Solubility Product Constant

In general, when ionic compounds dissolve in water, they go into solution as ions. When the solution becomes saturated with ions, that is, unable to hold any more, the excess solid settles to the bottom of the container and an equilibrium is established between the undissolved solid and the dissolved ions.

For example, when enough calcium oxalate is introduced into solution for it to become saturated, the following equilibrium is established.

$$\mathbf{CaC_2O_{4(s)} \rightleftarrows Ca^{+2}_{(aq)} + C_2O_4{}^{-2}_{(aq)}}$$

If we write an equilibrium expression for this situation, we obtain:

$$\mathbf{K_{sp} = [Ca^{+2}][C_2O_4{}^{-2}]}$$

Note that the solid itself does not appear as a denominator in the expression since it is a it is not in the same phase as the aqueous ions.

In general, the **solubility product constant (K_{sp}),** is *the equilibrium constant for the solubility equilibrium of a slightly soluble ionic compound.*

Like all equilibrium constants, the K_{sp} is temperature dependent, but at a given temperature it remains relatively constant.

It also noteworthy, that, just like any equilibrium expression, each ion concentration in the expression is raised to the power of its coefficient in the solubility equation.

For example, the K_{sp} expression for $\mathbf{CaCO_{3(s)} \rightleftarrows Ca^{+2}{}_{(aq)} + CO_3{}^{-2}{}_{(aq)}}$ is

$$\mathbf{K_{sp} = [Ca^{+2}][CO_3{}^{-2}]}$$

but for the equation $\mathbf{PbI_{2(s)} \rightleftarrows Pb^{+2}{}_{(aq)} + 2\ I^{-1}{}_{(aq)}}$

$$\mathbf{K_{sp} = [Pb^{+2}][I^{-1}]^2}$$

note that the *concentration of the iodide ion is squared.*

Calculating K_{sp} from the Solubility

Suppose the solubility of silver chloride, AgCl, is 1.9×10^{-3} g/L. Calculate its K_{sp}.

$$1.9 \text{ x } 10^{-3} \text{ grams AgCl}\left(\frac{1 \text{ mole AgCl}}{143.4 \text{ grams AgCl}}\right) = 1.33x10^{-5} \text{ moles AgCl}$$

So, if we were to mix solid AgCl in a liter of solution, 1.33×10^{-5} mol will dissolve to form 1.33×10^{-5} mol of each ion. If we substitute these equilibrium concentrations into the K_{sp} expression, we obtain;

$$AgCl_{(s)} \rightleftarrows Ag^{+1}{}_{(aq)} + Cl^{-1}{}_{(aq)}$$

$$\mathbf{K_{sp} = [Ag^{+1}][Cl^{-1}] = (1.33 \text{ x } 10^{-5})\ (1.33 \text{ x } 10^{-5}) = 1.76 \text{ x } 10^{-10}}$$

A more complex problem is proposed when the salt we're dissolving contains more than multiples of a given ion..

For example

The solubility of Lead(II)arsenate, $Pb_3(AsO_4)_2$, is 3.0 x 10^{-5} g/L. Calculate its K_{sp}

$$3.0 \text{ x } 10^{-5} \text{ grams } Pb_3(AsO_4)_2\left(\frac{1 \text{ mole } Pb(AsO_4)_2}{899.44 \text{ grams}}\right) = 3.34x10^{-8} \text{ moles } Pb(AsO_4)_2$$

In this case, however, the equation describing the dissolution of lead arsenate indicates that we obtain twice as many moles of the arsenate ion as we do lead ions.

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

So, if we were to mix solid $Pb_3(AsO_4)_2$ in a liter of solution, 3.34 x 10^{-8} mol will dissolve to form **3 x** (3.34 x 10^{-8}) mol of the lead ion, or 1.00 x 10^{-7} mol of Pb^{+2} and **2 x** (3.34 x 10^{-8}) mol of the arsenate, or 6.67 x 10^{-8} mol AsO_4^{-3}.

In addition to tripling the number of moles of the lead ion and doubling the number of moles of the arsenate ion, you must remember that the lead ion concentration is **cubed** and the arsenate concentration is **squared** in the K_{sp} expression. If we substitute these equilibrium concentrations into the K_{sp} expression, we obtain;

$$\mathbf{K_{sp} = [Pb^{+2}]^3[AsO_4^{-3}]^2 = (1.00 \times 10^{-7})^3\ (6.67 \times 10^{-8})^2 = 4.45 \times 10^{-36}}$$

Calculating Solubility from the K_{sp}

Calculate the solubility in g/L of calcium sulfate, $CaSO_4$, given that its K_{sp} is 2.4 x 10^{-5}.

