

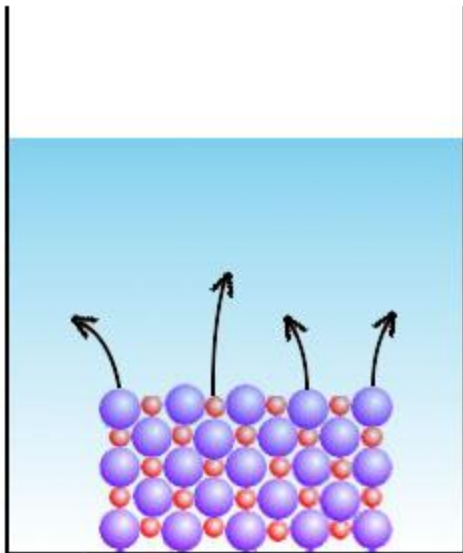


Solubility Product Constant

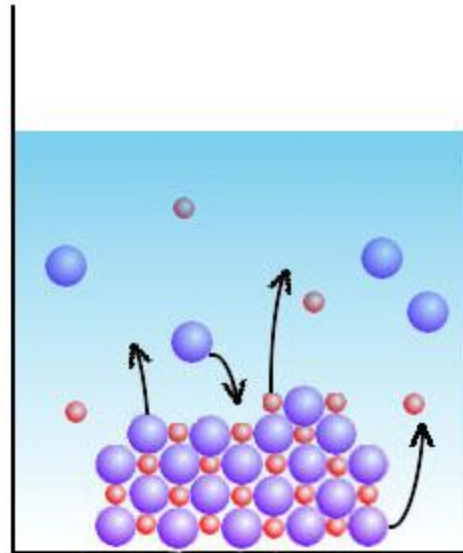
**K<sub>sp</sub>**

# K<sub>sp</sub>, the solubility-product constant.

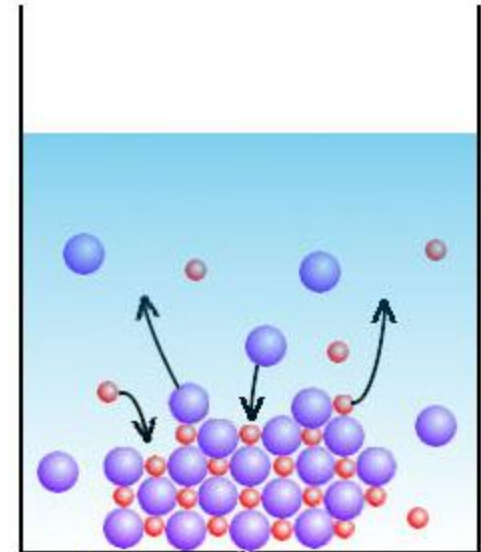
An equilibrium can exist between a partially soluble substance and its solution:



Salt is initially put into the water and begins dissolving.

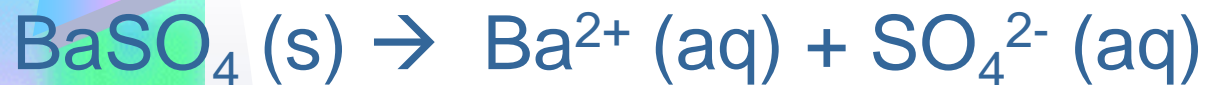


Salt continues to dissolve; however, dissolved ions will also precipitate. Because the salt dissolves faster than its ions precipitate, the net movement is towards dissolution.



Eventually, the rate of dissolution will equal the rate of precipitation. The solution will be in equilibrium, but the ions will continue to dissolve and precipitate.

For example:



- When writing the equilibrium constant expression for the dissolution of  $\text{BaSO}_4$ , we remember that the concentration of a solid is constant.

The equilibrium expression is therefore:

$$K = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$K = K_{\text{sp}}$ , the solubility-product constant.

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$



# The Solubility Expression



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



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

❖ The greater the  $k_{sp}$  the more soluble the solid is in  $H_2O$ .



