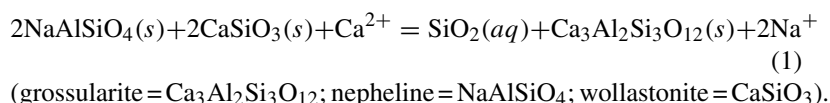
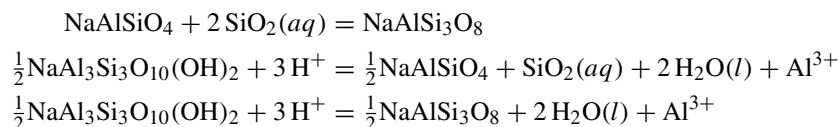


Chapter 16 Problems

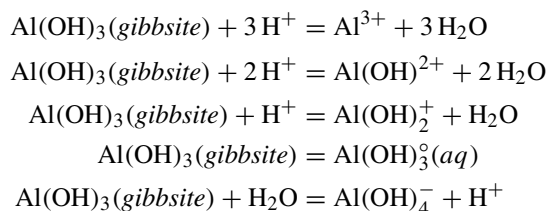
1. Calculate the solubility product of gibbsite. What would be the trivalent aluminum concentration of a solution in equilibrium with gibbsite at a pH of 6.0?
2. (a) What is an appropriate diagram to use to consider the relationship between water compositions and rocks containing nepheline, wollastonite, and grossularite? What is the slope of the grossularite \rightarrow nepheline + wollastonite boundary on this diagram?



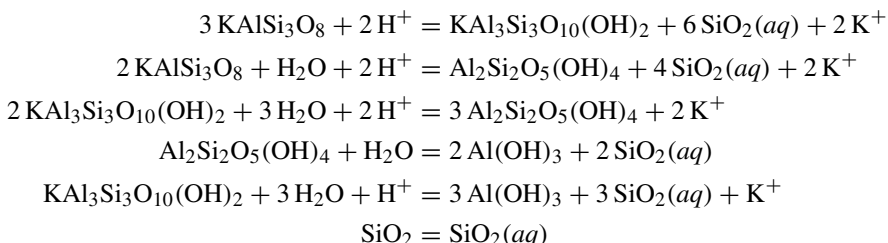
- (b) What is buffered by coexisting grossularite + nepheline + wollastonite?
3. (a) Calculate equilibrium constants at 25°C for the following reactions, where NaAlSiO_4 is nepheline, $\text{NaAlSi}_3\text{O}_8$ is albite, and $\text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ is paragonite:



- (b) Use these equilibrium constants to sketch a diagram showing the stability fields of the three minerals as a function of $\log(a_{\text{Al}^{3+}}/a_{\text{H}^+}^3)$ and $\log a_{\text{SiO}_2(aq)}$. The boundaries of the three phase fields intersect at a point. Calculate the value of the two parameters at this point.
- (c) After sketching this diagram, you become aware that there is yet another sodium aluminum silicate mineral—analclime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), which has been neglected. Without knowing its thermodynamic properties, sketch a revised diagram, showing how it might fit in. Remember that the formulae for nepheline, analclime, and albite can be written with the same amounts of Na and Al but increasing amounts of Si. Note too that for the purposes of this question, you can disregard the H_2O in the analclime formula.
- (d) Calculate and plot the quartz solubility line and the amorphous silica solubility line.
4. (a) Calculate the equilibrium constants for the following equations:



- (b) Derive an equation suitable for plotting each reaction on a graph having \log activity of dissolved Al species and pH as axes.
5. Use SUPCRT92 to obtain equilibrium constants for the following reactions at 100°C on the liquid-vapor curve for water, and draw a full-page graph of $\log(a_{K^+}/a_{H^+})$ vs. $\log a_{SiO_2}(aq)$, including a line indicating the solubility of quartz.

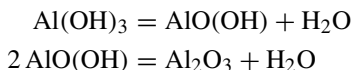


where

KAlSi_3O_8 is microcline
 $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ is muscovite
 $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ is kaolinite
 $\text{Al}(\text{OH})_3$ is gibbsite
 SiO_2 is quartz

6. Consider a hot-spring solution in contact with a rock containing microcline, muscovite, kaolinite, quartz, and other minerals (an altered granite) at 100°C. You have no analysis of this water, but you have your $\log(a_{K^+}/a_{H^+})$ vs. $\log a_{SiO_2}(aq)$ diagram. What does the diagram tell you about the composition of the solution,
- if quartz does not equilibrate with the solution?
 - if quartz equilibrates with the solution?
 - If this hot-spring solution had a pH of 5.0 and was observed or believed to be altering the microcline in the granite to kaolinite, what could you say about the activity and the concentration (in ppm) of K^+ in the solution? (Note for nongeologists: one of the minerals in all granites is quartz).
7. Gibbsite is a principal mineral in bauxite, which is mined as a source of aluminum. Would you expect to find quartz in bauxite? Would you expect to find kaolinite? Why?
8. (a) How would a change in redox conditions affect the reactions in Question 5?
- (b) What would be the potassium ion activity in groundwater in a soil containing microcline, kaolinite, and quartz, at a pH of 5.5, assuming (metastable) equilibrium?
- (c) If you measured the a_{K^+} in such a groundwater and found a different result, what reason would you suspect?

