An X-Ray Study of the Structure of Liquid Benzene, Cyclohexane and Their Mixtures*

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Carefully purified benzene and cyclohexane exhibit x-ray diffraction peaks corresponding to preferred spacings of 4.68A and 5.09A, respectively, which are interpreted as the effective thicknesses of the respective rings. Mixtures of these two hydrocarbons give rise to two independent diffraction peaks indicating emulsion-type solutions, in which the disperse phase is too small to show even a Tyndall effect.

INTRODUCTION

STUDIES of the x-ray diffraction effects exhibited by liquids have given much information concerning the nature of the liquid state. These studies, at least in the case of liquids composed of molecules not having spherical symmetry, appear to substantiate Stewart's cybotactic theory.[1]

The spacings corresponding to the diffraction peaks exhibited by liquids composed of disk shaped molecules, such as benzene and cyclohexane, have been shown[2] to correspond to the effective thicknesses of the respective rings or disks. The positions of the diffraction peaks given by these two liquids have been measured also by other workers[3] with fairly concordant results.

Several binary liquid systems have been studied.[4, 5, 6] The earlier work of Wyckoff[6] indicates a pure addition of the diffraction effects of the components. Krishnamurti[4] finds some cases belonging to this class and postulates the coexistence of the original groupings, as: $AAAA$, $BBBB$. For other solutions he finds one halo or diffraction peak for the solution located at a continuously variable position between those corresponding to the components; for this (second) class, groupings such as $ABABAB$, $A_m B$, $A_m B_n$, AB_n are postulated. Meyer,[5] however, finds all of the systems studied by him, excepting phenol-water below the critical solution temperature, belonging to Krishnamurti's second class. Other studies of liquid solutions include, in addition to binary liquid systems, also cases of solid solutes in various solvents, chiefly water.[7]

Krishnamurti[4] suggests that the action of a solution toward the salting out effect (he here refers to aqueous solutions) might serve to indicate to which class the solution belongs. Meyer,[5] however, perhaps more logically, places

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For other reviews see: C. Brucker, Phys. Zeits. **29**, 373 (1928); W. Good, Helv. Phys. Acta **3**, 205 (1930).

[2] G. W. Stewart, Phys. Rev. **33**, 889 (1929).

[3] P. Debye and P. Scherrer, Nachr. Kgl. Ges. Wiss. Göttingen (1916); p. 1.

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C. W. Hewlett, Phys. Rev. **22**, 688 (1922).

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P. Krishnamurti, Ind. J. Phys. **4**, 104 (1928).

C. V. Raman and C. M. Sogani, Nature **119**, 601, (1927).

S. S. Ramasubramanyam, Ind. J. Phys. **3**, 127 (1928).

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C. M. Sogani, Ind. J. Phys. **1**, 357 (1927); **2**, 97 (1927).

E. W. Skinner, Phys. Rev. **36**, 1625 (1930).

[4] P. Krishnamurti, Ind. J. Phys. **3**, 331 (1929); **3**, 507 (1929).

[5] A. W. Meyer, Phys. Rev. **38**, 1083 (1931).

[6] R. W. G. Wyckoff, Am. J. Sci. **5**, 455 (1923).

[7] K. Banerjee, Ind. J. Phys. **3**, 399 (1929).

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H. Shiba and T. Watanabe, Sci. Papers. Inst. Phys. Chem. Research (Tokyo) **10**, 187 (1929).

M. Ishino, S. Tanaka and A. Tsuji, Mem. Coll. Sci. Kyoto Imp. Univ. **13**, 27 (1930).

solutions into the two classes: emulsion type and true solution type. In the former, two distinct types of cybotactic groups are postulated to exist, while in the latter both components enter into the same cybotactic groups, supposedly the groups have about the same composition as the macro-composition of the solution.

There is no reason to doubt the technique, results, or interpretation of any of the workers as there is little duplication in the systems studied by the different workers. However, only qualitative agreement exists between the work of Meyer and of Krishnamurti on the two systems: phenol-water and tetranitromethane-cyclohexane.

