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THE EFFECT OF PRESSURE ON COMPLEX ION EQUILIBRIA

By A. H. Ewald* and S. D. Hamann*

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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 $1\cdot6\times10^{-3}$ mol kg^{-1} at atmospheric pressure to $1\cdot2\times10^{-3}$ 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 *iso*propyl 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)

$$\underset{\text{pink}}{2\mathrm{Co}^{++}}+4\mathrm{Cl}^-\rightleftharpoons\underset{\text{blue}}{\mathrm{CoCl}_4^=}+\mathrm{Co}^{++}. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

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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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 *iso*propyl 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 *iso*propyl 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 *iso*propyl alcohol (0·00604 mol kg^{-1} $CoCl_2$) 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 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 *iso*propyl 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

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

† The compressibility of aqueous *iso*propyl 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**).

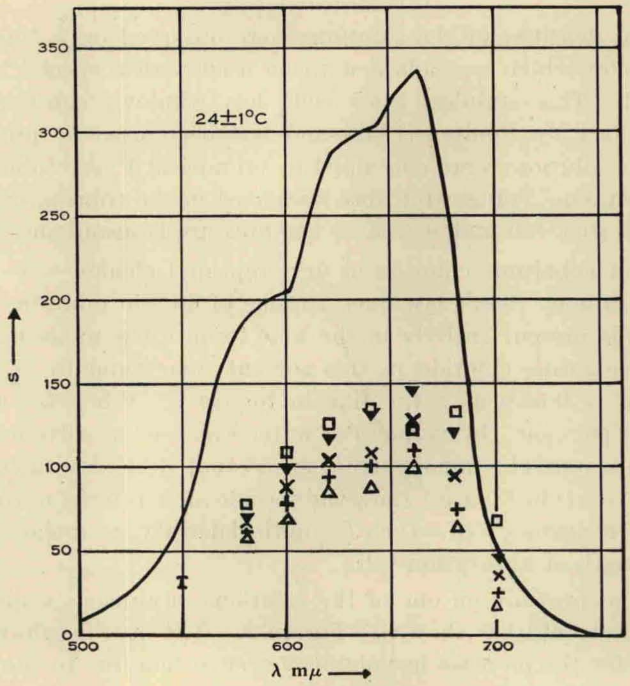

Fig. 1.—Absorption spectrum of $CoCl_2$ solutions.

Curve : molecular absorption coefficient of $CoCl_2$ in dry *i*-PrOH. The points denote specific absorption of solutions in *i*-PrOH$+2\cdot91$ per cent. H_2O. □ $62\cdot24\times10^{-3}$ mol kg^{-1} $CoCl_2$; ▼ $35\cdot50\times10^{-3}$ mol kg^{-1} $CoCl_2$; × $18\cdot15\times10^{-3}$ mol kg^{-1} $CoCl_2$; + $9\cdot075\times10^{-3}$ mol kg^{-1} $CoCl_2$; △ $3\cdot029\times10^{-3}$ mol kg^{-1} $CoCl_2$. Temperature 24 ± 1 °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.

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* *Note added in Proof.*—Since this paper was submitted for publication we have observed that a $0\cdot05$ mol kg^{-1} solution of copper sulphate in $2\cdot5$ 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 mμ 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 $CuCl_4^{--}$ 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.

Ham (1954) studied the effect of pressure on the complexes formed between iodine and some benzene homologues and found it to be not very large. The effect of temperature on the equilibrium (**2**)

$$I_3^- \rightleftharpoons I_2 + I^-, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{2})$$

in water-*tert.*-butyl alcohol was recently studied by Katzin and Gebert (1954) who rather surprisingly found the dissociation constant to decrease with a rise in temperature.

