

SOLUTION: Homogeneous mixture of substances Solutions contain:

SOLUTE: Component(s) of a solution present in small amount

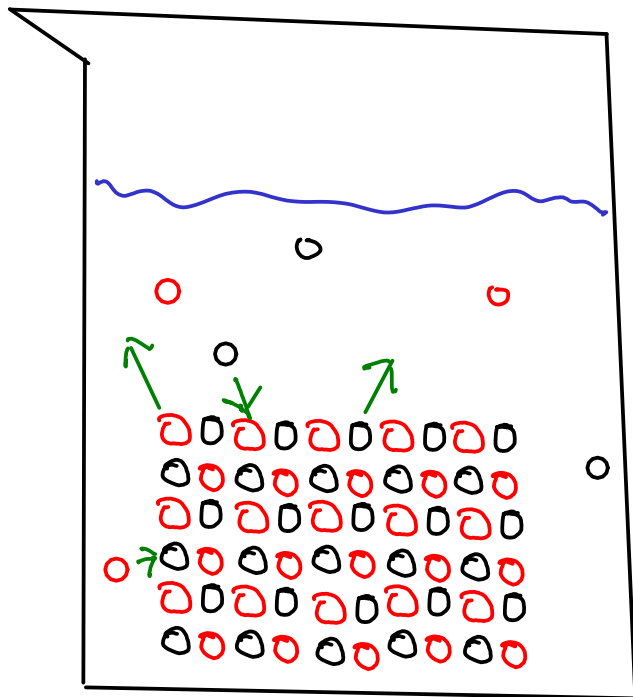
SOLVENT: Component of a solution present in greatest amount

We usually call water the solvent in aqueous mixtures, even if the water is present in smaller amount than another component

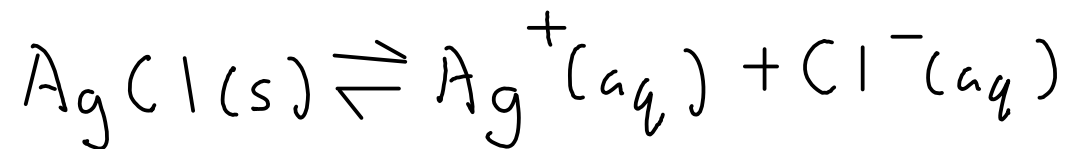
SOLUBILITY: The amount of a solute that will dissolve in a given volume of solvent

SATURATED SOLUTION: Contains the maximum amount of solute that it is possible to dissolve in a given volume of solvent!

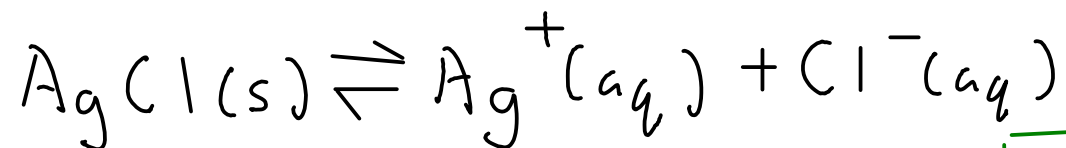
A SATURATED SOLUTION is a solution where dissolved solute exists in an EQUILIBRIUM with undissolved solute!



Example: Consider a saturated solution of silver chloride:

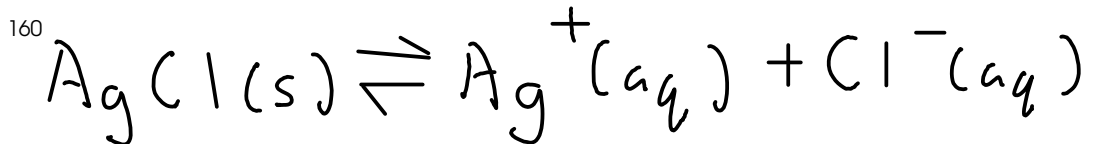


At equilibrium, the rate of dissolving equals the rate of crystallization!



$$K_c = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$$

... what does this equilibrium constant tell us? That silver chloride isn't very soluble!



