

## 3.7. $K_{sp}$ and Precipitate Formation

The value of  $K_{sp}$  is the point between the ions precipitating or the ions remaining soluble.

At exactly  $K_{sp}$ , the ions will *just* start to precipitate. You have just arrived at the saturation point.

# 3.7. Ksp and Precipitate Formation

a) *“Trial Ksp” aka. “The Ion Product” aka. “Q”*

i) this is a Ksp value for the ion concentrations before mixing with other ion(s).

ii) we will have to calculate a Trial Ksp value using the initial ion concentrations, to determine if mixing will result in a precipitate.

**Q < Ksp**      Then the ions will stay in solution.  
Not enough ions to precipitate.

**Q > Ksp**      Then the solution cannot dissolve more ions.  
The undissolved ions will join and precipitate.

**Q = Ksp**      There are just enough ions to barely form a saturated solution.  
You are at the saturation point.

# 3.7. $K_{sp}$ and Precipitate Formation

## *b) Predicting Precipitate Calculations*

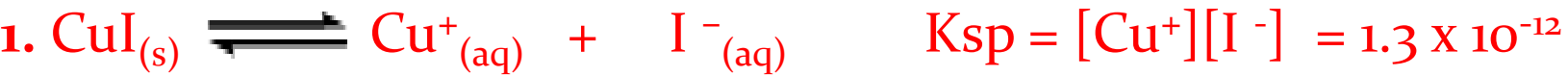
**Type 1 (will the ions precipitate when mixed together?)**

General Strategy:

1. Write equilibrium equation and find  $K_{sp}$
2. Find ion concentration
3. Find  $Q$
4. Compare  $Q$  with  $K_{sp}$

# 3.7. Ksp and Precipitate Formation

**Example:** Will a precipitate form when 4.5 mL of  $5.0 \times 10^{-4}$  M  $\text{Cu}^+$  is mixed with 2.0 mL of  $6.0 \times 10^{-5}$  M  $\text{I}^-$ ?



## 2. Find ion concentrations:

Mixing the two solutions results in a dilution, so we must recalculate the concentrations.

$$[\text{Cu}^+] \quad C_1V_1 = C_2V_2 \quad (5.0 \times 10^{-4} \text{ M})(4.5\text{mL}) = C_2(6.5\text{mL}); [\text{Cu}^+] = 3.5 \times 10^{-4} \text{ M}$$

$$[\text{I}^-] \quad C_1V_1 = C_2V_2 \quad (6.0 \times 10^{-5} \text{ M})(2.0\text{mL}) = C_2(6.5\text{mL}); [\text{I}^-] = 1.8 \times 10^{-5} \text{ M}$$

## 3. Find Q:

$$Q = [\text{Cu}^+][\text{I}^-] = [3.5 \times 10^{-4} \text{ M}][1.8 \times 10^{-5} \text{ M}] = 6.0 \times 10^{-9}$$

## 4. Compare to Ksp:

$$Q > K_{sp}$$

$$(6.0 \times 10^{-9}) > (1.3 \times 10^{-12})$$

**Thus, a precipitate will form!**

## 3.7. Ksp and Precipitate Formation

**Example:** Will a precipitate form when 12.0 mL of  $1.3 \times 10^{-3}$  M  $\text{Sr}^{+2}$  is mixed with 4.0 mL  $2.0 \times 10^{-9}$  M  $\text{SO}_4^{-2}$ ?



2.  $[\text{Sr}^{+2}] = (12.0 \text{ mL})(1.3 \times 10^{-3}) / 16.0 \text{ mL} = 9.8 \times 10^{-4} \text{ M}$

$[\text{SO}_4^{-2}] = (4.0 \text{ mL})(2.0 \times 10^{-9}) / 16.0 \text{ mL} = 5.0 \times 10^{-10} \text{ M}$

3.  $Q = [\text{Sr}^{+2}] [\text{SO}_4^{-2}] = (9.8 \times 10^{-4} \text{ M})(5.0 \times 10^{-10} \text{ M}) = 4.9 \times 10^{-13}$

4.  $K_{\text{sp}} > Q$  Thus, a precipitate will NOT form!  
 $(3.4 \times 10^{-7}) > (4.9 \times 10^{-13})$

## 3.7. K<sub>sp</sub> and Precipitate Formation

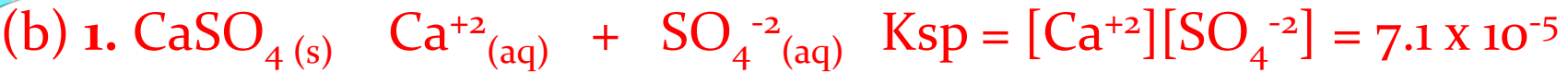
**Example:** If 20.0 mL of  $5.0 \times 10^{-3}$  M  $\text{Ca}(\text{NO}_3)_2$  is mixed with 10.0 mL of  $2.5 \times 10^{-2}$  M  $\text{Sn}(\text{SO}_4)_2$ :

**(a) What precipitate is possible?**

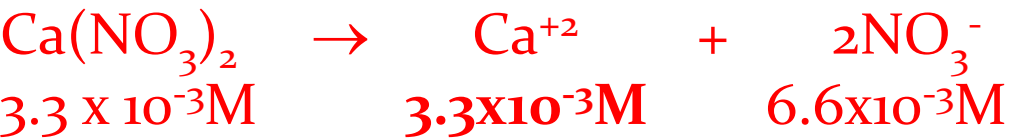
**(b) Will this precipitate form at the given concentrations?**

(a)  $\text{CaSO}_4$  is the only combo of ions that will potentially precipitate according to the solubility table. ( $\text{Sn}(\text{NO}_3)_4$  is soluble at all concentrations)

