 + \log [\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ for the reaction $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 1\text{e}^-$

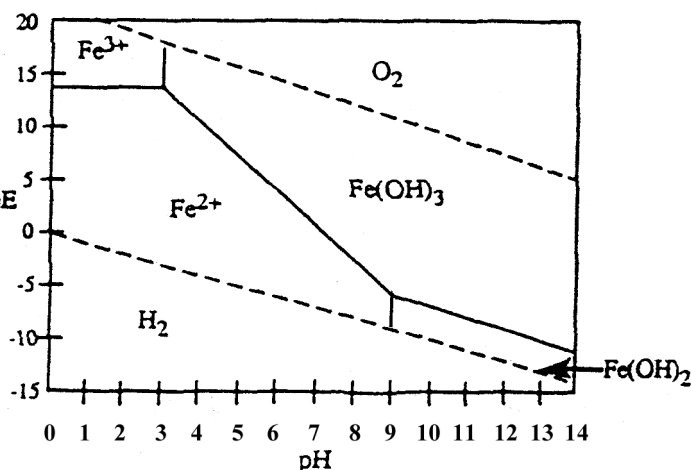


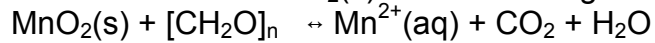
Figure 4.4 Simplified pE-pH diagram for iron in water. The maximum soluble iron concentration is 1.00×10^{-5} M.

GG325 -- GEOCHEMISTRY

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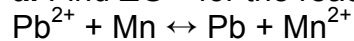
6. a) What is the role of $\text{MnO}_2(\text{s})$ in the following reaction?



b) How are microorganisms involved in this reaction?

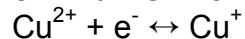
7. Thermodynamics of Redox reactions

a. Find ΔG – for the reaction:



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)

c. Find ΔG – for the reaction:



d. What is the pe° for this reaction?

8. Write the chemical formula and sketch the structure of 2-hydroxy-propanoic acid (lactic acid).

9. The first and second acidity constants of oxalic acid ($(\text{COOH})_2$) are $\text{pK}_{\text{a}1} = 1.23$ and $\text{pK}_{\text{a}2} = 4.19$. What is the pH of a solution formed by dissolving 0.1 mole of oxalic acid in 1 kg of water?

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Table 3.3. $E_{H^{\circ}}$ and pE° for some Half-cell Reactions

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

*CH₂O refers to carbohydrate, the basic product of photosynthesis.