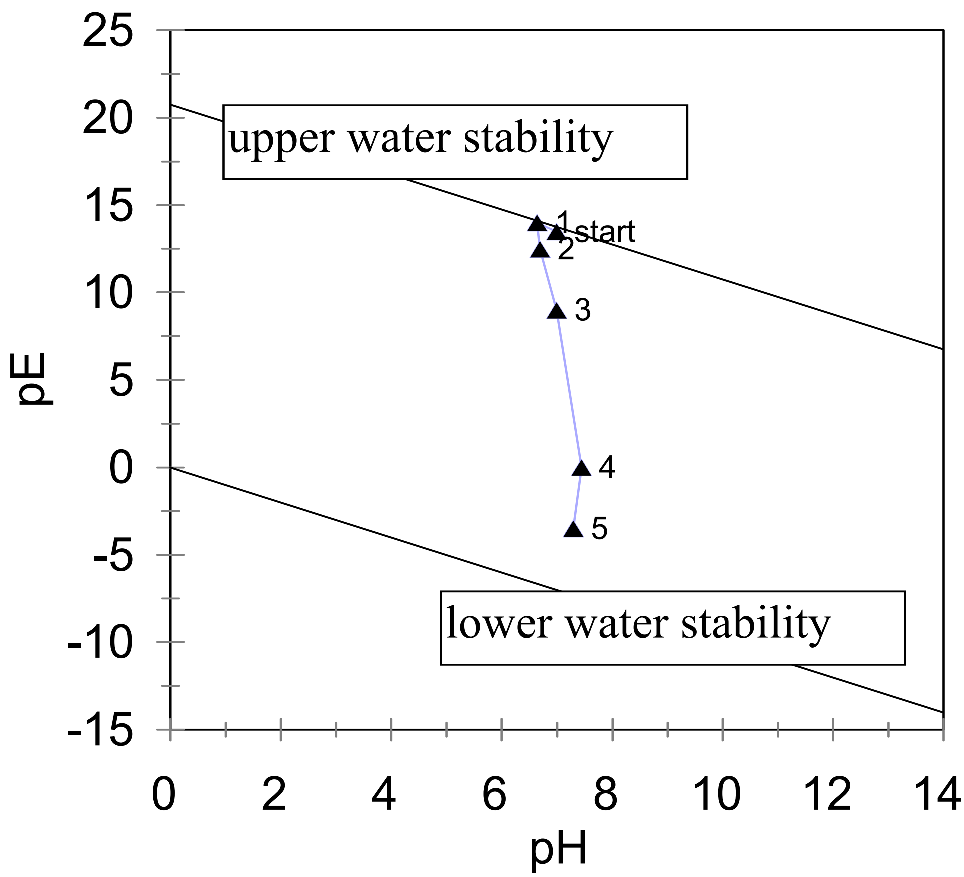
GG325 -- GEOCHEMISTRY
SPRING 2009
Homework set #2 answers, *11 pts each except 9, which is worth 12 pts*

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.

I've numbered the steps in the sequence on the diagram. Notice that this



biological redox sequence makes a mostly vertical line.

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

The standard hydrogen electrode potential: $2H^+ + 2e^- \rightarrow H_2$ *or* $H^+ + e^- \rightarrow \frac{1}{2}H_2$

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

$CH_3COOH + H_2O \leftrightarrow H_3O^+ + CH_3COO^-$

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

$CH_3COOH \rightarrow H^+ + CH_3COO^-$

$H^+ + H_2O \rightarrow H_3O^+$

b) Next, break the reaction 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^-. $Fe^{2+} + H^+ \leftrightarrow Fe^{3+} + \frac{1}{2}H_2$ (don't forget to balance the equation first)

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$H^+ + e^- \rightarrow \frac{1}{2}H_2$

hydrogen ions in part a are analogous to electrons in part b, in that they are both *transferred from one material to the other in an exchange reaction*

4. What determines the oxidizing and reducing limits for the thermodynamic stability of water (and thus, the exogenic hydrosphere?

reducing limit $2H_2O \leftrightarrow O_2 + 4H^+ + 4e^-$ (pE = 20.75)

oxidizing limit $4H_2O + 4e^- \leftrightarrow 2H_2 + 4OH^-$ (pE =0)

