

to be solvated and it is possible that they will be present as ion pairs in solvents of low dielectric constant. Some qualitative observations of the effect of pressure on the absorption spectrum of aqueous cobaltous chloride solutions have previously been reported by Wick (1923).

(a) Measurements

The optical densities of the solutions were observed on a Unicam S.P.500 spectrophotometer which was adapted to be used with a special high pressure absorption cell. This stainless steel cell* has windows constructed on the principle described by Poulter (1932) and has been used at pressures up to 1500 atm. The solutions were contained in cylindrical Pyrex tubes which were closed by "Neoprene" plugs and were immersed in the transparent paraffin oil which filled the steel cell and served as the pressure transmitting medium.

Solutions of cobaltous chloride in dry *isopropyl* alcohol were found to be deep blue and to obey Beer's law over a range of 36-fold dilution. This shows that the salt was present entirely in the blue form. The molecular absorption coefficient of cobaltous chloride in this solvent was found to be independent of pressure and is shown as a full line in Figure 1. When *isopropyl* alcohol containing 2.91 per cent. (by volume) of water was used as solvent it was found that the solutions were of a much paler blue and that Beer's law no longer applied to them. The points in Figure 1 show the specific absorption S of these solutions at various concentrations. ($S = D/cl$, D = optical density, c = molar concentration of CoCl_2 , l = length of absorption cell.)

The effect of pressure on one of the solutions in aqueous *isopropyl* alcohol ($0.00604 \text{ mol kg}^{-1} \text{ CoCl}_2$) is shown in Figure 2. The specific absorptions have been corrected for the increase in volume concentration due to the compression of the solution.†

The enthalpy of dissociation of the complex ion at atmospheric pressure was found to be $-4.6 \text{ kcal mol}^{-1}$ from the change of optical density of one of the solutions between 70°C and room temperature.

(b) Discussion

The effect of pressure on the solutions in aqueous *isopropyl* alcohol can be understood in terms of the change in the free energy of solvation accompanying the formation of the complex ion (Buchanan and Hamann 1953). Since this formation involves a decrease in the number of ionic charges there will be a decrease in the magnitude of the free energy of solvation. Pressure can be shown to favour an increase in the magnitude of the free energy of solvation and one would therefore expect the complex formation to be suppressed by pressure. Qualitatively this theory is therefore in agreement with the experimental results shown in Figure 2 which indicate that the concentration of the blue

* The authors wish to thank Mr. H. G. David of this laboratory for designing the high pressure equipment.

† The compressibility of aqueous *isopropyl* alcohol was measured in this laboratory by Mr. J. E. Stutchbury. At 1500 atm the correction amounted to 9 per cent.

complex decreases with pressure.* Unfortunately a quantitative test of the theory is not possible in this case since no equilibrium constant based on the simple equilibrium (1) could be found to fit the results. It is suggested that ion pair formation is superimposed on the equilibrium described by (1).

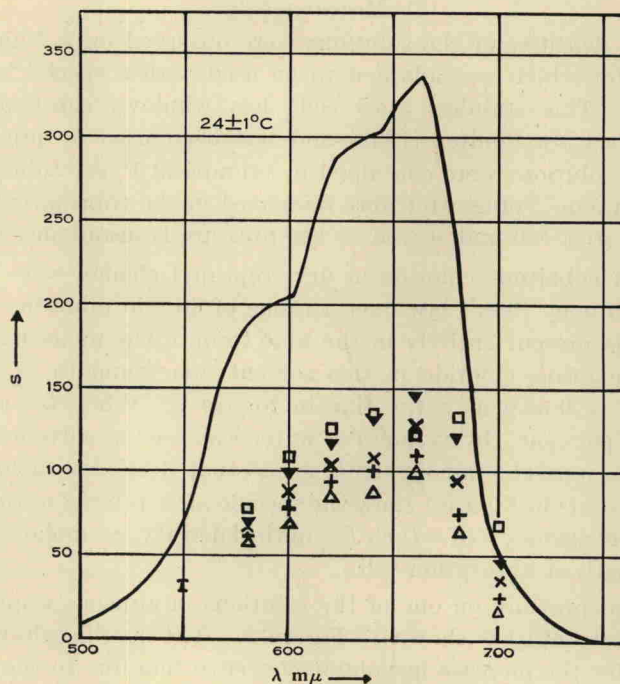


Fig. 1.—Absorption spectrum of CoCl_2 solutions.

Curve: molecular absorption coefficient of CoCl_2 in dry *i*-PrOH. The points denote specific absorption of solutions in *i*-PrOH + 2.91 per cent. H_2O . □ $62.24 \times 10^{-3} \text{ mol kg}^{-1} \text{ CoCl}_2$; ▼ $35.50 \times 10^{-3} \text{ mol kg}^{-1} \text{ CoCl}_2$; × $18.15 \times 10^{-3} \text{ mol kg}^{-1} \text{ CoCl}_2$; + $9.075 \times 10^{-3} \text{ mol kg}^{-1} \text{ CoCl}_2$; Δ $3.029 \times 10^{-3} \text{ mol kg}^{-1} \text{ CoCl}_2$. Temperature $24 \pm 1^\circ \text{C}$.

III. IODINE SOLUTIONS

The effect of pressure on the formation of tri-iodide ions in aqueous solutions containing both iodine and iodide is of interest not only in itself, but also in connexion with the study of the rates of reactions involving iodine.

* *Note added in Proof.*—Since this paper was submitted for publication we have observed that a 0.05 mol kg^{-1} solution of copper sulphate in 2.5 mol kg^{-1} aqueous hydrochloric acid shows colour changes with temperature and pressure similar to those of cobalt chloride solutions. At atmospheric pressure such a solution is blue-green at room temperature but becomes yellow on heating. On compressing to 1600 atm the absorption at $400 \text{ m}\mu$ decreases to about half of its value at 1 atm. It is suggested that this absorption in the blue region of the spectrum is due to the complex CuCl_4^{2-} ion which is in equilibrium with Cu^{++} and Cl^- ions. As in the case of the cobalt solutions the concentration of the complex ion is decreased by pressure.