

THE DIFFRACTION OF X-RAYS BY SUBSTANCES IN THE REGION OF THE CRITICAL POINT¹

WILLIAM H. BARNES

Department of Chemistry, McGill University, Montreal, Quebec, Canada

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INTRODUCTION

Before considering the data at present available on the diffraction of x-rays by substances in the region of the critical point, it is appropriate to review briefly the salient features of the scattering of x-rays by gases and by liquids under conditions not approaching the critical. It is the object of this paper, therefore, to present a brief review² of such x-ray data for gases, liquids, and fluids in the critical region, and to consider the generally accepted theories designed to account for the observed effects, in the hope that this review will be of value particularly to those whose chief interests do not lie in the field of x-ray analysis but who are interested in all phenomena associated with the critical state.

GASES

The most characteristic feature of the scattering of x-rays by gases is the relatively high intensity exhibited at small angles from the direction of the incident beam. Typical intensity curves (reference 17, pages 55 and 69) are reproduced in figure 1a for a monatomic gas (argon) and in figure 1b for a polyatomic gas (carbon tetrachloride), respectively. Without going into details the scattering of x-rays by gases has been satisfactorily explained, largely by Debye, from the following considerations. The intensity of the scattered radiation and its variation with angle depend on the electronic structure of the atoms concerned and, in polyatomic gases, on the relative arrangements and relative sizes of the atoms in the

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² In the preparation of this paper valuable assistance has been derived from Randall's treatise (17), from Wollan's excellent review of "X-ray Scattering and Atomic Structure" (28), and from the papers cited at the end of this review. Figures 1, 2, and 5 are reproduced from Mr. J. T. Randall's book (17) with the kind permission of the author and the publishers. Grateful acknowledgment is also made to Dr. B. E. Warren for permission to use figures 3 and 7, to Professor G. W. Stewart for figures 4 and 6, and to Dr. G. G. Harvey for figure 8.

molecules. The undulatory nature of the curves for polyatomic gases is introduced by the molecular structure. Since the molecules in a gas are separated by comparatively large distances and are characterized by a random distribution and orientation in space, the observed effects are due

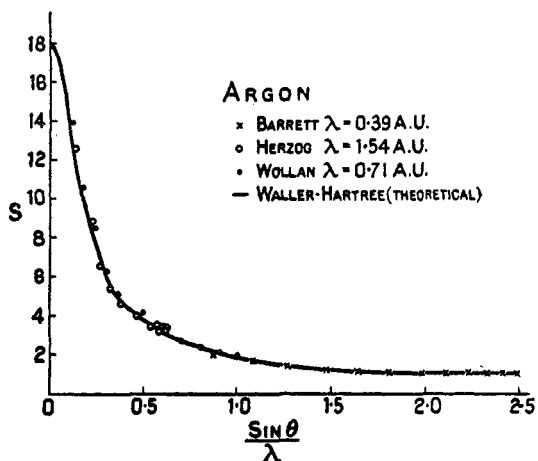


Fig. 1a. X-ray scattering curve for argon (from Randall (17) after Wollan (28))

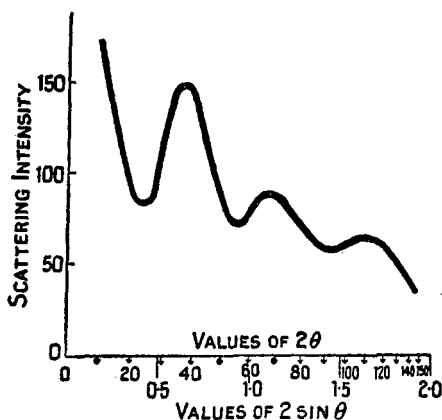


Fig. 1b. X-ray scattering curve for carbon tetrachloride (from Randall (17) after Debye)

solely to interference phenomena among waves scattered by the atoms within the molecules. There is no resultant effect of interference among waves scattered from neighboring molecules. The observed effects, therefore, are intramolecular. Intermolecular interference is negligible. Satisfactory quantitative agreement exists between intensities calculated from

equations based on these conceptions and experimentally observed data. Wollan's review (28) should be consulted for further details.

LIQUIDS

The scattering of x-rays by liquids resembles that by solids much more closely than it does that by gases. There is no doubt that the observed effects are due both to intermolecular and to intramolecular interference. It has frequently been shown, as for example in figure 2 (reference 17, page 116), that the observed intensity curves for liquids closely resemble

