

The Structure of Liquid Carbon Tetrachloride

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X-ray diffraction patterns of liquid CCl_4 at 27°C have been obtained by both the photographic and G-M counter methods. The corrected patterns were subjected to a Fourier analysis to obtain the electron density distribution function for the liquid. In addition to showing the C-Cl and Cl-Cl distances within the molecule, the intermolecular distances and concentrations are indicated as well. The latent heat of vaporization has been calculated from the distribution function and found to be in reasonably good agreement with the measured value.

INTRODUCTION

CARBON tetrachloride has the distinction of having been among the first polyatomic molecules subjected to an early structural analysis by means of diffraction methods. X-ray and electron diffraction studies^{1,2} of the vapor have shown the molecular structure to be tetrahedral, having a central carbon atom surrounded by four equidistant chlorine neighbors. The most recent electron diffraction investigations³ give as the Cl-Cl distance 2.98Å from which the C-Cl distance of 1.83Å may be derived. A qualitative picture of the liquid structure has been obtained⁴ by comparing the x-ray diffraction pattern of the liquid with a calculated pattern which assumes a mercury-like (close-packed) molecular distribution.

A determination of the liquid atomic structure as characterized by the atomic distribution function cannot in general be carried out with a high degree of accuracy for other than the monatomic liquids. This is due largely to the unknown natures of the exact molecular scattering factors whereas the monatomic scattering factors are well known.⁵ Many polyatomic liquids have been investigated and approximate atomic distribution functions obtained by assuming (1) that the liquid is essentially monatomic,⁶ which is justified in such cases where the

scattering power of one type of atom is large compared to that of the other atoms (C_6H_6 , H_2O , etc.) or (2) where the molecular scattering factor can be approximated by a sum of the individual atomic scattering factors.

The second method seems to offer the best approach to a structural analysis of carbon tetrachloride for the scattering power of the Cl atom is less than three times that of the C atom. Also, the tetrahedral molecular structure should show enough spherical symmetry to justify using the second approximation. Thus, an analysis based on the x-ray diffraction pattern of the liquid should result in an electron distribution function which shows, in addition to the interatomic Cl-Cl and C-Cl distances, the intermolecular concentrations and distances as well.

EXPERIMENTAL

The x-ray diffraction patterns used in this study were obtained by allowing a beam of

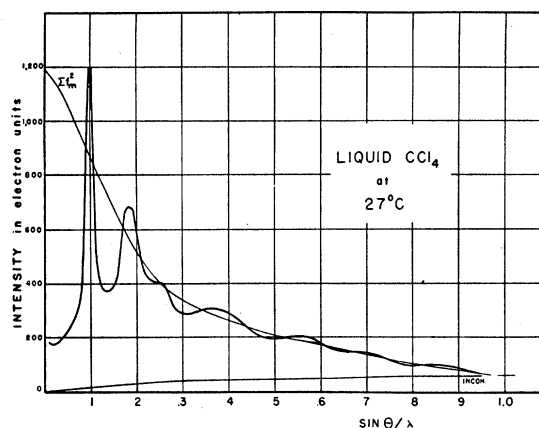


FIG. 1. Corrected x-ray diffraction pattern of liquid CCl_4 at 27°C .

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¹ P. Debye, L. Bewillogua, and F. Ehrhardt, *Physik. Zeits.* **30**, 84 (1929).

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³ S. B. Hendricks, L. R. Maxwell, V. L. Mosley, and M. E. Jefferson, *J. Chem. Phys.* **1**, 549 (1933).

⁴ H. Menke, *Physik. Zeits.* **33**, 593 (1932).

⁵ A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, New York, 1935).

⁶ J. Morgan and B. E. Warren, *J. Chem. Phys.* **6**, 66 (1938).

