Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET THREE SOLUTIONS DUE SEPTEMBER 26, 2007

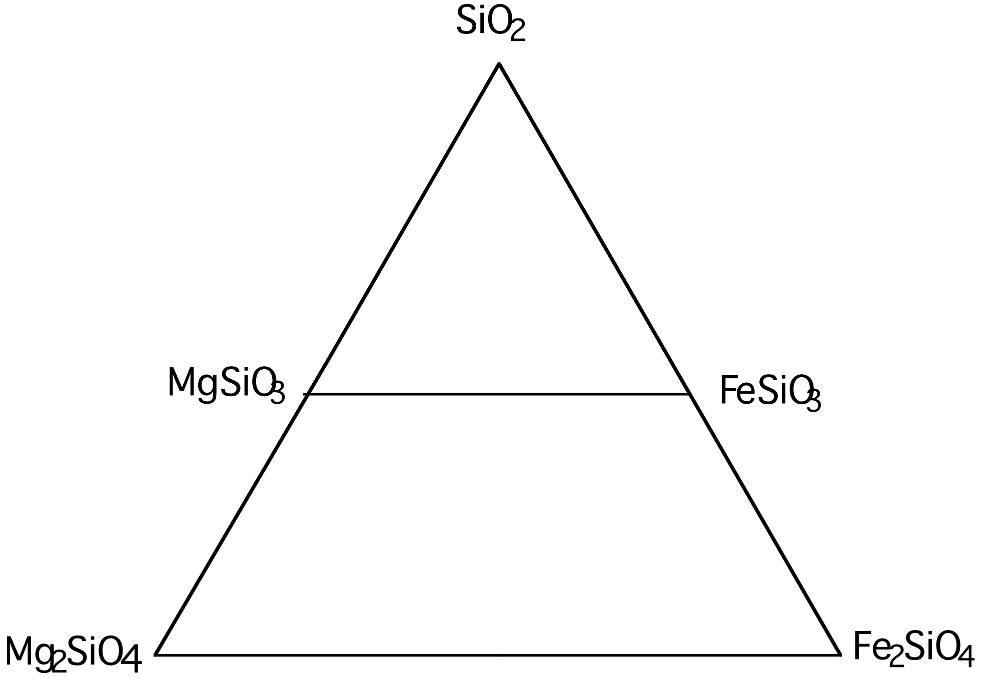
1. In section 3.2.1.3, we showed that a system containing H_2O, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, and OH^- could be described in terms of components CO_3^{2-}, H^+, and OH^-. Find a different set of components that describe the system equally well. Show that each of these species is an algebraic sum of your components.

In Section 3.10, we noted that H^+ and H_2O should be chosen as components in aqueous systems. So those should be our first two choices. Essentially, any of the 3 carbonate species could be chosen as a component, as an example, we'll chose H_2CO_3 (though CO_3^{2-} might be a better choice). The remaining species can then be constructed as:

$$OH^- = H_2O - H^+$$
$$HCO_3^- = H_2CO_3 - H^+$$
$$CO_3^{2-} = H_2CO_3 - 2H^+$$

2. Consider a system consisting of olivine of variable composition ($(Mg,Fe)_2SiO_4$) and orthopyroxene of variable composition ($(Mg,Fe)SiO_3$). What is the *minimum* number of components needed to describe this system?

Best to use the graphical method to answer this one. As the graph below shows, three components are the minimum. These could be SiO_2, Mg_2SiO_4, and Fe_2SiO_4 as shown, or they could be SiO_2, MgO, and FeO. Possible compositions of olivine and orthopyroxene line on the two horizontal lines.



3. Write the equilibrium constant expression for the reaction:

$$CaCO_{3(s)} + 2H^+_{(aq)} + SO_4^{-2} + H_2O_{(liq)} \leftrightarrows CaSO_4 \cdot 2H_2O_{(s)} + CO_{2(g)}$$

assuming the solids are pure crystalline phases and that the gas is ideal.

$$K = \frac{a_{CaSO_4 \cdot 2H_2O_{(s)}} \cdot a_{CO_{2(g)}}}{a_{CaCO_{3(s)}} a^2_{H^+_{aq}} \cdot a_{SO_4^{2-}} a_{H_2O}} = \frac{P_{CO_{2(g)}}}{a^2_{H^+_{aq}} \cdot a_{SO_4^{2-}} a_{H_2O}}$$

