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X-Ray Analysis of the Structure of Water

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X-ray diffraction patterns of water were obtained at five temperatures: 1.5°, 13°, 30°, 62°, and 83°C. The radiation was Cu $K\alpha$ and Mo $K\alpha$, monochromated by reflection from a rocksalt crystal. Radial distribution curves for water at the five temperatures were obtained by a Fourier analysis of the x-ray intensity curves. The first peak is only partially resolved, and it is not possible to interpret the distribution curves uniquely in terms of a definite number of neighbors at definite distances. The results can be interpreted in terms of a structure in which the tendency of a water molecule to bond itself tetrahedrally to 4 neighboring molecules is only partially satisfied.

INTRODUCTION

X-RAY diffraction studies of water have been carried out by Stewart,¹ Amaldi,² Meyer,³ and Katzoff.⁴ A quantitative interpretation of the experimental data has been given by Bernal and Fowler⁵ and Katzoff.⁴ Most of the subsequent work on the structure of water has been inspired and influenced by the pioneer work of Bernal and Fowler. Their method consisted of building up various molecular structures for water and finding the structure which gave the best agreement between the calculated and observed x-ray diffraction patterns. In this way they were able to verify the essentially tetrahedral structure of water, in which each water molecule has approximately four nearest neighboring molecules.

Katzoff was the first to apply to water the more straightforward method of Fourier analysis. With this method, one starts with the experimental intensity curve, and by a direct calculation obtains a radial distribution curve giving the number of water molecules to be found at any distance from a given molecule. Katzoff has given the distribution curves for two temperatures: 3° and 90°C. At both temperatures the area of the first peak indicated that each water molecule had roughly four nearest neighboring molecules.

The interest in the structure of water is so great, that it has seemed worth while to carry

through the x-ray analysis for five different temperatures. In this way one can hope to follow any significant temperature changes in the structure. Although our results are in essential agreement with those of Bernal and Fowler, and Katzoff, the more extensive data have allowed more precise conclusions to be drawn.

EXPERIMENTAL

X-ray diffraction patterns of water were obtained for five temperatures: 1.5°, 13°, 30°, 62°, and 83°C. The usual sources of inaccuracy were eliminated in the following ways: (a) The patterns were obtained in a large-sized brass camera of 5.57 cm radius, and in an atmosphere of hydrogen to minimize gas scattering. (b) The sample was in the form of a free stream of liquid of diameter 1.7 mm. (c) The radiation employed was Cu $K\alpha$ and Mo $K\alpha$ monochromated by reflection from a rocksalt crystal. (d) The apparatus was constructed so as to eliminate the vapor scattering at the higher temperatures.

The essential features of the camera are shown in Fig. 1. The stream of liquid emerging from the nozzle *N* is supplied from the reservoir *R*, where it is held at a constant height, and either warmed or cooled to the desired temperature. The reservoir is thermally insulated from the camera, so that the film is kept at room temperature. The monochromating rocksalt crystal is mounted on the table *T* and adjusted so that the reflected $K\alpha$ line passes through the collimator *C*. The transmitted main beam passes into the exit tube *B*. At the higher temperatures, the exit tube was extended nearly to the water stream to

¹ G. W. Stewart, *Phys. Rev.* **37**, 9 (1931).

² E. Amaldi, *Physik. Zeits.* **32**, 914 (1931).

³ H. H. Meyer, *Ann. d. Physik* **5**, 701 (1930).

⁴ S. Katzoff, *J. Chem. Phys.* **2**, 841 (1934).

⁵ J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).

minimize the scattering of the main beam by water vapor. The liquid stream falls into the receiving cup *D*, and is then pumped back to the reservoir. Hydrogen is circulated through the camera to eliminate air scattering.

The film was placed on the outside of the brass cylinder, and received the diffracted x-rays through a horizontal slot cut around the mid-section of the camera. To prevent wet hydrogen from reaching the film, this slot was covered with aluminum foil. A lead jacket which surrounded the camera, protected the film from stray radiation from outside.

