Problem Set #4
1.76 - Aquatic

Problem 1

a) $KAlSi_3O_8(s) \longrightarrow Al(OH)_3(s)$

$+ 3H_2SiO_3$ — balance Si with H_2SiO_3

$+ 4H_2O$ — balance O with H_2O

$+ H^+$ — balance H with H^+

$+ K^+$ — balance K with K^+

$$KAlSi_3O_8(s) + 4H_2O + H^+ \rightleftharpoons Al(OH)_3(s) + 3H_2SiO_3 + K^+$$

b) Book rxn:

$$\frac{7}{20}\text{Albite} + \frac{3}{5}H^+ + H_2O \rightleftharpoons \frac{1}{20}\text{Na-mnte} + H_2SiO_3 + \frac{3}{5}Na^+$$

Rewritten so Na^+, H^+ have coefficients of 1:

Multiply above rxn by $5/3$

$$\frac{35}{60}\text{Albite} + H^+ + \frac{5}{3}H_2O \rightleftharpoons \frac{5}{60}\text{Na-mnte} + \frac{5}{3}H_2SiO_3 + Na^+$$

Which reduces to

$$\frac{7}{12}\text{Albite} + H^+ + \frac{5}{3}H_2O \rightleftharpoons \frac{1}{12}\text{Na-mnte} + \frac{5}{3}H_2SiO_3 + Na^+$$

c) Using information in Table 5.4

	log K
$\frac{7}{6}\left(\frac{1}{2}\text{Albite} + H^+ + \frac{5}{2}H_2O = \frac{1}{2}\text{kaolinite} + 2H_2SiO_3 + Na^+\right)$	$\frac{7}{6}(-0.168)$
$-\frac{1}{6}\left(\frac{1}{2}\text{Na-mtte} + H^+ + \frac{15}{2}H_2O = \frac{7}{2}\text{kaol.} + 4H_2SiO_3 + Na^+\right)$	$-\frac{1}{6}(-9.1)$

multiply through + reduce:

$\frac{7}{12}$ Albite + ~~$\frac{6}{6}=1$ $\frac{7}{12}$ H^+~~ + ~~$\frac{20}{12}=\frac{5}{3}$ $\frac{5}{12}$ H_2O~~ = ~~$\frac{7}{12}$ kaol.~~ + ~~$\frac{11}{6}=\frac{5}{3}$ $\frac{10}{6}$ H_2SiO_3~~ + ~~$\frac{6}{6}=1$ $\frac{7}{6}$ Na^+~~ $\quad -0.793$

~~$\frac{7}{12}$ kaol.~~ + ~~$\frac{1}{6}$ H_2SiO_3~~ + ~~$\frac{1}{6}$ Na^+~~ = $\frac{1}{12}$ Na-mtte + ~~$\frac{1}{6}$ H^+~~ + ~~$\frac{15}{12}$ H_2O~~ $\quad 1.515$

$\frac{7}{12}$Albite + H^+ + $\frac{5}{3}H_2O$ = $\frac{1}{12}$Na-mtte + $\frac{5}{3}H_2SiO_3$ + Na^+ $\quad 0.723$

as desired.

$$K_{eq} = 10^{0.723} = \frac{[H_2SiO_3]^{5/3}[Na^+]}{[H^+]}$$

d) Assume $[Na^+]_T = [Na^+] = 10^{-2}$ M

Given $[H_2SiO_3]_T = [H_2SiO_3] + [HSiO_3^-] + [SiO_3^{2-}]$

$$K_{a_1} = \frac{[HSiO_3^-][H^+]}{[H_2SiO_3]} = 10^{-9.86}$$

$$K_{a_2} = \frac{[SiO_3^{2-}][H^+]}{[HSiO_3^-]} = 10^{-13.1}$$

$$[HSiO_3^-] = (10^{-9.86})[H_2SiO_3]/[H^+]$$

$$[SiO_3^{2-}] = (10^{-13.1})[HSiO_3^-]/[H^+] = (10^{-13.1})(10^{-9.86})[H_2SiO_3]/[H^+]^2$$

$$[H_2SiO_3]_T = [H_2SiO_3] + [HSiO_3^-] + [SiO_3^{2-}]$$

$$= [H_2SiO_3]\left(1 + 10^{-9.86}/[H^+] + (10^{-9.86})(10^{-13.1})/[H^+]^2\right)$$

$$[H_2SiO_3] = [H_2SiO_3]_T \Big/ \left(1 + 10^{-9.86+pH} + 10^{-22.96+2pH}\right) \quad \text{(Eqn 1)}$$

Using $K_{eq} = \dfrac{[H_2SiO_3]^{5/3}[Na^+]}{[H^+]}$ and Eqn 1,

⇒ we can solve for H^+ by trial + error, but the system won't converge!!