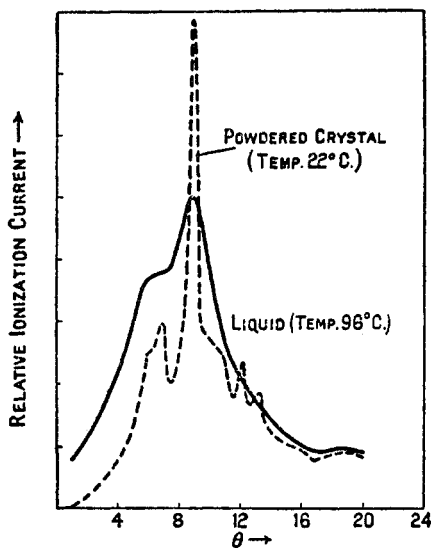


FIG. 2

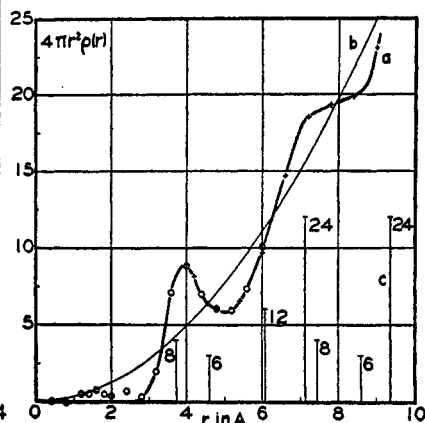


FIG. 3

FIG. 2. X-ray diffraction curves for equal masses of liquid and powdered triphenylmethane (from Randall (17) after Stewart (19)).

FIG. 3. a, radial distribution curve for liquid sodium; b, average density curve for liquid sodium; c, distribution of neighbors in crystalline sodium (Tarasov and Warren (24)).

smoothed-out, diffused curves for the corresponding crystalline solids. A liquid, therefore, appears to possess a "structure," as distinct from the chaos characteristic of a gas. The very nature of a liquid, however, precludes any idea of the comparatively rigid structure obtaining in a crystal. O. Maass has proposed the rather apt term "dynamic structure" to distinguish the condition of the liquid from what he calls the "static structure" of the crystal.

Apart from an attempt by Raman and Ramanathan to account for the scattering of x-rays by liquids in terms of the Smoluchowski-Einstein

treatment of the scattering of visible light, the most important, and at present generally accepted, methods of considering the x-ray data are due to Zernike and Prins, Debye, and Stewart. Zernike and Prins and Debye have approached the problem mathematically, while Stewart has explained the effects descriptively.

The viewpoint of Zernike and Prins and of Debye is that of an essentially homogeneous liquid possessing a "structure" which may be represented by means of a calculable distribution function. The distribution of atoms or molecules throughout the liquid resembles that in the crystal but is, of course, much more mobile. Zernike and Prins evaluate the distribution function empirically and compare intensities calculated therefrom with observed data. The distribution function may then be adjusted until reasonable agreement with experimental results is obtained. Debye calculates the distribution function directly from the experimental data and thus obtains a *probable* distribution. Among the more recent applications of these methods to specific problems may be mentioned the work of Bernal and Fowler (3) on the "structure" of water, of Katzoff (9) on water and certain organic liquids, and of Tarasov and Warren (24) on liquid sodium. Reference to these papers³ will illustrate the type of calculations involved. Figure 3 (from the paper of Tarasov and Warren (24)) shows (a) the average density of sodium atoms surrounding a given atom (given by $4\pi r^2\rho(r)$, where $4\pi r^2\rho(r)dr$ is the number of atoms between distances r and $r + dr$), (b) the average density curve (given by $4\pi r^2\rho_0$, where ρ_0 is the average density of the sample in atoms per unit volume), and (c) numbered ordinates representing the distribution of neighbors in crystalline sodium.⁴ As Tarasov and Warren (24) point out, "It is very evident that the density curve of the liquid [curve (a)] is essentially a smoothed out distribution curve for the crystalline phase." The last paragraph of their paper (24) is pertinent to the present review and is worth quoting *verbatim et literatim*. "The density curve . . . [Fig. 3 (a)] . . . represents the 'structure' of liquid sodium as specifically as this quantity can be represented. It should perhaps be emphasized that this curve is obtained directly from the experimental x-ray curve, without making any *a priori* assumptions as to the atomic arrangement in the liquid. It is evident that there is such a thing as a 'structure' in a liquid, a structure

³ See also "A General Discussion on Structure and Molecular Forces in (a) Pure Liquids and (b) Solutions," *Trans. Faraday Soc.* **33**, 1-282 (1937), particularly pp. 27-45, 105-9, 110-12.

⁴ The ordinate, numbered 6, at $r = 4.6$ should appear at $r = 4.3$, according to a private communication from Dr. Warren. There is also an error of about 2.5 per cent in the scale of abscissae for curve *a* (radial distribution curve), so that all distances read from figure 3a should be 2.5 per cent smaller (Warren: *J. Applied Phys.* **8**, 651 (1937)).

which has to do with the average distribution of neighboring atoms about any one atom. There appears to be no necessity for postulating a crystalline type of structure⁵ in the liquid, to explain a distribution curve such as . . . [Figure 3]."

G. W. Stewart employs a qualitatively descriptive method to explain the observed scattering phenomena. He considers the liquid to be composed of regions in which the molecules possess mutual orientation separated by regions in which the molecules are distributed in a completely random manner as in a gas. This condition is termed "cybotaxis" and the orderly regions of molecular aggregates are called "cybotactic groups." The viewpoint is similar to that embodied in Maass' conception of "regional orientation" (10).

