What Do You Mean, "It Is Soluble After All?" Exploring Solubility Equilibrium

OBJECTIVE

Students will learn to apply general equilibrium problem-solving techniques to solubility equilibrium.

LEVEL

Chemistry

NATIONAL STANDARDS

UCP.1, UCP.2, UCP.3, UCP.4, B.3, B.6

CONNECTIONS TO AP

AP Chemistry:

III. Reaction types A. Reaction types C. Equilibrium 1. Concept of dynamic equilibrium, physical and chemical; equilibrium constants 2. Quantitative treatment b. Equilibrium constants for reactions in solution

TIME FRAME

90 minutes

MATERIALS

calculator paper and pencil

TEACHER NOTES

This activity is designed as a classroom lesson and will require a direct teach. Students should be guided through the general concepts and definitions of chemical equilibrium as it relates to solubility. This activity should follow the lesson on general equilibrium expressions and the RICE-table method of problem solving. You should guide the students through the example problems found on the student answer pages. It is also assumed that students know their solubility rules by this time in the course.

There are many types of equilibrium including: concentration, gas, acid-base and solubility. This lesson is designed as an introduction to the basic skills and concepts involving solubility equilibrium. Much of what is presented here is probably absent from your high school chemistry textbook. However, the first question in the free-response section of the AP* Chemistry exam is always an equilibrium problem. Your students will benefit from an introduction to solubility equilibrium in your first-year course.

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ANSWERS TO THE CONCLUSION QUESTIONS

Emphasize to students that the value of an equilibrium constant does figure into their decision regarding how many significant digits to report in their answers since it is a *derived* constant rather than a defined constant.

- 1. In a saturated solution of $Ag_2C_2O_4$, the concentration of silver ion is 2.1×10^{-4} mol L⁻¹. From this information, calculate the solubility product constant, K_{sp} of $Ag_2C_2O_4$.
 - $\operatorname{Ag}_{2}C_{2}O_{4}(s) \rightleftharpoons 2 \operatorname{Ag}^{+}(aq) + C_{2}O_{4}^{2-}(aq)$ $K_{sp} = \left[\operatorname{Ag}^{+}\right]^{2} \left[C_{2}O_{4}^{2-}\right] = \left[2x\right]^{2} \left[x\right]$ $\left[\operatorname{Ag}^{+}\right] = 2x = 2.1 \times 10^{-4} \frac{\operatorname{mol}}{\mathrm{L}}, \quad x = \left[C_{2}O_{4}^{2-}\right] = 1.05 \times 10^{-5} \frac{\operatorname{mol}}{\mathrm{L}}$ • $\therefore K_{sp} = \left[2.1 \times 10^{-4}\right]^{2} \left[1.05 \times 10^{-5}\right] = 4.6 \times 10^{-12}$
 - Remind students to leave all numbers in the calculator and round at the end.
- 2. What amount of chloride ion must be exceeded before silver chloride will precipitate out of a solution in which the concentration of silver ion is 2.7×10^{-5} mol/L? K_{sp} for AgCl is 1.8×10^{-10} at 25°C.

• Solve for
$$[Cl^{-}]$$

AgCl(s) \iff Ag⁺(aq) + Cl⁻(aq)
 $K_{sp} = 1.8 \times 10^{-10} = [Ag^{+}][Cl^{-}]$

•
$$\therefore [Cl^{-}] = \frac{K_{sp}}{[Ag^{+}]} = \frac{1.8 \times 10^{-10}}{[2.7 \times 10^{-5}]} = 6.7 \times 10^{-6} \frac{\text{mol}}{\text{L}}$$

- So, more than $6.7 \times 10^{-6} \frac{\text{mol}}{\text{L}}$ of chloride ion must be added to the mixture for a precipitate of silver chloride to form.
- Remind students to leave all numbers in the calculator and round at the end.

What Do You Mean, "It Is Soluble After All?"

