interface it should enter for the bubble pressure method also. But there are reasons why the effect should be smaller for the bubble pressure apparatus. The capillaries are of Pyrex instead of fused silica and it is probable that the Pyrex-solution zeta potential is smaller than for fused silica. In addition the capillary is larger by a factor of three than that of Jones and Ray and this will also decrease the importance of the zeta potential contribution. A third point is that the position of the meniscus is quite different for the bubble pressure method. In the capillary height apparatus the meniscus is formed completely within the capillary tube. In the bubble pressure apparatus the bubble extends down into the bulk of the solution and is in contact with glass only at the end of the tube. Although as formulated by Langmuir the effect of the zeta potential is treated in terms of a layer of solution along the capillary it can alternatively be discussed in terms of its effect on the radius at the lowest point of the meniscus. Because the region of close approach of the meniscus to the capillary wall is much less for the bubble pressure method it is

very probable that the perturbation from the wall-solution zeta potential will be less. Thus the difference between the two methods of measurement seems likely to be due to a difference in the extent of the contribution of the zeta potential.

Summary

1. A differential maximum bubble pressure apparatus for the precise measurement of relative surface tensions is described. The relative surface tension values for dilute aqueous sucrose solutions, obtained with the apparatus, are similar to those obtained by the capillary height method.

2. The relative surface tension of potassium chloride solutions is considerably different from that obtained by previous workers. No minimum in the surface tension–concentration curve is observed and the results agree fairly well with the Onsager–Samaras predictions.

3. Explanations for the lack of agreement of the various results are considered and it is concluded that the most likely is the effect of the zeta potential as postulated by Langmuir.

ITHACA, N. Y.   RECEIVED AUGUST 19, 1942

The Heat Capacity of Benzene-d_6[1,2]

BY WALDEMAR T. ZIEGLER AND D. H. ANDREWS

Several years ago Lord, Ahlberg and Andrews made a semitheoretical calculation[3] of the heat capacities of crystalline benzene and benzene-d_6 based upon the spectroscopically determined frequencies[4] of the molecules in the gaseous state and certain assumptions concerning the contribution of lattice vibrations and the process of lattice expansion to the heat capacity. The agreement between the calculated and experimental values of C_p for crystalline benzene over the temperature range 4–270°K. may be described as very good, clearly indicating the general correctness of the frequency assignments for benzene.

At that time certain of the fundamental frequencies of both benzene and benzene-d_6 were in doubt. Since then, the work of Langseth and Lord on the deuterated benzenes[5] has appeared which resulted in several changes in the frequency assignments previously made. These changes produce an almost insignificant change in the calculated values of C_p for crystalline benzene,[6] but decrease the calculated C_p values for benzene-d_6 by about 2% at 270°K.

It seemed to us of interest to determine the heat capacity of crystalline benzene-d_6 in order that the results might be compared with those predicted by a calculation of the type described above. Through the kindness of Dr. C. K. Ingold of University College, London, we obtained a loan of about 5 ml. of benzene-d_6 with which to carry out the measurements. The semi-micro heat conduction

(1) From a dissertation submitted to the Board of University Studies of the Johns Hopkins University in 1938 by W. T. Ziegler in conformity with the requirements for the degree of Doctor of Philosophy.

(2) Part of this research was presented in a paper with Dr. R. C. Lord, Jr., at the Boston meeting of the American Chemical Society, September, 1939.

(3) Lord, Ahlberg and Andrews, J. Chem. Phys., 5, 649 (1937). For a more complete exposition of the method used see Lord, J. Chem. Phys., 9, 693, 700 (1941).

(4) Lord and Andrews, J. Phys. Chem., 41, 149 (1937).

(5) Langseth and Lord, Kgl. Danske Videnskab. Selskab. Math-fys. Medd., Vol. 16, No. 6 (1938).

(6) Brucksch and Ziegler, J. Chem. Phys., to be published shortly.

calorimeter described by Stull[7] was used for the experimental determination of the heat capacity as it required only a 5-ml. sample, yet gave results accurate to 1–2%. Measurements were made throughout the temperature range 100–320°K.

