

17.3: Factors That Affect Solubility

Learning Objectives

- To understand the factors that determine the solubility of ionic compounds.

The solubility product of an ionic compound describes the concentrations of *ions* in equilibrium with a solid, but what happens if some of the cations become associated with anions rather than being completely surrounded by solvent? Then predictions of the total solubility of the compound based on the assumption that the solute exists solely as discrete ions would differ substantially from the actual solubility, as would predictions of ionic concentrations. In general, four situations explain why the solubility of a compound may be other than expected: ion pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH. The first two situations are described in this section, the formation of complex ions is discussed in [Section 17.3](#), and changes in pH are discussed in [Section 17.4](#).

Ion-Pair Formation

An ion pair consists of a cation and an anion that are in intimate contact in solution rather than separated by solvent. An ion pair can be viewed as a species that is intermediate between the ionic solid and the completely dissociated ions in solution. The ions in an ion pair are held together by the same attractive electrostatic forces that we discussed in [Chapter 4](#) for ionic solids. As a result, the ions in an ion pair migrate as a single unit, whose net charge is the sum of the charges on the ions. In many ways, we can view an ion pair as a species intermediate between the ionic solid (in which each ion participates in many cation–anion interactions that hold the ions in a rigid array) and the completely dissociated ions in solution (where each is fully surrounded by water molecules and free to migrate independently).

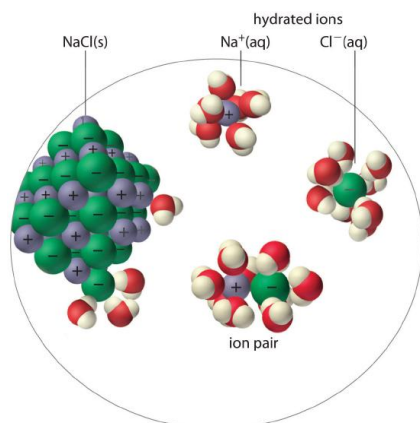
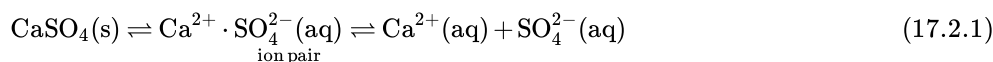


Figure 17.2.1 Ion-Pair **Formation** In an ion pair, the cation and the anion are in intimate contact in solution and migrate as a single unit. They are not completely dissociated and individually surrounded by solvent molecules, as are the hydrated ions, which are free to migrate independently.

As illustrated for calcium sulfate in the following equation, a second equilibrium must be included to describe the solubility of salts that form ion pairs:



The ion pair is represented by the symbols of the individual ions separated by a dot, which indicates that they are associated in solution. The formation of an ion pair is a dynamic process, just like any other equilibrium, so a particular ion pair may exist only briefly before dissociating into the free ions, each of which may later associate briefly with other ions.

Ion-pair formation can have a major effect on the measured solubility of a salt. For example, the measured K_{sp} for calcium sulfate is 4.93×10^{-5} at 25°C. The solubility of CaSO_4 should be 7.02×10^{-3} M if the only equilibrium involved were as follows:



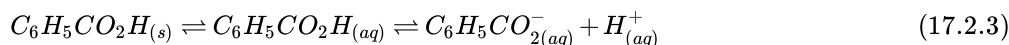
In fact, the experimentally measured solubility of calcium sulfate at 25°C is 1.6×10^{-2} M, almost twice the value predicted from its K_{sp} . The reason for the discrepancy is that the concentration of ion pairs in a saturated CaSO_4 solution is almost as high as the concentration of the hydrated ions. Recall that the magnitude of attractive electrostatic interactions is greatest for small, highly charged ions. Hence ion pair formation is most important for salts that contain M^{2+} and M^{3+} ions, such as Ca^{2+} and La^{3+} , and is relatively unimportant for salts that contain monovalent cations, except for the smallest, Li^+ . We therefore expect a saturated solution of CaSO_4 to contain a high concentration of ion pairs and its solubility to be greater than predicted from its K_{sp} .

Note the Pattern

The formation of ion pairs increases the solubility of a salt.