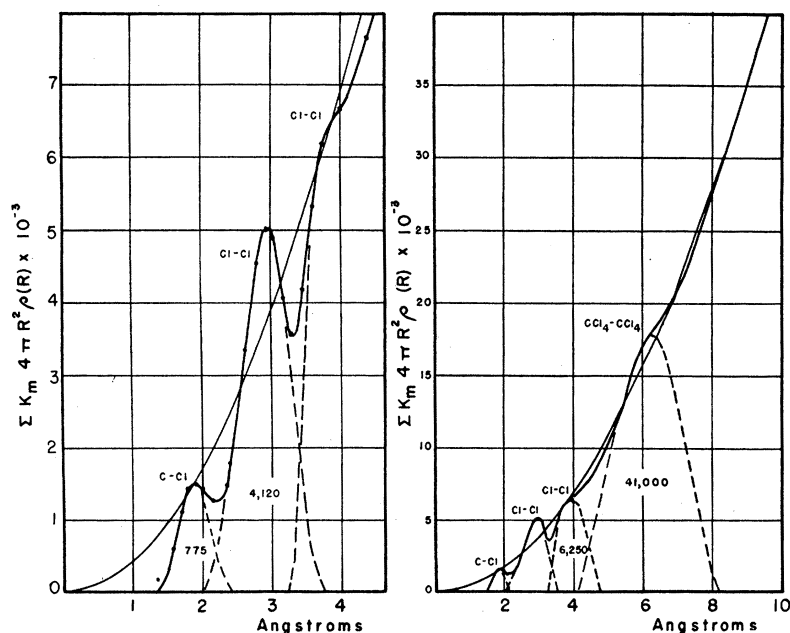


FIG. 2. Electron distribution function of liquid CCl_4 showing the interatomic C-Cl and Cl-Cl concentrations and distances, as well as the intermolecular CCl_4 - CCl_4 structure.

monochromatic x-rays (rocksalt reflected) of 0.71Å wave-length to fall upon a cylindrical sample of the liquid. The diffracted x-rays were recorded photographically or by means of a Geiger-Mueller counter. A Pyrex glass capillary having walls 0.02 mm thick and a diameter of 0.94 mm was filled with chemically pure CCl_4 and sealed off at atmospheric pressure for use as a sample. Suitable diffraction photographs were recorded in 22 hours by use of a camera of 5.377-cm radius and a high intensity x-ray tube.⁷ These diffraction patterns of the liquid at 27°C have been investigated to a value of $\sin \theta/\lambda = 1.1$ and show seven diffraction maxima in this region.

The liquid small angle scattering was recorded with the G-M counter method. In this, the sample was held at the center of an evacuated camera which in turn was mounted at the center of an x-ray spectrometer, the general set-up being quite similar to that used for liquid argon.⁸ Patterns obtained in this manner showed five distinct peaks; the sixth was obtained only with

difficulty since the weak scattered intensity in this region presents a probable error in counting of nearly the same magnitude as this prominence. No attempt was made to find the seventh peak. When compared over the same regions, both methods of detecting the scattered x-rays yield very nearly the same diffraction pattern. Figure 1 shows the corrected x-ray diffraction pattern formed by combining the small angle pattern as obtained by the G-M counter method with the large angle pattern recorded photographically. The experimental pattern has been corrected for polarization and absorption in the sample, the incoherent scattering has been subtracted, and the intensity is plotted in terms of electron units per molecule.

As will be explained in detail in the next section, an attempt has been made to correlate the position of the first diffraction peak with the intermolecular distance. In order that this correlation may be checked in an approximate manner, the sample was heated to a temperature of about 240°C under a calculated pressure of 26 atmos. Under these conditions of pressure and temperature the position of the first peak was again observed by the G-M counter method.

⁷ A. Eisenstein, *Rev. Sci. Inst.* **13**, 208 (1942).

⁸ A. Eisenstein and N. S. Gingrich, *Phys. Rev.* **62**, 261 (1942).