If the solution is sufficiently dilute that the activity of water may be taken as 1, the equation is:

$$K = \frac{P_{CO_{2\,(g)}}}{a^2_{H^+_{aq}} \cdot a_{SO_4^{2-}}}$$

4. The equilibrium constant for the dissolution of galena:

$$PbS_{solid} + 2H^+ \rightleftarrows Pb^{2+}_{aq} + H_2S_{aq}$$

is 9.12×10^{-7} at 80° C. Using the $\gamma_{Pb^{2+}} = 0.11$ and $\gamma_{H_2S} = 1.77$, calculate the equilibrium concentration of Pb^{2+} in aqueous solution at this temperature and at pH's of 6, 5 and 4. Assume the dissolution of galena is the only source of Pb and H_2S in the solution and that there is no significant dissociation of H_2S. *Hint:* mass balance requires that $[H_2S] = [Pb^{2+}]$.

Expressed in log form, the equilibrium constant expression for this reaction is:

$$\log K = 2pH + \log a_{Pb^{2+}} + \log a_{H_2S} = 2pH + \log[Pb^{2+}] + \log\gamma_{Pb^{2+}} + \log[H_2S] + \log\gamma_{H_2S}$$

(assuming PbS is a pure phase). Since $[H_2S] = [Pb^{2+}]$, we may write:

$$\log K = 2pH + 2\log[Pb^{2+}] + \log\gamma_{Pb^{2+}} + \log[H_2S] + \log\gamma_{H_2S}$$

Rearranging:

$$\log[Pb^{2+}] = \frac{\log K - \log\gamma_{Pb^{2+}} - \log[H_2S] + \log\gamma_{H_2S}}{2} - pH$$

We obtain the following answers:

pH	$[Pb^{2+}]$ M
6	2.16×10^{-9}
5	2.16×10^{-8}
4	2.16×10^{-7}

5. Find $\Delta\bar{G}$ for the reaction:

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

Which side of the reaction is favored under standard state conditions? (HINT: use the data in Table 3.3)

The E° for the two reactions is listed in Table 4.3 as -0.13 and -1.18 V respectively. Subtracting one from the other, the E° for this reaction is 1.05 V. According to equ. 4.41a, $\Delta G^\circ = -nFE^\circ$. n will be two since two electrons are exchanged. F is 96,485 J/V. so ΔG° for this reaction is **–202.6 kJ/mol.** The right side of the reaction is favored.

6. What is the $\Delta\bar{G}$ for the reaction:

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

What is the $p\varepsilon^\circ$ for this reaction?

This reaction can be viewed as the difference of two reactions listed in Table 3.3:

$$Cu^{2+} + 2e^- \rightleftarrows Cu \qquad (1)$$
$$-(Cu^+ + e^- \rightleftarrows Cu) \qquad (2)$$
$$Cu^{2+} + e^- \rightleftarrows Cu^+$$

Using equation 3.105, we calculate ΔG for these reactions, and for the net reaction as the difference between the two. We can then use equation 3.105 to calculate ΔG for the net reaction:

Reaction	E (V)	ΔG (kJ)
(1)	0.34	-65.61
(2)	0.52	-50.17
net	-0.18	**17.37**

to calculate pε°, we use equation 3.115, and find **pε°=3.04.**

7. Construct a pε–pH diagram for the following species of sulfur: HSO_4^-, SO_4^{2-}, H_2S, HS^-, and S^{2-} at 25°C and 0.1 MPa. The following free energies of formation should provide sufficient information to complete this task.

species	ΔG_f^o	species	ΔG_f^o
S^{2-}	+85.81	H_2O	-237.19
HS^-	+12.09	H^+	0
H_2S	-27.82	H_2 (g)	0
SO_4^{2-}	-744.54	O_2 (g)	0
HSO_4^-	-755.92		

Values are in kJ/mole, standard state is 25°C and 0.1 MPa. R = 8.314 J/mole-K.

We start by writing the possible reactions between these species. Some general rules for writing these reactions are:

1. Use H^+ and e^- to balance charge
2. Use H_2O and H^+ for dissociation and hydration reactions ($(OH)^-$ may also be used, but it will complicate things slightly in many cases).
3. Write the species involved in the reaction on either side of the equation.
4. First balance the element of principal interest (S in this case).
5. Next balance any oxygen deficit using H_2O.
6. Balance any hydrogen deficit using H^+.
7. Balance any remaining charge deficit using e^-.

