N35 - SOLUTIONS

K_{sp}

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K_{sp}

Target: I can perform K_{sp} calculations to determine the solubility of different salts.

Just application of old info!

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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.

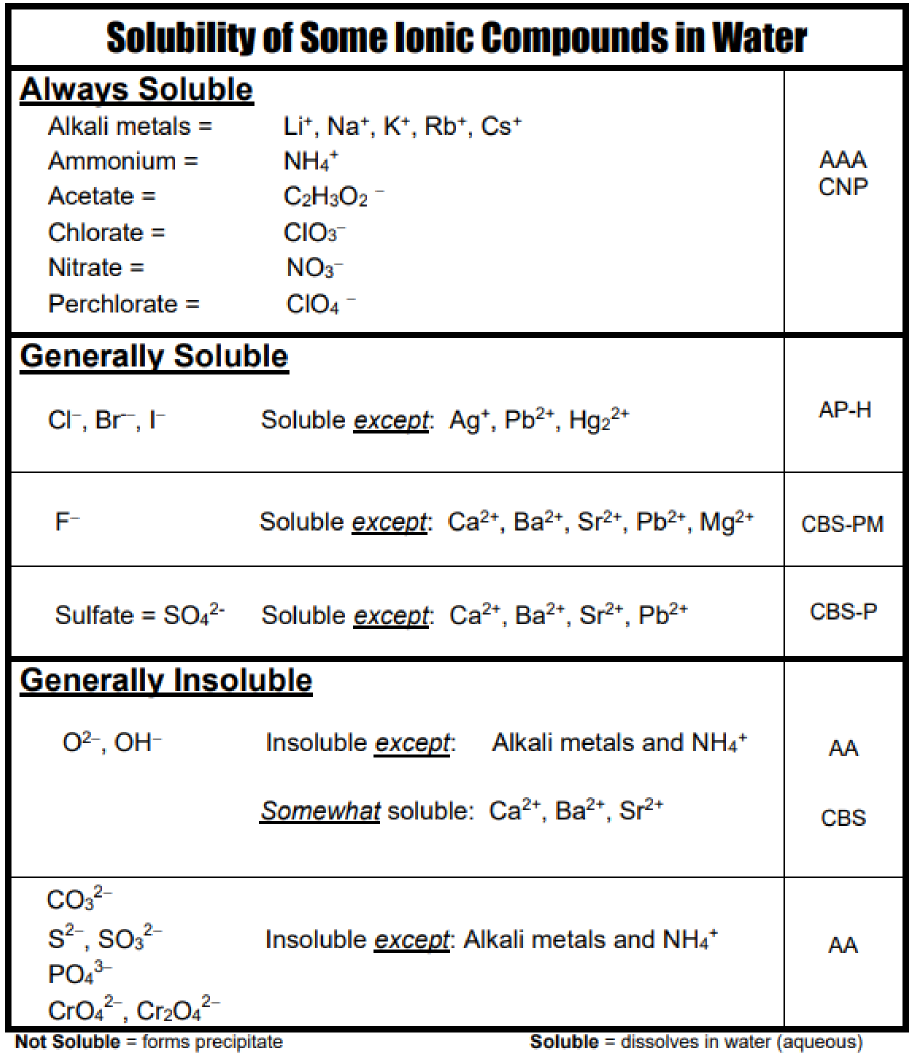
But that isn’t “new” – we’ve known that forever!

Solubility Chart

A solubility chart is a qualitative distinction!

When we say insoluble, we mean so little dissociates that it isn't practical. A few will still dissociate!

Can do math to see how much dissociates.



