Applications of Aqueous Equilibria

K_{sp} Values for Some Salts at 25°C

Name	Formula	K_{sp}
Barium carbonate	$BaCO_3$	2.6×10^{-9}
Barium chromate	$BaCrO_4$	1.2×10^{-10}
Barium sulfate	$BaSO_4$	1.1×10^{-10}
Calcium carbonate	$CaCO_3$	5.0×10^{-9}
Calcium oxalate	CaC_2O_4	2.3×10^{-9}
Calcium sulfate	$CaSO_4$	7.1×10^{-5}
Copper(I) iodide	CuI	1.3×10^{-12}
Copper(II) iodate	$Cu(IO_3)_2$	6.9×10^{-8}
Copper(II) sulfide	CuS	6.0×10^{-37}
Iron(II) hydroxide	$Fe(OH)_2$	4.9×10^{-17}
Iron(II) sulfide	FeS	6.0×10^{-19}
Iron(III) hydroxide	$Fe(OH)_3$	2.6×10^{-39}
Lead(II) bromide	$PbBr_2$	6.6×10^{-6}
Lead(II) chloride	$PbCl_2$	1.2×10^{-5}
Lead(II) iodate	$Pb(IO_3)_2$	3.7×10^{-13}
Lead(II) iodide	PbI_2	8.5×10^{-9}
Lead(II) sulfate	$PbSO_4$	1.8×10^{-8}

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Magnesium carbonate	$MgCO_3$	6.8×10^{-6}
Magnesium hydroxide	$Mg(OH)_2$	5.6×10^{-12}
Silver bromate	$AgBrO_3$	5.3×10^{-5}
Silver bromide	$AgBr$	5.4×10^{-13}
Silver carbonate	Ag_2CO_3	8.5×10^{-12}
Silver chloride	$AgCl$	1.8×10^{-10}
Silver chromate	Ag_2CrO_4	1.1×10^{-12}
Silver iodate	$AgIO_3$	3.2×10^{-8}
Silver iodide	AgI	8.5×10^{-17}
Strontium carbonate	$SrCO_3$	5.6×10^{-10}
Strontium fluoride	SrF_2	4.3×10^{-9}
Strontium sulfate	$SrSO_4$	3.4×10^{-7}
Zinc sulfide	ZnS	2.0×10^{-25}

Solving Solubility Problems

For the salt AgI at 25°C, $K_{sp} = 1.5 \times 10^{-16}$

$$AgI(s) \rightarrow Ag^{+}(aq) + I^{-}(aq)$$

I	0	0
C	$+x$	$+x$
E	x	x

$$1.5 \times 10^{-16} = x^2$$

x = solubility of AgI in mol/L = 1.2×10^{-8} M

Solving Solubility Problems

For the salt $PbCl_2$ at 25°C, $K_{sp} = 1.6 \times 10^{-5}$

$$PbCl_2(s) \rightarrow Pb^{2+}(aq) + 2Cl^{-}(aq)$$

I	0	0
C	$+x$	$+2x$
E	x	$2x$

$$1.6 \times 10^{-5} = (x)(2x)^2 = 4x^3$$

x = solubility of $PbCl_2$ in mol/L = 1.6×10^{-2} M

Solving Solubility with a Common Ion

For the salt AgI at 25°C, $K_{sp} = 1.5 \times 10^{-16}$
What is its solubility in 0.05 M NaI?

$$AgI(s) \rightarrow Ag^{+}(aq) + I^{-}(aq)$$

I	0	0.05
C	+x	0.05+x
E	x	0.05+x

$$1.5 \times 10^{-16} = (x)(0.05+x) \cong (x)(0.05)$$

x = solubility of AgI in mol/L = 3.0×10^{-15} M

[14] When solid BaF_2 is added to H_2O the following equilibrium is established.

