

Chemistry 132 NT

The most difficult thing to understand is the income tax.

Albert Einstein

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Chem 132 NT

Solubility and Complex-ion Equilibria

Module 1

Solubility Equilibria

- The Solubility Product Constant
- Solubility and the Common-Ion Effect
- Precipitation Calculations
- Effect of pH on Solubility



Reaction of zinc metal with hydrochloric acid.

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Solubility Equilibria

Many natural processes depend on the precipitation or dissolving of a slightly soluble salt.

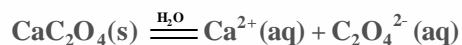
- In the next section, we look at the **equilibria** of slightly soluble, or nearly insoluble, ionic compounds.
- Their equilibrium constants can be used to answer questions regarding **solubility** and **precipitation**.

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The Solubility Product Constant

When an excess of a slightly soluble ionic compound is mixed with water, an equilibrium is established between the solid and the ions in the saturated solution.

For the salt calcium oxalate, CaC_2O_4 , you have the following equilibrium.

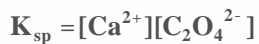


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The Solubility Product Constant

When an excess of a slightly soluble ionic compound is mixed with water, an equilibrium is established between the solid and the ions in the saturated solution.

The equilibrium constant for this process is called the **solubility product constant**.



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The Solubility Product Constant

In general, the solubility product constant is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound.

It equals the **product of the equilibrium concentrations** of the ions in the compound.

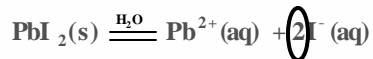
Each concentration is **raised to a power** equal to the number of such ions in the formula of the compound.

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The Solubility Product Constant

✎ In general, the solubility product constant is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound.

◆ For example, lead iodide, PbI_2 , is another slightly soluble salt. Its equilibrium is:



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The Solubility Product Constant

✎ In general, the solubility product constant is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound.

◆ The expression for the solubility product constant is:

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

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Calculating K_{sp} from the Solubility

✎ A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4 , contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.

◆ We must first convert the solubility of calcium oxalate from 0.0061 g/liter to moles per liter.

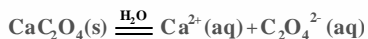
$$\begin{aligned} \text{M CaC}_2\text{O}_4 &= (0.0061 \text{ g CaC}_2\text{O}_4 / \text{L}) \cdot \frac{1 \text{ mol CaC}_2\text{O}_4}{128 \text{ g CaC}_2\text{O}_4} \\ &= 4.8 \cdot 10^{-5} \text{ mol CaC}_2\text{O}_4 / \text{L} \end{aligned}$$

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Calculating K_{sp} from the Solubility

✎ A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4 , contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.

◆ When 4.8×10^{-5} mol of solid dissolve it forms 4.8×10^{-5} mol of each ion.



Starting	0	0
Change	$+4.8 \times 10^{-5}$	$+4.8 \times 10^{-5}$
Equilibrium	4.8×10^{-5}	4.8×10^{-5}

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Calculating K_{sp} from the Solubility

✎ A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4 , contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.

◆ You can now substitute into the equilibrium-constant expression.

$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$$

$$K_{sp} = (4.8 \times 10^{-5})(4.8 \times 10^{-5})$$

$$K_{sp} = 2.3 \times 10^{-9}$$

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Calculating K_{sp} from the Solubility

✎ By experiment, it is found that 1.2×10^{-3} mol of lead(II) iodide, PbI_2 , dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?

◆ Note that in this example, you find that 1.2×10^{-3} mol of the solid dissolves to give 1.2×10^{-3} mol Pb^{2+} and 2.4 ($2 \times 1.2 \times 10^{-3}$) mol of I⁻.

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Calculating K_{sp} from the Solubility

By experiment, it is found that 1.2×10^{-3} mol of lead(II) iodide, PbI_2 , dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?

The following table summarizes.



Starting	0	0
Change	$+1.2 \times 10^{-3}$	$+2 \times (1.2 \times 10^{-3})$
Equilibrium	1.2×10^{-3}	$2 \times (1.2 \times 10^{-3})$

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Calculating K_{sp} from the Solubility

By experiment, it is found that 1.2×10^{-3} mol of lead(II) iodide, PbI_2 , dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?

