

An X-Ray Study of Sulphuric and Orthophosphoric Acids

THE study of X-ray diffraction patterns of liquids is one of the least indirect means of obtaining information concerning their structure, but the amount of information is restricted by the limitations of the theory. The straightforward application of the original Debye theory¹ leads to an expression for the intensity of scattering

$$I = I_0 \frac{e^4}{m^2 c^4} \cdot \frac{P}{R^2} F^2 \left[1 + \int_0^\infty 4\pi r^2 [g(r) - \rho] \frac{\sin sr}{sr} dr \right] \quad (1)$$

where I_0 is the intensity of the incident beam, P is the polarization factor, R the distance from specimen to point of observation; $4\pi r^2 g(r) dr$ represents the number of atoms or molecules lying within radii r and $r + dr$; ρ is the mean density in atoms or molecules per c.c., e , m and c have their usual significance, and $s = 4\pi \sin \theta/\lambda$, where θ is half the scattering angle.

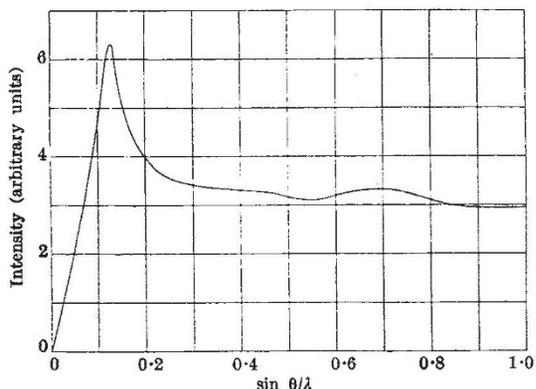


FIG. 1. Scattering of molybdenum $K\alpha$ radiation by orthophosphoric acid.

In the simple case of an atomic liquid, such as sodium, F^2 is identical with f^2 , the square of the atomic scattering power. By the use of Fourier inversion, it can be shown that:

$$4\pi r^2 g(r) = 4\pi r^2 \rho + \frac{2r}{\pi} \int_0^\infty s \varphi(s) \sin rs ds \quad (2)$$

where

$$\varphi(s) = \frac{(I/kP - f^2)}{f^2} \text{ and } k = \frac{I_0 e^4}{m^2 c^4} \cdot \frac{1}{R^2}$$

$\varphi(s)$ can be derived from a knowledge of f^2 and the experimental scattering curves, and it is therefore possible to obtain a Fourier analysis of the distribution of matter in the liquid^{2,3}.

For a molecular liquid

$$F^2 = \sum_p \sum_q f_p f_q \frac{\sin sr_{pq}}{sr_{pq}}$$

and a knowledge of the internal structure of the single molecule is necessary before (2) can be applied. $g(r)$ then gives the distance apart of molecular centres.

In the case of sulphuric and orthophosphoric acids, the rigid tetrahedral nature of the SO_4 and PO_4 groups is beyond question, and it was thought to be of interest to determine the arrangement of molecules in the liquids. (When f^2 becomes F^2 , $g(r)$ refers to molecules and not to atoms.) Strictly speaking,

orthophosphoric acid is a sticky solid, but a trace of water, about 1 per cent, is sufficient to turn it into a liquid.

The Fourier analysis is not yet complete, but it is clear that the scattering curves for the two liquids are almost identical, each having one main sharp diffraction band at an equivalent spacing of 3.85 Å. There are, however, minor differences between the curves at larger values of $\sin \theta/\lambda$. Fig. 1 shows the scattering curve for orthophosphoric acid, taken with molybdenum radiation, and corrected for lack of polarization in the incident beam.

Further studies of other acids and molecules of roughly spherical shape should be of interest. The theory takes no account of molecular rotation; in spherical molecules this effect should be of minor importance, and the Fourier analysis can be relied on to give a fairly accurate picture of the average distance apart of molecules in the liquid.

J. T. RANDALL.

Research Laboratories of the
General Electric Co., Ltd.,

Wembley.

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¹ Debye, *Ann. Phys.*, **46**, 809 (1915).

² Debye and Menke, *Phys. Z.*, **31**, 797 (1930).

³ Tarasov and Warren, *J. Chem. Phys.*, **4**, 236 (1936).

Specific Heat of a Liquid at Different Temperatures

It is possible to measure the specific heat of a liquid at a number of different temperatures by determining the power required to hold the temperature of a calorimeter and its contents stationary at different temperatures above that of the surroundings. The power is supplied electrically to a coil immersed in the liquid, and we have

$$-(Ms + W) d\theta/dt = E^2/RJ.$$

If a cooling curve is now taken, it can be shown that within the limits of experimental error,

$$-d\theta/dt = K\theta^n,$$

where n is nearly, but not exactly, equal to 5/4, K and n being determined by the use of a least-square or some equivalent method. We thus have

$$(Ms + W) K\theta^n = E^2/RJ,$$

giving the specific heat s in terms of the 20° calorie, if an experiment be performed with water at 20° C.

The method has proved to be surprisingly sensitive, and gives results which are reproducible with a very high degree of consistency. We have used the method to determine the specific heat of water over the range 15°–45° C., and, by the very great kindness of Imperial Chemical Industries Ltd., we were able to conduct an experiment with heavy water of 99.2 per cent purity over the same range. The sample of heavy water lent to us was 375 gm. in mass, and, although this is relatively a large quantity of a rare liquid, it is small compared with the quantity demanded by a continuous-flow experiment. The accompanying table gives results in terms of the 20° calorie:

Temp.	Water	Heavy water
15° C.	1.0010	1.009 ₆
20° C.	1.0000	1.007 ₆
25° C.	0.9991	1.005 ₆
30° C.	0.9986	1.004 ₆
35° C.	0.9984	1.003 ₆
40° C.	0.9984	1.003 ₆
45° C.	0.9986	1.003 ₆