The dissolution of calcium sulfate forms equal amounts of calcium ions and sulfate ions according to the following equation.

$$CaSO_{4(s)} \rightleftharpoons Ca^{+2}_{(aq)} + SO_4{}^{-2}_{(aq)}$$

If we let $[Ca^{+2}] = [SO_4^{-2}] = x$, then we can solve for the Molarity of calcium sulfate that would be soluble.

$$\mathbf{Ksp = [Ca^{+2}][SO_4^{-2}]}$$

$$2.4 \times 10^{-5} = (x)(x)$$

solving for x we get $[Ca^{+2}] = [SO_4^{-2}] = 4.90 \times 10^{-3}$ M

Since the equation above shows a 1:1 mole ratio of calcium sulfate to Ca^{+2} ions, we can assume that 4.90 x 10^{-3} moles of $CaSO_4$ will dissolve. Since $CaSO_4$ has a mass of 136.1 g/mol, this would equate to:

$$\mathbf{(4.90 \times 10^{-3} \text{ mol/L})\ \times\ (136.1 \text{ g/mol}) = 6.67 \times 10^{-1} \text{ grams/L}}$$

Solubility and the Common Ion Effect.

In the event that we would try to dissolve a salt in a solution of another salt containing the same cation or anion, this common ion has a cumulative effect on the solubility equilibrium.

For example, suppose we have a solution of Iron(II)sulfide. If we dissolve some sodium sulfide in the solution, the presence of the additional sulfide may cause the precipitation of FeS. The solution now contains less FeS. The decrease in the concentration of the FeS in a solution of Na_2S is an example of the ***common ion effect***. In general, any ionic equilibrium is affected by a substance producing an ion involved in the equilibrium.

Calculating the solubility of a Slightly Soluble Salt in a Solution of a Common Ion

(a) Calculate the **molar** solubility of barium fluoride, BaF_2, in water at 25°C. The K_{sp} at 25°C is 1.0 x 10^{-6}.

$$\mathbf{BaF_{2(s)}} \rightleftarrows \mathbf{Ba^{+2}_{(aq)}} + \mathbf{2\,F^{-1}_{(aq)}}$$

"x" "2x"
(at equilibrium)

$$\mathbf{Ksp = [Ba^{+2}][F^{-1}]^2}$$

$1.0 \times 10^{-6} = (x)\,(2x)^2 = 4x^3$ solving for x, we get: $\mathbf{x = 6.30 \times 10^{-3}\ M}$

Since "x" represents the molarity of the Ba^{+2} ion, and we get one mole of barium ions for each mole of barium fluoride that dissolves, we obtain a **molar solubility for BaF_2 of 6.30 x 10^{-3} M**.

Now, to illustrate the *common ion effect*.

(b) What is the **molar** solubility of barium fluoride in a solution that is 0.15 M NaF at 25°C.

Since the solution is already 0.15 M in F^{-1} ions, we must make an addition to our equilibrium concentrations.

$$\mathbf{BaF_{2(s)}} \rightleftarrows \mathbf{Ba^{+2}_{(aq)}} + \mathbf{2\,F^{-1}_{(aq)}}$$

"x" "2x + **0.15** "
(at equilibrium)

$$\mathbf{K_{sp} = [Ba^{+2}][F^{-1}]^2}$$

Because BaF_2 is only slightly soluble, you might expect "2x" to be negligible compared to 0.15. In that case

$(2x + 0.15) \cong (0.15)$ and substituting into the K_{sp} expression, we get

$1.0 \times 10^{-6} = (x)\,(0.15)^2$

solving for x, we get: $\mathbf{x = 4.44 \times 10^{-5}\ M}$

Note that "x" is indeed much smaller than 0.15, so our assumption was correct. Therefore the molar solubility of barium fluoride in 0.15 M NaF is only **4.44 x 10^{-5} M.** In pure water, the solubility is 6.3 x 10^{-3} M, which is over **140 times greater**

Precipitation Calculations

The K_{sp} for a salt can essentially tell you if precipitation will occur under conditions of ion concentration.

