

## Chapter 9 Answers

1.  $\log K = 143.29$ .  $\log f_{\text{CH}_4} = -145.4$  bar, equivalent to zero molecules per liter. Atmospheric  $\text{CH}_4$  is continuously produced by life processes and is obviously not at equilibrium with atmospheric oxygen.
2. The idea was to see that  $\Delta_r G^\circ (\text{J}) = -168600 + 75.729 T$  could be compared to  $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$ , giving  $\Delta_r H^\circ = -168.60 \text{ kJ mol}^{-1}$ ,  $\Delta_r S^\circ = -75.729 \text{ J deg}^{-1} \text{ mol}^{-1}$ .  $f_{\text{O}_2, 600\text{C}} = 10^{-12.26}$  bar.
3.  $f_{\text{H}_2\text{O}, 25\text{C}} = 10^{-1.499}$  bar, or 0.0317 bar.  
 $f_{\text{H}_2\text{O}, 100\text{C}} = 1.123$  bar.
4.  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}(s) = \text{Al}_2\text{O}_3(s) + \text{H}_2\text{O}(g)$ .  $\log K = -5.415$ .

$$0.0317 > 10^{-5.4}$$

and so diaspoire is stable. Or use

$$\Delta_r G^\circ + RT \ln Q = 30908 + 5708.04 \log(0.0317)$$

which is positive, and so diaspoire is stable.

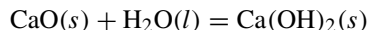
5.  $m_{\text{H}_4\text{SiO}_4} = 10^{-3.120}$ .
6.  $\log m_{\text{SiO}_2(aq)} = -5.83$ . at  $25^\circ\text{C}$ .
7. (a)  $\Delta_r G^\circ = -73070 \text{ J}$ . This shows that the reaction will indeed go in the direction of producing calcite in the cement blocks, at least if the  $\text{CO}_2$  pressure is 1 bar, and the other phases are pure, and for  $\text{CO}_2$  pressures down to that calculated in part (b).

(b)

$$\begin{aligned} \log K &= 73070 / (2.30259 \times 8.31451 \times 298.15) \\ &= 12.801 \\ K &= 6.33 \times 10^{12} \\ &= \frac{a_{\text{H}_2\text{O}} a_{\text{CaCO}_3}}{a_{\text{Ca}(\text{OH})_2} a_{\text{CO}_2}} \\ &= 1/f_{\text{CO}_2} \\ f_{\text{CO}_2} &= 10^{-12.80} \text{ bar} \\ &= 1.58 \times 10^{-13} \text{ bar} \end{aligned}$$

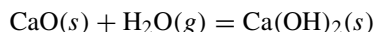
This is the fugacity or partial pressure of  $\text{CO}_2$  in equilibrium with both portlandite and calcite at  $25^\circ\text{C}$ . Any greater  $\text{CO}_2$  pressure will cause formation of calcite from portlandite. Any lesser pressure will cause formation of portlandite from calcite plus water. However, this is a very low value of fugacity, and so virtually any  $\text{CO}_2$  would react with portlandite.

- (c) The reaction to write is



for which  $\Delta_r G^\circ = -57.331 \text{ kJ}$ . This means, with no ambiguity, that CaO and water are not stable together. And, as water is present, CaO cannot be. Or, in other words, if CaO happened to be there, it would react with water to form portlandite until it was gone. Note that CaO and  $\text{Ca}(\text{OH})_2$  could theoretically coexist in the absence of water. However, as shown in part (d), it would have to be an extremely dry environment.

- (d) The reaction for this question is the same as the last one, *except* that the water must be gaseous, not liquid, because we want to calculate a water fugacity, not a water mole fraction. Only gas activities are in the form of fugacities or partial pressures. Thus the reaction is



$$\begin{aligned} \log K &= 65888 / (2.30259 \times 8.31451 \times 298.15) \\ &= 11.543 \\ K &= 3.49 \times 10^{11} \\ &= \frac{a_{\text{Ca}(\text{OH})_2}}{a_{\text{CaO}} a_{\text{H}_2\text{O}(g)}} \\ &= 1/f_{\text{H}_2\text{O}} \\ f_{\text{H}_2\text{O}} &= 10^{-11.54} \text{ bar, or} \\ &= 2.86 \times 10^{-12} \text{ bar} \end{aligned}$$

This is the fugacity or partial pressure of water vapor in equilibrium with CaO and portlandite. As in Question (b), it is a very low value. Most vacuum pumps cannot produce pressures this low. Therefore virtually any moisture in the air will cause lime to hydrate. Or you could use lime in a desiccator to produce extremely dry air.