Experimental

The experimental apparatus, operating procedure and method of calculation employed were identical with those described by Stull.[7]

Calibration of Calorimeter.—The temperature scale used by Stull was checked by determinations of the melting points of benzene, toluene, cyclohexane and aniline, and the transition in crystalline cyclohexane at 186°K. On the basis of these and other measurements described below we have estimated our temperature scale to be correct to ±0.3° below 180°K. and ±0.1° in the range 180–320°K. with respect to the International Temperature Scale (0°C. = 273.10°K.).

Benzene, 99.99 mole per cent. pure, was used as a primary standard for the calibration of the calorimeter. It was assumed to have the heat capacity values listed in Table II. The heat capacities of cyclohexane, aniline and toluene were measured to serve as a check on the operating procedure, since the heat capacities of these substances are known with good accuracy from absolute measurements.

Table I presents a summary of the melting points and heats of transition obtained for the various substances studied. The agreement with previously observed values is seen to be reasonably good, and served as another check on the accuracy of the calorimetric method.

On the basis of these comparisons it was concluded that the calorimeter would yield values of C_p benzene-d_6 probably accurate to about 2%.

Materials: Benzene.—A c. p. "thiophene-free" material was first distilled through a five-foot column made entirely of Pyrex glass and packed with small glass helices similar to those described by Young and Jasaitis.[8] The middle portion was then fractionally recrystallized six times, about one-fifth of the material being discarded each time. The resulting product was dried over phosphorus pentoxide for two weeks, refractionated and a fraction boiling over a range of about 0.03° collected. This material was used in all subsequent measurements. It melted very sharply, and from the observed premelting was judged to be 99.99 mole % pure.[8a]

Benzene-d_6.—This material was loaned to us by Professor C. K. Ingold of University College, London. As received, the sample (approximately 5 ml.) was labeled as being 99.8 mole per cent. pure benzene-d_6, but containing a trace of water. This was removed by distillation from phosphorus pentoxide in a vacuum. The sample was handled with all possible precautions to reduce exchange reactions to a minimum. From the observed premelting

of the dry sample its purity was calculated to be 99.8 mole %. The benzene-d_6 melted at 6.7°.

Cyclohexane.—An Eastman Kodak Co. product was fractionally recrystallized eight times and then fractionally distilled through a small Vigreux column. The purity calculated from the observed premelting was 99.9%.

Toluene.—C. P. toluene was twice distilled from the five-foot packed column previously described, dried over phosphorus pentoxide for three days and finally redistilled. From the observed premelting its purity was estimated to be 99.7 mole %.

Aniline.—A c. p. product was fractionally distilled through a Vigreux column, recrystallized twice, and finally refractionated through the Vigreux column. The product was water white, and from its premelting was judged to be 99.85 mole % pure.

Experimental Results

Measurements of the heat capacity of benzene-d_6 were made throughout the temperature range 100–320°K. at approximately 6° intervals. 4.537 g. (0.05392 mole) of benzene-d_6 was used in each of the three series of measurements made. The experimental results obtained at each temperature (i. e., mid-point of heating interval) in the three series of measurements were averaged[9] to obtain the values of C_p listed in Table II. The C_p values of crystalline benzene-d_6 listed in the last column of Table III were read from a smooth curve through the data of Table II.

The heats of fusion of benzene and benzene-d_6 were also measured, the results being 2370 and 2340 cal. mole⁻¹, respectively (see Table I). These values have been corrected for premelting and are probably accurate to 1–1.5%.