9. Calculate and plot the muscovite–gibbsite and kaolinite–gibbsite boundaries at 298.15 K and 373.15 K in Figure 16.7. You know you have the right answers when these two curves meet the muscovite–kaolinite boundary at a single point.
10. (a) Use the $\log K = 0$ option in SUPCRT92¹ to calculate the univariant temperatures for the reactions



at pressures from 200 to 500 bars at 50 bar intervals. Have the program search the temperature limits 100°C to 500°C.

- (b) You will find that SUPCRT92 thinks that gibbsite is stable up to about 150°C, then dehydrates to diaspore. Note that AlO(OH) has two polymorphs, diaspore and boehmite. Use SUPCRT92 to find if boehmite has a stability field.
11. According to the data in Appendix B, diaspore is more stable than gibbsite in water. Use your knowledge of Gibbs energy relationships to *predict* how substituting diaspore for gibbsite in Figures 16.8 and 16.9 will affect the position of the boundaries with muscovite and kaolinite. Calculate the boundaries to confirm your prediction.
12. Show why the saturation index for calcite must always be greater than that for aragonite.
13. Suppose you have dissolved some fluorite (CaF₂) in water at room temperature and pressure, so that the moles of F in solution is exactly twice the moles of Ca in solution, and the total fluorine molality (moles F per kg water) is 10^{−4}. You have adjusted the pH to 7.0, using something that does not react in any way with calcium or fluorine. You want to know how close the solution is to saturation with fluorite.

To do this you need to know, not the total amounts of Ca and F, but the activities of the Ca²⁺ and F[−] ions. Then you need to know the solubility product of fluorite, and calculate the Saturation Index.

To calculate the activities of the ions, you need to know

¹To do this, at SUPCRT92's second question ("choose file option...") respond with 3 ("build a new file"). Then give the following responses to the questions which appear on the screen:

- one phase region.
- Temperature, pressure.
- y. ("would you like to use univariant curve option?").
- 1. calculate T .
- 200,500,50 (these are the pressure min, max, intervals in bars suggested above).
- 0,100,500 (these are $\log K$, min T , max T , to be searched).
- "send to a file?" (y/n). As you wish, usually n.

The rest is as before ("existing rxn file, build new rxn file?").

- what ions there are in solution (besides Ca^{2+} and F^-), and
- the equilibrium constants for the formation of these ions, at the temperature and pressure you are considering.

The most important species in this case (not all the species known, just the most abundant ones) are CaF^+ and HF , and the reactions for which you need to know the equilibrium constants are



In addition you know that, because these are the only important ions,

$$m_{\text{Ca}^{2+}} + m_{\text{CaF}^+} = 5 \times 10^{-5} \quad (4)$$

$$m_{\text{F}^-} + m_{\text{HF}} = 10^{-4} \quad (5)$$

- Speciate this solution first “by hand”, with a calculator, and then compare with the results you get with the same problem from some speciation computer program. In the following, I assume you are using PHREEQC, but REACT, MINTEQA2, or any other such program will do. Assume all activity coefficients to be 1.0. In this case the approximation is very good, because the solution is very dilute (see the computer output for the calculated activity coefficients).
- Get the equilibrium constants at 25°C for reactions (1) and (2) from the database for PHREEQC, which is `llnl.dat`.
- Using equations (1) to (4), calculate the concentrations of the four main ions.
- Write an input file for PHREEQC to do the same thing, and compare the answers it provides. They should be virtually identical. The input file for PHREEQC is very simple.
- Look at the activity coefficients that PHREEQC has calculated. Why is the activity coefficient for F^- the same as that for CaF^+ ?
- Is Fluorite close to saturation? Calculate the Saturation Index.
 - Calculate the Solubility Product of Fluorite. To do this you can
 - Use SUPCRT92, or
 - Get the Gibbs free energies of Ca^{2+} , F^- , and Fluorite from Appendix B, or
 - Preferably, do both. If they are not exactly the same, then obviously they use different sources of data. If it was important, you would want to track this down.
 - Calculate the Ion activity Product (IAP) $[= a_{\text{Ca}^{2+}} \cdot a_{\text{F}^-}^2]$ in the solution from your speciation calculations, or from the PHREEQC results.

- iii. Calculate the Saturation Index, $SI = \log \frac{IAP}{K_{sp}}$. Compare with the one calculated by PHREEQC.
- (g) Get the same equilibrium constant data from program SUPCRT92, and use these data in program EQBRM or program SPECIES to solve the same problem. Compare the results.