- (e) There are at least three ways to do this. They all give about the same answer.

$$\Delta_r H^\circ = -113151 \text{ J.}$$

$$\Delta_r S^\circ = -134.32 \text{ J.}$$

$$\begin{aligned} \log K_{423} &= \log K_{298} + \frac{-113151}{(2.30259 \times 8.31451)} \left( \frac{1}{423.15} - \frac{1}{298.15} \right) \\ &= 12.80 - 5.856 \\ &= 6.94 \\ K &= 10^{6.94} \\ &= 8.71 \times 10^6 \end{aligned}$$

The reaction will be reversed when a temperature is reached at which  $\Delta_r G^\circ = 0$ , or  $\log K_T = 0$ . To find this  $T$ , write

$$\begin{aligned} 0 &= \log K_{298} + \frac{-113151}{(2.30259 \times 8.31451)} \left( \frac{1}{T} - \frac{1}{298.15} \right) \\ T &= 841.6 \text{ K} \\ &= 568^\circ\text{C} \end{aligned}$$

Or

$$\begin{aligned} \Delta_r G_T^\circ &= \Delta_r H_{298}^\circ - T \cdot \Delta_r S_{298}^\circ \\ &= -113151 - 423.15 \times (-134.32) \\ &= -56313.5 \text{ J} \end{aligned}$$

Then

$$\begin{aligned} \log K_{423} &= \frac{-(-56313.5)}{2.30259 \times 8.31451 \times 423.15} \\ &= 6.95 \end{aligned}$$

and

$$\begin{aligned} \Delta_r G_T^\circ - \Delta_r G_{298}^\circ &= -\Delta_r S_{298}^\circ (T - 298.15) \\ 0 - (-73070) &= -(-134.32)(T - 298.15) \\ T &= 842.2 \text{ K} \\ &= 569^\circ\text{C} \end{aligned}$$

Note that in doing this calculation we have ignored the fact that liquid water cannot exist at 1 bar at this high temperature. If we were really interested in this reaction at high  $T$ , we would switch to  $\text{H}_2\text{O}(g)$ , which *can* exist at 1 bar at high  $T$ . Also, we would have to check whether in fact portlandite was stable at this  $T$ . It is possible that the lime–portlandite reaction would reverse at high  $T$ , making  $\text{CaO}$  more stable than  $\text{Ca}(\text{OH})_2$ , even in the presence of water at 1 bar.

This raises the general point that there are at least two distinct aspects to doing calculations of this type. One is learning the mechanics—getting numbers from tables and correctly calculating a number for a *given* reaction. The second, and more difficult, is finding or writing the reaction most appropriate for a given problem. It must not only be balanced, but must fairly closely match what would actually happen. In other words, your model must reflect reality. Thermodynamics allows you to calculate an infinite number of results which, though correct, mean virtually nothing, such as our answer to this question.

8. (a)  $\log K_{150^\circ\text{C}} = 21.76$ .

(b)

$$\begin{aligned}\Delta_r G_{150\text{C}} &= \Delta_r G_{150\text{C}}^\circ + RT \ln Q \\ &= -176243 + 2.303 \times 423.15 \times 8.315 \log \frac{1 \times 1}{10^{-3} \times 10^{-6}} \\ &= -103332\end{aligned}$$

Negative, so PbS precipitates. Or calculate the equilibrium  $a_{\text{Pb}^{2+}}$  from  $K$ , and note that it is less than  $10^{-6}$ , and so PbS must precipitate.

(c)  $a_{\text{Pb}^{2+}} = 10^{-9.31}$ , PbS still precipitates.

(d)  $\log K_{sp} = -7.74$ .  $a_{\text{Pb}^{2+}} \cdot a_{\text{SO}_4^{2-}} = 10^{-12.31}$ , and so anglesite does not precipitate.  $a_{\text{Pb}^{2+}}$  would have to be  $> 10^{-4.74}$  to precipitate anglesite.

