American Academy of Arts and Sciences, with which some of the instruments used in this investigation were purchased.

Summary

1. An adiabatic calorimeter for measuring the specific heats of liquids accurately at elevated temperatures has been described.

2. The specific heats of 15 liquids have been determined over small temperature intervals from 30° to nearly 80°. The liquids are benzene, toluene, ethyl benzene, *o*-xylene, *m*-xylene, *p*-xylene, *iso*-propyl alcohol, ethyl alcohol, *iso*-amyl alcohol, *n*-butyl alcohol, *iso*-butyl alcohol, nitrobenzene, chloroform, carbon tetrachloride and heptane. The results have been recorded as graphs and as empirical equations.

3. Other physical properties of these liquids, related to heat capacity, have been tabulated.

4. The product of specific heat and density is approximately constant (about 0.35 calorie per cc.) for unassociated liquids. This relation is useful in predicting unknown specific heats and in studying the association of liquids.

5. Irregularities in specific heat-temperature curves indicate a change in equilibrium between different kinds of molecules in a liquid.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

X-RAY DIFFRACTION PATTERNS FROM CRYSTALLINE AND LIQUID BENZENE

BY E. D. EASTMAN

RECEIVED JANUARY 23, 1924

Broomé[1] has recently published X-ray diffraction data from powder photographs of crystalline benzene. Shortly before the appearance of his paper similar observations had been completed by the present writer. The more extended study of the crystal structure of benzene of which the latter measurements were to have been a part has been discontinued because its primary object, the determination of the molecular structure of benzene, now appears unlikely to be achieved by this method. The powder data are nevertheless of some interest and value. It is therefore deemed desirable to record here those obtained, especially since the experimental methods by which they were obtained differ considerably from Broomé's, and since certain minor differences in interpretation are indicated, although the two sets of results are in general in good agreement. In addition to the data concerning the crystals, a few observations on liquid benzene have been made and will be discussed.

---

[1] Broomé, *Physik. Z.*, **24**, 124 (1923).

The experimental method which was employed is that due to Hull.[2] The details of its application in the present case follow.

The source of X-rays was a molybdenum target, fine focus Coolidge tube of the "universal" type, operated at about 35 r.m.s. kilovolts and 6 milliamperes by a small transformer. The distance between the two defining slits was 10 cm. Their width was varied in the different experiments. A filter of zirconium oxide (0.05 g. per sq. cm.) with collodion as binding material was placed in front of the first slit. The benzene was contained in a very thin walled glass tube about 1.6 mm. in diameter, 1 cm. from the second slit and 21 cm. from the target. The photographic film, backed by a calcium tungstate intensifying screen, was held in a casette in a half circle of 15.95cm. radius with the tube of benzene as the center. Secondary radiation from the central spot of the film was cut off from the rest of the film by baffles.

The benzene used in the experiments was treated to remove thiophene and showed no appreciable test for this substance after the treatment. It was further purified by distillation and fractional crystallization, the latter being repeated until the desired degree of purity had been obtained, as indicated by the freezing point. The impurities most likely to have been present are toluene, and small amounts of water taken up from the atmosphere during the crystallization. The total amount of impurity in the last fraction was less than 0.2 mole-per cent., since its freezing point was 5.40, as compared with Richards and Shipley's[3] value of 5.493 ° for pure benzene in dry air.

The benzene was frozen and kept below its melting point during the passage of the X-rays by passing over it a stream of cold air. To accomplish this the tube of benzene was surrounded by a thin-walled tube of transparent celluloid connected to a thermally insulated delivery tube from a flask of liquid air directly below it. An electric heating coil was immersed in the liquid air and served to control the rate of evolution of the cold vapor. Suitable arrangements, including two other surrounding celluloid tubes, were used to prevent freezing out of atmospheric water on the cold surfaces. By these devices the benzene could be melted or frozen at will while in the apparatus, and could be maintained for long periods at a temperature low enough to prevent rapid sublimation and growth of large crystals at the expense of smaller. At the same time the benzene was always visible, and the only foreign materials which could cause scattering of the X-rays were glass and celluloid aggregating 0.1 mm. and 0.2 mm. in thickness, respectively.