Generally speaking, every program (every choice of database) will give a different answer, so in a sense, no one knows the “right” answer.

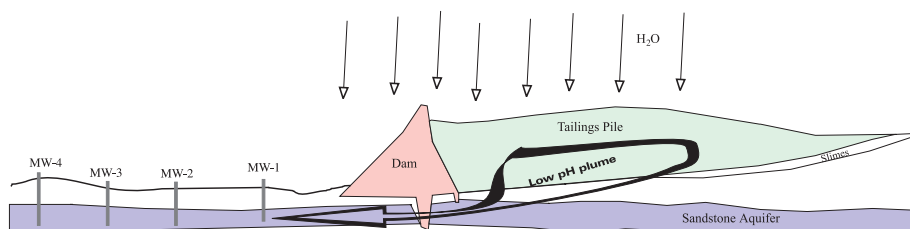


Figure 1: Cross-section through a mine tailings dump which is generating an acid plume in the underlying sandstone.

14. Figure 1 shows an example of a typical AMD (acid mine drainage) setting, in which water draining through a pile of rock containing sulfide minerals becomes extremely acid and iron-rich. This drainage water enters an underlying aquifer and contaminates it for some distance downstream. Four monitoring wells are used to obtain samples of the groundwater.

The aquifer is a sandstone, mostly quartz with a small percentage of other minerals, such as calcite $[CaCO_3]$ and K-feldspar $[KAlSi_3O_8]$. The acidic water tends to dissolve the calcite, and to alter the K-feldspar to kaolinite. It also precipitates ferric hydroxide $[Fe(OH)_3]$ in the sandstone, as the iron oxidizes.

No samples of the aquifer sandstone itself at this site have been examined, but it is suspected that the mineralogy of the aquifer changes in a systematic way downstream.

Analyses of solutions from the four wells are shown in Table 1. these have been speciated by program REACT.

- (a) Calculate the ionic strength of each sample in molal units
- (b) Calculate the activity coefficients of Ca^{2+} , Fe^{3+} , and CO_3^{2-} , using the Davies equation,

$$\log \gamma_{H_i} = \frac{-Az_i^2\sqrt{I}}{1 + \sqrt{I}} + 0.2Az_i^2I$$

- (c) Calculate the Solubility Product of ferric hydroxide, $Fe(OH)_3(s)$.²

²Don't forget that because you know the pH, and you know that $a_{H^+} \cdot a_{OH^-} = 10^{-14}$, you can calculate the a_{OH^-} of each sample.

- (d) Calculate the Saturation Index of calcite, quartz, and of ferric hydroxide in each of the four wells.³
- (e) Plot the Saturation Indices.
- (f) Make a comment on each SI profile.

species pH	MW-1 3.8	MW-2 4.5	MW-3 6.5	MW-4 6.7
Na+	0.1042	0.09159	0.02116	0.01994
SO ₄ --	0.09304	0.09217	0.01644	0.01387
MgSO ₄	0.02076	0.02064	0.003045	0.00141
Mg++	0.02022	0.02038	0.006776	0.003224
Al (SO ₄) 2-	0.01891	0.001718	1.403E-08	
Cl-	0.01522	0.01106	0.01024	0.00755
AlSO ₄ +	0.01355	0.001266	3.178E-08	
NaSO ₄ -	0.009255	0.008018	0.0006026	0.000522
Al+++	0.005244	0.0004949	2.308E-08	
CaSO ₄	0.003889	0.004748	0.005081	0.003967
Ca++	0.003754	0.004644	0.01002	0.007916
FeOH++	0.003411	0.002153	7.460E-08	
Fe (OH) 2+	0.001742	0.004922	2.460E-05	6.390E-06
K+	0.001365	0.001594	0.000442	0.0002955
Mn++	0.0006491	0.0006886	4.223E-06	6.005E-06
MnSO ₄	0.0005561	0.0005624	1.711E-06	2.347E-06
SiO ₂ (aq)	0.0005513	0.0004912	0.0001613	0.0001231
Fe+++	0.0003474	5.278E-05	6.000E-06	6.00E-08
HSO ₄ -	0.0003293	6.077E-05	1.730E-07	
O ₂ (aq)	0.0002736	0.0002899	0.0003161	0.0003309
KSO ₄ -	0.0001691	0.0001963	1.831E-05	1.137E-05
MgCl+	0.0001607	0.0001246	5.416E-05	2.099E-05
CO ₃ --	1.00E-08	1.00E-07	2.918E-06	2.350E-06

Table 1: Speciation by program REACT of water samples from the four monitoring wells. Units are molality. Sulfate has been adjusted for charge balance. The species are printed as they normally appear on computer output. The charge is indicated by the number of + or - signs; e.g., Fe (OH) 2+ has a charge of +1.

³Because quartz does not have a Solubility Product, its SI is simply the log of the SiO₂(aq) molality of the fluid divided by the equilibrium molality of SiO₂(aq) at the same *T*.