- 3. K_{sp} for HgS(s) is 1.6×10^{-54} at 25°C. If mercury(II) nitrate has a concentration of 2.0×10^{-25} mol L⁻¹, what is the maximum amount of sulfide ion that can exist in this solution at 25°C?
 - Solve for $[S^{2^{-}}]$ HgS(s) \longleftrightarrow Hg²⁺(aq) + S²⁻(aq) $K_{sp} = 1.6 \times 10^{-54} = [Hg^{2^{+}}][S^{2^{-}}]$ [Hg(NO₃)₂] = 2.0 × 10⁻²⁵ $\frac{\text{mol}}{L}$ $\therefore [Hg^{2^{+}}] = 2.0 \times 10^{-25} \frac{\text{mol}}{L}$ • $[S^{2^{-}}] = \frac{K_{sp}}{[Hg^{2^{+}}]} = \frac{1.6 \times 10^{-54}}{[2.0 \times 10^{-25}]} = 8.0 \times 10^{-30} \frac{\text{mol}}{L}$

4. Consider the reaction $\operatorname{SrCO}_3(s) \iff \operatorname{Sr}^{2^+}(aq) + \operatorname{CO}_3^{2^-}(aq)$. Given that the molar concentrations of the two ions in this reaction are both equal to 2.6×10^{-5} mol/L at 25°C, what is the value of K_{sp} for SrCO_3 at 25°C?

•
$$\operatorname{SrCO}_{3}(s) \rightleftharpoons \operatorname{Sr}^{2+}(aq) + \operatorname{CO}_{3}^{2-}(aq)$$

 $K_{sp} = \left[\operatorname{Sr}^{2+}\right] \left[\operatorname{CO}_{3}^{2-}\right]$
 $\left[\operatorname{Sr}^{2+}\right] = \left[\operatorname{CO}_{3}^{2-}\right] = 2.6 \times 10^{-5} \frac{\operatorname{mol}}{\mathrm{L}}$
• $\therefore K_{sp} = \left[2.6 \times 10^{-5}\right] \left[2.6 \times 10^{-5}\right] = \left[2.6 \times 10^{-5}\right]^{2} = 6.8 \times 10^{-10}$

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- 5. If the solubility product constant for AgBr is 5.0×10^{-13} at 25°C, and the molar concentration of Ag⁺ and Br⁻ are each 7.5×10^{-5} mol L⁻¹ in a solution of AgBr(*aq*) at 25°C, will there be a precipitate of AgBr formed?
 - Yes, since $Q_{sp} > K_{sp}$: a precipitate forms.

AgBr(s) \longrightarrow Ag⁺(aq) + Br⁻(aq) $\left[Ag^{+} \right] = \left[Br^{-} \right] = 7.5 \times 10^{-5} \frac{mol}{L}$

- $Q_{sp} = [Ag^+][Br^-] = [7.5 \times 10^{-5}]^2 = 5.6 \times 10^{-9}$ Compare Q_{sp} to K_{sp}
- Since $5.0 \times 10^{-9} > 5.0 \times 10^{-13}$, a precipitate forms.
- 6. Given that K_{sp} for Ca₃(PO₄)₂ is 1.3×10^{-32} at 25°C, what are the molar concentrations of Ca²⁺ and PO₄³⁻ in a saturated solution at 25°C?

•
$$\operatorname{Ca}_{3}(\operatorname{PO}_{4})_{2}(s) \rightleftharpoons 3 \operatorname{Ca}^{2+}(aq) + 2 \operatorname{PO}_{4}^{3-}(aq)$$

 $3x \quad 2x$
 $K_{sp} = \left[\operatorname{Ca}^{2+}\right]^{3} \left[\operatorname{PO}_{4}^{3-}\right]^{2} = \left[3x\right]^{3} \left[2x\right]^{2} = \left(27x^{3}\right)\left(4x^{2}\right) = 108x^{5}$
 $K_{sp} = 1.3 \times 10^{-32} = 108x^{5}$
 $x = \sqrt[5]{\frac{1.3 \times 10^{-32}}{108}} = 1.6 \times 10^{-7}$
• $\left[\operatorname{Ca}^{2+}\right] = 3x = 4.9 \times 10^{-7}$

•
$$\left[\operatorname{PO}_{4}^{3-}\right] = 2x = 3.3 \times 10^{-7}$$

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7. The solubility product of PbCl₂ at 25°C is 1.6×10^{-5} . If [Cl⁻] = 4.7×10^{-3} , what is the concentration of lead ion in equilibrium with the chloride ion at 25°C?

