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The Effect of Temperature on the Atomic Distribution in Liquid Potassium*

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X-ray diffraction patterns of liquid potassium at temperatures of 70°C, 200°C, 295°C and 395°C have been obtained, using Mo $K\alpha$ radiation. Three peaks appear in each pattern, and with increasing temperature, the peaks become somewhat less pronounced. The first, and most intense, peak appears at a scattering angle of $10^\circ 36'$ in the 70°C case, and it appears at $10^\circ 16'$ in the 395°C case. Fourier analysis applied to the above two cases gives the atomic distributions at these temperatures. In the 70°C distribution curve, the maximum of the first peak occurs at 4.64Å, that of the second peak at 9.0Å, and after this, the distribution rapidly becomes random. In the 395°C distribution curve, the maximum of the first peak occurs at 4.8Å, that of the second at 9.2Å, and beyond this the distribution becomes random more rapidly than in the 70°C case.

INTRODUCTION

THE so-called "structure" of a liquid can be given its most specific expression in the form of an atomic distribution curve. This curve represents the average distribution of atoms about a given atom. As a result of the theories of Zernike and Prins¹ and of Debye and Menke,² analysis of x-ray diffraction patterns of liquids leads to this atomic distribution curve. Determinations of this sort have been made for mercury,² for gallium³ and for sodium⁴ at two temperatures.⁵ It is of interest to investigate various liquids at different temperatures for the information that may be obtained concerning the liquid

state. In the present work, the effect of temperature upon the atomic distribution in liquid potassium has been investigated.

Previous work on the diffraction of x-rays by potassium has been done by Keesom⁶ and by Randall and Rooksby.⁷ They determined the position of the strongest peak in the pattern, and, making use of the Bragg equation for a crystalline solid,⁸ they attempt to correlate the value of " d " so calculated with the spacing of the 110 plane in the crystal. The rough correlation and comparison of the results of the above two workers is given elsewhere.⁹

For quantitative determination of the atomic distribution, it is necessary to have as complete a diffraction pattern as possible. Knowing this to

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** On leave of absence from the Missouri School of Mines and Metallurgy, University of Missouri, Rolla, Mo.

¹ Zernike and Prins, *Zeits. f. Physik* **41**, 184 (1927).

² Debye and Menke, *Erg. d. Tech. Röntgenkunde*, II (1931).

³ Menke, *Physik. Zeits.* **33**, 593 (1932).

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

⁵ Trimble and Gingrich, *Phys. Rev.* **53**, 278 (1938).

⁶ Keesom, *Amsterdam Akad.* **30**, 341 (1927).

⁷ Randall and Rooksby, *Nature* **130**, 473 (1932).

⁸ Bragg, *The Crystalline State* (Macmillan Company, 1934), p. 15.

⁹ Randall, *The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids and Gases*, (John Wiley and Sons, 1934) p. 130.

angles of diffraction so large that interferences no longer play an appreciable part in the pattern, makes it possible to place the observed pattern in units of intensity per electron. Straightforward calculations then lead to the distribution of atoms about a given atom.

EXPERIMENTAL

Diffraction patterns of liquid potassium at 70°C, 200°C, 295°C and 395°C have been obtained, using Mo $K\alpha$ radiation reflected from a rocksalt crystal. The samples were contained in very thin-walled Pyrex capillary tubes, they were heated electrically, and their temperatures were determined by means of an iron Advance thermocouple with one junction close to the point where the x-rays passed through the sample. The capillaries were filled in a manner practically the same as was used in the case of sodium.⁵ Because of the higher absorption of x-rays by potassium than by sodium, smaller diameter capillaries were used. This, however, required a reduction in the wall thickness of the capillaries in order to prevent excessive glass scattering. After several trials at 70°C, patterns were obtained with no perceptible rise in intensity at the point where the main peak of the glass pattern should appear. More difficulty was encountered in obtaining satisfactory patterns at the higher temperatures,

especially at 395°C. In this case, thin-walled capillaries as used at 70°C were unable to stand the high temperature. It was finally necessary to use a pattern on which there appeared a small amount of excess scattering due to the main peak for glass. Correction for this glass scattering was necessarily approximate, but it was based on an experimentally determined pattern for the glass used in these experiments.