For each temperature three patterns were made: a normal exposure with Cu radiation, a normal exposure with Mo radiation, and a very long exposure with Mo radiation. The latter was used to bring out the weak part of the pattern at large values of $\sin \theta/\lambda$. The Cu patterns gave better detail at small values of $\sin \theta/\lambda$, and the Mo patterns gave the best results at the high values. The final intensity curve was obtained by combining the results from the three films. Exposures were of the order of 50 hours.

RESULTS

A set of diffraction patterns taken with Mo radiation is shown in Fig. 2. All patterns were microphotometered along the equator, and the microphotometer record changed to an intensity curve in the usual way. Each intensity curve was then corrected for polarization⁶ and absorption.⁷ For each temperature, the three corrected intensity curves were combined to give the final curve. Fig. 3 shows the x-ray intensity curves for the five temperatures, the intensity being in arbitrary units.

A Fourier analysis of each of the intensity curves was made in the usual way. For a material containing only one kind of atom, the radial distribution function is given by the equation⁸

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty s i(s) \sin rs ds. \quad (1)$$

⁶ Using a rocksalt crystal as monochromator, the polarization factor is:

$$\begin{aligned} \frac{1}{2}(1 + 0.937 \cos^2 2\theta) & \text{ for Mo } K\alpha, \\ \frac{1}{2}(1 + 0.723 \cos^2 2\theta) & \text{ for Cu } K\alpha. \end{aligned}$$

⁷ *International Tables for the Determination of Crystal Structures*, Vol. II (Gebrüder Borntraeger, Berlin 1935), p. 584.

⁸ For a derivation of this equation see B. E. Warren, *J. App. Phys.* **8**, 645 (1937).

Since the scattering by hydrogen is almost completely Compton modified radiation, it is justifiable to treat water as a one atom substance. In Eq. (1) as applied to water:

r = distance from the center of any oxygen.

$4\pi r^2 \rho(r) dr$ = number of oxygens (or H₂O molecules) between distances r and $r + dr$ from the center of any given oxygen atom.

ρ_0 = density of water expressed in molecules per cubic angstrom.

$s = (4\pi \sin \theta)/\lambda$.

$i(s) = (I/Nf^2 - 1)$.

f = atomic scattering factor.

I/N = experimental intensity of unmodified scattering in electron units per molecule.

The intensity scale of the experimental curves in Fig. 3 is put upon an absolute basis (electron units per molecule) by adjusting the scale of

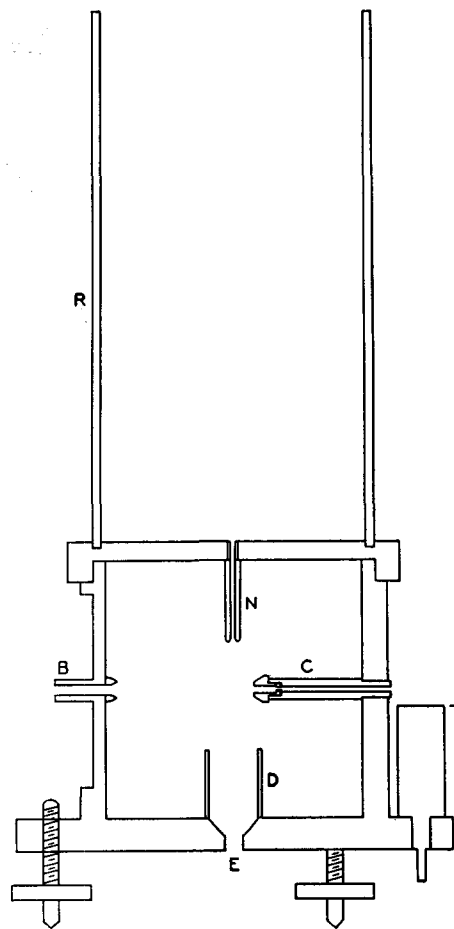


FIG. 1. Camera for x-ray diffraction study of water.