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

↶ This equilibrium constant is given a special name - the SOLUBILITY PRODUCT CONSTANT - because the equilibrium expression for the dissolving of a salt always appears as a PRODUCT of the concentrations of the ions in the compound!

Remember,  $K_{sp}$  is an equilibrium constant, so everything that applies to equilibrium constants applies to the solubility constant - including what to do with coefficients:

What is the solubility product constant expression for calcium phosphate?



$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

161 Solubility calculations and Ksp

You can calculate the solubility of a compound if you know Ksp!

Calculate the solubility (in g/L) of lead(II) iodide at 25C. FW = 461.0 g/mol  
 (See Appendix J in OpenStax for solubility product information!)

$$K_{sp} = [Pb^{2+}][I^-]^2 \quad PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

$$= 1.4 \times 10^{-8}, \text{ so } [Pb^{2+}][I^-]^2 = 1.4 \times 10^{-8}$$

Solve by making an equilibrium chart.

Species	[Initial]	$\Delta$	[Equilibrium]
$Pb^{2+}$	0	+x	x
$I^-$	0	+2x	2x

Let "x" equal the change in lead(II) ion concentration

$$(x)(2x)^2 = 1.4 \times 10^{-8}$$

$$4x^3 = 1.4 \times 10^{-8}$$

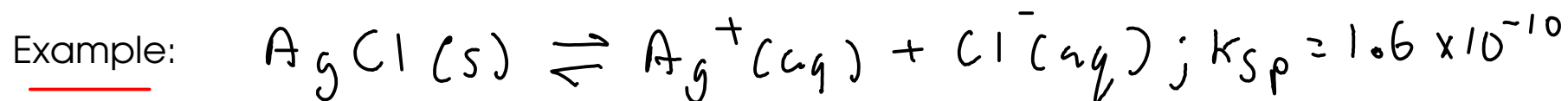
$$x = 0.0015182945 = [Pb^{2+}] = [PbI_2]_{\text{dissolved}}$$

We have the lead(II) iodide concentration in M units, but need g/L. Convert.

$$\frac{0.0015182945 \text{ mol } PbI_2}{L \text{ solution}} \times \frac{461.0 \text{ g } PbI_2}{\text{mol } PbI_2} = \boxed{0.70 \text{ g/L}}$$

## <sup>162</sup> Precipitation - also known as the reaction quotient

To predict whether a salt at a given concentration will precipitate out, calculate the reaction quotient  $Q$  and compare it to the  $K_{sp}$



$$Q = [Ag^+][Cl^-]$$

IF...

- \*  $Q < K_{sp}$  ; the reaction proceeds to produce more products (dissolved ions), so more solid is able to dissolve: NO PRECIPITATION
- \*  $Q > K_{sp}$  ; the reaction proceeds to produce more reactants (solid), so solid falls out of solution: PRECIPITATION OCCURS
- \*  $Q = K_{sp}$  ; the reaction is at equilibrium. PRECIPITATION IS JUST BEGINNING

Would a solution with  $(Ag^+) = 0.014$  M and  $(Cl^-) = 0.00042$  M precipitate?

$$Q = [Ag^+][Cl^-] = (0.014)(0.00042) = 5.88 \times 10^{-6}$$

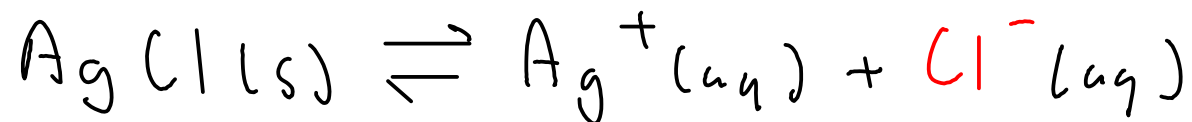
$$5.88 \times 10^{-6} > 1.6 \times 10^{-10}$$

$Q \quad > \quad K_{sp}$

Since  $Q > K_{sp}$ , this mixture will PRECIPITATE.

## <sup>163</sup> Le Chateleur's Principle

The "common ion effect" affects the solubility of a compound in solution. The presence of one of the ions in a salt in the solution will REDUCE THE SOLUBILITY of that salt!