The capillary containing potassium was centralized in a cylindrical camera of 8.85 cm radius, and using new type Agfa film,¹⁰ exposures of about 36 hours gave photographic densities high enough to measure with considerable certainty. The x-ray tube was operated at about 30 kv and 15 ma. Microphotometering the films, and converting to intensities in the usual manner resulted in the experimental intensity curves. The main peak in the 70°C case occurs at $\sin \theta/\lambda = 0.130$, corresponding to a diffraction angle of $10^\circ 36'$ and that in the 395°C case occurs at $\sin \theta/\lambda = 0.126$, corresponding to a diffraction angle of $10^\circ 16'$. These values are from curves corrected as mentioned below, but they are very little different from those taken from uncorrected curves. For intermediate temperatures, these quantities varied approximately linearly with the temperature. Further work was carried

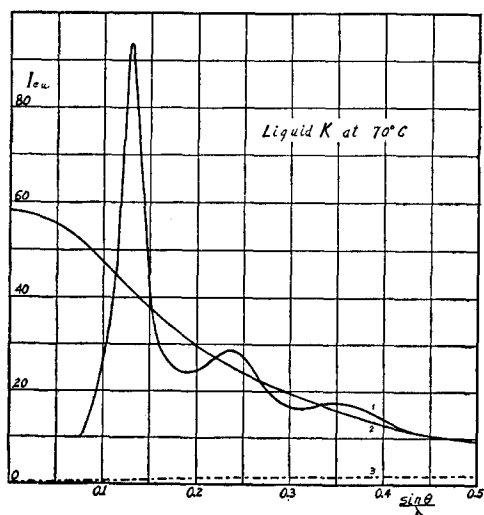


FIG. 1. Curve 1, corrected experimental intensity curve for liquid potassium at 70°C; curve 2, independent unmodified scattering; curve 3, incoherent scattering.

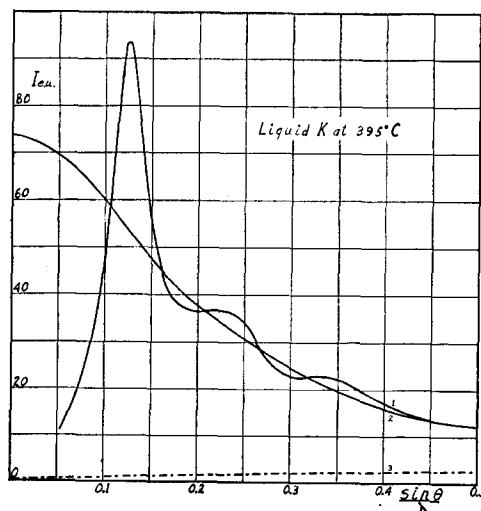


FIG. 2. Curve 1, corrected experimental intensity curve for liquid potassium at 395°C; curve 2, independent unmodified scattering; curve 3, incoherent scattering.

¹⁰ Gamertsfelder and Gingrich, Rev. Sci. Instr. 9, 154 (1938).

