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The Effect of Temperature on the Atomic Distribution in Liquid Sodium

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X-ray diffraction patterns of liquid sodium at eight temperatures ranging from 100°C to 400°C have been obtained with monochromatic Mo $K\alpha$ radiation. Fourier analyses of the 100°C and the 400°C intensity curves were made in order to obtain the atomic distribution functions. The distribution function at 400°C shows that at this temperature, the first concentration of atoms about any atom occurs at a distance of 3.90A and the second concentration of atoms occurs at about 7.2A. The peaks in this curve are broader, and the curve approaches the average density more rapidly, than in the 100°C case. For sodium at 100°C, the distance of closest approach of the atoms is 3.83A.

INTRODUCTION

THE atomic distribution functions for liquid mercury[1] and for liquid sodium[2] have been obtained for the liquids at one temperature, but no consistent attempt has been made to investigate the atomic distribution function in a liquid element at different temperatures. It is of interest to investigate this effect for the information it may give concerning interatomic forces or for the data it may supply in support of existing theories of the liquid state.

Analysis of x-ray diffraction patterns offers a direct means of obtaining the atomic distribution functions. In this method it is necessary to diffract monochromatic x-rays from the substance under investigation and obtain reliable values of the relative intensity *vs.* diffraction angle to as large values of the angle as possible. This relative intensity must be corrected for absorption in the sample, for polarization and for incoherent radiation. It is placed on an absolute basis in electron units by assuming that at sufficiently large angles of scattering so that interferences are completely washed out, the total radiation is the sum of the incoherent and the independent coherent radiations. From this fully corrected intensity curve in electron units, straightforward calculations on the basis of the theories of Zernike and Prins[3] and Debye and Menke[1] lead to the atomic distribution function Such analysis has been made not only in the case of liquids but also in the case of "amorphous" solids[4] and crystalline solids.[5]

A number of studies of the temperature effect upon the x-ray diffraction pattern of liquids have been made, but most of these studies have been made upon polyatomic liquids.[6] Liquid sulphur[7] has been investigated at a number of temperatures and some interesting conclusions were reached, but no determination of the atomic distribution function was made.

EXPERIMENTAL

In the present work, Mo $K\alpha$ radiation monochromatized by reflection from rocksalt was diffracted by liquid sodium contained in a very thin-walled Pyrex glass capillary of 2.8 mm diameter. Although the method described by Randall[8] for filling the capillary with sodium was first used, a simpler method was finally adopted. In this, freshly cut sodium was placed in one end of a glass tube with a series of about ten con-

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[1] Debye and Menke, Erg. d. Tech. Rontgenkunde, II.

[2] Tarasov and Warren, J. Chem. Phys. **4**, 236 (1937).

[3] Zernike and Prins, Zeits. f. Physik **41**, 184 (1927).

[4] Hultgren, Gingrich and Warren, J. Chem. Phys. **3**, 351 (1935).

[5] Warren and Gingrich, Phys. Rev. **46**, 368 (1934).

[6] Stewart and Morrow, Phys. Rev. **30**, 232 (1927). Zachariasen, J. Chem. Phys. **3**, 158 (1935). Harvey, Phys. Rev. **51**, 998 (1937). Katzoff, J. Chem. Phys. **2**, 841 (1934). Pierce, J. Chem. Phys. **3**, 252 (1935).

[7] Blatchford, Proc. Phys. Soc. London **45**, 493 (1933).

[8] Randall, *The Diffraction of X-Rays and Electrons by Amorphous Solids, Liquids and Gases.* (John Wiley & Sons, 1934) p. 129.

strictions and the capillary was sealed to the other end of the tube. After prolonged pumping and gentle heating, the sodium was melted and forced through the constrictions and into the capillary by means of helium at low pressure. This procedure in which the sodium has been subjected only to the removal of surface impurities has been justified in other work.[9] The sealed-off capillary filled with sodium and mounted in plaster of paris was encased in a heavy brass cylinder with entrance and exit holes for the x-rays. The brass cylinder was heated by means of a soldering iron element and the temperature of the capillary tube just above the point where the x-rays passed through was measured with a fine iron-advance thermocouple. The capillary was centralized in a cylindrical camera of 8.85 cm radius, which was measured mechanically and by a calibration run with rocksalt. The photographic film had suitable blackening after an exposure of 36 hours with the x-ray tube operated at 30 kv and 18 ma. Microphotometering the film and converting to intensities in the usual manner resulted in the experimental intensity curve.

