GEOL360 Homework 3 : Aqueous Geochemistry

Name: __________________________________________

Fill in the final answers in the blank spaces provided after each question. Staple all other pieces of paper which you have used to this page, and put in my mailbox (outside room 245) or give it to me in person by the end of class on **Tuesday March 26th**. There will be harsh penalties for late submission. **No credit will be given for answers that are not accompanied by calculations.**

Some questions use results from other questions – I give partial credit even if the final answer is wrong (as long as you provide a clear explanation of your calculations). Numbers for each question given in brackets. Total points available is **40** for this homework.

**Q1:** The solubility product (Ksp) of siderite, FeCO₃, is 10⁻¹₀.₇ at 25 °C.

(a) What is the solubility of siderite in pure water at this temperature? Express your answer (i) in mol l⁻¹, (ii) in g l⁻¹ and (iii) in ppm. [6]

**[Hint: take the atomic weight of Fe to be 55.85, use 12.0 for C and 16.0 for O]**

The solubility reaction is FeCO₃(s) = Fe²⁺(aq) + CO₃²⁻(aq)

\[ Ksp = \frac{[\text{products}]}{[\text{reactants}]} \]
\[ = \frac{[\text{Fe}^{2+}(aq)][\text{CO}_3^{2-}(aq)]}{[\text{FeCO}_3(s)]} \]
\[ = [\text{Fe}^{2+}(aq)][\text{CO}_3^{2-}(aq)] \text{ since the activity of solid phases is set to 1} \]

Now 1 mole of FeCO₃ gives 1 mole of Fe²⁺(aq) and 1 mole of CO₃²⁻(aq)

Therefore solubility of siderite is \([\text{Fe}^{2+}(aq)] = [\text{CO}_3^{2-}(aq)]\)

(i) \(\sqrt{10^{-10.7}} = 10^{-5.35} \text{ mol l}^{-1} \) or \(4.47 \times 10^{-6} \text{ mol l}^{-1}\)

This is equivalent to:

(ii) \(10^{-5.35} \times (55.85 + 12 + (3 \times 16)) = 517 \times 10^{-6} \text{ g liter}^{-1}\)

This is equivalent to:

(iii) \(517 \times 10^{-6} / 1000 \times 10^6 = 0.517 \text{ ppm}\)
(b) Calculate the solubility of siderite in river water which already contains 1 ppm Fe, assuming that all Fe is present as Fe\(^{2+}\). Again, give your answer in (i) mol l\(^{-1}\), (ii) g l\(^{-1}\) and (iii) ppm. [6]

[Hint: read about the common-ion effect, page 183]

1.0 ppm Fe initially present is equivalent to a concentration of \(10^{-3}\) g / liter

and an activity of \(1 \times 10^{-3} / (55.85)\)

(note we use the atomic weight of Fe, not FeCO\(_3\))

\[= 1.79 \times 10^{-5} \text{ mol l}^{-1} \text{ or } 10^{-4.75} \text{ mol l}^{-1}\]

Now [Fe\(^{2+}\)(aq)] \(\times\) [CO\(_3^{2-}\)(aq)] = \(10^{-10.7}\) as before, but this time there is some Fe already present.

Therefore [Fe\(^{2+}\)(added) + Fe\(^{2+}\)(initial)] \(\times\) [CO\(_3^{2-}\)(added)] = \(10^{-10.7}\)

where [Fe\(^{2+}\)(added)] = [CO\(_3^{2-}\)(added)] = solubility of siderite

So [Fe\(^{2+}\)(added) + 1.79 \times 10^{-5}] \(\times\) [Fe\(^{2+}\)(added)] = \(10^{-10.7}\)

This is a quadratic: if we say \(x = [\text{Fe}^{2+}(\text{added})]\) then

\[x^2 + (1.791 \times 10^{-5})x - 10^{-10.7} = 0\]

for an equation \(ax^2 + bx + c = 0\), use

\[x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\]

there is a positive solution and a negative solution to this, but a negative answer would be meaningless (can you have a negative activity, or a negative concentration?) so use the positive answer, which is \(1.053 \times 10^{-6}\).

