# EQUILIBRIUM AND SOLUBILITY

# EQUILIBRIUM AND SOLUBILITY

Solids form from solution when:

1. a solution is saturated

2. two solutions are mixed to form a precipitate

Both are dependent on an equilibrium between the solution and the solid.

# $K_{sp}$

$K_{sp}$ is the solubility product constant for solutions that can form a solid.

This is true for saturated solutions.

Why? Only at saturation point is equilibrium achieved.

# EQUILIBRIUM AND SOLUBILITY

## Example #1

Determine the $K_{sp}$ expressions for the following equilibria:

1. $Ag_2CrO_{4(s)} <====> 2\ Ag^+_{(aq)} + CrO_4{}^{2-}{}_{(aq)}$

   $$K_{sp} = [Ag^+_{(aq)}]^2\ [CrO_4{}^{2-}{}_{(aq)}]$$

2. $BaCrO_{4(s)} <====> Ba^{2+}{}_{(aq)} + CrO_4{}^{2-}{}_{(aq)}$

   $$K_{sp} = [Ba^{2+}{}_{(aq)}][CrO_4{}^{2-}{}_{(aq)}]$$

3. $Ag_3PO_{4(s)} <====> 3\ Ag^+_{(aq)} + PO_4{}^{3-}{}_{(aq)}$

   $$K_{sp} = [Ag^+_{(aq)}]^3[PO_4{}^{3-}{}_{(aq)}]$$

## Molar Solubility

The molar solubility for a compound is the concentration that is necessary for a solution to become saturated.

*Ex. One litre of water can dissolve $7.1 \times 10^{-7}$ mol of AgBr*

$K_{sp}$ values may be used to calculate molar solubility and vice versa.

# Example #2

Silver bromide, AgBr, is the light sensitive compound in nearly all photographic film. At 25°C, one litre of water can dissolve $7.1 \times 10^{-7}$ mol of AgBr. Calculate the $K_{sp}$ of AgBr at 25°C.

# EQUILIBRIUM AND SOLUBILITY

## Example #2

Silver bromide, AgBr, is the light sensitive compound in nearly all photographic film. At 25°C, one litre of water can dissolve $7.1\text{x}10^{-7}$ mol of AgBr. Calculate the $K_{sp}$ of AgBr at 25°C.

$$AgBr_{(s)} <=> Ag^{+}_{(aq)} + Br^{-}_{(aq)}$$

I
C
E

Changes when it dissolves, but it is a solid.

$$K_{sp} = [7.1\text{x}10^{-7}][7.1\text{x}10^{-7}]$$

$$K_{sp} = 5.0\text{x}10^{-13}$$

$$.: K_{sp} = 5.0\text{x}10^{-13}$$

# EQUILIBRIUM AND SOLUBILITY

## Example #3

At 25°C, the molar solubility of $PbCl_2$ in a 0.10 M NaCl solution is $1.7 \times 10^{-3}$ M. Calculate the $K_{sp}$ for $PbCl_2$.

# Example #3

At 25°C, the molar solubility of $PbCl_2$ in a 0.10 M NaCl solution is $1.7\text{x}10^{-3}$ M. Calculate the $K_{sp}$ for $PbCl_2$.

$$PbCl_{2(s)} <=> Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

I

C

E

**NOTE:** 0.1M $Na^{+}$ does not affect equilibrium

$$K_{sp} = [1.7\text{x}10^{-3}][0.1034]^2$$

$$K_{sp} = 1.8\text{x}10^{-5}$$

$$.: K_{sp} = 1.8\text{x}10^{-5}$$

## Example #4

The solubility of iron (II) hydroxide, $Fe(OH)_2$, is found to be $1.4 \times 10^{-3}$ g/L. What is the $K_{sp}$ value?

# Example #4

The solubility of iron (II) hydroxide, $Fe(OH)_2$, is found to be $1.4x10^{-3}$ g/L. What is the $K_{sp}$ value?

$$n = \frac{m}{M}$$

$$= \frac{(1.4x10^{-3}g)}{(89.861g/mol)}$$

$$= 1.557961741x10^{-5}mol$$

$$Fe(OH)_{2(s)} <=> Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)}$$

I

C

E

$$K_{sp} = [1.55796x10^{-5}][3.11592x10^{-5}]^2$$

$$K_{sp} = 1.5x10^{-14}$$

$$.: K_{sp} = 1.5x10^{-14}$$

## Example #5

What is the molar solubility of AgCl in pure water at 25°C when $K_{sp}$ = $1.8 \times 10^{-10}$?

## Example #5

What is the molar solubility of AgCl in pure water at 25°C when $K_{sp} = 1.8\times10^{-10}$.

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

I

C

E

$$K_{sp} = [x][x]$$

$$K_{sp} = x^2$$

$$1.8\times10^{-10} = x^2$$

$$1.34\times10^{-5}M = x$$

.: the molar solubility is $1.34\times10^{-5}$mol/L

# EQUILIBRIUM AND SOLUBILITY

## Example #6

The $K_{sp}$ for magnesium fluoride, $MgF_2$, has a value of $6.4 \times 10^{-9}$. What is its solubility in g/L?

# Example #6

The $K_{sp}$ for magnesium fluoride, $MgF_2$, has a value of $6.4 \times 10^{-9}$. What is its solubility in g/L?

$$MgF_{2(s)} <=> Mg^{2+}{}_{(aq)} + 2F^{-}{}_{(aq)}$$

I

C

E

$$K_{sp} = [x][2x]^2 = 6.4x10^{-9}$$

$$4x^3 = 6.4x10^{-9}$$

$$x = \sqrt[3]{\frac{6.4x10^{-9}}{4}}$$

$$x = 1.16x10^{-3} mol/L$$

.: the solubility is $7.2x10^{-2}$g/L

## Predicting Precipitation

Similar to $K_{eq}$ problems, calculating Q can be used to determine whether a precipitate will form when provided with $K_{sp}$.

