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

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[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).

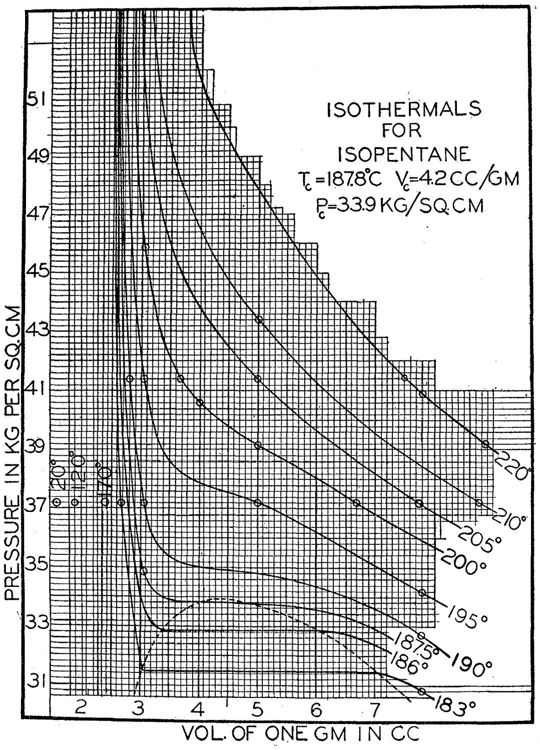

FIG. 1. P–V–T relations for isopentane in the region near the critical point, the observations reported by S. Young in 1899.

give the experimental diffraction curves for isopentane, the pressures, P, being expressed in kg/cm^2, the specific volume, V, cc/g, and the temperature, T, in degrees centigrade. θ is the angle through which the x-rays are diffracted.

Figs. 2 and 3 show the variation with temperature and specific volume at constant pressures of 37.2 and 41.4 kg/cm^2, both above the critical pressure of 33.9 kg/cm^2. There is a gradual change in the character of the diffraction curve with temperature and volume without any peculiarity in the neighborhood of the critical temperature, 187.8°.

In Fig. 4 the great variation in diffraction curves along an isotherm in Fig. 1 is shown by a comparison at 200°C of the curves with four pairs of values of pressures and specific volumes.

Figs. 5, 6, 7 and 8 enable one to compare the diffraction curves for the same specific volume and these show, first, that the curves for the same specific volume are similar and second, that any marked evidence of cybotactic grouping disappears at about 8 g/cc which is 90 percent greater than the critical specific volume.

Discussion

The interpretation of such diffraction curves depends upon the underlying view of the cause of the characteristic diffraction. In the present status of the subject two views are being considered, both of which are alike in requiring a certain regularity of molecular arrangement. One is descriptive, using crystal structure as a point of departure. The other is an attempt to set up models of scattering units that will by calculation give similar curves. Recently Ging-

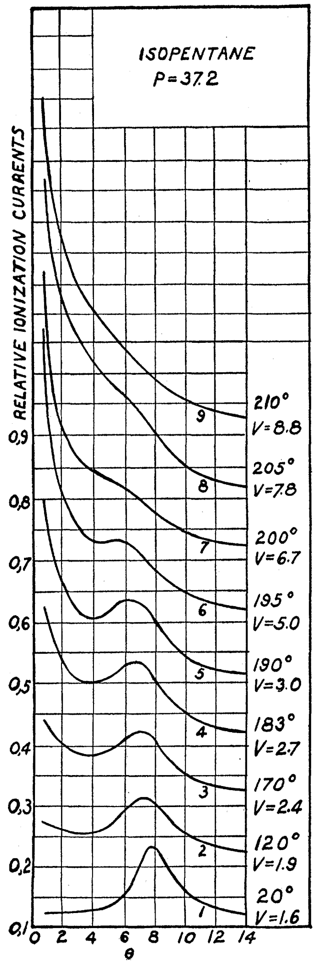

FIG. 2. X-ray diffraction of isopentane at a pressure of 37.2 kg/cm^2.

