Gravimetric analysis (Sec 27-1 and 27-2)

- To describe various techniques in gravimetric analysis to avoid over- or under-estimation of analyte concentration in gravimetric analysis (Do Exercise 27-1, -2, -5, -6, -7)
- To perform gravimetric calculations (Do Exercise 27-20)

Thermogravimetric analysis (TGA) (Sec 27-2)

To determine the composition of a substance by TGA. (Do Exercise 27-21)

Gravimetric analysis

Quantitative determination of an analyte conc. by weighing a product.

$$AgNO_3 + Cl^- \xrightarrow{H^+} AgCl\downarrow + NO_3^-$$

Precipitation occurs when the ionic product $[Ag^+][Cl^-]$ excess the solubility product $K_{sp}(AgCl)$.

Example in Sec. 27-1: A 10.0 mL solution containing Cl^- was treated with excess $AgNO_3$ to precipitate 0.4368 g of AgCl. What was the concentration of Cl^- in the unknown? (AgCl =143.321)

number of moles of Cl^- = number of moles of AgCl

$$= \frac{0.4368\ g}{143.321\ g/mol} = 3.048\times10^{-3}\ mol$$

Concentration of Cl^-

$$= \frac{3.048\times10^{-3}\ mol}{0.01000\ L} = 0.3048\ M$$

Techniques in gravimetric analysis

It is not so ideal in reality to have quantitative precipitation.

Adsorption: attachment of excess Ag^+ ions on AgCl, and excess NO_3^- around Ag^+, forming an ionic atmosphere.
So, tiny negatively charged AgCl particles (colloidal particles) repel each other.

Fig. 27-2 ionic atmosphere (Ag^+ and NO_3^- ions) around AgCl

Techniques in gravimetric analysis

- •Digestion(↓): Increase of temperature will raise the collision energy for colloidal particles to overcome Coulombic repulsion, leading to formation of larger particles (coalescence)
- •Use of electrolyte(↓): Coulombic repulsion is less in the presence of electrolyte because of a compression of the volume of the ionic atmosphere (e.g. AgCl precipitates in HNO_3)
- •Co-precipitation(↑): occurs when there are adsorbed or absorbed (included or occluded) impurities. Absorbed impurities: present within the bulk of the precipitate
  - •Inclusion: the impurities occupy the crystal lattice sites.
  - •Occlusion: the impurities (other ions or precipitates) are trapped inside the growing crystal
- •Re-precipitation: a procedure including washing away the mother liquor, redissolving the precipitate and precipitating the product again.
- •Peptization(↓): break up of the precipitate (AgCl) because of a loss of electrolyte (HNO_3) if the precipitate is washed by water.

(↑)over- estimation (↓)under-estimation

Thermogravimetric analysis (TGA)

A sample is heated, and its mass is measured as a function of temperature.

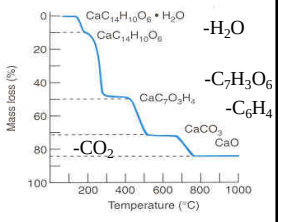

Figure 27-3 Thermogravimetric curve for calcium salicylate. [From G. Liptay, ed., *Atlas of Thermoanalytical Curves* (London: Heyden and Son, 1976).]

H_2O, $C_7H_3O_6$, C_6H_4, CO_2 are consecutively lost