

## Complex ions

- › Complex ions consist of a metal ion surrounded by attached ligands
  - › A ligand is a Lewis base
  - › The number of ligands is called the coordination number, which is commonly 2, 4, or 6
- › Complex ion equilibria in solution are described by formation (stability) constants
- › The formation of complex ions can be used to selectively dissolve solids in the qualitative analysis scheme

Review questions *Answers to the Review Questions can be found on the Student website (accessible from [www.cengagebrain.com](http://www.cengagebrain.com))*

1. To what reaction does the solubility product constant,  $K_{sp}$ , refer? Table 16.1 lists  $K_{sp}$  values for several ionic solids. For any of these ionic compounds, you should be able to calculate the solubility. What is the solubility of a salt, and what procedures do you follow to calculate the solubility of a salt? How would you calculate the  $K_{sp}$  value for a salt given the solubility?
2. Under what circumstances can you compare the relative solubilities of two salts directly by comparing the values of their solubility products? When can relative solubilities not be compared based on  $K_{sp}$  values?
3. What is a common ion and how does its presence affect the solubility?
4. List some salts whose solubility increases as the pH becomes more acidic. What is true about the anions in these salts? List some salts whose solubility remains unaffected by the solution pH. What is true about the anions in these salts?
5. What is the difference between the ion product,  $Q$ , and the solubility product,  $K_{sp}$ ? What happens when  $Q > K_{sp}$ ?  $Q < K_{sp}$ ?  $Q = K_{sp}$ ?
6. Mixtures of metal ions in aqueous solution can sometimes be separated by selective precipitation. What is selective precipitation? If a solution contained  $0.10\text{ M Mg}^{2+}$ ,  $0.10\text{ M Ca}^{2+}$ , and  $0.10\text{ M Ba}^{2+}$ , how could addition of NaF be used to separate the cations out of solution—that is, what would precipitate first, then second, then third? How could addition of  $K_3PO_4$  be used to separate out the cations in a solution that is  $1.0\text{ M Ag}^+$ ,  $1.0\text{ M Pb}^{2+}$ , and  $1.0\text{ M Sr}^{2+}$ ?
7. Figure 16.2 summarizes the classic method for separating a mixture of common cations by selective precipitation. Explain the chemistry involved with each of the four steps in the diagram.
8. What is a complex ion? The stepwise formation constants for the complex ion  $Cu(NH_3)_4^{2+}$  are  $K_1 \approx 1 \times 10^3$ ,  $K_2 \approx 1 \times 10^4$ ,  $K_3 \approx 1 \times 10^3$ , and  $K_4 \approx 1 \times 10^3$ . Write the reactions that refer to each of these formation constants. Given that the values of the formation constants are large, what can you deduce about the equilibrium concentration of  $Cu(NH_3)_4^{2+}$  versus the equilibrium concentration of  $Cu^{2+}$ ?
9. When  $5\text{ M}$  ammonia is added to a solution containing  $Cu(OH)_2(s)$ , the precipitate will eventually dissolve in solution. Why? If  $5\text{ M HNO}_3$  is then added, the  $Cu(OH)_2$  precipitate re-forms. Why? In general, what effect does the ability of a cation to form a complex ion have on the solubility of salts containing that cation?
10. Figure 16.3 outlines the classic scheme for separating a mixture of insoluble chloride salts from one another. Explain the chemistry involved in the various steps of the figure.

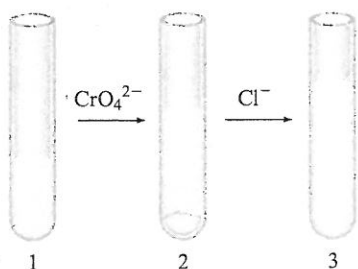
A discussion of the Active Learning Questions can be found online in the Instructor's Resource Guide and on PowerLecture. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

## Active Learning Questions

These questions are designed to be used by groups of students in class.

1. Which of the following will affect the total amount of solute that can dissolve in a given amount of solvent?
  - a. The solution is stirred.
  - b. The solute is ground to fine particles before dissolving.
  - c. The temperature changes.
2. Devise as many ways as you can to experimentally determine the  $K_{sp}$  value of a solid. Explain why each of these would work.
3. You are browsing through the *Handbook of Hypothetical Chemistry* when you come across a solid that is reported to have a  $K_{sp}$  value of zero in water at  $25^\circ\text{C}$ . What does this mean?
4. A friend tells you: "The constant  $K_{sp}$  of a salt is called the solubility product constant and is calculated from the concentrations of ions in the solution. Thus, if salt A dissolves to a greater extent than salt B, salt A must have a higher  $K_{sp}$  than salt B." Do you agree with your friend? Explain.
5. Explain the following phenomenon: You have a test tube with an aqueous solution of silver nitrate as shown in test tube 1 on the following page. A few drops of aqueous sodium chromate solution was added with the end result shown in test tube 2. A

few drops of aqueous sodium chloride solution was then added with the end result shown in test tube 3.



Use the  $K_{sp}$  values in the book to support your explanation, and include the balanced equations. Also, list the ions that are present in solution in each test tube.

- What happens to the  $K_{sp}$  value of a solid as the temperature of the solution changes? Consider both increasing and decreasing temperatures, and explain your answer.
- Which is more likely to dissolve in an acidic solution, silver sulfide or silver chloride? Why?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*, as found on PowerLecture.

## Questions

- For which of the following is the  $K_{sp}$  value of the ionic compound the largest? The smallest? Explain your answer.



- $\text{Ag}_2\text{S}(s)$  has a larger molar solubility than  $\text{CuS}$  even though  $\text{Ag}_2\text{S}$  has the smaller  $K_{sp}$  value. Explain how this is possible.
- Solubility is an equilibrium position, whereas  $K_{sp}$  is an equilibrium constant. Explain the difference.
- The salts in Table 16.1, with the possible exception of the hydroxide salts, generally have one of the following mathematical relationships between the  $K_{sp}$  value and the molar solubility  $s$ .
  - $K_{sp} = s^2$
  - $K_{sp} = 4s^3$
  - $K_{sp} = 27s^4$
  - $K_{sp} = 108s^5$
 For each mathematical relationship, give an example of a salt in Table 16.1 that exhibits that relationship.
- When  $\text{Na}_3\text{PO}_4(aq)$  is added to a solution containing a metal ion and a precipitate forms, the precipitate generally could be one of two possibilities. What are the two possibilities?
- The common ion effect for ionic solids (salts) is to significantly decrease the solubility of the ionic compound in water. Explain the common ion effect.

