

The Effect of Temperature on the Structure of Mercury

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second column are given the log K 's for water at 25° adjusted to this standard for comparison). In view of this discrepancy which might be expected from the discussion in Section II, it is surprising that a single value Y can be found for the dielectric constant for which the differences between the log K 's predicted from the equation $\log K_Y = \log K_X - c/YRT$, are equal to the differences between the log K_∞ 's. These values (with $Y=87.7$) are given in the last column of Table VI.

This correlation implies that the shift in the ratio of two dissociation constants in water on going at 25° ($1/D=0.01274$) to an imaginary solvent of $1/D=0.0114$, the slope of the log $K-1/D$ graphs being obtained from the temperature coefficients in water, is the same for all the dissociation constants listed, as the shift on going from water at 25° to an imaginary solvent with $1/D=0$, if the slopes are taken from the differences in log K' for different hydroxylic solvents. In terms of the Born equation, this means that the ionic radii to be obtained from the solvent shifts, are greater by a factor of about 9 than those from the temperature coefficients in water, and that this factor is the same for all acids. In this connection, it is suggestive that the values for ionic radii obtained

from the ratio of the differences in log K for uncharged and singly positively charged acids in water and *m*-cresol, would have to be given the high value 5A, if this ratio were interpreted by Born's equation.²⁸ Further data are needed to be sure that this correlation is not numerical coincidence.

The views advanced by Gurney provide therefore a valuable approximation to the problem of electrostatic influences on ionic dissociation, and predict values of the ionic radii of the correct order of magnitude. Exact test of these values is not at present possible. The equations deduced for the variation in heats of ionization with temperature are supported by the experimental data to within their probable error. The radii so obtained do not, however, account for changes in dissociation constant from solvent to solvent.

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²⁸ Brönsted, Delbanco and Tovborg-Jensen, *Zeits. f. physik. Chemie* **169A**, 361 (1934).

The Effect of Temperature on the Structure of Mercury

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X-ray diffraction patterns of mercury at eight temperatures ranging from -36°C to 250°C have been obtained using $\text{Mo } K\alpha$ radiation. The x-ray beam was diffracted from an open mercury surface using the small angle of incidence of $4^\circ 11'$, thus permitting observation of a previously unreported peak at a diffraction angle of about 10° . Fourier analyses of the intensity curves gave distribution functions showing the expected shifting and broadening of the maxima with increasing temperature. A small subsidiary peak, which changes position with temperature more rapidly than the others, occurs between the first and second main concentrations of atoms.

INTRODUCTION

THE atomic distribution functions for liquid sodium¹ and potassium² have been investigated over a considerable portion of their liquid

ranges, but no attempt has been made to investigate mercury above room temperature. Coster and Prins^{3, 4} and Debye and Menke^{5, 6}

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¹ F. H. Trimble and N. S. Gingrich, *Phys. Rev.* **53**, 278 (1938).

² C. D. Thomas and N. S. Gingrich, *J. Chem. Phys.* **6**, 411 (1938).

³ D. Coster and J. A. Prins, *J. de phys. et rad.* **9**, 153 (1928).

⁴ J. A. Prins, *Physik. Zeits.* **30**, 525 (1929).

⁵ P. Debye and H. Menke, *Erg. D. Tech. Röntgenkunde*, II.

⁶ H. Menke, *Physik. Zeits.* **33**, 593 (1932).

made studies of the structure of mercury at room temperature, and Danilov and Neimark⁷ took x-ray photographs near the freezing point (-38.87°C) but made no determination of the atomic distribution. Since mercury is frequently considered as a classical example of a monatomic liquid, it is of interest to investigate this function at various temperatures for the information it may give concerning interatomic forces and for the data it may supply to assist in evaluating existing theories of the liquid state. Such information promises to be very enlightening.⁸

Analysis of x-ray diffraction patterns gives a direct determination of the atomic distribution function. It is necessary, however, to have reliable values of corrected relative scattering intensities at large angles for which interferences no longer play a large part in the pattern; the observed pattern may then be placed on the basis of units of intensity per electron. From this point straightforward calculations using the methods outlined by Zernike and Prins⁹ and Debye and Menke⁵ lead to the distribution of atoms about a given central atom.

