Solubility Products Involving Silver Compounds

The work at the Colloidal Science Laboratory has certainly engendered world-wide comments. It is the purpose of this document to present our data and to restate what we believe is known from good scientific principles.

1. Silver metal is **insoluble** in water. This is well known and has been confirmed in our laboratory. Therefore, the only way silver can get into solution is in the form of ions. In a solution, when silver loses a $5s^1$ electron to form Ag^+, a corresponding anion must exist to maintain electrical neutrality. One of the comments we received indicated that the hydroxyl concentration in neutral water being 10^{-7} M, (moles/L), should allow silver ions to exist at a concentration of 0.15 M, due to the solubility product constant of AgOH. ($K_{sp} = 1.52$ x 10^{-8} for AgOH) This would be true by calculation, **if silver were water soluble**. (Refer back to line one of this paragraph.) If this were true, simply placing silver metal in neutral water would provide 16.42g/L of silver ions, or 16,420 ppm! This clearly **does not** happen! Silver nitrate, which has a very high solubility of 122 g/ 100 ml of water can contain 16000 ppm of silver ions in a **nitrate** environment, but this is not the case for insoluble silver metal.

       The 13.3 ppm value which was previously mentioned was for the specific case of silver hydroxide. The method by which one calculates the solubility of a weak electrolyte or a compound of low solubility is to **start with the compound** and let it dissociate in water, (see any good basic chemistry text, such as Petrucci & Harwood, {1}) as in the following calculation:

$$AgOH \rightleftarrows Ag^+ + OH^-$$
$$K_{sp} = 1.52 \text{ x } 10^{-8} = [Ag^+] \, [OH^-]$$

Since there is one Ag for every OH in the compound,

$$1.52 \text{ x } 10^{-8} = X^2, \therefore \ X = 1.23 \text{ x } 10^{-4} \text{ M}$$
$$(1.23 \text{ x } 10^{-4} \text{ M})(108g/mole) = 1.33 \text{ x } 10^{-2} \text{ g of Ag/L} = 13.3 \text{ ppm.}$$

2. Example of Solubility Product Calculation:

       Consider the solubility of Ag_2CO_3. The solubility equation is:

$$Ag_2CO_3 \rightleftarrows 2 \ Ag^+ + CO_3^{-2}$$

The solubility product is $K_{sp} = 6.15$ x $10^{-12} = [Ag^+]^2[CO_3^{-2}]$

Since there are two moles of Ag^+ for every mole of CO_3^{-2}, this becomes

$$6.15 \text{ x } 10^{-12} = [2x]^2[x] = 4 \ x^3$$
$$\text{or } 2x = Ag^+ = 2.3 \text{ x } 10^{-4} \text{ M}$$
$$x = CO_3^{-2} = 1.15 \text{ x } 10^{-4} \text{ M}$$

This means that Ag^+ can exist in a carbonate environment at a concentration of 2.3 x 10^{-4} M, or 24.8 ppm, **if** the carbonate concentration is 1.15 x 10^{-4} M or less.

3. With regard to the amount of silver ion allowed to exist in water due to carbon dioxide dissolving in water, the situation is complicated by the carbonic acid equilibrium:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows 2H^+ + CO_3^{-2}$$

The maximum solubility of CO_2 in water is 1.45 g /L at 25 °C and 1 atm., or 0.033 M. Given the acid dissociation constant for carbonic acid as 4.31 x 10^{-7}, one would expect CO_3^{-2} to have a maximum concentration of 2.16 x 10^{-5} M, which is clearly less than the

1.15 x 10^{-4} M value given above. According to Cotton & Wilkinson {2}, however, the published acid dissociation constant leads to erroneous results, due to the fact that the greater part of the CO_2 is only loosely hydrated, so that a better value to use is $K_{sp} = 2$ x 10^{-4}, which reflects the "true" activity of carbonic acid. Using this value, one calculates that the carbonate concentration should be 2.57 x 10^{-3} M, which would make the maximum allowable silver ion concentration 4.89 x 10^{-5} M, or 5.28 ppm from the above K_{sp} for silver carbonate.

4. Precipitation of Ag^+ ions in the presence of both hydroxide and carbonate:

　　　　This, of course, depends on the concentrations of both anions, but for illustrative purposes, let us assume the case in which $[OH^-] = [CO_3^{-2}] = 10^{-5}$ M, and silver ions, as $AgNO_3$ is added slowly to the mixture.

1. To precipitate AgOH :

$$[Ag^+] = \frac{1.52 \times 10^{-8}}{10^{-5}} = 1.52 \times 10^{-3} \text{ M}$$

2. To precipitate Ag_2CO_3 :

$$[Ag^+]^2 = \frac{6.15 \times 10^{-12}}{10^{-5}} \quad ? \quad [Ag^+] = 7.84 \times 10^{-4} \text{ M}$$

In other words, for slowly added $AgNO_3$, Ag_2CO_3 will start to precipitate when the silver ion concentration reaches 7.84 x 10^{-4} M, but AgOH will not start to precipitate until the silver ion concentration is at 1.52 x 10^{-3} M. Other examples can be worked out by the reader, using this calculation as a model.

{1} Petrucci & Harwood, "General Chemistry", 7th edition, chapter 19, Prentice Hall, (1997)

{2}Cotton & Wilkinson, " Advanced Inorganic Chemistry", p. 227, John Wiley & Sons, (1962)