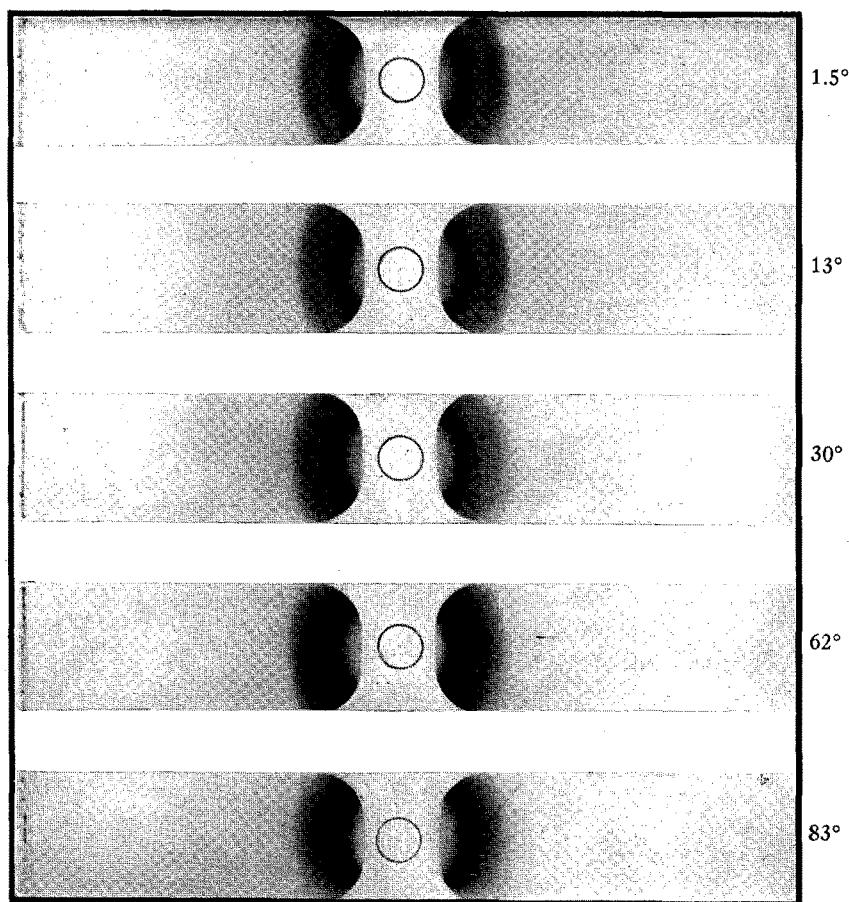


FIG. 2. X-ray diffraction patterns of water at temperatures 1.5°, 13°, 30°, 62°, and 83°C.

ordinates so that at large values of $\sin \theta/\lambda$ the experimental curve approaches the sum of the modified and independent unmodified scattering per molecule. The independent unmodified scattering was taken as that of oxygen alone (f_0^2). The modified scattering was taken as the sum of the modified scattering of one oxygen and two hydrogens. These quantities are available in tabulated form.⁹

Having put the experimental intensity curves upon an absolute basis, the curve $si(s)$ is plotted for each temperature, and the integration in Eq. (1) carried out with a harmonic analyzer. For each $si(s)$ curve the integral is evaluated for about thirty values of r . The resulting values of $4\pi r^2 \rho(r)$ plotted against r give the radial distribution curves shown in Fig. 4.

⁹ Compton and Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Co., Inc., New York 1935), pp. 781-782.

DISCUSSION OF RESULTS

The change in the diffraction pattern of water with rise in temperature is clearly shown in Fig. 3. At 1.5°C the first peak is at $\sin \theta/\lambda = 0.155\text{\AA}^{-1}$, and the second peak at 0.23\AA^{-1} . With rising temperature the second peak becomes less sharply resolved from the first peak. At 83°C the two peaks have practically merged into a single peak. About the only conclusion that can be drawn from the intensity curves of Fig. 3 is that there is a change in the structure of water with rise in temperature.

The radial distribution curves of Fig. 4 give directly as much information about the structure of water as can be obtained by x-ray diffraction study. It should be emphasized that these curves are obtained directly from the experimental intensity curves, and are therefore completely independent of any *a priori* assumptions as to

structure. The curves give the average distribution of neighboring molecules as a function of the distance from the center of any water molecule. The area under the curve between any two distances gives the number of neighboring water molecules in that range of distance.

