3. 7. Ksp and Precipitate Formation

The value of Ksp is the point between the ions precipitating or the ions remaining soluble.

At exactly Ksp, 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. Ksp and Precipitate Formation

b) Predicting Precipitate Calculations

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

General Strategy:

1. Write equilibrium equation and find Ksp
2. Find ion concentration
3. Find Q
4. Compare Q with Ksp

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^-?

1. $CuI_{(s)} \rightleftharpoons Cu^+_{(aq)} + I^-_{(aq)}$ $K_{sp} = [Cu^+][I^-] = 1.3 \times 10^{-12}$

2. Find ion concentrations:

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

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

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

3. Find Q:

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

4. Compare to Ksp:

Q > Ksp

(6.0×10^{-9}) (1.3×10^{-12})

Thus, a precipitate will form!

3. 7. Ksp and Precipitate Formation

Example: Will a precipitate form when 12.0 mL of 1.3×10^{-3} M Sr^{+2} is mixed with 4.0 mL 2.0×10^{-9} M SO_4^{-2}?

1. $SrSO_{4(s)} \quad Sr^{+2}_{(aq)} + SO_4^{-2}{}_{(aq)}$ $\quad Ksp = [Sr^{+2}]\,[SO_4^{-2}] = 3.4 \times 10^{-7}$

2. $[Sr^{+2}] = (12.0\text{ mL})(1.3 \times 10^{-3}) / 16.0\text{ mL} = 9.8 \times 10^{-4}\text{ M}$
   $[SO_4^{-2}] = (4.0\text{ mL})\,(2.0 \times 10^{-9}) / 16.0\text{ mL} = 5.0 \times 10^{-10}\text{ M}$

3. $Q = [Sr^{+2}]\,[SO_4^{-2}] = (9.8 \times 10^{-4}\text{ M})(5.0 \times 10^{-10}\text{ M}) = 4.9 \times 10^{-13}$

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

3. 7. Ksp and Precipitate Formation

Example: If 20.0 mL of 5.0 x 10^{-3} M $Ca(NO_3)_2$ is mixed with 10.0 mL of 2.5 x 10^{-2} M $Sn(SO_4)_2$:

(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. ($Sn(NO_3)_4$ is soluble at all concentrations)

3. 7. Ksp and Precipitate Formation

(b) **1.** $CaSO_{4\,(s)}$ $Ca^{+2}_{(aq)}$ + $SO_4{}^{-2}_{(aq)}$ Ksp = $[Ca^{+2}][SO_4{}^{-2}]$ = 7.1 x 10^{-5}

2. $[Ca(NO_3)_2]$ = (20.0 mL)(5.0 x 10^{-3}) / 30.0 mL = 3.3 x 10^{-3} M

$Ca(NO_3)_2$ → Ca^{+2} + $2NO_3{}^-$
3.3 x 10^{-3}M **3.3x10^{-3}M** 6.6x10^{-3}M

$[Sn(SO_4)_2]$ = (10.0 mL) (2.5 x 10^{-2}) / 30.0 mL = 8.3 x 10^{-3} M

$Sn(SO_4)_2$ → Sn^{+2} + $2SO_4{}^{-2}$
8.3 x 10^{-3}M 8.3x10^{-3}M **1.7x10^{-2}M**

3. Q = $[Ca^{+2}]$ $[SO_4{}^{-2}]$ = (3.3 x 10^{-3} M)(1.7 x 10^{-2} M) = 5.6 x 10^{-5}

4. Ksp > Q **Thus, a precipitate will NOT form!**
(7.1x10^{-5}) (5.6x10^{-5})

3. 7. Ksp and Precipitate Formation

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

General Strategy:

1. Write equilibrium equation and find Ksp
2. Know Q = Ksp at this particular [ion]
3. Solve Ksp 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 $[I^-]$ is required to just start the precipitation of $PbI_{2(s)}$ from the solution?

1. $PbI_{2(s)} \quad Pb^{+2}_{(aq)} + 2\,I^-_{(aq)}$

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

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

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

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

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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 $[Cl^-]$ with $AgNO_3$ solution.
2. The Ag^+ will precipitate out Cl^- as $AgCl_{(s)}$.
3. The point at which the moles of added Ag^+ = moles of Cl^- present is called the *Equivalence Point*.
4. The white $AgCl_{(s)}$ will stop forming at the equivalence point.
5. Difficult to see when $AgCl_{(s)}$ 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 $Ag_2CrO_{4\,(s)}$.

3. 8. Ksp and Precipitate Formation

Example: A 50.0 mL solution with an unknown [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 $Ag_2CrO_{4(s)}$.

b) What is the [Cl^-] in the 50.0 mL solution?

moles $AgNO_3$ = 0.25 M x 0.0328 L = 0.0082 moles

moles Ag^+ = moles $AgNO_3$ = 0.0082 moles

Since at equiv. point: moles Ag^+ = moles Cl^- = 0.0082 moles

[Cl^-] = 0.0082 moles / 0.050 L = **0.16 M**

3. 8. Ksp and Precipitate Formation

Example: A solution with a [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?

moles $AgNO_3$ = 0.50 M x 0.090 L = 0.045 moles

moles $AgNO_3$ = moles Ag^+ = moles Cl^- = 0.045 moles

volume Cl^- = 0.045 moles / 0.24 M = **0.19 L**

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