APPLICATION OF THE FOURIER METHOD

In applying the Fourier method, it is necessary to have the experimental intensity on an absolute basis, in electron units, and this is obtained by using the fully corrected intensity curve at so large a value of sin θ/λ that all the radiation may be considered as independent. For this point, the ratio of coherent radiation to total radiation is calculated, the incoherent is subtracted from the total, and this serves to place the experimental curve on the same scale as the coherent, which is given in tables[10] in electron units per atom. The experimental intensity curve was corrected for absorption (practically negligible in this case), for polarization, and for incoherent radiation. Fully corrected intensity curves for sodium at 100°C and 400°C are shown in Fig. 1, together with a dashed curve representing the total independent scattering per atom (for the 400°C case only) and a dotted curve representing the incoherent scattering.

For a liquid element, the average density of surrounding atoms is given by the relation[5]

$$4\pi r^2\rho(r)=4\pi r^2\rho_0+(2r/\pi)\left(\int_0^\infty si(s)\sin rs\,ds\right), \quad (1)$$

where $4\pi r^2\rho(r)dr$ is the number of atoms between distances r and $r+dr$.

ρ_0 = average density of sample in atoms per unit volume.
$s=4\pi\sin\theta/\lambda$.
$i(s)=(I/N-f^2)/f^2$.
I/N = unmodified intensity per atom in electron units.
f = atomic scattering factor.

The product $si(s)$ is plotted against ks where k is a constant so chosen as to give convenient points in the final distribution curve. Curves of this type are shown in Fig. 2 for the 100°C and the 400°C cases. The integral of Eq. (1) was evaluated with the help of a Coradi analyzer,[11]

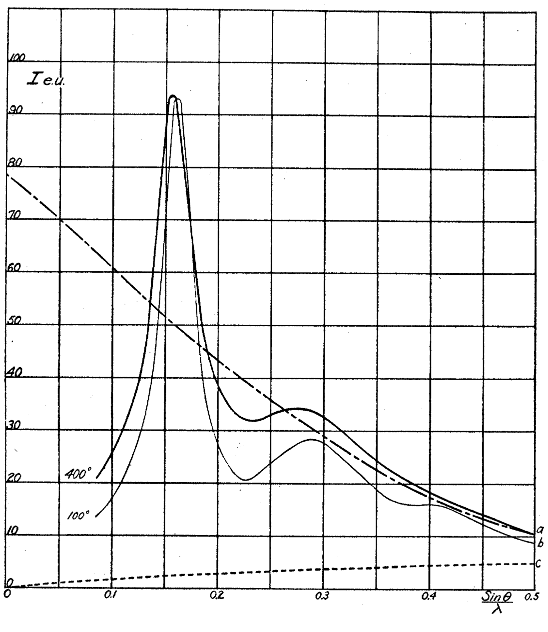

FIG. 1. Experimental intensity curves for x-ray diffraction from liquid sodium at 100°C and 400°C together with curves representing the incoherent radiation and the independent coherent radiation for the 400°C case.

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[9] Bent and Forziati, J. Am. Chem. Soc. **58**, 2220 (1936).

[10] From tables of f and Σf^2, Compton and Allison, *X-Rays in Theory and Experiment.* (D. Van Nostrand 1935) p. 781.

[11] We are indebted to Professor B. E. Warren for the use of the Coradi analyzer at Massachusetts Institute of Technology.