If we have a given set of concentration conditions we can calculate a solubility quotient, Q_c, and compare it to the K_{sp}. The **solubility quotient (often called the ion product)** *has the same form as the solubility constant expression, but the concentrations of the substances are not necessarily equilibrium values*. Rather, they are the concentrations at the start of the reaction. To predict the direction of the reaction, you compare Q_c with K_c.

If $Q_c < K_c$, the reaction will go in the forward direction (the solution is unsaturated)

If $Q_c = K_c$, the reaction mixture is at equilibrium.

If $Q_c > K_c$, the reaction should go in the reverse direction (precipitation occurs)

For example;

Suppose a solution has Ca^{+2} and SO_4^{-2} concentrations of 0.0052 M and 0.0041 M, respectively. If these concentrations were doubled by evaporating half the water in the solution, would precipitation of $CaSO_4$ occur given that the K_{sp} for calcium sulfate is 2.4 x 10^{-5}?

Since the K_{sp} expression for calcium sulfate is $K_{sp} = [Ca^{+2}]_{equil}[SO4^{-2}]_{equil}$, then $Q_c = [Ca^{+2}]_{init}[SO_4^{-2}]_{init}$.

Evaporating half of the water would double the initial concentrations of Ca^{+2} and SO_4^{-2} to 0.0104 M and 0.0081 M, respectively. Substituting these initial conditions into the expression for Q_c, we obtain

$$\mathbf{Q_c = (0.0104)\ (0.0082) = 8.53 \times 10^{-5}}$$

Since this value for Q_c is **greater** than the K_{sp}, ***you would expect precipitation to occur.***

Another example

A solution of 0.00016 M lead(II)nitrate, $Pb(NO_3)_2$, was poured into 456 mL of 0.00023 M sodium sulfate, Na_2SO_4. Would a precipitate of lead(II)sulfate, $PbSO_4$, be expected to form if 255 mL of the lead nitrate solution were added? (The Ksp for lead(II)sulfate is 1.7 x 10^{-8})

First we must calculate the initial concentrations of Pb^{+2} and SO_4^{-2} in the mixture.

(0.00016 mol/L)(0.255 L) = 4.08 x 10^{-5} mol Pb^{+2} (from the 255 mL of $Pb(NO_3)_2$)

(0.00023 mol/L)(0.456 L) =1.05 x 10^{-4} mol SO_4^{-2} (from the 456 mL of Na_2SO_4)

We must now divide each of these results by the cumulative volume of 255 mL + 456 mL = 711 mL

$$[Pb^{+2}] = \frac{4.08 \times 10^{-5}\ \text{mol } Pb^{+2}}{0.711\ \text{L}} = 5.74x10^{-5}M \qquad [SO_4^{-2}] = \frac{1.05 \times 10^{-4}\ \text{mol } SO_4^{-2}}{0.711\ \text{L}} = 1.48x10^{-4}M$$

Substituting these initial concentrations into the Q_c expression for $PbSO_4$, we get;

$Q_c = [Pb^{+2}][SO_4^{-2}] = (5.74 \times 10^{-5})\ (1.48 \times 10^{-4}) = 8.48 \times 10^{-9}$

Since this value is **less** than the K_{sp}, ***we would not expect precipitation to occur***

Completeness of Precipitation

In the real world, the concentration of certain ions in drinking water or surface water can be determined by precipitating the ion of interest, filtering it out of the solution, and simply weighing the dried solid. In order for this to be an accurate analysis, we must be assured that most of the ion of interest was precipitated and very little remained in solution.

For example, Lead chromate, $PbCrO_4$, is a yellow pigment used in paints. Suppose 0.50 L of a 1.0×10^{-5} M $Pb(C_2H_3O_2)$ and 0.50 L of a 1.0×10^{-3} M K_2CrO_4 solution are mixed. Calculate the equilibrium concentration of Pb^{+2} ion remaining in the solution after $PbCrO_4$ precipitates. What is the percentage of Pb^{+2} remaining in solution after the precipitation has occurred. (The K_{sp} for $PbCrO_4$ is 1.8×10^{-14})

First, let us assume a limiting reagent problem where all the lead chromate that is possible precipitates. Then using the K_{sp}, determine how much could redissolve.

