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EQUILIBRIA**

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Summary

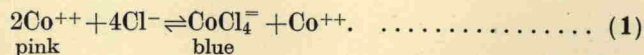
The effect of pressure on the formation of complex ions in solutions of cobaltous chloride and in solutions containing iodine and iodide has been shown to be in qualitative agreement with a theory (Buchanan and Hamann 1953) attributing these effects primarily to changes in the free energy of solvation of the ions. The dissociation constant of tri-iodide ions in water at 22 °C has been shown to decrease from 1.6×10^{-3} mol kg⁻¹ at atmospheric pressure to 1.2×10^{-3} mol kg⁻¹ at 1500 atm. The enthalpy of dissociation of the tri-iodide ion was found to be approximately -5 kcal mol⁻¹ and to be little affected by a pressure of 1500 atm.

I. INTRODUCTION

The effect of pressure on ionic equilibria has been the subject of several investigations in this laboratory (Buchanan and Hamann 1953; Hamann and Strauss 1955) and has been shown to be largely due to changes in the free energy of solvation of the ions. A very direct measure of this effect can be obtained by following colour changes induced by pressure in systems in which the participating ions absorb at characteristic wavelengths. This method has been used to investigate the formation of complex ions in a solution of cobaltous chloride in aqueous *isopropyl* alcohol and the formation of tri-iodide ions in a solution of iodine in aqueous potassium iodide. In the first of these systems the formation of the complex is accompanied by a decrease in the number of ionic charges, while this remains unchanged in the case of the iodine complex.

II. COBALTOUS CHLORIDE SOLUTIONS

Dilute aqueous solutions of cobaltous chloride are pink whereas concentrated aqueous solutions and solutions in organic solvents are blue. The nature of the ionic species causing the different colours has been widely discussed. The blue colour has been shown to be due to a complex anion and Sidgwick (1950) favours the theory of Donnan and Bassett that the equilibrium in a solution of cobaltous chloride is as shown in (1)



The absorption of the blue ion has been found to be many times stronger than that of the pink ion and the presence of very little of the blue complex ion can completely mask the pink colour of the solution. All the ions must be considered

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