

Abstract

After a short introduction, a search for a suitable method of chloride analysis is described. A colourimetric procedure involving mercuric thiocyanate was chosen. This and a direct spectrometric method were used to determine the Arrhenius parameters for a number of chloropentamine reactions. For the hydroxide substitution reaction of the chloropentamine cobalt(III) ion, $A = 1.51 \times 10^{20}$ l.m.⁻¹sec.⁻¹, $\Delta S = 27.2$ Kcals/mole. For the hydroxide substitution reaction of the chloropentamine rhodium(III) ion, $A = 3.15 \times 10^{17}$ l.m.⁻¹sec.⁻¹, $\Delta S = 26.5$ Kcals/mole. For the aquation of the chloropentamine rhodium(III) ion, $A = 2.47 \times 10^{10}$ sec.⁻¹, $\Delta S = 24.1$ Kcals/mole. For the reaction of chloride with the aquopentamine rhodium(III) ion, $A = 1.59 \times 10^{16}$ l.m.⁻¹sec.⁻¹, $\Delta S = 28.3$ Kcals/mole. Equilibrium measurements were carried out on acidic solutions containing chloropentamine rhodium(III), aquopentamine rhodium(III), and chloride ions. The enthalpy and entropy changes for the aquation of the chloropentamine rhodium(III) ion found by this method were:

$\Delta H = -5.1$ Kcals/mole, $\Delta S = -29.6$ calg/deg.mole.

All kinetic and equilibrium measurements were extrapolated to zero concentration.

The first subject of discussion is the reliability of the results; the three following sections are on the primary salt effect, the role of the amine groups, and the magnitude of pre-exponential terms. The results from this work and those in the literature have been used to develop a theory of aquation and hydroxide substitution in which the free energy of anion hydration is prominent. In the equilibrium discussion a contribution has been made to a method of estimating entropy changes in the reactions of co-ordination compounds. The discussion of the reaction of chloride with aquopentamine rhodium(III) ion is made difficult by the lack of comparable results, and of the necessary water exchange and ion association data.