•
$$\operatorname{PbCl}_{2}(s) \rightleftharpoons \operatorname{Pb}^{2+}(aq) + 2 \operatorname{Cl}^{-}(aq)$$

 $K_{sp} = 1.6 \times 10^{-5} = \left[\operatorname{Pb}^{2+}\right] \left[\operatorname{Cl}^{-}\right]^{2}$
• $\left[\operatorname{Pb}^{2+}\right] = \frac{K_{sp}}{\left[\operatorname{Cl}^{-}\right]^{2}} = \frac{1.6 \times 10^{-5}}{\left[4.7 \times 10^{-3}\right]^{2}} = 0.72 \frac{\operatorname{mol}}{\mathrm{L}}$

8. Calculate the molar solubility at 25°C of Ba(OH)₂ if it has a K_{sp} of 5.0 × 10⁻³ at 25°C?

•
$$\operatorname{Ba}(\operatorname{OH})_2(s) \rightleftharpoons \operatorname{Ba}^{2+}(aq) + 2 \operatorname{OH}^-(aq)$$

$$K_{sp} = \left[\text{Ba}^{2+} \right] \left[\text{OH}^{-} \right]^{2} = \left[x \right] \left[2x \right]^{2} = 4x^{3} = 5.0 \times 10^{-3}$$

•
$$x = \text{molar solubility} = \sqrt[3]{\frac{5.0 \times 10^{-3}}{4}} = 0.11 \frac{\text{mol}}{\text{L}}$$

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- 9. Will a precipitate form when 75.0 mL of 0.020 *M* BaCl₂ and 125 mL of 0.040 *M* Na₂SO₄ are mixed together at 25°C? K_{sp} of BaSO₄ = 1.5 × 10⁻⁹ at 25°C.
 - Solve for the concentration of each ion and calculate Q_{sp} and compare it to K_{sp} .

$$0.0750 \mathcal{L} \times \frac{0.020 \text{ mol}}{\mathcal{L}} \text{BaCl}_2 = 0.0015 \text{ mol BaCl}_2 = 0.0015 \text{ mol Ba}^{2+}$$
$$0.125 \mathcal{L} \times \frac{0.040 \text{ mol}}{\mathcal{L}} \text{Na}_2 \text{SO}_4 = 0.0050 \text{ mol Na}_2 \text{SO}_4 = 0.0050 \text{ mol SO}_4^{2-}$$

Total volume of solution = 200 mL = 0.200 L

$$BaSO_{4}(s) \xleftarrow{} Ba^{2+}(aq) + SO_{4}^{2-}(aq)$$
$$Q_{sp} = \left[Ba^{2+}\right] \left[SO_{4}^{2-}\right]$$
$$Q_{sp} = \left[\frac{0.0015}{0.200}\right] \left[\frac{0.0050}{0.200}\right] = 1.9 \times 10^{-4}$$

- Since $1.9 \times 10^{-4} > 1.5 \times 10^{-5}$ $Q_{sp} > K_{sp}$ \therefore precipitate forms.
- 10. Will a precipitate form when 100.0 mL of $0.020 M Pb(NO_3)_2$ is added to 100.0 mL of 0.020 *M* NaCl at 25°C? K_{sp} of PbCl₂ = 1.6 × 10⁻⁵ at 25°C.
 - $0.1000 \not{L} \times \frac{0.020 \text{ mol}}{\not{L}} \text{Pb}(\text{NO}_3)_2 = 0.0020 \text{ mol Pb}(\text{NO}_3)_2 = 0.0020 \text{ mol Pb}^{2+}$

