

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 or 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 CO₂ to the solution? Is Fe(OH)₂ still the dominant form of Fe? There is a figure in the lecture notes showing the Fe + CO₂ + S system that indicates that at some conditions siderite (FeCO₃) or pyrite (FeS₂) 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 CO₂ present in solution at low pE and basic pH, which material is less soluble, Fe(OH)₂ or FeCO₃. The least soluble phase will "dominate" the solids and be more abundant at the conditions specified.

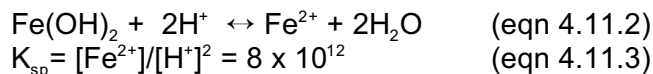
Let's solve.

First, note that at pH=9.5 and pE = -8.0 HCO₃⁻ (bicarbonate anion) is the dominant form of CO₂ in solution (Fig. 3.3 of Manahan).

There are two ways to now solve the problem.

- determine K for Fe(OH)₂ + HCO₃⁻ → FeCO₃ + H₂O + OH⁻ and see which side is favored at the conditions given (products or reactant)
- calculate [Fe²⁺] for K_{sp} of both Fe(OH)₂ and FeCO₃ at the conditions given and see which results in lower dissolved Fe²⁺. 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.*



$$K_{\text{sp}} = [\text{Fe}^{2+}]/[\text{H}^+]^2 = 8 \times 10^{12} \quad (\text{eqn 4.11.3})$$



$$K_{\text{sp}} = [\text{Fe}^{2+}][\text{CO}_3^{2-}] = 3.5 \times 10^{-11} \quad (\text{given in problem})$$

Fe(OH)₂ :

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

$$[\text{Fe}^{2+}] = 8 \times 10^{-7}$$

FeCO₃ :

$$[\text{Fe}^{2+}] = 3.5 \times 10^{-11}/[\text{CO}_3^{2-}]$$

I get [CO₃²⁻] from K_{a2} = 4.69 × 10⁻¹¹, (eqn 3.7.11). K_{a2} = [H⁺][CO₃²⁻]/[HCO₃⁻]

Using values given in the problem, [CO₃²⁻] = 1.48 × 10⁻⁴

$$[\text{Fe}^{2+}] = 3.5 \times 10^{-11}/1.48 \times 10^{-4} = 2.57 \times 10^{-7}$$

Therefore FeCO₃ dominates

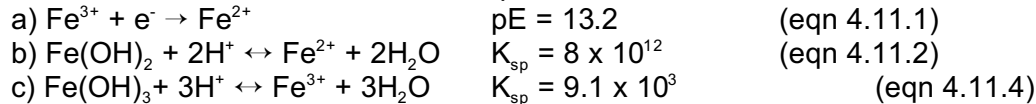
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Problem 6.

What is $[\text{Fe}^{3+}]$, pE and pH at place where $1 \times 10^{-5} = [\text{Fe}^{2+}] = [\text{Fe}(\text{OH})_2] = [\text{Fe}(\text{OH})_3]$
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+} , $\text{Fe}(\text{OH})_2$, and $\text{Fe}(\text{OH})_3$
From this one gets pH~9 and pE~5. But these are only approximate values.

To solve for 3 unknowns, we use 3 equations:



First, get $[\text{H}^+]$ from "b":

$$8 \times 10^{12} = [\text{Fe}^{2+}]/[\text{H}^+]^2. \text{ Using } [\text{Fe}^{2+}] = 10^{-5}, \text{ I get } [\text{H}^+] = 1.12 \times 10^{-9}, \text{ or } \mathbf{pH = 8.95}$$

Next, get $[\text{Fe}^{3+}]$ from "c":

$$9.1 \times 10^3 = [\text{Fe}^{3+}]/[\text{H}^+]^3 \qquad \mathbf{[\text{Fe}^{3+}] = 1.28 \times 10^{-23}} \text{ (really low)}$$

Finally, get pE from

$$pE = pE^0 + \log [\text{Fe}^{3+}]/[\text{Fe}^{2+}], \text{ where } pE^0 = 13.2 \qquad \text{(eqn 4.11.6)}$$

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

Problem 8.

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

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

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

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

$$\mathbf{pE = 3.2}$$