(Here, you can see why a coefficient 1 on H_2SiO_3 makes the problem simpler to solve by hand...)

Assume ① $[H_2SiO_3]_T = [H_2SiO_3]$, ② $[Na^+]_T = [Na^+]$:

$$[H^+] = \frac{[H_2SiO_3]_T^{5/3}[Na^+]_T}{K_{eq}} = \frac{(10^{-4.0})^{5/3}(10^{-2})}{10^{0.723}}$$

$$[H^+] = 4.08 \times 10^{-10}\ M$$

$$pH = 9.39$$

so assumption 1 isn't valid

(pretend it is... there was an error when the problem was written - the given $[H_2SiO_3]_T$ & $[Na^+]_T$ concentrations are not possible if you are in equilibrium with Albite + Na-mite)

~sorry~

e)

Rxn from b + info in Tab. 5.4 — log K

$\frac{7}{12}$ Albite + H^+ + $\frac{5}{3}H_2O \rightleftharpoons \frac{1}{12}$ Na-mtte + $\frac{5}{3}H_2SiO_3$ + Na^+ — 0.723

$-\frac{5}{3}\left(SiO_2(qtz) + H_2O \rightleftharpoons H_2SiO_3\right)$ — $-\frac{5}{3}(-4.00)$

$\frac{7}{12}$ Albite + $H^+ \rightleftharpoons \frac{1}{12}$ Na-mtte + $\frac{5}{3}SiO_2$ (q+z) + Na^+ — 7.39

$$K_{eq} = \frac{[Na^+]}{[H^+]} = 10^{7.39}$$

$$[H^+] = [Na^+]/K_{eq} = 10^{-2}/10^{7.39} = 10^{-9.39}$$

pH = 9.39 The same pH as before!!

→ fluid was in equilibrium with quartz also.

PROBLEM 2

$pCO_2 = 10^{-1.5}$ atm

Calcite: $CaCO_3$ $\quad 10^{-8.35} = K_{sp}$

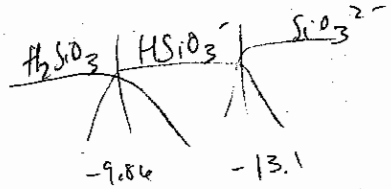
albite: $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$

Kaolinite: $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

$$\tfrac{1}{2}\underset{(Alb)}{Na_2O \cdot Al_2O_3 \cdot 6SiO_2}(s) + H^+ + \tfrac{5}{2}H_2O \rightleftharpoons \tfrac{1}{2}\underset{(Kaol.)}{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O}(s) + 2H_2SiO_3 + Na^+$$

$$10^{-0.68} = K_{eq.} = \frac{[H_2SiO_3]^2[Na^+]}{[H^+]}$$

$$\frac{[H^+][HSiO_3^-]}{[H_2SiO_3]} = 10^{-9.86} = Ka_1 \qquad \frac{[SiO_3^{2-}][H^+]}{[HSiO_3^-]} = 10^{-13.1} = Ka_2$$



$$[Ca^{2+}][CO_3^{2-}] = 10^{-8.35}$$

$$[H_2CO_3^*] = pCO_2 K_H = 10^{-1.5}\,10^{-1.46} = 10^{-2.96}\ M$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.33} \qquad \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 10^{-6.35}$$

$$K_W = 10^{-14} = [OH^-][H^+]$$

$H^+, OH^-, H_2O, H_2SiO_3, HSiO_3^-, \cancel{SiO_3^{2-}}$ (neglect), $Na^+, H_2CO_3^*, HCO_3^-, CO_3^{2-}, Ca^{2+}$

$$\left(H_2SiO_3 = \tfrac{1}{2}Alb + H^+ + \tfrac{5}{2}H_2O - \tfrac{1}{2}Kaol. = Na^+\right)\tfrac{1}{2}$$