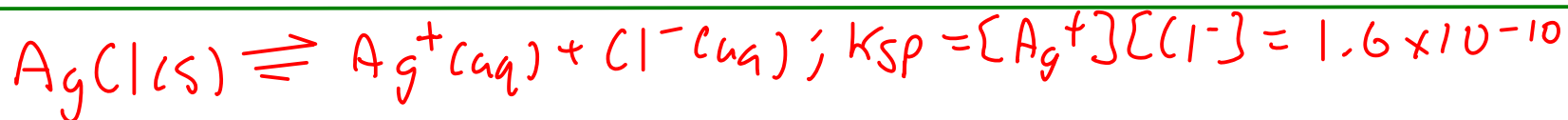


Silver chloride is much less soluble in a solution of 0.1 M NaCl than it is in distilled water. Why? The presence of CHLORIDE ION forces the solubility equilibrium back to the left, meaning less silver chloride can dissolve!

Solubility can also be affected by pH - depending on the acidic or basic properties of the salt!

A second example: Salicylic acid in the characterization lab

Calculate the solubility of AgCl (FW = 143.35 g/mol) in distilled water. Then, calculate the solubility of AgCl in 0.10 M NaCl solution. Report both answers in parts per million (mg/L)



Solve equilibrium...

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{Ag}^+$	0	+x	x
$\text{Cl}^-$	0	+x	x

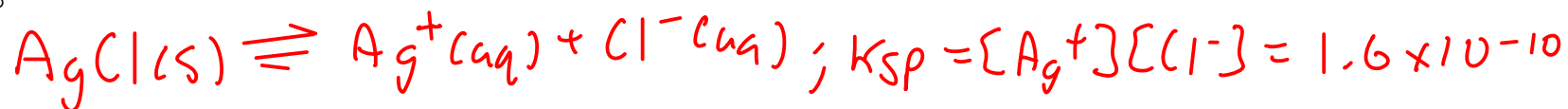
Let "x" equal the change in silver ion concentration

$$(x)(x) = 1.6 \times 10^{-10}$$

$$x^2 = 1.6 \times 10^{-10}$$

$$x = 1.264911064 \times 10^{-5} \text{ M} = [\text{Ag}^+] = [\text{AgCl}]_{\text{dissolved}}$$

$$\frac{1.264911064 \times 10^{-5} \text{ mol AgCl}}{\text{L}} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} = 0.0018 \frac{\text{g AgCl}}{\text{L}} = \boxed{1.8 \text{ ppm AgCl}}$$



Now solve for the AgCl dissolved in 0.10 M NaCl

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{Ag}^+$	0	+x	x
$\text{Cl}^-$	0.10	+x	0.10+x

Let "x" equal the change in silver ion concentration.

$$(x)(0.10+x) = 1.6 \times 10^{-10}$$

↓ Assume  $x \ll 0.10$

$$(x)(0.10) = 1.6 \times 10^{-10}$$

$$x = 1.6 \times 10^{-9} = [\text{Ag}^+] = [\text{AgCl}]_{\text{dissolved}}$$

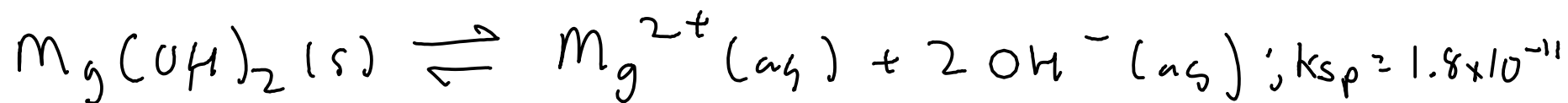
$$\frac{1.6 \times 10^{-9} \text{ mol AgCl}}{\text{L}} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} = 2.3 \times 10^{-7} \frac{\text{g}}{\text{L}} = \boxed{0.00023 \text{ ppm AgCl}}$$

Compare: Solubility in DI water was 1.8 ppm. Solubility in 0.10 M NaCl (common ion, Cl<sup>-</sup>) is 0.00023 ppm.

Conclusion: The presence of a common ion GREATLY decreases solubility.