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\,F^{-}(aq) \quad K_{sp} = 1.5\times10^{-6} \text{ at } 25\ °C$$

a. Calculate the molar solubility of barium fluoride at 25 °C.

b. Explain how adding each of the following substances affects the solubility of BaF_2 in water.
  i. 0.10 M $Ba(NO_3)_2$
  ii. 0.10 M HNO_3

c. In an experiment to determine the K_{sp} of PbF_2 a student starts with 0.10 M $Pb(NO_3)_2$ and 0.10 M KF and uses the method of serial dilutions to find the lowest $[Pb^{2+}]$ and $[F^{-}]$ that form a precipitate when mixed. If the student uses the concentration of the ions in the combined solution to determine K_{sp}, will the value of K_{sp} calculated be too large, too small or just right? Explain.
K_{sp} for $PbF_2 = 4.0 \times 10^{-8}$

d. i. In a solution of 0.010 M barium nitrate and 0.010 M lead(II) nitrate, which will precipitate first, BaF_2 or PbF_2, as NaF(s) is added? Assume volume changes are negligible. Explain (support your answer with calculations).
ii. When the more soluble fluoride begins to precipitate, what is the concentration of the cation for the less soluble fluoride that remains in solution?

a. If S = molar solubility of BaF_2 (s), then $[Ba^{2+}] = S$, $[F^-] = 2S$

$K_{sp} = [Ba^{2+}][F^-]^2 = (S)(2S)^2 = 4S^3 = 1.5 \times 10^{-6}$

$S = 0.00721$ mol/L

b. i. Adding Ba^{2+} ion will decrease the molar solubility of BaF_2 due to the common ion effect.

ii. Adding H^+ will increase the molar solubility of BaF_2 as the F^- ion will react with H^+ to form HF, thereby causing more BaF_2 to dissolve by Le Chatelier's Principle.

c. The calculated K_{sp} will be too large because the student is relying on seeing the formation of a precipitate at the moment that Q exceeds K_{sp}. The student will miss the exact moment that happens, so the calculated value of K_{sp} will be too large.

Other possible issues: Protolysis will decrease the concentration of fluoride, so more fluoride will need to be added to cause precipitation; therefore measured K_{sp} will be too large. Likewise, some complex ions such as PbF^+ or PbF_2 (aq) may form, again leading to an experimental value that is too large.

d. i. As both BaF_2 and PbF_2 are 1:2 compounds, and the concentrations of the metal ions are both 0.010 M, you can tell that PbF_2 will precipitate first, because it has the lower K_{sp}. For calculations to support this:

For PbF_2, $4.0 \text{ x } 10^{-8} = (0.01)[F^-]^2$ $[F^-]^2 = 4.0 \text{ x } 10^{-6}$ $[F^-] = 2.0 \text{ x } 10^{-3}$ M

For BaF_2, $1.5 \text{ x } 10^{-6} = (0.01)[F^-]^2$ $[F^-]^2 = 1.5 \text{ x } 10^{-4}$ $[F^-] = 1.2 \text{ x } 10^{-2}$ M

The PbF_2 will precipitate first because a lower value for the concentration of fluoride is needed.

ii. From part (i) we know that the BaF_2 precipitates second, when the $[F^-]$ reaches $1.2 \text{ x } 10^{-2}$ M

Since PbF_2 (s) is present, then $[Pb^{2+}][F^-]^2 = K_{sp} = 4.0 \text{ x } 10^{-8}$

$[Pb^{2+}](1.2 \text{ x } 10^{-2})^2 = 4.0 \times 10^{-8}$

$[Pb^{2+}] = 2.8 \times 10^{-4}$ M

The molar solubility of PbI_2 is 1.50×10^{-3} M. Calculate the value of K_{sp} for PbI_2.

