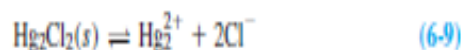


6-3 Solubility Product

In chemical analysis, we encounter solubility in precipitation titrations, electrochemical reference cells, and gravimetric analysis. The effect of acid on the solubility of minerals and the effect of atmospheric CO₂ on the solubility (and death) of coral reefs are important in environmental science.

The **solubility product** is the equilibrium constant for the reaction in which a solid salt dissolves to give its constituent ions in solution. Solid is omitted from the equilibrium constant because it is in its standard state. Appendix F lists solubility products.

As an example, consider the dissolution of mercury(I) chloride (Hg₂Cl₂, also called mercurous chloride) in water. The reaction is



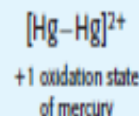
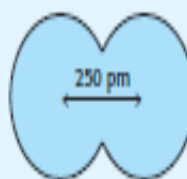
for which the solubility product, K_{sp} , is

$$K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = 1.2 \times 10^{-18} \quad (6-10)$$

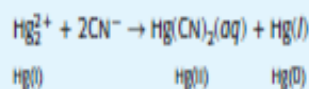
A solution containing excess, undissolved solid is said to be **saturated** with that solid. The solution contains all the solid capable of being dissolved under the prevailing conditions.

The physical meaning of the solubility product is this: If an aqueous solution is left in contact with excess solid Hg₂Cl₂, the solid will dissolve until the condition $[\text{Hg}_2^{2+}][\text{Cl}^-]^2 = K_{sp}$ is satisfied. Thereafter, the amount of undissolved solid remains constant. Unless excess solid remains, there is no guarantee that $[\text{Hg}_2^{2+}][\text{Cl}^-]^2 = K_{sp}$. If Hg₂²⁺ and Cl⁻ are mixed together (with appropriate counterions) such that the product $[\text{Hg}_2^{2+}][\text{Cl}^-]^2$ exceeds K_{sp} , then Hg₂Cl₂ will precipitate.

Mercurous ion, Hg₂²⁺, is a *dimer* (pronounced DIE mer), which means that it consists of two identical units bound together:



OH⁻, S²⁻, and CN⁻ stabilize Hg(II), thereby converting Hg(I) into Hg(0) and Hg(II):

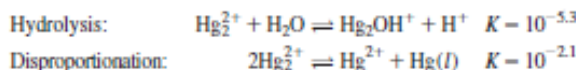


Disproportionation is the process in which an element in an intermediate oxidation state gives products in both higher and lower oxidation states.

BOX 6-1 Solubility Is Governed by More Than the Solubility Product

If we want to know how much Hg_2^{2+} is dissolved in a saturated solution of Hg_2Cl_2 , we are tempted to look at Reaction 6-9 and to note that two Cl^- are created for each Hg_2^{2+} . If we let x be the concentration of Hg_2^{2+} , we could say that the concentration of Cl^- is $2x$. Substituting these values into the solubility product expression 6-10, we could write $K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (x)(2x)^2$, and we would find $[\text{Hg}_2^{2+}] = x = 6.7 \times 10^{-7} \text{ M}$.

However, this answer is incorrect because we have not accounted for other reactions, such as



Both reactions consume Hg_2^{2+} . By Le Chatelier's principle, if Hg_2^{2+} is consumed, more Hg_2Cl_2 will dissolve. We need to know all significant chemical reactions to compute the solubility of a compound.

We most commonly use the solubility product to find the concentration of one ion when the concentration of the other is known or fixed by some means. For example, what is the concentration of Hg_2^{2+} in equilibrium with 0.10 M Cl^- in a solution of KCl containing excess, undissolved $\text{Hg}_2\text{Cl}_2(s)$? To answer this question, we rearrange Equation 6-10 to find

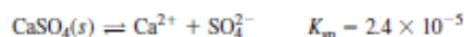
$$[\text{Hg}_2^{2+}] = \frac{K_{\text{sp}}}{[\text{Cl}^-]^2} = \frac{1.2 \times 10^{-18}}{0.10^2} = 1.2 \times 10^{-16} \text{ M}$$

Because Hg_2Cl_2 is so slightly soluble, additional Cl^- obtained from Hg_2Cl_2 is negligible compared with 0.10 M Cl^- .