9.  $2\text{S}(\text{orthorhombic}) = \text{S}_2(\text{g})$ .

$$f_{\text{S}_2} = 10^{-12.15}.$$

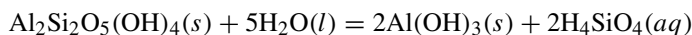
10.  $\log K = a_{\text{H}^+}^4 / a_{\text{Zn}^{2+}}^2 = -17.84$ . At  $\text{pH} = 5.0$ ,  $a_{\text{Zn}^{2+}}$  at equilibrium is 0.083. So if  $a_{\text{Zn}^{2+}}$  is 0.173, reaction goes to the right, and willemite precipitates. Or

$$\begin{aligned}\Delta_r G &= \Delta_r G^\circ + RT \ln Q \\ &= 101858 + 5708.042 \log \frac{(10^{-5})^4}{(10^{-0.76})^2} \\ &= -3626.6\end{aligned}$$

Negative, reaction goes to the right, and willemite precipitates.

11.  $\log f_{\text{O}_2} = -211.64$  for equilibrium between Ca and CaO, which is so low that metallic Ca never occurs naturally on Earth. Similar calculations and conclusions for BaS(s) and other compounds.

12. The reaction is



The value of  $\Delta_f G^\circ$  for  $\text{Al}(\text{OH})_3$  is one half the tabulated value for  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ .  $m_{\text{H}_4\text{SiO}_4} = 10^{-5.238}$ .

13.  $100 \text{ ppm} = 10^{-2.78} m \text{ SiO}_2$  or  $\text{H}_4\text{SiO}_4$ . At equilibrium,  $a_{\text{H}_4\text{SiO}_4} = 10^{-5.238}$ ; therefore kaolinite is expected.

14.  $\text{CaMg}(\text{CO}_3)_2(\text{s}) + 2\text{SiO}_2(\text{s}) = \text{CaMgSi}_2\text{O}_6(\text{s}) + 2\text{CO}_2(\text{g})$ .

$\Delta_r G^\circ = 55962 \text{ J mol}^{-1}$ ; reaction does not proceed.  $f_{\text{CO}_2} = 10^{-4.90}$  at 1 bar,  $25^\circ\text{C}$ .  $f_{\text{CO}_2} = 1$  bar at  $194^\circ\text{C}$ .

15.  $m_{\text{H}_2\text{S}} = 0.0991$  at  $25^\circ\text{C}$ , 0.020 at  $100^\circ\text{C}$ .

16. (a)  $m_{\text{SiO}_2} = 10^{-3.029}$ .

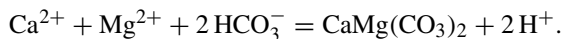
(b)  $\Delta_f G_{\text{H}_4\text{SiO}_4(\text{aq})}^\circ = -1302554 \text{ J mol}^{-1}$ ;  $\Delta_f G_{\text{SiO}_2(\text{aq})}^\circ = -828246 \text{ J mol}^{-1}$ .

17. (a)  $\text{H}_2\text{S}(aq) = \text{H}^+ + \text{HS}^-$ ;  $\log K_1 = -6.992$ .  
 $\text{HS}^- = \text{H}^+ + \text{S}^{2-}$ ;  $\log K_2 = -12.915$ . Overall,  $K = K_1 K_2 = 10^{-19.907}$ .  
(c)  $\text{PbS}(s) = \text{Pb}^{2+} + \text{S}^{2-}$ ;  $\log K_{sp} = -28.043$ .  
 $m_{\text{Pb}^{2+}} = 10^{-16.136}$ .
18.  $\text{CH}_3\text{OOH}(aq) = \text{CH}_3\text{OO}^- + \text{H}^+$ .  $\log K_{25\text{C}} = -4.757$ .  $\log K_{100\text{C}} = -4.783$ .
19.  $(f_{\text{NO}_2}^2/f_{\text{N}_2\text{O}_4}) = 0.148$ ;  $f_{\text{NO}_2} + f_{\text{N}_2\text{O}_4} = 1.0$  bar; so  $f_{\text{NO}_2} = X_{\text{NO}_2} = 0.318$ ;  
 $f_{\text{N}_2\text{O}_4} = X_{\text{N}_2\text{O}_4} = 0.682$ .
20.  $\text{CaCO}_3(\text{calcite}) + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$ .