- Sulfide precipitates are generally grouped as sulfides insoluble in acidic solution and sulfides insoluble in basic solution. Explain why there is a difference between the two groups of sulfide precipitates.
- List some ways one can increase the solubility of a salt in water.
- The stepwise formation constants for a complex ion usually have values much greater than 1. What is the significance of this?
- Silver chloride dissolves readily in  $2\text{ M NH}_3$  but is quite insoluble in  $2\text{ M NH}_4\text{NO}_3$ . Explain.
- If a solution contains either  $\text{Pb}^{2+}(aq)$  or  $\text{Ag}^{+}(aq)$ , how can temperature be manipulated to help identify the ion in solution?

## Exercises

In this section similar exercises are paired.

### Solubility Equilibria

- Write balanced equations for the dissolution reactions and the corresponding solubility product expressions for each of the following solids.
  - $\text{Ag}_2\text{C}_2\text{H}_3\text{O}_2$
  - $\text{Al}(\text{OH})_3$
  - $\text{Ca}_3(\text{PO}_4)_2$
- Write balanced equations for the dissolution reactions and the corresponding solubility product expressions for each of the following solids.
  - $\text{Ag}_2\text{CO}_3$
  - $\text{Ce}(\text{IO}_3)_3$
  - $\text{BaF}_2$
- Use the following data to calculate the  $K_{sp}$  value for each solid.
  - The solubility of  $\text{CaC}_2\text{O}_4$  is  $4.8 \times 10^{-5}\text{ mol/L}$ .
  - The solubility of  $\text{BiI}_3$  is  $1.32 \times 10^{-5}\text{ mol/L}$ .
- Use the following data to calculate the  $K_{sp}$  value for each solid.
  - The solubility of  $\text{Pb}_3(\text{PO}_4)_2$  is  $6.2 \times 10^{-12}\text{ mol/L}$ .
  - The solubility of  $\text{Li}_2\text{CO}_3$  is  $7.4 \times 10^{-2}\text{ mol/L}$ .
- Approximately  $0.14\text{ g}$  nickel(II) hydroxide,  $\text{Ni}(\text{OH})_2(s)$ , dissolves per liter of water at  $20^\circ\text{C}$ . Calculate  $K_{sp}$  for  $\text{Ni}(\text{OH})_2(s)$  at this temperature.
- The solubility of the ionic compound  $\text{M}_2\text{X}_3$ , having a molar mass of  $288\text{ g/mol}$ , is  $3.60 \times 10^{-7}\text{ g/L}$ . Calculate the  $K_{sp}$  of the compound.
- The concentration of  $\text{Pb}^{2+}$  in a solution saturated with  $\text{PbBr}_2(s)$  is  $2.14 \times 10^{-2}\text{ M}$ . Calculate  $K_{sp}$  for  $\text{PbBr}_2$ .
- The concentration of  $\text{Ag}^{+}$  in a solution saturated with  $\text{Ag}_2\text{C}_2\text{O}_4(s)$  is  $2.2 \times 10^{-4}\text{ M}$ . Calculate  $K_{sp}$  for  $\text{Ag}_2\text{C}_2\text{O}_4$ .
- Calculate the solubility of each of the following compounds in moles per liter. Ignore any acid–base properties.
  - $\text{Ag}_3\text{PO}_4$ ,  $K_{sp} = 1.8 \times 10^{-18}$
  - $\text{CaCO}_3$ ,  $K_{sp} = 8.7 \times 10^{-9}$
  - $\text{Hg}_2\text{Cl}_2$ ,  $K_{sp} = 1.1 \times 10^{-18}$  ( $\text{Hg}_2^{2+}$  is the cation in solution.)
- Calculate the solubility of each of the following compounds in moles per liter. Ignore any acid–base properties.
  - $\text{PbI}_2$ ,  $K_{sp} = 1.4 \times 10^{-8}$
  - $\text{CdCO}_3$ ,  $K_{sp} = 5.2 \times 10^{-12}$
  - $\text{Sr}_3(\text{PO}_4)_2$ ,  $K_{sp} = 1 \times 10^{-31}$

