# Solubility Product Constant
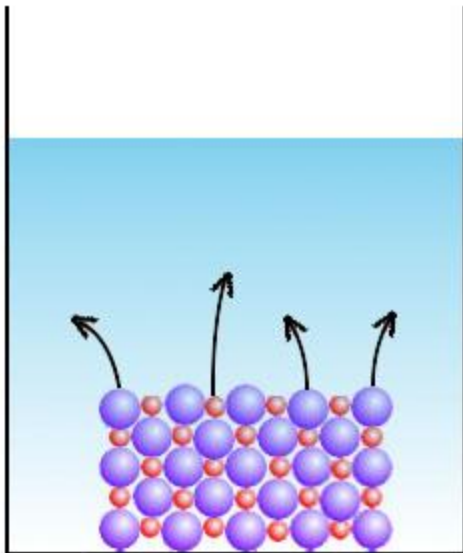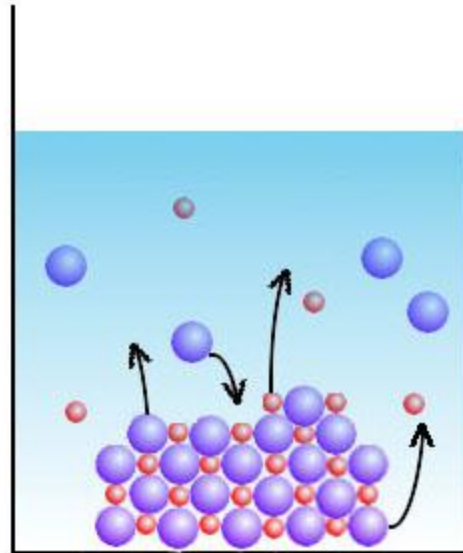
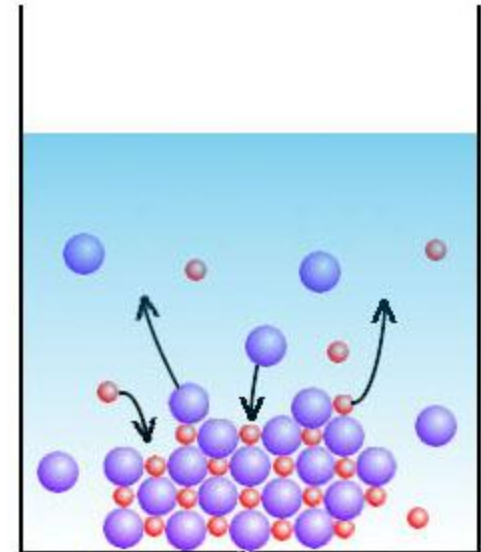# Ksp

# Ksp, 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 wil continue to dissolve and precipitate.

# For example:

$BaSO_4 (s) \rightarrow Ba^{2+} (aq) + SO_4^{2-} (aq)$
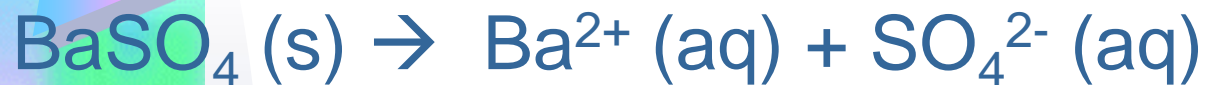
- **When writing the equilibrium constant expression for the dissolution of $BaSO_4$, we remember that the concentration of a solid is constant.**

**The equilibrium expression is therefore:**

$$K = [Ba^{2+}][SO_4^{2-}]$$

**K = Ksp, the** solubility-product constant.

$$Ksp = [Ba^{2+}][SO_4^{2-}]$$

# The Solubility Expression

$$A_aB_b(s) \longleftrightarrow aA^{b+}(aq) + bB^{a-}(aq)$$

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

Example: $PbI_2(s) \longleftrightarrow Pb^{2+} + 2 I^-$

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

❖ **The greater the ksp the more soluble the solid is in $H_2O$.**

# Solubility and Ksp

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) Ksp (solubility product): **the equilibrium constant for the equilibrium between an ionic solid and its saturated solution**

# Calculating Molar Solubility

**Calculate the molar solubility of $Ag_2SO_4$ in one liter of water. $Ksp = 1.4 \times 10^{-5}$**

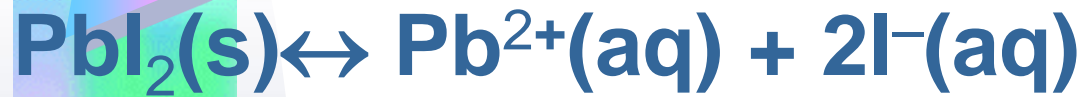$$Ag_2SO_4 \longleftrightarrow 2Ag^+ + SO_4^{2-}$$

| | | $2Ag^+$ | $SO_4^{2-}$ |
|---|---|---|---|
| **Initial** | | 0 | 0 |
| **Change** | | +2x | +x |
| **Equilb** | | 2x | x |

$Ksp = [Ag^+]^2[SO_4^{2-}] = (2x)^2(x) = 1.4 \times 10^{-5}$

$X = 1.5 \times 10^{-2}$ mol $Ag_2SO_4$ /L (molar solubility)

# Common ion Effect

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

**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 $PbI_2$ **if the** concentration of $NaI$ is 0.10?  $Ksp = 7.9 \times 10^{-9}$
So $[I-] = 0.10$ M

|   | $PbI_2(s)$ | $Pb^{2+}(aq)$ | $I^-(aq)$ |
|---|---|---|---|
| R |   | 1 | 2 |
| I |   | 0 | 0.10 |
| C |   | x | 2x |
| E |   | x | 0.10 + 2x |