## pH AND SOLUBILITY



This compound's solubility is pH dependent. How?

\* In a BASIC solution, the concentration of hydroxide ion in solution is high, so solubility is LOWER than in pure water.

\* In an ACIDIC solution, we have a significant amount of hydronium, which can react with hydroxide. This lowers the hydroxide concentration and makes magnesium hydroxide MORE SOLUBLE

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### Generalizing

If a compound is BASIC, then it will be LESS SOLUBLE in basic solutions, and MORE SOLUBLE in acidic solutions!

If a compound is ACIDIC, then it will be MORE SOLUBLE in basic solutions, and LESS SOLUBLE in acidic solutions!

If a compound is NEUTRAL (neither acidic nor basic), then its solubility will be UNAFFECTED by pH

## LEWIS THEORY

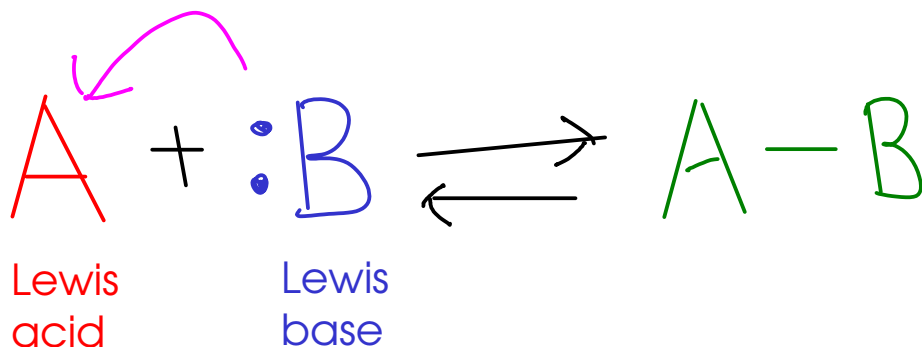
- Lewis theory treats acid-base chemistry as ELECTRON-TRANSFER chemistry involving pairs of electrons
- Lewis acid-base reactions form new covalent bonds (of interest to organic chemists!)

ACIDS are ACCEPTORS of electron pairs

... this is why some METAL IONS, even though they contain no hydrogen ions, can exhibit ACIDIC character. Many metal ions can accept a pair of electrons to form a COMPLEX with a Lewis base! ex:  $Ag(NH_3)_2^+$

BASES are DONORS of electron pairs.