Three possibilities:

1. Q <
2. Q =
3. Q >

## Example #7

A student wished to prepare 1.0 L of a solution containing 0.015 mol of NaCl and 0.15 mol of $Pb(NO_3)_2$. Knowing from the solubility rules that the chloride of $Pb^{2+}$ is insoluble, there was a concern that $PbCl_2$ might form. If the $K_{sp}$ for this reaction is $1.7 \times 10^{-5}$, will a ppt form?

# EQUILIBRIUM AND SOLUBILITY

## Example #7

A student wished to prepare 1.0 L of a solution containing 0.015 mol of NaCl and 0.15 mol of $Pb(NO_3)_2$. Knowing from the solubility rules that the chloride of $Pb^{2+}$ is insoluble, there was a concern that $PbCl_2$ might form. If the $K_{sp}$ for this reaction is $1.7x10^{-5}$, will a ppt form?

$$PbCl_{2(s)} <=> Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

0.15 0.015

$$K_{sp} = [Pb^{2+}_{(aq)}][Cl^{-}_{(aq)}]^2$$

$$Q = [Pb^{2+}_{(aq)}][Cl^{-}_{(aq)}]^2$$

$$Q = [0.15][0.015]^2$$

$$Q = 3.375x10^{-5}$$

$Q > K_{sp}$, so a precipitate WILL form

.: a precipitate will form

## Example #8

What possible precipitate might form by mixing 50.0 mL of 0.0010 M $CaCl_2$ with 50.0 mL of 0.010 M $Na_2SO_4$? Will the precipitate form? ($K_{sp} = 7.1 \times 10^{-5}$)

# Example #8

What possible precipitate might form by mixing 50.0 mL of 0.0010 M $CaCl_2$ with 50.0 mL of 0.010 M $Na_2SO_4$? Will the precipitate form? ($K_{sp}$ = 7.1x$10^{-5}$)

| Ion | Solubility | Exceptions |
|---|---|---|
| $NO_3^-$ | soluble | none |
| $ClO_4^-$ | soluble | none |
| $Cl^-$ | soluble | except $Ag^+$, $Hg_2^{2+}$, *$Pb^{2+}$ |
| $I^-$ | soluble | except $Ag^+$, $Hg_2^{2+}$, $Pb^{2+}$ |
| $SO_4^{2-}$ | soluble | except $Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Ag^+$ |
| $CO_3^{2-}$ | insoluble | except Group IA and $NH_4^+$ |
| $PO_4^{3-}$ | insoluble | except Group IA and $NH_4^+$ |
| $^-OH$ | insoluble | except Group IA, *$Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$ |
| $S^{2-}$ | insoluble | except Group IA, IIA and $NH_4^+$ |
| $Na^+$ | soluble | none |
| $NH_4^+$ | soluble | none |
| $K^+$ | soluble | none |

*slightly soluble

$CaSO_4$ has low solubility.

# EQUILIBRIUM AND SOLUBILITY

## Example #8

What possible precipitate might form by mixing 50.0 mL of 0.0010 M $CaCl_2$ with 50.0 mL of 0.010 M $Na_2SO_4$? Will the precipitate form? ($K_{sp}$ = 7.1x10$^{-5}$)

$$CaSO_{4(s)} <=> Ca^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

$$C_1V_1=C_2V_2$$

$$C_2=\frac{C_1V_1}{V_2}$$

$$C_2=\frac{0.0010M \times 0.050L}{0.100L}$$

$$C_2= 5x10^{-4}M$$

$$C_2=\frac{C_1V_1}{V_2}$$

$$C_2= 5x10^{-3}M$$

$$Q = [Ca^{2+}{}_{(aq)}][SO_4{}^{2-}{}_{(aq)}]$$

$$Q = [0.0005][0.005]$$

$$Q = 2.5x10^{-6}$$

$Q < K_{sp}$, so a precipitate will NOT form (unsaturated)

.: the possible precipitate, $CaSO_4$, will not form

## Example #9

Will a precipitate form if 20.0 mL of 0.010 M $CaCl_2$ are mixed with 30.0 mL of 0.0080 M $Na_2SO_4$? ($K_{sp} = 2.45 \times 10^{-5}$)

# EQUILIBRIUM AND SOLUBILITY

## Example #9

Will a precipitate form if 20.0 mL of 0.010 M $CaCl_2$ are mixed with 30.0 mL of 0.0080 M $Na_2SO_4$? ($K_{sp}$ = 2.45x10$^{-5}$)

$$CaSO_{4(s)} <=> Ca^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

$$C_2 = \frac{C_1V_1}{V_2} \qquad C_2 = \frac{C_1V_1}{V_2}$$

$$C_2 = \frac{0.010M \text{ x } 0.020L}{0.050L} \qquad C_2 = \frac{0.0080M \text{ x } 0.030L}{0.050L}$$

$$C_2 = 4x10^{-3}M \qquad C_2 = 4.8x10^{-3}M$$

$$Q = [Ca^{2+}{}_{(aq)}][SO_4{}^{2-}{}_{(aq)}]$$

$$Q = [0.004][0.0048]$$

$$Q = 1.92x10^{-5}$$

$Q < K_{sp}$, so a precipitate will NOT form (unsaturated)

.: a precipitate will not form