40S Chemistry

Solubility

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Outcomes . . .

- Describe and write a balanced chemical equation to represent the equilibrium in a saturated aqueous solution of an ionic compound.
- Write a solubility product expression, given a balanced chemical equation for a solubility reaction.
- Distinguish between solubility and solubility product constant(K_{sp}).
- Calculate the solubility product, given the solubility of a compound in water, and vice versa.

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Introduction

- When placed into water, slightly soluble substances establish an equilibrium between the solid and dissolved ions in a saturated solution. This equilibrium is described by the solubility product.
- Using the solubility product, we can calculate the ion concentrations and the solubility of the substance.

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- when a solution is saturated, there exists an equilibrium between the dissolved solute particles and the solid solute particles.
- For an ionic compound, such as sodium chloride, we express the equilibrium in terms of a chemical equation:
  - $NaCl(s) \rightleftarrows Na^{+}(aq) + Cl^{-}(aq)$
- This equilibrium is dynamic, since the rate of dissolving of each ion is equal to the crystallization of each ion.

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The Solubility Product

- Substances chemists believed to be insoluble in water, by experiment, were shown to be slightly soluble.
- With sensitive instruments, chemists are able to show that substances that would not dissolve in water actually do dissolve to a very small extent.

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- When a sparingly soluble ionic solid is dissolved in water to form a saturated solution the general equilibrium equation is

$$A_aB_b(s) \rightleftharpoons aA^+(aq) + bB^-(aq)$$

- Where A is a positively charged ion and B is a negatively charged ion.

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- At a given temperature, the equilibrium law for this reaction is given as

$$K_C = \frac{[A+]^a [B-]^b}{[A_aB_b]}$$

$$K_C \bullet [A_aB_b] = [A+]^a [B-]^b$$

- However, the term $K_C[A_aB_b]$ can be replaced by a new constant, **K_{sp}**, called the **solubility product**.

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$$K_{sp} = [A^+]^a[B^-]^b$$

- The **solubility product constant** is the product of ion concentrations in a saturated solution. The solubility product constant takes into account the presence of the solid.

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The Solubility Product Expression

- Recall that the general form of the solubility product expression is
  - $K_{sp} = [A^+]^a[B^-]^b$
- for the dissociation equation
  - $A_aB_b(s) \rightleftharpoons aA^+(aq) + bB^-(aq)$

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Example 1

- Write the dissociation equation and the expression for the solubility product constant for calcium hydroxide.

Solution

- Write the chemical formula for calcium hydroxide, $Ca(OH)_2$.

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- Write the dissociation equation, remembering that the subscript indicates two hydroxide ions dissociate for every calcium ion:

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ OH^{-}(aq)$$

- When writing the solubility product expression, the molar coefficient in the dissociation equation becomes the exponent.
  - $K_{sp} = [Ca^{2+}][OH^{-}]^2$

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Example 2

- Write the solubility product expression for $Pb_3(PO_4)_2$.
- **Solution**
- Write the dissociation equation first.

$$Pb_3(PO_4)_2(s) \quad 3\ Pb^{2+}(aq) + 2\ PO_4^{3-}(aq)$$

- Use the molar coefficients to write the solubility product expression.

$$K_{sp} = [Pb^{2+}]^3[PO_4^{3-}]^2$$

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Calculating Solubility Product

Example 3

- If at equilibrium, the concentration of silver ions is 1.3×10^{-5} mol/L and the concentration of chloride ions is 1.3×10^{-5} mol/L, what is the K_{sp} of silver chloride?

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- **Solution**
- Write out the dissociation equation:

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

- Write the solubility product expression:

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

- Substitute given values:
- $K_{sp} = (1.3 \times 10^{-5})(1.3 \times 10^{-5})$
- $K_{sp} = 1.7 \times 10^{-10}$

***NOTE: K_{sp} has no units.**

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Solubility

- Solubility and solubility product are two different terms.
- **Solubility** is the maximum amount of solute that can dissolve in a certain amount of solvent at a certain temperature.
- Solubility has an infinite number of possible values, depending on temperature and other solutes present.

