The Cybotactic Condition of Ethyl Ether in the Region of the Critical Point

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X-ray diffraction-ionization current curves have been taken at thirty-seven combinations of values of pressure, temperature and specific volume in the neighborhood of the critical point of ethyl ether. The results have been interpreted on the basis of the cybotactic view of molecular organization in liquids. It has been found that the groups are very sensitive to changes in specific volume but show much less dependence on temperature and pressure; that the groups disappear at approximately the same specific volume at various values of temperature and pressure; that groups may appear in the gaseous state; and that beyond a certain specific volume no groups appear and the curves are of the gas type. Using the cybotactic view one secures a rather definite picture of what occurs in fluid in the neighborhood of its critical point.

NOLL[1] reported the first results of x-ray diffraction in ethyl ether when in the region of the critical point. It is generally known[2] 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 the computations, based on a homogeneous conception of a liquid, such as that of Gingrich and Warren[3] to which reference is made in a succeeding paper. Another[4] is that the liquid is nonhomogeneous 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. It is the latter view which is used in this discussion.

In Noll's investigation of what takes place in the transition of gas to liquid only one pressure was used. At this pressure he found that the x-ray diffraction peaks indicative of structure decreased rapidly with temperature and specific volume in the region of the critical temperature and disappeared a few degrees above that temperature. The questions arising and serving as the origin of the present work were: (1) What relation has the critical temperature or either of the other critical constants to the disappearance of the liquid diffraction peaks? (2) What is the most effective single factor in the formation of cybotactic groups, pressure, specific volume, or temperature? (3) Is there any change in the diffraction effect as one goes from below to above the critical temperature if the specific volume remains the same?

EXPERIMENTAL

The major difficulties encountered were the uncorrected differential absorption by the aluminum container, sufficiently accurate temperature measurements, and uniform conditions in the ether specimen. The first difficulty was overcome by making use of double filters;[5] the second and third by modifications of the Noll apparatus.

The arrangement of the x-ray tube, of the Soller slits, and of the ionization chamber was like that previously used in this laboratory.[6] The detail of the apparatus, used to hold and

[1] W. Noll, Phys. Rev. **42**, 336 (1932).
[2] See papers by Stewart and co-workers, Phys. Rev. (1927–34); for a complete review of the literature see Debye, Ergebnisse der tech. Röntgenkunde **2**, 1 (1931).
[3] Gingrich and Warren, Phys. Rev. **45**, 292 (1933).
[4] See for instance, Stewart, J. Chem. Phys. **2**, 147 (1934).
[5] P. A. Ross, Phys. Rev. **21**, 426 (1926); J. O. S. A. **16**, 433 (1928).
[6] Stewart and Morrow, Phys. Rev. **30**, 232 (1927), and subsequent papers.

