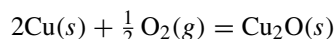


## Chapter 9 Problems

1. Write an equation for the reaction of methane and oxygen to give carbon dioxide and liquid water. Calculate the equilibrium constant. Given the partial pressures of  $\text{CO}_2(g)$  and oxygen (Chapter 7, Question 4), what is the equilibrium amount of methane in the atmosphere? Compare with the amount in the table. Why the discrepancy?
2. The standard Gibbs energy change for the reaction

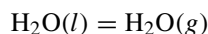


as a function of temperature is sometimes given as

$$\Delta_r G^\circ \text{ J mol}^{-1} = -168600 + 75.729 T (\text{K})$$

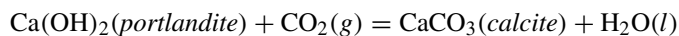
What are the  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  of this reaction? (You can tell this directly from the equation given, or you can work it out from the tables, or both). What is the  $f_{\text{O}_2}$  in equilibrium with Cu and  $\text{Cu}_2\text{O}$  at  $600^\circ\text{C}$ ?

3. Calculate the vapor pressure of water at 25 and  $100^\circ\text{C}$ . The reaction is simply



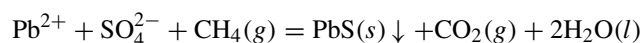
4. Write a reaction for the dehydration of diaspore to form corundum and gaseous water (water vapor). Calculate the equilibrium constant. If the fugacity of water in the atmosphere is controlled by evaporation as in Question 3, which way will the reaction go?
5. Calculate the solubility of amorphous silica (i.e., the concentration of  $\text{H}_4\text{SiO}_4$ ) in a solution having a water activity of 0.9.
6. Calculate the molality of silica ( $m_{\text{H}_4\text{SiO}_4}$  or  $m_{\text{SiO}_2(aq)}$ ) in water that equilibrates with nepheline and albite at  $25^\circ\text{C}$ , 1 bar. Do the same for  $100^\circ\text{C}$ , 1 bar.
7. In a recent large-scale experiment,  $\text{CO}_2(g)$  produced from the oxidation of organic material in soils seemed to be far less than expected. Then someone suggested that perhaps cement blocks, which contain  $\text{Ca}(\text{OH})_2$  (*portlandite*) and were enclosing the experiment, were soaking up  $\text{CO}_2(g)$  in the form of calcite.

- (a) Show that this is indeed possible from the reaction

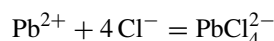


- (b) What would be the equilibrium partial pressure of  $\text{CO}_2(g)$  in a room containing both calcite and portlandite?
- (c) Show that in the presence of liquid water, lime  $[\text{CaO}(s)]$  would not be expected in the cement blocks.

- (d) What would be the partial pressure of water at equilibrium with lime (CaO) and portlandite?
- (e) What is the equilibrium constant of the reaction in part (a) at 150°C? At what temperature would the reaction direction be reversed, i.e., the temperature above which calcite could not form from portlandite and CO<sub>2</sub>(g) at atmospheric pressure?
8. One hypothesis for the formation of lead ores, in which the lead occurs as galena (PbS), is that hot, saline solutions carrying both lead ions (Pb<sup>2+</sup>) and sulfate ions (SO<sub>4</sub><sup>2-</sup>), circulating in the crust of the Earth, pass through a rock unit containing methane [CH<sub>4</sub>(g)], produced by the heating of organic material in the sedimentary rocks. The reaction could be written



- (a) Calculate the equilibrium constant for this reaction at 150°C.
- (b) Consider the solution as it enters the methane-bearing rock. If the fugacity of both methane and CO<sub>2</sub> is 1 bar, the sulfate ion concentration is 0.001 molal, and the lead ion concentration is 10<sup>-6</sup> molal, will galena precipitate? Assume that activity coefficients are 1.0 and that the water is sufficiently pure to have unit activity.
- (c) After doing this calculation, you realize that probably the figure of 10<sup>-6</sup> molal for lead refers to the *total* lead in solution, not the lead ion itself. In a saline solution, most of the lead will be carried as PbCl<sub>4</sub><sup>2-</sup>, and the relation of this to the lead ion is