Solubility of Some Ionic Compounds in Water

Always Soluble		
Alkali metals =	Li^+, Na^+, K^+, Rb^+, Cs^+	AAA CNP
Ammonium =	NH_4^+	
Acetate =	$C_2H_3O_2^-$	
Chlorate =	ClO_3^-	
Nitrate =	NO_3^-	
Perchlorate =	ClO_4^-	
Generally Soluble		
Cl^-, Br^-, I^-	Soluble *except*: Ag^+, Pb^{2+}, Hg_2^{2+}	AP-H
F^-	Soluble *except*: Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+}, Mg^{2+}	CBS-PM
Sulfate = SO_4^{2-}	Soluble *except*: Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+}	CBS-P
Generally Insoluble		
O^{2-}, OH^-	Insoluble *except*: Alkali metals and NH_4^+	AA
	Somewhat soluble: Ca^{2+}, Ba^{2+}, Sr^{2+}	CBS
CO_3^{2-} S^{2-}, SO_3^{2-} PO_4^{3-} CrO_4^{2-}, $Cr_2O_4^{2-}$	Insoluble *except*: Alkali metals and NH_4^+	AA

Not Soluble = forms precipitate

Soluble = dissolves in water (aqueous)

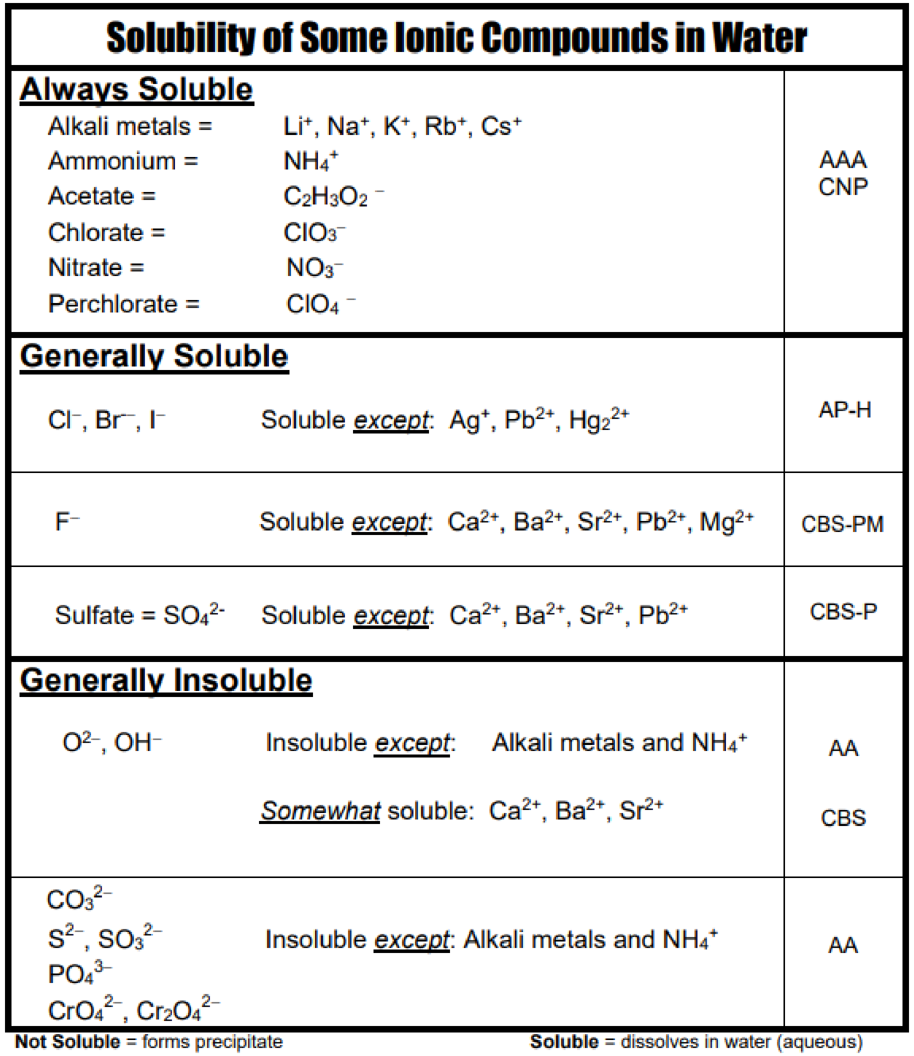
Solubility Product

K_{sp} is called the solubility product

Example:

$$AgBr_{(s)} \rightarrow Ag^+_{(aq)} + Br^-_{(aq)}$$

$$K_{sp} = [Ag^+][Br^-]$$



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Not Soluble = forms precipitate

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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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Lead(II) sulfate	$PbSO_4$	1.8×10^{-8}
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}

K_{sp} isn't always the most useful value

You can't always *directly* compare the solubility of substances based on their K_{sp} values because the stoichiometry comes into play also.

