

## Chapter 18

# Solubility and Complex-Ion Equilibria

### Concept Check 18.1

Lead compounds have been used as pigments to make paint. Several factors are important to consider in contemplating the use of a compound as a paint pigment. Toxicity is one factor, and because of their toxicity, lead compounds are used less often today. Solubility of a compound is another factor; normally, the compound should be insoluble. Comparing solubility product constants, which of these compounds of lead is least soluble,  $\text{PbCrO}_4$ ,  $\text{PbSO}_4$ , or  $\text{PbS}$ ?

### Solution

Solubility and  $K_{sp}$  are related, although not directly. You can compare  $K_{sp}$ 's for a series of salts, however, if they have the same number of cations and anions in each of their formulas. (In that case,  $K_{sp}$  and solubility are related in the same way for each salt.) In this problem, each of the lead(II) compounds has one  $\text{Pb}^{2+}$  cation and one anion, so you can compare the  $K_{sp}$ 's directly. Lead(II) sulfide has the smallest  $K_{sp}$  and, therefore, is the least soluble of these lead(II) compounds.

### Concept Check 18.2

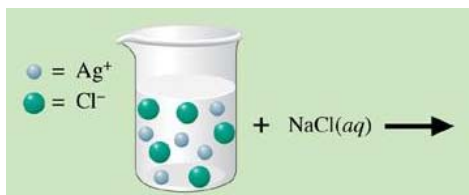
Suppose you have equal volumes of saturated solutions of  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{PbS}$ . Which solution would dissolve the most lead(II) sulfate,  $\text{PbSO}_4$ ?

### Solution

Let's look at each compound in turn.  $\text{NaNO}_3$  has no ion in common with  $\text{PbSO}_4$ , so it should have little effect on its solubility.  $\text{Na}_2\text{SO}_4$  is a soluble compound and provides the common ion  $\text{SO}_4^{2-}$ , which would repress the solubility of  $\text{PbSO}_4$ .  $\text{PbS}$  has an ion in common with  $\text{PbSO}_4$  ( $\text{Pb}^{2+}$ ), but the compound is so insoluble that very little of the  $\text{Pb}^{2+}$  ion is available. Because of this, the solubility of  $\text{PbSO}_4$  is little affected by the  $\text{PbS}$ . Therefore, only  $\text{Na}_2\text{SO}_4$  appreciably affects the solubility of  $\text{PbSO}_4$ .

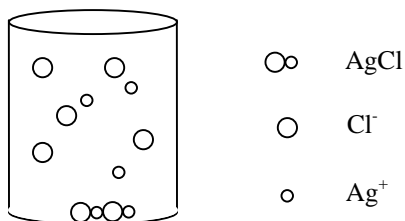
### Concept Check 18.3

Consider the beaker below that represents a saturated solution of  $\text{AgCl(aq)}$ . Draw a picture of the solution in the beaker after the addition of  $\text{NaCl(aq)}$ .



### Solution

If  $\text{NaCl}$  were added to a saturated  $\text{AgCl}$  solution, the equilibrium would shift to consume the added chloride ion, and some  $\text{AgCl}$  would precipitate. After the addition of two  $\text{Cl}^-$  ions, there would be five  $\text{Cl}^-$  ions, three  $\text{Ag}^+$  ions, and two  $\text{AgCl}$  molecules. The solution would look like the following ( $\text{Na}^+$  not shown for clarity).



### Concept Check 18.4

If you add a dilute acidic solution to a mixture containing magnesium oxalate and calcium oxalate, which of the two compounds is more likely to dissolve?

**Solution**

If you compare the  $K_{sp}$ 's for magnesium oxalate ( $8.5 \times 10^{-5}$ ) and calcium oxalate ( $2.3 \times 10^{-9}$ ), you can see that magnesium oxalate is much more soluble in water solution than the calcium salt (the  $K_{sp}$  is larger). This means that it provides a greater concentration of oxalate ion. In water solution, some of the magnesium oxalate dissolves, giving an oxalate ion concentration that tends to repress the dissolution of calcium oxalate (common ion effect). The addition of acid tends to remove oxalate ion, but this is replenished by the dissolution of more magnesium oxalate. Therefore, you would expect the magnesium oxalate to be more likely to dissolve.

**Conceptual Problem 18.11**

Which compound in each of the following pairs of compounds is the more soluble one?

- silver chloride or silver iodide
- magnesium hydroxide or copper(II) hydroxide

**Solution**

- Since both compounds contain the same number of ions, the salt with the larger  $K_{sp}$  value will be more soluble. The  $K_{sp}$  for AgCl is  $1.8 \times 10^{-10}$ , while for AgI, it is  $8.3 \times 10^{-17}$ . Therefore, silver chloride (AgCl) is more soluble.
- Since both compounds contain the same number of ions, the salt with the larger  $K_{sp}$  value will be more soluble. The  $K_{sp}$  for Mg(OH)<sub>2</sub> is  $1.8 \times 10^{-11}$ , while for Cu(OH)<sub>2</sub>, it is  $2.6 \times 10^{-19}$ . Therefore, magnesium hydroxide (Mg(OH)<sub>2</sub>) is more soluble.