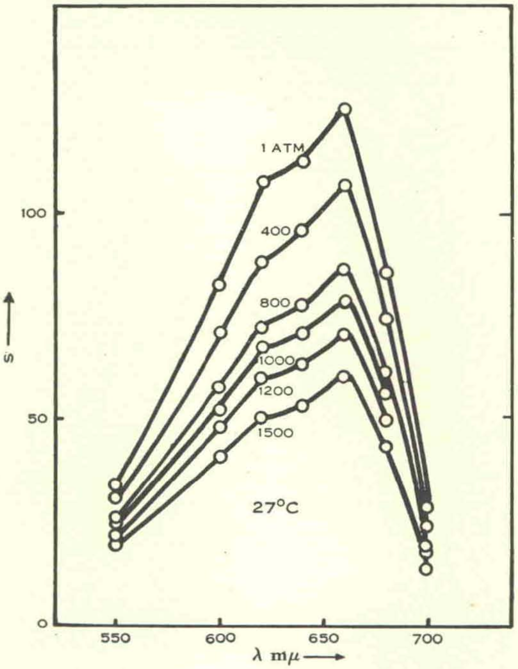

Fig. 2.—Effect of pressure on absorption spectrum of $CoCl_2$ solution at 27 °C $6 \cdot 04 \times 10^{-3}$ mol kg^{-1} $CoCl_2$ in *i*-PrOH+2·91% H_2O.

(*a*) *Measurements*

The apparatus used to investigate the iodine solutions was the same as that already described, except that a " Teflon " plug was used in the tube containing the iodine solution. The spectrum of the tri-iodide ions shows an absorption peak at 355 mμ, a wavelength at which neither iodine molecules nor iodide ions absorb appreciably, and it is therefore possible to measure the concentration of I_3^- spectrophotometrically (Awtrey and Connick 1951). The molecular absorption coefficient of I_3^- was determined in solutions containing a very large excess (10,000-fold) of iodide ions. These solutions were shown to obey Beer's law with reference to the iodine concentration, indicating that all the iodine was present as complex ions. The molecular absorption coefficient of the tri-iodide ion was found to be $2 \cdot 81 \times 10^4$ mol^{-1} l. cm^{-1} at 355 mμ and was found to be independent of temperature and pressure within the range and accuracy of the measurements.

Equilibria were measured in solutions containing between $0 \cdot 893 \times 10^{-4}$ and $2 \cdot 443 \times 10^{-4}$ mol kg^{-1} of iodine and between two and four times as much potassium iodide. The dissociation constants which were found at various pressures and have not been corrected for activity are shown in Figure 3. The results of measurements at various temperatures at 1 and at 1500 atm are shown in Figure 4.