	H_2O	H^+	$H_2CO_3^*$	$CaCO_3$ (s)	Albite (s)	Kaol. (s)	Na^+
H_2O	1						
H^+		1					
OH^-	1	-1					
$H_2CO_3^*$			1				
HCO_3^-	-1	-1	1				
CO_3^{2-}		-2	1				
Ca^{2+}		2	-1	1			
H_2SiO_3	5/4	1/2			1/4	-1/4	-1/2
$HSiO_3^-$	5/4	-1/2			1/4	-1/4	-1/2
Na^+							1

TOT H^+: $[H^+] - [OH^-] + \frac{1}{2}[H_2SiO_3] - \frac{1}{2}[HSiO_3^-] - [HCO_3^-] - 2[CO_3^{2-}] + 2[Ca^{2+}] = 0$

TOT Na^+: $-\frac{1}{2}[H_2SiO_3] - \frac{1}{2}[HSiO_3^-] + [Na^+] = 0$

From TOT H:

$$[H^+] - \frac{10^{-14}}{[H^+]} + \frac{1}{2}\left(\frac{(10^{-0.68})[H^+]}{[Na^+]}\right)^{1/2} - \frac{1}{2}\left(\frac{10^{-9.86}}{[H^+]^{1/2}}\left(\frac{10^{-0.68}}{[Na^+]}\right)^{1/2}\right)$$

$$- \frac{10^{-6.35}\,10^{-2.96}}{[H^+]} - 2\left(10^{-8.35}/[Ca^{2+}]\right) + 2[Ca^{2+}] = 0$$

$$[Ca^{2+}] = 10^{-8.35} / [CO_3^{2-}]$$

$$[CO_3^{2-}] = \frac{(10^{-10.33})[HCO_3^-]}{[H^+]} = \frac{(10^{-6.35})(10^{-10.33})(10^{-1.5})(10^{-1.46})}{[H^+]^2} = \frac{10^{-19.64}}{[H^+]^2}$$

$$[Ca^{2+}] = \frac{10^{-8.35}}{10^{-19.64}/[H^+]^2} = \frac{10^{-8.35}[H^+]^2}{10^{-19.64}} = 10^{11.29}[H^+]^2$$

To replace $[Na^+]$ in TOTH, use TOT Na:

$$-\frac{1}{2}\left(\frac{10^{-0.68}[H^+]}{[Na^+]}\right)^{1/2} - \frac{1}{2}\left(\frac{10^{-9.86}}{[H^+]^{1/2}}\left(\frac{10^{-0.68}}{[Na^+]}\right)^{1/2}\right) + [Na^+] = 0$$

$$-\frac{1}{2}\left(\frac{10^{-0.68}}{[Na^+]}\right)^{1/2}\left[[H^+]^{0.5} + \frac{10^{-9.86}}{[H^+]^{0.5}}\right] = -[Na^+]$$

(put $-\frac{1}{2}$ into exponent)

$$10^{-0.64}\left([H^+]^{0.5} + \frac{10^{-9.86}}{[H^+]^{0.5}}\right) = (-[Na^+])(-[Na^+]^{1/2}) = [Na^+]^{3/2}$$

(take the $\frac{2}{3}$rds root of both sides)

$$[Na^+] = \left(10^{-0.64}\left([H^+]^{0.5} + 10^{-9.86}[H^+]^{-0.5}\right)\right)^{2/3}$$

Choose a pH, solve for $[Na^+]$, $[Ca^{2+}]$, $[H_2SiO_3]$, $[HSiO_3^-]$, $[CO_3^{2-}]$, $[HCO_3^-]$, plug in to TOTH, find pH where TOTH = 0.

pH	[H+]	Ca2+	Na+	H2SiO3	HSiO3-	TOTH
7.0230	9.48418E-08	0.001753881	1.71E-03	0.003405044	4.95590E-06	3.8537E-05
7.0240	9.46237E-08	0.001745822	1.71E-03	0.003402428	4.96351E-06	9.1799E-06
7.0250	9.44061E-08	0.001737801	1.71E-03	0.003399814	4.97113E-06	-2.0130E-05
7.0260	9.41890E-08	0.001729816	1.71E-03	0.003397202	4.97876E-06	-4.9393E-05
7.0270	9.39723E-08	0.001721869	1.70E-03	0.003394591	4.98640E-06	-7.8608E-05
7.0280	9.37562E-08	0.001713957	1.70E-03	0.003391983	4.99406E-06	-1.0778E-04
7.0290	9.35406E-08	0.001706082	1.70E-03	0.003389377	5.00173E-06	-1.3690E-04
7.0300	9.33254E-08	0.001698244	1.70E-03	0.003386773	5.00940E-06	-1.6598E-04
7.0310	9.31108E-08	0.001690441	1.70E-03	0.00338417	5.01709E-06	-1.9501E-04
7.0320	9.28966E-08	0.001682674	1.70E-03	0.00338157	5.02480E-06	-2.2400E-04
7.0330	9.26830E-08	0.001674943	1.70E-03	0.003378972	5.03251E-06	-2.5295E-04
7.0340	9.24698E-08	0.001667247	1.69E-03	0.003376375	5.04023E-06	-2.8194E-04
LOG (spp)	-7.02E+00	-2.76E+00	-2.77E+00	-2.47E+00	-5.30E+00	