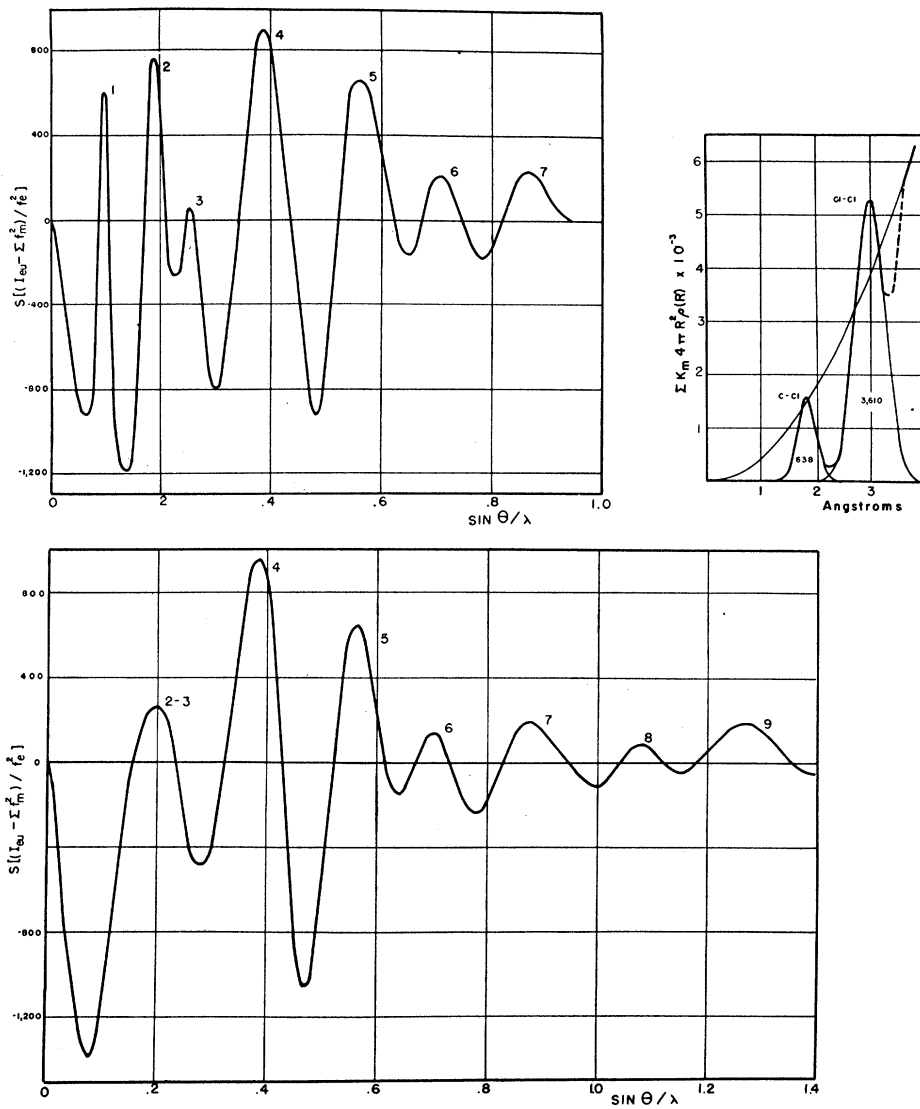


FIG. 3 (A—Upper left) Experimental intensity function. (B—Upper right) Idealized electron distribution. (C—Lower) Intensity function calculated from (B) using Eq. (2).

RESULTS

The fully corrected intensity function of Fig. 1 has been subjected to an analysis to obtain the electron density distribution function by the method⁹ indicated below.

$$\sum K_m 4\pi R^2 \rho_m(R) = \sum K_m 4\pi R^2 \rho_0 + (2R/\pi) \times \int_0^\infty S[(I_{eu} - \sum f_m^2)/f_e^2] \sin SR dS. \quad (1)$$

⁹ B. E. Warren, H. M. Krutter, and O. Morningstar, J. Am. Ceramic Soc. **19**, 202 (1936).