In a recent paper from Stewart's laboratory Spangler (18) has presented the following summary of the "cybotactic" view and of the essential difference between it and that of Zernicke, Prins, and Debye. "It is generally known that liquids show a structure simulating, but by no means approaching, that found in crystals. There are at least two views as to the nature of this 'liquid structure.' One is illustrated by computations, based on a homogeneous conception of a liquid. . . . Another is that the liquid is non-homogeneous but, at any instant, there are enough molecules in groups, simulating crystalline structure, called cybotactic groups, to indicate this temporary and vacillating structure when investigated by x-rays. These groups do not have definite boundaries but are temporary regions of orderliness shading off into regions of little orderliness. The former view is quantitatively successful in matching the experimental curves. The latter view is not so easily subjected to mathematical treatment and is content to point out the simulation of crystal structure for which the theory is well known. Both views are approximate, the former adjusting the view to the theory then to be applied and the latter using the crystal theory already established as an approximate guide to an understanding as to what occurs within the liquid."

Stewart (19, 21) suggests that the cybotactic groups may comprise from twenty-five or fifty to one thousand molecules each, "that they are not perfectly regular, that there is a fluctuating density in the liquid, and that the shape of the molecules cannot be considered as constant" (reference 19, page 985). At ordinary temperatures he estimates that "the percentage of molecules not in such groups at any instant is small. For example, in

⁵ "By a *crystalline structure* one means an array of atoms in which some unit of structure repeats itself identically at regular intervals in three dimensions. In using terms such as 'structure' it is necessary to state precisely whether crystalline structure is meant, or whether the term is being used in a more general sense" (Tarasov and Warren).

the case of ethyl ether at room temperature it appears that perhaps 7 to 10 per cent of the molecules scatter x-rays as would a gas" (reference 19, page 988). It is of interest to note in passing that Stewart considers "liquid crystals" to be composed of aggregates of modified cybotactic groups containing something of the order of 10^6 to 10^9 molecules each (19, 21).

In general the scattering of x-rays by liquids differs from that by gases in the much lower intensities exhibited at small angles (compare figures 1 and 2). It is with this small angle scattering (i.e., within about 15°) that the following section is concerned.

FLUIDS IN THE REGION OF THE CRITICAL POINT

Although the number of substances which have been subjected to x-ray examination in the critical region is at present very limited, the results that have been obtained to date are of very great interest and give promise of important developments in the future. In the laboratory of G. W. Stewart, Noll (16) and Spangler (18) have investigated the scattering of x-rays by ethyl ether, and Benz and Stewart (1) have studied the effects from isopentane. Elsewhere Harvey (8) has obtained some important results from nitrogen at high pressures, and Gingrich and Warren (7) have considered the mathematical problem of interpreting the scattering of x-rays by a fluid at high densities with a modification of the methods of Zernike and Prins.

Typical experimental results obtained by Spangler (18) and by Benz and Stewart (1) are shown in figures 4, 5, and 6. For reference purposes the critical constants of ethyl ether are as follows: T_c , 194.6°C .; P_c , 36.7 kg. per square centimeter; V_c , 3.77 cc. per gram; and for isopentane T_c , 187.8°C .; P_c , 33.9 kg. per square centimeter; V_c , 4.2 cc. per gram (18, 1).

Figure 4 for isopentane at a constant pressure above P_c shows the effect of increasing temperatures and specific volumes (1). As the temperature and the specific volume increase, the scattering intensity curve characteristic of a liquid exhibited at temperatures and specific volumes considerably below the critical (curve 1) changes gradually and continuously into that characteristic of a gas exhibited at temperatures and specific volumes considerably above the critical (curve 9). The same trend appears in similar sets of curves for ethyl ether and isopentane at various constant pressures, the peak in the curve characteristic of a "liquid structure" disappearing at high temperatures and specific volumes. Of particular importance is the fact that at constant pressures above P_c the "liquid structure" (i.e., a peak in the intensity curve) persists above T_c and V_c in both isopentane and ethyl ether. This will be referred to again later.

At a constant temperature (above T_c) the peak diminishes and disappears with increasing specific volume and decreasing pressure (figure 5 (18; 17, page 169)).

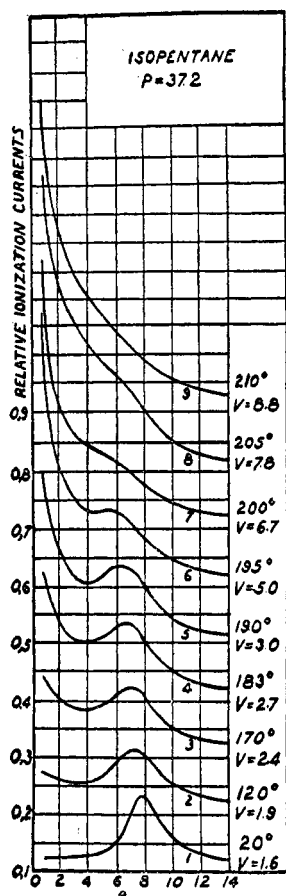


FIG. 4

FIG. 4. X-ray scattering curves for isopentane at a constant pressure of 37.2 kg. per square centimeter (Benz and Stewart (1)).