TOTH = 0 somewhere in this pH range,

pH = 7.02

$[H^+] = 10^{-7.02}$ M

$[OH^-] = 10^{-6.98}$ M

$[Ca^{2+}] = 10^{-2.76}$ M

$[Na^+] = 10^{-2.77}$ M

$[H_2SiO_3] = 10^{-2.47}$ M

$[HSiO_3^-] = 10^{-5.30}$ M

$[H_2CO_3^*] = 10^{-2.96}$ M

$[HCO_3^-] = 10^{-2.29}$ M

$[CO_3^{2-}] = 10^{-5.60}$ M

PROBLEM #3

Rxn 1: $CaCO_3(s) + CO_2(g) + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$

As $CO_2(g)$ escapes, $CaCO_3(s)$ ppts (rxn goes left, ↑pH, ↑ $CaCO_3$ preservation).
The outgassing of CO_2 will have no effect on the alkalinity ($\Delta Alk = 0$ ($\Delta CO_2(g)$)).
The outgassing of CO_2 will increase the pH, as this rxn

Rxn 2: $H_2O + CO_2(g) \rightleftharpoons H_2CO_3^* \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$
is driven left. (pH↑, shift toward CO_3^{2-}, ↑ $CaCO_3$ ppt.)

C_T will begin to decrease, as $C_T = H_2CO_3^* + HCO_3^- + CO_3^{2-}$
and we are decreasing $H_2CO_3^*$ (↓ HCO_3^- ↓ CO_3^{2-}, pulling Rxn 2 to the left)

According to rxn 1, $CaCO_3(s)$ will begin to ppt, and for every $CaCO_3$ removed, Alk ↓ by 2 equivalents.
($\Delta Alk = \Delta(-TOTH) = \Delta HCO_3^- = -2$ mol Alk / mol $CaCO_3$).

C_T will continue to decrease as more CO_2 outgasses + $CaCO_3(s)$ ppts, since you are removing CO_3^{2-} and $H_2CO_3^*$. The pH should increase, as rxn 1 is going left, ↓ HCO_3^- ($HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$), thereby ↓ H^+, and ↑ pH.

$\Delta C_T = -1(CaCO_3 ppt) - 1(CO_2 escaped)$

Freshwater - ignore ionic strength effects

$$pCO_2 = \left(\frac{350\times10^{-6}\ ml}{mL\ air}\right)\left(\frac{L}{1000\ mL\ CO_2}\right)\left(\frac{mol}{22.4\ L}\right)\left(\frac{1000\ mL}{L\ air}\right)(298\ K)\left(\frac{8.2\times10^{-2}\ L\cdot atm}{mol\cdot K}\right)$$

$= 3.82\times10^{-4}$ atm $= 10^{-3.4}$ atm = typical atmospheric pCO_2.

As $10^{-3.4} = pCO_{2,atm} < pCO_{2,groundwater} = 10^{-1.5}$ atm, our water will be supersaturated with respect to CO_2.

Assume: • we are no longer in eq. w/albite or kaolinite
• there are no sources/sinks of Na^+ or $H_2SiO_{3,T}$

Solve using charge balance (why not try something new?):

Charged spps: H^+, OH^- $HSiO_3^-$, ~~SiO_3^{2-}~~ (neglect @ pH<12.9), HCO_3^-, CO_3^{2-}, Na^+, Ca^{2+}

Charge Balance:

$$0 = [H^+] + [Na^+] + 2[Ca^{2+}] - [OH^-] - [HSiO_3^-] - 2[CO_3^{2-}] - [HCO_3^-]$$

We will rewrite species in terms of $[H^+]$ and solve by trial & error using a spreadsheet.