APPARATUS

X-radiation

A molybdenum anode Coolidge type x-ray tube (G. E. X-ray Corp.) was operated at 20 milli-amperes and at about 30 kilovolts r.m.s. The usual zirconium oxide in celluloid filter (supplied by G. E. Company) transmits selectively the $K\alpha$ group of molybdenum (7.10A), however, there is an appreciable transmission of the white radiation at about 0.4A. This was corrected for by the use of a balanced strontium oxide filter[8] made by soaking several pieces of blotting paper, free from filler containing heavy atoms, in strontium nitrate solution, drying, and assembling with the use of Duco Household Cement. The whole filter was then impregnated with celluloid.

Spectrometer

The spectrometer was constructed with an horizontal axis of rotation in order that it may be used for certain studies planned for the future. Essential features of the spectrometer are given by Fig. 1. The scale given in the figure applies only in directions parallel to the x-ray beam. Dashed lines have been used to indicate an alternative position of the spectrometer arm. The mirror, lamp and scale used for the measurement of the angles of diffraction have not been indicated. The Soller slits[9] used for both colli-mator and ionization chamber each consist of

[8] P. A. Ross, Phys. Rev. **28**, 425A (1926).
W. C. Pierce, ibid. **38**, 1409 (1931).
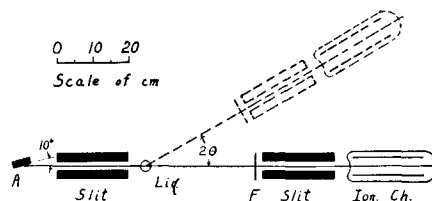[9] W. Soller, Phys. Rev. **24**, 159 (1924).

FIG. 1. Diagram of spectrometer. (Scale applies only to directions parallel to the x-ray beam.) A, Mo anode of Coolidge type x-ray tube. *Slit*, Soller type slit (see text). *Liq.*, Liquid being measured. F, ZrO_2 or SrO filter (see text). *Ion.Ch.*, ionization chamber.

ten parallel slits 19.7 cm long by 0.0795 cm wide by 1.27 cm, with lacquered iron foil 0.0076 cm thick as separators.

Sample holder

The sample holder was made of nickel plated brass with cellophane windows, cemented on with Duco Household Cement. The sample holder could be filled, emptied and washed without removing it from its position on the spectrometer. The spacing (1.3 cm) between the two cellophane windows is definitely less than the optimum thickness (about 1.6 cm) in order to avoid undue filtration effect on the x-ray beam by the sample.

Ionization chamber

The ionization chamber used (see Fig. 2) was blown from Pyrex with a Pyrex window about 0.1 to 0.2 mm thick and was filled with methyl bromide at 74 cm pressure. Electrodes made from
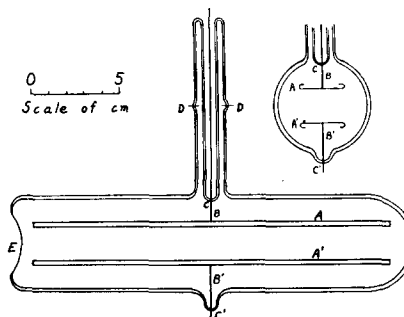

FIG. 2. Ionization chamber. A, A', Electrodes made of 10 mil (0.25 mm) sheet nickel (polished). B, B', 40 mil (1.0 mm) stub nickel leads electrically welded to electrodes (A, A') and to 40 mil tungsten leads used to make the metal-to-Pyrex seals. C, C', Tungsten-to-Pyrex seals. DD', Copper disk-to-Pyrex seals (see text). E, Thin Pyrex window.

polished sheet nickel each 20 cm long by 2.6 cm wide and about 2.0 cm apart were used. A copper disk sealed[10] into the Pyrex side tube provides electrical guarding for the collector electrode and lead. The side tube used for preliminary evacuation, testing for leaks, filling of the chamber is not shown; this was later sealed off.

Vacuum tube electrometer

The vacuum tube electrometer used to measure the ionization currents is shown schematically in Fig. 3. This amplifier uses the General Electric
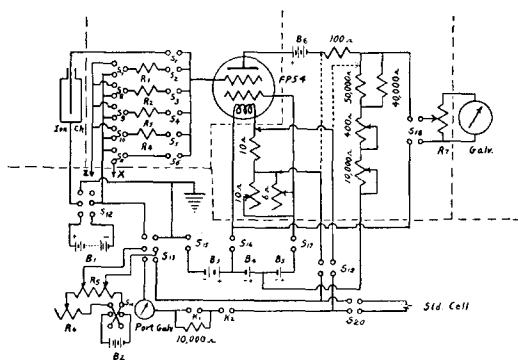