The first peak in the distribution curves represents the nearest neighboring molecules, and the position of the peak gives the average distance of separation of closest neighbors. In ice the dis-

tance between neighboring water molecules is 2.76Å. From the distribution curves it is seen that in water the distance between closest neighbors is 2.90Å at 1.5°C increasing to about 3.05Å at 83°C. The intermolecular distance is therefore slightly greater in water and increases with temperature. The area under the first peak is rather indefinite since the peak is not well resolved on the right-hand side. However, by taking the maximum of the peak as the mid-position, and

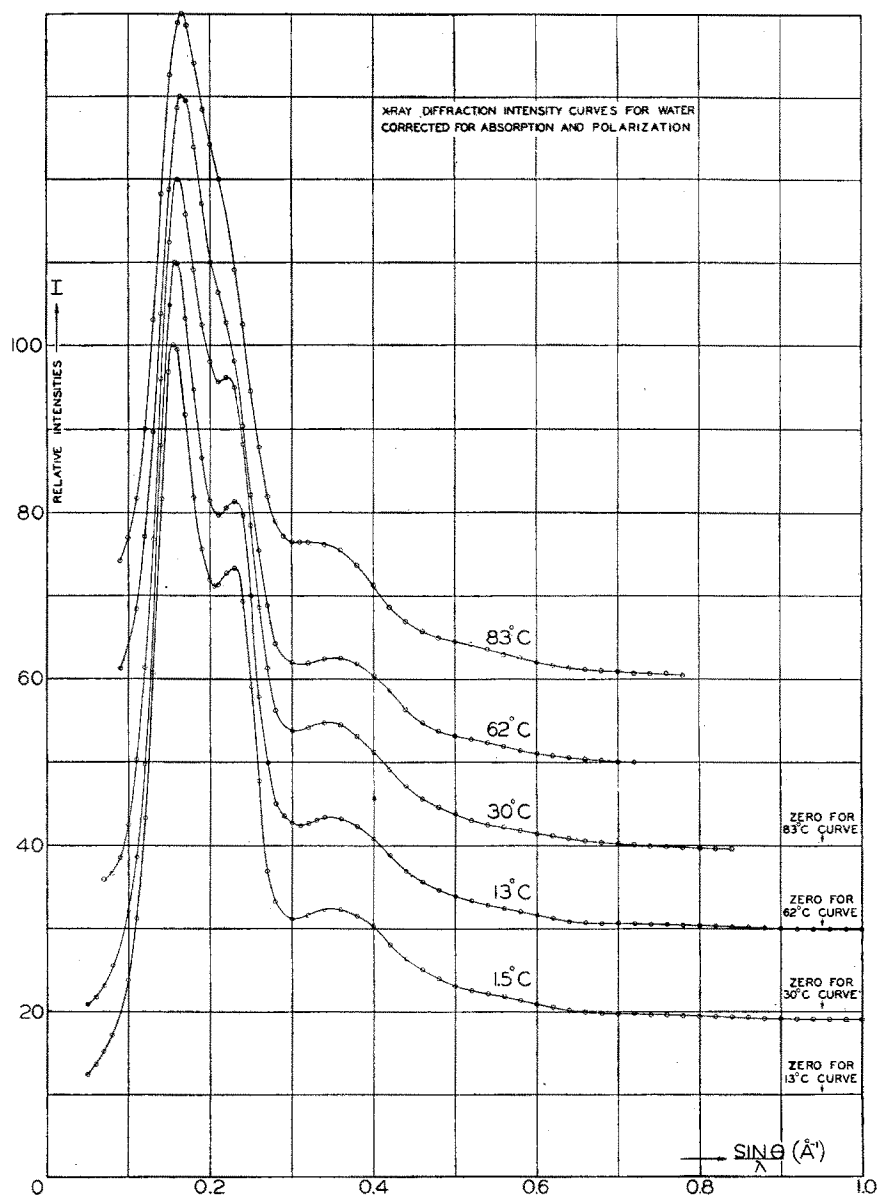


FIG. 3. X-ray intensity curves for water, corrected for absorption and polarization. The intensity is in arbitrary units.

