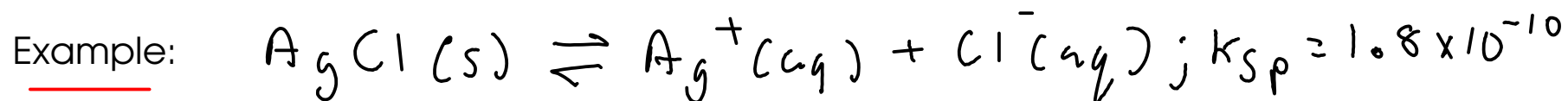


Precipitation - also known as the reaction quotient

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 $[Ag^+] = 0.014 \text{ M}$ and $[Cl^-] = 0.00042 \text{ M}$ precipitate?

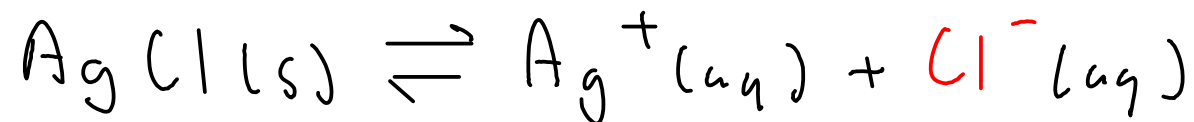
$$Q = [Ag^+][Cl^-] = (0.014)(0.00042) = 5.88 \times 10^{-6}$$

$$Q = 5.88 \times 10^{-6} > 1.8 \times 10^{-10}$$

Since $Q > K_{sp}$, precipitation will occur!

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!

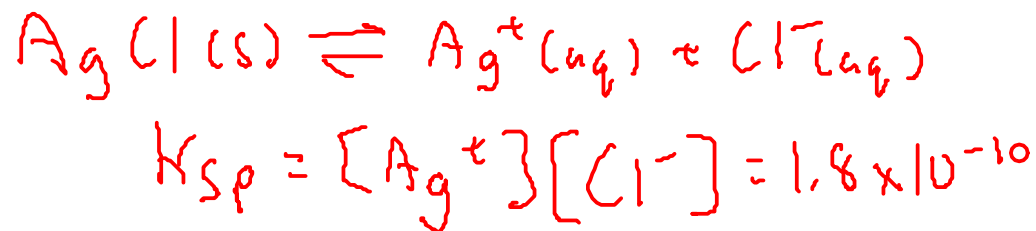


Silver chloride is much less soluble in a solution of 0.1 M NaCl than it is in distilled water. Why? The presence of CHLORIDE ION forces the solubility equilibrium back to the left, meaning less silver chloride can dissolve!

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



For distilled water,

Species	[Init]	Δ	[Equil]
Ag^+	0	+x	x
Cl^-	0	+x	x

$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.341640786 \times 10^{-5} \text{ M} = [\text{Ag}^+] = [\text{AgCl}]_{\text{dissolved}}$$

$$\frac{1.341640786 \times 10^{-5} \text{ mol AgCl}}{\text{L}} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} \times \frac{\text{mg}}{10^{-3} \text{ g}} = 1.9 \text{ ppm AgCl}$$

(in distilled water)

AgCl:

$$\text{Ag} = 1 \times 107.8$$

$$\text{Cl} = 1 \times 35.45$$

$$\underline{143.35 \text{ g/mol}}$$



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

For 0.10 M NaCl,



Species	[Init]	Δ	[Equl]
Ag^+	0	+x	x
Cl^-	0.10	+x	0.10 + x

$$(x)(0.10 + x) = 1.8 \times 10^{-10}$$

\downarrow $x \ll 0.10$, so $0.10 + x \approx 0.10$

$$0.10x = 1.8 \times 10^{-10}$$

$$x = 1.8 \times 10^{-9} = [\text{Ag}^+] = [\text{AgCl}] \text{ dissolved}$$

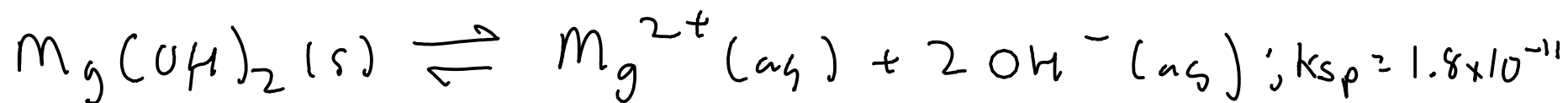
$$\frac{1.8 \times 10^{-9} \text{ mol AgCl}}{\text{L}} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} \times \frac{\text{mg}}{10^{-3} \text{ g}} = 2.6 \times 10^{-4} \text{ ppm} \quad (0.00026 \text{ ppm})$$

