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**)

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

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.

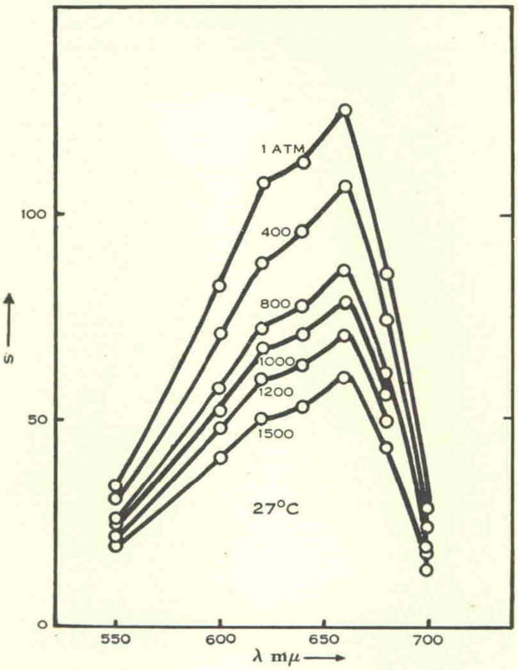

Fig. 2.—Effect of pressure on absorption spectrum of $CoCl_2$ solution at 27 °C $6{\cdot}04 \times 10^{-3}$ mol kg^{-1} $CoCl_2$ in *i*-PrOH+2·91% H_2O.

(*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.

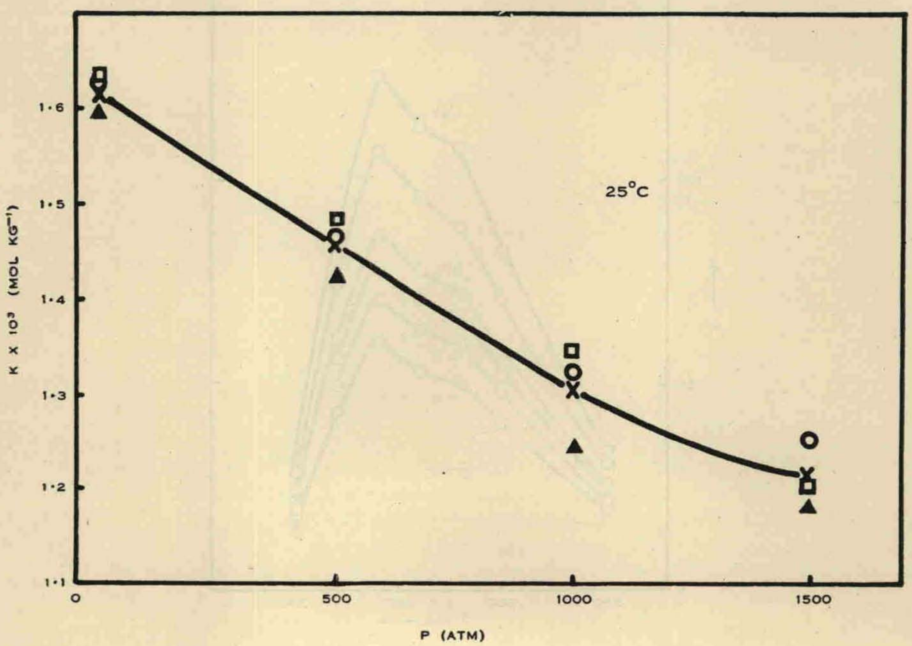

Fig. 3.—Effect of pressure on dissociation constant

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

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