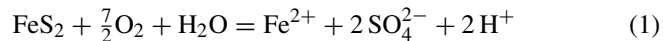


If the solution is 3 molal in NaCl ( $a_{\text{Cl}^-} = 3$ ), and the activity of PbCl<sub>4</sub><sup>2-</sup> is 10<sup>-6</sup>, what is  $a_{\text{Pb}^{2+}}$ ? Does this change your previous answer? Do the calculation for 25°C, not 150°C.  $\Delta_f G^\circ$  for aqueous PbCl<sub>4</sub><sup>2-</sup> is -557560 J mol<sup>-1</sup> at 25°C.

- (d) Then it occurs to you that with so much lead and sulfate in solution, maybe anglesite (PbSO<sub>4</sub>) should precipitate. Test this idea by calculating the solubility product for anglesite, assuming that the sulfate activity remains at 0.001. What lead ion activity would be required to precipitate anglesite? Use 25°C.
9. Calculate the vapor pressure (i.e., the  $f_{\text{S}_2}$ ) of orthorhombic sulfur at 50°C.
10. If a solution having a zinc concentration of 0.173 *m* at a *pH* of 5.0 was in contact with quartz, would willemite [Zn<sub>2</sub>SiO<sub>4</sub>(s)] precipitate? A relevant reaction would be
- $$2\text{Zn}^{2+} + \text{SiO}_2(\text{quartz}) + 2\text{H}_2\text{O}(l) = \text{Zn}_2\text{SiO}_4(s) + 4\text{H}^+$$
11. Calculate the fugacity of oxygen in equilibrium with solid Ca and solid CaO (lime). Why is pure solid Ca never found in the Earth's crust?

12. Suppose that meteoric water that is percolating down through a bauxite deposit comes to equilibrium with gibbsite and kaolinite. What would be the silica concentration in the water?
13. At another bauxite deposit close to the one in the last question, the groundwater in the bauxite is also in contact with granite boulders containing quartz and feldspars. The weathering of these boulders results in a silica  $[\text{SiO}_2(aq)]$  concentration in the groundwater of 100 ppm. Would you expect to find kaolinite or gibbsite in the bauxite? Or is there another aluminum oxide or hydroxide you would expect?
14. When carbonate rocks are metamorphosed, dolomite  $[\text{CaMg}(\text{CO}_3)_2]$  and quartz  $[\text{SiO}_2]$  often react to form diopside  $[\text{CaMg}(\text{SiO}_3)_2]$  and carbon dioxide. Write a balanced reaction for this process, and show whether this reaction should proceed at  $25^\circ\text{C}$  or not. If the three minerals were at equilibrium together at  $25^\circ\text{C}$ , what would be the fugacity of  $\text{CO}_2$ ? At what temperature would  $f_{\text{CO}_2}$  become equal to 1 bar? Sketch  $G$  vs.  $T$  for this system, showing two curves, one for diopside +  $\text{CO}_2$  and one for dolomite + quartz.
15. Calculate the solubility of  $\text{H}_2\text{S}$  in water if  $f_{\text{H}_2\text{S}} = 1$  bar, at  $25^\circ\text{C}$  and at  $100^\circ\text{C}$ .
16. (a) Calculate the concentration of silica in the ocean, assuming that it is controlled by the solubility of radiolaria shells, which are made of amorphous silica.  
(b) The  $\text{SiO}_2$  concentration in sea-water is actually about 7 ppm. Use this number to calculate the Gibbs energy of formation of  $\text{H}_4\text{SiO}_4(aq)$  and of  $\text{SiO}_2(aq)$  from the elements, assuming equilibrium with amorphous silica.
17. (a) Calculate the first and second ionization constants of aqueous hydrogen sulfide  $[\text{H}_2\text{S}(aq)]$ . Combine these to get the equilibrium constant for the reaction
 