•
$$0.1000 \, \cancel{k} \times \frac{0.020 \text{ mol}}{\cancel{k}} \text{ NaCl} = 0.0020 \text{ mol NaCl} = 0.0020 \text{ mol Cl}^-$$

Total volume of solution = 200 mL = 0.200 L

$$PbCl_{2}(s) \longleftrightarrow Pb^{2+}(aq) + 2 Cl^{-}(aq)$$
$$Q_{sp} = \left[Pb^{2+}\right] \left[Cl^{-}\right]^{2}$$
$$Q_{sp} = \left[\frac{0.0020}{0.200}\right] \left[\frac{0.0020}{0.200}\right]^{2} = 1.0 \times 10^{-6}$$

• $Q_{sp} = \left[\frac{1}{0.200}\right] \left[\frac{1}{0.200}\right] = 1.0 \times 10^{-10}$ • $Q_{sp} < K_{sp} \therefore$ NO precipitate forms. --1 Fm

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Laying the Foundation in Chemistry

What Do You Mean, "It Is Soluble After All?" Exploring Solubility Equilibrium

In this activity, we explore a new kind of K, K_{sp} , where the "sp" stands for "solubility product". This is where we confess our sins as chemistry teachers [gasp!]. Remember those solubility rules we keep harping about? Well, some of those compounds deemed insoluble actually dissolve a bit. We haven't *exactly* been lying to you, since the future attorneys among you probably read the fine print where "soluble" has a qualifier of 3.0 grams dissolving in 100. mL of water. This qualifier means that if only 2.9 grams dissolves in 100. mL of water the compound or salt is deemed insoluble. What does this really mean? It means that nothing is completely insoluble, even silver chloride!

DETERMINIG THE SOLUBILITY PRODUCT CONSTANT, KSP

If a precipitate is visible in a container, then a saturated solution is present. Saturated solutions of salts represent a type of chemical equilibria. Slightly soluble salts establish a dynamic equilibrium with the hydrated cations and anions in solution. No ions are initially present when the solid is first added to water. As dissolution proceeds, the concentration of ions increases until equilibrium is established. This occurs when the solution is saturated. All of these equilibria follow this general reaction pattern:

solid + H₂O(
$$\lambda$$
) \rightleftharpoons cation⁺(*aq*) + anion⁻(*aq*)

Since water is a pure liquid, it does NOT appear in the equilibrium constant expression. And neither does the solid. That means that the K_{sp} expression is simply the product of the ions in solution since the concentration of water is not appreciably changing and is thus considered to be "one".

Consider a saturated solution of AgCl, the simplified equation would be (notice the water is left out of the simplified equation):

$$\operatorname{AgCl}(s) \longleftrightarrow \operatorname{Ag}^+(aq) + \operatorname{Cl}^-(aq)$$

The solubility product expression would be:

$$K_{sp} = [Ag^+][C1^-] = 1.8 \times 10^{-10}$$

Remember, K of any variety represents both a number *and* a relationship. K_{sp} values are published in many different sources including your textbook. Since they are experimentally determined, you will notice disagreement among sources. It is also important to note that the number of significant digits on K_{sp} values *do* factor into your decisions about the number of significant digits to report since they are *derived* rather than *defined* constants.

DETERMINING KSP FROM EXPERIMENTAL MEASUREMENTS

In the laboratory a K_{sp} is determined by careful laboratory measurements using various spectroscopic methods.

Example 1

Lead(II) chloride dissolves to a slight extent in water according to the equation:

$$PbCl_2(s) \iff Pb^{+2}(aq) + 2 Cl^{-}(aq)$$

Calculate the K_{sp} if the lead ion concentration has been found to be $1.62 \times 10^{-2} M$.