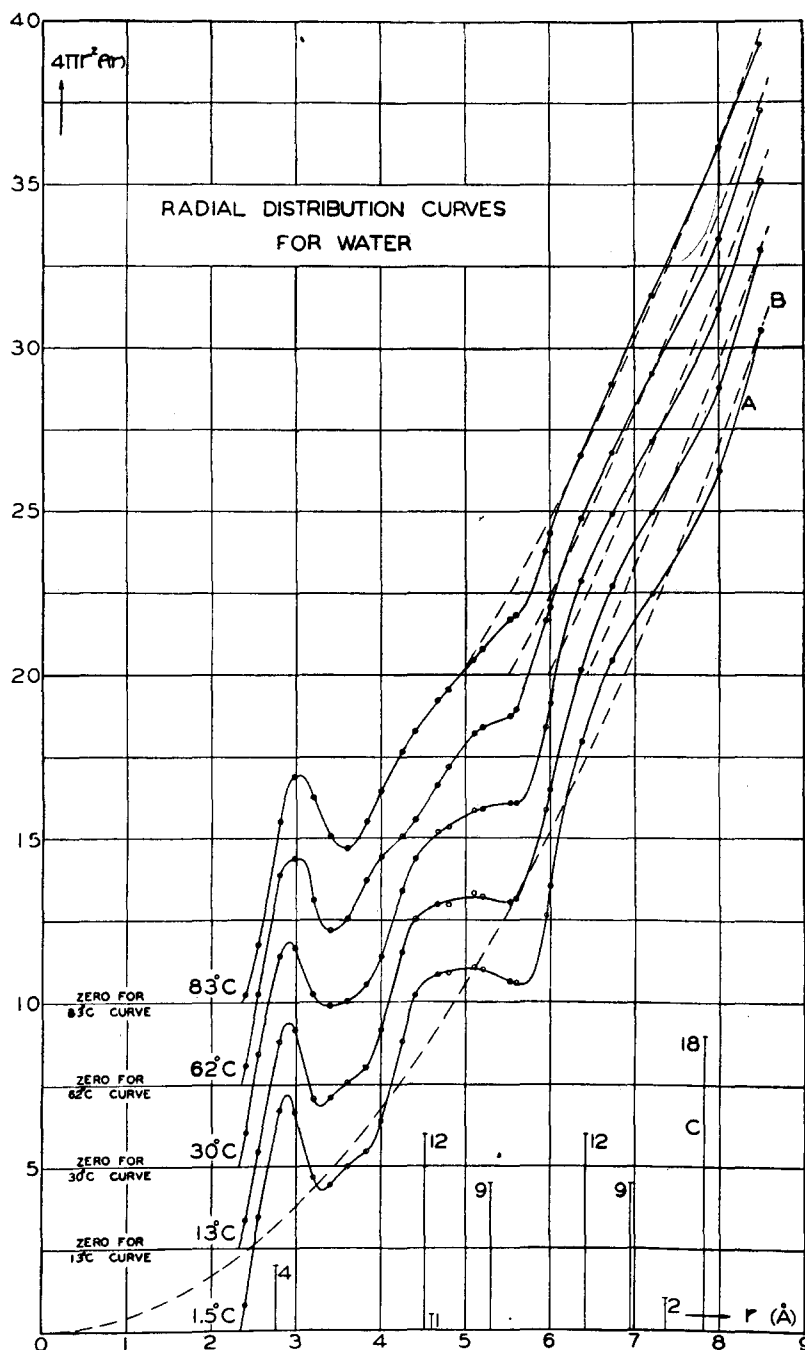


FIG. 4. Radial distribution curves for water. The vertical lines at the bottom give the number and position of the neighbors in ice.

drawing in the right-hand side symmetrical with the left-hand side, one gets what seems to be a fair assignment of peak area. The numbers of nearest neighbors as calculated from the peak areas are given in Table I.