$AgCl$ vs $CaCl_2$

2 ions 3 ions

Instead we will use a value that we calculate that allows us to compare the solubility of two compounds more directly.

Expressing Solubility

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

Moles / Liter - *0.25 moles will dissociate in 1 L sol’n*
Grams / Liter
Etc…

(Always check what units it wants answers in!)

This value is called the Molar Solubility
Usually represented by “s”

Solving Solubility Problems

Calculate molar solubility for 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

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

Nothing on the denominator because the reactant was a solid!

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

x = s = molar solubility of AgI in mol/L

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

Meaning:

1.2×10^{-8} moles of Ag^+ and I^- can be present per 1 L of sol'n before the sol'n is saturated.

*Or...you can get 1.2×10^{-8} moles of **AgI** to dissociate per L of sol'n*

Solving Solubility Problems

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E	s	s

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

s = molar solubility of AgI in mol/L

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

Meaning:

1.2×10^{-8} moles of Ag^{+} and I^{-} can be present per 1 L of sol'n before the sol'n is saturated.

Or...you can get 1.2×10^{-8} moles of AgI to dissociate per L of sol'n

Solving Solubility Problems When Not 1:1

Calculate molar solubility for $PbCl_2$ at 25°C, $K_{sp} = 1.6 \times 10^{-5}$

Meaning:

1.6×10^{-2} mol of Pb^{2+} and 3.2×10^{-2} mol of Cl^- can be present per 1 L of sol'n before the sol'n is saturated.

Or...you can get 1.6×10^{-2} moles of $PbCl_2$ to dissociate per L of solution

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

I	0	0
C	+s	+2s
E	s	2s

Be careful with the stoichiometry!

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

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

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

$PbI_{2\,(s)}$	↔	$Pb^{2+}_{(aq)}$	+	$2I^{-}_{(aq)}$
-		0		0
-		+ s		+ 2s

$$K_{sp} = (s)(2s)^2$$

$$K_{sp} = 4(s)^3$$

$$K_{sp} = 4\left(1.5 \times 10^{-3}\right)^3$$

$$K_{sp} = 1.35\ x\ 10^{-8}$$

Will Something Precipitate?

Have to check Q versus K !

$Q < K_{sp}$	**No precipitate yet! The solution is unsaturated.** **All ions are still dissociated.**
$Q = K_{sp}$	**No precipitate yet! The solution is saturated.** **The maximum amount of ions are dissociated.**
$Q > K_{sp}$	**A precipitate will form!** **The maximum amount of ions are already dissociated, so the extra will “crash out” as a solid precipitate.**

Note *Supersaturated solutions have* $Q > K_{sp}$ *but a ppt hasn’t crashed out yet because it was made at a higher temperature and slowly cooled down. It is unstable and the ppt will crash out once the sol’n is disturbed.*

Precipitation[2]

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!

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

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

s = solubility of AgI in mol/L

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

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

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	+s	+s
E	s	0.05+s

5% rule!

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

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

Qualitatively describing how adding something changes solubility

Another Salt:

Look to see if the dissociated ions are in common

$BaCl_2$ + NaCl
Ba^{2+} $2Cl^-$ Na^+ Cl^- Cl^- is in common with $BaCl_2$, so it will decrease the solubility.

$BaCl_2$ + NaF
Ba^{2+} $2Cl^-$ Na^+ F^- F^- is NOT in common with $BaCl_2$, so it will not change the solubility.

Qualitatively describing how adding something changes solubility

Adding an Acid: Look to see if the dissociated ions will react with one of the ions from the salt.