# Solubility and $K_{sp}$

Three important definitions:

- 1) solubility: **quantity of a substance that dissolves to form a saturated solution**
- 2) molar solubility: **the number of moles of the solute that dissolves to form a liter of saturated solution**
- 3)  $K_{sp}$  (solubility product): **the equilibrium constant for the equilibrium between an ionic solid and its saturated solution**



## Calculating Molar Solubility

Calculate the molar solubility of  $\text{Ag}_2\text{SO}_4$  in one liter of water.  $K_{sp} = 1.4 \times 10^{-5}$

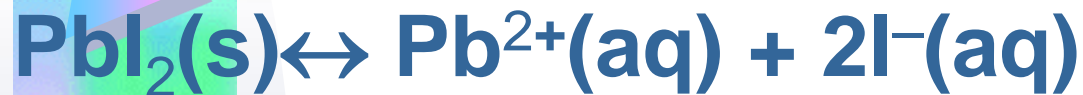


Initial	0	0
Change	+2x	+x
Equilb	2x	x

$$K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (2x)^2(x) = 1.4 \times 10^{-5}$$

$$X = 1.5 \times 10^{-2} \text{ mol Ag}_2\text{SO}_4 / \text{L (molar solubility)}$$

# Common ion Effect



Common ion: “The ion in a mixture of ionic substances that is common to the formulas of at least two.”

Common ion effect: “The solubility of one salt is reduced by the presence of another having a common ion”

# Example #1

What is the Molar solubility of  $\text{PbI}_2$  if the concentration of  $\text{NaI}$  is  $0.10$ ?  $K_{\text{sp}} = 7.9 \times 10^{-9}$

So  $[\text{I}^-] = 0.10 \text{ M}$

	$\text{PbI}_2(\text{s})$	$\text{Pb}^{2+}(\text{aq})$	$\text{I}^-(\text{aq})$
R		1	2
I		0	0.10
C		x	2x
E		x	$0.10 + 2x$

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

$$K_{\text{sp}} = [x] [0.10 + 2x]^2 = 7.9 \times 10^{-9}$$

x is small, thus we can ignore 2x in  $0.10 + 2x$

$$K_{\text{sp}} = [x] [0.10]^2 = 7.9 \times 10^{-9}, \quad x = 7.9 \times 10^{-7} \text{ M}$$





## Common Ion Effect

- Thus the solubility of the  $\text{PbI}_2$  is reduced by the presence of the  $\text{NaI}$ .

$K_{sp}$  of  $\text{PbI}_2 = 7.9 \times 10^{-9}$ , so the molar solubility is  $7.9 \times 10^{-9} = (x)(2x)^2 = 4x^3$

$$X = 1.3 \times 10^{-3}$$

Which is much greater than  $7.9 \times 10^{-7}$  when  $0.10 \text{ M NaI}$  is in solution.

## Example #2

**Molar solubility of AgI?  $K_{sp} = 8.3 \times 10^{-17}$**

**Concentration of NaI is 0.20, thus  $[I^-] = 0.20$**

	AgI(s)	Ag <sup>+</sup> (aq)	I <sup>-</sup> (aq)
R		1	1
I		0	0.20
C		x	x
E		x	0.20 + x

$$K_{sp} = [Ag^+(aq)] [I^-(aq)]$$

$$K_{sp} = [x] [0.20 + x] = 8.3 \times 10^{-17}$$

x is small, thus we can ignore it in 0.20 + x

$$K_{sp} = [x] [0.20] = 8.3 \times 10^{-17}, x = 4.2 \times 10^{-16}$$



## Common Ion Effect

- When two salt solutions that share a common ion are mixed the salt with the lower  $K_{sp}$  will precipitate first.

Example:  $\text{AgCl } K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$

$$[\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$$

$$X^2 = 1.6 \times 10^{-10}$$

$$X = [\text{Ag}^+] = [\text{Cl}^-] = 1.3 \times 10^{-5} \text{ M}$$



# Common Ion Effect

Add 0.10 M NaCl to a saturated AgCl solution.

$[\text{Cl}^-] = 0.10$  (common ion)

$$[\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$$

$$[\text{Ag}^+][0.10 + x] = 1.6 \times 10^{-10} \quad (x \text{ is small})$$

$$[\text{Ag}^+] = 1.6 \times 10^{-10} / 0.10 \text{ M}$$

$$[\text{Ag}^+] = 1.6 \times 10^{-9}$$

❖  $[\text{Ag}^+] = 1.3 \times 10^{-5}$  from the previous slide

So, some AgCl will precipitate when the NaCl is added because the molar solubility of the solution is now less than the that of AgCl alone.