**Conceptual Problem 18.12**

You are given two mineral samples: halite, which is NaCl, and fluorite, which is CaF<sub>2</sub>. Describe a simple test you could use to discover which mineral is fluorite.

**Solution**

Dissolve a sample of each mineral in water in separate containers. NaCl is soluble in water, and CaF<sub>2</sub> is insoluble in water ( $K_{sp} = 3.4 \times 10^{-11}$ ), so the sample that dissolves is NaCl, while the sample that doesn't dissolve is CaF<sub>2</sub>.

**Conceptual Problem 18.13**

You are given a saturated solution of lead(II) chloride. Which one of the following solutions would be most effective in yielding a precipitate when added to the lead(II) chloride solution?

- 0.1 M NaCl(aq)

- b.  $0.1\text{ M Na}_2\text{SO}_4(aq)$
- c. saturated  $\text{PbS}(aq)$

### Solution

$0.1\text{ M NaCl}$  will be most effective in causing a precipitate from a saturated solution of  $\text{PbCl}_2$ , since it is completely soluble, and contains the common ion  $\text{Cl}^-$ . Therefore, the answer is a.

### Conceptual Problem 18.14

Which of the following pictures best represents a solution made by adding 10 g of silver chloride,  $\text{AgCl}$ , to a liter of water? In these pictures, the dark spheres represent  $\text{Ag}^+$  and the light spheres represent chloride ions. For clarity, water molecules are not shown.



### Solution

The beaker on the left depicts all of the  $\text{AgCl}$  as individual formula units in solution. This implies that  $\text{AgCl}$  is a soluble nonelectrolyte, which is not the case since  $\text{AgCl}$  is a slightly soluble ionic compound. The center beaker depicts  $\text{AgCl}$  as a soluble ionic compound that completely dissolves in solution leaving no  $\text{AgCl}(s)$ . Once again, this cannot be correct since  $\text{AgCl}$  is slightly soluble. The beaker on the right indicates that there are ions of  $\text{Ag}^+$  and  $\text{Cl}^-$  present in the solution along with solid  $\text{AgCl}$ . This is consistent with  $\text{AgCl}$  being a slightly soluble ionic compound.

### Conceptual Problem 18.15

Which of the following pictures best represents an unsaturated solution of sodium chloride,  $\text{NaCl}$ ? In these pictures, the dark spheres represent  $\text{Na}^+$  ions and the light spheres represent chloride ions. For clarity, water molecules are not shown.



### Solution

The beaker on the left depicts all of the NaCl as individual formula units in solution. This implies that NaCl is a soluble nonelectrolyte, which is not the case since NaCl is a very soluble ionic compound that produces ions in solution. The center beaker depicts NaCl as a soluble ionic compound that completely dissolves in solution producing only  $\text{Na}^+(aq)$  and  $\text{Cl}^-(aq)$ . This must be correct since NaCl is a very soluble ionic compound. The beaker on the right indicates that there are ions of  $\text{Na}^+$  and  $\text{Cl}^-$  present in the solution along with solid NaCl. The presence of solid is not consistent with NaCl being a very soluble ionic compound.

### Conceptual Problem 18.16

When ammonia is first added to a solution of copper(II) nitrate, a pale blue precipitate of copper(II) hydroxide forms. As more ammonia is added, however, this precipitate dissolves. Describe what is happening.

### Solution

When first added to a solution of copper(II) nitrate, the ammonia causes a pale blue precipitate of  $\text{Cu}(\text{OH})_2$  to form ( $K_{sp} = 2.6 \times 10^{-19}$ ). After enough ammonia has been added, however, the complex ion  $\text{Cu}(\text{NH}_3)_4^{2+}$  forms ( $K_f = 4.8 \times 10^{12}$ ), and the precipitate dissolves.

### Conceptual Problem 18.17

You are given a solution of the ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Ba}^{2+}$ . Devise a scheme to separate these ions using sodium sulfate. Note that magnesium sulfate is soluble.

### Solution

Add just enough  $\text{Na}_2\text{SO}_4$  to precipitate all of the  $\text{Ba}^{2+}$ ; filter off the  $\text{BaSO}_4$ ; add more  $\text{Na}_2\text{SO}_4$  to precipitate all of the  $\text{Ca}^{2+}$ ; filter off the  $\text{CaSO}_4$ ;  $\text{Mg}^{2+}$  remains in the solution.

### Conceptual Problem 18.18

You add dilute hydrochloric acid to a solution containing a metal ion. No precipitate forms. After the acidity is adjusted to  $0.3\text{ M}$  hydronium ion, you bubble hydrogen sulfide into the solution. Again no precipitate forms. Is it possible that the original solution contained silver ion? Could it have contained copper(II) ion?

**Solution**

When a precipitate fails to form when HCl is added to the solution, this indicates that no silver ion is present. When a precipitate fails to form when the solution is acidified and  $\text{H}_2\text{S}$  is added, this indicates that no copper(II) ion is present in the solution.