Therefore [Fe\(^{2+}\)(added)], and siderite solubility, = \textbf{1.053 \times 10^{-6} mol l}^{-1} \text{ or } \textbf{10^{-5.98} M}\n
which is \(1.053 \times 10^{-6} \times 115.85 = 0.122 \times 10^{-3} \text{ g l}^{-1}\), or 0.122 mg l\(^{-1}\) or \textbf{0.122 ppm}\n
Q2: The water half-electrode is: \[ \text{H}_2\text{O}(l) = 2\text{H}^+ + 1/2\text{O}_2 + 2\text{e}^- \]

The relevant Nernst equation \( (\text{Eh} = E^0 + \frac{RT}{NF \ln K}) \) reduces to:

\[ \text{Eh} = 1.23 + 0.01479 \log[\text{O}_2] - 0.05916 \text{pH} \]

where \( \log[\text{O}_2] = f_{\text{O}_2} \)

In class, we used this to determine the upper and lower bounds of water stability on Eh-pH diagrams. Under conditions of twice atmospheric pressure (i.e. 202 650 Pa), would the upper and lower limits of water stability on the Eh-pH diagram remain the same or change?

[Assume that the equilibrium constant for the reaction \( \text{H}_2\text{O}(l) = \text{H}^+ + \text{OH}^- \) remains \( 10^{-14} \) at the new pressure].

You only need to say whether the stability limits would change or not, and briefly explain why. [3]

Consider upper and lower limits for \( \text{Eh} = 1.23 - 0.05916 \text{pH} + 0.015 \log (p\text{O}_2) \)

The limits are determined by the requirement that, at equilibrium,

\[ [\text{O}_2(g)] [\text{H}_2(g)]^2 = 10^{43.1} \] (see your notes if you are unclear where this came from)

Under a total pressure of 2 atm, the upper limit for \( p\text{O}_2 \) is now 2 atm.

**Eh = 1.23 - 0.05916 \text{pH} + 0.015 \log (2) \) so \( \text{Eh} = 1.2345 -0.05916 \text{pH} \)

(not a very significant change)

Under a total pressure of 2 atm, the upper limit for \( pH_2 \) is also now 2 atm, so the minimum fugacity of \( \text{O}_2 \) is reduced to \( 2 \times 10^{-84} \). Hence the lower limit also remains approximately the same:

**Eh = 1.23 - 0.05916 \text{pH} + 0.015 \log (2 \times 10^{-84}) \) so \( \text{Eh} = -0.026 -0.05916 \text{pH} \)

In brief, the limits do change but not very much

(A larger pressure change might affect the equilibrium constants and \( \Delta Gr \), in which case the value of Eh and the relation between Eh and pH would also change.)
Q3: From the list of standard potentials for half-reactions given in Brownlow (Table 4-3, page 192), give the value of Eh for the following reactions at standard temperature and pressure, and say whether the reaction will go to the left or to the right. Make sure you say whether Eh is positive or negative.

(i) \( \text{Fe}^{2+} + \text{Cu}^{2+} = \text{Fe}^{3+} + \text{Cu}^{+} \)

*This reaction results from adding the following half-reactions:*

\[
\begin{align*}
\text{Fe}^{2+} &= \text{Fe}^{3+} + e^- & E^0 &= +0.77 \text{ V} \\
\text{Cu}^{2+} + e^- &= \text{Cu}^{+} & E^0 &= -0.16 \text{ V}
\end{align*}
\]

[Note that the opposite reaction is given in table 4-3; we reverse the reaction and the sign of \( E^0 \).]

Summing these we get \( Eh = +0.61 \text{ V} \), and since reactions with positive potentials go to the left, this reaction goes to the left and produces \( \text{Fe}^{2+} + \text{Cu}^{2+} \).

\[ \text{Eh} = +0.61 \text{ V} \quad \text{Reaction goes to the LEFT} \]

(ii) \( \text{H}_2\text{S} (g) + 2 \text{O}_2 (g) = \text{SO}_4^{2-} + 2 \text{H}^+ \)

*This reaction results from adding the following half-reactions:*

\[
\begin{align*}
\text{H}_2\text{S} (g) + 4 \text{H}_2\text{O} &= \text{SO}_4^{2-} + 10 \text{H}^+ + 8 e^- & E^0 &= -0.34 \text{ V} \\
2 \text{O}_2 (g) + 8 \text{H}^+ + 8 e^- &= 4 \text{H}_2\text{O} & E^0 &= -1.23 \text{ V}
\end{align*}
\]

[Note that the opposite reaction is given in table 4-3; we reverse the reaction and the sign of \( E^0 \). In addition, we have multiplied this reaction by two to balance out the number of electrons. However, the value of \( E^0 \) does not depend on how the reaction is written, and stays the same.]