29. Cream of tartar, a common ingredient in cooking, is the common name for potassium bitartrate (abbreviated KBT, molar mass = 188.2 g/mol). Historically, KBT was a crystalline solid that formed on the casks of wine barrels during the fermentation process. Calculate the maximum mass of KBT that can dissolve in 250.0 mL of solution to make a saturated solution. The  $K_{sp}$  value for KBT is  $3.8 \times 10^{-4}$ .
30. Barium sulfate is a contrast agent for X-ray scans that are most often associated with the gastrointestinal tract. Calculate the mass of  $\text{BaSO}_4$  that can dissolve in 100.0 mL of solution. The  $K_{sp}$  value for  $\text{BaSO}_4$  is  $1.5 \times 10^{-9}$ .
31. Calculate the molar solubility of  $\text{Mg}(\text{OH})_2$ ,  $K_{sp} = 8.9 \times 10^{-12}$ .
32. Calculate the molar solubility of  $\text{Cd}(\text{OH})_2$ ,  $K_{sp} = 5.9 \times 10^{-11}$ .
33. Calculate the molar solubility of  $\text{Al}(\text{OH})_3$ ,  $K_{sp} = 2 \times 10^{-32}$ .
34. Calculate the molar solubility of  $\text{Co}(\text{OH})_3$ ,  $K_{sp} = 2.5 \times 10^{-43}$ .
35. For each of the following pairs of solids, determine which solid has the smallest molar solubility.
- $\text{CaF}_2(s)$ ,  $K_{sp} = 4.0 \times 10^{-11}$ , or  $\text{BaF}_2(s)$ ,  $K_{sp} = 2.4 \times 10^{-5}$
  - $\text{Ca}_3(\text{PO}_4)_2(s)$ ,  $K_{sp} = 1.3 \times 10^{-32}$ , or  $\text{FePO}_4(s)$ ,  $K_{sp} = 1.0 \times 10^{-22}$
36. For each of the following pairs of solids, determine which solid has the smallest molar solubility.
- $\text{FeC}_2\text{O}_4$ ,  $K_{sp} = 2.1 \times 10^{-7}$ , or  $\text{Cu}(\text{IO}_4)_2$ ,  $K_{sp} = 1.4 \times 10^{-7}$
  - $\text{Ag}_2\text{CO}_3$ ,  $K_{sp} = 8.1 \times 10^{-12}$ , or  $\text{Mn}(\text{OH})_2$ ,  $K_{sp} = 2 \times 10^{-13}$
37. Calculate the solubility (in moles per liter) of  $\text{Fe}(\text{OH})_3$  ( $K_{sp} = 4 \times 10^{-38}$ ) in each of the following.
- water
  - a solution buffered at pH = 5.0
  - a solution buffered at pH = 11.0
38. Calculate the solubility of  $\text{Co}(\text{OH})_2(s)$  ( $K_{sp} = 2.5 \times 10^{-16}$ ) in a buffered solution with a pH of 11.00.
39. The  $K_{sp}$  for silver sulfate ( $\text{Ag}_2\text{SO}_4$ ) is  $1.2 \times 10^{-5}$ . Calculate the solubility of silver sulfate in each of the following.
- water
  - 0.10 M  $\text{AgNO}_3$
  - 0.20 M  $\text{K}_2\text{SO}_4$
40. The  $K_{sp}$  for lead iodide ( $\text{PbI}_2$ ) is  $1.4 \times 10^{-8}$ . Calculate the solubility of lead iodide in each of the following.
- water
  - 0.10 M  $\text{Pb}(\text{NO}_3)_2$
  - 0.010 M  $\text{NaI}$
41. Calculate the solubility of solid  $\text{Ca}_3(\text{PO}_4)_2$  ( $K_{sp} = 1.3 \times 10^{-32}$ ) in a 0.20-M  $\text{Na}_3\text{PO}_4$  solution.
42. Calculate the solubility of solid  $\text{Pb}_3(\text{PO}_4)_2$  ( $K_{sp} = 1 \times 10^{-54}$ ) in a 0.10-M  $\text{Pb}(\text{NO}_3)_2$  solution.
43. The solubility of  $\text{Ce}(\text{IO}_3)_3$  in a 0.20-M  $\text{KIO}_3$  solution is  $4.4 \times 10^{-8}$  mol/L. Calculate  $K_{sp}$  for  $\text{Ce}(\text{IO}_3)_3$ .
44. The solubility of  $\text{Pb}(\text{IO}_3)_2(s)$  in a 0.10-M  $\text{KIO}_3$  solution is  $2.6 \times 10^{-11}$  mol/L. Calculate  $K_{sp}$  for  $\text{Pb}(\text{IO}_3)_2(s)$ .

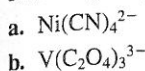
45. Which of the substances in Exercises 27 and 28 show increased solubility as the pH of the solution becomes more acidic? Write equations for the reactions that occur to increase the solubility.
46. For which salt in each of the following groups will the solubility depend on pH?
- $\text{AgF}$ ,  $\text{AgCl}$ ,  $\text{AgBr}$
  - $\text{Pb}(\text{OH})_2$ ,  $\text{PbCl}_2$
  - $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_2)_2$
  - $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{CN})_2$

### Precipitation Conditions

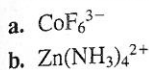
47. What mass of  $\text{ZnS}$  ( $K_{sp} = 2.5 \times 10^{-22}$ ) will dissolve in 300.0 mL of 0.050 M  $\text{Zn}(\text{NO}_3)_2$ ? Ignore the basic properties of  $\text{S}^{2-}$ .
48. The concentration of  $\text{Mg}^{2+}$  in seawater is 0.052 M. At what pH will 99% of the  $\text{Mg}^{2+}$  be precipitated as the hydroxide salt? [ $K_{sp}$  for  $\text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12}$ .]
49. Will a precipitate form when 100.0 mL of  $4.0 \times 10^{-4}$  M  $\text{Mg}(\text{NO}_3)_2$  is added to 100.0 mL of  $2.0 \times 10^{-4}$  M  $\text{NaOH}$ ?
50. A solution contains  $1.0 \times 10^{-5}$  M  $\text{Ag}^+$  and  $2.0 \times 10^{-6}$  M  $\text{CN}^-$ . Will  $\text{AgCN}(s)$  precipitate? ( $K_{sp}$  for  $\text{AgCN}(s)$  is  $2.2 \times 10^{-12}$ .)
51. A solution is prepared by mixing 100.0 mL of  $1.0 \times 10^{-2}$  M  $\text{Pb}(\text{NO}_3)_2$  and 100.0 mL of  $1.0 \times 10^{-3}$  M  $\text{NaF}$ . Will  $\text{PbF}_2(s)$  ( $K_{sp} = 4 \times 10^{-8}$ ) precipitate?
52. A solution contains  $2.0 \times 10^{-3}$  M  $\text{Ce}^{3+}$  and  $1.0 \times 10^{-2}$  M  $\text{IO}_3^{3-}$ . Will  $\text{Ce}(\text{IO}_3)_3(s)$  precipitate? [ $K_{sp}$  for  $\text{Ce}(\text{IO}_3)_3$  is  $3.2 \times 10^{-10}$ .]
53. Calculate the final concentrations of  $\text{K}^+(aq)$ ,  $\text{C}_2\text{O}_4^{2-}(aq)$ ,  $\text{Ba}^{2+}(aq)$ , and  $\text{Br}^-(aq)$  in a solution prepared by adding 0.100 L of 0.200 M  $\text{K}_2\text{C}_2\text{O}_4$  to 0.150 L of 0.250 M  $\text{BaBr}_2$ . (For  $\text{BaC}_2\text{O}_4$ ,  $K_{sp} = 2.3 \times 10^{-8}$ .)
54. A solution is prepared by mixing 75.0 mL of 0.020 M  $\text{BaCl}_2$  and 125 mL of 0.040 M  $\text{K}_2\text{SO}_4$ . What are the concentrations of barium and sulfate ions in this solution? Assume only  $\text{SO}_4^{2-}$  ions (no  $\text{HSO}_4^-$ ) are present.
55. A 50.0-mL sample of 0.00200 M  $\text{AgNO}_3$  is added to 50.0 mL of 0.0100 M  $\text{NaIO}_3$ . What is the equilibrium concentration of  $\text{Ag}^+$  in solution? ( $K_{sp}$  for  $\text{AgIO}_3$  is  $3.0 \times 10^{-8}$ .)
56. A solution is prepared by mixing 50.0 mL of 0.10 M  $\text{Pb}(\text{NO}_3)_2$  with 50.0 mL of 1.0 M  $\text{KCl}$ . Calculate the concentrations of  $\text{Pb}^{2+}$  and  $\text{Cl}^-$  at equilibrium. [ $K_{sp}$  for  $\text{PbCl}_2(s)$  is  $1.6 \times 10^{-5}$ .]
57. A solution contains  $1.0 \times 10^{-5}$  M  $\text{Na}_3\text{PO}_4$ . What is the minimum concentration of  $\text{AgNO}_3$  that would cause precipitation of solid  $\text{Ag}_3\text{PO}_4$  ( $K_{sp} = 1.8 \times 10^{-18}$ )?
58. The  $K_{sp}$  of  $\text{Al}(\text{OH})_3$  is  $2 \times 10^{-32}$ . At what pH will a 0.2-M  $\text{Al}^{3+}$  solution begin to show precipitation of  $\text{Al}(\text{OH})_3$ ?
59. A solution is  $1 \times 10^{-4}$  M in  $\text{NaF}$ ,  $\text{Na}_2\text{S}$ , and  $\text{Na}_3\text{PO}_4$ . What would be the order of precipitation as a source of  $\text{Pb}^{2+}$  is added gradually to the solution? The relevant  $K_{sp}$  values are  $K_{sp}(\text{PbF}_2) = 4 \times 10^{-8}$ ,  $K_{sp}(\text{PbS}) = 7 \times 10^{-29}$ , and  $K_{sp}[\text{Pb}_3(\text{PO}_4)_2] = 1 \times 10^{-54}$ .
60. A solution contains 0.25 M  $\text{Ni}(\text{NO}_3)_2$  and 0.25 M  $\text{Cu}(\text{NO}_3)_2$ . Can the metal ions be separated by slowly adding  $\text{Na}_2\text{CO}_3$ ? Assume that for successful separation 99% of the metal ion must be precipitated before the other metal ion begins to precipitate, and assume no volume change on addition of  $\text{Na}_2\text{CO}_3$ .