To assist in securing a disordered arrangement of small crystals the freezing of the benzene was made as rapid as possible, and it was melted and refrozen many times during the long exposures which were necessary. Very often in the freezing supercooling would occur, and crystallization, when it finally took place, would be very rapid throughout the mass. Nevertheless, the crystals obtained in this way were either too large or possessed more or less ordered orientations. This was shown by the irregular character of the diffraction pattern produced in an exposure of 430 hours, during which the benzene was refrozen 25 times. More nearly equal

---

[2] Hull, *Phys. Rev.*, **10,** 661 (1917); **17,** 571 (1921).

[3] Richards and Shipley, THIS JOURNAL, **41,** 2022 (1919).

opportunity of reflection among the various crystalline planes was finally secured by continuous mechanical rotation and up and down displacement (through a distance of 1.5 cm.) of the benzene tube during runs.

Several exposures using slits 1.5 mm. in width were made. The resolution was not high and the lines on these films could be identified without uncertainty caused by imperfect separation only for the larger angles of diffraction. The spacings so obtained agree within the error of measurements with Broomé's results in this region, and will not be given in detail. The measurements upon which most reliance is placed are the results of

TABLE I

OBSERVED AND CALCULATED SPACING OF PLANES, IN ÅNGSTROM UNITS, AND OBSERVED INTENSITIES OF REFLECTION

Observed spacings, d/n −20° (Eastman)	Observed intensities (Eastman)	Observed spacings, d/n −80° (Broomé)	Observed intensities (Broomé)	Calculated spacings d/n (−20°)	Indices of planes	n
..	..	[(5.35)]	20	..	....	...
4.83	80	(4.90)	80	4.83	010	2
4.55	100	4.46	100	4.52	111	1
4.22	5	[(4.13)]	10	4.06	120	1
3.97	20	[(3.90)]	10	3.98	021	1
3.74	15	3.71	60	3.74	100	2
				3.50	001	2
3.50	30	(3.44)	70	3.50	121	1
				3.49	210	1
3.15	50	3.11	90	3.17	102	1
				3.11	211	1
				3.00	112	1
2.98	15	(2.95)	40	2.96	110	2
				2.95	130	1
2.82	15	(2.81)	10	2.84	011	2
2.70	15	2.69	60	2.72	131	1
				2.72	221	1
2.62	15	2.61	50	2.64	122	1
..	..	2.52	40	2.56	101	2
.	..	2.43	50	2.47	212	1
2.40	15	2.38	50	2.43	230	1
				2.41	310	1
		(2.25)	30	2.28	311	1
2.25	5			2.27	013	1
		(2.22)	30	2.26	111	2
				2.25	132	1
2.15	5	2.12	20	2.16	113	1
		2.10	20	2.09	023	1
				2.03	120	2
2.02	10	2.00	60	2.02	123	1
				2.02	302	1
1.94	5	1.91	40	1.93	213	1
..	..	1.86	40	..	...	..
1.82	10	1.79	40	1.83	223	1

an exposure with 0.4mm. slits for 330 hours, during which the benzene was refrozen 30 times. Seventeen lines, uniform in character and of apparently equal intensities on the two sides of the central image, appeared on the film with sufficient intensity for measurement. The positions of the centers of these lines could be reproducibly measured to 1% or better. The planar spacings, (*d* divided by the order, *n*, of the diffraction), corresponding to the experimental pattern are given in the first column of Table I. In calculating these spacings, the average wave length of the $K\alpha$ doublet of molybdenum was taken as 0.710 Å. The estimated intensities of each of the lines appear in the second column, on the basis of 100 for the most intense line. For comparison the figures which Broomé gives for the positions and intensities of the lines in this region are shown in the third and fourth columns of the table.

The density and axial ratios of the crystals are required in the interpretation of the X-ray data. Broomé has determined the density as 1.004 at 0°. The value given by Richards, Bartlett and Hodges[4] appears to be more accurate and has been used in this work. It is 1.0151 g./cc. at the melting point. Broomé's work permits an estimate of the average coefficient of expansion of the crystals between 0° and —80°. From the high probability that the largest expansion occurs in the upper portion of this range, and from analogy with naphthalene and paraffin over similar ranges below their melting points, it is estimated that at the temperature of the above measurements, about —20°, the density is 1.025 ± 0.5%. Groth[5] places benzene in the class of highest symmetry in the rhombic system, and from measurements which he describes as rough approximations only, obtains axial ratios of 0.891 : 1 : 0.799.