A 3.38E^{-9}

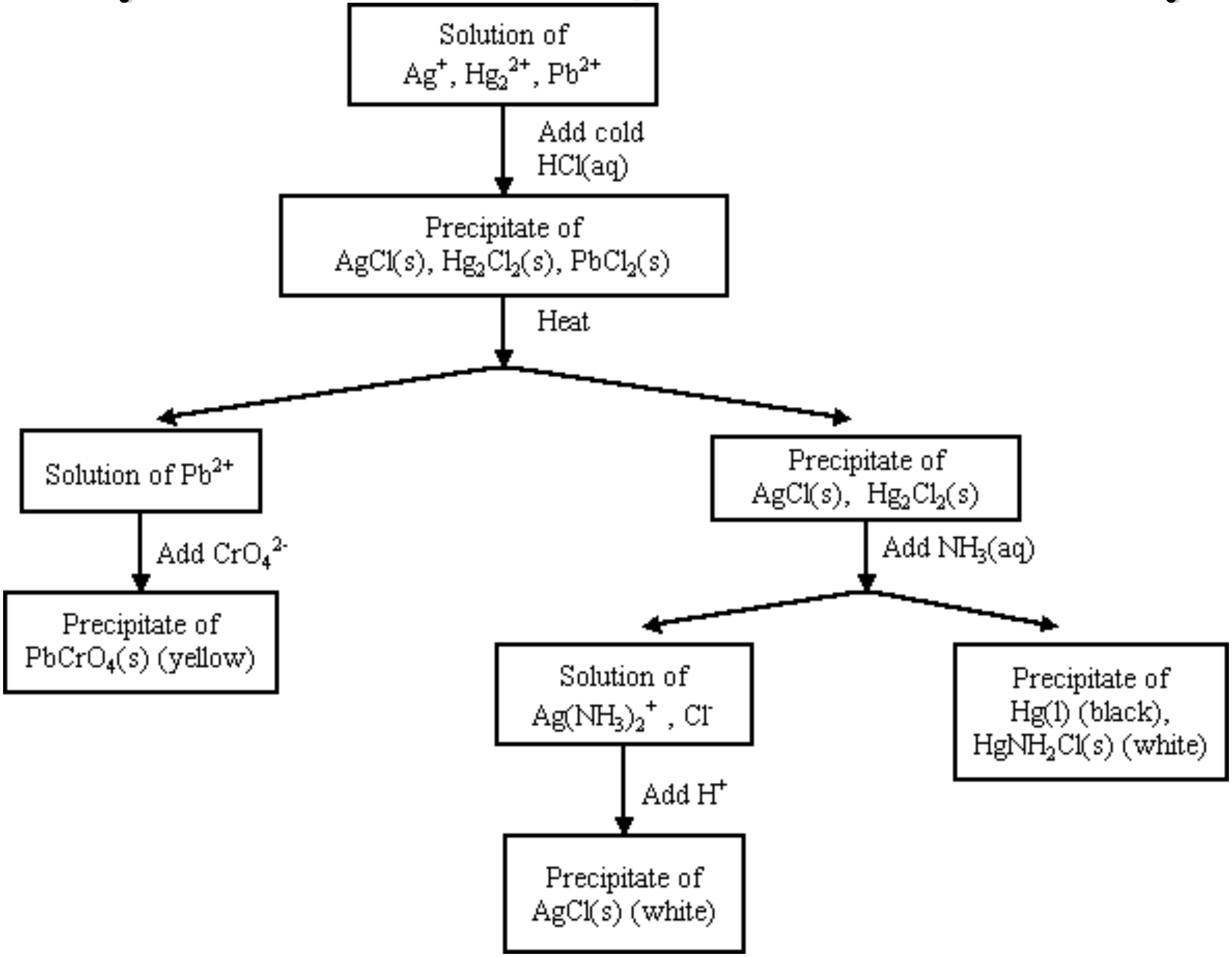
B 4.50E^{-6}

C 1.35E^{-8}

D 1.50E^{-3}

E none of these

Precipitation and Qualitative Analysis



Solution of Ag^+, Hg_2^{2+}, Pb^{2+}

Add cold $HCl(aq)$

Precipitate of $AgCl(s)$, $Hg_2Cl_2(s)$, $PbCl_2(s)$

Heat

Solution of Pb^{2+}

Add CrO_4^{2-}

Precipitate of $PbCrO_4(s)$ (yellow)