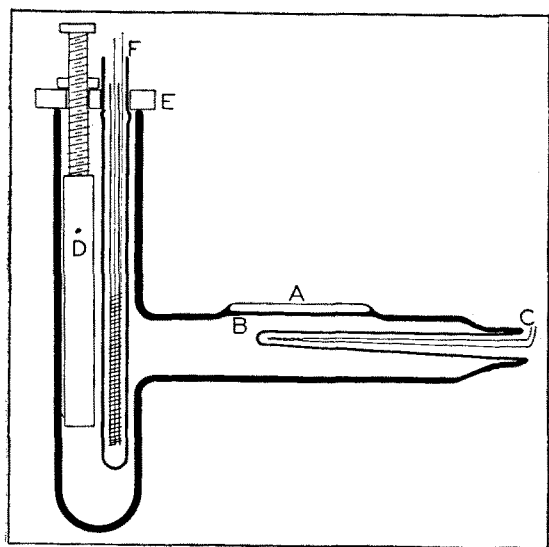


FIG. 1. Mercury container with open surface at *A*.

⁷ V. I. Danilov and V. E. Neimark, *J. Exp. Theoret. Phys. (U.S.S.R.)*, **5**, 724 (1935).

⁸ J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933); J. H. Hildebrand, *J. Chem. Phys.*, **7**, 1 (1939).

⁹ F. Zernike and J. A. Prins, *Zeits. f. Physik* **41**, 184 (1927).

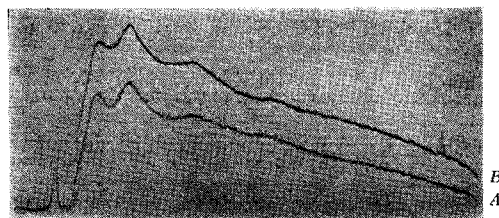


FIG. 2. Microphotometer tracings for mercury diffraction at 30°C . *B*, curve for eight-hour exposure; *A*, curve for four-hour exposure.

EXPERIMENTAL

Diffraction patterns of liquid mercury at -36°C , -34°C , 0°C , 30°C , 75°C , 125°C , 175°C and 250°C have been obtained using $\text{Mo } K\alpha$ radiation filtered through a ZrO_2 layer. The method used was essentially the same as that employed by the previous workers,^{3, 5} that is, diffraction was obtained by allowing the x-ray beam to impinge on the mercury surface. The angle of incidence on the level mercury surface was carefully measured and found to be $4^{\circ} 11'$. This angle was considerably smaller than that used by all previous investigators and made possible the observation of an intensity maximum appearing at an angle of diffraction of about 10° , not previously reported. (See peak on intensity curve in vicinity of $(\sin \theta)/\lambda = 0.1 - 0.15$, Fig. 3.)

Mercury samples were contained in the tube shown in Fig. 1, and diffraction occurred in the mercury which was made to bulge out of the open part, *A*, by means of the plunger, *D*. The opening was roughly rectangular, about 3 cm by 5 cm in dimensions, and was large enough to give a flat mercury surface. This was necessary for application of the absorption correction calculated by Debye and Menke.⁵ The temperature was measured by means of a copper-constantan thermocouple with one junction in the small tube, *B-C*, in the mercury. An electrical heating element, *F*, used for high temperatures was replaced for the low temperatures by a U-tube attached to a refrigerating system in which circulated acetone cooled in an acetone-solid CO_2 mixture. The mercury tube was mounted in front of a specially constructed x-ray camera so that the x-ray beam was diffracted from the mercury at the exact center of curvature of the film in the camera. The

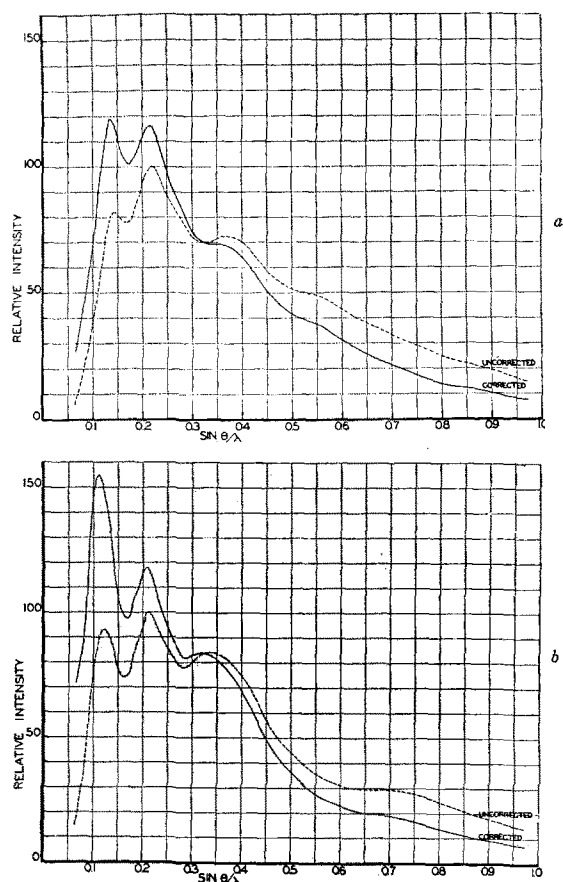


FIG. 3. Relative intensity distribution for mercury diffraction at 34°C and 175°C. Uncorrected (broken line) and corrected for polarization and absorption (solid line). (a) Temperature 34°C. (b) Temperature 175°C.

radius of curvature of the film was 7.00 cm. A nickel foil placed halfway between the sample and the film served to cut out the L radiation from the mercury.