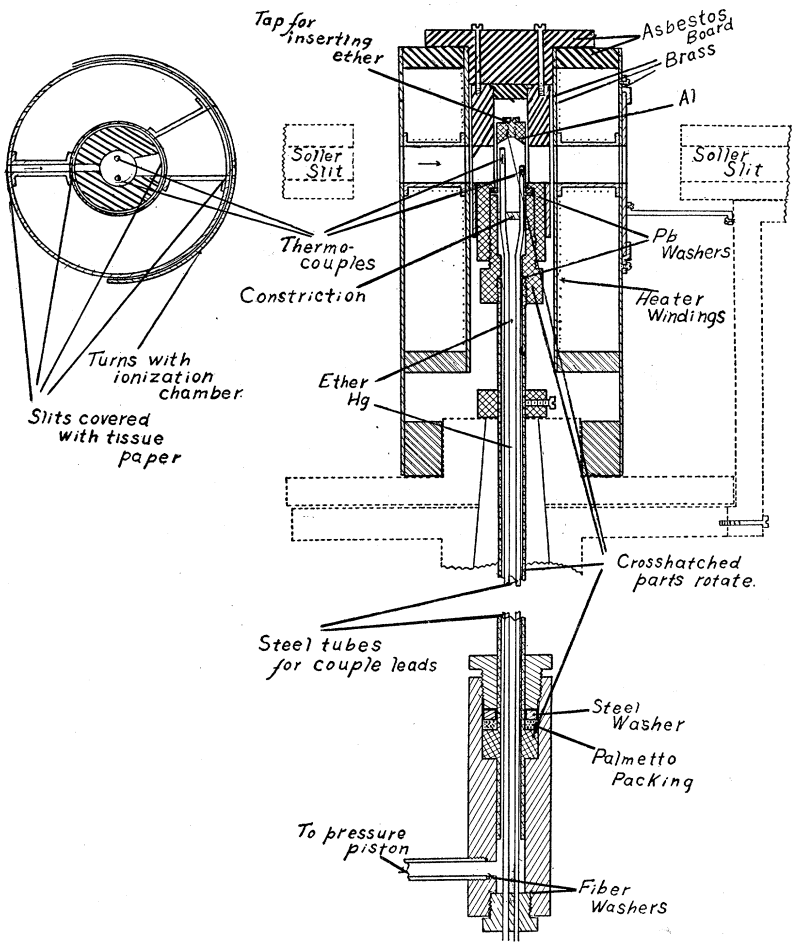

FIG. 1. Horizontal and longitudinal sections of apparatus used to heat and hold ether under pressure.

stir the ether and to permit temperature and pressure measurements, is shown in Fig. 1. The ether was held in an aluminum tube[7] which had an inside diameter of 1.27 cm, and a wall thickness of about 0.027 cm. Two thermocouples were held along the side of the x-ray beam by small steel tubes which remained stationary while the aluminum tube rotated thus stirring the ether. Temperatures were accurate to within 0.5 percent. The pressure was produced and maintained by a dead weight pressure piston of the type used to calibrate pressure gauges and was transmitted to the ether by a column of oil and mercury. Pressures were measured with an estimated accuracy of 0.6 percent. The specific volume was determined by reference to a P–V–T diagram[8] for ether. A reduced copy of the graph used is shown in Fig. 2. The small circles represent points at which diffraction curves were taken. A part of the observations were made with a Compton electrometer using the rate of drift method, and the remainder with a direct current amplifier using an FP-54 tube.[9] A re-

[7] Containers made of magnesium and of Dow metal were tried, but they did not withstand the pressure at the temperatures used here. There seemed to be a decided weakening of each at about 170°C. Containers of a beryllium-aluminum alloy were tried by Noll, but the material was porous so that the ether passed directly through the walls.

[8] Data taken from Schroer, Zeits. f. physik. Chemie **140**, 381 (1929).

[9] L. A. DuBridge, Phys. Rev. **37**, 392 (1931).

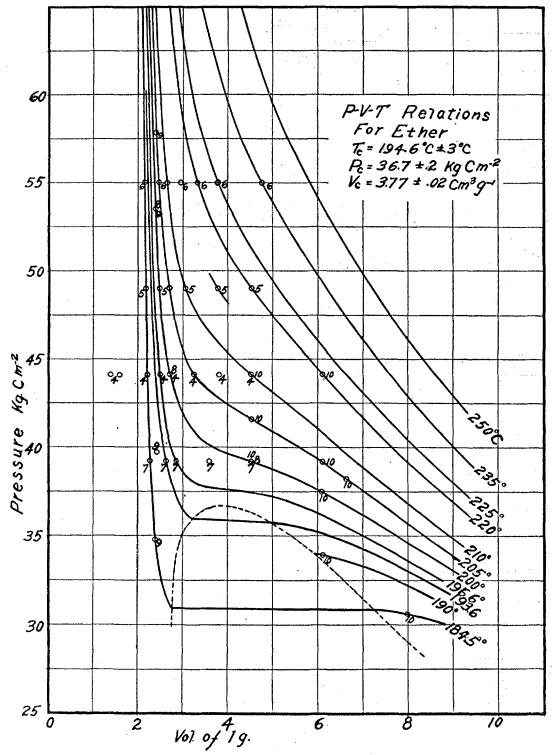

FIG. 2. *P–V–T* relations for ether. The small circles represent points at which observations were made. The numbers at each point refer to the figure in which the data taken at the point are found.

sistance of 8.4×10^{10} ohms as used in the grid circuit. It was found necessary to build a close fitting shield around the tube and the grid connections and dehydrate this with P_2O_5 in order to obtain stability. With the amplifier, observations could be taken with a great saving of time and a large number of tests showed this method as reliable as that of the electrometer.