$$\begin{aligned}\Delta_r G &= \Delta_r G^\circ + RT \ln Q \\ &= -11560 + 5708.042 \log \left( \frac{10^{-6} \times 0.09}{10^{-8}} \right) \\ &= -6113.14 \text{ J}\end{aligned}$$

Negative, therefore calcite will not precipitate. Or calculate that

$$IAP = 10^{-9.38} < K_{sp}$$



$$\log K = -3.245.$$

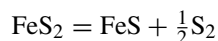
$a_{\text{Mg}^{2+}} = 10^{-4.66}$  at equilibrium, so  $a_{\text{Mg}^{2+}} > 10^{-4.66}$  will precipitate dolomite. This is much less than the actual magnesium ion activity, and so the oceans are supersaturated with dolomite.

21. (a)  $a_{\text{Ca}^{2+}} = 0.249$ .  
(b)  $a_{\text{Ca}^{2+}} = 0.378$ .

With both minerals in the same solution at 1 bar, aragonite will always require a greater  $a_{\text{Ca}^{2+}}$  for equilibrium than will calcite, no matter what the conditions. Therefore, it should continue to dissolve while calcite precipitates until it is used up. This is consistent with the free energy relations, which say that aragonite should change to calcite spontaneously at 1 bar. The dissolution/precipitation simply provides a mechanism to do this.

22. (a)  $m_{\text{O}_2} = 0.00134$ .  
(b)  $K_1 = 10^{213.97}$ ;  $K_2 = 10^{95.099}$ ;  $K_3 = 10^{7.77}$ .  
No amount of aqueous molecular oxygen can equilibrate with pyrite under these conditions.

23. (a) The reaction is



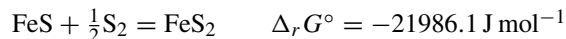
for which

$$\begin{aligned}
 K &= a_{\text{FeS}}(f_{\text{S}_2})^{0.5} \\
 &= 0.46 \times (10^{-1.95})^{0.5} \\
 &= 0.04872 \\
 \ln K &= -3.0215
 \end{aligned}$$

then

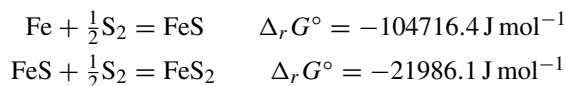
$$\begin{aligned}
 \Delta_r G^\circ &= -RT \ln K \\
 &= -8.31451 \times 875.15 \times (-3.0215) \\
 &= 21986.1 \text{ J mol}^{-1}
 \end{aligned}$$

and for the opposite reaction,



(b) The pyrrhotite in this  $\Delta_r G^\circ$  term is stoichiometric FeS, *not* Fe<sub>0.92</sub>S, because the calculated  $\Delta G^\circ$  is between standard states.

(c) Given



then adding the reactions,



(d) All products (pyrite) and reactants (Fe and S<sub>2</sub>(g)) are at the same temperature, so this is a traditional  $\Delta_f G^\circ$ . This is confirmed by the fact that the apparent  $\Delta_a G^\circ$  from SUPCRT92 at 602°C is quite different ( $-216278 \text{ J mol}^{-1}$ ), while  $\Delta_f G^\circ$  from the RHF tables<sup>1</sup> is about the same ( $-140641 \text{ J mol}^{-1}$  at 800 K,  $-120936 \text{ J mol}^{-1}$  at 900 K). To make an exact comparison, get the heat capacity equations for Fe, S<sub>2</sub>(g) and pyrite from the Tables and use them to calculate  $\Delta_f G^\circ_{875}$ . The equation relating their coefficients to  $\Delta_f G^\circ$  is given in Anderson and Crerar (1993), Appendix B.

24. (a)  $f_{\text{CO}_2} = 135$  bars.

(b) One way would be to use the fugacity of pure CO<sub>2</sub> at 749 K, 2 kbar, and assume the Lewis fugacity Rule (equation (8.14)).

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<sup>1</sup>Robie, R.A., Hemingway, B.S., and Fisher, J.R., 1978, Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (10<sup>5</sup> Pascals) Pressure and at Higher Temperatures. U.S. Geol. Survey Bull. 1452, 456 pp.