Incomplete Dissociation

A molecular solute may also be more soluble than predicted by the measured concentrations of ions in solution due to *incomplete dissociation*. This is particularly common with weak organic acids. (For more information about weak organic acids, see [Chapter 16](#)). Although strong acids (HA) dissociate completely into their constituent ions (H^+ and A^-) in water, weak acids such as carboxylic acids do not ($K_a = 1.5 \times 10^{-5}$). However, the molecular (undissociated) form of a weak acid (HA) is often quite soluble in water; for example, acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) is completely miscible with water. Many carboxylic acids, however, have only limited solubility in water, such as benzoic acid ($\text{C}_6\text{H}_5\text{CO}_2\text{H}$), with $K_a = 6.25 \times 10^{-5}$. Just as with calcium sulfate, we need to include an additional equilibrium to describe the solubility of benzoic acid:



In a case like this, measuring only the concentration of the ions grossly underestimates the total concentration of the organic acid in solution. In the case of benzoic acid, for example, the pH of a saturated solution at 25°C is 2.85, corresponding to $[\text{H}^+] = [\text{C}_6\text{H}_5\text{CO}_2^-] = 1.4 \times 10^{-3}$ M. The total concentration of benzoic acid in the solution, however, is 2.8×10^{-2} M. Thus approximately 95% of the benzoic acid in solution is in the form of hydrated neutral molecules— $\text{C}_6\text{H}_5\text{CO}_2\text{H}_{(aq)}$ —and only about 5% is present as the dissociated ions ([Figure 17.2.2](#)).

Note the Pattern

Incomplete dissociation of a molecular solute that is miscible with water can increase the solubility of the solute.

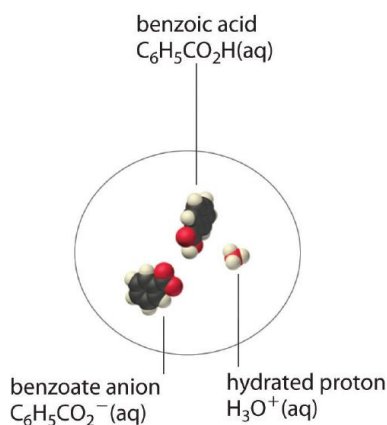


Figure 17.2.2 Incomplete Dissociation of a Molecular Solute In a saturated solution of benzoic acid in water at 25°C, only about 5% of the dissolved benzoic acid molecules are dissociated to form benzoate anions and hydrated protons. The remaining 95% exists in solution in the form of hydrated neutral molecules. (H_2O molecules are omitted for clarity.)

Although ion pairs, such as $\text{Ca}^{2+} \cdot \text{SO}_4^{2-}$, and undissociated electrolytes, such as $\text{C}_6\text{H}_5\text{CO}_2\text{H}$, are both electrically neutral, there is a major difference in the forces responsible for their formation. Simple electrostatic attractive forces between the cation and the anion hold the ion pair together, whereas a polar covalent O–H bond holds together the undissociated electrolyte.

Summary

There are four explanations why the solubility of a compound can differ from the solubility indicated by the concentrations of ions: (1) **ion pair** formation, in which an anion and a cation are in intimate contact in solution and not separated by solvent, (2) the incomplete dissociation of molecular solutes, (3) the formation of complex ions, and (4) changes in pH. An ion pair is held together

by electrostatic attractive forces between the cation and the anion, whereas incomplete dissociation results from intramolecular forces, such as polar covalent O–H bonds.

Key Takeaway

- Ion-pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH all affect solubility.

Conceptual Problems

1. Do you expect the actual molar solubility of LaPO_4 to be greater than, the same as, or less than the value calculated from its K_{sp} ? Explain your reasoning.
2. Do you expect the difference between the calculated molar solubility and the actual molar solubility of $\text{Ca}_3(\text{PO}_4)_2$ to be greater than or less than the difference in the solubilities of $\text{Mg}_3(\text{PO}_4)_2$? Why?
3. Write chemical equations to describe the interactions in a solution that contains $\text{Mg}(\text{OH})_2$, which forms ion pairs, and in one that contains propanoic acid ($\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$), which forms a hydrated neutral molecule.
4. Draw representations of $\text{Ca}(\text{IO}_3)_2$ in solution
 1. as an ionic solid.
 2. in the form of ion pairs.
 3. as discrete ions.

Numerical Problem

1. Ferric phosphate has a molar solubility of 5.44×10^{-16} in 1.82 M Na_3PO_4 . Predict its K_{sp} . The actual K_{sp} is 1.3×10^{-22} . Explain this discrepancy.

Answer

1. 9.90×10^{-16} ; the solubility is much higher than predicted by K_{sp} due to the formation of ion pairs (and/or phosphate complexes) in the sodium phosphate solution.

Contributors

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