$[Na^+] = 10^{-2.77}$ M, as in Problem 2

$$[HSiO_3^-] = [H_2SiO_3]_T \Big/ \left(1 + [H^+]/10^{-9.86}\right); \quad [H_2SiO_3]_T = 10^{-2.47}\ M, \text{ as in Prob 2.}$$

$$[Ca^{2+}] = K_{sp,CaCO_3(s)}/[CO_3^{2-}] = 10^{-8.35}/[CO_3^{2-}]$$

$$[HCO_3^-] = \frac{[H_2CO_3^*]K_{a1}}{[H^+]} = \frac{(\phi CO_2)(K_H)K_{a1}}{[H^+]} = \frac{(10^{-3.4})(10^{-1.46})(10^{-6.35})}{10^{-pH}}$$

$$[CO_3^{2-}] = \frac{[HCO_3^-]K_{a2}}{[H^+]} = \frac{(\phi CO_2)(K_H)(K_{a1})(K_{a2})}{[H^+]} = \frac{(10^{-3.4})(10^{-1.46})(10^{-6.35})(10^{-11.33})}{10^{-2pH}}$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-pH}} = 10^{-14+pH}$$

$pH = 8.48$

$C_T = 10^{-2.72}$ M

$Alk = 10^{-2.77}$ eq/l

$Ca^{2+} = 10^{-3.76}$ M

Alk Tableau

	H_2O	H^+	$CaCO_3$	$H_2CO_3^*$	H_2SiO_3	Na^+
H_2O	1					
H^+		1				
OH^-	1	-1				
$H_2CO_3^*$				1		
HCO_3^-		-1		1		
CO_3^{2-}		-2		1		
Ca^{2+}		+2	1	-1		
H_2SiO_3					1	
$HSiO_3^-$		-1			1	
Na^+						1

$$Alk = -TOTH = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - 2[Ca^{2+}] + [HSiO_3^-]$$

PROBLEM #4

a) $[Fe^{2+}]_T = 10^{-6} M$

complex	$\log\beta$
$FeOH^+$	4.5
$Fe(OH)_2$	7.4
$Fe(OH)_3^-$	11.0

$$[Fe(II)]_T = [Fe^{2+}] + [FeOH^+] + [Fe(OH)_2] + [Fe(OH)_3^-]$$

$$= [Fe^{2+}] + \beta_{FeOH^+}[Fe^{2+}][OH^-] + \beta_{Fe(OH)_2}[Fe^{2+}][OH^-]^2 + \beta_{Fe(OH)_3^-}[Fe^{2+}][OH^-]^3$$

$$= [Fe^{2+}]\left(1 + \beta_{FeOH^+}[OH^-] + \beta_{Fe(OH)_2}[OH^-]^2 + \beta_{Fe(OH)_3^-}[OH^-]^3\right)$$

$$[Fe^{2+}] = [Fe(II)]_T \Big/ \left(1 + 10^{4.5}\frac{K_w}{[H^+]} + 10^{7.4}\left(\frac{K_w}{[H^+]}\right)^2 + 10^{11.0}\left(\frac{K_w}{[H^+]}\right)^3\right) \quad (\text{Eqn 1})$$

$$[FeOH^+] = \beta_{FeOH^+}[Fe^{2+}][OH^-] = 10^{4.5}\frac{K_w}{[H^+]}[Fe^{2+}] \quad (\text{Eqn 2})$$

$$[Fe(OH)_2] = \beta_{Fe(OH)_2}[Fe^{2+}][OH^-]^2 = 10^{7.4}\left(\frac{K_w}{[H^+]}\right)^2[Fe^{2+}] \quad (\text{Eqn 3})$$

$$[Fe(OH)_3^-] = \beta_{Fe(OH)_3^-}[Fe^{2+}][OH^-]^3 = 10^{11.0}\left(\frac{K_w}{[H^+]}\right)^3[Fe^{2+}] \quad (\text{Eqn 4})$$

$$[H^+] = 10^{-pH}$$

$$[OH^-] = K_w/[H^+] = 10^{-14+pH}$$

$$K_w = 10^{-14}$$

Equations 1-4 used to generate plot.