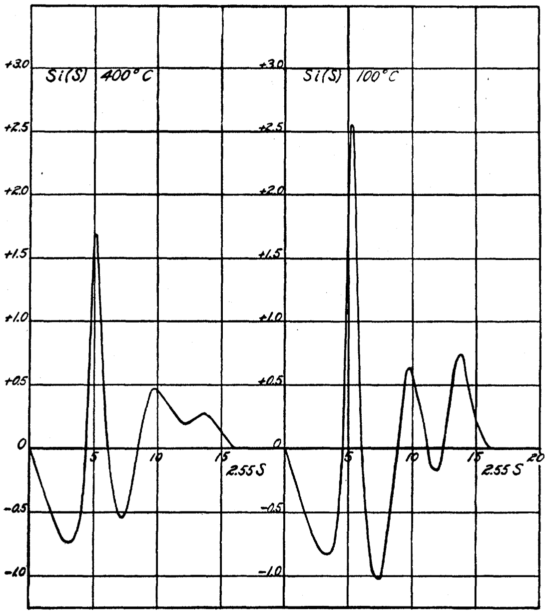

FIG. 2. Curves showing the *si*(*s*) function for liquid sodium at 100°C and 400°C.

and the values for certain points were checked by graphical computation. The analysis resulted in the curves shown in Fig. 3 and Fig. 4. These distribution curves are plotted together with the curves for constant density.

DISCUSSION OF RESULTS

The effect of temperature upon the diffraction pattern of a liquid is shown in Fig. 1. For the same intensity of the main peak, the scattering at large angles is higher for the higher temperature, the second peak is less prominent and the third peak is almost absent. There is, in addition, a slight shift of the positions of the maxima in the high temperature case to smaller angles than in the low temperature case. Perhaps the most effective graphical representation of the temperature effect is shown in Fig. 2. In this the oscillations of the *si*(*s*) function are highly damped in the 400°C case. For temperatures between 100°C and 400°C, there was a consistent, gradual transition in the shape of the *si*(*s*) function. Complete analyses of these intermediate cases were not made.

The radial density curve for liquid sodium at 100°C shown in Fig. 4 confirms that obtained by Tarasov and Warren[2] except for a consistent difference in the abscissa values. This shows up most prominently for the first peak, which in their work appeared at 3.96A and in the present work appears at 3.83A.[12] The interpretation of the curve of Fig. 4 is that an atom at $r=0$ is surrounded on the average, by an atomic population between distances r and $r+dr$ given by the area under the curve between r and $r+dr$. The distance from $r=0$ to the position of the maximum of the first peak is interpreted as being the most probable distance to the nearest neighbors. Beyond this distance, the distribution curve oscillates about the curve of constant density but never approaches zero. In similar curves for glass, however, the distribution curve does reach zero after the first peak. The significance of this has been pointed out by Warren,[13] for in vitreous SiO_2, a silicon atom, for example, has four definite and permanent neighbors, while in liquids, neighbors are temporary and any distances of approach above the minimum are possible, although the probability of finding a neighbor at the "contact distance" is higher than for other distances. Beyond the first peak there is a fairly well defined average concentration of atoms at about 7.0A.

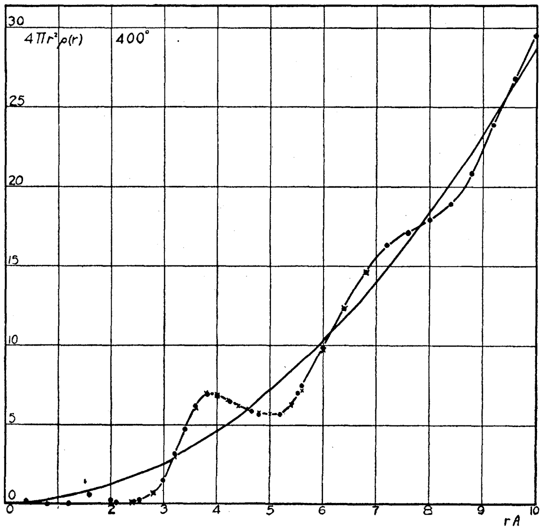

FIG. 3. The radial density distribution of atoms about any one atom in liquid sodium at 400°C.

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[12] In a private communication, Professor Warren stated that there was an error of 2.6 percent in their microphotometer enlarging ratio. Correcting for this, their value becomes 3.86A, in essential agreement with the value obtained in the present work.