$Ksp = [Pb^{2+}(aq)] \, [I^-(aq)]^2$

$Ksp = [x] \, [0.10 + 2x]^2 = 7.9 \times 10^{-9}$

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

$Ksp = [x] \, [0.10]^2 = 7.9 \times 10^{-9}$ , $x = 7.9 \times 10^{-7}$ *M*

# Common Ion Effect

- **Thus the solubility of the $PbI_2$ is reduced by the presence of the NaI.**

**Ksp of $PbI_2$ = 7.9 x $10^{-9}$, so the molar solubility is 7.9 x $10^{-9}$ = $(x)(2x)^2$ = $4x^3$**

**X = 1.3 x $10^{-3}$**

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

# Example #2

**Molar solubility of AgI?  Ksp = 8.3 x 10$^{-17}$**
**Concentration of NaI is 0.20, thus [I$^-$] = 0.20**

|   | AgI(s) | Ag$^+$(aq) | I$^-$(aq) |
|---|--------|-----------|-----------|
| R |        | 1         | 1         |
| I |        | 0         | 0.20      |
| C |        | x         | x         |
| E |        | x         | 0.20 + x  |

Ksp = [Ag$^+$(aq)] [I$^-$(aq)]
Ksp = [x] [0.20 + x] = 8.3 x 10$^{-17}$
 x is small, thus we can ignore it in 0.20 + x
Ksp = [x] [0.20] = 8.3 x 10$^{-17}$, x = 4.2 x 10$^{-16}$

# Common Ion Effect

- **When two salt solutions that share a common ion are mixed the salt with the lower ksp will precipitate first.**

**Example: AgCl ksp = $[Ag^+][Cl^-]$ = 1.6 x$10^{-10}$**

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

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

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

# Common Ion Effect

Add 0.10 M NaCl to a saturated AgCl solution.

[Cl-] = 0.10 (common ion)

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

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

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

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

❖ [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 $Na_2CrO_4$ is added to 225 ml of 0.00015 M $AgNO_3$, will a precipitate form?

$Ag_2CrO_4$ (s) → $2Ag^+ + CrO_4^{2-}$

Determine the initial concentration of ions.

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

$CrO_4^{2-} = 1.00 \times 10^{-3}$ g / MM = $6.17 \times 10^{-6}$ mol
$CrO_4^{2-}$/ .225 L = $2.74 \times 10^{-5}$ M

# Will a Precipitation Occur?

- **Compare the initial concentration to the solubility product constant**

**Initial concentration of ions: $(Ag^+)^2$ $(CrO_4^{2-})$**

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

**$Ag_2CrO_4$ 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:**

$Ag_2CrO_4(s) \leftrightarrow 2Ag^+(aq) + CrO_4^{2-}(aq)$

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

$Ksp = [Ag^+]^2[CrO_4^{2-}] = 1.2 \times 10^{-12}$

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

$[Ag^+]^2[CrO_4^{2-}] = [4.8 \times 10^{-5}]^2[3.4 \times 10^{-4}]$

$= 7.8 \times 10^{-13}$

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

# Formation Constants for Complex Ions

- $K_{form} = \dfrac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4}$

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

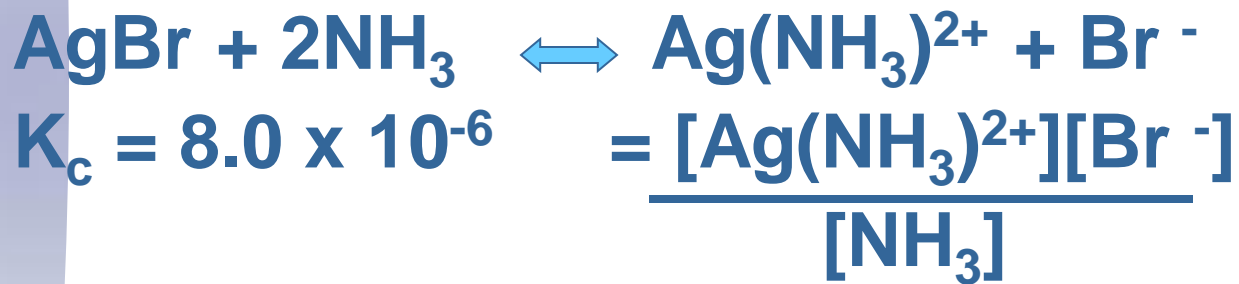$AgBr\ (s) \Longleftrightarrow Ag^+ + Br^-$      $K_{sp} = 5.0 \times 10^{-13}$

Add $NH_3$

$Ag^+ + 2NH_3 \Longleftrightarrow Ag(NH_3)_2{}^+$    $kf_{orm} = 1.6 \times 10^7$

# Formation Constants for Complex Ions

- **The very soluble silver complex ion removes Ag+ from the solution and shifts the equilibrium to the right increasing the solubility of AgCl.**

**$AgBr + 2NH_3 \longleftrightarrow Ag(NH_3)^{2+} + Br^-$**

**$K_c = 8.0 \times 10^{-6} = \dfrac{[Ag(NH_3)^{2+}][Br^-]}{[NH_3]}$**

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

**$= 8.0 \times 10^{-6}$**

# Example

- **How many moles of AgBr can dissolve in 1 L of 1.0 M $NH_3$?**

$$AgBr + 2NH_3 \Longleftrightarrow Ag(NH_3)^{2+} + Br^-$$

| | 1.0 | 0 | 0 |
|---|---|---|---|
| | -2x | +x | +x |
| | 1.0-2x | x | x |

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

$X = 2.8 \times 10^{-3}$, $2.8 \times 10^{-3}$ mol of AgBr dissolves in 1L of $NH_3$