Chem 321 Lecture 7 - Gravimetric Analysis

9/17/13

Student Learning Objectives

Your first unknown in lab will be a sample that contains chloride ion. You will analyze this sample by dissolving it in water and quantitatively precipitating the chloride as AgCl.

$$Cl^-(aq) \quad + \quad Ag^+(aq) \;\overset{K}{\rightleftharpoons}\; AgCl(s)$$

Recall that for this reaction, $K = 1/K_{sp} = 1/\,(1.8 \times 10^{-10}) = 5.6 \times 10^{9}$. This means that the precipitation strongly favors the product (i.e., AgCl is not very soluble) and, in principle, it should be possible to quantitatively recover the chloride this way. The solubility of the AgCl is reduced further by adding an excess of Ag^+ to the solution containing the dissolved chloride. The AgCl precipitate will be recovered, dried and weighed. From the mass of AgCl it is possible to calculate the amount of chloride in your sample and finally the mass percent chloride in your unknown. This is an example of what is known as **gravimetric analysis**. The basic measurement that you make in this experiment is that of mass. Since the mass measurements will typically have less than 1 ppth error associated with them (for example, 0.5491 ± 0.0001 g), the mass percent results can be quite accurate. Care must be taken, however, in the forming, collecting and drying of the precipitate.

Slightly soluble salt equilibria (review)

The solubility of ionic compounds that dissolve only slightly in water can be estimated by considering the chemical equilibrium established between the compound and its constituent ions in solution. A table of initial and equilibrium concentrations is created and those values at equilibrium are substituted in the reaction quotient and set equal to K_{sp}. For AgCl this is done as follows.

	$AgCl(s)$	$\rightleftharpoons$	$Ag^+(aq)$	$+$	$Cl^-(aq)$
init			0		0
equil			x		x

where x equals the increase in the $[Ag^+]$ as a result of the dissolving process. Note that no concentration information for AgCl(s) is needed because solids never appear in reaction quotients. Substituting into the reaction quotient and setting it equal to K_{sp} gives

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

The solution of this simple quadratic equation is $x = 1.3_4 \times 10^{-5}$ M. Since all of the Ag^+ is coming from the dissolution of the salt, this equilibrium concentration also represents the solubility of AgCl.

Note this approach to the calculation of solubility ignores other possible reactions such as the hydrolysis of the product ions or the formation of **ion pairs**. An ion pair is a closely associated pair of ions, such as AgCl(aq), that behaves as one species in solution. Salts containing only +1 and -1 ions generally dissociate almost completely.

In the above example, if either Ag^+ or Cl^- is added to this solution at equilibrium, **Le Chatelier's principle** indicates that the reverse reaction will occur to restore equilibrium. That is, less salt will dissolve. This is known as the **common ion effect**: the solubility of a salt will be decreased if one of its constituent ions is present in solution. In such a case the initial concentration of this ion will not be zero and this initial concentration will usually be a much more significant source of this ion than that coming from the dissolution of a slightly soluble salt.

Check for Understanding 4.1 Solutions

1. Calculate the solubility of AgCl in a solution containing $[Ag^+] = 0.0060$ M.
2. What mass of AgCl is unprecipitated in 200. mL of a solution with an excess $[Ag^+] = 0.0060$ M?

Precipitate formation

The precipitate formed in a gravimetric analysis should have not only a low solubility, but also form large, easily filtered particles, be pure and be stable (so that it can be dried easily). The particle size that is produced in a precipitation reaction depends on the chemical composition of the precipitate and the conditions at the time of its formation. Precipitate formation occurs by two processes: **nucleation** and **particle growth**. Nucleation involves some minimum number of particles coming together to form a stable solid phase. Particle growth is the deposition of additional particles on these aggregates. If nucleation predominates a large number of very fine particles results. If particle growth predominates, a smaller number of larger particles is obtained. Experimentally it is found that nucleation occurs more rapidly than particle growth when the solution has a large **relative supersaturation** - a measure of how much extra solute is present in solution compared to that expected at equilibrium. The relative supersaturation can be evaluated by

$$\textit{relative supersaturation} = \frac{Q - S}{S}$$

where Q is the solute concentration in solution at any instant and S is the equilibrium solubility of the precipitate. A large relative supersaturation often results in the formation of a colloid, a suspension of particles 1-100 nm in size, that does not settle and is not retained in common filtering. Consequently, to promote the formation of large precipitate particles, one wants to reduce the relative supersaturation (decrease Q, increase S).

<u>Ways to reduce the relative supersaturation (and promote large particle size)</u>

- precipitate from dilute solution (lowers Q)
- add precipitating agent slowly with stirring (lowers average value of Q)
- precipitate from hot solution (increases S)
- adjust solvent; for example, make the solution acidic (to increase S)

Check for Understanding 4.2 **Solution**

1. Does the presence of HNO_3 in the sample solution increase the solubility of the AgCl precipitate? Explain.

Note that in the gravimetric chloride experiment a relatively large volume of water is used to dissolve the unknown sample (lowers Q) and the $AgNO_3$ solution used as a source of silver ion is diluted to 0.2 M before slowly adding it to the dissolved sample (lowers Q).

Despite these efforts to promote the formation of large particles, a colloidal suspension of AgCl forms. These colloidal particles must coagulate in order to recover the precipitate by filtering.