## Complex Ion Equilibria

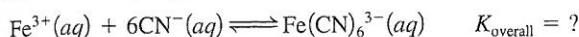
61. Write equations for the stepwise formation of each of the following complex ions.



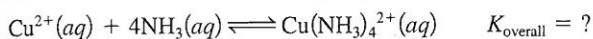
62. Write equations for the stepwise formation of each of the following complex ions.



63. In the presence of  $\text{CN}^-$ ,  $\text{Fe}^{3+}$  forms the complex ion  $\text{Fe}(\text{CN})_6^{3-}$ . The equilibrium concentrations of  $\text{Fe}^{3+}$  and  $\text{Fe}(\text{CN})_6^{3-}$  are  $8.5 \times 10^{-40} \text{ M}$  and  $1.5 \times 10^{-3} \text{ M}$ , respectively, in a  $0.11\text{-M}$  KCN solution. Calculate the value for the overall formation constant of  $\text{Fe}(\text{CN})_6^{3-}$ .



64. In the presence of  $\text{NH}_3$ ,  $\text{Cu}^{2+}$  forms the complex ion  $\text{Cu}(\text{NH}_3)_4^{2+}$ . If the equilibrium concentrations of  $\text{Cu}^{2+}$  and  $\text{Cu}(\text{NH}_3)_4^{2+}$  are  $1.8 \times 10^{-17} \text{ M}$  and  $1.0 \times 10^{-3} \text{ M}$ , respectively, in a  $1.5\text{-M}$   $\text{NH}_3$  solution, calculate the value for the overall formation constant of  $\text{Cu}(\text{NH}_3)_4^{2+}$ .



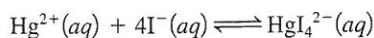
65. When aqueous KI is added gradually to mercury(II) nitrate, an orange precipitate forms. Continued addition of KI causes the precipitate to dissolve. Write balanced equations to explain these observations. (*Hint*:  $\text{Hg}^{2+}$  reacts with  $\text{I}^-$  to form  $\text{HgI}_4^{2-}$ .)

66. As sodium chloride solution is added to a solution of silver nitrate, a white precipitate forms. Ammonia is added to the mixture and the precipitate dissolves. When potassium bromide solution is then added, a pale yellow precipitate appears. When a solution of sodium thiosulfate is added, the yellow precipitate dissolves. Finally, potassium iodide is added to the solution and a yellow precipitate forms. Write equations for all the changes mentioned above. What conclusions can you draw concerning the sizes of the  $K_{\text{sp}}$  values for  $\text{AgCl}$ ,  $\text{AgBr}$ , and  $\text{AgI}$ ?

67. The overall formation constant for  $\text{HgI}_4^{2-}$  is  $1.0 \times 10^{30}$ . That is,

$$1.0 \times 10^{30} = \frac{[\text{HgI}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4}$$

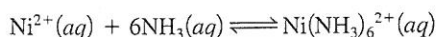
What is the concentration of  $\text{Hg}^{2+}$  in  $500.0 \text{ mL}$  of a solution that was originally  $0.010 \text{ M}$   $\text{Hg}^{2+}$  and  $0.78 \text{ M}$   $\text{I}^-$ ? The reaction is



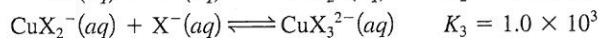
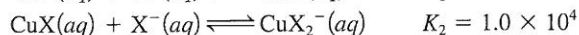
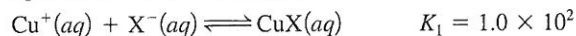
68. A solution is prepared by adding  $0.10$  mole of  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$  to  $0.50 \text{ L}$  of  $3.0 \text{ M}$   $\text{NH}_3$ . Calculate  $[\text{Ni}(\text{NH}_3)_6^{2+}]$  and  $[\text{Ni}^{2+}]$  in this solution.  $K_{\text{overall}}$  for  $\text{Ni}(\text{NH}_3)_6^{2+}$  is  $5.5 \times 10^8$ . That is,

$$5.5 \times 10^8 = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}]}{[\text{Ni}^{2+}][\text{NH}_3]^6}$$

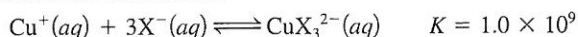
for the overall reaction



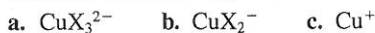
69. A solution is formed by mixing  $50.0 \text{ mL}$  of  $10.0 \text{ M}$   $\text{NaX}$  with  $50.0 \text{ mL}$  of  $2.0 \times 10^{-3} \text{ M}$   $\text{CuNO}_3$ . Assume that  $\text{Cu}^+$  forms complex ions with  $\text{X}^-$  as follows:



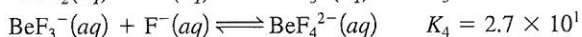
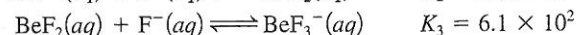
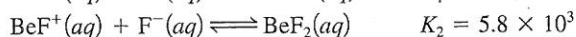
with an overall reaction



Calculate the following concentrations at equilibrium.