Solution:

If lead's concentration is equal to "x", then chloride's concentration is equal to "2x". You must respect the stoichiometry of the reaction when assigning x values.

$$K_{sp} = [Pb^{+2}][Cl^{-}]^2 = (1.62 \times 10^{-2})(3.24 \times 10^{-2})^2 = 1.70 \times 10^{-5}$$

ESTIMATING SALT SOLUBILITY FROM KSP

Example 2

The K_{sp} for CaCO₃ is 3.8×10^{-9} at 25°C. Calculate the solubility of calcium carbonate in pure water in a. moles per liter

b. grams per liter

Solution:

a. First, write the balanced chemical equation for the dissolution:

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

Next, write the K_{sp} expression and set it equal to the value you were given in the problem. Substitute "x" for each ion, this one is easy since the ion:ion ratio is 1:1.

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 3.8 \times 10^{-9}$$
 therefore,
 $K_{sp} = [x][x] = x^2 = 3.8 \times 10^{-9}$ finally, solve for "x"
 $x = \sqrt{3.8 \times 10^{-9}} = 6.2 \times 10^{-5} M$

Why is this the solubility of $CaCO_3(s)$ in moles per liter? Think back to the RICE tables. In this chemical equation, all of the substances have coefficients of one. So, when one CaCO₃ formula unit dissolves it forms one each of the ions. That means that the $[CaCO_3] = [either ion]$. Any time you've solved for "*x*", you have the solubility of the solid in moles per liter.

b. Just use dimensional analysis:

$$\left(\frac{6.2 \times 10^{-5} \text{moles}}{\text{liter}}\right) \times \left(\frac{100. \text{ g}}{\text{mole}}\right) = 6.2 \times 10^{-2} \frac{\text{g}}{\text{liter}}$$

Don't forget solubility changes with temperature! Some substances become less soluble at low temperatures while some become more soluble. This graph is a classic.



TO PRECIPITATE OR NOT TO PRECIPITATE?

To answer this question we must first be introduced to the concept of the reaction quotient, Q. We can use the value of Q to decide whether or not a precipitate will form. We can also determine the concentration of the ion in question, when precipitation begins. Q, the reaction quotient, is calculated exactly as you calculate K. What does the value of Q_{sp} mean when compared to the value of K_{sp} ?

- 1. $Q_{sp} < K_{sp}$, the system is not at equilibrium (*un*saturated)
- 2. $Q_{sp} = K_{sp}$, the system is at equilibrium (saturated)
- 3. $Q_{sp} > K_{sp}$, the system is not at equilibrium (*super*saturated)

Precipitates form when the solution is supersaturated!

Example 3

At 25°C, the value of K_{sp} for PbF₂(s) is 4.0×10^{-8} . If 50.0 mL of 0.020 *M* KF(*aq*) is added to 50.0 mL of 0.060 *M* Pb(NO₃)(*aq*), will a precipitate form? Assume that the volumes are additive.

Solution:

"Assume the volumes are additive" is your clue that the molarities of the ions need to be recalculated. The total volume of the solution is 50.0 mL + 50.0 mL = 100.0 mL = 0.100 L

moles of $F^- = M \times L = (0.020 \text{ mol/L})(0.050 \text{ L}) = 0.0010 \text{ moles } F^-$

$$[F^{-}] = \frac{0.0010 \text{ moles}}{0.100 \text{ L}} = 0.010 M$$

moles of $Pb^{2+} = M \times L = (0.060 \text{ mol/L})(0.050 \text{ L}) = 0.0030 \text{ moles } Pb^{2+}$

$$[Pb^{2^+}] = \frac{0.0030 \text{ moles}}{0.100 \text{ L}} = 0.030 M$$

Calculate Q_{sp} and compare it to K_{sp} to determine if a precipitate occurs.

PbF₂(s)
$$\rightleftharpoons$$
 Pb²⁺(aq) + 2 F⁻(aq)
 $Q_{sp} = [Pb^{2+}][F^{-}]^2 = [0.030][0.010]^2 = 3.0 \times 10^{-6}$

Compare Q_{sp} to K_{sp} . Since Q_{sp} is greater than K_{sp} , a precipitate forms.