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- **Solubility product** is an equilibrium constant and has only one value for a given solid at a particular temperature.
- **Example 4**
- The solubility of PbF_2 is 0.466 g/L. What is the value of the solubility product?

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Solution

Step 1: Determine the number of moles/L of PbF_2.

PbF_2 = 207.19g + 2(19.00g) = 245.19g

0.466g/L PbF_2 x $\frac{1 \text{ mol } PbF_2}{245.19\text{g } PbF_2}$ = 1.90×10^{-3} mol/L

So, the concentration of PbF_2 is 1.90×10^{-3} mol/L.

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- Step 2: Write the dissociation equation.

$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ F^{-}(aq)$

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- Step 3: Calculate ion concentrations.
- The concentration of PbF_2 an Pb^{2+} ions will be equal since their stoichiometry is 1:1.
- $[PbF_2] = [Pb^{2+}] = 1.90 \times 10^{-3}$ mol/L
- From the stoichiometry,
- $[F^{-}] = 2 \times [Pb^{2+}] = 3.80 \times 10^{-3}$ mol/L

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- Step 4: Write the solubility product expression and calculate.
- $K_{sp} = [Pb^{2+}][F^{-}]^2$
- $K_{sp} = (1.90 \times 10^{-3})(3.80 \times 10^{-3})^2$
- **$K_{sp} = 2.74 \times 10^{-8}$**
- Therefore, the solubility product of PbF_2 is 2.74×10^{-8}.

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Determining Ion Concentrations from K_{sp}

Example 5

- The K_{sp} of magnesium hydroxide is 8.9×10^{-12}. What will be the equilibrium concentrations of the dissolved ions in a saturated solution of $Mg(OH)_2$?

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Solution

Step 1: Write the dissolution equation.

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

Step 2: Assign variables to the ion [].

- The initial concentrations of the ions, before dissolving, is zero.
- The equilibrium concentrations are unknown, so we will assign them a value of "*x*".

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- The OH^- is assigned a value of 2*x* because of the stoichiometry.

Step 3: Substitute values into K_{sp} expression and solve for *x*.

$$Ksp = [Mg^{2+}][OH^-]^2$$

$$8.9 \times 10^{-12} = (x)(2x)^2$$

$$8.9 \times 10^{-12} = 4x^3$$

$$\frac{8.9 \times 10^{-12}}{4} = \frac{4x^3}{4}$$

$$1.3 \times 10^{-4} = x$$

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Step 4: Calculate ion concentrations from the value of *x*.

- **$[Mg^{2+}] = x = 1.3 \times 10^{-4}$ mol/L**
- **$[OH^-] = 2x = 2.6 \times 10^{-4}$ mol/L**

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In Summary . . .

- Substances which are insoluble are actually slightly soluble.
- The solubility product, K_{sp}, describes the product of ion concentrations in saturated solutions.
- Solubility can be determined from the solubility product.

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Assignment

- Complete Solubility *Assignment 1*
- Complete Solubility *Assignment 2*

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Solubility Rules

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Solubility Rules

- Insoluble compounds are generally described as those that precipitate upon mixing equal volumes of solutions which are 0.10 mol/L in the respective ions.
- A **precipitate** is the solid that forms when two solutions are mixed. A precipitate will usually cause a mixture to appear cloudy.

- Video 1

- Video 2

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Predicting if a Precipitate Forms

- Not all reactions produce a precipitate. If the volume of solution is large enough, and the amount of solute is small enough no precipitate will form.
- The **reaction quotient**, ***Qsp***, to predict whether a precipitate forms. The form of the reaction quotient is the same as the K_{sp}.

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- By comparing the value of the reaction quotient with the solubility product, we can determine if an aqueous solution is saturated or unsaturated . . .