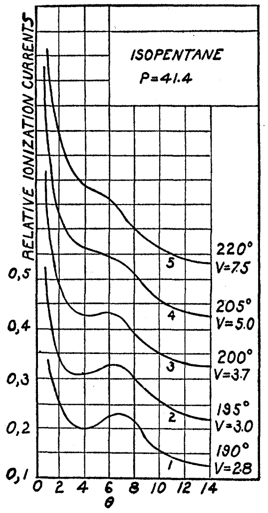

FIG. 3.

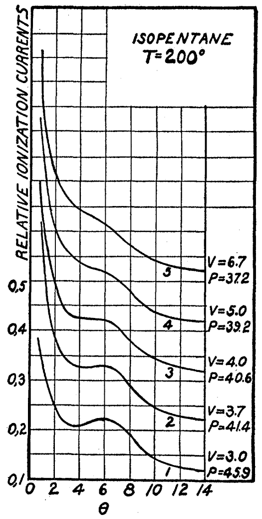

FIG. 4.

FIG. 3. X-ray diffraction of isopentane at a pressure of 41.4 kg/cm².

FIG. 4. X-ray diffraction of isopentane at a temperature of 200°C.

rich and Warren[4] have by the latter method been able to secure diffraction curves closely like those of ethyl ether. As the authors state, they have taken the case of spherical atoms and have made approximations to the density distribution of atoms about any one atom. This treatment for spherical atoms could be rigorous with a complete knowledge of the density distribution. The model of these authors is not the only one possible, nevertheless it is helpful in adding to our confidence in a liquid structure and hence to the descriptive view presently to be mentioned. In this model the molecules are treated as spherical, a smallest distance of approach of molecules is adopted, a concentration of scattering units in a spherical shell is assumed at this distance and then, beginning at a distance eighteen percent greater, the density of the units is regarded as constant throughout the remainder of the fluid. The expression for the scattered intensity is found to be dependent upon the density of the sample. The model is adjusted so that there is fair agreement between the calculated and the observed relative scattering intensities.

The view based upon similarity to crystalline structure, used by Spangler,[1] gives an excellent picture of what occurs in the fluid in the region of the critical point. In these two liquids, at room conditions, the arrangement of molecules simulates the crystalline structure of the substance but a definite arrangement is not maintained on account of instability, permitting mobility and constant shifting of molecules from one degree of regularity of arrangement to another.

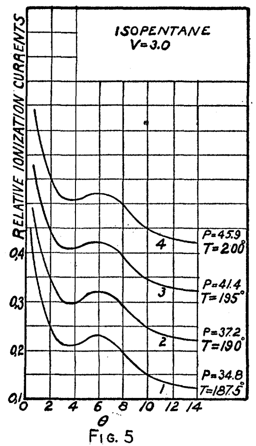

FIG. 5

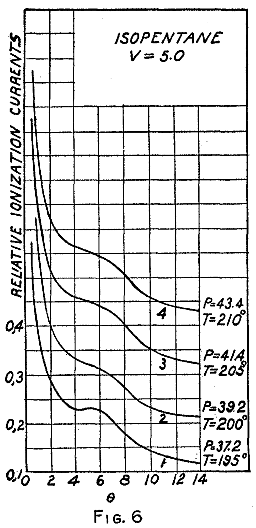

FIG. 6

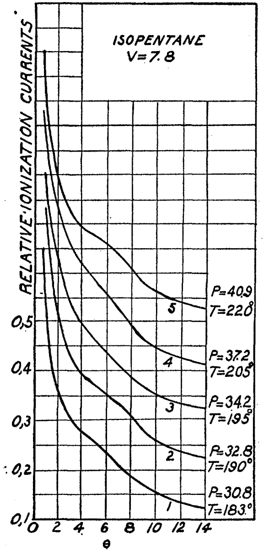

FIG. 7

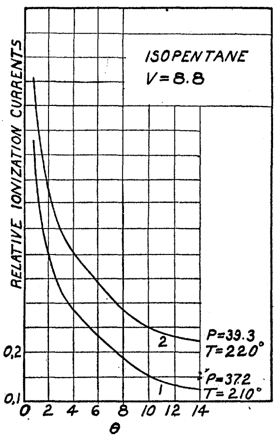

FIG. 8

FIG. 5. X-ray diffraction of isopentane at a specific volume of 3.0 cc/g.