Fig. 3. Vacuum tube electrometer. R_1, 7×10^{11} ohms. R_2, 2.5×10^9 ohms. R_3, 10 megohms. R_4, 1.0 megohm. R_5, L. and N. student potentiometer. R_6, L. and N. dial decade resistance box $9(100+10+1+0.1)$ ohms. R_7, Galvanometer shunt—$10+100+1000+10,000$ ohm fixed resistors in series with an inductance switch connected to all junctions. S_1 to S_6, Sealing wax insulated switches with mercury-copper contacts. S_7 to S_{20}, Switches of suitable mechanical construction—"jack" knife, and Pyrex insulated mercury copper contacts (these in the filament circuit).

electrometer tube—Pliotron FP54.[11] A number of circuits using this tube have been described recently,[12] being used for various purposes. The overall sensitivity of the amplifier here described is about 6×10^{-16} amperes per division using a rugged galvanometer* having a sensitivity of

1.3 × 10⁻⁸ 1.3×10^{-8} amperes per division. This has been accomplished without recourse to rate of deflection technique, usually used for the higher current sensitivities.

The several sections of the circuit have been separately shielded as indicated by the dashed lines. The ionization chamber battery (B_1) is also separately shielded, similarly the several storage batteries (B_2 to B_6) are shielded as a unit. Shielded flexible wires are used between the several shield boxes. All shielding and electrical guarding are connected together and jointly grounded.

Sealing wax insulators made from a tested supply of sealing wax have been used throughout the high insulation part of the circuit. For measuring currents of various magnitudes any one of several grid leaks (R_1, R_2, R_3, R_4) may be selected by suitable switches (S_2 to S_{10}). Resistors supplied commercially† have been found satisfactory for use as grid leaks. Good quality commerical wire wound resistors have been used elsewhere in the circuit, excepting those used for protection purposes only. Potential for the ionization chamber is supplied by a number of large radio B batteries in series (B_1), while other voltages required are supplied by storage batteries of large capacity (B_2 to B_6).

Leads X and Z, normally connected to ground, have been provided for test purposes and the intercomparison of the several grid leaks when using the FP54 as the indicating instrument.[13] The filament current of the FP54 may be measured with the potentiometer (R_5) by the IR drop through a 10 ohm resistor in the filament circuit. When desired the plate (anode) current may be measured by transferring these leads to the 100 ohm resistor in the plate circuit as indicated by the dotted lines.

MATERIALS

Benzene

Benzene was purified by successive treatments with sulfuric acid, treating with mercury, washing with water, drying, distillation, and several fractional recrystallizations. This method is

[10] W. G. Housekeeper, Trans. Am. Inst. Elect. Eng. **42**, 870 (1923).

[11] G. F. Metcalf and B. J. Thompson, Phys. Rev. **36**, 1489 (1930).
A. W. Hull, Physics **2**, 409 (1932).

[12] A. DuBridge, Phys. Rev. **37**, 392 (1931).
Heil and Edwards, Phys. Rev. **43**, 1 (1933).
S. E. Hill, Science **73**, 529 (1931).
F. J. Moles, Genl. Elec. Rev. **36**, 156 (1933).
W. Soller, Rev. Sci. Inst. **3**, 416 (1932).
* Leeds and Northrup—Catalog number 2400a.

† S. S. White Dental Supply Co., 154 W. 42nd St., New York, N. Y.
[13] G. M. Rose, Rev. Sci. Inst. **2**, 810 (1931).

similar to that used by Richards and coworkers.[14] It had a boiling point of 80°C (uncorrected), a freezing point of 5.49°±0.02°C, and an index of refraction ($n_0{}^{20}$) of 1.5008 as determined by an Abbe refractometer.

Cyclohexane

Cyclohexane was thought to contain benzene as one of its impurities, so it was first nitrated (cyclohexane is not affected) with an equal volume of a mixture consisting of two parts of sulfuric acid and one part of nitric acid to one part of water. Then the cyclohexane was given several successive treatments with sulfuric acid, washed with water, dilute sodium hydroxide solution, and several more water washes. At this stage a test portion did not discolor clean mercury upon prolonged shaking. The cyclohexane was then dried with calcium chloride, distilled, and further purified by several fractional recrystallizations. It had a boiling point of 80°C (uncorrected), a freezing point of 6.45°±0.05°C, and $n_0{}^{20} = 1.4262$.