The formation of dew or frost on the mercury was prevented at the lower temperatures by blowing on the surface a stream of air dried by passing through a liquid-air trap. At high temperatures mercury vapor was removed by means of a funnel-shaped tube inverted a short distance over the mercury and attached to a vacuum. Mercury oxide which was formed was sucked off periodically with a tipped tube and the level restored by means of the plunger.

Using new type Agfa film¹⁰ exposures of eight or ten hours gave photographs of proper densities when the tube was operated at 30 kv

¹⁰ C. Gamertsfelder and N. S. Gingrich, *Rev. Sci. Inst.* **9**, 154 (1938).

and 20 ma. Half the film was given half the exposure to facilitate relative intensity conversion with a correction of variations of film development, and the microphotometer tracing all in one step. Both parts of the film were microphotometered on the same plate, as shown in Fig. 2, which is for mercury at 30°C (A is four hours, B is eight hours); and intensity measurements were made with a ratiometer described by Langstroth,¹¹ using the half-time tracing to make the calibration curve. The relative intensity curves were corrected for absorption and polarization in the usual manner. Sample uncorrected and corrected curves for mercury at -34°C and 175°C are shown in Fig. 3.

APPLICATION OF THE FOURIER METHOD

The application of the Fourier method requires that the experimental scattering intensity curves, corrected for polarization and absorption, be placed on an absolute basis, in electron units per atom. To do this it is considered that the scattering becomes independent at a large value of $(\sin \theta)/\lambda$ and equal to the sum of the modified and independent unmodified scattering of N atoms. This sum is readily determined from tables of f and Σf_n^2 ,¹² in electron units per atom.

The experimental curve is then placed on an absolute basis by multiplying the arbitrary units

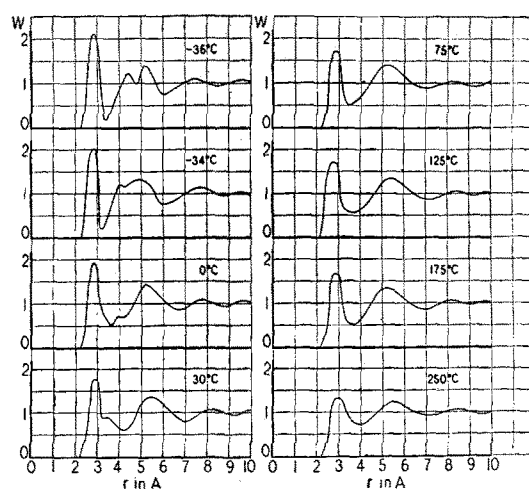


FIG. 4. Menke's W function for mercury.

¹¹ G. O. Langstroth, *Rev. Sci. Inst.* **5**, 255 (1934).

¹² A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, 1935), pp. 781, 782.

by a constant. This constant is the ratio of the sum of the modified and independent unmodified intensities (in electron units per atom) at a large value of $(\sin \theta)/\lambda$ to the experimental intensity (in arbitrary units) at the same point. The correction for modified scattering was almost negligible due to the high atomic number of mercury. The value $(\sin \theta)/\lambda = 0.971$ was chosen in practically all cases.

Warren and Gingrich¹³ have outlined the theory of the mathematical treatment. The equation used 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 the distances r and $r+dr$ for a given central atom, ρ_0 = average density of scattering matter 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, and f = atomic scattering factor.

The function $si(s)$ was plotted against various scales of s , and the integral in Eq. (1) evaluated by means of a Bardsley harmonic analyzer. Any variations caused by the choice of $(\sin \theta)/\lambda$ would be long period ones affecting only the first few harmonics, which are known to be zero from the almost complete impenetrability of the atoms. From these values, the probability function of Menke, W ,⁶ was determined (Fig. 4) and finally values of $4\pi r^2 \rho(r)$ as a function of r were obtained (Fig. 5).

DISCUSSION

Since no calculation has been made for the distribution of mercury atoms at any other temperature than room temperature, it is not possible to make a direct comparison between the results appearing here and those of other authors. The distribution obtained for 30°C corresponds approximately to that obtained by Coster and Prins³ and Debye and Menke,⁵ with the exception of the small subsidiary peak which appears in the vicinity of 4Å. The first maximum in the experimental intensity pattern has not been mentioned by investigators on this liquid; their experimental arrangements appear to be

¹³ B. G. Warren and N. S. Gingrich, Phys. Rev. **46**, 368 (1934).