FIG. 6. X-ray diffraction of isopentane at a specific volume of 5.0 cc/g.

FIG. 7. X-ray diffraction of isopentane at a specific volume of 7.8 cc/g.

FIG. 8. X-ray diffraction of isopentane at a specific volume of 8.8 cc/g.

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[4] Gingrich and Warren, Phys. Rev. **45**, 292 (1933).

The liquid diffraction curve of ether and also of isopentane shows but one periodicity and presumably this is produced by an approximate parallelism of molecules. This liquid structure[5] or condition of cybotaxis[6] may be regarded as being more or less in evidence, depending upon the volume and temperature. The diffraction curve at the lowest temperature shown in these two fluids is typical of a liquid having an unsymmetrical molecule. The peak in these curves is gradually metamorphosed into a typical gas curve where the molecules are practically at random and where the variation in intensity depends solely upon the molecular scattering factor. With this descriptive view it is not necessary to regard the fluid as strictly homogeneous at any time. Indeed, at any instant there are regions in which a structure is distinctly more marked and those in which it is less. The former may be called "groups." There are then two ways in which these groups may be thought to change, one in size and the other in regularity. One cannot use the diffraction curves to express these changes quantitatively but qualitatively the variation in the curves is what one would reasonably expect. For purposes of discussion, however, one may regard the disappearance of the typical liquid peaks as the vanishing of any marked cybotaxis.

The gradual formation of aggregates in the process of liquefaction has been suggested many times. In these experiments the internal evidence has been secured. There seems to be no adequate reason, however, to suggest the discontinuance of the use of the critical temperature isotherm as an arbitrary boundary between the "liquid" and the "gaseous" states, for neither of these terms can be used to connote a definite character of the interior of a fluid. These x-ray diffraction experiments give some comprehension of the aggregating phenomenon on the interior and at the same time show that the magnitude of this phenomenon is not determined by the relation of the pressure, volume and temperature to the critical values.

The most striking difference between the results for isopentane and ethyl ether is that, with the former, the cybotactic grouping disappears at a specific volume much larger than the critical volume, whereas in the latter the disappearance occurs at almost the critical volume. Obviously the critical volume has no direct connection with cybotactic groupings, for the former has to do with two phases in equilibrium and the latter with the noticeable formation of cybotactic groups. The difference between the two fluids just stated would at once be attributed to differences in molecular forces. The ether is distinctly polar, having a moment of approximately 1.1×10^{-18} c.g.s. units, whereas the isopentane has no measurable moment. It is the non-polar compound that seems to have the more persistent group-forming ability as the separation of the molecules is increased. Thus 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.

The results with the two liquids are alike in two respects:

(1) In the neighborhood of the critical point and above the critical pressure the formation of cybotactic groups is not dependent upon the critical temperature but most importantly upon the specific volume. An isometric on the $P-V-T$ diagram is the only line designating conditions for diffraction having like typical liquid peaks.

(2) With the pressure above the critical one, the formation of groups increases with decrease in specific volume.

The authors desire to express their thanks to the research laboratory of the Phillips Petroleum Company for the isopentane.

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[5] The term "structure" is used with reference to a liquid without any inference that it is crystalline. "Structure" is a common term already applied as "atomic structure" and "crystal structure" and evident value should indicate its general use.

[6] "Cybotaxis" and "cybotactic" refer, in derivation, to space arrangement in liquids and has been found very convenient in referring to the condition of structure in liquids.