70. A solution is prepared by mixing  $100.0 \text{ mL}$  of  $1.0 \times 10^{-4} \text{ M}$   $\text{Be}(\text{NO}_3)_2$  and  $100.0 \text{ mL}$  of  $8.0 \text{ M}$   $\text{NaF}$ .



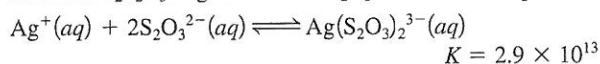
Calculate the equilibrium concentrations of  $\text{F}^-$ ,  $\text{Be}^{2+}$ ,  $\text{BeF}^+$ ,  $\text{BeF}_2$ ,  $\text{BeF}_3^-$ , and  $\text{BeF}_4^{2-}$  in this solution.

71. a. Calculate the molar solubility of  $\text{AgI}$  in pure water.  $K_{\text{sp}}$  for  $\text{AgI}$  is  $1.5 \times 10^{-16}$ .

- b. Calculate the molar solubility of  $\text{AgI}$  in  $3.0 \text{ M}$   $\text{NH}_3$ . The overall formation constant for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ .

- c. Compare the calculated solubilities from parts a and b. Explain any differences.

72. Solutions of sodium thiosulfate are used to dissolve unexposed  $\text{AgBr}$  ( $K_{\text{sp}} = 5.0 \times 10^{-13}$ ) in the developing process for black-and-white film. What mass of  $\text{AgBr}$  can dissolve in  $1.00 \text{ L}$  of  $0.500 \text{ M}$   $\text{Na}_2\text{S}_2\text{O}_3$ ?  $\text{Ag}^+$  reacts with  $\text{S}_2\text{O}_3^{2-}$  to form a complex ion:



73.  $K_f$  for the complex ion  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ .  $K_{\text{sp}}$  for  $\text{AgCl}$  is  $1.6 \times 10^{-10}$ . Calculate the molar solubility of  $\text{AgCl}$  in  $1.0 \text{ M}$   $\text{NH}_3$ .

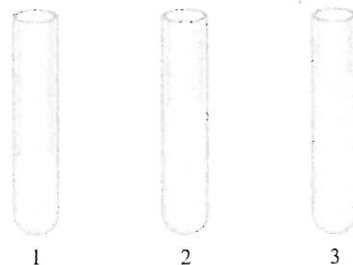
74. The copper(I) ion forms a chloride salt that has  $K_{\text{sp}} = 1.2 \times 10^{-6}$ . Copper(I) also forms a complex ion with  $\text{Cl}^-$ :



- a. Calculate the solubility of copper(I) chloride in pure water. (Ignore  $\text{CuCl}_2^-$  formation for part a.)

- b. Calculate the solubility of copper(I) chloride in  $0.10 \text{ M}$   $\text{NaCl}$ .

75. A series of chemicals were added to some  $\text{AgNO}_3(\text{aq})$ .  $\text{NaCl}(\text{aq})$  was added first to the silver nitrate solution with the end result shown below in test tube 1,  $\text{NH}_3(\text{aq})$  was then added with the end result shown in test tube 2, and  $\text{HNO}_3(\text{aq})$  was added last with the end result shown in test tube 3.



Explain the results shown in each test tube. Include a balanced equation for the reaction(s) taking place.

76. The solubility of copper(II) hydroxide in water can be increased by adding either the base  $\text{NH}_3$  or the acid  $\text{HNO}_3$ . Explain. Would added  $\text{NH}_3$  or  $\text{HNO}_3$  have the same effect on the solubility of silver acetate or silver chloride? Explain.

### Additional Exercises

77. A solution contains 0.018 mole each of  $\text{I}^-$ ,  $\text{Br}^-$ , and  $\text{Cl}^-$ . When the solution is mixed with 200. mL of 0.24 M  $\text{AgNO}_3$ , what mass of  $\text{AgCl}(s)$  precipitates out, and what is  $[\text{Ag}^+]$ ? Assume no volume change.

$$\text{AgI}: K_{\text{sp}} = 1.5 \times 10^{-16}$$

$$\text{AgBr}: K_{\text{sp}} = 5.0 \times 10^{-13}$$

$$\text{AgCl}: K_{\text{sp}} = 1.6 \times 10^{-10}$$

78. You have two salts,  $\text{AgX}$  and  $\text{AgY}$ , with very similar  $K_{\text{sp}}$  values. You know that  $K_a$  for  $\text{HX}$  is much greater than  $K_a$  for  $\text{HY}$ . Which salt is more soluble in acidic solution? Explain.

79. Tooth enamel is composed of the mineral hydroxyapatite. The  $K_{\text{sp}}$  of hydroxyapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , is  $6.8 \times 10^{-37}$ . Calculate the solubility of hydroxyapatite in pure water in moles per liter. How is the solubility of hydroxyapatite affected by adding acid? When hydroxyapatite is treated with fluoride, the mineral fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , forms. The  $K_{\text{sp}}$  of this substance is  $1 \times 10^{-60}$ . Calculate the solubility of fluorapatite in water. How do these calculations provide a rationale for the fluoridation of drinking water?

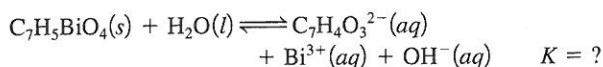
80. The U.S. Public Health Service recommends the fluoridation of water as a means for preventing tooth decay. The recommended concentration is 1 mg  $\text{F}^-$  per liter. The presence of calcium ions in hard water can precipitate the added fluoride. What is the maximum molarity of calcium ions in hard water if the fluoride concentration is at the USPHS recommended level? ( $K_{\text{sp}}$  for  $\text{CaF}_2 = 4.0 \times 10^{-11}$ )

81. What mass of  $\text{Ca}(\text{NO}_3)_2$  must be added to 1.0 L of a 1.0-M HF solution to begin precipitation of  $\text{CaF}_2(s)$ ? For  $\text{CaF}_2$ ,  $K_{\text{sp}} = 4.0 \times 10^{-11}$  and  $K_a$  for HF =  $7.2 \times 10^{-4}$ . Assume no volume change on addition of  $\text{Ca}(\text{NO}_3)_2(s)$ .