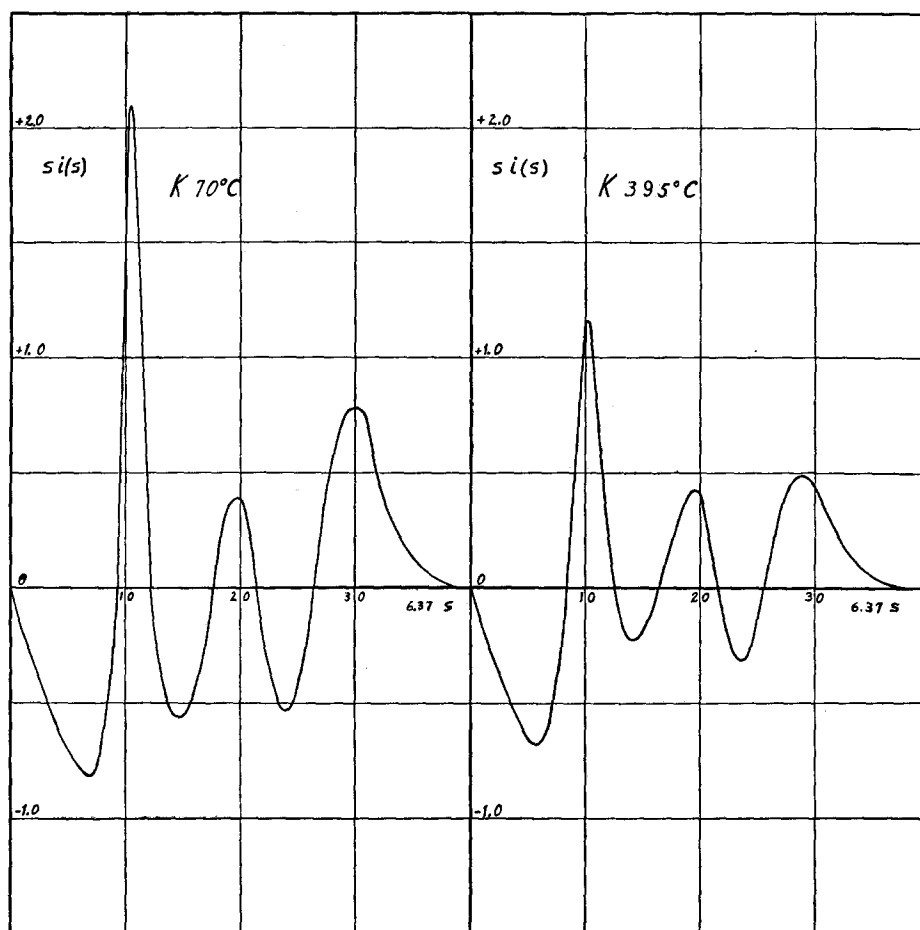


FIG. 3. Curves showing $si(s)$ functions for liquid potassium at 70°C and at 395°C.

out only for the two extreme temperatures, 70°C and 395°C.

APPLICATION OF THE FOURIER METHOD

The experimental intensity curves were corrected for absorption in the sample, for polarization both by crystal reflection and by diffraction from the sample, and for incoherent scattering from the sample. The absorption correction applied is that given by Blake.¹¹ The ratio of incoherent to total radiation was calculated from tables of " f " and " Σf^2 ".¹² The fully corrected intensity curve for the 70°C case is shown in Fig. 1, and that for the 395°C case is shown in Fig. 2. In both of these, 1 is the fully corrected

intensity curve, 2 is the Nf^2 , or coherent, curve, and 3 is the curve for the incoherent correction.

An outline of the theory may be found elsewhere,¹³ but the equation used here is

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

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.

¹¹ Blake, Rev. Mod. Phys. 5, 169 (1933).

¹² Compton and Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, 1935), p. 781.

¹³ Warren and Gingrich, Phys. Rev. 46, 368 (1934).

The quantity $si(s)$ is plotted against ks where k is a constant chosen for convenience in the use of the Coradi analyzer for evaluating the integral of Eq. (1). These curves are shown in Fig. 3 to illustrate the effect of temperature upon this function. Evaluation of the integral of Eq. (1) for various values of r leads to values of $4\pi r^2\rho(r)$ as a function of r .

DISCUSSION OF RESULTS

The results of this analysis are shown in Fig. 4 for the 70°C case and in Fig. 5 for the 395°C case. The curve, $4\pi r^2\rho_0$ is shown in each case and it can be seen that the actual distribution approaches the average distribution more rapidly at the high temperature than at the low temperature. For 70°C, the maximum of the first peak occurs at 4.64Å, and that for the second peak at about 9.0Å. For 395°C, these maxima are shifted to 4.76Å and 9.2Å, respectively. If an arbitrary line is drawn along the large r slope of the first peak and extended to the axis in such a manner as to form a symmetrical, isolated curve, this curve covers an area of about 8 units in each case. This indicates that, on the average, there are roughly 8 atoms surrounding a given atom, but it is important to note that the distribution curves do

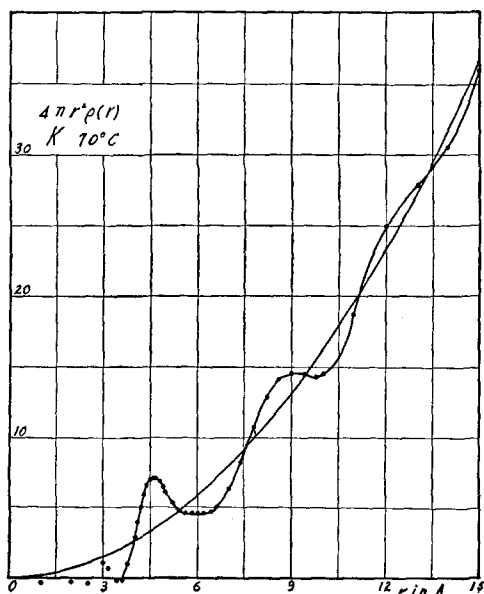


FIG. 4. The radial density distribution of atoms about any one atom in liquid potassium at 70°C.

not approach the axis between the first and second peaks. This indicates that there is a continual interchange of neighbors.