\sum denotes the summation over all the atoms of the molecule; $K_m = f_m/f_e$ or the effective number of electrons in the type m atom; f_m = atomic scattering factor of the type m atom; $f_e = \sum f_m / \sum Z_m$ or the average f per electron; Z_m = atomic number of type m atom; $\rho_m(R)$ = density of atoms of type m at a distance R from a given atom; ρ_0 = mean electron density of scattering matter; R = distance from the origin atom; $S = 4\pi \sin \theta / \lambda$; I_{eu} = intensity of unmodified scattering in electron units per molecule.

The harmonic analysis required to evaluate

the integral was performed by means of a Coradi† analyzer. Figure 2 shows a plot of $\sum K_m 4\pi R^2 \rho_m(R)$ which represents a superimposed electron distribution function such as would be obtained by placing each atom in turn at the origin and summing over all the resulting electron distributions. On the right may be seen the complete distribution curve out to 10A while at the left an enlarged portion of this curve is shown to better illustrate the interatomic structure. The first electron concentration shows a maximum at 1.85A thus representing the C-Cl distance; the second concentration occurs at 2.95A which indicates the interatomic Cl-Cl separation. The manner in which the peaks are drawn in is somewhat arbitrary, especially for those prominences representing the intermolecular distances. Despite this, reasonable agreement has been obtained in comparing the peak areas with the calculated electron concentrations. For example, the measured area of the C-Cl peak $775e^2$ is to be compared to $2(K_C \times 4K_{Cl}) = 648e^2$ where $K_C = 4.60$ and $K_{Cl} = 17.34$. The Cl-Cl peak area of $4129e^2$ compares similarly to $4(K_{Cl} \times 3K_{Cl}) = 3610e^2$. In addition to this interatomic structure, a peak at 3.9A having an area of $6250e^2$ may be interpreted as representing a further Cl-Cl concentration, these Cl atoms belonging presumably to neighboring molecules. By use of the measured area of this peak the number of Cl neighbors surrounding each Cl atom at this distance may be calculated as follows: $8(K_{Cl} \times nK_{Cl}) = 6250$ from which n has the value 2.6 indicating 2 to 3 neighbors in adjacent molecules. The fourth peak at 6.2A represents a concentration which at this large distance is probably due to the molecules themselves, CCl_4-CCl_4 . Under this premise the number of molecular neighbors n may be obtained from $2(K_{CCl_4} \times nK_{CCl_4}) = 41,000e^2$ and has the value of 3.7 or approximately 4.

In the process of evaluating the integral of Eq. (1), the intensity function $S(I - \sum f_m^2)/f_c^2$ must be assumed to be negligible beyond a certain arbitrary point. Experience shows, however, that in most cases the experimental difficulty in evaluating this function at large scatter-

ing angles prohibits setting the vanishing point with a high degree of accuracy.¹⁰ Certain considerations lead to the belief that this intensity function at large angles is determined chiefly by the atomic structure at small values of R or in this case by the C-Cl and Cl-Cl concentrations.

An attempt, based on these assumptions, has been made to calculate the above function for scattering angles to 180° . It has been measured experimentally to 103° , a plot of which is shown in Fig. 3A. An idealized interatomic structure has been chosen, the C-Cl and Cl-Cl peaks being represented by Gaussian error functions having the proper area and position of maxima. Beyond 3.6A the distribution represents that of a completely homogeneous liquid. This structure is shown in Fig. 3B and is used to calculate the intensity function by the use of Eq. (2), derivable from (1).

$$S(I - \sum f_m^2)/f_c^2 = \int_0^\infty (1/R) (\sum K_m 4\pi R^2 \rho_m(R) - \sum K_m 4\pi R^2 \rho_0) \sin SR dR. \quad (2)$$

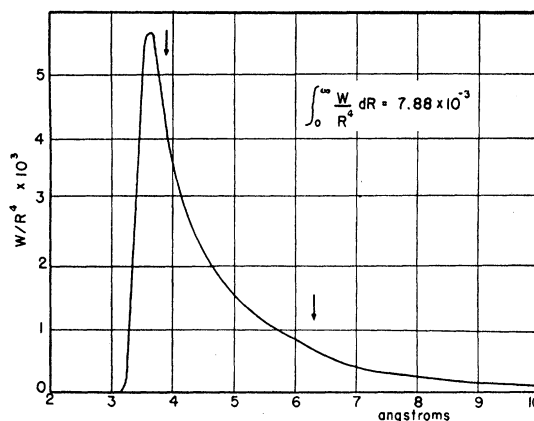


FIG. 4. The function W/R^4 vs. R used in evaluating the latent heat. Arrows indicate the intermolecular Cl-Cl and CCl_4-CCl_4 distances.