Precipitate of $AgCl(s)$, $Hg_2Cl_2(s)$

Add $NH_3(aq)$

Solution of $Ag(NH_3)_2^+$, Cl^-

Add H^+

Precipitate of $AgCl(s)$ (white)

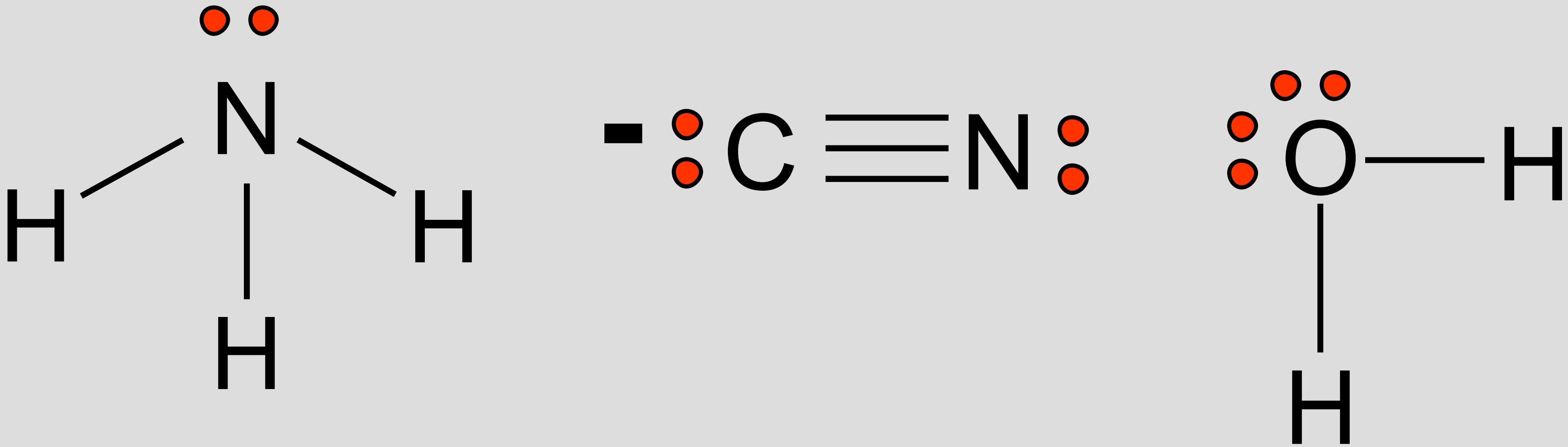
Precipitate of $Hg(l)$ (black), $HgNH_2Cl(s)$ (white)

FYI - Complex Ions

A *Complex ion* is a charged species composed of:

1. A metallic cation
2. *Ligands* – Lewis bases that have a lone electron pair that can form a covalent bond with an empty orbital belonging to the metallic cation

NH_3, CN^-, and H_2O are Common Ligands



Coordination Number

- ☐ Coordination number refers to the number of ligands attached to the cation
- ☐ 2, 4, and 6 are the most common coordination numbers

Coordination number	Example(s)
2	$Ag(NH_3)_2^+$
4	$CoCl_4^{2-}$ $Cu(NH_3)_4^{2+}$
6	$Co(H_2O)_6^{2+}$ $Ni(NH_3)_6^{2+}$

Complex Ions and Solubility

$$AgCl(s) \leftrightarrows \cancel{Ag^+} + Cl^- \qquad K_{sp} = 1.6 \times 10^{-10}$$

$$\cancel{Ag^+} + NH_3 \leftrightarrows \cancel{Ag(NH_3)^+} \qquad K_1 = 2.1 \times 10^3$$

$$\cancel{Ag(NH_3)^+}\ NH_3 \leftrightarrows Ag(NH_3)_2^+ \qquad K_2 = 8.2 \times 10^3$$

$$AgCl + 2NH_3 \leftrightarrows Ag(NH_3)_2^+ + Cl^- \qquad K = K_{sp} \cdot K_1 \cdot K_2$$

$$K = 2.8\,x\,10^{-3} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$