The filters used were made of $SrCO_3$ and of ZrO_2. They were balanced by taking the diffraction curve of Al and adjusting the relative effective thicknesses by turning one of them about an axis perpendicular to the direction of the x-ray beam, so that the same intensity was obtained through each of them for the $K\beta$ and the general radiation. A curve representing the transmission of the filters when balanced is shown in Fig. 3. The crosses represent the intensity from Al with the $SrCO_3$ and the circles the intensity with the ZrO_2, respectively, in the beam.

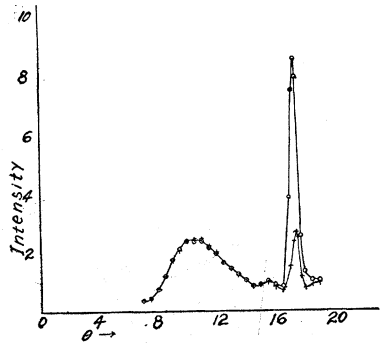

FIG. 3. Transmission through ZrO_2 and $SrCO_3$ filters.

EXPERIMENTAL RESULTS

The results of the experiments are shown in Figs. 4 to 10. θ is the angle between the direction of the incident beam and that of the scattered one. Ionization currents are relative values, yet the comparative values from one curve to another in any figure are as actually measured. The ordinates in the figures are readings with the ZrO_2 filter minus those with the $SrCO_3$ in the beam. To save space, several curves are on each plot, but with zero ordinates shifted as indicated on the left of each graph. Each curve is the average of at least six separate determinations.

CORRECTIONS

All curves were corrected for scattering from air the Soller slits and from the aluminum container. Corrections for natural electrometer drifts were taken care of automatically by the balanced filters. Corrections were made for difference in absorption and for the difference in the number of molecules acting as scattering units at different densities. That is, all the curves in any one figure are corrected so that they represent scattering from the same number of molecules, and thus makes them comparable. A correction for the incoherent scattering was not needed.

DISCUSSION

Several different types of curves appear in Figs. 4 to 10 ranging from those with a very pronounced peak and with little intensity at small angles to those with no peak and increasing

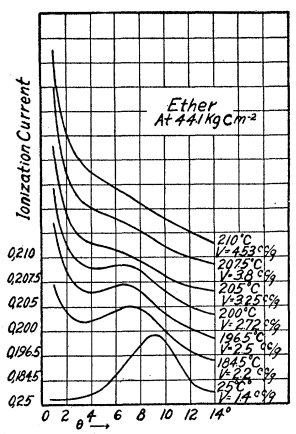

FIG. 4.

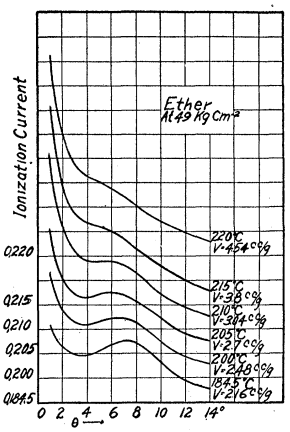

FIG. 5.

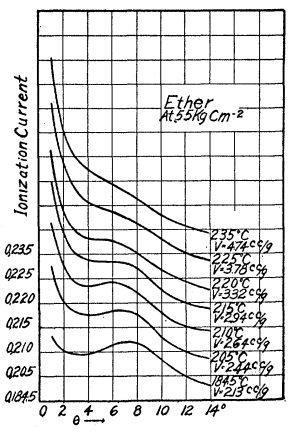

FIG. 6.

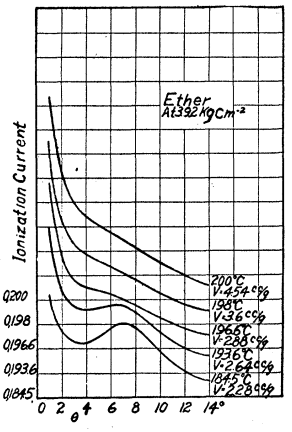

FIG. 7.

FIG. 4. X-ray diffraction of ethyl ether at 44.1 kg/cm². Data taken with amplifier.
FIG. 5. X-ray diffraction of ether at the constant pressure of 49 kg/cm². Data taken with amplifier.
FIG. 6. X-ray diffraction of ether at the constant pressure of 55 kg/cm². Data taken with amplifier.
FIG. 7. X-ray diffraction of ether at the constant pressure of 39.2 kg/cm². Data taken with amplifier.

intensity at small angles. The former are typical liquid diffraction curves, the peaks appearing as a result of the cybotactic molecular grouping of the molecules in the liquid. The latter are typical gas curves signifying a random distribution of molecules. Other curves have a shape which corresponds to neither a liquid nor a gas but appears to be equivalent to a combination of the two types—liquid and gas.