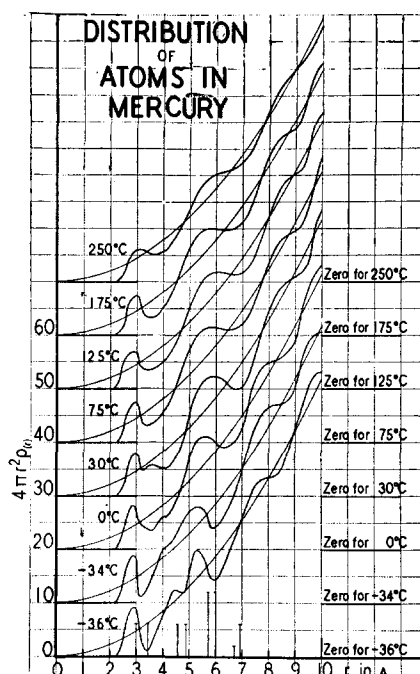


FIG. 5. Radial density distribution of atoms about any one atom in mercury. Solid lines below -36°C curve show distribution in the solid.

such that it was impossible or unlikely for them to observe such a peak in the intensity pattern.

The fact that this first maximum had not been reported was known when it was first observed and attempts were made to eliminate it. The suggestion that it might have been due to gas scattering led to taking photographs with a stream of helium passing through the camera, but this failed to solve the discrepancy. The convincing argument in favor of its being due to scattering from the liquid mercury was that the peak was found to shift in relation to the other peaks, when the temperature was changed. (See Fig. 3.)

In Fig. 5 are given the atomic distribution curves for the various temperatures, together with the corresponding $4\pi r^2 \rho_0$ curves. It can be seen in every case that the actual distribution approaches the average at the larger distances, and more rapidly as the temperature increases. The peaks become broader and less pronounced for the higher temperatures, and the positions of the maxima shift to larger distances in accordance with the increased expansion of the liquid.

The area under the first peak gives the number of atoms which may be considered as closest neighbors of any given atom, though there is a constant interchange of atoms in the liquid. The rhombohedral structure of solid mercury¹⁴ gives six atoms as closest neighbors, as is shown by the solid distribution indicated by the vertical lines in Fig. 5. As might have been expected, six atoms were found for the liquid for -36°C , and likewise for all the higher temperatures. However, in considering the structure of a liquid, a distribution curve as presented here should be regarded as a measure of the probability of finding an atomic center at some particular distance.

This probability, and the changes with temperature, are very clearly shown in the curves of Fig. 4. The line, $W=1$, corresponds to $4\pi r^2\rho_0$. Again, it can be seen that the peaks broaden and decrease in height, while the minima rise, as the temperature increases, indicating a less pronounced structure as the atomic motions become more violent. All the curves are similar in displaying a trend toward a value of unity at large distances, and for the high temperatures the trend is evident at smaller distances. A W curve for a completely random arrangement of the atoms would show a rapid rise to unity, and outside of a possible small peak would remain unity. The curve for 250°C , at least, indicates an approach to this condition.

In Fig. 5 a subsidiary peak is observed between the first and second main maxima at the lower temperatures. The position of this small maximum changes in a regular manner with change in temperature although its direction of displacement is contrary to that for the other peaks.

¹⁴ L. W. McKeehan and P. P. Cioffi, *Phys. Rev.* **19**, 444 (1922); H. Terrey and C. M. Wright, *Phil. Mag.* **6**, 1055 (1928); M. Wolf, *Zeits. f. Physik* **53**, 72 (1929).

This fact, together with the further one that all the low temperature atomic distributions showed this subsidiary maximum, indicate that the effect is real and not one arising out of mathematical discrepancies in the Fourier analysis. A possible reason for its shift is that the "defence" of the volume of the first shell by the closest neighbors breaks down as the temperature is raised, permitting the closer approach of a few atoms, an effect which is observable until finally the broadening of the principal peak obscures the minor one.

A consideration of the mathematical theory behind the calculation of a distribution function such as that plotted in Fig. 5 will indicate that no simple relationship exists between the positions of maxima or minima in the experimental intensity pattern and the peaks in the final atomic distribution function. Determination of a most probable distance, d , by means of the Bragg equation from the intensity peak positions gives values which do not correspond at all to those obtained by the Fourier method. Most probable interatomic distances in a liquid cannot be determined by a gross inspection of an intensity pattern for this reason, and a more careful mathematical analysis should be made before far-reaching conclusions concerning liquid structures are drawn.

Some applications of the results reported here will be presented in a later paper.

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