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

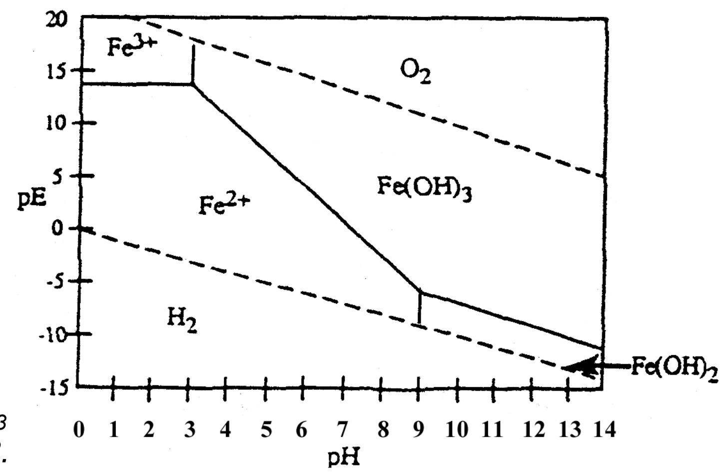


Figure 4.4 Simplified pE-pH diagram for iron in water. The maximum soluble iron concentration is 1.00 x 10^{-5} M.

Solve for [Fe^{3+}] using the equations given. To do this, one needs to estimate one parameter by reading it from the plot below (either pH or pE). Looking at the diagram, one can see that at this so-called triple point of Fe^{2+}- $Fe(OH)_2$ - $Fe(OH)_3$ equilibrium, pH = 9 and pE~4.7 or 4.8. The other thing one needs to consider is that this triple point is really far from the Fe^{3+} stability field, meaning $a_{Fe2+} \sim a_{FeTOTAL}$. If you don't want to make this estimate, you could solve for [Fe^{3+}] at these conditions using the K_{sp} given using estimates of pH and pE from the plot. It is really low (< 10^{-10}).

OK, let's find out [Fe^{3+}] and pE using the equations and pH = 9 (read off the plot).

I'm going to get pE first

$pE = 13.2 + \log K_{sp} [H^+]^3/[Fe^{2+}]$

..... ***pH=9*** *is $[H^+] = 10^{-9}$. I'm also assuming $[Fe^{2+}] = [Fe_{total}] = 10^{-5}$*

$pE = 13.2 + \log 9.1x10^3 (1x10^{-9})^3/(1x10^{-5})$ → → → ***pE = -4.8***

then I get [Fe^{3+}]

$pE = 13.2 + \log [Fe^{3+}]/[Fe^{2+}]$

$-4.8 = 13.2 + \log [Fe^{3+}]/10^{-5}$ → → → ***[Fe^{3+}] = 1x10^{-23}***

Note, you could have gotten Fe^{3+} first from writing and then solving the K_{sp} expression and then used this to solve for pE second.

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^{-5} M?

this point on the diagram is also far from the Fe^{3+} stability field, meaning $a_{Fe2+} \sim a_{FeTOTAL}$. you can get Fe^{3+} from either of the two equations. This time, I'll use the K_{sp} expression for fun. $K_{sp} = 9.1x10^3 = [Fe^{3+}]/[H^+]^3$ at pH =5, I can solve this to get $[Fe^{3+}] = 9.1x10^{-12}$ Then, substituting that into $pE = 13.2 + \log [Fe^{3+}]/[Fe^{2+}]$ and assuming $[Fe^{2+}] = 10^{-5}$, I get ***pE = 7.2***

c) Calculate the pE at this same point for total Fe in solution of 10^{-4} M. *Use the same equation but use 10^{-4} rather than 10^{-5} for [Fe^{2+}]. Then, you get* ***pE = 6.2***

A factor of 10 change in total Fe resulted in a factor of 10 change in E_H (or 1 pE unit).

6. a) What is the role of $MnO_2(s)$ in the following reaction?

$MnO_2(s) + [CH_2O]_n \leftrightarrow Mn^{2+}(aq) + CO_2 + H_2O$

MnO_2 is an oxidizing agent (aka electron receptor).

b) How do organisms play a role in this reaction?

MnO_2 is used by organisms in a manner that is analogous to how respiring organisms like ourselves use O_2 to oxidize organic matter and release chemical energy from the bonds in "fixed organic carbon".