TABLE I

Substance	Melting point, °C. This research	Melting point, °C. Others	Heat of fusion (cal. mole⁻¹) This research	Heat of fusion (cal. mole⁻¹) Others
Benzene	5.50	5.50[a]	2370	2349[a]
Benzene-d_6	6.70	6.8[b]	2340	
Cyclohexane[g]	−86.8	−87.2[c]	1630	1604[c]
	6.2	6.2[c]	652	623[c]
Toluene	−95.2	−95.15[d]	1565	1582[d]
Aniline	− 5.9	− 6.0[e]		
		− 6.3[f]	2610	2521[f]

[a] Huffman, Parks and Daniels, THIS JOURNAL, 52, 1547 (1930). [b] Ingold, Raisin and Wilson, J. Chem. Soc., 915 (1936), state that C_6D_6 melts 1.3° above benzene. [c] Parks, Huffman and Thomas, THIS JOURNAL, 52, 1032 (1930). [d] Kelley, ibid., 51, 2738 (1929). [e] Lang, Proc. Roy. Soc. (London), A118, 138 (1928). [f] Parks, Huffman and Barmore, THIS JOURNAL, 55, 2733 (1933). [g] The data in the first line for cyclohexane are for a crystalline transition.

(7) Stull, THIS JOURNAL, 59, 2726 (1937).

(8) Young and Jasaitis, ibid., 58, 377 (1936).

(8a) The estimation of purity from the observed premelting was based upon the assumption that no solid solution was formed and that all of the impurity was present in (ideal) solution after a small fraction of the benzene had melted. The purity of the other substances studied was estimated in a similar manner.

(9) This averaging is possible when measurements are made with a heat conduction calorimeter due to the fact that the temperature intervals traversed are always the same.

TABLE II

EXPERIMENTAL VALUES OF C_p FOR BENZENE-d_6

(0°C. = 273.10 °K.; 1 calorie = 4.1833 int. joules)

	C_p (cal. mole^{-1} deg.$^{-1}$)			C_p (cal. mole^{-1} deg.$^{-1}$)	
T, °K.	Benzene[a]	Ben-zene-d_6	T, °K.	Benzene	Ben-zene-d_6
101.9	12.10	12.4	234.6	24.10	28.0
112.0	12.76	13.7	240.4	24.85	28.7
121.6	13.42	14.4	246.0	25.59	29.4
130.6	14.06	15.2	251.6	26.37	30.3
139.2	14.68	16.1	257.1	27.25	31.0
147.4	15.28	17.3	262.5	28.15	32.0
155.3	15.94	18.3	267.8	29.10	33.1
162.9	16.53	18.3	273.1	30.15	34.3
170.3	17.13	19.3		M. p. 279.8°K.	
177.5	17.76	20.0	283.5	31.55	34.9
184.4	18.44	21.0	288.5	31.75	34.2
191.2	19.11	21.8	293.6	31.92	35.4
197.8	19.77	22.7	298.5	32.19	35.7
204.3	20.53	23.2	303.4	32.45	35.9
210.6	21.28	24.6	308.3	32.76	36.3
216.8	22.00	25.5	313.1	33.12	36.4
222.8	22.64	26.3	317.9	33.50	36.9
228.8	23.37	27.1	322.6	34.45	36.9

[a] These values were obtained by interpolation from a large-scale plot of the experimental data of (a) Ahlberg, Blanchard and Lundberg, J. Chem. Phys., 5, 539 (1937); (b) Nernst, Ann. Physik, 36, 395 (1911); (c) Huffman, Parks and Daniels, THIS JOURNAL, 52, 1547 (1930); (d) Daniels and Williams, ibid., 46, 903 (1924); (e) Richards and Wallace, ibid., 54, 2705 (1932).

Discussion of Results

The experimental values of C_p for crystalline benzene-d_6 have been compared with those calculated by means of the expression (see ref. 3)

$$C_p = C_v + [aC_{v(L)} + bC_{v(Vib.)}]^2 T \qquad (1)$$

In this expression $C_v = C_{v(L)} + C_{v(Vib.)}$ and T is the absolute temperature. $C_{v(L)}$ represents the contribution of torsional and translational motions of the molecules, considered as units of the molecular lattice, to the heat capacity at constant volume, and is assumed to be given by the expression $6D(\Theta/T)$, where $D(\Theta/T)$ is the Debye heat capacity function for one degree of freedom. Θ has been taken as 140°.[3]

$$C_{v(Vib.)} = \sum_{i=30} E(\Theta_i/T),$$ where $E(\Theta/T)$ is the Einstein heat capacity function, represents the contribution of the internal vibrational frequencies of the molecule to the heat capacity (at constant volume). The internal frequency assignments used were those of Langseth and Lord.[10]

