Chapter 17: Solubility Equilibria

Sections 17.1 - 17.2: Solubility Equilibria and the K_{sp} Table

In this chapter, we consider the equilibrium associated with the dissociation of solids to form aqueous solutions. Our discussion is limited to ionic solids, which release cations and anions upon dissociation in water.

For example: Consider the equilibrium dissolution of $BaSO_4$.

$$BaSO_{4\,(s)} \leftrightarrows Ba^{+2}_{(aq)} + SO_4^{-2}{}_{(aq)}$$

Initially, before solid $BaSO_4$ is added to water, the Ba^{+2} and SO_4^{-2} ions are tightly bound to each other in the crystalline lattice of the solid. When the salt is placed in water, some of its Ba^{+2} and SO_4^{-2} ions are released into the solution.

This is expressed as: $BaSO_{4\,(s)} \rightarrow Ba^{+2}_{(aq)} + SO_4^{-2}{}_{(aq)}$

Now, if water is allowed to evaporate from the solution, the molarities of Ba^{+2} and SO_4^{-2} ions in solution may increase to the point where these ions prefer to exist in combination as $BaSO_4$ solid.

This is expressed as: $Ba^{+2}_{(aq)} + SO_4^{-2}{}_{(aq)} \rightarrow BaSO_{4\,(s)}$

In summary, as $BaSO_4$ is dissolved in water and the concentrations of Ba^{+2} and SO_4^{-2} in solution increase, a point may be reached where the solid and the solution are in equilibrium.

This is expressed as: $BaSO_{4\,(s)} \leftrightarrows Ba^{+2}_{(aq)} + SO_4^{-2}{}_{(aq)}$

The point at which it becomes impossible to dissolve any further amount of solid $BaSO_4$ in the solution is called the saturation point. We say that the solution is **saturated**.

The equilibrium constant for this dissolution process is expressed as:

$$K_{sp} = [Ba^{+2}][SO_4^{-2}]$$

Note: Solids are not included in the equilibrium constant expression.

K_{sp} is called the "**solubility product constant**" or simply the "**solubility product**."

Note: Once the equilibrium is established, adding more solid $BaSO_4$ to the solution will not shift the position of the equilibrium.

To view the table of K_{sp} values, go to Section 17.1 on the DVD.

The **Solubility** of an ionic solid measures the maximum amount of this solid that can be dissolved in water at a given temperature. The Solubility of an ionic solid is an equilibrium property. Thus, in pure water at a given temperature, an ionic solid has a particular Solubility. Solubility is expressed by the symbol "S." Solubility is expressed in the units of mol.L^{-1} or Molarity (M).

Example 1: Careful measurements reveal the solubility of $BaSO_4$ in pure H_2O to be 1.04×10^{-5} M. Calculate K_{sp} for $BaSO_4$.

First, always write the dissociation equation for the ionic solid.

$$BaSO_{4\,(s)} \leftrightarrows Ba^{+2}_{(aq)} + SO_4{}^{-2}_{(aq)}$$

If "S" is the solubility of $BaSO_4$, then, from the reaction stoichiometry we conclude that:

$[Ba^{+2}] = S$ and $[SO_4{}^{-2}] = S$

Thus, $K_{sp} = [Ba^{+2}]\,[SO_4{}^{-2}]$

$K_{sp} = S^2$

$K_{sp} = (1.04 \times 10^{-5})^2$

$K_{sp} = 1.08 \times 10^{-10}$

Example 2: If Bi_2S_3 has a solubility of 1.0×10^{-15} mol.L^{-1}, calculate its K_{sp}.

First, write the equation for the dissociation of Bi_2S_3.

$$Bi_2S_{3\,(s)} \leftrightarrows 2\,Bi^{+3}_{(aq)} + 3\,S^{-2}_{(aq)}$$

If "S" is the solubility of Bi_2S_3, then, from the reaction stoichiometry we conclude that:

$[Bi^{+3}] = 2S$ and $[S^{-2}] = 3S$

Thus, $K_{sp} = [Bi^{+3}]^2 [S^{-2}]^3$

$K_{sp} = (2S)^2(3S)^3$

$K_{sp} = (4S^2)(27S^3)$

$K_{sp} = 108\ S^5$

$K_{sp} = 108\ (1.0 \times 10^{-15})^5$

$K_{sp} = 1.1 \times 10^{-73}$

In Section 17.2, practice the Interactive Problems.