Ways to hasten aggregation of colloidal particles

- heat and stir the solution
- add an electrolyte to the precipitation solution

The individual particles in a typical colloidal suspension bear either a positive or negative charge due to **adsorption** of cations or anions on the surface. For an ionic solid, the ions on the particle surface have a partially unsatisfied bonding capacity by virtue of their surface location so they attract ions in the neighboring solution and chemical bond them. Empirically it is observed that lattice ions are more strongly adsorbed on the particle surface. Thus, in a solution with excess Ag^+, the colloidal AgCl particles are positively charged. This charged surface electrostatically attracts oppositely-charged ions in the surrounding solution, forming an **electric double layer** (see Fig. 4.1). This double layer will exert repulsive forces toward similar particles, thus preventing coagulation of the colloid.

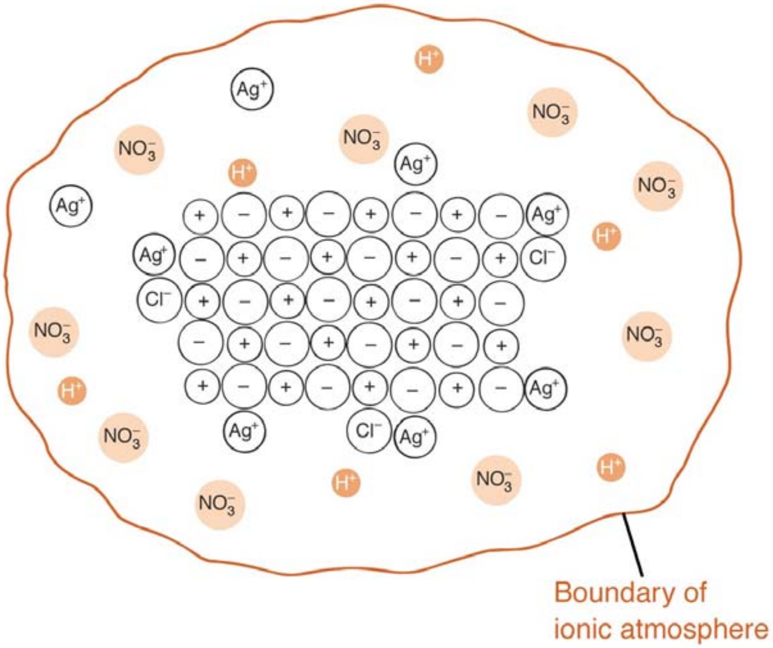

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Figure 4.1 A colloidal particle of AgCl in a solution containing excess Ag^+, H^+ and NO_3^-.

Aggregation of the colloidal particles requires a reduction in the repulsive force of the double layer. Heating and stirring lead to a net decrease of adsorbed ions and increase the kinetic energy of the particles so they approach more closely. The addition of an electrolyte reduces the volume of solution needed to contain enough ions to neutralize the charge of the adsorbed ions, thus shrinking the double layer and allowing closer approach of the particles. In the chloride analysis, the addition of HNO_3 to the sample solution prior to precipitation is done, in part, to provide this electrolyte. HNO_3 is a good choice for the electrolyte because it makes the precipitation solution acidic, which prevents competing precipitation reactions involving Ag^+ which might otherwise occur in a basic solution.

The particle size of the coagulated colloid can be further increased by a process called **digestion**. In this context, digestion refers to letting the precipitate stand in its "mother liquor" (the solution in which it is formed), usually at elevated temperatures. The smaller precipitate particles tend to dissolve faster than large ones and re-precipitate onto larger particles. This relatively slow dissolution/re-precipitation process also tends to remove foreign ions that have been trapped inside rapidly growing precipitate particles. Letting the AgCl precipitate stand at room temperature between lab periods will generally result in a complete settling of the AgCl and a clearing of the **supernatant** (the liquid above the precipitate).

Co-precipitation occurs when normally soluble substances are carried down during precipitation. One type of co-precipitation involves the adsorption of ions on the precipitate particle surface. This can be a serious problem for colloidal precipitates because of the large surface area of colloidal particles. This effect can be used analytically to recover an ion in solution that is present at too low a concentration to allow for its direct precipitation.

In the gravimetric analysis of chloride experiment, the AgCl precipitate must be quantitatively recovered and then washed to remove excess Ag^+. Washing the precipitate with pure water can result in **peptization** of the precipitate - the breakup of the coagulated colloid into colloidal particles. This occurs as the electric double layer increases as electrolyte is washed from the precipitate. Peptization is minimized by washing with a solution containing a volatile electrolyte. HNO_3 is added to the wash solution for this reason.

Check for Understanding 4.3

Solution

1. What mass (in g) of AgCl is lost when this precipitate is washed with 60.0 mL of water? Assume equilibration between the solid and the dissolved form. How many ppth error does this introduce? Assume a sample size of 0.25 g that is 50% chloride by mass.

The gravimetric method is one of the most accurate methods of analysis. It is usually applied when the analyte concentration exceeds 1%. One distinct advantage is that no standard is required. However, precipitations may not be very specific (you may get group precipitations), although organic precipitating agents tend to be more specific (e.g., dimethylglyoxime selectively precipitates Ni^{2+}).

Exercises for Gravimetric Analysis