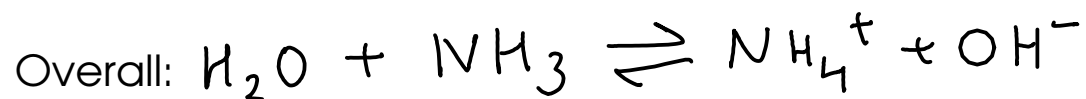
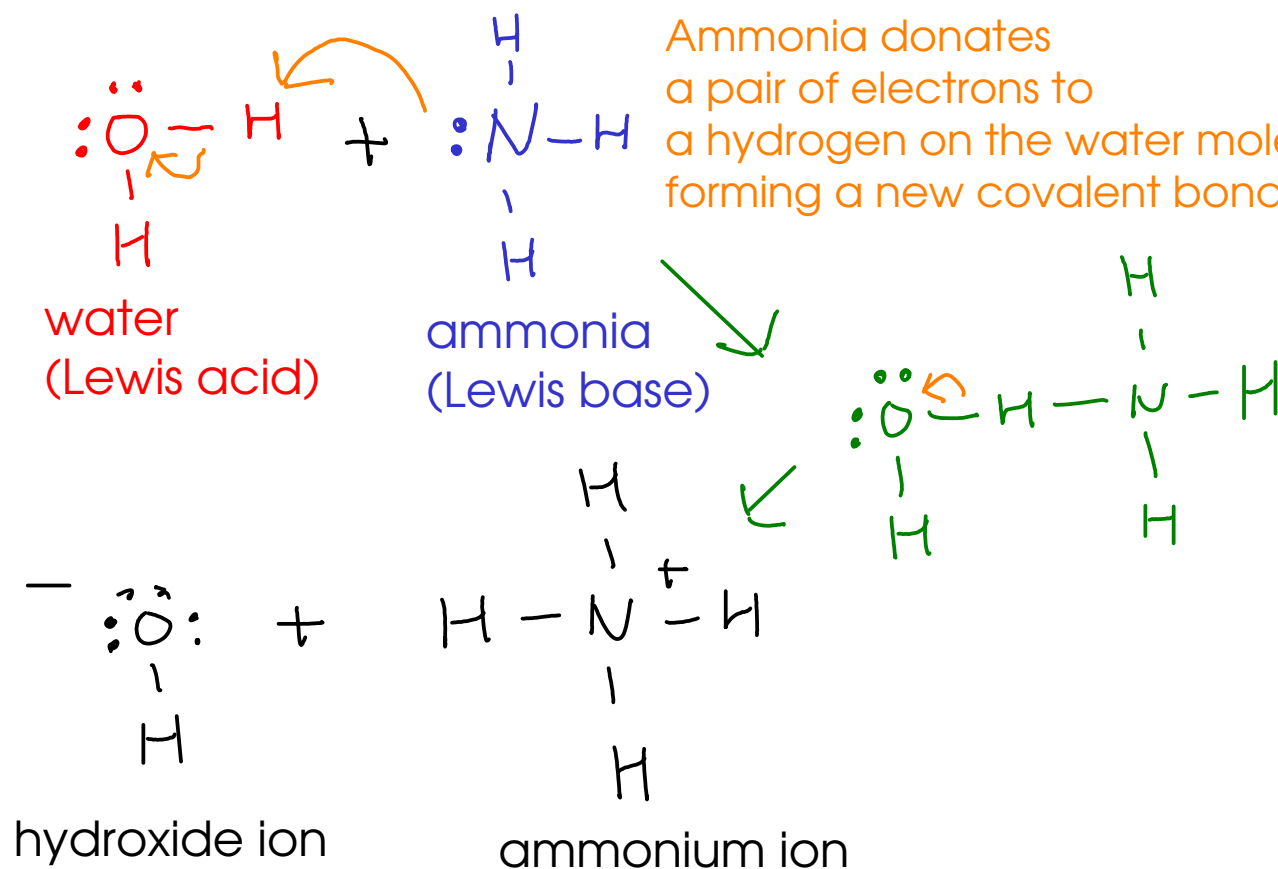
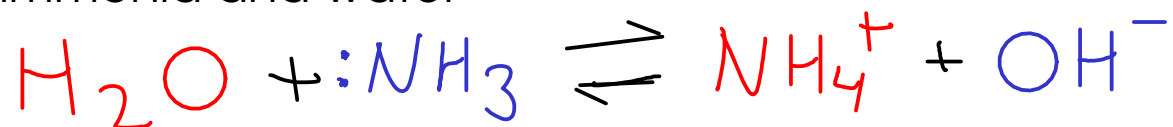
... so, Lewis bases have LONE PAIRS OF ELECTRONS in their Lewis structures



... In a Lewis acid-base reaction, electrons are donated from the Lewis base to the Lewis acid. This forms a new COVALENT BOND between the acid and the base.

LEWIS THEORY

Example: ammonia and water



## COMPARING THE THEORIES

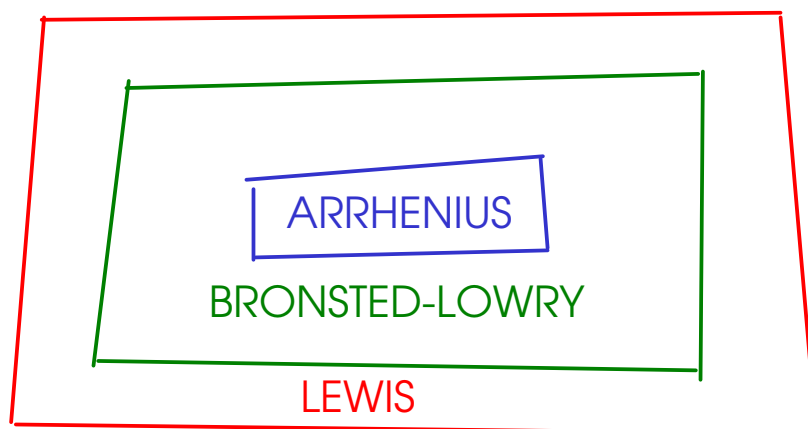
- From Arrhenius to Lewis, the definitions get broader as you go along. In other words, the later definitions include MORE SUBSTANCES under the acid/base umbrella.