$BaCl_2 + HNO_3$	$CaF_2 + HNO_3$
Ba^{2+} $2Cl^-$ H^+ NO_3^- H^+ and Cl^- make a strong acid which stays dissociated. Doesn't affect the solubility of $BaCl_2$	Ca^{2+} $2F^-$ H^+ NO_3^- H^+ and F^- make a weak acid which doesn't dissociate fully! Removes F^- ions from solution. Increases the solubility of CaF_2, trying to replace F^- ions

In which solution is $BaSO_4$ most soluble?

A A solution that is 0.10 M in $Ba(NO_3)_2$

B A solution that is 0.10 M in Na_2SO_4

C A solution that is 0.10 M in $NaNO_3$

D None of these, solubility never changes, it is a set value

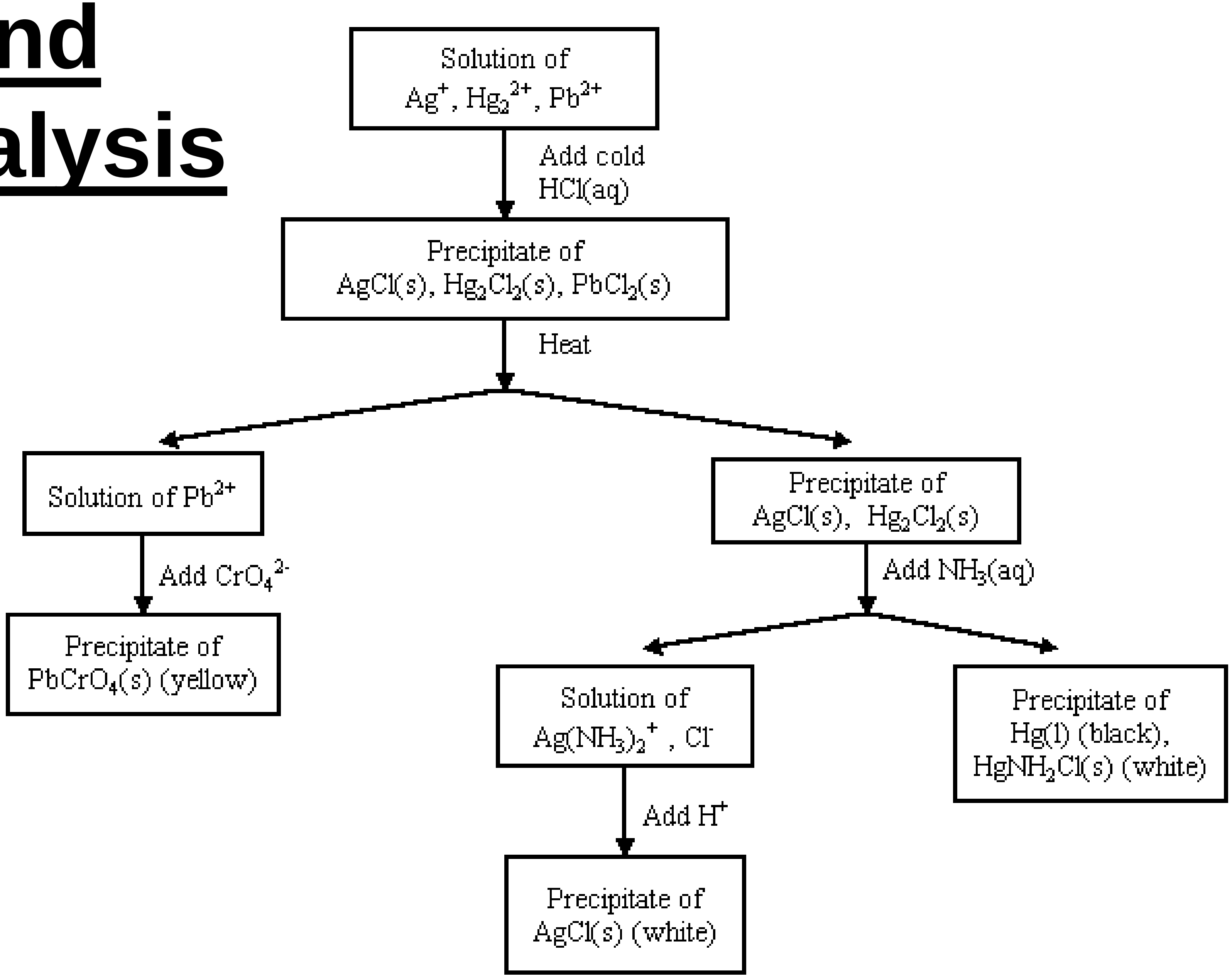
In which solution is $BaSO_4$ most soluble?