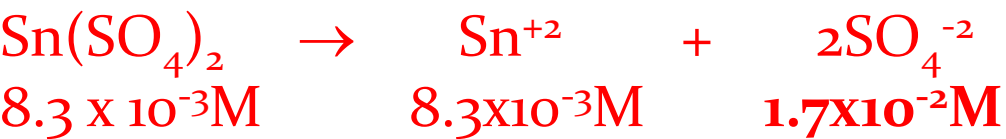
# 3.7. Ksp and Precipitate Formation



2.  $[\text{Ca}(\text{NO}_3)_2] = (20.0 \text{ mL})(5.0 \times 10^{-3}) / 30.0 \text{ mL} = 3.3 \times 10^{-3} \text{ M}$



$[\text{Sn}(\text{SO}_4)_2] = (10.0 \text{ mL})(2.5 \times 10^{-2}) / 30.0 \text{ mL} = 8.3 \times 10^{-3} \text{ M}$



3.  $Q = [\text{Ca}^{+2}][\text{SO}_4^{-2}] = (3.3 \times 10^{-3} \text{ M})(1.7 \times 10^{-2} \text{ M}) = 5.6 \times 10^{-5}$

4.  $K_{sp} > Q$       **Thus, a precipitate will NOT form!**  
 $(7.1 \times 10^{-5}) > (5.6 \times 10^{-5})$

# 3.7. $K_{sp}$ and Precipitate Formation

**Type 2 (what [ion] is required to precipitate out the other ion?)**

General Strategy:

1. Write equilibrium equation and find  $K_{sp}$
2. Know  $Q = K_{sp}$  at this particular [ion]
3. Solve  $K_{sp}$  equation for other [ion]



## 3.7. Ksp and Precipitate Formation

**Example:** If we have a  $3.0 \times 10^{-4}$  M solution of  $\text{Pb}^{+2}$ , what  $[\text{I}^-]$  is required to just start the precipitation of  $\text{PbI}_{2(s)}$  from the solution?



$$K_{sp} = [\text{Pb}^{+2}][\text{I}^-]^2 = 8.5 \times 10^{-9}$$

2.  $Q = K_{sp} = 8.5 \times 10^{-9}$  (this means we can use the  $[\text{Pb}^{+2}]$  given)

3.  $[\text{I}^-]^2 = K_{sp} / [\text{Pb}^{+2}] = 8.5 \times 10^{-9} / 3.0 \times 10^{-4} = 2.8 \times 10^{-5}$

$$[\text{I}^-] = \sqrt{(2.8 \times 10^{-5})} = \mathbf{5.3 \times 10^{-3} \text{ M}}$$

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# 3. 8. Ksp and Precipitate Formation

## c) Precipitates and Titration

i) What is the purpose of “titration”?

procedure used to determine concentration of one substance by slowly adding another substance with a known concentration.

ii) Theory:

1. The most useful example is titrating for an unknown  $[\text{Cl}^-]$  with  $\text{AgNO}_3$  solution.
2. The  $\text{Ag}^+$  will precipitate out  $\text{Cl}^-$  as  $\text{AgCl}_{(s)}$ .
3. The point at which the moles of added  $\text{Ag}^+$  = moles of  $\text{Cl}^-$  present is called the *Equivalence Point*.
4. The white  $\text{AgCl}_{(s)}$  will stop forming at the equivalence point.
5. Difficult to see when  $\text{AgCl}_{(s)}$  stops forming, so add a chromate indicator. The  $\text{Ag}^+$  will react with  $\text{CrO}_4^{2-}$  when the  $\text{Cl}^-$  is used up, to form the easily visible red precipitate of  $\text{Ag}_2\text{CrO}_{4(s)}$ .

## 3. 8. Ksp and Precipitate Formation

**Example:** A 50.0 mL solution with an unknown  $[\text{Cl}^-]$ , was titrated with 0.25 M  $\text{AgNO}_3$ . A precipitate started to form after 32.8 mL of  $\text{AgNO}_3$  was added.

a) What is a precipitate that definitely forms at the equivalence point?

Excess  $\text{Ag}^+$  reacts with the chromate indicator to form  $\text{Ag}_2\text{CrO}_{4(s)}$ .

b) What is the  $[\text{Cl}^-]$  in the 50.0 mL solution?

moles  $\text{AgNO}_3 = 0.25 \text{ M} \times 0.0328 \text{ L} = 0.0082 \text{ moles}$

moles  $\text{Ag}^+ = \text{moles } \text{AgNO}_3 = 0.0082 \text{ moles}$

Since at equiv. point: moles  $\text{Ag}^+ = \text{moles } \text{Cl}^- = 0.0082 \text{ moles}$

$[\text{Cl}^-] = 0.0082 \text{ moles} / 0.050 \text{ L} = \mathbf{0.16 \text{ M}}$

## 3. 8. Ksp and Precipitate Formation

**Example:** A solution with a  $[\text{Cl}^-]$  of 0.24 M, was titrated with 0.50 M  $\text{AgNO}_3$ . A precipitate started to form after 90.0 mL of  $\text{AgNO}_3$  was added. What is the volume of the chloride solution?

$$\text{moles AgNO}_3 = 0.50 \text{ M} \times 0.090 \text{ L} = 0.045 \text{ moles}$$

$$\text{moles AgNO}_3 = \text{moles Ag}^+ = \text{moles Cl}^- = 0.045 \text{ moles}$$

$$\text{volume Cl}^- = 0.045 \text{ moles} / 0.24 \text{ M} = 0.19 \text{ L}$$

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