Sections 17.3 - 17.4: Solubility Calculations from K_{sp}

Example 1: **Consider the dissociation equilibrium of $PbSO_4$ ($K_{sp} = 1.3 \times 10^{-8}$) and calculate its molar solubility.**

First, write the dissociation equilibrium for $PbSO_4$.

$$PbSO_{4\,(s)} \leftrightarrows Pb^{+2}_{(aq)} + SO_4{}^{-2}_{(aq)}$$

If “S” is the solubility of $PbSO_4$, then,

$$[Pb^{+2}] = S \text{ and } [SO_4{}^{-2}] = S$$

The solubility product is expressed as:

$$K_{sp} = [Ba^{+2}]\,[SO_4{}^{-2}]$$

Substituting the concentrations by their respective values, we get:

$$K_{sp} = S^2 \text{ and } K_{sp} = 1.3 \times 10^{-8}$$

$$\text{Hence, } S^2 = 1.3 \times 10^{-8}$$

$$S = (1.3 \times 10^{-8})^{1/2}$$

$$S = 1.1 \times 10^{-4}\ M$$

Example 2: Calculate the molar solubility of $Pb_3(AsO_4)_2$ from the solubility product for $Pb_3(AsO_4)_2$ ($K_{sp} = 4.1 \times 10^{-36}$).

First, write the dissociation equilibrium for $PbSO_4$.

$$Pb_3(AsO_4)_{2\,(s)} \leftrightarrows 3\,Pb^{+2}_{(aq)} + 2\,AsO_4{}^{-3}_{(aq)}$$

If “S” is the solubility of $Pb_3(AsO_4)_2$, then,

$$[Pb^{+2}] = 3S \text{ and } [AsO_4{}^{-3}] = 2S$$

The solubility product is expressed as:

$$K_{sp} = [Pb^{+2}]^3\,[AsO_4{}^{-3}]^2$$

Substituting the concentrations by their respective values, we get:

$$K_{sp} = (3S)^3 (2S)^2 = 108\ S^5 \quad \text{and} \quad K_{sp} = 4.1 \times 10^{-36}$$

$$\text{Hence, } 108\ S^5 = 4.1 \times 10^{-36}$$

$$S = \left[\frac{4.1 \times 10^{-36}}{108}\right]^{\frac{1}{5}}$$

$$S = 3.3 \times 10^{-8}\ M$$

In Section 17.4 practice the Interactive Problems.

Sections 17.5 - 17.6: The Common Ion Effect in Solubility Problems

Let us consider a saturated solution of $BaSO_4$. The dissolution equilibrium for $BaSO_4$ is represented as:

$$BaSO_{4\,(s)} \leftrightarrows Ba^{+2}{}_{(aq)} + SO_4{}^{-2}{}_{(aq)}$$

In a saturated solution of $BaSO_4$, the concentration of Ba^{+2} and SO_4^{-2} ions are equal to the molar solubility of $BaSO_4$.

Now, what happens to this equilibrium if we add Na_2SO_4 or $BaCl_2$? Both Na_2SO_4 and $BaCl_2$ are highly soluble in H_2O. For example, let's add Na_2SO_4 to the saturated solution of $BaSO_4$. The dissociation equation for Na_2SO_4 is written as:

$$Na_2SO_{4\,(s)} \rightarrow 2\ Na^{+}{}_{(aq)} + SO_4{}^{-2}{}_{(aq)}$$

Thus, adding Na_2SO_4 to a saturated solution of $BaSO_4$ results in an increase in the concentration of SO_4^{-2}.

Recall Le Châtelier's Principle:

> "If a change is imposed on a system at equilibrium, the system will react by shifting in the direction that counteracts the change."

Thus, by increasing the concentration of SO_4^{-2} ions in solution, the dissolution equilibrium shifts to the left (favoring the formation of $BaSO_4$).

Similarly, adding $BaCl_2$ to a saturated solution of $BaSO_4$ results in an increase in the concentration of Ba^{+2}. Hence, adding $BaCl_2$ will result in a shift of the dissolution equilibrium for $BaSO_4$ in the direction that consumes Ba^{+2}.