Compare: 1.9 ppm AgCl in distilled water
0.00026 ppm AgCl in 0.10 M NaCl

in 0.10 M NaCl

Conclusion: The presence of a common ion greatly decreases the solubility!

pH AND SOLUBILITY



This salt'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

Generalizing

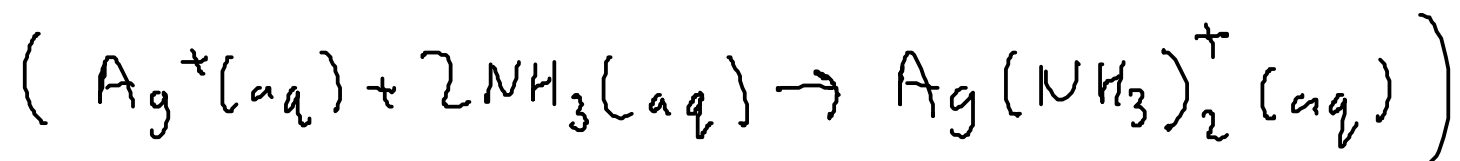
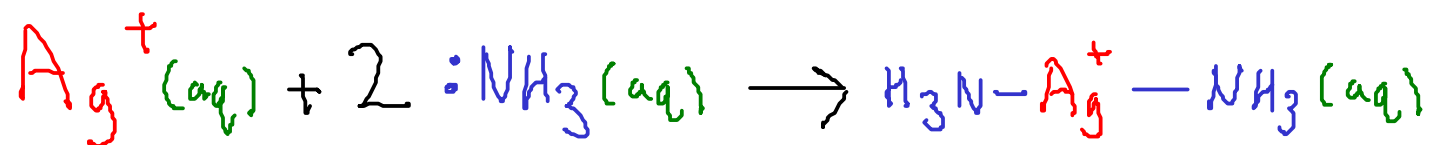
If a compound is BASIC, then it will be LESS SOLUBLE in basic solutions, and MORE SOLUBLE in acidic solutions!

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

COMPLEX IONS

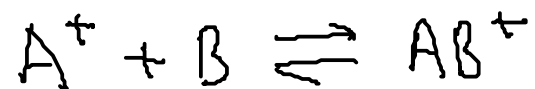
- are ions that result from the reaction of a Lewis base (like water, ammonia, hydroxide ion, etc.) with a metal ion
- The Lewis base attaches to the metal ion by forming a COORDINATE COVALENT BOND with the metal ion.



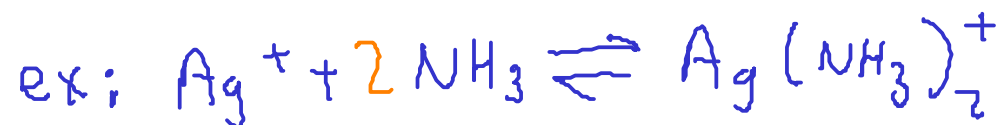
- The product of the reaction is called a "COMPLEX", and the attached Lewis bases are called "LIGANDS"