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If,

- $Qsp = K_{sp}$, the solution is just saturated and no precipitate forms.
- $Qsp > K_{sp}$, the solution is saturated and **a precipitate forms**.
- $Qsp < K_{sp}$, the solution is unsaturated and no precipitate forms.

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Determining if a Solution is Saturated

- The reaction quotient can be used to determine if adding a specific amount of solute to a solvent produces a saturated solution.

Example 4

- The K_{sp} of lead (II) chloride is 1.6×10^{-5}. If 0.57 g of lead (II) chloride are added to 1500 mL of water, is the solution saturated? Assume no volume change.

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Solution

Step 1: Write out the dissociation equation for lead (II) chloride.

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

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Step 2: Determine the concentration of the $PbCl_2$.

$PbCl_2$ = 207.19g/mol + 2(35.45g/mol) = 278.09g/mol

$$0.57g\ PbCl_2 \times \frac{1\ mol\ PbCl_2}{278.09g\ PbCl_2} = 0.00204\ mol\ PbCl_2$$

$$M = \frac{mol}{L} = \frac{0.00204\ mol\ PbCl_2}{1.5L} = 1.37\times10^{-3}\ mol/L$$

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Step 3: Calculate the value of the reaction quotient.

Determine the concentration of each ion:

$[Pb^{2+}] = [PbCl_2] = 1.37 \times 10^{-3}$ mol/L

$[Cl^-] = 2 \times [Pb^{2+}] = 2.74 \times 10^{-3}$ mol/L

$Qsp = [Pb^{2+}]\,[Cl^-]^2$

$Qsp = (1.37 \times 10^{-3})\,(2.74 \times 10^{-3})^2$

$Qsp = 1.03 \times 10^{-8} = 1.0 \times 10^{-8}$

Since Qsp<Ksp, the solution is unsaturated.

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Does a Precipitate Form?

Example 5

If 20.0 mL of a 0.0010 mol/L silver nitrate solution is mixed with 20.0 mL of a 3.0×10^{-5} mol/L potassium bromide solution, does silver bromide ($K_{sp} = 5.0 \times 10^{-13}$) precipitate? Assume the volumes are additive.

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Solution

Step 1: Write the dissociation equation for silver bromide.

$$AgBr(s) \rightleftharpoons Ag^{+}(aq) + Br^{-}(aq)$$

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Step 2: Determine the ion concentrations.

Since the solutions are mixed, we will assume the new volume will be the sum of the two.

New volume = 20.0 mL + 20.0 mL = 40.0 mL or 0.0400 L

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Calculate the silver ion and bromide ion concentrations by using the dilution formula:

$$[Ag^{+}] = \frac{C_1V_1}{V_2} = \frac{(0.0010\ \text{mol/L})(0.0200\ \text{L})}{(0.0400\ \text{L})} = 5.0\times10^{-4}\ \text{mol/L}\ Ag^{+}$$

$$[Br^{-}] = \frac{C_1V_1}{V_2} = \frac{(3.0\times10^{-5}\ \text{mol/L})(0.0200\ \text{L})}{(0.0400\ \text{L})} = 1.5\times10^{-5}\ \text{mol/L}\ Br^{-}$$

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Step 3: Calculate the reaction quotient.

$$\begin{aligned} Q_{sp} &= [Ag^{+}][Br^{-}] \\ &= (5.0\times10^{-4})(1.5\times10^{-5}) \\ &= 7.5\times10^{-9} \end{aligned}$$

$Qsp>K_{sp}$, the solution is saturated and a precipitate forms.

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In Summary . . .

- Substances which are insoluble are actually slightly soluble.
- The solubility product, K_{sp}, describes the product of ion concentrations in saturated solutions.
- Solubility can be determined from the solubility product.

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Lesson Summary

- When two solutions of ionic compounds are mixed, a solid with low solubility may precipitate from the mixture.
- The trial K_{sp}, or reaction quotient can be used to predict if a precipitate forms.

