GG425 -- ENVIRONMENTAL GEOCHEMISTRY
Homework set #2 (partial answers)

Here are answers to a few of the homework problems (the ones most people found to be more difficult). Please let me know if any of this is unclear of if you would like assistance with one of the other problems.

Problem 2

From Fig. 4.4, we see that Fe in pure water of pH=9.5 and pE = -8.0 that Fe is as $Fe(OH)_2$. Fe is in the +2 oxidation state.

What happens when we add CO_2 to the solution? Is $Fe(OH)_2$ still the dominant form of Fe? There is a figure in the lecture notes showing the Fe + CO_2 + S system that indicates that at some conditions siderite ($FeCO_3$) or pyrite (FeS_2) are more favored (the "dominant phase").

We have no sulfur, so we needn't worry about pyrite.

Siderite could form, however, in the problem 2 scenario. Notice that Fe is in the +2 oxidation state in this compound as well.

So, the question is not a redox problem, it is a solubility one. With CO_2 present in solution at low pE and basic pH, which material is less soluble, $Fe(OH)_2$ or $FeCO_3$. The least soluble phase will "dominate" the solids and be more abundant at the conditions specified.

Let's solve.
First, note that at pH=9.5 and pE = -8.0 HCO_3^- (bicarbonate anion) is the dominant form of CO_2 in solution (Fig. 3.3 of Manahan).

There are two ways to now solve the problem.
a) determine K for $Fe(OH)_2 + HCO_3^- \leftrightarrow FeCO_3 + H_2O + OH^-$ and see which side is favored at the conditions given (products or reactant)
b) calculate $[Fe^{2+}]$ for Ksp of both $Fe(OH)_2$ and $FeCO_3$ at the conditions given and see which results in lower dissolved Fe^{2+}. The one with the lower dissolved Fe is the "more favored" solid.

I chose method "b". *Please note: [a] means "the concentration of a" in my answer.*

$Fe(OH)_2 + 2H^+ \leftrightarrow Fe^{2+} + 2H_2O$ (eqn 4.11.2)
$K_{sp} = [Fe^{2+}]/[H^+]^2 = 8 \times 10^{12}$ (eqn 4.11.3)

$FeCO_3 \leftrightarrow Fe^{2+} + CO_3^{2-}$
$K_{sp} = [Fe^{2+}][CO_3^{2-}] = 3.5 \times 10^{-11}$ (given in problem)

$Fe(OH)_2$:
$[Fe^{2+}] = 8 \times 10^{12} \times (H^+)^2$, where $(H^+) = 10^{-9.5}$ from the equation $pH = -\log(H^+)$.
$[Fe^{2+}] = 8 \times 10^{-7}$

$FeCO_3$:
$[Fe^{2+}] = 3.5 \times 10^{-11}/[CO_3^{2-}]$
I get $[CO_3^{2-}]$ from $K_{a2} = 4.69\ \ 10^{-11}$, (eqn 3.7.11). $K_{a2} = [H^+][CO_3^{2-}]/[HCO_3^-]$
Using values given in the problem, $[CO_3^{2-}] = 1.48 \times 10^{-4}$
$[Fe^{2+}] = 3.5 \times 10^{-11}/1.48 \times 10^{-4} = 2.57 \times 10^{-7}$

Therefore $FeCO_3$ dominates

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Problem 6.
What is $[Fe^{3+}]$, pE and ph at place where $1 \times 10^{-5} = [Fe^{2+}] = [Fe(OH)_2] = [Fe(OH)_3]$
Use Fig. 4.4

One can estimate pH and pE by reading of the chart the x and y axis values at the "triple" point intersection of the stability files for Fe^{2+}, $Fe(OH)_2$, and $Fe(OH)_3$
From this one gets pH~9 and pE~5. But these are only approximate values.

To solve for 3 unknowns, we use 3 equations:

a) $Fe^{3+} + e^- \rightarrow Fe^{2+}$	pE = 13.2	(eqn 4.11.1)
b) $Fe(OH)_2 + 2H^+ \leftrightarrow Fe^{2+} + 2H_2O$	$K_{sp} = 8 \times 10^{12}$	(eqn 4.11.2)
c) $Fe(OH)_3 + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$	$K_{sp} = 9.1 \times 10^3$	(eqn 4.11.4)

First, get $[H^+]$ from "b":
$8 \times 10^{12} = [Fe^{2+}]/[H^+]^2$. Using $[Fe^{2+}] = 10^{-5}$, I get $[H^+] = 1.12 \times 10^{-9}$, or **pH = 8.95**

Next, get $[Fe^{3+}]$ from "c":
$9.1 \times 10^3 = [Fe^{3+}]/[H^+]^3$ **$[Fe^{3+}] = 1.28 \times 10^{-23}$** (really low)

Finally, get pE from
$pE = pE^o + \log [Fe^{3+}]/[Fe^{2+}]$, where $pE^o = 13.2$ (eqn 4.11.6)

$pE = 13.2 + \log (1.28 \times 10^{-23}/10^{-5})$, **or pE = - 4.7**

Problem 8.
What is pE at pH=6 on the Fe^{2+} - $Fe(OH)_3$ boundary line in Fig 4.4 for total Fe of 10^{-4}

To solve, use equations 4.11.5 and 4.11.6 combined...

$pE = 13.2 + \log (9.1 \times 10^3 [H^+]^3 / [Fe^{2+}]$

$pE = 13.2 + \log (9.1 \times 10^3 [10^{-6}]^3 / [10^{-4}]$

pE = 3.2