As Broomé points out, the positions of the lines in the powder spectrum are in harmony with the ratios given by Groth only if a large number of molecules per unit cell and a peculiar distribution of intensity of reflection among the different planes are assumed. Better agreement with the observed planar spacings and more reasonable intensity relations are found if the first, fifth and sixth lines in Column 1 of Table I are taken as second order reflections from the faces of the unit cell. This procedure would ascribe a minimum of four molecules to the unit cell, and give axial ratios of 0.775 : 1 : 0.725 (as compared with 0.757 : 1 : 0.702 obtained by Broomé in the same way). The planar spacings, d/n, calculated assuming these axial ratios to be correct, are shown in the fifth column of Table I, and the indices of the planes to which they correspond, in the sixth. The assumed order of the spectrum lines is shown in the last column of the table. This "order" may indicate reflection from planes with spacings $1/n$ times

---

[4] Richards, Bartlett and Hodges, THIS JOURNAL, **43**, 1538 (1921).

[5] Groth, "Chemische Krystallographie," Leipzig, **4**, 3 (1917); *Ber.*, **3**, 450 (1870); *Ann. Physik*, **141**, 33 (1870).

that to be expected from a simple lattice having a unit cell containing one molecule and of the same dimensions as the cell with four, or may be the real order of the reflection.

The agreement in position of the observed lines with those calculated as above, is entirely within the experimental error, with the possible exception of the third line in Column 1. As the lines above were obtained using filtered radiation from molybdenum, as compared with unfiltered radiations from iron in Broomé's work, a check upon the lines which Broomé considered to be due to K_β radiation is afforded. The figures in the third column of Table I, which might be interpreted as K_β lines are enclosed in parentheses. Those which were so interpreted by Broomé are bracketted in addition. Broomé's conclusions in this regard are substantiated in most instances, though not in all. Lines 4 and 5 of his spectrum also appear, though weakly, in the results obtained here, and hence were not due entirely to K_β reflections. Broomé states that studies by the Laue spot method have been undertaken by him. It is clear that such studies are necessary, together with a redetermination of the axial ratios, before any safe conclusions may be drawn concerning the character of the unit cell in benzene.

In concluding this note it is desired to draw attention to the interesting coincidence in the angles of diffraction obtained with liquid benzene and those with the crystals. Interference maxima from liquids have been obtained by several observers. The maxima are not in general as sharply marked as those from crystals, and usually only a single broadened line has been observed. Debye and Scherrer,[6] however, by photometric measurements, showed the presence of a number of such maxima in photographs obtained with liquid benzene. The theory proposed by Debye and Scherrer, and by Ehrenfest[7] to account for such maxima is quite different from that pertaining to crystals. To show the coincidence of the lines of the liquid with those of the crystals, however, the "planar spacings" corresponding to the maxima in Debye and Scherrer's intensity chart have been

TABLE II

REFLECTIONS FROM CRYSTALLINE AND LIQUID BENZENE

Crystals, Å..........	...	4.90[a] 4.83[b]	2.69[a] 2.70[b]	2.00[a] 2.02[b]	1.54[a]
Liquid, Å...........	(9.8[c] ?)	4.97[c] 4.83[b]	2.73[c]	2.00[c]	1.50[c]

[a] Broomé. [b] Eastman. [c] Debye and Scherrer.

calculated by the usual formula for crystals, and are compared in Table II with spacings in the same region of reflection in the crystals. Within the

---

[6] Debye and Scherrer, *Nachr. Kgl. Ges. Wiss. Göttingen*, **1916**.

[7] Ehrenfest, *Verslag Akad. Wetenschappen Amsterdam*, **27**, 1184 (1919).

limits of error the maxima[8] in the liquids correspond in position with lines from the crystals.