COMPLEX ION EQUILIBRIUM

- Described by the FORMATION CONSTANT, K_f



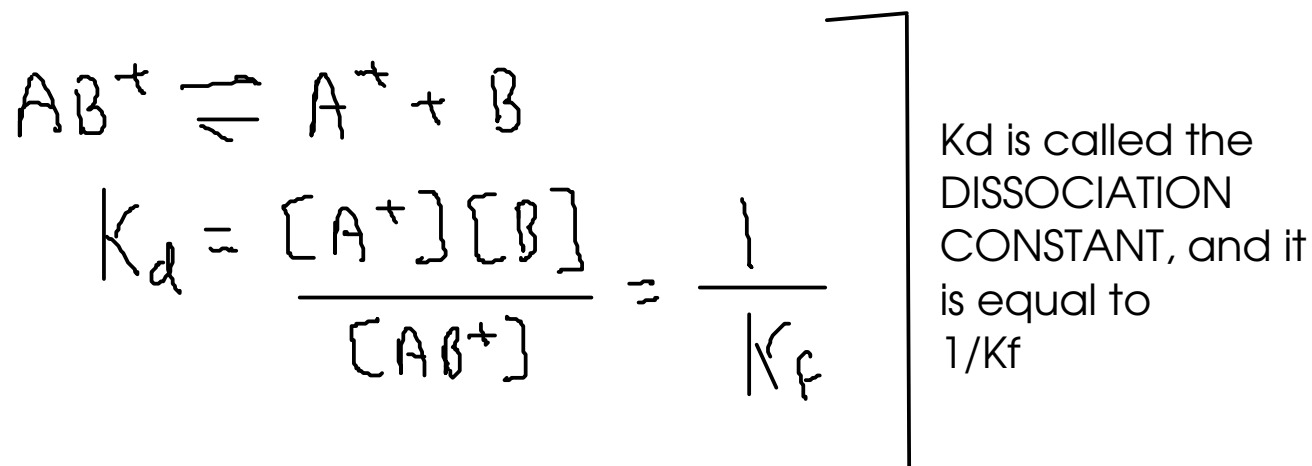
$$K_f = \frac{[AB^+]}{[A^+][B]}$$



$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7$$

What does this value for the equilibrium constant say about the favorability of the formation of the complex ion?

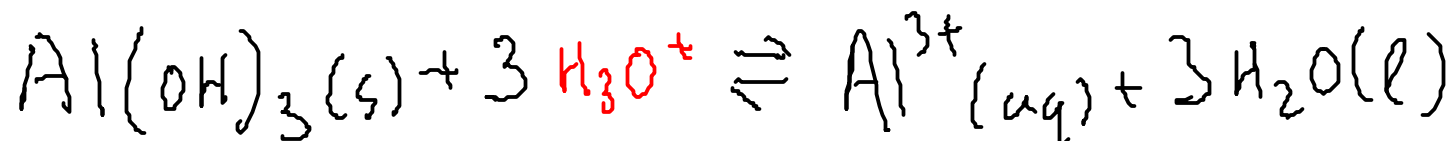
Since the formation of these complex ions is so favorable, we often assume that these reactions go to completion, and instead look at the small amount of complex ion that DISSOCIATES!



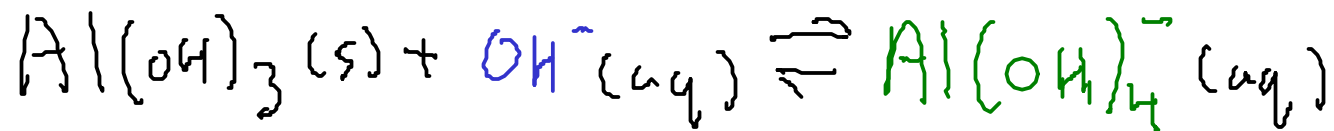
$$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{1}{1.7 \times 10^7} = 5.9 \times 10^{-8}$$

AMPHOTERIC COMPOUNDS

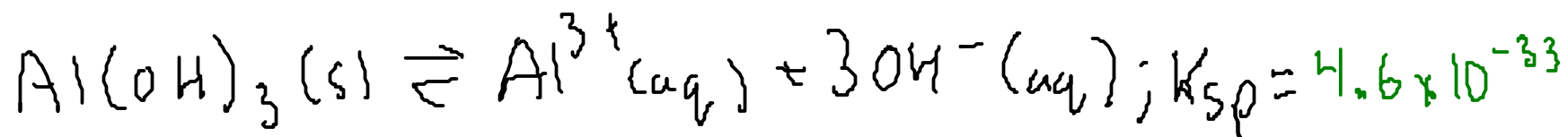
- All metal hydroxides react with ACIDS, but SOME metal hydroxides can react with BASES by forming a complex ion.



... Aluminum hydroxide is soluble in acidic solutions.



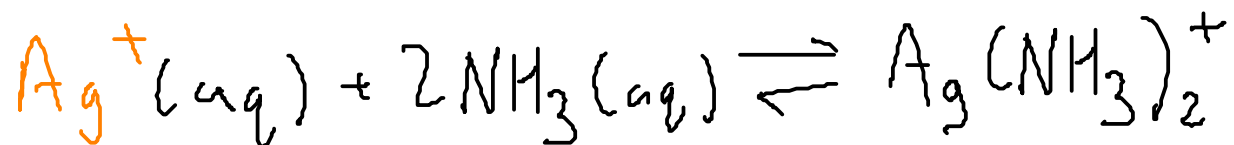
... And it is also soluble in bases due to the formation of this complex ion!



- So aluminum hydroxide is relatively insoluble in pure water, but its solubility increases greatly if the pH goes either up or down.

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!