

N41 – Acid Base

Ksp

K_{sp} Values for Some Salts at 25°C

Name	Formula	K _{sp}
Barium carbonate	BaCO ₃	2.6 x 10 ⁻⁹
Barium chromate	BaCrO ₄	1.2 x 10 ⁻¹⁰
Barium sulfate	BaSO ₄	1.1 x 10 ⁻¹⁰
Calcium carbonate	CaCO ₃	5.0 x 10 ⁻⁹
Calcium oxalate	CaC ₂ O ₄	2.3 x 10 ⁻⁹
Calcium sulfate	CaSO ₄	7.1 x 10 ⁻⁵
Copper(I) iodide	CuI	1.3 x 10 ⁻¹²
Copper(II) iodate	Cu(IO ₃) ₂	6.9 x 10 ⁻⁸
Copper(II) sulfide	CuS	6.0 x 10 ⁻³⁷
Iron(II) hydroxide	Fe(OH) ₂	4.9 x 10 ⁻¹⁷
Iron(II) sulfide	FeS	6.0 x 10 ⁻¹⁹
Iron(III) hydroxide	Fe(OH) ₃	2.6 x 10 ⁻³⁹
Lead(II) bromide	PbBr ₂	6.6 x 10 ⁻⁶
Lead(II) chloride	PbCl ₂	1.2 x 10 ⁻⁵
Lead(II) iodate	Pb(IO ₃) ₂	3.7 x 10 ⁻¹³
Lead(II) iodide	PbI ₂	8.5 x 10 ⁻⁹
Lead(II) sulfate	PbSO ₄	1.8 x 10 ⁻⁸

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Magnesium carbonate	MgCO ₃	6.8 x 10 ⁻⁶
Magnesium hydroxide	Mg(OH) ₂	5.6 x 10 ⁻¹²
Silver bromate	AgBrO ₃	5.3 x 10 ⁻⁵
Silver bromide	AgBr	5.4 x 10 ⁻¹³
Silver carbonate	Ag ₂ CO ₃	8.5 x 10 ⁻¹²
Silver chloride	AgCl	1.8 x 10 ⁻¹⁰
Silver chromate	Ag ₂ CrO ₄	1.1 x 10 ⁻¹²
Silver iodate	AgIO ₃	3.2 x 10 ⁻⁸
Silver iodide	AgI	8.5 x 10 ⁻¹⁷
Strontium carbonate	SrCO ₃	5.6 x 10 ⁻¹⁰
Strontium fluoride	SrF ₂	4.3 x 10 ⁻⁹
Strontium sulfate	SrSO ₄	3.4 x 10 ⁻⁷
Zinc sulfide	ZnS	2.0 x 10 ⁻²⁵

Mostly Review!

Equilibrium constants and ICE Tables.

Only real difference is that your reactant is always a solid so it doesn't show up in the Law of Mass Action.

But that isn't "new" – we've known that forever!

Solubility

We typically describe the solubility in how much solute can you dissolve in how much solvent.

Moles / Liter

Grams / Liter

Etc...

Always check what units it wants answers in!

Usually represented by “S”

Solving Solubility Problems

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



I	0	0
C	+x	+x
E	x	x

$$K_{sp} = [\text{Ag}^+][\text{I}^-]$$

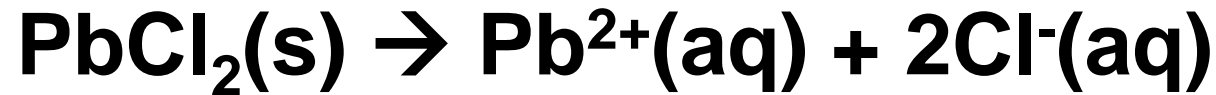
*Nothing on the denominator
because the reactant was a solid!*

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

$$x = \text{solubility of AgI in mol/L} = 1.2 \times 10^{-8} \text{ M}$$

Solving Solubility Problems When Not 1:1

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



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

Be careful with the stoichiometry!