$$\text{H}_2\text{S}(aq) = 2 \text{H}^+ + \text{S}^{2-}$$
 (b) Calculate this equilibrium constant directly. It should be identical.  
(c) Use the solubility product of  $\text{PbS}$  and this equilibrium constant to calculate the lead ion content of a solution saturated with hydrogen sulfide at  $25^\circ\text{C}$ , 1 bar ( $m_{\text{H}_2\text{S}(aq)} = 0.1$ ) and a  $p\text{H}$  of 4.0. Assume all activity coefficients are 1.0.
18. Calculate the ionization constant of acetic acid at 25 and  $100^\circ\text{C}$ .
19. Calculate the proportions (mole fractions) of an equilibrium mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  gases at  $25^\circ\text{C}$ , 1 bar.
20. A sample of seawater has a bicarbonate concentration of  $0.09\text{ m}$  ( $\approx a_{\text{HCO}_3^-}$ ), a  $p\text{H}$  of 8.0, and a calcium ion activity ( $a_{\text{Ca}^{2+}}$ ) of  $10^{-6}$ . Will calcite precipitate? What activity of  $\text{Mg}^{2+}$  would be required to precipitate dolomite?

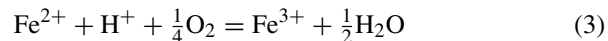
21. Calculate the calcium ion concentration in a solution having  $a_{\text{H}_2\text{CO}_3(aq)} = 0.1$  at a pH of 5.0, and in equilibrium with (a) calcite; (b) aragonite. What should happen if this same solution was in contact with both minerals? Is this consistent with their values of  $\Delta_f G^\circ$ ?
22. (a) Calculate the oxygen concentration in water in equilibrium with the atmosphere ( $f_{\text{O}_2} = 0.21$  bar) under standard conditions (25°C, 1 atm).  
 (b) There are two main reactions in the oxidation of pyrite at the Earth's surface. One of course involves oxygen,



The other involves ferric iron as oxidant,



The ferric iron in this reaction is produced from the oxidation of ferrous iron by oxygen,



All three reactions, along with countless others, proceed simultaneously in the mine waste environment. Calculate the equilibrium constant for each of these reactions using an aqueous standard state for oxygen [ $\text{O}_2(aq)$ ]. What do you conclude about the equilibrium level of molecular oxygen ( $\text{O}_2$ ) in groundwaters in contact with pyrite and dissolved ferrous and ferric iron?

23. (a) The fugacity of  $\text{S}_2$  in equilibrium with pyrite and pyrrhotite at 602°C, 1 bar is  $10^{-1.95}$  bar. The pyrrhotite in this equilibrium is  $\text{Fe}_{0.92}\text{S}$ , which may be considered as a solid solution composition in the system  $\text{FeS} - \text{S}_2$ . The activity of  $\text{FeS}$  in this pyrrhotite is 0.46 based on a standard state of pure stoichiometric  $\text{FeS}$  at the same  $P$  and  $T$ . The pyrite is pure stoichiometric  $\text{FeS}_2$ . Calculate  $\Delta_r G^\circ$  for the reaction in which pyrite breaks down to form pyrrhotite and  $\text{S}_2$  gas at this  $P$ ,  $T$ .  
 (b) Is the pyrrhotite involved in this  $\Delta_r G^\circ$  term  $\text{FeS}$  or  $\text{Fe}_{0.92}\text{S}$ ?  
 (c) The fugacity of sulfur in equilibrium with iron and stoichiometric  $\text{FeS}$  at 602°C, 1 atm. is  $10^{-12.5}$  atm. Calculate the standard Gibbs energy of formation of pyrite from its elements at 602°C, 1 atm.  
 (d) Is this a traditional or an apparent Gibbs energy of formation?

24. A wollastonite-bearing contact metamorphic zone is observed adjacent to a granite which has intruded a quartz-bearing limestone horizon. Heat-flow calculations indicate that the maximum temperature achieved at a given distance from the contact is given by

$$T = 760 - 7.66d + 0.0396d^2$$

where  $T$  is the temperature in °C, and  $d$  is the distance in feet. Stratigraphic considerations put the pressure at the time of intrusion at 2000 bars.

- (a) If the contact zone is 50 feet wide, what was the  $f_{\text{CO}_2}$  in the pore fluid of the limestone?
- (b) If you assume that the pore fluid was a  $\text{H}_2\text{O} - \text{CO}_2$  solution, what do you need to know to calculate its composition?