Summing these we get \( Eh = -1.57 \text{ V} \), and since reactions with negative potentials go to the right, this reaction goes to the right and produces \( \text{SO}_4^{2-} + \text{H}^+ \).

\[ \text{Eh} = -1.57 \text{ V} \quad \text{Reaction goes to the RIGHT} \]
Q4: A stream containing dissolved manganese (Mn) has an Eh value of +0.80. What is the ratio of Mn$^{3+}$ to Mn$^{2+}$ in the stream? [4]

[Hint: the half-reaction Mn$^{2+}$ = Mn$^{3+}$ + e$^{-}$ has an $E^0$ of +1.51 V]

Note the measured Eh of the stream is less oxidizing than the half-reaction. Hence we would expect most Mn to be in the form Mn$^{2+}$.

The Nernst equation allows us to be quantitative:

\[ E = E^0 + \frac{RT}{NF} \ln K \]

so \[ +0.80 = +1.51 + \left( \frac{8.31 \times 298.15}{96500} \right) \times \ln \left( \frac{[Mn^{3+}]}{[Mn^{2+}]} \right) \]

(note $N = 1$ and the values for $R, T$ and $F$ are all in S.I. units)

i.e. \[ -0.71 = 0.025675 \ln \left( \frac{[Mn^{3+}]}{[Mn^{2+}]} \right) \]

\[ \ln \left( \frac{[Mn^{3+}]}{[Mn^{2+}]} \right) = -27.65 \]

and

\[ \frac{[Mn^{3+}]}{[Mn^{2+}]} = 9.78 \times 10^{-13} \]

Q5: The copper-zinc cell shown below has $E^0$ = + 1.101 V.

\[ \text{Zn (s)} + \text{Cu}^{2+} (aq) \rightarrow \text{Cu(s)} + \text{Zn}^{2+} (aq) \]

If the reaction is done in a cell in 5.00 M Zn$^{2+}$ and 0.30 M Cu$^{2+}$ at 25 °C, what is the cell voltage? [4]

First, work out the reaction quotient $Q$. Since zinc and copper metals are solids, they don’t show up in the reaction quotient

\[ Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} \]

\[ Q = \frac{5.00}{0.30} \]

\[ Q = 16.7 \]

Two electrons are transferred between the zinc and copper, so $n=2$. Plug everything in

\[ E = E^0 + \left( 0.0257/n \right) \times \ln(Q) \]

\[ E = + 1.101 V + \left( 0.0257 \times 2 \right) \times \ln(16.7) \]

\[ E = + 1.101 V + 0.036 V \]

\[ E = + 1.137 V \]

Voltage = +1.137 V
Q6: The reaction shown below has $E^0 = +1.46 \text{ V}$.

$$\text{Pb}^{2+} + 2\text{H}_2\text{O} = \text{PbO}_2 (s) + 4\text{H}^+ + 2e^-$$

(a) If groundwater with a pH of 7 and an Eh of 0.6 V passed through a lead ore deposit, how much Pb$^{2+}$ in solution would be necessary to cause precipitation of plattnerite (PbO$_2$)? Give your answer in terms of molarity.

