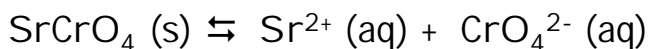


Solubility Equilibria

Chem 36
Spring 2002

Definitions

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



$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{CrO}_4^{2-}] = 4.0 \times 10^{-5}$$

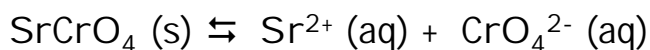
solubility product constant

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 SrCrO₄?



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

Plugging into K_{sp}:

$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{CrO}_4^{2-}] = \mathbf{S^2} = 4.0 \times 10^{-5}$$

$$\mathbf{S = 6.3 \times 10^{-3} \text{ mol SrCrO}_4/\text{L}}$$

←
molar solubility

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Gram Solubility?

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

$$\frac{6.325 \times 10^{-3} \text{ mol SrCrO}_4}{\text{L}} \times \frac{203.61 \text{ g SrCrO}_4}{\text{mol SrCrO}_4} = 1.29 \frac{\text{g SrCrO}_4}{\text{L}}$$

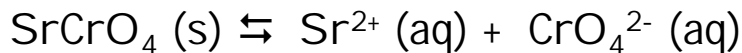
$$= \underline{\underline{1.3 \text{ g SrCrO}_4/\text{L}}}$$

How would a common ion affect solubility?

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Common Ion Effect

- What is the solubility of SrCrO_4 in $0.1000 \text{ M K}_2\text{CrO}_4$?



I	-	0.1000 M
C	+S	+S
E	S	0.1000 + S

$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{CrO}_4^{2-}] = \mathbf{S(0.1000 + S)} = 4.0 \times 10^{-5}$$

Assume: $S \ll 0.1000 \Rightarrow S' (0.1000) = 4.0 \times 10^{-5}$

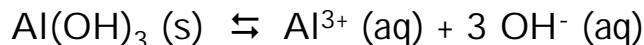
$$S' = \mathbf{4.0 \times 10^{-4} \text{ M}} \quad (\text{assumption checks!})$$

$$\mathbf{= 8.1 \times 10^{-2} \text{ g SrCrO}_4/\text{L}}$$

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More Common Ions

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



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

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

$$S = \mathbf{1.1 \times 10^{-4} \text{ mol Al(OH)}_3/\text{L}}$$

What about OH^- ?

At pH=7, $[\text{OH}^-]_{\text{H}_2\text{O}} \ll S$ (safe to ignore)

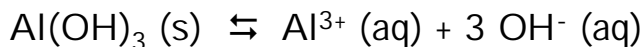
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How 'bout at pH=12.00?

➤ Now we've got LOTS of OH⁻!

pH = 12.00, so pOH = 2.00:

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



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

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

$$\text{S}' = \underline{\underline{3.7 \times 10^{-9} \text{ mol Al}(\text{OH})_3/\text{L}}} \text{ (assumption checks!)}$$

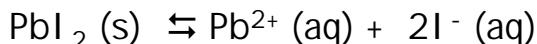
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When Precipitation Happens

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

Example:

If we mix 50.0 mL 0.010 M $\text{Pb}(\text{NO}_3)_2$ and 50.0 mL 0.010 M KI, will ***PbI₂*** ($K_{\text{sp}} = 1.4 \times 10^{-8}$) precipitate?



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

$$C_{\text{Pb}^{2+}} = C_{\text{I}^-} = 0.50 \text{ mmol}/100.0 \text{ mL} = 5.0 \times 10^{-3} \text{ M}$$

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

$Q > K_{\text{sp}}$ so ***PbI₂* will precipitate**

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Differential Solubility

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

Example:

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

$$K_{\text{sp}} (\text{BaCrO}_4) = 2.4 \times 10^{-10}$$

$$K_{\text{sp}} (\text{SrCrO}_4) = 3.6 \times 10^{-5}$$

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

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Quantitatively!

- BaCrO_4 will begin to precipitate when:

$$[\text{CrO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{Ba}^{2+}]} = \frac{2.4 \times 10^{-10}}{1.0 \times 10^{-3}} = 2.4 \times 10^{-7} \text{ M}$$

$[\text{CrO}_4^{2-}]$ when precipitation *begins*

- SrCrO_4 will begin to precipitate when:

$$[\text{CrO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{Sr}^{2+}]} = \frac{3.6 \times 10^{-5}}{1.0 \times 10^{-3}} = 3.6 \times 10^{-2} \text{ M}$$

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Leftovers?

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

When SrCrO_4 begins to precipitate:

$$[\text{CrO}_4^{2-}] = 3.6 \times 10^{-2} \text{ M}$$

So: $[\text{Ba}^{2+}] = \frac{K_{\text{sp}}}{[\text{CrO}_4^{2-}]} = \frac{2.4 \times 10^{-10}}{3.6 \times 10^{-2}} = \mathbf{6.7 \times 10^{-9} \text{ M}}$

% Ba^{2+} remaining:

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

Ba^{2+} remaining