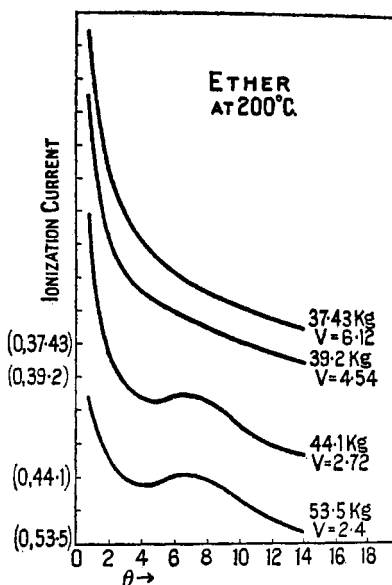


FIG. 5

FIG. 5. X-ray scattering curves for ethyl ether at a constant temperature of 200°C. (from Randall (17) after Spangler (18) and Stewart (19)).

On the other hand, at constant specific volume (above or below V_c) no significant change occurs in the appearance of the curves with change in temperature and pressure (figure 6 (18)). As Spangler (18) points out, this behavior is unique because a variation along any line of the P-V-T

diagram with the sole exception of an isometric produces a marked change in the scattering phenomena observed.

With both ethyl ether and isopentane the persistence of a "structure" above the critical pressure depends most importantly on specific volume and not on the critical temperature. With either fluid above the critical

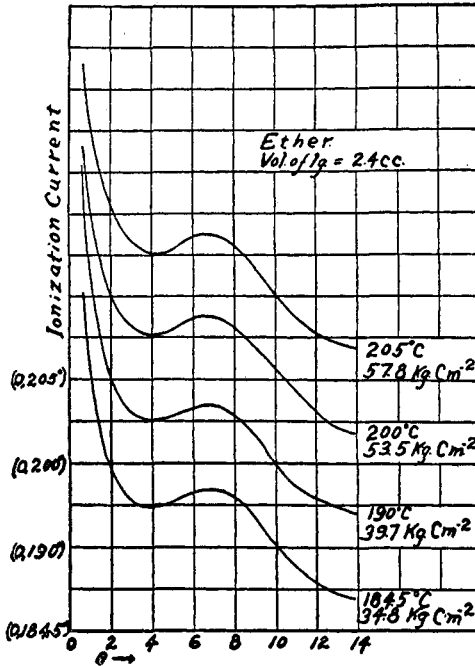


FIG. 6a

FIG. 6a. X-ray scattering curves for ethyl ether at a constant specific volume of 2.4 cc. per gram (Spangler (18)).

FIG. 6b. X-ray scattering curves for ethyl ether at specific volumes greater than 4 cc. per gram (Spangler (18)).

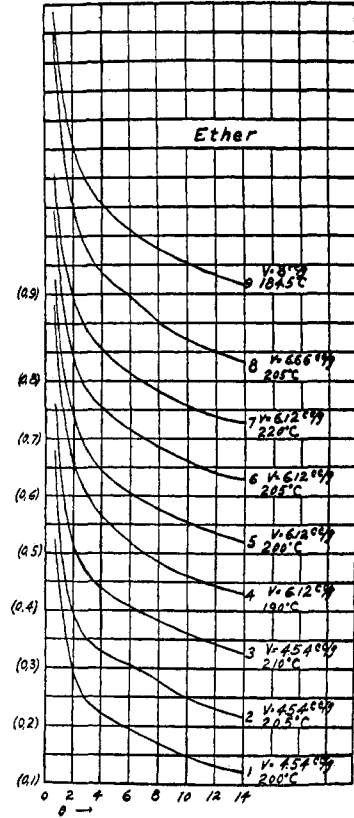


FIG. 6b

pressure, decreasing the specific volume results in a more pronounced peak in the intensity curve.

Benz and Stewart (1) point out that the most striking difference between the results for ethyl ether and those for isopentane is that the "liquid structure" persists to a specific volume much larger (by about 90 per cent)

than V_c in the case of isopentane, whereas it disappears at about the critical volume in the case of ethyl ether. This is somewhat surprising since isopentane has no measurable dipole moment, whereas ethyl ether is definitely polar. Benz and Stewart (1) conclude, therefore, that "the forces arising from polarity seem to be of minor importance in the comparison of the two liquids or in a consideration of the molecular forces."

Spangler (18) and Benz and Stewart (1) explain their results in terms of the cybotactic groups previously mentioned. They consider that, at least "for purposes of discussion, . . . one may regard the disappearance of the typical liquid peaks as the vanishing of any marked cybotaxis" (reference 1, page 706) and "the presence of peaks, with or without gaseous diffraction (i.e., high intensities at very small angles, e.g., the first portions of the intermediate curves in figure 4), is assumed to indicate the formation of some cybotactic groups, the incipient ones, of course, not being in size or structure alike throughout the experiments" (reference 1, page 703). The dependence of the peaks on specific volume is considered to arise from the operation of molecular forces. Since these forces "undoubtedly vary rapidly with the distance of separation of the molecules" (reference 18, page 702), peaks should be present in all curves for specific volumes less than a certain value (characteristic of the substance concerned and not necessarily equal to V_c), whereas at higher specific volumes typical "gas" curves should be obtained the general character of which should be independent of temperature, pressure, and volume (e.g., compare figure 6a and figure 6b). As Spangler says, "This corresponds to the view that, after a certain distance of separation of the molecules has been obtained, the molecular forces are no longer effective in producing orderliness among the molecules" (reference 18, page 702). A careful examination of the various curves in the papers of Spangler (18) and Benz and Stewart (1) shows that they may all be explained satisfactorily in terms of "cybotactic groups," or "regional orientation" of molecules, and changes in size or regularity which such groups, or regions, might be expected to undergo under changing conditions.