The solubility product does not tell the entire story of solubility. In addition to complications described in Box 6-1, most salts form soluble *ion pairs* to some extent. That is, $\text{MX}(s)$ can give $\text{MX}(aq)$ as well as $\text{M}^+(aq)$ and $\text{X}^-(aq)$. In a saturated solution of CaSO_4 , for example, two-thirds of the dissolved calcium is Ca^{2+} and one third is $\text{CaSO}_4(aq)$.⁷ The $\text{CaSO}_4(aq)$ **ion pair** is a closely associated pair of ions that behaves as one species in solution. Appendix J and Box 7-1 provide information on ion pairs.⁸

Common Ion Effect

For the ionic solubility reaction



the product $[\text{Ca}^{2+}][\text{SO}_4^{2-}]$ is constant at equilibrium in the presence of excess solid CaSO_4 . If the concentration of Ca^{2+} were increased by adding another source of Ca^{2+} , such as CaCl_2 , then the concentration of SO_4^{2-} must decrease so that the product $[\text{Ca}^{2+}][\text{SO}_4^{2-}]$ remains constant. In other words, less $\text{CaSO}_4(s)$ will dissolve if Ca^{2+} or SO_4^{2-} is already present from some other source. Figure 6-1 shows how the solubility of CaSO_4 decreases in the presence of dissolved CaCl_2 .

This application of Le Chatelier's principle is called the **common ion effect**. A salt will be less soluble if one of its constituent ions is already present in the solution.

A salt is any ionic solid, such as Hg_2Cl_2 or CaSO_4 .

Common ion effect: A salt is less soluble if one of its ions is already present in the solution. Demonstration 6-1 illustrates the common ion effect.

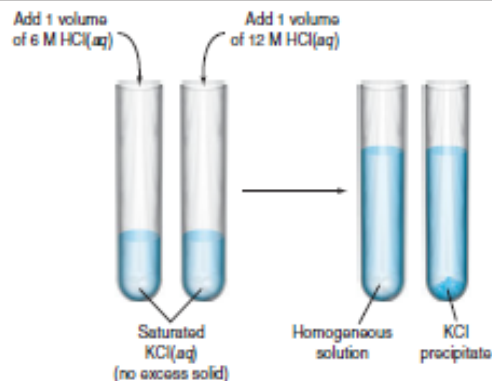
DEMONSTRATION 6-1 Common Ion Effect^{9,10}

Fill two large test tubes about one-third full with saturated aqueous KCl containing no excess solid. The solubility of KCl is approximately 3.7 M , so the solubility product (ignoring activity effects introduced later) is

$$K_{\text{sp}} = [\text{K}^+][\text{Cl}^-] = (3.7)(3.7) = 13.7$$

Now add one-third of a test tube of 6 M HCl to one test tube and an equal volume of 12 M HCl to the other. Even though a common ion, Cl^- , is added in each case, KCl precipitates only in one tube.

To understand your observations, calculate the concentrations of K^+ and Cl^- in each tube after HCl addition. Then evaluate the reaction quotient, $Q = [\text{K}^+][\text{Cl}^-]$, for each tube. Explain your observations.