The constants a and b (assumed temperature independent) were given the values 0.0090 cal.$^{-1/2}$

(10) See ref. 5, Table XVIII. Frequencies no. 14 and 15 were taken as 1550 and 850 cm^{-1}, respectively.

and 0.0057 cal.$^{-1/2}$, respectively, by analogy with crystalline benzene (see ref. 6).

The results of the calculation are presented in Table III together with the experimental values. The calculations also have been made for the range 10–100°K. in order to show the relative importance of the terms $C_{v(L)}$, $C_{v(Vib.)}$ and $C_p - C_v$.

TABLE III

HEAT CAPACITY OF BENZENE-d_6

T, °K.	C_v lattice	C_v vibration	$C_p - C_v$	C_p calcd.[a]	C_p obs.
10	0.34			0.34	
15	1.10			1.10	
20	2.28		0.01	2.29	
25	3.64		.02	3.66	
30	4.89		.03	4.92	
40	6.91		.15	7.06	
50	8.30	0.02	.28	8.60	
60	9.24	.07	.41	9.72	
70	9.84	.17	.56	10.57	
80	10.28	.34	.71	11.33	
90	10.60	.59	.88	12.07	
100	10.85	.91	1.06	12.82	12.8
110	11.01	1.31	1.25	13.57	13.6
120	11.14	1.78	1.46	14.38	14.4
130	11.24	2.33	1.70	15.27	15.2
140	11.32	2.95	1.97	16.24	16.1
150	11.38	3.64	2.27	17.29	17.1
160	11.44	4.36	2.62	18.42	18.1
170	11.50	5.15	3.00	19.65	19.2
180	11.55	5.98	3.43	20.96	20.3
190	11.60	6.38	3.90	22.33	21.6
200	11.64	7.71	4.42	23.77	23.0
210	11.67	8.61	4.99	25.27	24.4
220	11.69	9.52	5.60	26.81	25.8
230	11.71	10.43	6.25	28.39	27.2
240	11.73	11.32	6.94	29.99	28.5
250	11.74	12.30	7.73	31.77	30.0
260	11.75	13.15	8.49	33.39	31.6
270	11.76	14.05	9.33	35.14	33.6

[a] Calculated from Eq. (1).

Examination of Table III shows that there is good agreement (within experimental error) between the calculated and observed values of C_p in the range 100–170°K., but that there is a general trend for the calculated values of C_p to become greater than the observed for increasing temperatures, the calculated value of C_p being about 6% too large in the neighborhood of the melting point.

The reason for this discrepancy is not immediately apparent. Since the agreement is quite good in the range 100–170°K., it seems likely that both the contributions arising from lattice vibrations and from the lowest internal frequencies have been accurately evaluated. Above 170°K. the higher frequencies as well as the expansion term $(C_p - C_v)$ begin to play a more important role,

so that discrepancies at the higher temperatures presumably have their origin in one or both of these components of C_p. We conclude, then, that one or more of the medium-valued frequencies, possibly ν 17,[11] have been assigned values somewhat too low, and/or that the constant b in the expansion formula[12] has been set somewhat too high.

Acknowledgment.—The authors wish to thank Dr. R. C. Lord, Jr., of the Department of Chemistry for many helpful discussions.

(11) See ref. 5, p. 68.
(12) The constant a which gives the lattice portion of the expansion term, presumably is essentially correct because of the satisfactory agreement below 170°K.

Summary

1. The heat capacity of benzene-d_6 has been measured throughout the temperature range 100–320°K. with an accuracy of about 2%.

2. A comparison of the experimentally observed values of C_p with those calculated by a semi-theoretical method indicates that the low frequencies in the benzene-d_6 molecule have been correctly assigned.