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Assignment

- Complete Solubility *Assignment 3*

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Common Ion Effect

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Introduction

- we have studied the solubility of ionic solids in pure water and precipitates from mixtures.
- What happens to solubility of an ionic compound if the water contains an ion in common with the ionic solid?

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Outcome

- Calculate the solubility of an ionic compound in the presence of an ion in common with the ionic compound.

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Common Ions

- When an ionic compound dissolves in pure water, the initial concentration of each ion is zero.
- If an ionic compound dissolves in a solution that has an ion in common with the compound, this is not the case.
- Even though the starting concentrations may not be zero, the product of the ions must still equal the solubility product constant.

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- How would the solubility of silver chloride in pure water change if we try dissolving it in tap water?

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

- Tap water often has chlorine added to kill bacteria. The chlorine exists as chloride ions, so when we dissolve silver chloride in tap water, chloride ions are present.

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- According to Le Chatelier's Principle, Adding more chloride ions to a saturated solution would cause the equilibrium to shift to the left to use up the excess product.
- This would result in more solid formed, and a decreased solubility.

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Solubility in the Presence of a Common Ion

- Le Chatelier's Principle predicts that the solubility of an ionic solid in a solution containing a common ion decreases its solubility.
- Will our calculations support this?

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Example 1

- Determine the solubility of silver chloride in pure water and in a solution of 0.10 mol/L sodium chloride. The K_{sp} of AgCl is 1.7×10^{-10}.

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Solution

Step 1: Solubility of AgCl in pure water.

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

$$Ksp = [Ag^{+}]\,[Cl^{-}] = 1.7 \times 10^{-10}$$

$$[Ag^{+}] = [Cl^{-}] = x$$

x = molar solubility

$$(x)\,(x) = 1.7 \times 10^{-10}$$

$$x^2 = 1.7 \times 10^{-10}$$

$$x = 1.3 \times 10^{-5}$$

Since [AgCl] = x, the solubility of AgCl in pure water is 1.3×10^{-5} mol/L.

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Step 2: Determine the $[Cl^-]$ in solution.

- The sodium chloride solution will have an initial chloride ion concentration of 0.10 mol/L.
- This must be added to the $[Cl^-]$ from the AgCl solution . . .

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$Ksp = [Ag^+] [Cl^-] = 1.7 \times 10^{-10}$

Let x = molar solubility

$[Ag^+] = x$, $[Cl^-] = 0.10 + x$

$(x)(0.10 + x) = 1.7 \times 10^{-10}$

$0.10x = 1.7 \times 10^{-10}$

$x = 1.7 \times 10^{-9}$ mol/L

The value of x is considered insignificant because the Ksp is so small

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- AgCl is 1.7×10^{-9} mol/L in 0.10 mol/L NaCl and 1.3×10^{-5} mol/L in pure water.
- The solubility decreases, just as predicted.

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Solubility in the Presence of a Common Ion

Example 2

- The K_{sp} of lead (II) chloride, $PbCl_2$, is 1.6×10^{-5}. What is the solubility of lead (II) chloride in a 0.10 mol/L solution of magnesium chloride, $MgCl_2$?

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Solution

Step 1: Determine the concentration of the common ion, Cl^-.

$$MgCl_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ Cl^-(aq)$$

- From the dissociation of magnesium chloride,
- $[Cl^-] = 2 \times [MgCl_2] = 0.20$ mol/L

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Step 2: Determine the $[Cl^-]$ in solution.

- The magnesium chloride solution will have an initial chloride ion concentration of 0.20 mol/L.
- This must be added to the $[Cl^-]$ from the $PbCl_2$ solution . . .