82. Calculate the mass of manganese hydroxide present in 1300 mL of a saturated manganese hydroxide solution. For  $\text{Mn}(\text{OH})_2$ ,  $K_{\text{sp}} = 2.0 \times 10^{-13}$ .

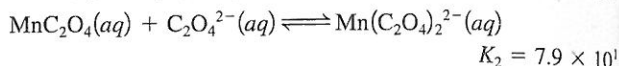
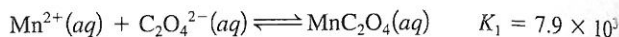
83. On a hot day, a 200.0-mL sample of a saturated solution of  $\text{PbI}_2$  was allowed to evaporate until dry. If 240 mg of solid  $\text{PbI}_2$  was collected after evaporation was complete, calculate the  $K_{\text{sp}}$  value for  $\text{PbI}_2$  on this hot day.

84. The active ingredient of Pepto-Bismol is the compound bismuth subsalicylate, which undergoes the following dissociation when added to water:



If the maximum amount of bismuth subsalicylate that reacts by this reaction is  $3.2 \times 10^{-19}$  mol/L, calculate the equilibrium constant for the preceding reaction.

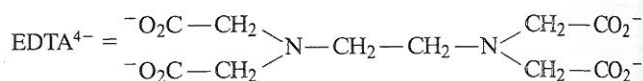
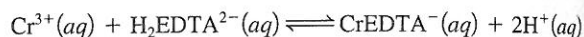
85. Nanotechnology has become an important field, with applications ranging from high-density data storage to the design of "nano machines." One common building block of nanostructured architectures is manganese oxide nanoparticles. The particles can be formed from manganese oxalate nanorods, the formation of which can be described as follows:



Calculate the value for the overall formation constant for  $\text{Mn}(\text{C}_2\text{O}_4)_2^{2-}$ :

$$K = \frac{[\text{Mn}(\text{C}_2\text{O}_4)_2^{2-}]}{[\text{Mn}^{2+}][\text{C}_2\text{O}_4^{2-}]^2}$$

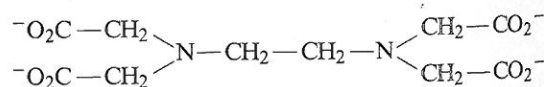
86. The equilibrium constant for the following reaction is  $1.0 \times 10^{23}$ :



Ethylenediaminetetraacetate

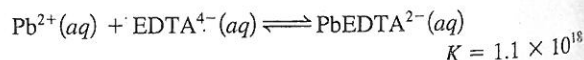
EDTA is used as a complexing agent in chemical analysis. Solutions of EDTA, usually containing the disodium salt  $\text{Na}_2\text{H}_2\text{EDTA}$ , are used to treat heavy metal poisoning. Calculate  $[\text{Cr}^{3+}]$  at equilibrium in a solution originally 0.0010 M in  $\text{Cr}^{3+}$  and 0.050 M in  $\text{H}_2\text{EDTA}^{2-}$  and buffered at pH = 6.00.

87. Calculate the concentration of  $\text{Pb}^{2+}$  in each of the following
- a saturated solution of  $\text{Pb}(\text{OH})_2$ ,  $K_{\text{sp}} = 1.2 \times 10^{-15}$
  - a saturated solution of  $\text{Pb}(\text{OH})_2$  buffered at pH = 13.00
  - Ethylenediaminetetraacetate ( $\text{EDTA}^{4-}$ ) is used as a complexing agent in chemical analysis and has the following structure:



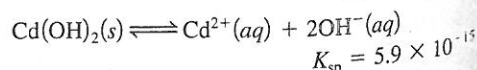
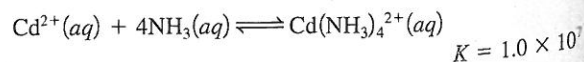
Ethylenediaminetetraacetate

Solutions of  $\text{EDTA}^{4-}$  are used to treat heavy metal poisoning by removing the heavy metal in the form of a soluble complex ion. The reaction of  $\text{EDTA}^{4-}$  with  $\text{Pb}^{2+}$  is

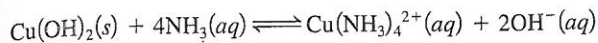


Consider a solution with 0.010 mole of  $\text{Pb}(\text{NO}_3)_2$  added to 1.0 L of an aqueous solution buffered at pH = 13.00 and containing 0.050 M  $\text{Na}_4\text{EDTA}$ . Does  $\text{Pb}(\text{OH})_2$  precipitate from this solution?

88. Will a precipitate of  $\text{Cd}(\text{OH})_2$  form if 1.0 mL of 1.0 M  $\text{Cd}(\text{NO}_3)_2$  is added to 1.0 L of 5.0 M  $\text{NH}_3$ ?



89. a. Using the  $K_{sp}$  value for  $\text{Cu}(\text{OH})_2$  ( $1.6 \times 10^{-19}$ ) and the overall formation constant for  $\text{Cu}(\text{NH}_3)_4^{2+}$  ( $1.0 \times 10^{13}$ ), calculate the value for the equilibrium constant for the following reaction:



- b. Use the value of the equilibrium constant you calculated in part a to calculate the solubility (in mol/L) of  $\text{Cu}(\text{OH})_2$  in 5.0 M  $\text{NH}_3$ . In 5.0 M  $\text{NH}_3$  the concentration of  $\text{OH}^-$  is 0.0095 M.
90. Describe how you could separate the ions in each of the following groups by selective precipitation.
- a.  $\text{Ag}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$     c.  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$   
 b.  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$
91. The solubility rules outlined in Chapter 4 say that  $\text{Ba}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ , and  $\text{Ca}(\text{OH})_2$  are marginally soluble hydroxides. Calculate the pH of a saturated solution of each of these marginally soluble hydroxides.
92. In the chapter discussion of precipitate formation, we ran the precipitation reaction to completion and then let some of the precipitate redissolve to get back to equilibrium. To see why, redo Example 16.6, where