[13] Warren, J. App. Phys. **8**, 645 (1937).

The radial density curve for liquid sodium at 400°C shown in Fig. 3 shows much less pronounced concentrations of atoms. The first concentration has a peak value at 3.90A and the second at about 7.2 A, while the dip between these two peaks is less than that in the case of sodium at 100°C. In order to compare the distributions at 100°C and 400°C more conveniently and effectively, $\rho(r)$, the actual density, as a function of r is shown for the two temperatures in Fig. 5. The solid curve for 400°C, is shown oscillating about the straight line representing the average density at 400°C. The dotted curve is the $\rho(r)$ for 100°C with its ordinate scale shifted since it would normally oscillate about the average density of sodium at 100°C. The concentrations and deficiencies of atoms are less pronounced in the 400°C case than in the 100°C case. Furthermore, at 400°C, the curve has positive values at values of r less than that for the 100°C case. The reality of this slight difference depends upon the accuracy with which the diffraction patterns in the two cases are known. Some support is given to this effect, however, from the fact that all the patterns obtained at various temperatures showed a consistent trend in such a manner as to indicate the reality of this effect.

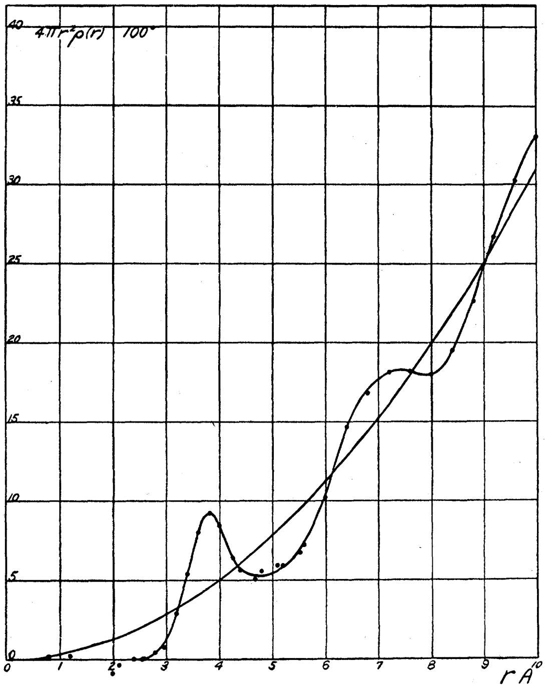

FIG. 4. The radial density distribution of atoms about any one atom in liquid sodium at 100°C.

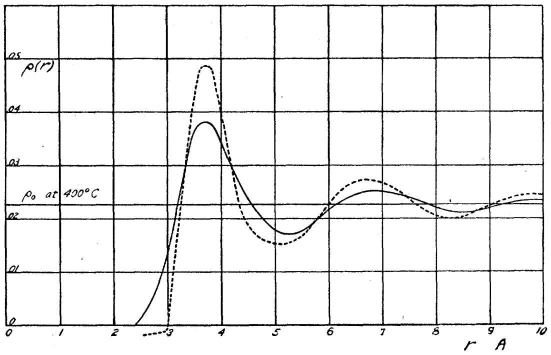

FIG. 5. The actual density in atoms per unit volume as a function of distance from any one atom in liquid sodium at 400°C. The dotted curve (with slightly shifted ordinate) shows that for liquid sodium at 100°C.

The impossibility of interpenetration of sodium atoms and the existence of interatomic binding requires that certain arrangements of these atoms with respect to their neighbors are more probable than others. These results show that the arrangement of sodium atoms is not wholly random, and they indicate the extent to which the atoms assume temporary arrangements due to their packing together. They show further, that the tendency to assume these temporary arrangements is less when the temperature is high than when it is low, and the curves shown in Fig. 3, Fig. 4 and Fig. 5 provide a measure of how much less this tendency is. They are in accord with the kinetic picture of a liquid, and on this picture, they may be given rough qualitative interpretation but it is possible that they may eventually lead to quantitative results concerning the interatomic binding forces or energies.

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