Solutions

Three solutions (or mixtures) of benzene and cyclohexane were made up by volume from the purified components. The refractive index of each was determined at 20°C by means of an Abbe refractometer. Table I gives the composition and refractive index of each. Weight and mol percentages are calculated from the volume percentages and the densities of the components.

TABLE I.

Liquid	Percent Cyclohexane			Refractive Index
	Volume	Weight	Mol	
Benzene	0.0	——	——	1.5008
Solution No. 1	25.0	22.8	21.5	1.4790
Solution No. 2	50.0	47.0	45.2	1.4595
Solution No. 3	75.0	72.8	71.3	1.4413
Cyclohexane	100.0	——	——	1.4262

EXPERIMENTAL PROCEDURE

The amplifier was warmed up by operation for about one hour before use in the measurement of ionization currents. During this period the

[14] T. W. Richards, J.A.C.S. **36**, 1825 (1914); **41**, 2019 (1919).

amplifier was balanced by the adjustment of the variable 10,000 ohm and 400 ohm resistors in the plate circuit, after adjusting the filament current of the FP54 Pliotron to 0.110 ampere. The ionization current for the zero beam was checked periodically using low sensitivity at this time; however, no appreciable change was found over the period of this work. Then for the rest of the warm-up period, the collector electrode was tied to the control grid of the FP54 and the rest of the grid circuit connected for highest sensitivity, i.e., grid connected to ground through R_1 and R_5 in series. After the warm-up period the initial current was balanced out with the use of R_5; this initial current is due in part to the grid current of the FP54 and in part to the natural ionization in the ionization chamber in the absence of x-rays.

Ionization currents were then measured by direct deflection of the galvanometer, waiting a period of one minute between readings. This wait is required since the relaxation time RC, (where R is in ohms and C is in farads the time unit will be seconds) of the grid circuit is longer than the galvanometer period and hence determines the speed of response of the system. This method of operation is speedier than the null method under these conditions (namely, with a grid leak of over 10^{10} ohms), and introduces no errors since the galvanometer deflection-grid voltage curve is linear over the range involved. The drift after the first hour of operation (warm-up) is negligible over a period of fifteen minutes or more under the worst conditions encountered during the work.

At each setting of the spectrometer the intensity of the diffracted x-rays passed by each of the filters was measured by the vacuum tube electrometer and ionization chamber. The ionization current obtained using the strontium oxide filter was then subtracted from that obtained using the zirconium oxide filter giving that due to the molybdenum $K\alpha$ radiation alone. This follows since they have the same transmission factor for the white radiation and the ZrO_2 filter selectively transmits this spectral group. Zero readings in each were obtained by inserting a lead screen in the path of the x-ray beam. At least three checking deflections were obtained at each setting of the spectrometer arm with each filter, and the three sets of readings were averaged.

In measuring the diffraction curves, the spectrometer arm was moved to the several positions. The angles were measured by a lamp and scale, and determined by calculations on the basis of the geometry of the lamp and scale system.

Each diffraction curve was measured both in the direction of increasing and in the direction of decreasing angles. Both of the curves checked within the precision of measurement in all cases. The curves given herewith (Fig. 4) are the average curves obtained from these pairs.
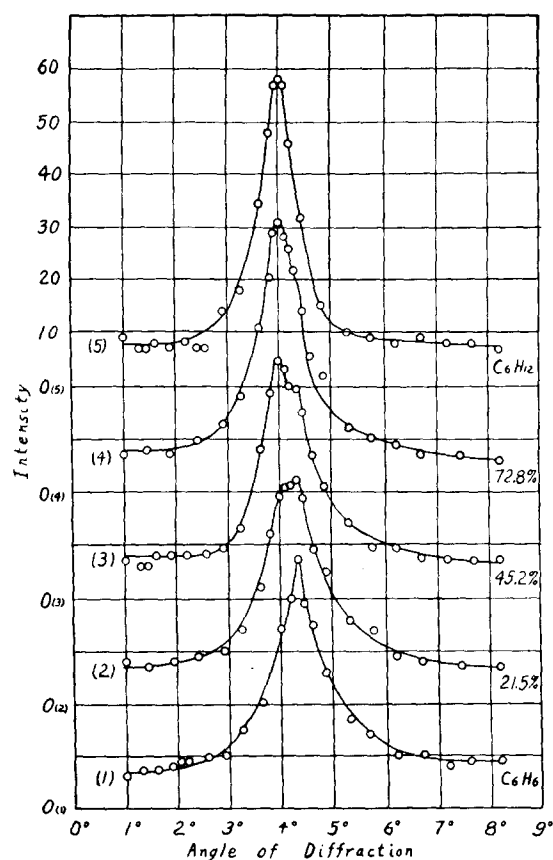

FIG. 4. Diffraction curves.

