

14.13: The Solubilities of Salts of Weak Acids

In many chemical operations it is an advantage not only to be able to form a precipitate but to be able to redissolve it. Fortunately, there is a wide class of sparingly soluble salts which can almost always be redissolved by adding acid. These are precipitates in which the anion is basic; i.e., they are the salts of weak acids. An example of such a precipitate is calcium carbonate, whose solubility equilibrium is

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

If acid is now added to this solution, some of the carbonate ions become protonated and transformed into HCO_3^- ions. As a result, the concentration of the carbonate ion is reduced. In accord with Le Chatelier's principle, the system will respond to this reduction by trying to produce more carbonate ions. Some solid $CaCO_3$ will dissolve, and the equilibrium will be shifted to the right. If enough acid is added, the carbonate-ion concentration in the solution can be reduced so as to make the ion product $(Q = c_{Ca2})^2$ smaller than the solubility product K_{Sp} so that the precipitate dissolves.

A similar behavior is shown by other precipitates involving basic anions. Virtually all the carbonates, sulfides, hydroxides, and phosphates which are sparingly soluble in water can be dissolved in acid. Thus, for instance, we can dissolve precipitates like ZnS, $Mg(OH)_2$, and $Ca_2(PO_4)_3$ because all the following equilibria

$$\mathrm{ZnS}\left(s
ight)
ightleftharpoons \mathrm{Zn}^{2+}(aq) + \mathrm{S}^{2-}(aq)$$
 $\mathrm{Mg}(\mathrm{OH})_{2}\left(s
ight)
ightleftharpoons \mathrm{Mg}^{2+}(aq) + 2\mathrm{OH}^{-}(aq)$
 $\mathrm{Ca}_{3}(\mathrm{PO}_{4})_{2}\left(s
ight)
ightleftharpoons \mathrm{3Ca}^{2+}(aq) + 2\mathrm{PO}_{4}^{3-}(aq)$

can be shifted to the right by attacking the basic species S^{2-} , OH^- , and PO_4^{3-} with hydronium ions. Very occasionally we find an exception to this rule. Mercury(II) sulfide, HgS, is notorious for being insoluble. The solubility product for the equilibrium

$$\mathrm{HgS}\left(s
ight)
ightleftharpoons \mathrm{Hg}^{2+}(aq) + \mathrm{S}^{2-}(aq)$$

is so minute that not even concentrated acid will reduce the sulfide ion sufficiently to make Q smaller than $K_{\rm SD}$.

Occasionally the shift in a solubility-product equilibrium caused by a decrease in pH may be undesirable. One example of this was mentioned in the section on chalcogens. Acid rainfall can occur when oxides of sulfur and other acidic air pollutants are removed from the atmosphere. In some parts of the United States pH values as low as 4.0 have been observed. These acid solutions dissolve marble and limestone (CaCO₃) causing considerable property damage. This is especially true in Europe, where some statues and other works of art have been almost completely destroyed over the last half century.

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