If something is an Arrhenius acid, it is also an acid in the Bronsted or Lewis picture.

If something is an Arrhenius base, it is also a base in the Bronsted or Lewis picture.

All Bronsted acids are Lewis acids, and all Bronsted bases are Lewis bases.

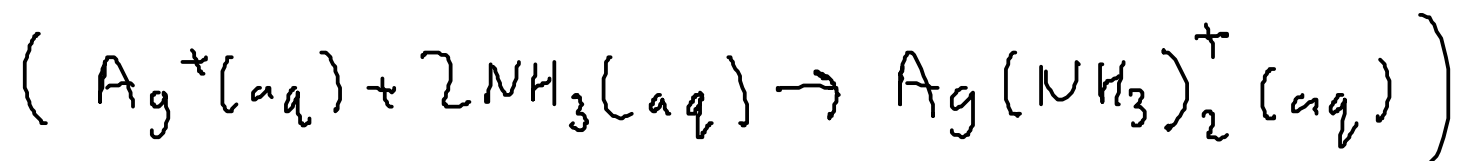
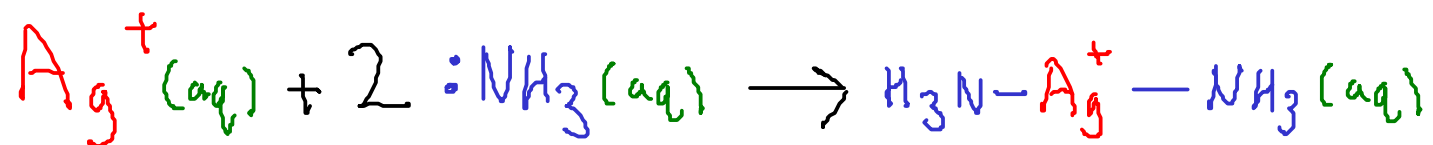
... but not all Lewis acids/bases (like the metal ions) are Bronsted or Arrhenius acids/bases.



... We have mostly used BRONSTED-LOWRY theory to this point in the course!

## 170 COMPLEX IONS

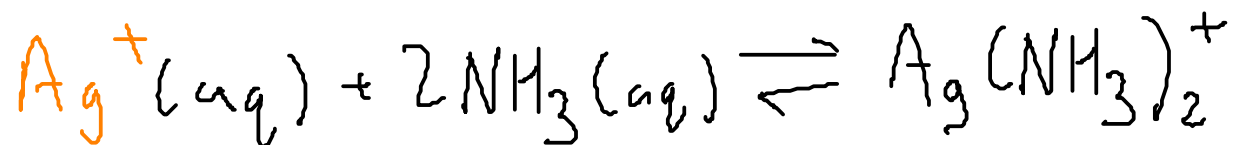
- are ions that result from the reaction of a Lewis base (like water, ammonia, hydroxide ion, etc.) with a metal ion
- The Lewis base attaches to the metal ion by forming a COORDINATE COVALENT BOND with the metal ion.



- The product of the reaction is called a "COMPLEX", and the attached Lewis bases are called "LIGANDS"

## COMPLEX IONS AND SOLUBILITY

- What is the effect of complex formation on solubility?



What will the presence of ammonia do to the solubility of silver chloride?

- ① Since the formation of the silver-ammonia complex is favorable, we expect that any dissolved silver ion would react with ammonia to make the complex.
- ② This will REDUCE the concentration of free silver ion.
- ③ The reduction of free silver ion will cause more silver chloride to dissolve (Le Chateleur's principle - the equilibrium will try to produce more free silver ion to replace what the ammonia has removed)

So, the presence of a ligand which can form a complex with an ion from a salt will greatly INCREASE the solubility of that salt!