Over the range included in this study the correction for scattering by the collimator slit and the cellophane windows of the sample holder is negligible as determined by experiment. At smaller angles the correction is not negligible and at larger angles has not been determined.

RESULTS AND DISCUSSION

Diffraction curves for benzene, cyclohexane, and their solutions are given in Fig. 4. All curves have been plotted to the same scale, hence comparisons may be made between the several curves. The angles of diffraction as given are one-half the respective angles of deviations and are thus equivalent to θ in the Bragg formula

$$n\lambda = 2d \sin \theta. \tag{1}$$

The x-ray diffraction curves for the solutions indicate the presence of each peak, although they are close enough together so that the resolution is not perfect. The curves for the 21.5 and 45.2 mol percent cyclohexane solutions show clearly both peaks in both of the original experimental curves for each solution. In the case of the 71.3 mol percent cyclohexane solution, the top of the peak is identical in position with that of the pure cyclohexane while the central portion is asymmetrical with respect to the top. This asymmetry is present in both of the original experimental curves while none of the curves for pure benzene or cyclohexane is asymmetrical in this region. This shows that the diffraction curves for the solutions arise from the combined effects of two preferred spacings, which are identical with those of the two pure components.

Positions of the diffraction peaks for benzene, cyclohexane, and their mixtures are given in Table II. The positions of the secondary peaks

TABLE II.

Liquid	Main Peak θ	d	Side peak θ	d
Benzene	4.33°	4.68A	——	——
Solution No. 1	4.33	4.68	4.00°	5.09A
Solution No. 2	4.00	5.09	4.33	4.68
Solution No. 3	4.00	5.09	4.33	4.68
Cyclohexane	4.00	5.09	——	——

are, of course, not so well defined as those of the main peaks but are given as those of the components from which they arise, with which the curves are consistent. Table III gives the peak limits and widths (half intensity used arbitrarily). The values given in parentheses for the mixtures are the corresponding values for curves calculated by assuming that the diffraction effects of the

TABLE III.[1]

Liquid	Peak limits (at half intensity)				Peak width (at half intensity)
Benzene	3.73°		4.93°		1.20°
Solution No. 1	3.53	(3.50)*	5.04	(5.00)	——
Solution No. 2	3.50	(3.50)	4.78	(4.70)	——
Solution No. 3	3.48	(3.50)	4.63	(4.65)	——
Cyclohexane	3.52		4.48		0.95

* Values in parentheses are from curves calculated by assuming strict addition of the diffraction effects of the components.

[1] Quotation from laboratory notebook.

θ	C_6H_6	C_6H_{12}	Synthetic		
			1-1	1-3	3-1
1.0	7	8	8	8	7
1.5	7	8	8	8	7
2.0	8	8	8	8	8
2.5	9	9	9	9	9
3.0	12	14	13	14	12
3.3	16	21	$18\frac{1}{2}$	20	17
3.6	20	32	26	29	23
3.8	26	45	$35\frac{1}{2}$	40	31
3.9	30	55	$42\frac{1}{2}$	49	36
4.0	33	58	$45\frac{1}{2}$	52	39
4.1	36	55	$45\frac{1}{2}$	50	41
4.2	40	46	43	44	42
4.3	46	39	$42\frac{1}{2}$	41	44
4.4	44	33	$38\frac{1}{2}$	37	41
4.5	38	28	33	31	35
4.6	34	18	26	22	30
4.8	28	15	$21\frac{1}{2}$	18	25
5.0	23	12	$17\frac{1}{2}$	15	20
5.5	16	9	$12\frac{1}{2}$	11	14
6.0	12	9	$10\frac{1}{2}$	10	11
6.5	10	8	9	8	10
7.0	9	8	9	8	9
7.5	9	8	8	8	9
8.0	9	8	8	8	9

