Solubility Equilibria

Chem 36

Spring 2002

Definitions

- "Insoluble" ionic solids are *actually* sparingly soluble:

$$SrCrO_4\ (s) \leftrightarrows Sr^{2+}\ (aq) + CrO_4^{2-}\ (aq)$$

$$\mathbf{K_{sp}} = [Sr^{2+}][CrO_4^{2-}] = 4.0 \times 10^{-5}$$

solubility product constant

K_{sp} and solubility are NOT the same!

➢ **Solubility:** amount (*moles* or *grams*) of a compound that is soluble in ***1.00 L*** of solution.

Calculating Solubility

- **What is the solubility of $SrCrO_4$?**

$$SrCrO_4\,(s) \leftrightarrows Sr^{2+}\,(aq) + CrO_4^{2-}\,(aq)$$

Equilib: **S** **S**

Plugging into K_{sp}:

$$K_{sp} = [Sr^{2+}][CrO_4^{2-}] = \mathbf{S^2} = 4.0 \times 10^{-5}$$

$$\mathbf{S} = \underline{\boldsymbol{6.3 \times 10^{-3}}} \text{ mol } SrCrO_4/L$$

molar solubility

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Gram Solubility?

- Convert *molar* solubility to **mass**:

$$\frac{6.325 \times 10^{-3} \text{ mol } SrCrO_4}{L} \times \frac{203.61 \text{ g } SrCrO_4}{\text{mol } SrCrO_4} = 1.29\ \frac{g\ SrCrO_4}{L}$$

$$= \underline{\boldsymbol{1.3\ g\ SrCrO_4/L}}$$

How would a <u>common ion</u> affect solubility?

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Common Ion Effect

- What is the solubility of $SrCrO_4$ in *0.1000 M K_2CrO_4*?

$$SrCrO_4\ (s) \leftrightarrows Sr^{2+}\ (aq) + CrO_4^{2-}\ (aq)$$

		Sr^{2+}	CrO_4^{2-}
I		**-**	0.1000 *M*
C		+S	+S
E		*S*	*0.1000 + S*

$K_{sp} = [Sr^{2+}][CrO_4^{2-}] = \mathbf{S(0.1000 + S)} = 4.0 \times 10^{-5}$

<u>Assume:</u> S << 0.1000 $\Rightarrow$ S' (0.1000) = 4.0×10^{-5}

S' = <u>***4.0×10^{-4} M***</u> *(assumption checks!)*

<u>***(= 8.1×10^{-2} g $SrCrO_4$/L)***</u>

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More Common Ions

- Sometimes the *common ion* is one that is <u>commonly found</u> in water: e.g., OH^-

$$Al(OH)_3\ (s) \leftrightarrows Al^{3+}\ (aq) + 3\ OH^-\ (aq)$$

E **S** **3S**

$K_{sp} = [Al^{3+}][OH^-]^3 = S(3S)^3 = 3.7 \times 10^{-15}$

$27S^4 = 3.7 \times 10^{-15}$

S = <u>***1.1×10^{-4} mol $Al(OH)_3$/L***</u>

<u>What about OH^-?</u>

At pH=7, $[OH^-]_{H2O}$ << S (safe to ignore)

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How 'bout at pH=12.00?

- Now we've got LOTS of OH^-!

  pH = 12.00, so pOH = 2.00:

  $[OH^-] = 1.0 \times 10^{-2}\ M$

$$Al(OH)_3\ (s) \leftrightarrows Al^{3+}\ (aq) + 3\ OH^-\ (aq)$$

E **S** *1.0 x 10^-2^* + **3S**

$K_{sp} = [Al^{3+}][OH^-]^3 = \mathbf{S(0.010 + 3S)^3} = 3.7 \times 10^{-15}$

Assume: $3S \ll 0.010 \Rightarrow S'\ (0.010)^3 = 3.7 \times 10^{-15}$

S' = ***3.7 x 10^-9^ mol Al(OH)~3~/L*** *(assumption checks!)*

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When Precipitation Happens

- Will a *precipitate* form when we mix two solutions?

Example:

If we mix 50.0 mL 0.010 *M* $Pb(NO_3)_2$ and 50.0 mL 0.010 *M* KI, will $\boldsymbol{PbI_2}$ **($\boldsymbol{K_{sp} = 1.4 \times 10^{-8}}$)** precipitate?

$$PbI_2\ (s) \leftrightarrows Pb^{2+}\ (aq) + 2I^-\ (aq)$$

50.0 mL 0.010 *M* = *0.50 mmol* Pb^{2+} and I^-

$C_{Pb2+} = C_{I-} = 0.50\ mmol/100.0\ mL = 5.0 \times 10^{-3}\ M$

$Q = (C_{Pb2+})(C_{I-})^2 = (5.0 \times 10^{-3})(5.0 \times 10^{-3})^2 = \boldsymbol{1.25 \times 10^{-7}}$

$Q > K_{sp}$ so ***PbI_2 will precipitate***

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Differential Solubility

- Suppose *two* cations are in solution; which will precipitate first?

<u>Example:</u>

Suppose we add CrO_4^{2-} to a solution containing *both* Ba^{2+} and Sr^{2+} at **1.0 x 10^{-3} *M***. Which ion will precipitate first?

K_{sp} ($BaCrO_4$) = 2.4 x 10^{-10}
K_{sp} ($SrCrO_4$) = 3.6 x 10^{-5}

- With identical amounts of both ions, cmpd with the *smallest K_{sp}* will precipitate first: Ba^{2+}

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Quantitatively!

- $BaCrO_4$ will begin to precipitate when:

$$[CrO_4^{2-}] = \frac{K_{sp}}{[Ba^{2+}]} = \frac{2.4 \times 10^{-10}}{1.0 \times 10^{-3}} = \mathbf{2.4 \times 10^{-7}\ \mathit{M}}$$

$[CrO_4^{2-}]$ when precipitation *begins*

- $SrCrO_4$ will begin to precipitate when:

$$[CrO_4^{2-}] = \frac{K_{sp}}{[Sr^{2+}]} = \frac{3.6 \times 10^{-5}}{1.0 \times 10^{-3}} = \mathbf{3.6 \times 10^{-2}\ \mathit{M}}$$

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Leftovers?

- How much Ba^{2+} **remains** when $SrCrO_4$ *begins* to precipitate?

When $SrCrO_4$ begins to precipitate:

$$[CrO_4^{2-}] = 3.6 \times 10^{-2}\ M$$

So: $$[Ba^{2+}] = \frac{K_{sp}}{[CrO_4^{2-}]} = \frac{2.4 \times 10^{-10}}{3.6 \times 10^{-2}} = \mathbf{6.7 \times 10^{-9}\ M}$$

Ba^{2+} remaining

% Ba^{2+} remaining:

$$\frac{[Ba^{2+}]}{C_{Ba2+}} = \frac{6.7 \times 10^{-9}}{1.0 \times 10^{-3}} \times 100 = \boldsymbol{6.7 \times 10^{-4}\ \%}$$

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