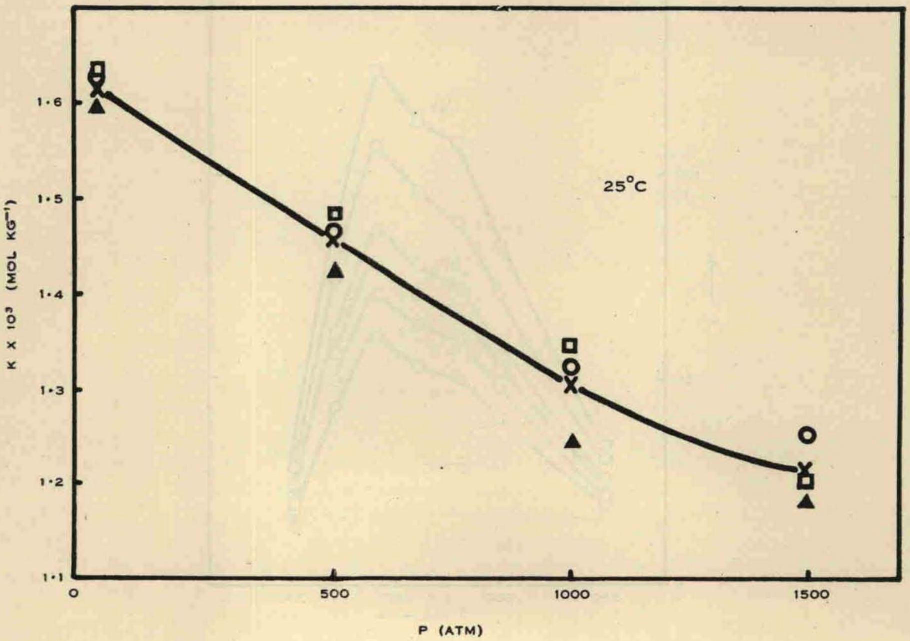

Fig. 3.—Effect of pressure on dissociation constant

$$K = \frac{[I_2][I^-]}{[I_3^-]} \text{ mol kg}^{-1} \text{ at } 25\ ^\circ\text{C}.$$

The points denote the following molal concentrations: □ $1 \cdot 218 \times 10^{-4}$ I_2($4 \cdot 816 \times 10^{-4}$ KI); ○ $2 \cdot 443 \times 10^{-4}$ ($4 \cdot 842 \times 10^{-4}$); ▲ $1 \cdot 218 \times 10^{-4}$ ($2 \cdot 414 \times 10^{-4}$); × mean values.

(*b*) *Discussion*

The results shown in Figure 4 indicate that the dissociation constant of the tri-iodide ion increases with temperature contrary to the findings of Katzin and Gebert. The slopes of the two curves show that the enthalpy of dissociation is approximately −5 kcal mol^{-1} and is little affected by a pressure of 1500 atmospheres.

The effect of pressure on the dissociation constant of the tri-iodide ion is small, amounting to a decrease of about 20 per cent. at 1000 atm. The change in partial molar volume accompanying the dissociation can be estimated from the slope of a plot of the logarithm of the dissociation constant against pressure and is found to be $+5\cdot4$ cm^3 mol^{-1}. It is interesting to compare this value with the volume change calculated on the basis of simple models of the ions involved in the dissociation. Using crystallographic data for the distances between iodine atoms in the iodine molecule (2·66Å) and the tri-iodide ion (2·95Å), and using ionic and van der Waals radii for the size of the ions (2·16Å) and atoms (1·77Å), one finds a volume change of $+4\cdot92$ cm^3 mol^{-1} for the dissociation.

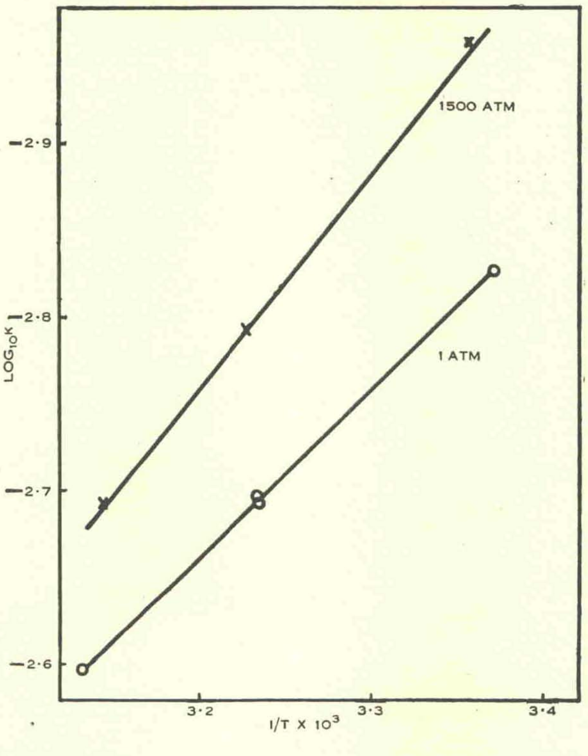

Fig. 4.—Effect of temperature on dissociation of tri-iodide ion.

It is thus apparent that most of the effect of pressure on the dissociation can be attributed to the change in the volume of the reacting species. The energy of solvation can therefore be only little affected by pressure, as would indeed be expected theoretically, since there is no change in the number of ionic charges in the dissociation.

IV. ACKNOWLEDGMENTS

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