The integral was again evaluated with the aid of the Coradi analyzer. Figure 3C shows this calculated function. A comparison of the measured and calculated curves may be most easily facilitated by numbering the maxima, each of which has its counterpart in the diffraction pattern. Peaks 4, 5, 6, and 7 are reproduced in

† The Coradi analyzer was made available for this work by the Aeronautics Department of the Massachusetts Institute of Technology.

¹⁰ N. S. Gingrich, Phys. Rev. **59**, 290 (1941).

both instances with a noticeable fidelity. This is consistent with the basic assumption as to the origin of the scattering at large angle. Peaks 8 and 9 have also been obtained and their magnitudes indicate that the vanishing point chosen for the initial analysis is not truly valid, although probably justifiable.

At small angles the fine structure, peaks 1, 2, and 3, of the experimental function is not present in the calculated function. This is taken to indicate that this fine structure, particularly peak 1, arises directly from intermolecular interference. When the position of this first prominence ($\sin \theta/\lambda = 0.10$) is substituted into Ehrenfest's diffraction equation¹¹ to calculate the recurring distance giving rise to this diffraction peak, the resulting value is 6.2Å. By applying this approximate method of calculation to the position of the first diffraction peak from the liquid at 240°C and 26 atmos. the intermolecular distance is found to be 7.3Å showing an increase proportional to T^3 .

The relationship between the atomic distribution function and the latent heat of vaporization L , has been shown¹² to assume the form

$$L = RT - 2\pi N\rho_0 \int_0^\infty R^2 V(R)(\rho(R)/\rho_0) dR, \quad (3)$$

where R is the gas constant, T the absolute temperature, N Avogadro's number, $V(R)$ the intermolecular potential, $\rho(R)$ the atomic distribution function, and ρ_0 the average molecular density. Heretofore, the application of this relationship has been made only to monatomic liquids, but since the molecular distribution function of CCl_4 is available from the curves of Fig. 2 by subtracting off the interatomic concentrations C—Cl and Cl—Cl, an attempt has been made to evaluate the latent heat. Only the van der Waals' attractive forces will be considered in this calculation in which the form $V(R)$

$= -kR^{-6}$ is assumed. The proportionality constant k has been related to the molecular polarizability α by the equation¹³

$$k = (3/8)hem^3\alpha^3N^3, \quad (4)$$

where N is the total number of electrons in the molecule and h , e , and m have their conventional significance. If one uses for the molecular polarizability $\alpha = 11.2 \times 10^{-24}$ cc, he finds the constant k assumes the value 12.6×10^{-10} erg Å⁶.

The integral of Eq. (3) has been evaluated graphically by plotting W divided by R^4 vs. R , where W , the probability function, equals $\rho(R)/\rho_0$. This curve is shown in Fig. 4, the arrows indicating the intermolecular Cl—Cl and CCl_4 — CCl_4 distances. From this, the contribution to the intermolecular cohesive energy due to the neighboring Cl atoms of different molecules at 3.9Å may be compared to that contributed by the remainder of the molecule. The fact that the maximum of this curve does not correspond exactly to this Cl—Cl distance is probably due to the neglected repulsive terms of the potential function. From the area under the curve, 7.88×10^{-3} , the latent heat of vaporization is found to be 6.24 kcal./mole as compared to the observed value 7.09 kcal./mole. The discrepancy between these values is of the same order of magnitude as that existing between the calculated and experimentally observed electron concentrations. These inconsistencies are believed to arise primarily from the basic assumptions involving the nature of the molecular scattering factor.

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