

# **SOLUBILITY CONSTANT – 2**

# **PREDICTING PRECIPITATION**

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# PREDICTING PRECIPITATION

- Precipitation can be predicted by calculating reaction quotient.
- Compare the reaction quotient ( $Q_{sp}$ ) to the  $K_{sp}$



$Q_{sp} = [\text{M}^{n+}]_i [\text{X}^{-}]_i^n$  - where "i" designates the initial concentration

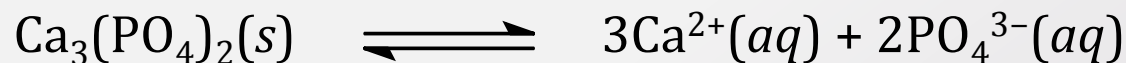
$Q_{sp} \leq K_{sp}$  no precipitate will form

$Q_{sp} > K_{sp}$  precipitate will form until  $Q_{sp} = K_{sp}$

# EXAMPLE: PREDICTING PRECIPITATION -1

One form of kidney stones is calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , which has a  $K_{sp}$  of  $1.0 \times 10^{-26}$ . A sample of urine contains  $1.0 \times 10^{-3} \text{ M Ca}^{2+}$  and  $1.0 \times 10^{-8} \text{ M PO}_4^{3-}$  ion. Calculate  $Q_{sp}$  and predict whether  $\text{Ca}_3(\text{PO}_4)_2$  will precipitate.

**Solution:**



$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

$$K_{sp} = 1.0 \times 10^{-26}$$

$$Q_{sp} = (1.0 \times 10^{-3})^3 (1.0 \times 10^{-8})^2$$

$$Q_{sp} = 1.0 \times 10^{-25}$$

$$K_{sp} < Q_{sp} \text{ OR } Q_{sp} > K_{sp}$$

A precipitate will form.

# EXAMPLE: PREDICTING PRECIPITATION -2

Exactly 0.400 L of 0.500 M  $\text{Pb}^{2+}$  and 1.60 L of  $2.50 \times 10^{-2}$  M  $\text{Cl}^-$  are mixed together to form 2.00 L of solution. Calculate  $Q_{sp}$  and predict whether  $\text{PbCl}_2$  will precipitate.  $K_{sp}$  for  $\text{PbCl}_2$  is  $1.6 \times 10^{-5}$ .

**Solution:**

$$[\text{Pb}^{2+}] = \frac{(0.500 \text{ M})(0.400 \text{ L})}{(2.00 \text{ L})} = 0.100 \text{ M}$$

$$[\text{Cl}^-] = \frac{(2.50 \times 10^{-2} \text{ M})(1.60 \text{ L})}{(2.00 \text{ L})} = 0.0200 \text{ M}$$



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

$$Q_{sp} = (0.100)(0.0200)^2 = 4.00 \times 10^{-5}$$

$$K_{sp} < Q_{sp} \text{ OR } Q_{sp} > K_{sp}$$

A precipitate will form.

# FACTORS AFFECTING SOLUBILITY

1) **The Common Effect** – an example of LeChâtelier's principle

- The presence of a second salt that produces an ion common to a solubility equilibrium will reduce solubility.
  - Example: AgCl in a solution of AgNO<sub>3</sub>
- The concentration of a product ion is increased forcing the solubility reaction toward reactant, the solid.
  - Example: Ag<sup>+</sup> from the AgNO<sub>3</sub>, reverses the solubility reaction.

2) **pH** – some salts are more soluble in acids or bases; hydroxide salt solubility is affected by pH – addition of acid will increase solubility of hydroxide because of acid base reaction.

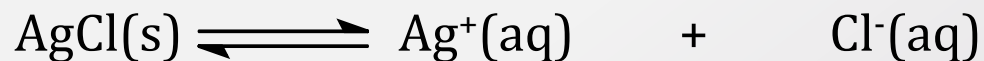
- If ion in solution is conjugate base then addition of acid will increase solubility.
- If ion in solution is conjugate acid then addition of base will increase solubility.

# EXAMPLE: COMMON ION EFFECT - 1

What is the molar solubility of silver chloride in 1.0 L of solution that contains  $2.0 \times 10^{-2}$  mol of HCl?  $K_{sp}$  for AgCl at 25°C is  $1.8 \times 10^{-10}$

## Solution:

Initial  $[\text{Cl}^-] = 0.020$  M. We then solve for x, the molar solubility.



|         |    |           |
|---------|----|-----------|
| Initial | 0  | 0.020     |
| Change  | +s | +s        |
| Eq conc | s  | 0.020 + s |

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

$$1.8 \times 10^{-10} = s(0.020 + s) \quad (\text{Assumption, } s \text{ is negligible: } 0.020 + x \approx 0.020)$$

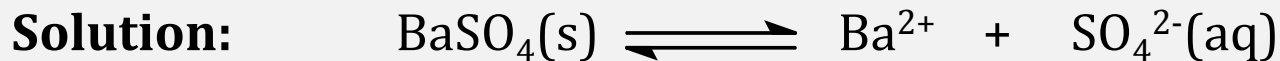
$$1.8 \times 10^{-10} = 0.020s; \quad \text{so } s = 9.0 \times 10^{-9} \text{ M}$$

Solubility of AgCl in water is  $K_{sp} = s^2$  so  $1.8 \times 10^{-10} = s^2$  and  $s = 1.3 \times 10^{-5} \text{ M}$

**The solubility was reduced by a factor of about 1400 in presence of HCl!**

# EXAMPLE: COMMON ION EFFECT - 2

Calculate the molar solubility of  $\text{BaSO}_4$  in  $0.0010\text{ M Na}_2\text{SO}_4$ .