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

$$x = \text{solubility of } \text{PbCl}_2 \text{ in mol/L} = 1.6 \times 10^{-2} \text{ M}$$

Common Ion Effect

What happens to the solubility of a substance if one of its ions is already present in the solution?

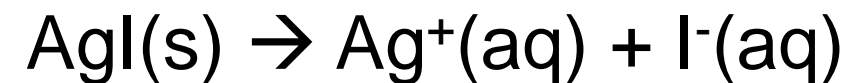
Will the solubility increase or decrease????

It decreases!

Let's redo this problem but this time let's have some I⁻ already

in the solution. x should end up less than 1.2×10^{-8} mol/L

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



x = solubility of AgI in mol/L

$$= 1.2 \times 10^{-8} \text{ M}$$

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?



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

$$1.5 \times 10^{-16} = (x)(0.05+x) \cong (x)(0.05) \quad \text{5\% rule!}$$

$$x = \text{solubility of AgI in mol/L} = 3.0 \times 10^{-15} \text{ M}$$

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

- A** $3.38\text{E-}9$
- B** $4.50\text{E-}6$
- C** $1.35\text{E-}8$
- D** $1.50\text{E-}3$
- E** none of these

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- B** 4.50E^{-6}
- C** 1.35E^{-8}
- D** 1.50E^{-3}
- E** none of these

PbI_2 (s)	\leftrightarrow	Pb^{2+} (aq)	+	2I^- (aq)
-		0		0
-		+ x		+ 2x

$$K_{\text{sp}} = (x)(2x)^2$$

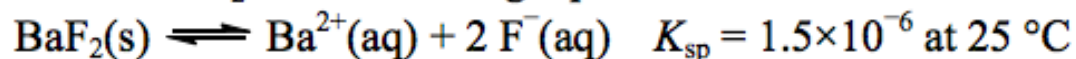
$$1.50 \times 10^{-3} = (x)(2x)^2$$

$$1.50 \times 10^{-3} = 4x^3$$

$$x = 1.35 \times 10^{-8}$$

Practice to Glue In

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



- Calculate the molar solubility of barium fluoride at $25 \text{ }^\circ\text{C}$.
- Explain how adding each of the following substances affects the solubility of BaF_2 in water.
 - $0.10 \text{ M Ba}(\text{NO}_3)_2$
 - 0.10 M HNO_3
- In an experiment to determine the K_{sp} of PbF_2 a student starts with $0.10 \text{ M Pb}(\text{NO}_3)_2$ and 0.10 M KF and uses the method of serial dilutions to find the lowest $[\text{Pb}^{2+}]$ and $[\text{F}^{-}]$ 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 $\text{PbF}_2 = 4.0 \times 10^{-8}$
- 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 $\text{NaF}(\text{s})$ is added? Assume volume changes are negligible. Explain (support your answer with calculations).
 - When the more soluble fluoride begins to precipitate, what is the concentration of the cation for the less soluble fluoride that remains in solution?

Key

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

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

$$S = 0.00721 \text{ mol/L}$$

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.

Key

- 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:

$$\text{For } \text{PbF}_2, \quad 4.0 \times 10^{-8} = (0.01)[\text{F}^-]^2 \quad [\text{F}^-]^2 = 4.0 \times 10^{-6} \quad [\text{F}^-] = 2.0 \times 10^{-3} \text{ M}$$

$$\text{For } \text{BaF}_2, \quad 1.5 \times 10^{-6} = (0.01)[\text{F}^-]^2 \quad [\text{F}^-]^2 = 1.5 \times 10^{-4} \quad [\text{F}^-] = 1.2 \times 10^{-2} \text{ M}$$