SOLUBILITY AND THE COMMON ION EFFECT

Experiments show that the solubility of any salt is always less in the presence of a "common ion". Why? LeChâtelier's Principle, that's why! Be reasonable and use approximations when you can. The pH can also affect solubility. Evaluate the balanced chemical equation to see which species would "react" with the addition of acid or base.

Example 4

Would magnesium hydroxide be more soluble in an acid or a base? Why?

$$Mg(OH)_2(s) \iff Mg^{2+}(aq) + 2 OH^{-}(aq)$$

Solution:

Addition of a base would shift the equilibrium to the left, decreasing the solubility since more solid magnesium hydroxide forms as a result of the increase in OH⁻ ions. Addition of an acid will remove OH⁻ ions as water is formed. This will shift the equilibrium to the right, decreasing the amount of solid magnesium hydroxide making it *more* soluble.

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PURPOSE

In this activity you will learn to write solubility equilibrium constant expressions and solve solubility equilibrium problems. You will also become familiar with the terms such as molar solubility and the reaction quotient, Q.

MATERIALS

calculator paper and pencil

PROCEDURE

Solve the problems found on your student answer page. Be sure to show all work paying attention to the proper use of significant digits and units.

Name			

What Do You Mean, "It Is Soluble After All?" Exploring Solubility Equilibrium

Period

CONCLUSION QUESTIONS

It is suggested that you leave all numbers in the calculator as you solve the following problems. As always, take care to round to the appropriate number of significant digits when reporting your answer.

- 1. In a saturated solution of $Ag_2C_2O_4$, the concentration of silver ion is 2.1×10^{-4} mol L⁻¹. From this information, calculate the solubility product constant, K_{sp} of $Ag_2C_2O_4$.
- 2. What amount of chloride ion must be exceeded before silver chloride will precipitate out of a solution in which the concentration of silver ion is 2.7×10^{-5} mol/L? K_{sp} for AgCl is 1.8×10^{-10} at 25°C.
- 3. K_{sp} for HgS(s) is 1.6×10^{-54} at 25°C. If mercury(II) nitrate has a concentration of 2.0×10^{-25} mol L⁻¹, what is the maximum amount of sulfide ion that can exist in this solution at 25°C?
- 4. Consider the reaction $SrCO_3(s) \iff Sr^{2+}(aq) + CO_3^{2-}(aq)$. Given that the molar concentrations of the two ions in this reaction are both equal to 2.6×10^{-5} mol/L at 25°C, what is the value of K_{sp} for SrCO₃ at 25°C?
- 5. If the solubility product constant for AgBr is 5.0×10^{-13} at 25°C, and the molar concentration of Ag⁺ and Br⁻ are each 7.5×10^{-5} mol L⁻¹ in a solution of AgBr(*aq*) at 25°C, will there be a precipitate of AgBr formed?
- 6. Given that K_{sp} for Ca₃(PO₄)₂ is 1.3×10^{-32} at 25°C, what are the molar concentrations of Ca²⁺ and PO₄³⁻ in a saturated solution at 25°C?
- 7. The solubility product of PbCl₂ at 25°C is 1.6×10^{-5} . If [Cl⁻] = 4.7×10^{-3} , what is the concentration of lead ion in equilibrium with the chloride ion at 25°C?
- 8. Calculate the molar solubility at 25°C of Ba(OH)₂ if it has a K_{sp} of 5.0 × 10⁻³ at 25°C?
- 9. Will a precipitate form when 75.0 mL of 0.020 *M* BaCl₂ and 125 mL of 0.040 *M* Na₂SO₄ are mixed together at 25°C? K_{sp} of BaSO₄ = 1.5 × 10⁻⁹ at 25°C.
- 10. Will a precipitate form when 100.0 mL of $0.020 M Pb(NO_3)_2$ is added to 100.0 mL of 0.020 M NaCl at 25°C? K_{sp} of PbCl₂ = 1.6 × 10⁻⁵ at 25°C.

Laying the Foundation in Chemistry