15.5 Silver Salt Equilibrium and LeChatlier's principle

Subject: Solubility-K_{sp}, precipitation reactions, complex ions, Le Chatlier's principle

Description: A precipitate of silver chloride is dissolved upon addition of a clear liquid. Adding a second clear liquid produces a precipitate again.

Materials:
200 mL water
500 mL beaker
10 mL 0.1 M silver nitrate‡
30 mL 1.0 M sodium chloride‡
35 mL 6.0 M aqueous Ammonia‡
Acetic acid
Stir bar
Stir plate*
2 graduated cylinders (1 50 ml, 1 10 ml)

‡Solutions are located on the solutions shelves. Ammonia and acetic acid are located in the cabinets under the hood.

*Shared item: located in the top drawer of the central bench opposite the chemical storage cabinets or on the center bench.

Pre-class preparation:
1. Prepare the silver chloride precipitate. Place 200 mL of water in a 600 mL beaker. Add 10 mL 0.1 M silver nitrate and 30 mL 1.0 sodium chloride to the beaker to form the precipitate.

Procedure:
1. Add the ammonia to dissolve the silver chloride and produce the soluble silver ammonia complex ion.
2. Have the students predict what will happen upon addition of the acetic acid. Add the acetic acid.

Discussion:
Step 1 (pre-class step): Addition of sodium chloride to the silver nitrate solution forms a precipitate of silver chloride.

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

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

$$AgCl(s) \Leftrightarrow Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.8 \times 10^{-10}$$

Step 2: When aqueous ammonia is added the silver chloride precipitate dissolves in favor of formation of the silver ammonia complex ion.

$$Ag^+(aq) + 2NH_3(aq) \Leftrightarrow [Ag(NH_3)_2^+] (aq) \qquad K_f = 1.6 \times 10^7$$

Net reaction: $AgCl(s) + 2NH_3(aq) \Leftrightarrow [Ag(NH_3)_2^+] (aq) + Cl^-(aq)$

$$K_{net} = K_{sp} \times K_f = (1.8 \times 10^{-10})(1.6 \times 10^7) = 2.9 \times 10^{-3}$$

$$K_{net} = 2.9 \times 10^{-3} = \{[Ag(NH_3)_2^+](Cl^-)\}/ [NH_3]^2$$

Using a large concentration of NH_3 will produce a large concentration of the complex ion in solution and thus the solubility of silver chloride is much higher in an aqueous ammonia solution than in water.

Step 3: Acetic acid is added pushing the reaction back towards the reactant, silver chloride, reforming the precipitate.

$$[Ag(NH_3)_2]^+(aq) + Cl^- + 2CH_3CO_2H(aq) \Leftrightarrow AgCl(s) + 2CH_3CO_2NH_4(aq)$$

LeChatlier's principle states that a system will change to reduce or counteract the effects of a change to the equilibrium conditions. In this case, acetic was added to the solution, disturbing the equilibrium of silver chloride and ammonia. The acetate ions react with the ammonia ions to produce ammonium acetate, increasing the silver ion concentration, leading to a common ion effect. Taking the ammonia and acetic acid out of the equation produces the original equation for the dissociation of silver chloride. The increase in silver ion product concentration pushes the reaction to the left, creating more insoluble silver chloride.

$$AgCl(s) \Leftrightarrow Ag^+(aq) + Cl^-(aq)$$

Safety: Silver nitrate and its solutions and concentrated ammonia solutions can be irritating to the skin and can cause burns. Use proper protective equipment, including gloves and glasses when performing these experiments

Disposal: Dispose of solution in an appropriate aqueous waste container.

References:

1. B.Z. Shakhashiri; *Chemical Demonstrations: A Handbook for Teachers of Chemistry*; Volume 1; Wisconsin; 1983; p. 307-313 (variation)
2. Kotz, Treichel, Townsend. *Chemistry & Chemical Reactivity, 7th* Ed ;Teachers Ed; Brooks/Cole; 2009
3. L. Summerlin, C. Borgford, J. Ealy; *Chemical Demonstrations: A Sourcebook for Teachers*; Volume 2; 1987; p. 80 (simpler version producing AgCl and $[Ag(NH_3)_2]^+$ only)

4. Prof. Fermann – acetic acid variation