- A A solution that is 0.10 M in $Ba(NO_3)_2$
- B A solution that is 0.10 M in Na_2SO_4
- C A solution that is 0.10 M in $NaNO_3$
- D None of these, solubility never changes, it is a set value

The others have common ions that would drive equilibrium position to the left, resulting in less dissociation of the ions

Precipitation and Qualitative Analysis

Not in the class anymore!



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)

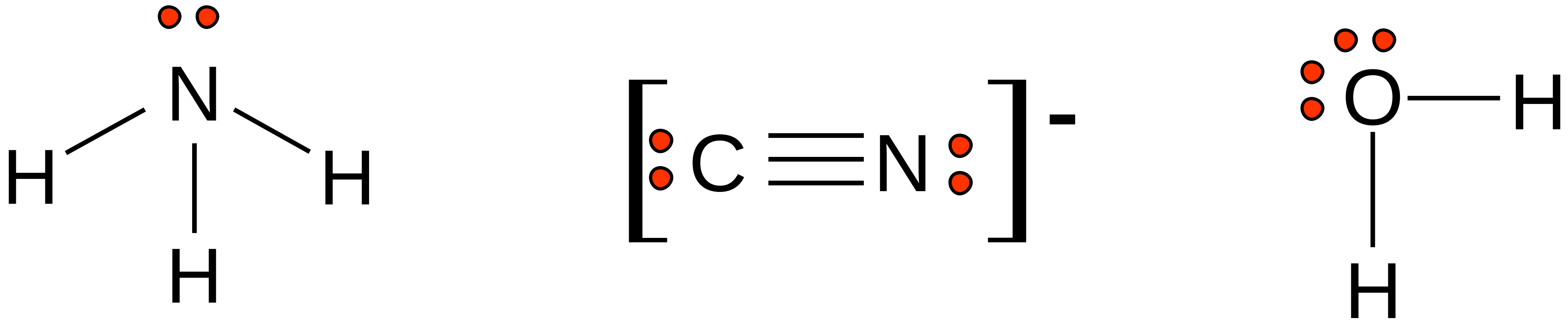
FYI - Complex Ions

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

NH_3, CN^-, and H_2O 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 or Solutions chapters.

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

Complex Ions and Solubility

$$\begin{array}{rl}
AgCl(s) \leftrightarrows \cancel{Ag^+} + Cl^- & K_{sp} = 1.6 \times 10^{-10} \\
\cancel{Ag^+} + NH_3 \leftrightarrows \cancel{Ag(NH_3)^+} & K_1 = 2.1 \times 10^3 \\
\cancel{Ag(NH_3)^+}\ NH_3 \leftrightarrows Ag(NH_3)_2^+ & K_2 = 8.2 \times 10^3 \\
\hline
AgCl + 2NH_3 \leftrightarrows Ag(NH_3)_2^+ + Cl^- & K = K_{sp} \cdot K_1 \cdot K_2
\end{array}$$

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

Some more pretty precipitation videos if you are interested ☺

Precipitation[3]

[illegible]

[illegible]

Precipitation IV

[illegible] Chemistry

Precipitation V

[illegible]

YouTube Link to Presentation

This is an old version of the lecture, back when it used to be in the Acid Base chapter. If I get time I will update this with a new video for this AP lecture.

https://youtu.be/LWIR91gx-ac