Initial  $\qquad\qquad\qquad 0 \qquad\qquad 0.0010\text{ M}$

Change  $\qquad\qquad\qquad +s \qquad\qquad +s$

Eq conc  $\qquad\qquad\qquad s \qquad\qquad 0.0010 + s$

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$$

$$(s)(0.00100\text{ M} + s) \approx (s)(0.00100\text{ M}) = 1.1 \times 10^{-10}$$

$$s = 1.1 \times 10^{-7}\text{ M}$$

Solubility of  $\text{BaSO}_4$  in water is  $K_{\text{sp}} = s^2$  so  $1.1 \times 10^{-10} = s^2$  and  $s = 1.0 \times 10^{-5}\text{ M}$

**Note again: solubility decreases 100 fold with a little common ion!!**

# EXAMPLE: SOLUBILITY AND pH

Consider the two slightly soluble salts barium fluoride and silver bromide. Which of these would have its solubility more affected by the addition of strong acid? Would the solubility of that salt increase or decrease?

## **Solution:**

Addition of acid to  $\text{BaF}_2$  will produce HF which is a weak acid, and  
Addition of acid to  $\text{AgBr}$  will produce HBr which is a strong acid.

→  $\text{BaF}_2$  is more soluble in an acidic solution.

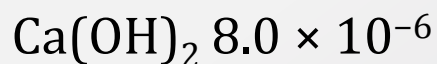
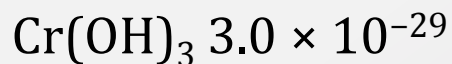
→  $\text{AgBr}$  is unaffected by an acidic solution.



# FRACTIONAL PRECIPITATION

- Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another ion, and so forth.
- A mixture of ions can be separated on the basis of this unequal solubility.
- In lab fractional precipitation can be used to separate ions and identify them – this is called “qualitative analysis”.
- For example: separating salts of chromium (III), calcium and iron (II) ions.

We can begin by identifying the value of  $K_{sp}$  for each compound:



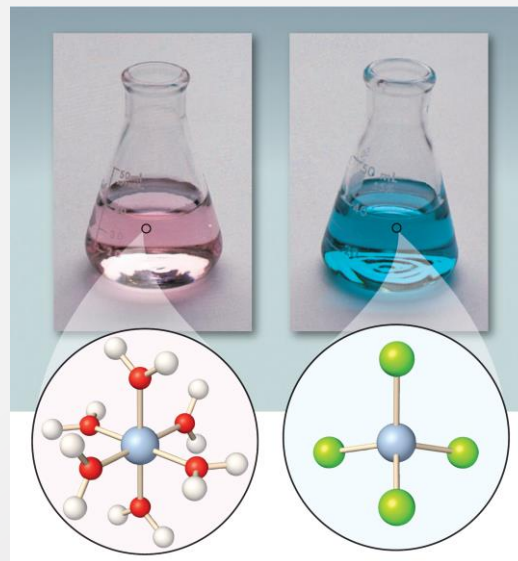
# COMPLEX IONS

- Some cations form soluble complex ions.
- Metal ions that form complex ions include  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ .
- Complexing agents, called ligands, are Lewis bases. They include  $\text{CN}^-$ ,  $\text{NH}_3$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{OH}^-$ .
- In each case, an equilibrium is established, called the complex-ion formation equilibrium.
- Example:  $\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(\text{aq})$

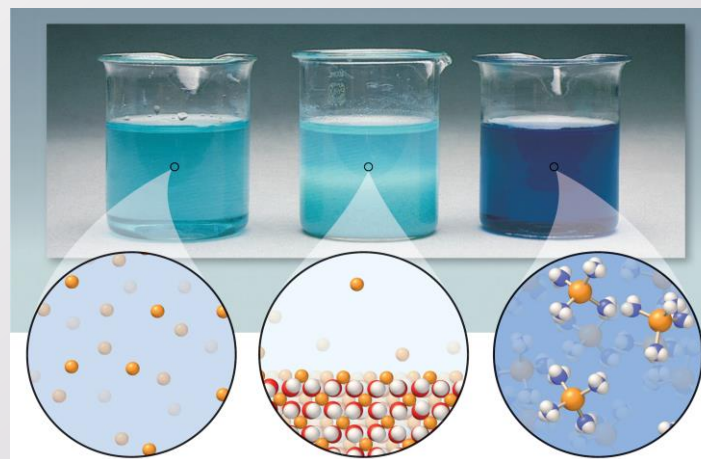
$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

# COMPLEX IONS

- Examples of forming complex ions.
- Effect of Addition of HCl to an Aqueous Solution of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$



- Effect of Addition of  $\text{NH}_3$  to an Aqueous Solution of  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$



# KEY CONCEPTS

- Predict precipitation by using solubility quotient.
- Predict solubility in common ion and pH of solutions.