

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 $+5.4 \text{ cm}^3 \text{ mol}^{-1}$. 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 (2.66 \AA) and the tri-iodide ion (2.95 \AA), and using ionic and van der Waals radii for the size of the ions (2.16 \AA) and atoms (1.77 \AA), one finds a volume change of $+4.92 \text{ cm}^3 \text{ mol}^{-1}$ for the dissociation.

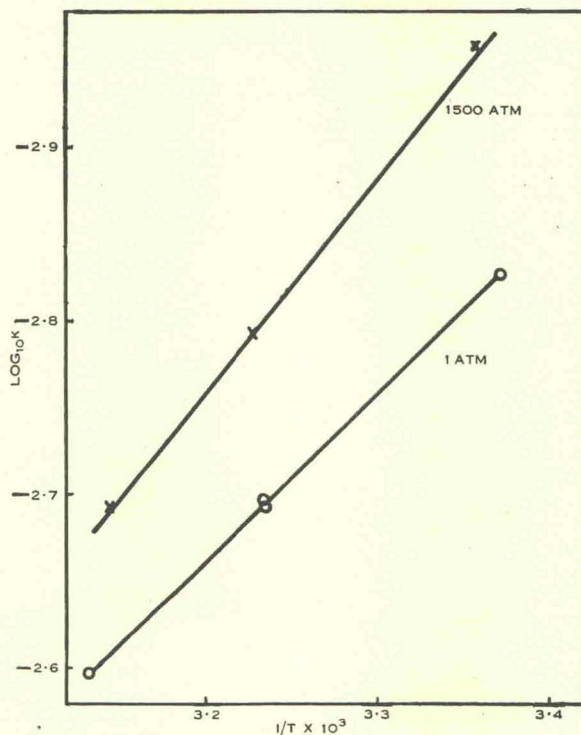


Fig. 4.—Effect of temperature on dissociation of tri-iodide ion.

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.

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V. REFERENCES

- AWTREY, A. D., and CONNICK, R. E. (1951).—*J. Amer. Chem. Soc.* **73** : 1842.
BUCHANAN, J., and HAMANN, S. D. (1953).—*Trans. Faraday Soc.* **49** : 1425.
HAM, J. (1954).—*J. Amer. Chem. Soc.* **76** : 3881.
HAMANN, S. D., and STRAUSS, W. (1955).—*Trans. Faraday Soc.* (in press).
KATZIN, L. I., and GEBERT, E. (1954).—*J. Amer. Chem. Soc.* **76** : 2049.
POULTER, T. C. (1932).—*Phys. Rev.* **40** : 860.
SIDGWICK, N. V. (1950).—"The Chemical Elements and their Compounds." Vol. 2, p. 1390.
(Oxford Univ. Press.)
WICK, F. G. (1923).—*Proc. Amer. Acad.* **58** : 555.

