

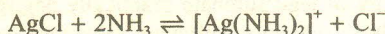
2 Solution reactions: fundamental theory

which has a value of $1.0 \times 10^{-21} \text{ mol}^2 \text{ L}^{-2}$ at the ordinary temperature. By inspection of this expression, and bearing in mind that excess cyanide ion is present, it is evident the silver ion concentration must be very small, so small in fact that the solubility product of silver cyanide is not exceeded.

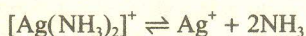
The inverse of equation (2.31) gives us the stability constant or formation constant of the complex ion

$$K = \frac{[\{\text{Ag}(\text{CN})_2\}^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 10^{21} \text{ mol}^{-2} \text{ L}^2 \quad (2.32)$$

Consider now a somewhat different type of complex ion formation, namely the production of a complex ion with constituents other than the common ion present in the solution. This is exemplified by the solubility of silver chloride in ammonia solution. The reaction is



Here again electrolysis, or treatment with hydrogen sulphide, shows that silver ions are present in solution. The dissociation of the complex ion is represented by



and the dissociation constant is given by

$$K_{\text{diss}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\{\text{Ag}(\text{NH}_3)_2\}^+]} = 6.8 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2}$$

The stability constant $K = 1/K_{\text{diss}} = 1.5 \times 10^7 \text{ mol}^{-2} \text{ L}^2$

The magnitude of the dissociation constant clearly shows that only a very small silver ion concentration is produced by the dissociation of the complex ion.

The stability of complex ions varies within very wide limits. It is quantitatively expressed by means of the **stability constant**. The more stable the complex, the greater the stability constant, i.e. the smaller the tendency of the complex ion to dissociate into its constituent ions. When the complex ion is very stable, e.g. the hexacyanoferrate(II) ion $[\text{Fe}(\text{CN})_6]^{4-}$, the ordinary ionic reactions of the components are not shown.

The application of complex ion formation in chemical separations depends upon the fact that one component may be transformed into a complex ion which no longer reacts with a given reagent, whereas another component does react. One example concerns the separation of cadmium and copper. Excess of potassium cyanide solution is added to the solution containing the two salts when the complex ions $(\text{Cd}(\text{CN})_4]^{2-}$ and $[\text{Cu}(\text{CN})_4]^{3-}$ are formed. Upon passing hydrogen sulphide into the solution containing excess of CN^- ions, a precipitate of cadmium sulphide is produced. Despite the higher solubility product of CdS ($1.4 \times 10^{-28} \text{ mol}^2 \text{ L}^{-2}$ as against $6.5 \times 10^{-45} \text{ mol}^2 \text{ L}^{-2}$ for copper(II) sulphide), the CdS is precipitated because the complex cyanocuprate(I) ion has a greater stability constant ($2 \times 10^{27} \text{ mol}^{-4} \text{ L}^4$ as compared with $7 \times 10^{10} \text{ mol}^{-4} \text{ L}^4$ for the cadmium complex).

2.22 Complexation

The processes of complex ion formation can be described by the general term **complexation**. A complexation reaction with a metal ion involves the replacement of one or more of the coordinated solvent molecules by other nucleophilic groups. The groups bound to the central ion are called ligands and in aqueous solution the reaction can be represented by the equation