3. The possibility that one or more of the medium-valued frequencies have been assigned values which are too low is presented.

BALTIMORE, MD.   RECEIVED JUNE 27, 1942

The Halogenation of m-Diphenylbenzene. II. The Monoiodo Derivative[1]

BY WALTER A. COOK AND KATHRYN HARTKOFF COOK

In a previous communication[2] the authors reported the preparation and proof of structure of the monochloro and monobromo derivatives of m-diphenylbenzene. The present communication describes the preparation of the analogous mono-iodo derivative from the corresponding amine. The latter compound was prepared by ammonolysis of the monochloro and monobromo derivatives.

Experimental

Ammonolysis Experiment.—The ammonolysis studies were carried out in a steel bomb of 500-ml. capacity, electrically heated and equipped with a bimetallic thermoregulator, safety diaphragm valve, pressure gage and Hoke pressure regulator valve. The details of a typical run are given as follows: 12 g. of 4-chloro-m-diphenylbenzene, 340 ml. of 28% aqueous ammonia, 2 g. of cuprous chloride, 1.26 g. of calcium oxide and 2 g. of copper tinsel were heated with continuous agitation for thirty hours at 190° and 800–850 pounds pressure. After cooling the bomb contents were transferred to a 600-ml. beaker, the aqueous ammonia layer decanted and the reaction residue washed with water. The reaction product was dissolved in ether, filtered and saturated with dry hydrogen chloride gas. The precipitated and dried crude 4-amino-m-diphenylbenzene hydrochloride weighed 6 g. The ether layer, after subsequent washing with water and evaporation, yielded 2.5 g. of unreacted monochloro derivative. The combined yields of crude amine hydrochloride from several runs was purified by moistening with dil. hydrochloric acid and allowed to stand for several hours in contact with glacial acetic acid. After filtration it was washed with diluted hydrochloric acid and water. It was then converted into the free base with 6 N potassium hydroxide solution containing a trace of ammonium hydroxide and filtered. Recrystallization from 95% ethanol yielded pure 4-amino-m-diphenylbenzene, m. p. 74°. Similarly a specimen of the amine prepared by the Wardner and Lowy[3] method, and purified as described above, melted at 74°, although these authors reported a value of 64°. Mixed melting points of these products as well as a specimen of the amine prepared by Dr. Russell Jenkins[4] of Monsanto Chemical Co. agree with our value of 74°. The structure of the amine was recently reported by France, Heilbron and Hey,[5] although they were unable to solidify their specimen. A phenylthiourea derivative of 4-amino-m-diphenylbenzene was prepared in the usual way; m. p. 135°.

Anal. Calcd. for $C_{25}H_{20}N_2S$: N, 7.36; S, 8.43. Found: N, 7.51; S, 8.60.

4-Iodo-m-diphenylbenzene.—From 28 g. of the corresponding amine hydrochloride, 18.6 g. of a pale yellow oil b. p. (1 mm.) 235–240° (cor.) was obtained by diazotization and treatment with potassium iodide in the usual manner. The oil solidified after standing for several days and on crystallization from absolute ethanol melted at 67°.

Anal. Calcd. for $C_{18}H_{13}I$: I, 35.65. Found: I, 35.41.

Attempts to oxidize this compound to a substituted phenylbenzoic acid resulted in such small yield of product that it could not be isolated.

The authors acknowledge the helpful assistance of Professor D. E. Anderson in the design and construction of the bomb in which the ammonolysis studies were undertaken.

Summary

1. The preparation and properties of 4-iodo-m-diphenylbenzene are described.

(1) Presented before the Division of Organic Chemistry at the Memphis meeting of the American Chemical Society, in April, 1942.
(2) Cook and Cook, THIS JOURNAL, **55**, 1212 (1933).
(3) Wardner and Lowy, *ibid.*, **54**, 2510 (1932).
(4) Private communication to the authors.
(5) France, Heilbron and Hey, *J. Chem. Soc.*, 1283–1292 (1939).