# Will a Precipitation Occur?

If 1.00 mg of  $\text{Na}_2\text{CrO}_4$  is added to 225 ml of 0.00015 M  $\text{AgNO}_3$ , will a precipitate form?



Determine the initial concentration of ions.

$$\text{Ag}^+ = 1.5 \times 10^{-4}$$

$$\text{CrO}_4^{2-} = 1.00 \times 10^{-3} \text{ g} / \text{MM} = 6.17 \times 10^{-6} \text{ mol}$$

$$\text{CrO}_4^{2-} / .225 \text{ L} = 2.74 \times 10^{-5} \text{ M}$$



## Will a Precipitation Occur?

- Compare the initial concentration to the solubility product constant

Initial concentration of ions:  $(\text{Ag}^+)^2$   
 $(\text{CrO}_4^{2-})$

$$(1.5 \times 10^{-4})^2 (2.74 \times 10^{-5} \text{ M}) = 6.2 \times 10^{-13}$$

$$\text{Ag}_2\text{CrO}_4 \text{ Ksp} = 1.1 \times 10^{-12}$$

- No precipitation will occur because the initial concentration is less than the Ksp.

# Predicting if Precipitation Occurs

**Step 1: write the balanced equilibrium:**



**Step 2: Write the Ksp equation:**

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 1.2 \times 10^{-12}$$

**Step 3: Determine the initial concentration of ions**

$$\begin{aligned} [\text{Ag}^+]^2[\text{CrO}_4^{2-}] &= [4.8 \times 10^{-5}]^2[3.4 \times 10^{-4}] \\ &= 7.8 \times 10^{-13} \end{aligned}$$

**ion product is less than Ksp, thus no precipitate will form (more could be dissolved)**

# Formation Constants for Complex Ions

- $$K_{\text{form}} = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

The solution of a slightly soluble salt increase when one of its ions can be changed to a soluble complex ion.



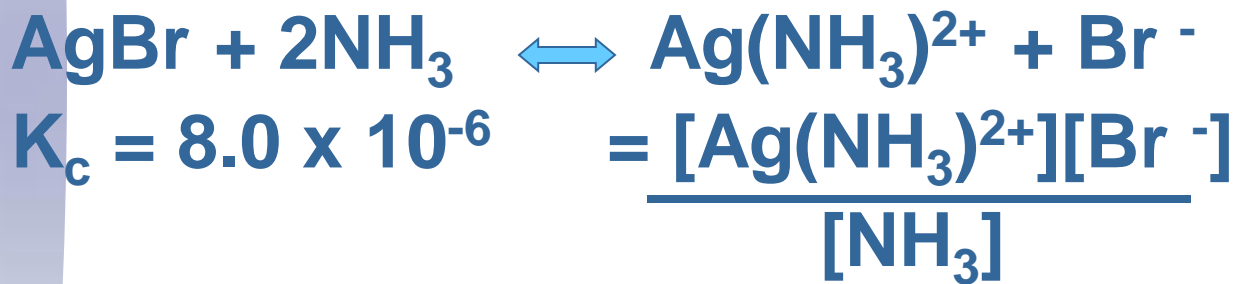
Add  $\text{NH}_3$





# Formation Constants for Complex Ions

- The very soluble silver complex ion removes  $\text{Ag}^+$  from the solution and shifts the equilibrium to the right increasing the solubility of  $\text{AgCl}$ .



$$K_c = k_{\text{form}} \times k_{\text{sp}} = (1.6 \times 10^7)(5.0 \times 10^{-13})$$
$$= 8.0 \times 10^{-6}$$

## Example

- How many moles of AgBr can dissolve in 1 L of 1.0 M NH<sub>3</sub>?



1.0	0	0
-2x	+x	+x
<hr/>		
1.0-2x	x	x

$$K_c = \frac{x^2}{(1.0-2x)^2} = 8.0 \times 10^{-6}$$

$X = 2.8 \times 10^{-3}$ ,  $2.8 \times 10^{-3}$  mol of AgBr dissolves in 1L of NH<sub>3</sub>