In conclusion: the net effect of adding a common ion to the saturated solution of a slightly soluble ionic compound is to decrease its solubility (S) at a given temperature.

Example 1: Calculate the solubility of $Ca(OH)_2$ in water ($K_{sp} = 1.3 \times 10^{-6}$ for $Ca(OH)_2$).

First, write the equation expressing the equilibrium dissolution of $Ca(OH)_2$.

$$Ca(OH)_{2\ (s)} \leftrightarrows Ca^{+2}_{(aq)} + 2\ OH^{-}_{(aq)}$$

If "S" is the solubility of $Ca(OH)_2$, then,

$$[Ca^{+2}] = S \text{ and } [OH^{-}] = 2S$$

The solubility product is expressed as:

$$K_{sp} = [Ca^{+2}]\,[OH^{-}]^2$$

Substituting the concentrations by their respective values, we get:

$$K_{sp} = (S)\,(2S)^2 = 4\,S^3 \quad \text{and} \quad K_{sp} = 1.3 \times 10^{-6}$$

$$\text{Hence, } 4\,S^3 = 1.3 \times 10^{-6}$$

$$S = \left[\frac{1.3 \times 10^{-6}}{4}\right]^{\frac{1}{3}}$$

$$S = 6.9 \times 10^{-3}\ M$$

Example 2: Calculate the solubility of $Ca(OH)_2$ in water in the presence of 0.10 M $Ca(NO_3)_2$ ($K_{sp} = 1.3 \times 10^{-6}$ for $Ca(OH)_2$).

$Ca(NO_3)_2$ is highly soluble in water.

$$Ca(NO_3)_{2\ (s)} \rightarrow Ca^{+2}_{(aq)} + 2\ NO_3^{-}{}_{(aq)}$$

From the information given and the stoichiometry of the dissociation reaction, we conclude that $[Ca^{+2}] = 0.10$ M

Now, look at the equation for the equilibrium dissociation of $Ca(OH)_2$.

	$Ca(OH)_{2\ (s)}$	$\leftrightarrows$	$Ca^{+2}_{(aq)}$	+	$2\ OH^{-}_{(aq)}$
Initial			0.10 M		0 M

If S is now the solubility of $Ca(OH)_2$ in the presence of 0.10 M $Ca(NO_3)_2$, then, the changes in concentration for Ca^{+2} and OH^- due to the dissociation of $Ca(OH)_2$ and the equilibrium concentrations of these ions are given by:

$$Ca(OH)_{2\ (s)} \leftrightarrows Ca^{+2}_{(aq)} + 2\ OH^-_{(aq)}$$

Initial	0.10 M	0 M
Change	S	2S
Equilibrium	(S + 0.10)	(2S)

The solubility product is expressed as:

$$K_{sp} = [Ca^{+2}]\ [OH^-]^2$$

Substituting the concentrations by their respective values, we get:

$$K_{sp} = (S + 0.10)\ (2S)^2 \quad \text{and} \quad K_{sp} = 1.3 \times 10^{-6}$$

Now, if we assume that S is much smaller than 0.10 M, then, we can neglect S in the term S + 0.10.

$$\text{Hence, } (S + 0.10)\ (2S)^2 \sim 0.4\ S^2 = 1.3 \times 10^{-6}$$

$$S = \left[\frac{1.3 \times 10^{-6}}{0.4}\right]^{\frac{1}{2}}$$

$$S = 1.8 \times 10^{-3}\ M$$

Note: Without $Ca(NO_3)_2$ $S = 6.9 \times 10^{-3}$ M

and with 0.10 M $Ca(NO_3)_2$ $S = 1.8 \times 10^{-3}$ M

The solubility S of calcium hydroxide is decreased when a common ion (Ca^{+2}) is added to a calcium hydroxide solution.

In Section 17.6, practice the Interactive Problems.

Section 17.7: The Effect of pH on Solubility

Consider a saturated solution of $CaCO_3$. The equation representing the dissolution equilibrium for $CaCO_3$ is:

$$CaCO_{3\ (s)} \leftrightarrows Ca^{+2}{}_{(aq)} + CO_3{}^{-2}{}_{(aq)}$$

Now, $CO_3{}^{-2}$ is the conjugate **base** of carbonic **acid**, H_2CO_3. How do we know that? This only comes through practice!!! You should be familiar with strong, as well as weak, **acids** and **bases**.