Substituting into the equilibrium-constant expression:

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

$$K_{sp} = (1.2 \times 10^{-3})(2 \times (1.2 \times 10^{-3}))^2$$

$$K_{sp} = 6.9 \times 10^{-9}$$

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Calculating K_{sp} from the Solubility

By experiment, it is found that 1.2×10^{-3} mol of lead(II) iodide, PbI_2 , dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?

A table in your text lists the solubility product constants for various ionic compounds.

If the solubility product constant is known, the solubility of the compound can be calculated.

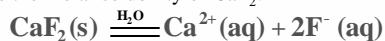
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Calculating the Solubility from

$$K_{sp}$$

✎ The mineral fluorite is calcium fluoride, CaF_2 . Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})

◆ Let x be the molar solubility of CaF_2 .



Starting	0	0
Change	+x	+2x
Equilibrium	x	2x

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Calculating the Solubility from

$$K_{sp}$$

✎ The mineral fluorite is calcium fluoride, CaF_2 . Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})

◆ You substitute into the equilibrium-constant equation

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

$$(x)(2x)^2 = 3.4 \times 10^{-11}$$

$$4x^3 = 3.4 \times 10^{-11}$$

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Calculating the Solubility from

$$K_{sp}$$

✎ The mineral fluorite is calcium fluoride, CaF_2 . Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})

◆ You now solve for x .

$$x = \sqrt[3]{\frac{3.4 \times 10^{-11}}{4}} = 2.0 \times 10^{-4} \text{ mol CaF}_2/\text{L}$$

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Calculating the Solubility from K_{sp}

✎ The mineral fluorite is calcium fluoride, CaF_2 . Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})

◆ Convert to g/L (CaF_2 78.1 g/mol).

$$\begin{aligned} \text{solubility} &= 2.0 \times 10^{-4} \text{ mol/L} \cdot \frac{78.1 \text{ g CaF}_2}{1 \text{ mol CaF}_2} \\ &= 1.6 \times 10^{-2} \text{ g CaF}_2 / \text{L} \end{aligned}$$

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Solubility and the Common-Ion Effect

✎ In this section we will look at calculating solubilities in the presence of other ions.

◆ The importance of the K_{sp} becomes apparent when you consider the solubility of one salt in the solution of another **having the same cation**.

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Solubility and the Common-Ion Effect

✎ In this section we will look at calculating solubilities in the presence of other ions.

◆ For example, suppose you wish to know the solubility of calcium oxalate in a solution of calcium chloride.

◆ Each salt contributes the same cation (Ca^{2+})

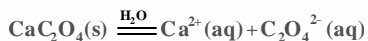
◆ The effect is to make calcium oxalate **less soluble than it would be in pure water**.

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A Problem To Consider

What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9} .

Note that before the calcium oxalate dissolves, there is already 0.15 M Ca^{2+} in the solution.



Starting	0.15	0
Change	+x	+x
Equilibrium	0.15 + x	x

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A Problem To Consider

What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9} .

You substitute into the equilibrium-constant equation

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

$$(0.15 + x)(x) = 2.3 \times 10^{-9}$$

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A Problem To Consider

What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9} .

Now rearrange this equation to give

$$x = \frac{2.3 \times 10^{-9}}{0.15 + x} \quad @ \quad \frac{2.3 \times 10^{-9}}{0.15}$$

We expect x to be negligible compared to 0.15.

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A Problem To Consider

What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9} .

Now rearrange this equation to give

$$x = \frac{2.3 \times 10^{-9}}{0.15 + x} \approx \frac{2.3 \times 10^{-9}}{0.15}$$

$$x = 1.5 \times 10^{-8}$$

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A Problem To Consider

What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9} .

Therefore, the molar solubility of calcium oxalate in 0.15 M CaCl_2 is 1.5×10^{-8} M.

In pure water, the molarity was 4.8×10^{-5} M, which is over **3000 times greater**.

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Precipitation Calculations

Precipitation is merely another way of looking at solubility equilibrium.

Rather than considering how much of a substance will dissolve, we ask: **Will precipitation occur for a given starting ion concentration?**

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Criteria for Precipitation

✎ To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c** .