7.a. Find ΔG – for the reaction:

$Pb^{2+} + Mn \leftrightarrow Pb + Mn^{2+}$

This is a redox reaction with two half rxns:

$Pb^{2+} + 2e \leftrightarrow Pb$ *and* $Mn \leftrightarrow Mn^{2+} + 2e$

Using table 3.3, we get electrode potential values (ϵ^o) of -0.13 and 1.18 (the sign on the latter is reversed because it is an oxidation). Adding the two we get ϵ^o_{rxn} = 1.05 volts. $\Delta G = -n\mathcal{F}\Delta\epsilon$, n=2, $\mathcal{F}$ = 96485 coulomb/mole

ΔG^o = 2 96485 coulomb/mole*1.05 volts = 202618 coulomb-volts/mol = 202618 joule/mol =* ***-202.6 kJ/mol***

b. Which side of the reaction is favored? (HINT: use the data in White Table 3.3)

ΔG^o is negative, products are favored. (Remember = -RT lnK, so negative ΔG^o means lnK is positive and K >1)

c. Find ΔG – for the reaction:

$Cu^{2+} + e^- \leftrightarrow Cu^+$

Using table 3.3, we find

$Cu^{2+} + 2e^- \leftrightarrow Cu$ ϵ^o = 0.34 and $Cu^+ + e^- \leftrightarrow Cu$ ϵ^o = 0.52 (or $Cu \leftrightarrow Cu^+ + e^-$ ϵ^o = -0.52)
Adding the two half reactions yields the new reaction and the number of electrons transferred is correct (1). Using eqn 3.110, Page 104, white Chap 3 $\epsilon^o_{net} = 1/n_{net} \sum n_i \epsilon^o_i$ we get ϵ^o = 1x(2x0.34 - 1x0.52) = 0.16volt

Then using $\Delta G = -n\mathcal{F}\Delta\epsilon$ we get ***ΔG = -15.4 kJ/mol***

d. What is the pe° for this reaction?

pe = ϵ/0.059 = 0.16/0.059 = ***2.7***

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

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     OH   O
     |    ||
H3C-CH-C-OH                          C3O3H6
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9. The the first and second acidity constants of oxalic acid ($(COOH)_2$) are pK_{a1} = 1.23 and pK_{a2} = 4.19. What is the pH of a solution formed by dissolving 1 mole of oxalic acid in 1 kg of water?

I know this problem was difficult for some of you, so I've written a long, detailed answer. This is basically an algebra problem, and in these types of problems the starting point is always to determine the number if unknowns and equations needed.

Oxalic acid is a diprotic acid (i.e., $H_2Ox \leftrightarrow HOX^- + H^+ \leftrightarrow OX^{2-} + H^+$

(See the lecture 7-8 notes). Solving this problem is easier if you have a "feeling" for the relative proportions on acid, conjugate base$_1$ and conjugate base$_2$ as a function of pH and the pK_a values. Such insights can be gained from the dissociation expressions or a graphical representation (i.e., Bjerrum plot), such as the for the carbonic system on Lect 7-8, page 4. The locations of the vertical lines are somewhat different for carbonic and oxalic acids (because the pK_a values are different), but the curve shapes are the same).

the K_a expressions for the 1st and 2nd acid dissociations can be rewritten as

$K_{a1} = [H^+][HOx^-]/[H_2Ox]$	*or*	$pK_{a1} = pH - \log [HOx^-]/[H_2Ox]$
$K_{a2} = [H^+][Ox^{2-}]/[HOx^-]$	*or*	$pK_{a2} = pH - \log[Ox^{2-}]/[HOx^-]$

There are lots of ways to solve this problem. First we need to recognize that it is an algebra problem, and that we need to have as many equations as we have unknowns. I am going to solve this problem by writing 4 equations, then use an estimate method to hone in on the answer. In such cases, you can check your estimate at the end by plugging it back into the original expressions. If it gives a different value than the one you estimated, you redo the calculations with the new value and converge on the result (this is called iterations).