Insofar as the x-ray data alone are concerned Gingrich and Warren (7) and Harvey (8) have shown that the hypothesis of "cybotaxis" or "regional orientation" is not essential for the interpretation of the observed scattering of x-rays by fluids at relatively high densities.

Gingrich and Warren (7) have employed a modification of the method of Zernike and Prins by deriving a more suitable equation for the intensity which involves a distribution function more in accord with the density distribution to be expected from Morse's potential energy curves (15). For a monatomic gas the density distribution is such that about any one atom there are no atoms closer than a certain minimum distance; there is

a slight concentration of atoms at this distance, after which the density rapidly becomes constant. For a liquid with approximately close-packed atoms there is the same minimum distance of closest approach, a marked concentration at this distance with a corresponding deficiency just beyond, after which the density distribution curve oscillates about the average density a few times before becoming constant. By suitable and reasonable adjustment of certain factors in the intensity equation Gingrich and Warren (7) have been able to construct curves for ethyl ether at various

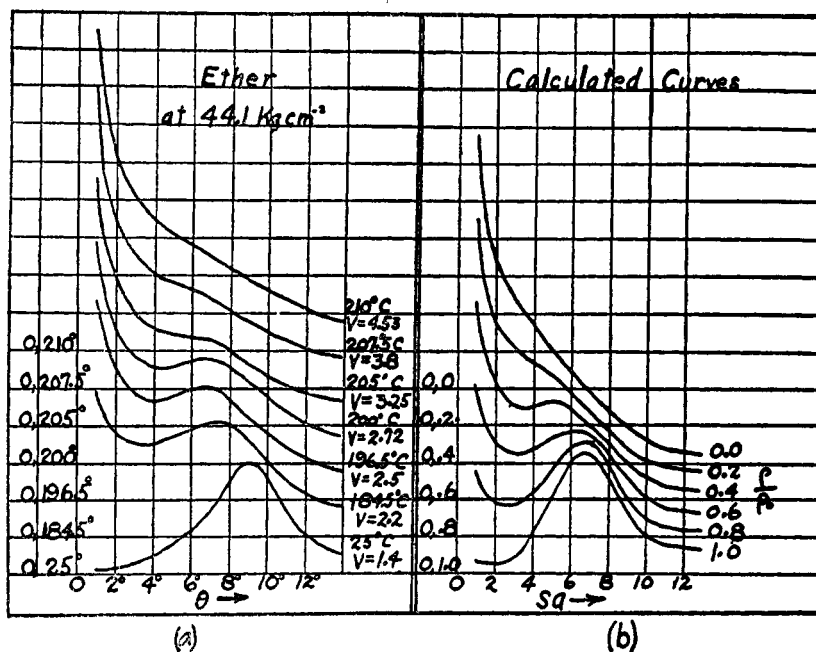


FIG. 7. X-ray scattering curves for ethyl ether at a constant pressure of 44.1 kg. per square centimeter. a, observed (after Spangler (18)); b, calculated (Gingrich and Warren (7)).

densities (figure 7) which are in very satisfactory agreement with those obtained experimentally by Spangler (18).

Harvey (8) has measured the intensities of x-rays scattered at angles less than about 10° from nitrogen at pressures corresponding to 60, 80, and 100 atm. at 0°C. A pronounced peak in the curve was obtained in each instance (figure 8). The critical constants for nitrogen are given in the International Critical Tables⁶ as P_c , 33.5 atm.; T_c , -147.1°C.; d_c ,

⁶ Volume III, page 248.

0.311 g. cm.⁻³. The pressures employed by Harvey, therefore, were all greater than P_c . Harvey shows that his experimental values are in good agreement with theoretical curves based on Debye's equation for a diatomic gas. This assumes no molecules closer to a given molecule than the diameter of the molecular sphere of influence and a uniform density distribution thereafter. Harvey, therefore, concludes, with Gingrich and Warren (7), that the "decrease in scattering at small angles is due merely