Our reactions are:

1.) $S^{2-} + H^+ \rightleftarrows HS^-$ $\log K = \log[S^{2-}]/[HS^-] + pH$

2.) $H^+ + HS^- \rightleftarrows H_2S$ $\log K = \log[H_2S]/[HS^-] + pH$

3.) $8e^- + 10H^+ + SO_4^{2-} \rightleftarrows H_2S + 4H_2O$ $\log K = \log[H_2S]/[SO_4^{2-}] + 10pH + 8p\varepsilon$

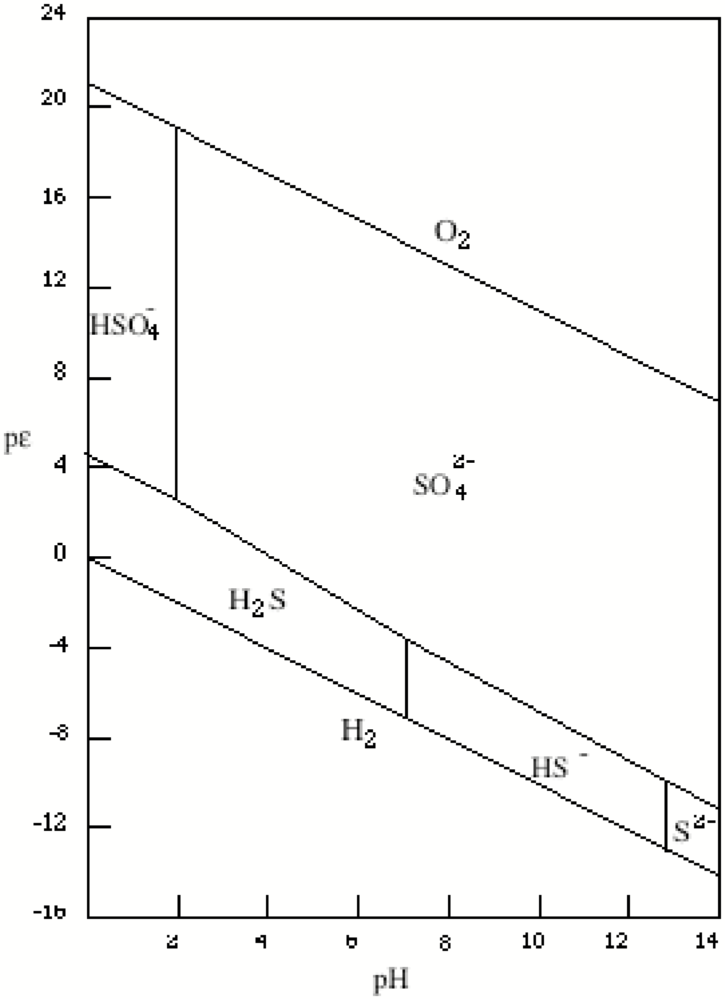
4.) $8e^- + 9H^+ + SO_4^{2-} \rightleftarrows HS^- + 4H_2O$ $\log K = \log[HS^-]/[SO_4^{2-}] + 9pH + 8p\varepsilon$

5.) $H^+ + SO_4^{2-} \rightleftarrows HSO_4^-$

6.) $8e^- + 8H^+ + SO_4^{2-} \rightleftarrows S^{2-} + 4H_2O$

7.) $H_2S + 4H_2O \rightleftarrows HSO_4^- + 9H^+ + 8e^-$

Values of log K can be calculated using
$\ln K = -\Delta G_r/RT$:
1.) 12.92
2.) 6.98
3.) 40.7
4.) 33.7
5.) 1.99
6.) 20.76
7.) -38.68



For equal activities, we have
1.) log K = pH =12.92
2.) log K = pH = 6.99
3.) log K = 10 pH + 8 pε or pε = (log K -10 pH)/8 = 5.08 –1.25 pH
4.) log K = 9 pH + 8 pε or pε = (log K - 9 pH)/8 = 4.210 - 1.13 pH
5.) log K = pH = 1.99
6.) log K = 8 pH + 8 pε or pε = log K/8 - pH = 2.59 – pH
7.) log K =-9pH-8pε or pε = 4.83-1.125pH