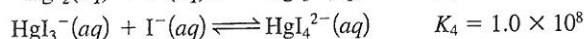
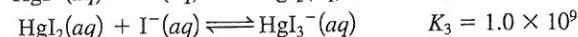
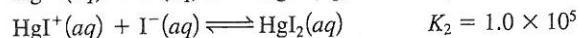
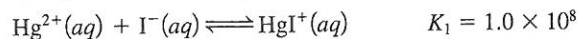
Initial Concentration (mol/L)	Equilibrium Concentration (mol/L)
$[\text{Mg}^{2+}]_0 = 3.75 \times 10^{-3}$	$[\text{Mg}^{2+}] = 3.75 \times 10^{-3} - y$
$[\text{F}^-]_0 = 6.25 \times 10^{-2}$	$[\text{F}^-] = 6.25 \times 10^{-2} - 2y$
$\xrightarrow[\text{from MgF}_2]{y \text{ mol/Mg}^{2+} \text{ reacts to}}$	

## ChemWork Problems

These multiconcept problems (and additional ones) are found interactively online with the same type of assistance a student would get from an instructor.

93. Assuming that the solubility of  $\text{Ca}_3(\text{PO}_4)_2(s)$  is  $1.6 \times 10^{-7}$  mol/L at 25°C, calculate the  $K_{sp}$  for this salt. Ignore any potential reactions of the ions with water.
94. Order the following solids (a–d) from least soluble to most soluble. Ignore any potential reactions of the ions with water.
- a.  $\text{AgCl}$      $K_{sp} = 1.6 \times 10^{-10}$   
 b.  $\text{Ag}_2\text{S}$      $K_{sp} = 1.6 \times 10^{-49}$   
 c.  $\text{CaF}_2$      $K_{sp} = 4.0 \times 10^{-11}$   
 d.  $\text{CuS}$      $K_{sp} = 8.5 \times 10^{-45}$
95. The  $K_{sp}$  for  $\text{PbI}_2(s)$  is  $1.4 \times 10^{-8}$ . Calculate the solubility of  $\text{PbI}_2(s)$  in 0.048 M NaI.
96. The solubility of  $\text{Pb}(\text{IO}_3)_2(s)$  in a  $7.2 \times 10^{-2}$ -M  $\text{KIO}_3$  solution is  $6.0 \times 10^{-9}$  mol/L. Calculate the  $K_{sp}$  value for  $\text{Pb}(\text{IO}_3)_2(s)$ .
97. A 50.0-mL sample of 0.0413 M  $\text{AgNO}_3(aq)$  is added to 50.0 mL of 0.100 M  $\text{NaIO}_3(aq)$ . Calculate the  $[\text{Ag}^+]$  at equilibrium in the resulting solution. [ $K_{sp}$  for  $\text{AgIO}_3(s) = 3.17 \times 10^{-8}$ .]

98. The  $\text{Hg}^{2+}$  ion forms complex ions with  $\text{I}^-$  as follows:

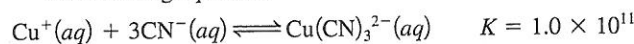


A solution is prepared by dissolving 0.088 mole of  $\text{Hg}(\text{NO}_3)_2$  and 5.00 mole of NaI in enough water to make 1.0 L of solution.

- a. Calculate the equilibrium concentration of  $[\text{HgI}_4^{2-}]$ .  
 b. Calculate the equilibrium concentration of  $[\text{I}^-]$ .  
 c. Calculate the equilibrium concentration of  $[\text{Hg}^{2+}]$ .

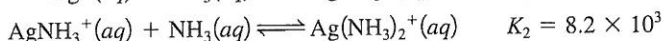
## Challenge Problems

99. The copper(I) ion forms a complex ion with  $\text{CN}^-$  according to the following equation:



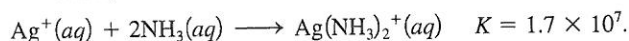
- a. Calculate the solubility of  $\text{CuBr}(s)$  ( $K_{sp} = 1.0 \times 10^{-5}$ ) in 1.0 L of 1.0 M NaCN.  
 b. Calculate the concentration of  $\text{Br}^-$  at equilibrium.  
 c. Calculate the concentration of  $\text{CN}^-$  at equilibrium.

100. Consider a solution made by mixing 500.0 mL of 4.0 M  $\text{NH}_3$  and 500.0 mL of 0.40 M  $\text{AgNO}_3$ .  $\text{Ag}^+$  reacts with  $\text{NH}_3$  to form  $\text{AgNH}_3^+$  and  $\text{Ag}(\text{NH}_3)_2^+$ :

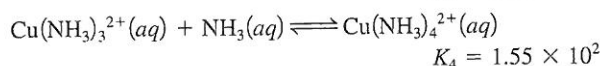
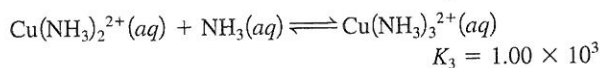
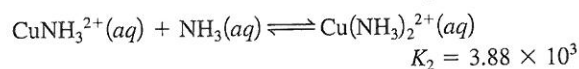
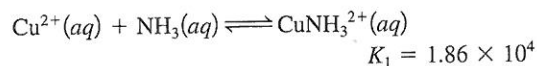


Determine the concentration of all species in solution.

101. a. Calculate the molar solubility of  $\text{AgBr}$  in pure water.  $K_{sp}$  for  $\text{AgBr}$  is  $5.0 \times 10^{-13}$ .  
 b. Calculate the molar solubility of  $\text{AgBr}$  in 3.0 M  $\text{NH}_3$ . The overall formation constant for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ , that is,



- c. Compare the calculated solubilities from parts a and b. Explain any differences.  
 d. What mass of  $\text{AgBr}$  will dissolve in 250.0 mL of 3.0 M  $\text{NH}_3$ ?  
 e. What effect does adding  $\text{HNO}_3$  have on the solubilities calculated in parts a and b?
102. Calculate the equilibrium concentrations of  $\text{NH}_3$ ,  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{NH}_3)^{2+}$ ,  $\text{Cu}(\text{NH}_3)_2^{2+}$ ,  $\text{Cu}(\text{NH}_3)_3^{2+}$ , and  $\text{Cu}(\text{NH}_3)_4^{2+}$  in a solution prepared by mixing 500.0 mL of 3.00 M  $\text{NH}_3$  with 500.0 mL of  $2.00 \times 10^{-3}$  M  $\text{Cu}(\text{NO}_3)_2$ . The stepwise equilibria are