b) $Fe(OH)_2(s) = Fe^{2+} + 2OH^-$ $\quad K_{sp} = 10^{-15.1} = [Fe^{2+}][OH^-]^2$

$$[Fe^{2+}]_{\substack{eq.\ w/ \\ Fe(OH)_2(s)}} = K_{sp}/[OH^-]^2 = K_{sp}\left(\frac{[H^+]}{K_w}\right)^2 = \frac{(10^{-15.1})(10^{-2pH})}{10^{-28}}$$

$Fe(OH)_2(s)$ will ppt when

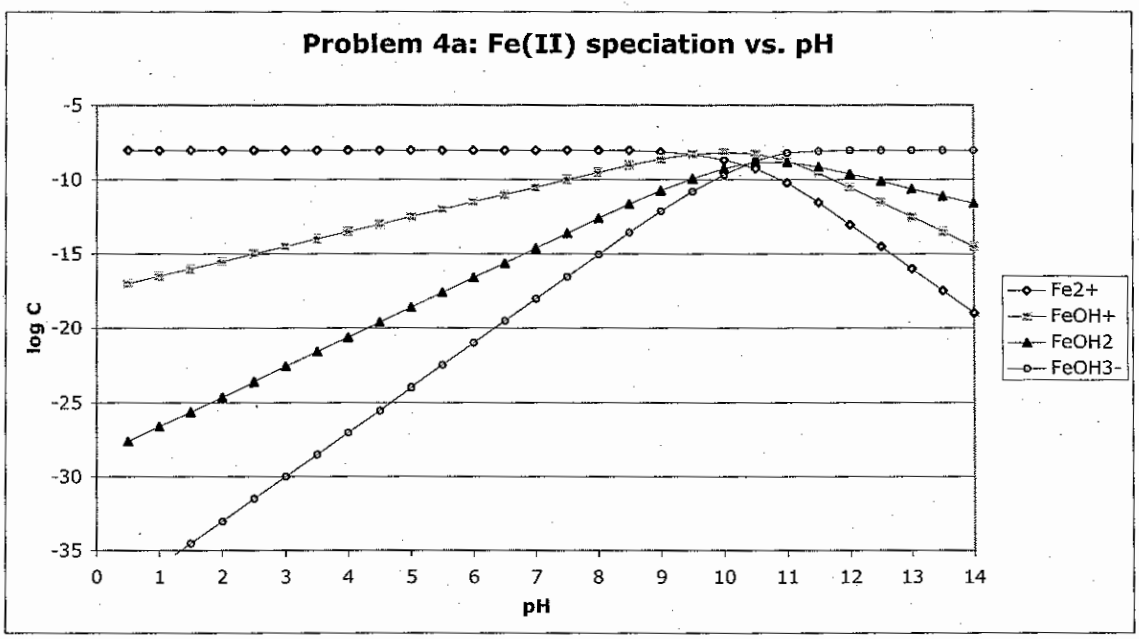
$$[Fe^{2+}]_{\substack{eq.\ w/ \\ Fe(OH)_2(s)}} \leq [Fe^{2+}]_{free}$$