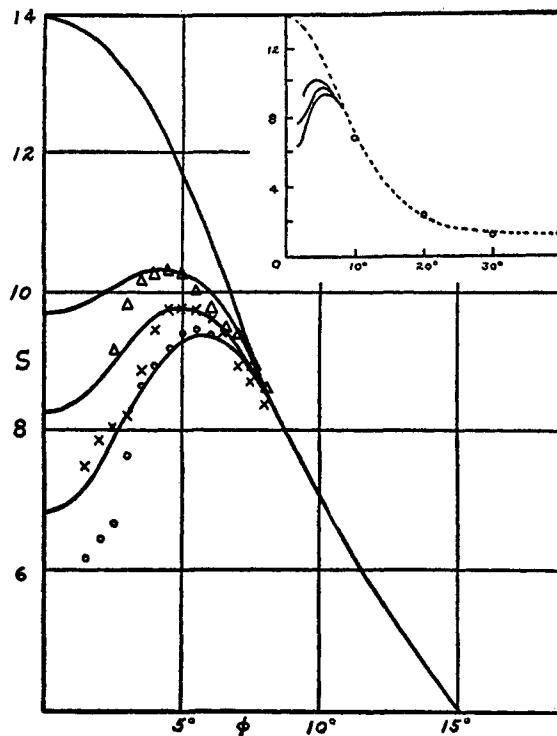


FIG. 8. X-ray scattering curves for nitrogen. Solid curves according to Debye's theory for 0, 60, 80, and 100 atm. Experimental points: Δ , 60 atm.; \times , 80 atm.; \circ , 100 atm. (Harvey (8)).

to the fact that there are a large number of scattering centers within a small space, rather than to any preferred grouping of the molecules, since the existence of such groups would be very unlikely in a gas so far from the liquid state" (reference 8, page 445).

DISCUSSION

It has already been emphasized by Bernal (2) and by Stewart (20) that x-ray scattering data alone are insufficient to determine the "structure"

of a liquid uniquely. This fact is brought out forcibly by the satisfactory nature of each of the two different points of view at present utilized for the interpretation of the x-ray results,—namely, the mathematical treatment in terms of the distribution of the molecules in a liquid with, or without, a non-uniform density distribution, and the qualitative description of the liquid state in terms of cybotactic groups or regional orientation of molecules. From either of these viewpoints a liquid possesses a “structure,” whether it be due simply to an optimum distribution of molecules due to their relatively close proximity to each other, or whether it consists of transitory regions of semi-order merging into and separated by regions of completely random orientation. Furthermore, there is strong evidence for the continued existence of such a “structure” above the critical point as normally defined.

The results of a series of physicochemical investigations by A. L. Clark (5) and, during the past few years, by O. Maass and his coworkers (12, 22, 27, 23, 14, 6, 13, 11) on fluids in the region of the critical point have shown that the assumption of a “liquid structure” and its persistence under certain conditions above the critical temperature is necessary to account for the data obtained. For example, among the interesting facts which have emerged from Maass’ investigations are the following: When ethylene, dimethyl ether, or propylene is heated above T_c a difference in density between the regions above and below that where the meniscus disappears persists to temperatures considerably above T_c . This has been shown not to be due to a gravitational or temperature gradient effect. Furthermore, when the gas is cooled from very high temperatures where a uniform density exists, no density difference is reestablished until the meniscus reappears. These results indicate that a “liquid structure” persists above T_c when the approach is from lower temperatures, but that when the approach is from a higher temperature this “structure” does not become evident until an appreciably lower temperature is reached than that at which the “structure” previously was broken up. This is in agreement with the well-known fact that it is more difficult to establish order in a system than it is to create chaos. It has also been shown that the time required to establish equilibrium in the critical region along an isobar is greater when a point is approached from high temperatures than it is when the fluid is initially at lower temperatures. Other results have shown that a marked difference in the dielectric constants of fluids between the liquid and vapor regions persists above the critical temperature and follows the density differences mentioned above. Further evidence for the persistence of the “liquid structure” is to be found in the shape of the sorption curves for dimethyl ether and propylene, respectively, on

alumina. For further details reference should be made to the original papers (12, 22, 27, 23, 14, 6, 13, 11).

A density difference above the critical temperature has also been observed by Traube (26) and Teichner (25), and H. L. Callendar (4) has presented strong evidence for a discontinuity of state above T_c in the case of water-steam. For example, on the total heat versus pressure diagram the steam saturation line does not coincide with the water saturation line, and on the density versus temperature curves the water density curve does not meet the steam density curve, until a temperature of about 380.5°C. is reached in each case, whereas T_c is equal to 374°C.

The x-ray data, therefore, are in agreement with physicochemical evidence that a liquid must possess a "structure" as distinct from the state of disorder characteristic of a gas. At the present time the two theories which appear to be in best agreement with the various observations available are those already outlined. The fact that the observed scattering of x-rays by fluids in the critical region can be accounted for satisfactorily in terms of the possible distribution of molecules relative to one another does not automatically preclude preferred orientation of molecules in more or less discrete regions. The results of Harvey (8) on nitrogen constitute the only positive experimental evidence apparently against the conception of cybotactic groups being necessary to produce the x-ray scattering observed. Further experiments on other gases at high pressures but at temperatures far removed from T_c , therefore, are urgently needed. On the other hand the results from Maass' laboratory, particularly those on densities and on the times required for equilibrium conditions to be established, are very difficult to understand from the point of view of a mere distribution function without any orientation factor. These results would seem to be more reasonable if the appearance and disappearance of a "liquid structure" involved not only a disintegration and formation of a preferred coördination number of molecules but, in addition, the disruption and reformation of groups having a mutually established direction of preferred orientation.