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

$$Ksp = [Pb^{2+}]\ [Cl^-]^2 = 1.6 \times 10^{-5}$$

Let x = molar solubility

$[Pb^{2+}] = x$, $[Cl^-] = 0.20 + 2x$

$$(x)\ (0.20 + 2x)^2 = 1.6 \times 10^{-5}$$

$$0.040x = 1.6 \times 10^{-5}$$

$$x = 4.0 \times 10^{-4}\ mol/L$$

The value of x is considered insignificant because the Ksp is so small

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- The solubility of $PbCl_2$ is 4.0×10^{-4} mol/L in 0.10 mol/L $MgCl_2$ solution.

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Solubility in the Presence of a Common Ion

Example 3

- The K_{sp} of lead (II) chloride is 1.6×10^{-5}. What is the solubility of lead (II) chloride in a 0.10 mol/L solution of lead (II) nitrate, $Pb(NO_3)_2$?

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Solution

Step 1: Determine the concentration of the common ion, Pb^{2+}

- $Pb(NO_3)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ NO_3^{-}(aq)$
- From the dissociation of lead (II) nitrate,
- $[Pb^{2+}] = [Pb(NO_3)_2] = 0.10$ mol/L

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Step 2: Determine the $[Pb^{2+}]$ in solution.

- The lead (II) chloride solution will have an initial lead ion concentration of 0.10 mol/L.
- This must be added to the $[Pb^{2+}]$ from the $Pb(NO_3)_2$ solution . . .

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$Ksp = [Pb^{2+}] [Cl^-]^2 = 1.6 \times 10^{-5}$

Let x = molar solubility

$[Pb^{2+}] = 0.10 + x$, $[Cl^-] = 2x$

$(2x)^2 (0.10 + x) = 1.6 \times 10^{-5}$

$0.40x^2 = 1.6 \times 10^{-5}$

$x = 6.3 \times 10^{-3}$ mol/L

The value of x is considered insignificant because the Ksp is so small

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- The solubility of $PbCl_2$ is 6.3×10^{-3} mol/L in 0.10 mol/L $Pb(NO_3)_2$.

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Alternate Method:

- Ksp problems can also be solved using an ICE table.
- The solution, with ICE table, for **Example 3** is shown on the following slides.
- The first step and some of step 2 are identical to the original solution. But as we progress further . . .

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Solution

Step 1: Determine the concentration of the common ion, Pb^{2+}

- $Pb(NO_3)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ NO_3^{-}(aq)$
- From the dissociation of lead (II) nitrate,
- $[Pb^{2+}] = [Pb(NO_3)_2] = 0.10$ mol/L

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Step 2: Determine the $[Pb^{+}]$ in solution.

- The lead (II) chloride solution will have an initial chloride ion concentration of 0.10 mol/L.
- This must be added to the $[Pb^{2+}]$ from the $Pb(NO_3)_2$ solution . . .

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- Set up an ICE table:

$PbCl_{2\,(s)} \rightleftarrows Pb^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)}$

I	**Solid**	**0.10**	**0**
C	**Solid**	**+x**	**+2x**
E	**solid**	**0.10 + x**	**2x**

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I	**Solid**	**0.10**	**0**
C	**Solid**	**+x**	**+2x**
E	**solid**	**0.10 + x**	**2x**

$Ksp = [Pb^{2+}]\,[Cl^{-}]^2 = 1.6 \times 10^{-5}$

$(0.10 + x)\,(2x)^2 = 1.6 \times 10^{-5}$

$0.40x^2 = 1.6 \times 10^{-5}$

$x = 6.3 \times 10^{-3}$ mol/L

The value of x is considered insignificant because the Ksp is so small

The solubility of $PbCl_2$ is 6.3×10^{-3} mol/L in 0.10 mol/L $Pb(NO_3)_2$.

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Lesson Summary

- The solubility of an ionic solid decreases in the presence of an ion in common with the ionic solid.
- Solving problems requires determining the molar solubility and substituting values into the solubility product expression.

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Assignment

- Complete worksheets: *Ksp Assignments #1-5*

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