Column 1 headed θ represents various selected angles of the spectrometer. Column 2 headed C_6H_6 gives values of the intensity of the diffracted beam for the angles given in column 1. These intensities are read from the smooth curve drawn through the experimental points found for benzene. Column 3 gives corresponding values of the intensity of the diffracted beam from cyclohexane. Columns 4, 5 and 6 give the calculated values for 3 mixtures. In column 4 the values are obtained by adding 50 percent of the values in column 2 to 50 percent of the value in column 3. Column 5 is obtained by adding $\frac{1}{4}$ of the values in column 2 to $\frac{3}{4}$ of the value in column 3. Column 6 is obtained by adding $\frac{3}{4}$ of the values of column 2 to $\frac{1}{4}$ of the value of colume 3. The values in parentheses in Table III come from plots of the values in the last three columns which were then treated as if they were real data.

two components are strictly additive. These differences are more apparent than real as may be shown by plotting the experimental points on top of the synthetic curves. Trial shows no difference in any portion of any of the curves large enough to be significant.

It will be noted that the peak for cyclohexane is distinctly higher and its width is distinctly less than in the case of benzene. There are over seventeen percent less molecules per unit volume of cyclohexane than of benzene, and since the same thickness of sample was used in each case, it means that there were less cyclohexane molecules in the diffracting volume. While the comparative diffracting power of the benzene and cyclohexane molecules acting as diffracting centers is not known, it is probable that the diffracting power of the cyclohexane molecule is not more than about fifteen percent greater than that of the benzene molecule. The sharper peak means that the semi-orderly arrangement in cyclohexane is more orderly than in the case of benzene and that probably a greater fraction of the cyclohexane molecules (more intense diffraction) are included in the cybotactic groupings. It was noticed that during the recrystallization the crystal nuclei of cyclohexane were much more persistent above the melting point than those of benzene. This is consistent with theory.[15]

The spacings corresponding to the diffraction peaks exhibited by benzene and cyclohexane have been shown[2] to be the effective thicknesses of the respective rings. This is an intermolecular spacing as contrasted with an intramolecular spacing.* Hence it may be seen that the cybotactic groups of both benzene and cyclohexane coexist in their mixtures. Thus we may picture benzene-cyclohexane solutions as submicroscopic emulsions. The minimum size of the groups which are able to give rise to regular x-ray diffraction is smaller than the limit of resolution of an ultra-microscope even for the case where the difference of refractive indices is larger than for the liquids used here. The extreme smallness of the cybotactic groups in the present experiments is shown

[15] W. P. Davey, Trans. Am. Soc. Steel Treating (1933).

* If, as it seems unlikely, the peak corresponds to an intramolecular spacing, the following interpretation of the data taken on the solutions is not demanded, but it is still not inconsistent with the data.

by the fact that the ordinary rough tests showed no Tyndall effect in any of the solutions. It is believed that such emulsions are described here for the first time.

The independent existence of the cybotactic groups of benzene and cyclohexane molecules in their solutions may be possibly connected with their deviations from the laws of perfect solutions in very dilute solution. Professor M. R. Fenske and Mr. M. R. Cannon[16] have found that the cryoscopically determined molecular weight of benzene in cyclohexane is nearly twice normal. It is here suggested that some of the cybotactic groups may have a regular enough structure to act as single molecules in their effects on the thermodynamic (vapor pressure connected) properties of solutions, thus making it appear that the solute molecules are associated. True association should give rise to secondary peaks corresponding to distances in the associated molecule such as has been found, for example by Stewart[1, 17] in the case of some polar compounds such as certain of the aliphatic alcohols.

SUMMARY

1. Carefully purified benzene and cyclohexane give x-ray diffraction peaks at 4.68 and 5.09A, respectively.

2. A possible connection between the shape and intensity of the x-ray diffraction peaks given by liquids and the persistence of crystal nuclei above the melting point has been suggested.

3. Solutions of benzene and cyclohexane have an emulsion type structure, in which the disperse phase is considerably too small to be seen with a microscope, and too small to show a perceptible Tyndall effect.

4. A possible connection between the deviations from the laws of perfect solutions and the x-ray diffraction patterns of solutions has been suggested.

5. A vacuum tube electrometer has been designed and tested, which has a direct deflection (or null method if desired) sensitivity of 6×10^{-16} ampere per division.

[16] Private communication, July, 1933.

[17] G. W. Stewart, Phys. Rev. **35**, 296 (1930).