I gave you the pKa values, so this gives us 2 equations and 4 unknowns:
$[H^+]$, $[H_2Ox]$, $[HOx^-]$, and $[Ox^{2-}]$

1mole in 1 kg (~1 liter) = 1M oxalic acid in all of it's forms, so this gives us a third equation $[H_2Ox] + [HOX^-] + [OX^{2-}] = 1$

We need at least one other equation to solve this problem
The equation we use relates to the stoichiometry of the reactions:

for the 1st dissociation, $[H^+]_1 = [HOx^-]$
(because one mole H_2Ox dissociates to form 1 mol each of H^+ and Hox^-)
for the second dissociation $[H^+]_2 = [OX^{2-}]$ (for the same reasons).

Thus our 4th equation is $[H^+] =[H^+]_1 + [H^+]_2 =[HOx^-] + [OX^{2-}]$
now it turns out that $K_{a2} << K_{a1}$ (it is 1000x smaller, so that the $[OX^{2-}]$ contribution to $[H^+]$ is really small (~0.001 of the HOx^- contribution), so let's simply our last equation by ignoring this (convince yourself of this using the carbonic acid plots on lect 7-8 page 4. In fact, you can convince yourself that the ratio of 1st conjugate base to second conjugate base can be determined roughly from (K_{a1}/K_{a2}), in the oxalic acid case it is 3 orders of magnitude and for carbonic acid it is 4 orders of magnitude. Then...

$$[H^+] =[H^+]_1 = [HOx^-]$$

OK, let's solve
let x= $[H^+] = [HOx^-]$.
now, $[H_2Ox] + [HOX^-] + [OX^{2-}] = 1$ so that $[H_2Ox] + x + \sim 0 = 1$ (again, assuming $[OX^{2-}]$ is very small, so that $[H_2Ox] = 1 - x$
substituting into the K_{a1} expression we get

$$K_{a1} = x^2/1-x \quad .. \text{ Or } K_{a1} - K_{a1}x= x^2 \text{ .. Or } x^2 + K_{a1}x- K_{a1} = 0$$

using the quadratic formula, which in this case will be ... $x= [-K_{a1} \pm (K_{a1}^2 - 4(-K_{a1}))^{½}]/2$
so that= -0.274 or 0.215 (using $K_{a1} = 10^{-pKa1} = 10^{-1.23} = 0.0589$). We can reject the

negative root so that x= 0.215 M and thus
pH = -log (0.215) = 0.668

Let's check the assumption that $[OX^{2-}]$ is small by using the K_{a2} expression assuming
Let the amount of 2^{nd} dissociation $[H^+]_2 = y$
$K_{a2} = [H^+][Ox^{2-}]/[HOx^-] = y^2/(0.215-y)$
$K_{a2} = 10^{-4.19} = 6.46x10^{-5} = y^2/(0.215-y)$
$y^2 + 6.46x10^{-5}\ y - 1.39\ x\ 10^{-5}$
that $y = 3.7x10^{-3}$ (which is indeed very low)

We can do one iteration, to refine our estimate, recognizing that $[H^+] =[H^+]_1 + [H^+]_2$ and that $[H^+]_2 = [Ox^{2-}]$, so that $[H^+] = 0.215 + 3.7x10^{-3}$

using the same x and y definitions.
$[H^+] =x+ y$ $[HOx^-] =x-y$ $[OX^{2-}] = y$ $[H_2Ox] = 1 -x-y$

then $K_{a1} = (x+y)(x-y)/(1-x-y)$
$10^{-1.23} = 0.0589 = [(x+ 3.7x10^{-3})(x- 3.7x10^{-3})]/(1-x- 3.7x10^{-3})$
$0.0589 = [x^2- 1.37x10^{-5}]/(1-x- 3.7x10^{-3})$
$0.0589 - 0.0589x - 2.18x10^{-4} = x^2 - 1.37x10^{-5}$
$0 = x^2 + 0.0589\ x - 0.0587$

$[H^+] = x = 0.2146$, showing that our estimate was indeed good
pH = -log (0.2146) = 0.668

Remember, the approximations I used ONLY work when $K_{a1} >> K_{a2}$, and it turns out, when there is a lot of acid in solution (i.e., >0.01M or so), otherwise the concentrations of H^+ and OH^- from the dissociation of water start to also matter

Also, other equations I could have written to help solve this problem are charge and proton balance equations. Both equations are the same in this case:

$[H^+] = [HO_x] + 2[Ox^{2-}]$