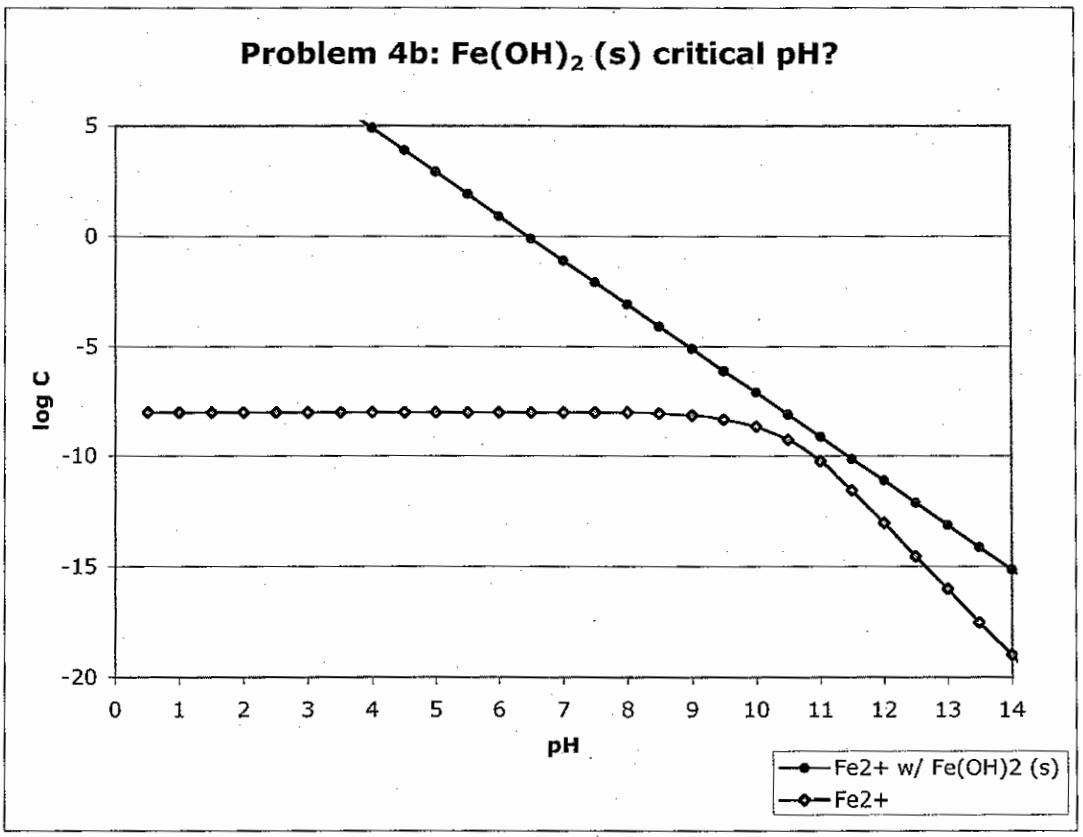
Plot $[Fe^{2+}]_{free}$ ($[Fe^{2+}]$) and $[Fe^{2+}]_{eq.\ w/\ Fe(OH)_2(s)}$,

solve for pH where

$[Fe^{2+}] = [Fe^{2+}]_{eq\ w/\ Fe(OH)_2(s)}$

From the plot, we see that $[Fe^{2+}] < [Fe^{2+}]_{eq\ w/\ FeOH_2(s)}$ for all pH, so $Fe(OH)_2$ does not ppt.


Problem 4a: Fe(II) speciation vs. pH
log C
pH
-5
-10
-15
-20
-25
-30
-35
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
Fe2+
FeOH+
FeOH2
FeOH3-


Problem 4b: Fe(OH)2 (s) critical pH?
log C
pH
5
0
-5
-10
-15
-20
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
Fe2+ w/ Fe(OH)2 (s)
Fe2+

c) $[H_2S]_T = [H_2S] + [HS^-] + [S^{2-}] = 10^{-5}\ M$

$$K_{a_1} = \frac{[HS^-][H^+]}{[H_2S]} = 10^{-7.02} \Rightarrow [H_2S] = \frac{[HS^-][H^+]}{10^{-7.02}} = \frac{[S^{2-}][H^+]^2}{(10^{-7.02})(10^{-13.9})}$$

$$K_{a_2} = \frac{[S^{2-}][H^+]}{[HS^-]} = 10^{-13.9} \Rightarrow [HS^-] = \frac{[S^{2-}][H^+]}{10^{-13.9}}$$

$$[H_2S]_T = \frac{[S^{2-}][H^+]^2}{(10^{-7.02})(10^{-13.9})} + \frac{[S^{2-}][H^+]}{10^{-13.9}} + [S^{2-}]$$

$$[S^{2-}] = [H_2S]_T \Big/ \left(1 + \frac{[H^+]}{10^{-13.9}} + \frac{[H^+]^2}{(10^{-7.02})(10^{-13.9})}\right)$$

$$[S^{2-}] = [H_2S]_T \Big/ \left(1 + 10^{-pH+13.9} + 10^{-2pH+20.92}\right) \quad (\text{Eqn 1})$$

$FeS(s) \rightleftharpoons Fe^{2+} + S^{2-} \qquad K_{sp} = 10^{-18.1} = [Fe^{2+}][S^{2-}]$

$$[Fe^{2+}]_{\substack{eq \\ w/FeS(s)}} = 10^{-18.1} \Big/ [S^{2-}] \quad (\text{Eqn 2})$$