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

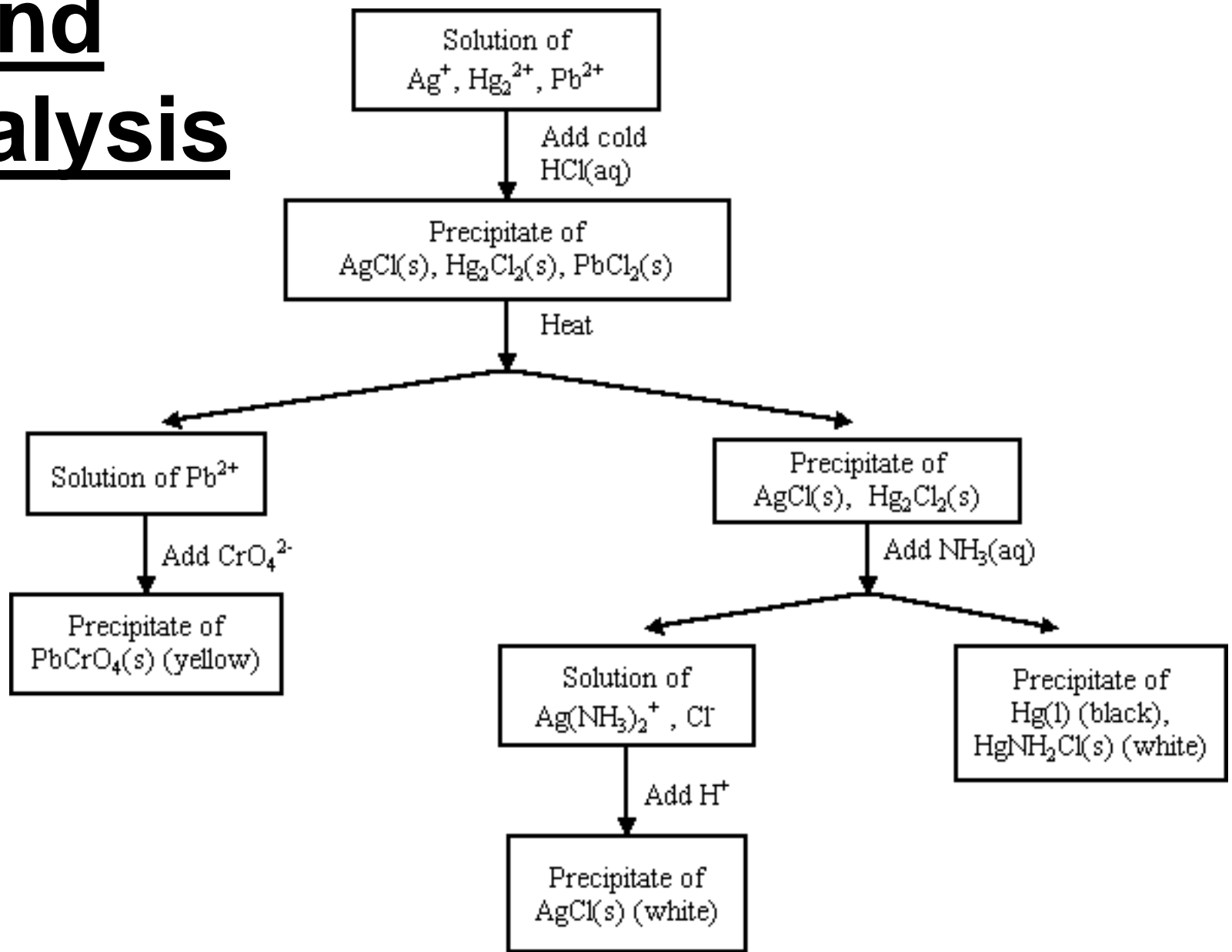
- ii. From part (i) we know that the BaF_2 precipitates second, when the $[\text{F}^-]$ reaches $1.2 \times 10^{-2} \text{ M}$

$$\text{Since } \text{PbF}_2 (\text{s}) \text{ is present, then } [\text{Pb}^{2+}][\text{F}^-]^2 = K_{\text{sp}} = 4.0 \times 10^{-8}$$