	$Pb^{+2}_{(aq)}$	$+$	$CrO_4^{-2}{}_{(aq)}$	$\longrightarrow$	$PbCrO_{4(s)}$
initial	5×10^{-6} mol		5×10^{-4} mol		0
final	0		$(5 \times 10^{-4}) - (5 \times 10^{-6})$ $= 4.95 \times 10^{-4}$ mol		5×10^{-4} mol

The cumulative volume of the two solutions is now 1.0 L, so we now have 5×10^{-4} mol solid $PbCrO_4$ in contact with a solution containing 4.95×10^{-4} M CrO_4^{-2} ions.

Let us now calculate how much of the solid lead chromate could possibly redissolve in the presence of this excess chromate ion.

	$PbCrO_{4(s)}$	$\rightleftarrows$	$Pb^{+2}_{(aq)}$	$+$	$CrO_4^{-2}{}_{(aq)}$
initial			0		4.95×10^{-4} M
change			$+x$		$+x$
equilibrium			x		4.95×10^{-4} M $+ x$

Substituting into the Ksp expression for lead chromate, we obtain

$Ksp = [Pb^{+2}][CrO_4^{-2}]$

$1.8 \times 10^{-14} = (x)(x + 4.95 \times 10^{-4}) = (x)(4.95 \times 10^{-4})$ .....assuming x is negligible compared to 4.95×10^{-4}

Solving for "x" we get $x = \frac{1.8x10^{-14}}{4.95x10^{-4}} = 3.64x10^{-11}\text{M Pb}^{+2}$ remaining in solution

The number of moles of Pb^{+2} in the solution prior to precipitation was 5.0×10^{-6} mol, so the percentage of Pb^{+2} remaining in the solution is:

$$\frac{3.64x10^{-11}}{5.0x10^{-6}}x100\% = 7.3x10^{-4}\%$$

and would generally be considered a complete precipitation.

Fractional Precipitation

Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.

For example, suppose a solution contains both Ba^{+2} ions and Sr^{+2} ions. As we slowly add a concentrated solution of potassium chromate, K_2CrO_4, to the solution, barium chromate precipitates first (since its K_{sp} is much less than that for strontium chromate). After most of the barium chromate has precipitated, strontium chromate begins to precipitate. It is therefore possible to separate Ba^{+2} ions from Sr^{+2} ions from a solution by fractional precipitation.

Effect of PH on Solubility

Suppose we wish to dissolve a salt whose cation or anion may undergo hydrolysis to form H^+ or OH^- in the solution. In this event, the pH of the solution may have a profound effect on the solubility of the salt.

For example, consider the equilibrium between solid calcium fluoride and its ions in aqueous solution.

$$CaF_{2(s)} \rightleftarrows Ca^{+2}_{(aq)} + 2\,F^{-1}_{(aq)}$$

Because the fluoride ion is the conjugate bas of a weak acid (HF), you would expect it to react with any H^+ ion that is added:

$$F^{-1}_{(aq)} + H^{+}_{(aq)} \rightleftarrows HF_{(aq)}$$

According to LeChatelier's Principle, as F^{-1} ions are removed by the reaction with H^+ ion, more calcium fluoride can dissolve to replenish the fluoride ions.

Therefore you expect calcium fluoride to be more soluble in acidic solution than in pure water.

In general, salts of weak acids should be expected to be more soluble in acidic solutions.

For example,

which salt would have its solubility more affected by changes in pH, silver chloride or silver cyanide?

Looking at the two dissolution equations

$$AgCl_{(s)} \rightleftarrows Ag^{+}_{(aq)} + Cl^{-1}_{(aq)}$$

$$AgCN_{(s)} \rightleftarrows Ag^{+}_{(aq)} + CN^{-1}_{(aq)}$$

we can assume that the chloride ion will not undergo hydrolysis since it is the conjugate base of the strong acid, HCl.

However, the cyanide ion is the conjugate base of the weak acid, HCN, and consequently will react with any H^+ ions present to reform HCN, thus removing cyanide ions from the solution.

$$CN^{-1}_{(aq)} + H^{+}_{(aq)} \rightleftarrows HCN_{(aq)}$$

Based on this, one would assume that ***the solubility of the silver cyanide would be more affected by changes in pH***.

Exam Review Topics

terms

Solubility Product Constant
Ion Product, Q_c
Fractional Precipitation
Complex Ion
Ligand
Formation Constant, K_f
Dissociation Constant, K_d

skills/operations

Writing Solubility Product Expressions
Calculating K_{sp} from Solubility
Calculating Solubility from K_{sp}
Calculating Solubility in presence of Common Ion
Predicting Precipitation
Determining Effect of pH on Solubility