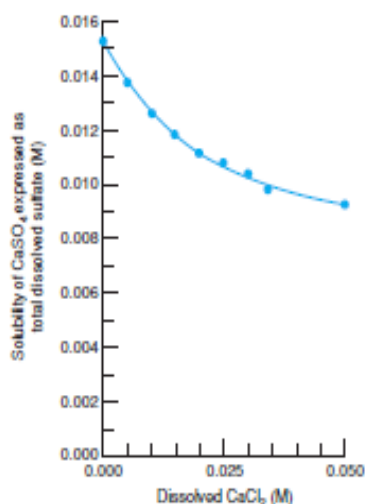


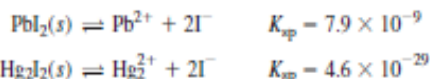
FIGURE 6-1 Solubility of CaSO_4 in solutions containing dissolved CaCl_2 . Solubility is expressed as total dissolved sulfate, which is present as free SO_4^{2-} and as the ion pair, $\text{CaSO}_4(\text{aq})$. [Data from reference B.]



FIGURE 6-2 A yellow solid, lead(II) iodide (PbI_2), precipitates when a colorless solution of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) is added to a colorless solution of potassium iodide (KI). [Photo by Chip Clark.]

Separation by Precipitation

Precipitation can sometimes be used to separate ions from each other.¹¹ For example, consider a solution containing lead(II) (Pb^{2+}) and mercury(I) (Hg_2^{2+}) ions, each at a concentration of 0.010 M. Each forms an insoluble iodide (Figure 6-2), but the mercury(I) iodide is considerably less soluble, as indicated by the smaller value of K_{sp} :



Is it possible to lower the concentration of Hg_2^{2+} by 99.990% by selective precipitation with I^- , without precipitating Pb^{2+} ?

We are asking whether we can lower $[\text{Hg}_2^{2+}]$ to 0.010% of 0.010 M = 1.0×10^{-6} M without precipitating Pb^{2+} . Here is the experiment: We add enough I^- to precipitate 99.990% of Hg_2^{2+} if all the I^- reacts with Hg_2^{2+} and none reacts with Pb^{2+} . To see if any Pb^{2+} should precipitate, we need to know the concentration of I^- in equilibrium with precipitated $\text{Hg}_2\text{I}_2(s)$ plus the remaining 1.0×10^{-6} M Hg_2^{2+} .

$$\begin{aligned} \text{Hg}_2\text{I}_2(s) &\rightleftharpoons \text{Hg}_2^{2+} + 2\text{I}^- \\ [\text{Hg}_2^{2+}][\text{I}^-]^2 &= K_{\text{sp}} \\ (1.0 \times 10^{-6})([\text{I}^-])^2 &= 4.6 \times 10^{-29} \\ [\text{I}^-] &= \sqrt{\frac{4.6 \times 10^{-29}}{1.0 \times 10^{-6}}} = 6.8 \times 10^{-12} \text{ M} \end{aligned}$$

Will this concentration of I^- cause 0.010 M Pb^{2+} to precipitate? That is, is the solubility product of PbI_2 exceeded?

$$\begin{aligned} Q &= [\text{Pb}^{2+}][\text{I}^-]^2 = (0.010)(6.8 \times 10^{-12})^2 \\ &= 4.6 \times 10^{-25} < K_{\text{sp}} \quad (\text{for } \text{PbI}_2) \end{aligned}$$

The reaction quotient, $Q = 4.6 \times 10^{-25}$ is less than K_{sp} for $\text{PbI}_2 = 7.9 \times 10^{-9}$. Therefore, Pb^{2+} will not precipitate and separation of Pb^{2+} and Hg_2^{2+} is feasible. We predict that adding I^- to a solution of Pb^{2+} and Hg_2^{2+} will precipitate virtually all the mercury(I) before any lead(II) precipitates.

Life should be so easy! We have just made a thermodynamic prediction. If the system comes to equilibrium, we can achieve the desired separation. However, occasionally one substance *coprecipitates* with the other. In **coprecipitation**, a substance whose solubility is not

The smaller K_{sp} implies a lower solubility for Hg_2I_2 because the stoichiometries of the two reactions are the same. If the stoichiometries were different, it does not follow that the smaller K_{sp} would imply lower solubility.