- ✦ To predict the direction of reaction, you **compare Q_c with K_c** (Equilibrium Chapter).
- ✦ The reaction quotient has the same form as the K_{sp} expression, but the concentrations of products are starting values.

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Criteria for Precipitation

✎ To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c** .

- ✦ Consider the following equilibrium.



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Criteria for Precipitation

✎ To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c** .

- ✦ The Q_c expression is

$$Q_c = [\text{Pb}^{2+}]_i [\text{Cl}^{-}]_i^2$$

where initial concentration is denoted by i

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Criteria for Precipitation

☛ To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c** .

- ◆ If Q_c exceeds the K_{sp} , precipitation occurs.
- ◆ If Q_c is less than K_{sp} , more solute can dissolve.
- ◆ If Q_c equals the K_{sp} , the solution is saturated.

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Predicting Whether Precipitation Will Occur

☛ The concentration of calcium ion in blood plasma is 0.0025 M. If the concentration of oxalate ion is 1.0×10^{-7} M, do you expect calcium oxalate to precipitate? K_{sp} for calcium oxalate is 2.3×10^{-9} .

◆ The ion product quotient, Q_c , is:

$$Q_c = [Ca^{2+}]_i [C_2O_4^{2-}]_i$$

$$Q_c = (0.0025) (1.0 \times 10^{-7})$$

$$Q_c = 2.5 \times 10^{-10}$$

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Predicting Whether Precipitation Will Occur

☛ The concentration of calcium ion in blood plasma is 0.0025 M. If the concentration of oxalate ion is 1.0×10^{-7} M, do you expect calcium oxalate to precipitate? K_{sp} for calcium oxalate is 2.3×10^{-9} .

◆ This value is smaller than the K_{sp} , so **you do not expect precipitation to occur.**

$$Q_c = 2.5 \times 10^{-10} < K_{sp}$$

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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, when you slowly add potassium chromate, K_2CrO_4 , to a solution containing Ba^{2+} and Sr^{2+} , **barium chromate precipitates first**.

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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.

◆ After most of the Ba^{2+} ion has precipitated, strontium chromate begins to precipitate.

◆ It is therefore possible to separate Ba^{2+} from Sr^{2+} by **fractional precipitation** using K_2CrO_4 .

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Effect of pH on Solubility

⚠ Sometimes it is necessary to account for other reactions aqueous ions might undergo.

◆ For example, if the anion is the **conjugate base of a weak acid**, it will react with H_3O^+ .

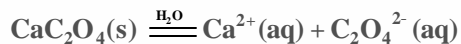
◆ You should expect the solubility to be affected by pH.

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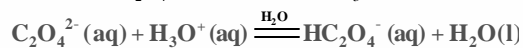
Effect of pH on Solubility

⚠ Sometimes it is necessary to account for other reactions aqueous ions might undergo.

◆ Consider the following equilibrium.



◆ Because the oxalate ion is conjugate to a weak acid (HC_2O_4^-), it will react with H_3O^+ .



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Effect of pH on Solubility

⚠ Sometimes it is necessary to account for other reactions aqueous ions might undergo.

◆ According to Le Chatelier's principle, as $\text{C}_2\text{O}_4^{2-}$ ion is removed by the reaction with H_3O^+ , more calcium oxalate dissolves.

◆ Therefore, you expect calcium oxalate to be **more soluble in acidic solution (low pH) than in pure water.**

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Separation of Metal Ions by Sulfide Precipitation

⚠ Many metal sulfides are insoluble in water but dissolve in acidic solution.

◆ **Qualitative analysis** uses this change in solubility of the metal sulfides with pH to separate a mixture of metal ions.

◆ By adjusting the pH in an aqueous solution of H_2S , you adjust the sulfide concentration to precipitate the least soluble metal sulfide first.

◆ **Qualitative analysis** is covered in your text.

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Operational Skills

- ✎ Writing solubility product expressions
- ✎ Calculating K_{sp} from the solubility, or vice versa.
- ✎ Calculating the solubility of a slightly soluble salt in a solution of a common ion.
- ✎ Predicting whether precipitation will occur
- ✎ Determining the qualitative effect of pH on solubility

Time for a few review questions

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