More x-ray data are required on other substances in the region of the critical point. Of particular interest would be the correlation of data on the scattering of x-rays by ethylene, propylene, and dimethyl ether with the results of Maass' investigations. These three substances have critical constants apparently suitable for the application of the technique and type of apparatus developed by Stewart. Their polarity increases in the order named, and in view of the results on ethyl ether (18) and isopentane (1) a systematic study of substances with various dipole moments would be of great importance. It would be interesting to know whether the prolonged

persistence of the "liquid structure" in isopentane as compared to ethyl ether is due perhaps to a peculiarity of the molecules concerned or whether it is really caused by the suggested lack of importance of polarity as a factor influencing the "liquid structure." If the latter suggestion is substantiated, then regional orientation presumably would involve the operation of non-uniform van der Waals forces.

In view of the density hysteresis effect observed in Maass' experiments an exceedingly interesting study could be made of the scattering of x-rays by ethylene at various temperatures approaching and passing the critical temperature and then at corresponding temperatures in the reverse order.

In conclusion, therefore, it is evident that liquids do possess a "structure" which persists under certain conditions above the critical temperature. This "structure" may consist simply of a preferential distribution of molecules throughout the fluid or of regions of preferred distribution and orientation. The results of Harvey favor the former view, the results of Clark and of Maass favor the latter. Interesting developments, therefore, may be expected in the future from further physicochemical investigations and from a more extended and directed examination of the diffraction of x-rays by substances in the region of the critical point.

REFERENCES

- (1) BENZ, C. A., AND STEWART, G. W.: *Phys. Rev.* **46**, 703-6 (1934).
- (2) BERNAL, J. D.: *Trans. Faraday Soc.* **29**, 1076 (1933).
- (3) BERNAL, J. D., AND FOWLER, R. H.: *J. Chem. Phys.* **1**, 515-48 (1933).
- (4) CALLENDAR, H. L.: *Proc. Roy. Soc. (London)* **A120**, 460-72 (1928); *World Power* **11**, 11-16 (1929).
- (5) CLARK, A. L.: *Trans. Roy. Soc. Canada* **III**, **9**, 43-67 (1915); **III**, **18**, 329-38 (1924).
- (6) EDWARDS, J., AND MAASS, O.: *Can. J. Research* **12**, 357-71 (1935); **13**, 133-39 (1935).
- (7) GINGRICH, N. S., AND WARREN, B. E.: *Phys. Rev.* **46**, 248-51 (1934).
- (8) HARVEY, G. G.: *Phys. Rev.* **45**, 848-9 (1934); **46**, 441-5 (1934).
- (9) KATZOFF, S. J.: *J. Chem. Phys.* **2**, 841-51 (1934).
- (10) MAASS, O.: *The Liquid State of Aggregation* (chapter IV of *A Treatise on Physical Chemistry*, edited by H. S. Taylor, Vol. I, pp. 107-46). D. Van Nostrand Co., New York (1924).
- (11) MAASS, O., AND GEDDES, A. L.: *Phil. Trans.* **A236**, 303-32 (1937).
- (12) MAASS, O., AND SIVERTZ, C.: *J. Am. Chem. Soc.* **47**, 2883 (1925).
- (13) MARSDEN, J., AND MAASS, O.: *Can. J. Research* **B13**, 296-307 (1935); **B14**, 90-5 (1936).
- (14) MORRIS, H. E., AND MAASS, O.: *Can. J. Research* **9**, 240-51 (1933).
- (15) MORSE, P. M.: *Phys. Rev.* **34**, 57-64 (1929).
- (16) NOLL, F. H. W.: *Phys. Rev.* **42**, 336-9 (1932).
- (17) RANDALL, J. T.: *The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids and Gases*. Chapman and Hall, London (1934).

- (18) SPANGLER, R. D.: *Phys. Rev.* **46**, 698-703 (1934).
- (19) STEWART, G. W.: *Trans. Faraday Soc.* **29**, 982-90 (1933).
- (20) STEWART, G. W.: *Trans. Faraday Soc.* **29**, 1077 (1933).
- (21) STEWART, G. W.: *J. Chem. Phys.* **4**, 231-6 (1936).
- (22) SUTHERLAND, H. S., AND MAASS, O.: *Can. J. Research* **5**, 48-63 (1931).
- (23) TAPP, J. S., STEACIE, E. W. R., AND MAASS, O.: *Can. J. Research* **9**, 217-39 (1933).
- (24) TARASOV, L. P., AND WARREN, B. E.: *J. Chem. Phys.* **4**, 236-8 (1936).
- (25) TEICHNER, G.: *Ann. Physik* [4] **13**, 595-610 (1904).
- (26) TRAUBE, I.: *Z. anorg. allgem. Chem.* **38**, 399-402 (1904).
- (27) WINKLER, C. A., AND MAASS, O.: *Can. J. Research* **6**, 438-70 (1932); **9**, 65-79, 610-12, 613-29 (1933).
- (28) WOLLAN, E. O.: *Rev. Modern Phys.* **4**, 205-58 (1932).