As the measurements from Debye and Scherrer's chart are approximate in character, and as some divergence appears in the positions of the most intense maximum as reported by other observers,[6,9] several exposures of liquid benzene were made in connection with the present study. The experiments were made with a water-cooled tube with a molybdenum target. The slits were 0.5mm. wide and 10 cm. apart. The benzene was contained in a thin-walled glass tube 2 mm. in diameter. The film was held in an arc of a circle of 14.95cm. radius. On exposure for 26 hours at 20 milliamperes and 35 kilovolts, very distinct maxima were obtained in the different photographs. There was always a good deal of general blackening, and only a single "line" or band could be surely distinguished (without photometric measurements). This line was of nearly uniform intensity over a region corresponding in width to that between the first two lines in Table I, but the average of the closely agreeing measurements on the two best films gave the position of its center as exactly the same as that of the first line in the spectrum of the crystals. In view of the difference in density of the liquid and crystalline forms, this apparently exact coincidence in spacing is perhaps partly fortuitous. It is possible that the band in the liquid really corresponds to the first two lines (unresolved) of the spectrum of the solid. It is, of course, also possible that nothing more than an approximate agreement in position exists for any of the lines in Table II. Nevertheless, the correspondence shown there is sufficient to warrant some consideration.

It is not certainly known at this time whether these maxima in liquids are due to scattering from centers having a regular spacing within the individual molecules, or from aggregates of molecules.[10] If the latter is the explanation, the presence in the liquid of crystal nuclei would appear to be indicated by the coincidence of lines from the liquid and the crystals. The failure of some of the crystal lines to appear would then be due perhaps to the possibly lamellar form of the aggregates in the liquid. If the maxima obtained with liquids arise from scattering centers within the molecule and if the same analytical treatment is applicable in both cases, the coincidence with the crystal reflections suggests that in the crystal

---

[8] In the third "line" of the liquid spectrum the width is so great that some doubt arises as to whether one maximum is involved or two. A single maximum has been assumed in the figures referred to above. The difference in temperature in the experiments with liquids and with crystals should also be noted.

[9] Keesom and Smedt, *J. phys. radium*, **4**, 144 (1923). Wyckoff, *Am. J. Sci.*, **5**, 455 (1923).

[10] The number of lines found by Debye and Scherrer seems to preclude the explanation of Keesom and Smedt, Ref. 9, that the maxima correspond to the average distances between single molecular centers, randomly arranged, in the liquid.

the packing of molecules, in some directions at least, is of the type in which separate molecules cannot be distinguished, that is, in which there is continuous bonding throughout the crystal.

Summary

Measurements of the planar spacings in crystalline benzene are described, and the results compared with those of Broomé.

Comment is made upon the interesting coincidence of some of the diffraction maxima found for liquid benzene with those of the crystals.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY, HARVARD UNIVERSITY]

THE AQUEOUS PRESSURE OF HYDRATED CRYSTALS. II. OXALIC ACID, SODIUM SULFATE, SODIUM ACETATE, SODIUM CARBONATE, DISODIUM PHOSPHATE, BARIUM CHLORIDE

BY GREGORY P. BAXTER AND WILLIAM C. COOPER, JR.

RECEIVED JANUARY 28, 1924

In a recent paper by Wilson[1] the critical discussion of methods for determining vapor pressures of salt hydrates contains the implication that in the gas-current method of determining vapor pressures, equilibrium may be established only from the side of under-saturation. That such an implication is unwarranted is shown by experiments described in this paper, in which equilibrium in the gas phase is approached from the side of over-saturation. The results of these experiments agree within the limit of error with those obtained in the usual way.

The apparatus used for our work corresponded very closely with that used by Baxter and Lansing[2] and for details their paper should be consulted.[3] Furthermore, two of the substances examined by them, oxalic acid and sodium sulfate, were re-investigated, as well as four others.

Two sets of experiments were made with each substance at each temperature. In one set, dry air was passed over the carefully prepared mixture of hydrated crystals containing at least one-tenth of the first product of efflorescence. In the other set the air was first drawn over sulfuric acid solution of considerably higher aqueous pressure than that of the crystals, and then over a mixture of dehydrated crystals with a liberal proportion of hydrated material. The aqueous pressure of the sulfuric acid could in no case have fallen below that of the crystals

---

[1] R. E. Wilson, THIS JOURNAL, **43**, 709 (1921).

[2] Baxter and Lansing, *ibid.*, **42**, 419 (1920).

[3] Schumb has recently suggested improvements on this method, *ibid.*, **45**, 342 (1923).