In a close packing of spheres each sphere is in contact with 12 neighboring spheres. In an approximately close packed liquid, made up of essentially spherical molecules, we would expect to find a number of nearest neighbors slightly less

than 12. For example, in liquid sodium¹⁰ the number of neighboring sodium atoms is roughly 10. The conclusion is therefore definite that water is not even approximately a close-packed liquid. In the crystalline structure of ice, each water molecule is tetrahedrally surrounded by 4 neighboring molecules. From the values in Table I it is evident that the water structure approximates more closely to the open tetrahedral type of structure in ice, than to a close-packed structure. Once we have determined that the intermolecular distances are roughly the same in ice and water, it follows immediately that the number of neighboring molecules must be roughly the same since the densities are not very different in ice and water.

If each water molecule were tetrahedrally surrounded by 4 water molecules, and each of these by 4, and so on, as in the crystalline structure of ice, each molecule would have a set of second nearest neighbors at a distance

$$r = 2.76(8/3)^{1/2} = 4.51\text{\AA}.$$

A marked concentration of neighbors at a distance of about 4.5\AA is clearly seen on the distribution curves for 1.5°, 13°, and 30°C. At the higher temperatures this concentration is much less marked. The concentration at 4.5\AA in the experimental curves is in good agreement with the existence of tetrahedral bonding in water. The disappearance of this concentration in the distribution curves indicates that the tetrahedral bonding becomes less sharply defined or less prevalent with rise in temperature. It should also be noted that the first peak becomes broader and more poorly defined with rise in temperature. This indicates that the nearest neighbors become less definitely defined as to number and distance of separation.

It is of interest to see how far we can go in giving a specific interpretation to the distribution curves of Fig. 4, and to see to what extent we can describe the structure of water in terms of a

TABLE I. Number of nearest neighbors.

Temp. °C	1.5	13	30	62	83
Number	4.4	4.4	4.6	4.9	4.9

¹⁰ L. P. Tarasov and B. E. Warren, J. Chem. Phys. 4, 236 (1936). F. H. Trimble and N. S. Gingrich, Phys. Rev. 53, 278 (1938).

definite number of neighbors at definite distances. It is evident at the start that this will not be very successful, since the first peak is not well resolved on the right-hand side. In a glass such as vitreous silica, each silicon is tetrahedrally surrounded by four oxygens. The silicon has a definite number of permanent neighbors at a definite distance, and the first peak of the distribution curve is completely resolved.⁸ All glasses so far studied show a first peak completely resolved, whereas for all liquids the first peak to represent an intermolecular distance is never more than partially resolved. This important difference has considerable bearing on the structure of liquids. It indicates that in a liquid we do not have a definite number of neighbors existing only at certain definite distances.

To illustrate the point that there is no simple unique interpretation of the distribution curves, we will consider a number of different ways of interpreting the 1.5°C curve. In Fig. 5 the distri-

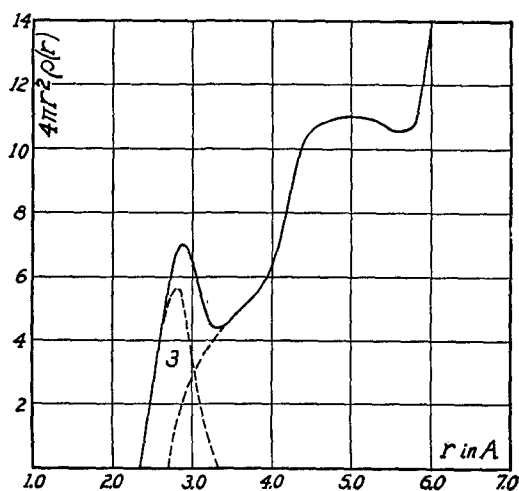


FIG. 5. Interpretation of 1.5°C distribution curve in terms of 3 nearest neighbors and others at a continuous variety of distances.

bution curve has been arbitrarily split up to indicate each molecule surrounded by 3 definite neighbors at a distance 2.8\AA and an indefinite number of neighbors at a continuous variety of larger distances. This could be interpreted in terms of a structure in which each water molecule is bonded on the average to 3 other molecules rather than to 4 as in ice. In addition to the bonded neighbors, there are an indefinite number of neighbors at a variety of distances.

