

Chapter 16 Answers

1. $\text{Al}(\text{OH})_3(\text{gibbsite}) = \text{Al}^{3+} + 3 (\text{OH})^-$.
 $\log K_{sp} = -34.75$.
 $a_{\text{Al}^{3+}} = 10^{-10.75}$. (Don't forget that $a_{\text{H}^+} \cdot a_{\text{OH}^-} = 10^{-14}$.)
2. (a) The reaction given suggests $\log(a_{\text{Na}^+}^2/a_{\text{Ca}^{2+}})$ vs. $\log a_{\text{SiO}_2(aq)}$. Slope = -1 .
 (b) Only the ratio $(a_{\text{Na}^+}^2 a_{\text{SiO}_2(aq)} / a_{\text{Ca}^{2+}})$ is buffered. If quartz is present, then the ratio $(a_{\text{Na}^+}^2 / a_{\text{Ca}^{2+}})$ is buffered.
3. (b) $\log(a_{\text{Al}^{3+}}/a_{\text{H}^+}^3) = 6.506$, $\log a_{\text{SiO}_2(aq)} = -5.518$.
4. (b)

$$\begin{aligned}\log a_{\text{Al}^{3+}} &= -3 \text{ pH} + 7.23 \\ \log a_{\text{Al}(\text{OH})^{2+}} &= -2 \text{ pH} + 2.253 \\ \log a_{\text{Al}(\text{OH})_2^+} &= -\text{pH} + 2.903 \\ \log a_{\text{Al}(\text{OH})_3^0} &= -9.53 \\ \log a_{\text{Al}(\text{OH})_4^-} &= \text{pH} - 14.932\end{aligned}$$

5. The diagram can be drawn just as in Chapter 16. It is interesting to note, however, that you could use appropriate versions of the PHREEQC input file used in the Phase Rule problem in Chapter 11 to calculate the position of the two three-phase intersection points (Kspar-muscovite-kaolinite) and (gibbsite-muscovite-kaolinite). Drawing lines through these points with the appropriate slopes then generates the diagram. You can get the values of a_{K^+} , a_{H^+} , and $a_{\text{SiO}_2(aq)}$ from the output and calculate the points, or you could add a few lines to the file and have PHREEQC provide the data directly. Setting the temperature to 100°C then allows a direct comparison with Figure 16.8 (see input file triple.in). Database lnl.dat uses a lot of SUPCRT92 data, so the comparison is very good.
6. This diagram represents equilibrium conditions among pure minerals. If the natural system (in this case granite and hot-spring water) is not near equilibrium, then the solution composition will not fall on the mineral field boundaries, and there may be too many minerals (the phase rule is not obeyed; see Chapter 11). In this case, with four components (K_2O , Al_2O_3 , SiO_2 , H_2O) and two degrees of freedom (T and P), there should be no more than four phases coexisting, that is, three minerals plus water. Therefore the four-mineral granite mentioned, plus water, cannot fit the model. This is also shown by the diagram, in which not more than three minerals can coexist.

Nevertheless, if a solution having values of $\log(a_{\text{K}^+}/a_{\text{H}^+})$ and $\log a_{\text{SiO}_2}$, which fall in the kaolinite field, is in contact with microcline, we can predict that microcline will react to form kaolinite and that the solution composition will move towards the microcline-kaolinite boundary. Most groundwaters do in fact plot in the kaolinite field, which is why feldspars are unstable in the weathering environment.

- (a) i. If quartz *and the other minerals* do not equilibrate with the solution, we can say little, except that the solution composition will not be on the quartz saturation line, except by accident. At low temperatures ($< \sim 150^\circ\text{C}$) solutions are quite often supersaturated and sometimes undersaturated with respect to quartz. At higher temperatures, saturation with quartz is the rule, and silica content may even be used as a geothermometer. However, if we assume that quartz is the only recalcitrant mineral, then the solution composition should migrate toward the intersection of the microcline, muscovite, and kaolinite fields.
- ii. If quartz does equilibrate, then the solution composition lies on the quartz saturation line, but we can say little else. One of the other three minerals (either microcline or kaolinite) must disappear before equilibrium can be achieved. If microcline disappears, the solution could equilibrate at the muscovite–kaolinite–quartz intersection.
- iii. The answer depends on what stable or metastable assemblage you assume would exist. If, for example, you assume that Kspar changes metastably to kaolinite while at equilibrium with muscovite, $a_{\text{K}^+} \leq 10^{-2.45}$. Other “correct” answers are possible.

You also can say nothing about the mineral *proportions*, even at equilibrium. That is, it makes no sense to say “the granite would be mostly microcline, with some muscovite and kaolinite.” If microcline is present in the system, its activity in the model is 1.0, whether it makes up 1% or 99% of the mineral mass present.

7. You would not expect to find much quartz in bauxite. Any you did see should be in the process of dissolving. Kaolinite could be present at equilibrium with gibbsite, but it might be disappearing too, if meteoric water with essentially zero silica is flowing through the bauxite.
8. (a) redox conditions have no effect.
(b)



$$\log K = 12.171$$

$$\log a_{\text{K}^+} = -4.72$$

- (c) lack of metastable equilibrium, possibly poor thermodynamic data.

13. The exact answers for hand calculation are:

Ca^{++}	4.9956e-5
F^-	9.9989e-5
HF	1.5133e-8
CaF^+	4.3504e-8

Activity coefficients from PHREEQC are:

Ca^{++}	0.9462
F^{-}	0.9863
HF	1.0
CaF^{+}	0.9863

14. Answers are in spreadsheet SI.xls.