For this reaction $N = 2$ and $[\text{H}_2\text{O}] = [\text{PbO}_2] = [e^-] = 1$

$$E = E^0 + \frac{RT}{NF} \ln \left( \frac{[C]^N[D]^M}{[A]^p[B]^q} \right)$$

$$+0.6 = +1.46 + \frac{(8.3145 \times 298.15)}{(2 \times 96500)} \ln \left( \frac{[\text{H}^+]^4}{[\text{Pb}^{2+}]} \right)$$

$$-0.86 = (8.3145 \times 298.15 \times 2.303) \ln \left( \frac{[\text{H}^+]^4}{[\text{Pb}^{2+}]} \right) \log \left( \frac{[\text{H}^+]^4}{[\text{Pb}^{2+}]} \right)$$

$$-0.86 = 0.0296 \log \left( \frac{[\text{H}^+]^4}{[\text{Pb}^{2+}]} \right)$$

$$-29.07 = \log \left( \frac{[\text{H}^+]^4}{[\text{Pb}^{2+}]} \right)$$

$$\log [\text{Pb}^{2+}] = \log ([\text{H}^+]^4) - 29.07$$

$$\log [\text{Pb}^{2+}] = 4 \log ([\text{H}^+]) + 29.07$$

$$\log [\text{Pb}^{2+}] = 29.07 - 4 \times 7$$

$$\log [\text{Pb}^{2+}] = +1.07$$

$$[\text{Pb}^{2+}] = 10^{+1.07} \text{ M or 11.75 M}$$

(note this is Question 8 in chapter 4 of Brownlow, who somehow gets $10^{-0.67}$ or 4.68 M)

(b) If the solution became more acidic, would the amount of PbO$_2$ precipitated increase or decrease? Why?

If the solution became more acidic, the amount of PbO$_2$ precipitated would decrease, because $[\text{H}^+]$ would be higher, and the reaction would tend to go farther to the left.

(look at the last line of working: $\log [\text{Pb}^{2+}] = 29.07 - 4pH$. A decrease in pH will lead to a higher concentration of dissolved Pb$^{2+}$, and a decrease in PbO$_2$ precipitated)
Q7: In class we calculated stability limits for water in terms of Eh and pH.

Now calculate the stability limits of metallic Fe, magnetite (Fe₃O₄), and hematite (Fe₂O₃), in the presence of water at 25°C, and write the two relevant equations below.

Also plot the stability limits (neatly and accurately, please!) on an Eh-pH diagram (use a sheet of graph paper), with upper and lower water stabilities (from the notes). Would you ever expect to find metallic iron forming in natural sedimentary environments?

Hints:
(i) you will want to use the reactions:
(a) \(3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8\text{e}^-\) \(E^0 = -0.086\) V
(b) \(2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = 3\text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}^-\) \(E^0 = +0.20\) V

(ii) Don’t forget to also plot the stability limits of water on the diagram!

The equations are: (please write them in here)

(a) metallic Fe - magnetite

\[
3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8\text{e}^- \quad E^0 = -0.086 \text{ V}
\]

\[
E = E^0 + \frac{RT}{NF} \ln \left(\frac{[C]^3[D]^8}{[A]^3[B]^8}\right)
\]

\[
E = -0.086 + \frac{8.3145 \times 298.15}{8 \times 96500} \ln ([\text{H}^+]^8)
\]

\[
= -0.086 + \frac{(8.3145 \times 298.15 \times 8 \times 2.303)}{(8 \times 96500)} \log [\text{H}^+]
\]

\[
E = -0.086 - 0.059 \text{ pH}
\]

(b) magnetite - hematite

\[
2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = 3\text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \quad E^0 = +0.20 \text{ V}
\]

\[
E = E^0 + \frac{RT}{NF} \ln \left(\frac{[C]^3[D]^8}{[A]^3[B]^8}\right)
\]

\[
E = +0.20 + \frac{8.3145 \times 298.15}{2 \times 96500} \ln ([\text{H}^+]^2)
\]

\[
= +0.20 + \frac{(8.3145 \times 298.15 \times 2 \times 2.303)}{(2 \times 96500)} \log [\text{H}^+]
\]

\[
E = +0.20 - 0.059 \text{ pH}
\]
You would *never* expect to find metallic iron forming in natural sedimentary environments, since metallic Fe and water are never stable under the same Eh-pH conditions.

[i.e. Metallic Fe would only form in environments substantially more reducing than natural sedimentary environments (exposed subaerially at the Earth’s surface, or at the bottom of a body of water), where water is always stable. Diagenetic environments (burial at depth) may become sufficiently reducing to deposit native Fe.]