The different groups of curves show the following:

(1) With constant pressure, 44.1 kg/cm², and increasing temperature and specific volume (see Fig. 4) the diffraction curve changes from that typical of a liquid, 25°C curve, Fig. 4, to that typical of a gas, 210°C curve, Fig. 4. Figs. 5, 6 and 7 show the same trend at pressures of 49, 55 and 39.2 kg/cm². Constant λ-ray intensities, the same amplifier sensitivity and correction for density make these curves comparable from figure to figure as well as from curve to curve.

(2) With constant temperature the peak decreases and disappears with increasing specific volume. This is shown for 200°C in Fig. 8.

(3) With constant specific volume no significant change is noticed with increasing temperature and pressure. This is shown for a specific volume of 2.4 cc/g in Fig. 9, for 4.54 and 6.12 cc/g in Fig. 10. This non-variability with constant volume is true as one passes from the liquid phase, the two lower curves, Fig. 9, where the ether is below the critical temperature, to the gaseous phase, two upper curves, Fig. 9, where the ether is above the critical temperature. It is to be noted here that the specific volume is unique in its effect, for a variation along an isometric produces no noticeable change in the diffraction effect, while a variation along an isothermal, Fig. 8, an isobar, Fig. 4, or along

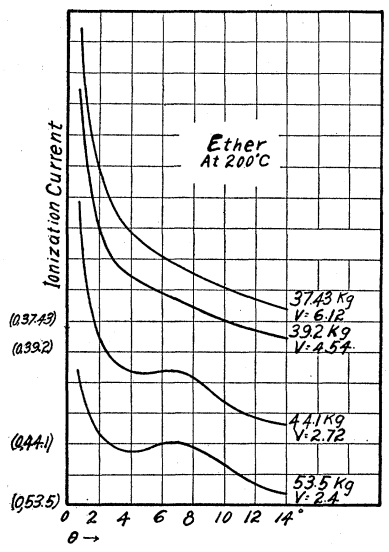

FIG. 8. X-ray diffraction of ether at the constant temperature of 200°C. Data taken with electrometer.

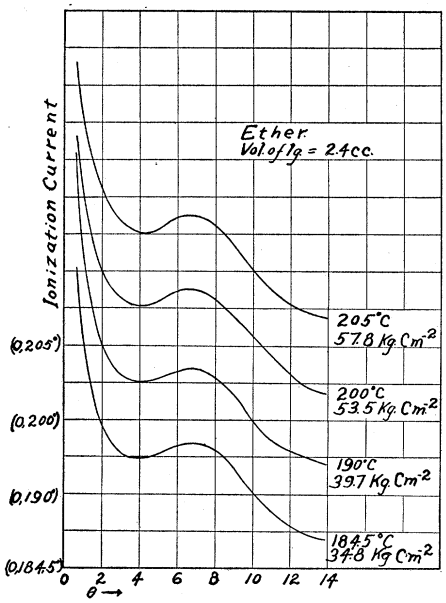

FIG. 9. X-ray diffraction of ethyl ether at the constant specific volume of 2.4 cc/g.

any line except an isometric does produce a change in the diffraction effect. This uniqueness of specific volume arises from the nature of the molecular forces which undoubtedly vary rapidly with the distance of separation of the molecules and thus the effect is not wholly unexpected. The similar curves for like specific volumes may be interpreted as representing the same condition of structure or extent of cybotactic groupings.

(4) Peaks are found with the ether in the gaseous state, i.e., in the region above the critical temperature, provided the pressure is great enough to produce a specific volume of the gas equal to that showing peaks at another pressure.