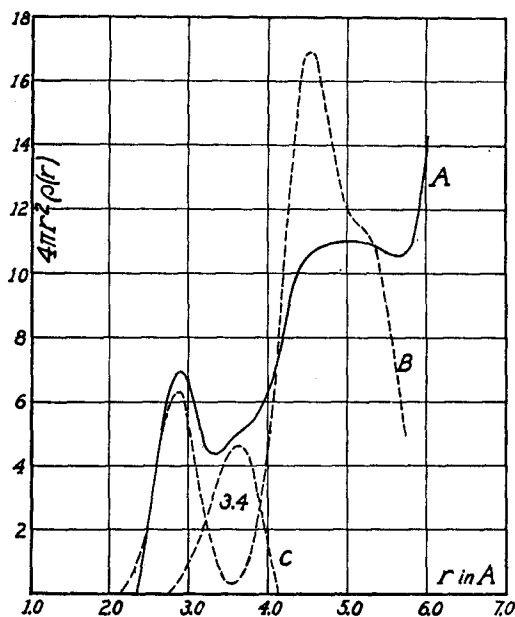


FIG. 6. Comparison of 1.5°C water distribution curve with an ice-like distribution. *A*, water distribution; *B*, calculated distribution; *C*, difference.

Another method of interpretation involves making a direct comparison with the distribution function of ice. Following Prins and Petersen¹¹ one can approximate the distribution in a liquid by smoothing out the distribution curve of the crystal by means of an error function

$$4\pi r^2 \rho(r) = \sum_k \frac{N_k a}{(\pi r_k^3)^{1/2}} \exp \left[-\frac{(a^2/r_k)(r-r_k)^2}{r_k^3} \right], \quad (2)$$

where N_k is the number of neighbors at a distance r_k . Fig. 6 shows this applied to the first three sets of neighbors in ice. The curve is calculated for 4 neighbors at 2.85 Å, 13 at 4.50 Å, and 9 at 5.30 Å. The first neighbor distance is taken as 2.85 rather than 2.76 Å to correspond more closely to the experimental curve. The constant a in Eq. (2) is chosen arbitrarily to give a first peak comparable in width to the distribution curve. As seen from Fig. 6, this method of representation fails to account for about 3.4 neighbors at a distance around 3.6 Å and gives too great a concentration at about 4.5 Å.

If one smooths out the distribution more drastically by applying the equation

¹¹ Prins and Petersen, *Physica* 3, 147 (1936).

$$4\pi r^2 \rho(r) = \sum_k \frac{N_k a}{(\pi r_k^3)^{1/2}} \exp \left[-\frac{(a^2/r_k^3)(r-r_k)^2}{r_k^3} \right] \quad (3)$$

to the structure of ice the curve of Fig. 7 is obtained. There is still a deficit of about 2.0 neighbors to be accounted for at distances between the nearest and next nearest neighbors. We conclude that an ideal 4 coordinated tetrahedral structure does not account for the neighbors which occur in water at distances between those of the first and second neighbors in ice. A structure involving partial tetrahedral bonding with continually changing neighbors seems to be the simplest interpretation of the x-ray distribution curves.

Following Bernal and Fowler's⁵ picture of the tetrahedral water molecule, we would expect that in water each molecule is continually striving to bond itself tetrahedrally to 4 neighboring molecules. The peak in the experimental curve at about 4.5 Å indicates that the desire for tetrahedral bonding is at least partially realized. At any instant a molecule might be bonded to 2 or 3 neighboring molecules, and have other neighbors moving toward it or away from it and therefore occurring at a continuous variety of distances. A picture such as this involving partial tetrahedral bonding is in agreement with results obtained by other methods. Raman spectrum studies¹² indicate that water is slightly more than 2 co-

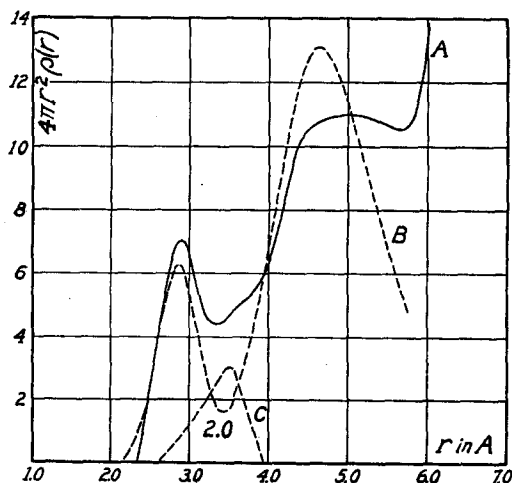


FIG. 7. Comparison of 1.5°C water distribution curve with a smoothed out ice-like distribution. *A*, water distribution; *B*, calculated distribution; *C*, difference.