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

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

Precipitation and Qualitative Analysis



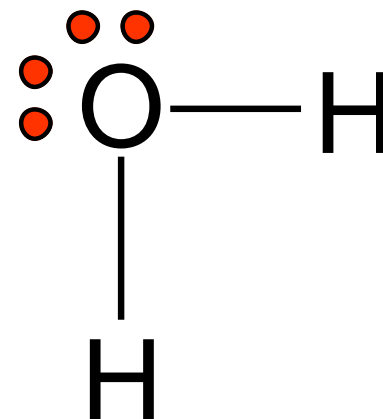
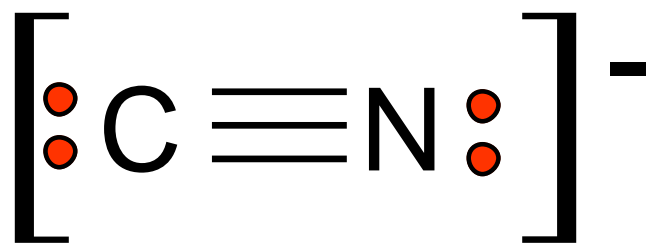
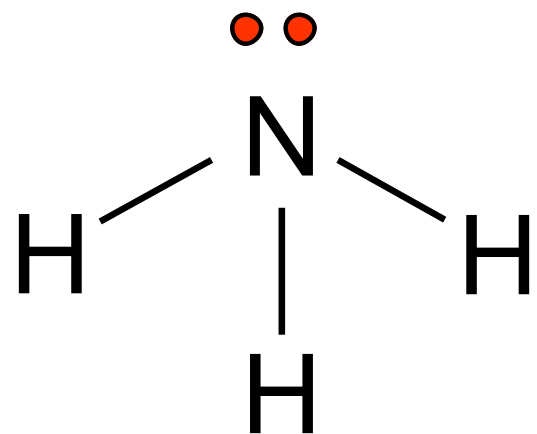
FYI - Complex Ions

Complex ion - a charged species composed of:

1. A metallic cation
2. Ligands

Ligand – Lewis bases that have a lone electron pair that can form a covalent bond with an empty orbital belonging to the metallic cation

NH₃, CN⁻, and H₂O are Common Ligands



NOTE A lot of Lewis acids/bases act as ligands. They are often involved in solubility problems, which is why we tend to put K_{sp} in the Acid Base chapter and not always Equilibrium chapter.

Coordination Number

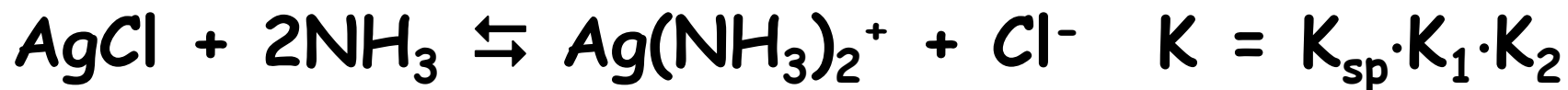
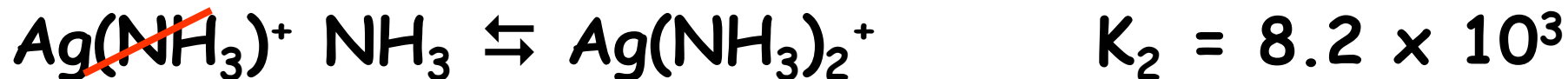
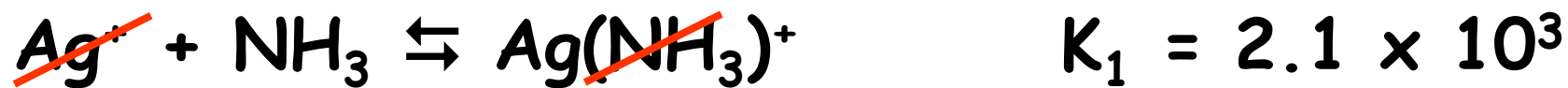
Coordination number

The number of ligands attached to the cation

- 2, 4, and 6 are the most common coordination numbers

Coordination #	Example(s)
2	$\text{Ag}(\text{NH}_3)_2^+$
4	CoCl_4^{2-} $\text{Cu}(\text{NH}_3)_4^{2+}$
6	$\text{Co}(\text{H}_2\text{O})_6^{2+}$ $\text{Ni}(\text{NH}_3)_6^{2+}$

Complex Ions and Solubility



$$K = 2.8 \times 10^{-3} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2}$$