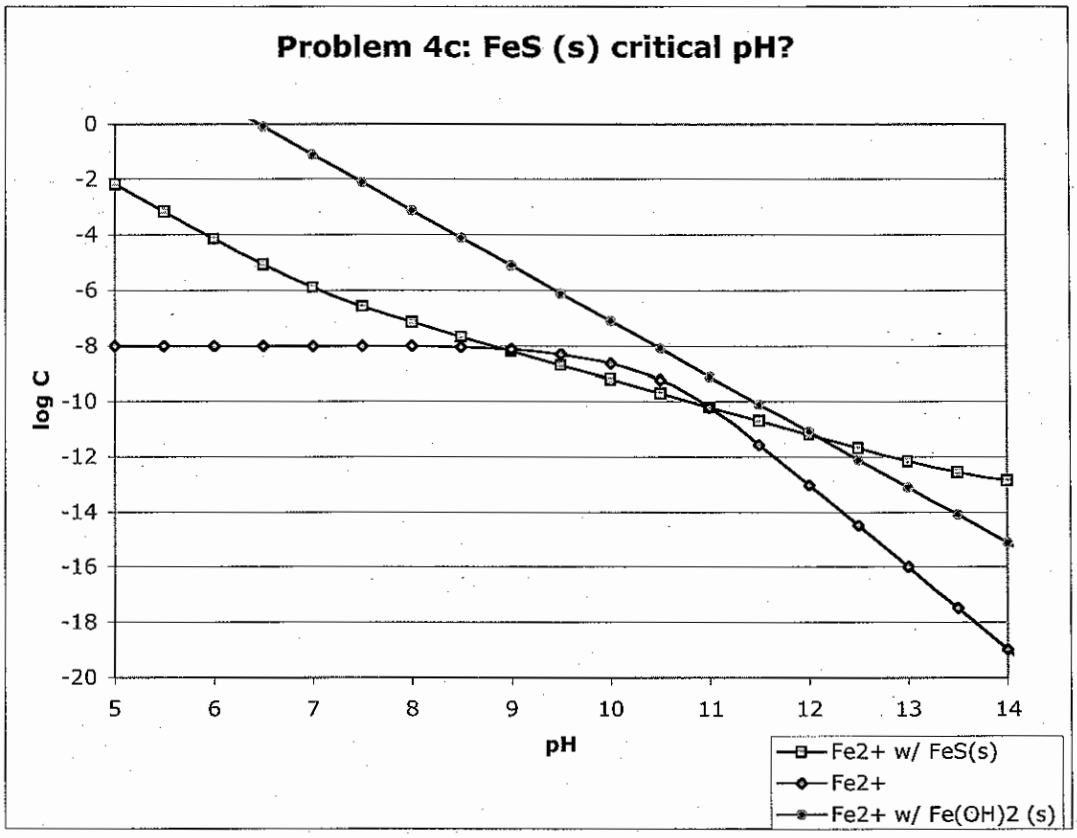
Plug Eqn 1 into Eqn 2 to generate $[Fe^{2+}]_{\substack{in\ eq. \\ w/FeS(s)}}$, plot with $[Fe^{2+}]_{free}$, $[Fe^{2+}]_{\substack{in\ eq. \\ w/Fe(OH)_2(s)}}$.

The critical pH is the pH where

$[Fe^{2+}]_{\substack{eq.\ w \\ FeS(s)}} \leq [Fe^{2+}]_{free}$, $[Fe^{2+}]_{\substack{in\ eq. \\ w/Fe(OH)_2(s)}}$.

$pH \doteq 8.8$.

(note: used solver, did not read off plot)


Problem 4c: FeS (s) critical pH?
log C
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
5
6
7
8
9
10
11
12
13
14
pH
Fe2+ w/ FeS(s)
Fe2+
Fe2+ w/ Fe(OH)2 (s)

d) $FeS(s)$ is more stable at pH values < 12

(as $[Fe^{2+}]_{\text{in eq. w/ } FeS(s)} < [Fe^{2+}]_{\text{in eq w/ } Fe(OH)_2}$ for all pH values < 12.

e) Ignoring complexing $[Fe^{2+}] = [Fe^{2+}]_T$,

and $Fe(OH)_2(s)$ will ppt when $[Fe^{2+}][OH^-]^2 \geq K_{sp} = 10^{-15.1}$

$$[OH^-] = \sqrt{[OH^-]^2} = \sqrt{K_{sp}/[Fe^{2+}]_T} = \sqrt{\frac{10^{-15.1}}{10^{-8}}} = 10^{-3.55}\ M$$

$$pOH = 3.55$$

$$14 - pOH = pH = 10.45$$

Aqueous complexing increases the solubility of $Fe(OH)_2(s)$ (but does not change K_{sp}), by lowering the $[Fe^{2+}]_{free}$.