

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. K_{sp} and Precipitate Formation

a) *“Trial K_{sp} ” aka. “The Ion Product” aka. “ Q ”*

i) this is a K_{sp} value for the ion concentrations before mixing with other ion(s).

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

$Q < K_{sp}$ Then the ions will stay in solution.
Not enough ions to precipitate.

$Q > K_{sp}$ Then the solution cannot dissolve more ions.
The undissolved ions will join and precipitate.

$Q = K_{sp}$ 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

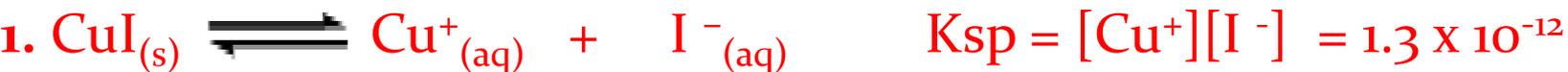
Type 1 (will the ions precipitate when mixed together?)

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 5.0×10^{-4} M Cu^+ is mixed with 2.0 mL of 6.0×10^{-5} M 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!

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Example: Will a precipitate form when 12.0 mL of 1.3×10^{-3} M Sr^{+2} is mixed with 4.0 mL 2.0×10^{-9} M 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_{sp} and Precipitate Formation

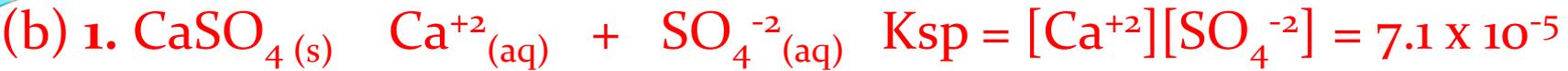
Example: If 20.0 mL of 5.0×10^{-3} M $\text{Ca}(\text{NO}_3)_2$ is mixed with 10.0 mL of 2.5×10^{-2} M $\text{Sn}(\text{SO}_4)_2$:

(a) What precipitate is possible?

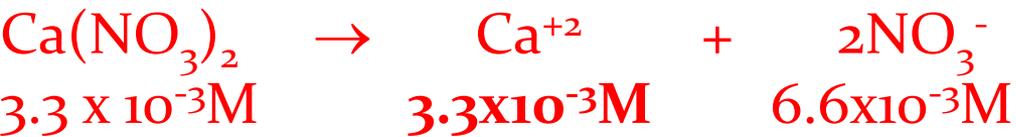
(b) Will this precipitate form at the given concentrations?

(a) 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)

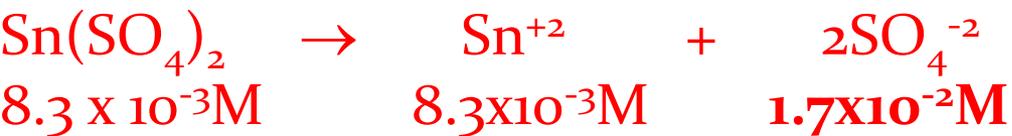
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2. $[\text{Ca}(\text{NO}_3)_2] = (20.0 \text{ mL})(5.0 \times 10^{-3}) / 30.0 \text{ mL} = 3.3 \times 10^{-3} \text{ M}$



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



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!**
(7.1×10^{-5}) (5.6×10^{-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 3.0×10^{-4} M solution of 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 AgNO_3 solution.
2. The Ag^+ will precipitate out Cl^- as $\text{AgCl}_{(s)}$.
3. The point at which the moles of added Ag^+ = moles of 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 Ag^+ will react with CrO_4^{2-} when the 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 AgNO_3 . A precipitate started to form after 32.8 mL of AgNO_3 was added.

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

Excess 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 AgNO_3 . A precipitate started to form after 90.0 mL of 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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