103. Calculate the solubility of  $\text{AgCN}(s)$  ( $K_{\text{sp}} = 2.2 \times 10^{-12}$ ) in a solution containing  $1.0 \text{ M H}^+$ . ( $K_{\text{a}}$  for  $\text{HCN}$  is  $6.2 \times 10^{-10}$ .)
104. Calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) is relatively insoluble in water ( $K_{\text{sp}} = 2 \times 10^{-9}$ ). However, calcium oxalate is more soluble in acidic solution. How much more soluble is calcium oxalate in  $0.10 \text{ M H}^+$  than in pure water? In pure water, ignore the basic properties of  $\text{C}_2\text{O}_4^{2-}$ .
105. What is the maximum possible concentration of  $\text{Ni}^{2+}$  ion in water at  $25^\circ\text{C}$  that is saturated with  $0.10 \text{ M H}_2\text{S}$  and maintained at  $\text{pH } 3.0$  with  $\text{HCl}$ ?
106. A mixture contains  $1.0 \times 10^{-3} \text{ M Cu}^{2+}$  and  $1.0 \times 10^{-3} \text{ M Mn}^{2+}$  and is saturated with  $0.10 \text{ M H}_2\text{S}$ . Determine a  $\text{pH}$  where  $\text{CuS}$  precipitates but  $\text{MnS}$  does not precipitate.  $K_{\text{sp}}$  for  $\text{CuS} = 8.5 \times 10^{-45}$  and  $K_{\text{sp}}$  for  $\text{MnS} = 2.3 \times 10^{-13}$ .
107. Sodium tripolyphosphate ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ) is used in many synthetic detergents. Its major effect is to soften the water by complexing  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions. It also increases the efficiency of surfactants, or wetting agents that lower a liquid's surface tension. The  $K$  value for the formation of  $\text{MgP}_3\text{O}_{10}^{3-}$  is  $4.0 \times 10^8$ . The reaction is  $\text{Mg}^{2+}(aq) + \text{P}_3\text{O}_{10}^{5-}(aq) \rightleftharpoons \text{MgP}_3\text{O}_{10}^{3-}(aq)$ . Calculate the concentration of  $\text{Mg}^{2+}$  in a solution that was originally  $50. \text{ ppm Mg}^{2+}$  ( $50. \text{ mg/L}$  of solution) after  $40. \text{ g Na}_5\text{P}_3\text{O}_{10}$  is added to  $1.0 \text{ L}$  of the solution.
108. You add an excess of solid  $\text{MX}$  in  $250 \text{ g}$  water. You measure the freezing point and find it to be  $-0.028^\circ\text{C}$ . What is the  $K_{\text{sp}}$  of the solid? Assume the density of the solution is  $1.0 \text{ g/cm}^3$ .
109. a. Calculate the molar solubility of  $\text{SrF}_2$  in water, ignoring the basic properties of  $\text{F}^-$ . (For  $\text{SrF}_2$ ,  $K_{\text{sp}} = 7.9 \times 10^{-10}$ .)  
 b. Would the measured molar solubility of  $\text{SrF}_2$  be greater than or less than the value calculated in part a? Explain.  
 c. Calculate the molar solubility of  $\text{SrF}_2$  in a solution buffered at  $\text{pH} = 2.00$ . ( $K_{\text{a}}$  for  $\text{HF}$  is  $7.2 \times 10^{-4}$ .)
111. Consider  $1.0 \text{ L}$  of an aqueous solution that contains  $0.10 \text{ M}$  sulfuric acid to which  $0.30 \text{ mole}$  of barium nitrate is added. Assuming no change in volume of the solution, determine the  $\text{pH}$ , the concentration of barium ions in the final solution, and the mass of solid formed.
112. The  $K_{\text{sp}}$  for  $Q$ , a slightly soluble ionic compound composed of  $\text{M}_2^{2+}$  and  $\text{X}^-$  ions, is  $4.5 \times 10^{-29}$ . The electron configuration of  $\text{M}^+$  is  $[\text{Xe}]6s^14f^{14}5d^{10}$ . The  $\text{X}^-$  anion has 54 electrons. What is the molar solubility of  $Q$  in a solution of  $\text{NaX}$  prepared by dissolving  $1.98 \text{ g NaX}$  in  $150. \text{ mL}$  solution?

### Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation.

113. Aluminum ions react with the hydroxide ion to form the precipitate  $\text{Al}(\text{OH})_3(s)$ , but can also react to form the soluble complex ion  $\text{Al}(\text{OH})_4^-$ . In terms of solubility,  $\text{Al}(\text{OH})_3(s)$  will be more soluble in very acidic solutions as well as more soluble in very basic solutions.
- Write equations for the reactions that occur to increase the solubility of  $\text{Al}(\text{OH})_3(s)$  in very acidic solutions and in very basic solutions.
  - Let's study the  $\text{pH}$  dependence of the solubility of  $\text{Al}(\text{OH})_3(s)$  in more detail. Show that the solubility of  $\text{Al}(\text{OH})_3$ , as a function of  $[\text{H}^+]$ , obeys the equation
 
$$S = [\text{H}^+]^3 K_{\text{sp}} / K_{\text{w}}^3 + KK_{\text{w}} / [\text{H}^+]$$
 where  $S = \text{solubility} = [\text{Al}^{3+}] + [\text{Al}(\text{OH})_4^-]$  and  $K$  is the equilibrium constant for
 
$$\text{Al}(\text{OH})_3(s) + \text{OH}^-(aq) \rightleftharpoons \text{Al}(\text{OH})_4^-(aq)$$
  - The value of  $K$  is  $40.0$  and  $K_{\text{sp}}$  for  $\text{Al}(\text{OH})_3$  is  $2 \times 10^{-32}$ . Plot the solubility of  $\text{Al}(\text{OH})_3$  in the  $\text{pH}$  range  $4\text{--}12$ .

### Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

110. A solution saturated with a salt of the type  $\text{M}_3\text{X}_2$  has an osmotic pressure of  $2.64 \times 10^{-2} \text{ atm}$  at  $25^\circ\text{C}$ . Calculate the  $K_{\text{sp}}$  value for the salt, assuming ideal behavior.

Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.