(5) While the specific volume is the controlling factor in the formation of the liquid structure at volumes less than about 4 cc/g it has no noticeable effect at specific volumes greater than this value, for all of the typical "gas" curves, those corresponding to a specific volume of about 4 cc/g or greater, show the same features independent of temperature, pressure and volume. These curves are shown in Fig. 10. They show that over a wide range of temperature, pressure and specific volume there is no marked alteration in the type of curve

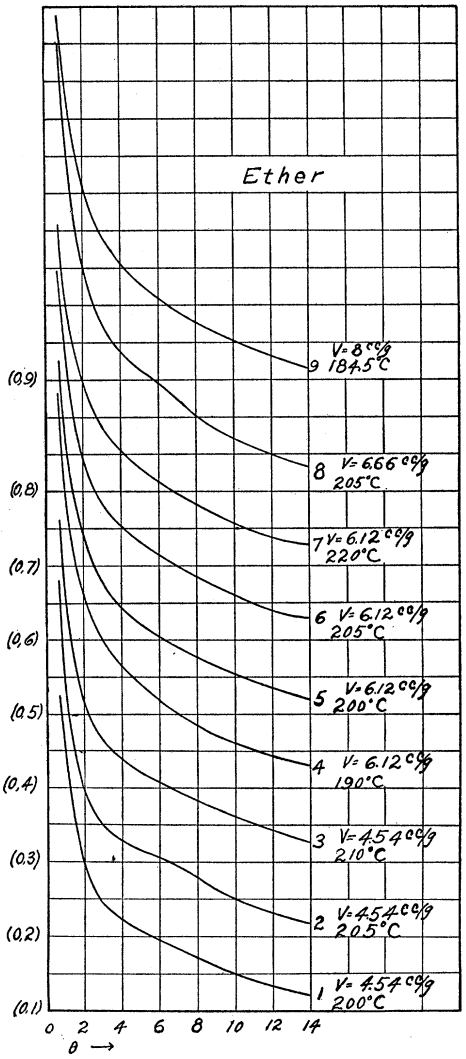

FIG. 10. X-ray diffraction of ether at specific volumes greater than 4 cc/g.

obtained. While one would not expect pressure alone to affect the character of the curve, it is significant that a change in specific volume does not alter it. 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.

(6) At approximately the specific volume of 3.8 cc/g the liquid structure is yet in evidence but at 4.54 cc/g its presence can no longer be certain. At 6.12 cc/g there is no detectable

indication. These facts are brought out in Figs. 4, 5, 6 and 7. The fact that the critical specific volume is 3.77 cc/g does not lead to a definite connection between the critical specific volume and that corresponding to the disappearance of the peaks. The values of both are dependent upon molecular forces but they arise from different circumstances. The liquid structure is wholly in the interior of the liquid, whereas the critical specific volume is the volume at which two phases in equilibrium become possible at the critical temperature.

In the foregoing the presence of peaks, with or without gaseous diffraction, 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. Thus is shown what transpires in the sample as its pressure, temperature and volume are altered. One may not, however, conclude from the size of the peaks the exact extent to which the cybotactic condition prevails. Nevertheless, what occurs on the interior with change in pressure, temperature and volume is now more easily apprehended through the exhibition of the interior through x-ray diffraction.

In conclusion the writer wishes to express his thanks to Professor G. W. Stewart who suggested this problem and under whose direction the work was done.

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The Cybotactic Condition of Isopentane in the Region of the Critical Point

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X-ray diffraction-ionization curves have been obtained, at various values of pressure, volume and temperature, of isopentane near the critical point. The results are: (1) that, as is the case with ethyl ether, the specific volume is unique in determining the extent of cybotactic groups; (2) that the specific volume at which these groups disappear is ninety percent greater than the critical volume; (3) that the internal description of liquefaction above the critical pressure, as the fluid passes from gas to liquid, is the same for both isopentane and ethyl ether.

THE experimental work of Spangler[1] in the foregoing paper enables one to describe what occurs in a fluid near the critical point. The present paper is supplementary thereto, reporting the results of investigation of a second fluid, isopentane, this being selected[2] because the necessary values of temperature, pressure and specific volume were available and because the demands were within the limitations of the equipment, particularly that of a thin-walled cylinder enclosing the fluid.

The apparatus is essentially similar to that of Spangler[1] except that measurements were made entirely with an electrometer and an improved ionization chamber with an interior wire cage to reduce the α-particle ionization. The two sets of equipment were entirely separate but they gave identical results as was demonstrated by repeating some of the ethyl ether data with the isopentane apparatus. The experimental curves have been corrected as described in the foregoing article of Spangler.

RESULTS

Fig. 1 is the P–V–T diagram[3] for isopentane and was used to obtain the critical volume from the other two measured quantities. Figs. 2 to 8

[1] Spangler, preceding article in this journal.

[2] The isopentane was kindly supplied by the research department of the Phillips Petroleum Company. It was 99.7 percent pure.

[3] S. Young, Proc. Phys. Soc. London **13**, 602 (1899).