The effect of temperature can be shown very conveniently by plotting $\rho(r)$, the actual density, as a function of r . This is shown in Fig. 6. The horizontal line ρ_0 represents the average density at 70°C and the solid curve represents the actual density as a function of distance from a given atom at this temperature. At a distance of 15Å from an atom, the actual density nearly equals the average density. The dotted curve for 395°C has its ordinates shifted so that it will oscillate about ρ_0 at 70°C. The maximum for the first peak for the 70°C curve occurs at 4.50Å, and that for the 395°C curve occurs at 4.60Å. It is to be noted that an increase in temperature causes all peak

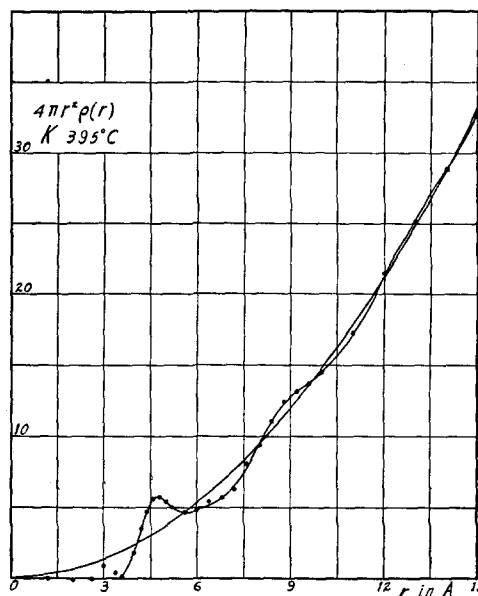


FIG. 5. The radial density distribution of atoms about any one atom in liquid potassium at 395°C.

positions to be shifted to larger values of r , and that the high temperature curve is more highly damped.

As might be expected, these results are similar to those for sodium.⁵ The peaks in the distribution curve occur at larger values of r in this case, due to the larger volume occupied by the potassium atom, but the general features of the curves for sodium and potassium are the same. The temperature effect in the two elements is

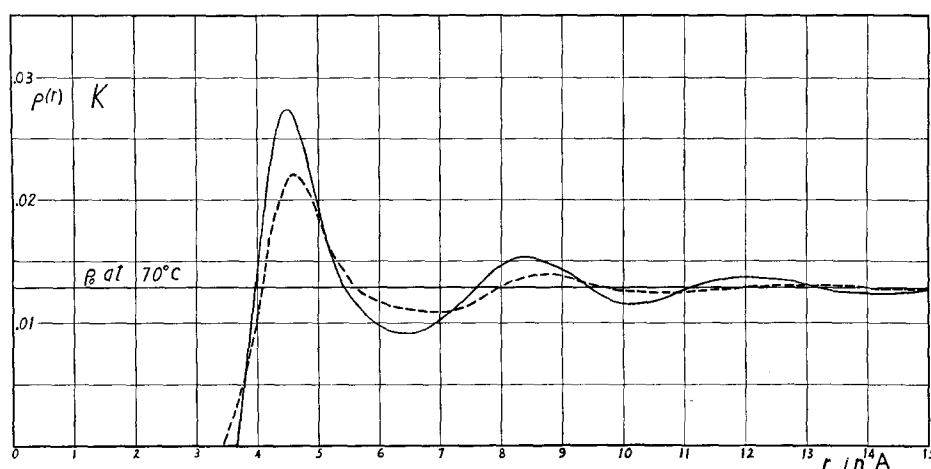


FIG. 6. The actual density in atoms per unit volume as a function of distance from any one atom in liquid potassium at 70°C. The dotted curve (with slightly shifted ordinate) shows that for liquid potassium at 395°C.

essentially the same. Although the distribution of atoms about a given atom retains a certain resemblance to that for the substance in the crystalline form for a few interatomic distances, the distribution rapidly becomes random beyond this region. An increase in temperature of the liquid reduces this resemblance, and it causes the random distribution to set in at smaller distances. That the general form of these curves can be explained on the basis of a mechanical model using steel balls has been pointed out by Debye and Menke.² An ingenious attempt to reconstruct the form of the density curve by experiment has

been reported by Hildebrand.¹⁴ It seems evident that the method here used to analyze diffraction patterns offers the most quantitative determination of the structure of a liquid, given by the atomic distribution function. These functions may also lead to the determination of interatomic forces in the liquid state.

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¹⁴ Hildebrand, Science **80**, 125 (1934).