Carbonic **acid**, H_2CO_3, is a weak **acid**. Hence, $CO_3{}^{-2}$ is a weak **base**. Thus, if a strong **acid** is added to the $CaCO_3$ solution, then $CO_3{}^{-2}$ would accept a proton from the **acid**.

Note: The addition of a strong acid reduces the pH. The reaction between $CO_3{}^{-2}$ and H^+ is written as:

$$H^+{}_{(aq)} + CO_3{}^{-2}{}_{(aq)} \leftrightarrows HCO_3{}^-{}_{(aq)}$$

If a sufficient amount of H^+ is added, (that is if the pH is lowered even further), then:

$$H^+{}_{(aq)} + HCO_3{}^-{}_{(aq)} \leftrightarrows H_2CO_{3(aq)}$$

In conclusion, decreasing the pH results in the consumption of $CO_3{}^{-2}$. Hence, decreasing the pH leads to a shift of the equilibrium dissolution for $CaCO_3$ favoring further dissolution of the solid $CaCO_3$. We say that decreasing the pH leads to an increase in the solubility of $CaCO_3$.

In general, “If an ionic compound contains the anion of a weak **acid**, the addition of a strong **acid** increases its solubility.”

Section 17.8: Predicting the Formation of a Precipitate

In the chapter on Equilibrium, we learned about the relationship between the reaction quotient, Q, and the equilibrium constant, K. The relationship between Q and K tells us the direction in which a reaction must proceed for the system to reach equilibrium. The same approach is used here to discuss the formation of a precipitate. If Q and K are the reaction quotient and the equilibrium constant, respectively, then Q_{sp} and K_{sp} are the solubility product quotient and the solubility product constant, respectively.

Let us consider the dissolution equilibrium for a general ionic solid MX.

$$MX_{(s)} \leftrightarrows M^{+}_{(aq)} + X^{-}_{(aq)}$$

When we refer to the “saturated” aqueous solution of an ionic compound, we imply that this solution is at equilibrium. The concentrations of M^+ and X^- in the saturated solution are the equilibrium concentrations, $[M^+]_{(eq)}$ and $[X^-]_{(eq)}$.

If we call S, the molar solubility of MX, then, for a saturated solution:

$$[M^+] = [M^+]_{(eq)} = S \text{ and } [X^-] = [X^-]_{(eq)} = S$$

For a non-saturated solution, the ion concentrations are:

$$[M^+] \neq [M^+]_{(eq)} \text{ and } [X^-] \neq [X^-]_{(eq)}$$

The solubility product quotient and constant are then expressed as:

$$Q_{sp} = [M^+]\,[X^-] \text{ and } K_{sp} = [M^+]_{(eq)}\,[X^-]_{(eq)} = S^2$$

Hence, for a saturated solution $Q_{sp} = K_{sp}$ (equilibrium chemical system).

When the concentrations of ions in solution are such that $[M^+][X^-] > [M^+]_{eq}[X^-]_{eq}$, that is $Q_{sp} > K_{sp}$, the solution is said to be “**supersaturated**.” The reaction proceeds in the direction in which $M^+_{(aq)}$ and $X^-_{(aq)}$ are consumed and the precipitate $MX_{(s)}$ forms.

Hence, precipitation results in a decrease of the reaction quotient, Q_{sp}. The precipitation continues until Q_{sp} reaches its equilibrium value, K_{sp}. At this point, the solution becomes **saturated** ($Q_{sp} = K_{sp}$).

When the concentrations of ions in solution are such that $[M^+][X^-] < [M^+]_{eq}[X^-]_{eq}$, that is $Q_{sp} < K_{sp}$, the solution is said to be “**unsaturated**.”

What happens depends on whether any solid MX is present in solution.

Assuming some solid is present in solution:

> The solid will dissolve, thereby increasing the concentrations of M^+ and X^- ions in solution and the reaction quotient, Q_{sp}. The dissolution continues until Q_{sp} reaches its equilibrium value, K_{sp}. At this point, the solution becomes saturated ($Q_{sp} = K_{sp}$).

Assuming no solid is present in solution:

> As no solid dissolves, the solution remains “unsaturated.”

In this section, practice the Interactive Problem.

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