Calculate $[Ag^+]$ at equilibrium when concentrated ammonia, $NH_3$, is added to $0.010 \, M \, AgNO_3$ to give $[NH_3]_{equl} = 0.20 \, M$. $AgNO_3$ dissociates completely. Neglect the volume change.

Assume $AgNO_3$ dissociates 100% (it is a strong electrolyte) and all the $Ag^+$ forms the complex ion.

$AgNO_3(aq) \rightarrow Ag^+(aq) + NO_3^-(aq)$

$$Ag^+(aq) + 2 \, NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

Initial:
- $0.010$
- $0.22$
- $0$

Reaction:
- $-0.010$
- $-0.020$
- $+0.010$

New Initial:
- $0$
- $0.20$
- $0.010$

Change:
- $+x$
- $+2x$
- $-x$

Equilibrium:
- $x$
- $0.20 + 2x$
- $(0.010 - x)$

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

$$1.7 \times 10^7 = \frac{(0.010-x)}{(x)(0.20 + 2x)^2}$$

$$1.7 \times 10^7 = \frac{(0.010)}{(x)(0.20)^2}$$

$x = \frac{(0.010)}{(1.7 \times 10^7)(0.040)}$

$x = 1.47 \times 10^{-8} \, M$ $[Ag^+]$ at equilibrium, free $[Ag^+]$

Proof that you can ignore the $x$ above:

$0.20 + 2x = 0.20 + 2(1.5 \times 10^{-8}) = 0.20 + 3.0 \times 10^{-8}$

$0.20 + 0.0000000030$ Significant figure (SF) rule for addition

$0.2000000030$ limits you to the places after the decimal (2SF)

This method is used to calculate the free ion.
This method is used to calculate the molar solubility of a slightly soluble salt in the presence of a given amount of ligand.

- What is the molar solubility of AgCl in 15 M NH₃?
  
  As above, Ag⁺ is involved in both the solubility equilibrium and complex ion formation.

  When you add chemical equations, you multiply the Ks.

  \[ K = K_{sp}K_f = (1.8 \times 10^{-10})(1.6 \times 10^7) = 2.9 \times 10^{-3} \]

  \[
  \begin{align*}
  \text{AgCl(s)} & \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \\
  \text{Ag}^+(aq) + 2 \text{NH}_3(aq) & \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) \\
  \text{AgCl(s)} + 2 \text{NH}_3(aq) & \rightleftharpoons \text{Ag(NH}_3)_2^+(aq) + \text{Cl}^-(aq)
  \end{align*}
  \]

  \[
  \begin{array}{c|c|c|c|c|c}
  \text{Initial} & & & & & \\
  \hline
  \text{AgCl} & 15 & & & 0 & 0 \\
  \text{NH}_3 & & 0 & & & \\
  \hline
  \text{Change} & -x & 2x & +x & +x & \\
  \text{AgCl} & (15-2x) & x & x & x & \\
  \hline
  \text{K} = \frac{[\text{Ag(NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = \left(2.9 \times 10^{-3}\right)\left(\frac{x^2}{(15-2x)^2}\right) = \frac{0.054}{(15-2x)} \\
  \end{array}
  \]

  \[ x = 0.73 \text{ M} \]

- The molar solubility of AgCl in water is \(1.3 \times 10^{-5}\)
- Note how the solubility increases to 0.73 M
- Decreasing the concentration of free metal ion in solution by complexing it with a ligand will increase the solubility of the insoluble salt.

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)
\]

\[
K_{sp} = 8 \times 10^{-17}
\]

\[1.8 \times 10^{-10} = (x)(x)\]

\[x = 1.3 \times 10^{-5} \text{ M}\]

Note:

- AgCl in H₂O \(\Rightarrow 1.3 \times 10^{-5} \text{ M}\)
- AgCl in 15 M NH₃ \(\Rightarrow 0.73 \text{ M}\)
- Quite an increase!