SYMPOSIUM ON THE LESS FAMILIAR ELEMENTS

In addition to the papers printed in this Journal¹ the program of the Second Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society on "The Less Familiar Elements," held at Cleveland, Ohio, December 27, 28, and 29, 1937, contained the following papers. References are given for such of these papers as have been published; for some others the probable medium of publication is listed.

- General Introduction to the Symposium. H. S. Booth, Western Reserve University, Cleveland, Ohio.
- The Non-terrestrial Occurrence of the Less Familiar Elements. J. Papish, Cornell University, Ithaca, New York.
- Occurrence of the Less Familiar Elements in Everyday Materials. B. F. Scribner, National Bureau of Standards, Washington, D. C. (Probably to be published in *Industrial and Engineering Chemistry, Analytical Edition*.)
- Economics of Some of the Less Familiar Elements. H. Conrad Meyer, Foote Mineral Company, Philadelphia, Pennsylvania. (*Ind. Eng. Chem.* **30**, 431 (1938).)
- The Carbonyls of the Less Familiar Elements. Arthur A. Blanchard, Massachusetts Institute of Technology, Cambridge, Massachusetts. (Cf. "Volatile Metal Carbonyls," *Chem. Rev.* **21**, 3 (1937).)
- The Hydrous Oxides of Some Rarer Metals. H. B. Weiser and W. O. Milligan, Rice Institute, Houston, Texas. (*J. Phys. Chem.* **42**, 673 (1938).)
- Newer Developments in Beryllium. C. B. Sawyer and B. R. Kjellgren, The Brush Beryllium Company, Cleveland, Ohio. (*Ind. Eng. Chem.* **30**, 501 (1938).)
- Metallurgy of Tungsten and Molybdenum. Zay Jeffries and W. P. Sykes, General Electric Company, Cleveland, Ohio. (To be published in the *Journal of Chemical Education*.)
- Recent Developments in Tantalum and Columbium. Clarence W. Balke, Fansteel Metallurgical Corporation, North Chicago, Illinois. (*Ind. Eng. Chem.* **30**, 251 (1938).)
- The Platinum Group Metals. Fred E. Carter, Baker and Company, Inc., Newark, New Jersey.
- Indium. Occurrence, Recovery and Uses. R. E. Lawrence and L. R. Westbrook, Grasselli Chemicals Department, E. I. du Pont de Nemours and Company, Cleveland, Ohio. (*Ind. Eng. Chem.* **30**, 611 (1938).)
- Optical Lithium Fluoride. H. C. Kremers, The Harshaw Chemical Company, Cleveland, Ohio. (Probably to be published in *Industrial and Engineering Chemistry*.)
- Organometallic Compounds of Indium. Walter C. Schumb and H. Irving Crane, Massachusetts Institute of Technology, Cambridge, Massachusetts. (*J. Am. Chem. Soc.* **60**, 306 (1938).)

¹ *Chem. Rev.* **23**, 47-191 (1938).

- Gallium. Laurence S. Foster, Brown University, Providence, Rhode Island. (Probably to be published in the *Journal of Chemical Education*.)
- Magnetic Measurements in Rare Earth Chemistry. P. W. Selwood, Northwestern University, Evanston, Illinois. (Probably to be published in the *Journal of the American Chemical Society*.)
- The Use of the Arc Spectra for the Quantitative Determination of the Members of the Rare Earth Group. C. N. McCarty, L. R. Scribner, and Margaret Lawrenz with B. S. Hopkins, University of Illinois, Urbana, Illinois. (*Ind. Eng. Chem., Anal. Ed.* **10**, 184 (1938).)
- The Chemistry of Germanium and its Compounds. Warren C. Johnson, University of Chicago, Chicago, Illinois.
- The Analytical Chemistry of Columbium and Tantalum. Thomas R. Cunningham, Union Carbide and Carbon Research Laboratories, Inc., Niagara Falls, New York. (*Ind. Eng. Chem., Anal. Ed.* **10**, 233 (1938).)
- Distribution of Rhenium. Clarence Hiskey and Loren C. Hurd, University of Wisconsin, Madison, Wisconsin. (To be published in *Industrial and Engineering Chemistry, Analytical Edition*.)
- Behavior of Rhenium in Analysis. G. E. F. Lundell and H. B. Knowles, National Bureau of Standards, Washington, D. C.
- Osmium Tetroxide. Don M. Yost and LeRoy H. Anderson, California Institute of Technology, Pasadena, California. (To be published in the *Journal of the American Chemical Society* as "The Properties of Osmium Tetroxide in Carbon Tetrachloride Solution. The Thermodynamic Constants of Osmium Tetroxide.")
- Use of Less Familiar Elements in Vitreous Enamel Frits. Glenn H. McIntyre, Ferro Enamel Corporation, Cleveland, Ohio. (To be published by the Technical Staff of the Ferro Enamel Corporation, 4150 East 56th Street, Cleveland, Ohio.)
- Use of Less Familiar Elements in Ceramic Pigments. Carl J. Harbert, The Harshaw Chemical Company, Cleveland, Ohio. (Published as "Less Familiar Elements in Ceramic Pigments," *Ind. Eng. Chem.* **30**, 770 (1938).)