¹² Cross, Burnham and Leighton, *J. Am. Chem. Soc.* 59, 1134 (1937).

ordinated in the range 25° to 90° . Viscosity studies¹³ indicate that the average coordination in water is $2\frac{1}{2}$ at 0° , $1\frac{1}{2}$ at 50° , and 1 at 100°C .

We could attempt to explain the latent heat of fusion of ice in at least two ways. If we assumed that in water at 0°C each molecule is tetrahedrally bonded to 4 others exactly as in ice, the x-ray distribution curves show that the average intermolecular separation is about 2.90\AA rather than 2.76\AA as in ice. On the other hand, if we assume that each molecule is bonded to less than 4 neighboring molecules, the latent heat will be partly due to the work of breaking some of the bonds in the ice structure. From either point of view there is a definite difference between the ice and the liquid.

When ice melts, the volume decreases by 9 percent, in spite of the fact that the distribution curves show that the intermolecular distance actually increases from 2.76 to 2.90\AA . This is not as anomalous as it might seem, if we remember that the density of a substance depends upon the interatomic distances and also upon the scheme of packing or coordination number. Ice is an unusually open structure with a coordination number of four. In water the tetrahedral scheme of structure is partly broken down, and neighbors can occur at a variety of distances. As seen from Figs. 6 and 7, this effectively increases the number of approximate neighbors, and the increase in density due to this "filling in" effect more than compensates for the decrease in density due to the larger intermolecular distance. In Fig. 8 this point is illustrated schematically. Fig. 8a represents a very open type of structure with each molecule bonded to 3 neighbors at a definite distance. In Fig. 8b we have a closer scheme of packing, each molecule has 2 nearest neighbors at the same distance as in 8a, and 2 next nearest neighbors at a distance 10 percent larger. The average intermolecular distance is therefore greater in 8b. Due to the closer scheme of packing the density of 8b is 27 percent larger than 8a.

As the temperature of water is raised above 0°C we can think of two opposite effects going on.

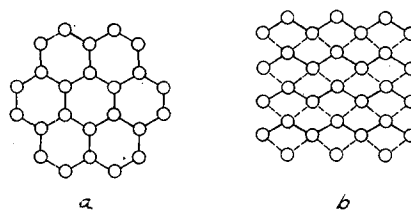


FIG. 8. Illustration of increase in density due to closer scheme of packing.

The progressive breaking down of the fourfold tetrahedral structure allows more neighboring molecules, and this "filling in" increases the density. The increase in intermolecular distance, as shown by the distribution curves for the different temperatures, tends to decrease the density. The minimum volume of water at 4°C is the result of these two opposing effects.

The higher density of water has been treated by Bernal and Fowler by calling water "quartz-like" and ice "tridymite-like." From the "quartz-like" point of view the higher density of water would be due to the next nearest neighbors moving in from 4.5 to about 4.2\AA . The second peak of the distribution curve, however, corresponds to a distance of 4.5\AA or slightly larger, rather than to 4.2\AA . The increased density of water is due not to closer next nearest neighbors, but rather to a "filling in" between the first and second neighbors of the ideal tetrahedral structure. The term "quartz-like" is therefore not a good description of the water structure.

The x-ray results show the essentially tetrahedral nature of the water structure, but cannot be interpreted uniquely in terms of a definite number of neighbors at certain definite distances. This is probably inherent in the nature of the liquid state. Water is well described by the term "broken down ice structure." By this we mean a structure in which each water molecule is striving to bond itself tetrahedrally to 4 neighboring molecules just as in ice, but in which bonds are continually breaking and reforming, so that at any instant a molecule will be bonded to less than 4 neighboring molecules, and have other neighbors at a continuous variety of distances.

¹³ Ewell and Eyring, *J. Chem. Phys.* **5**, 726 (1937).