normal fluorides whose freezing points are reported to be: lithium fluoride, 870°; sodium fluoride, 980–997°; potassium fluoride, 880°; rubidium fluoride, 760°; cesium fluoride, 684°. Item (2) is illustrated by the heats of formation of the acid fluorides of the type MF·HF from the solid fluorides of the type MF·HF from the solid fluoride of the metal and gaseous hydrogen fluoride. Values given by de Forcrand[6] for the salts progressing from that of sodium to that of cesium are in calories per mole: 17.10, 21.56, 22.58, 23.57. Further evidence for increasing stability is furnished by the temperatures at which the MF·HF compounds decompose to give solid MF and hydrogen fluoride vapor at one atmosphere pressure. The lithium and sodium salts decompose without melting at "below 200°"[7] and at 278°,[8] respectively. Potassium acid fluoride, KF·HF, melts, and the liquid must be heated to about 400°,[4,8] to cause the vapor pressure of hydrogen fluoride to be one atmosphere. The corresponding salts of rubidium and cesium require still higher, but at present unknown, temperatures. Item (3) is illustrated by the formulas for the highest known acid fluorides: LiF·HF, NaF·HF, KF·4HF, RbF·3HF (others may yet be found), CsF·6HF.

Both KF·HF and CsF·HF undergo transitions involving large heat effects. In the case of the former, the heat of transition is larger than the heat of fusion and the modification existing above the transition point is much softer than the low temperature form. The cause of the transition is not known, but it may possibly involve rotation of the HF_2^- ion.

Summary

Cesium fluoride and hydrogen fluoride form the compounds: CsF·HF, CsF·2HF, CsF·3HF and CsF·6HF.

Seattle 5, Washington Received August 8, 1947

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[6] M. de Forcrand, *Compt. rend.*, **152**, 1557 (1911).

[7] H. V. Wartenberg and O. Bosse, *Z. Elektrochem.*, **28**, 386 (1922).

[8] Fredenhagen and Cadenback, *Z. anorg. allgem. Chem.*, **178**, 289 (1928).

[Contribution No. 9 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines]

The Heat Capacity, Heat of Fusion and Entropy of Benzene[1]

By George D. Oliver, Margaret Eaton and Hugh M. Huffman

Because of the importance of benzene in organic chemistry and in industry the Bureau of Mines has considered it desirable to include this material in its research program involving determination of the thermodynamic properties of hydrocarbons and their derivatives.

Low-temperature measurements have been made on benzene by several investigators. Nernst[2] made measurements over the temperature range 20 to 80°K. Huffman, Parks and Daniels[3] made measurements over the temperature range 92 to 300°K. More recently Ahlberg, Blanchard and Lundberg[4] made measurements from 4 to 93°K. These authors used their data, combined with those of Huffman, Parks and Daniels,[3] to calculate the entropy of liquid benzene at 298.1°K. Hence the best experimental value of the entropy of benzene is the resultant of measurements made in different laboratories. It seemed desirable to obtain the value of the entropy from a single set of precise data in order to make a reliable comparison with the entropy calculated from spectroscopic and molecular data.

The Apparatus.—The measurements were made in the apparatus described by Ruehrwein and Huffman.[5] Very briefly, the method is as follows: About 0.6 mole of the material under investigation was contained in a sealed copper calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the environment was maintained at that of the calorimeter to prevent heat interchange. The initial and final temperatures of the calorimeter were measured by means of a platinum resistance thermometer. The electrical measurements required for determination of the resistance of the thermometer and for electrical energy were made on a "White" double potentiometer in conjunction with a high-sensitivity galvanometer and accurately calibrated resistances. The potential was in terms of a bank of six saturated cadmium cells which had been certified by the National Bureau of Standards. Time measurements were made with an electric stop clock driven by alternating current, the frequency of which was controlled to about 0.001%. The precision of the measurements was in general better than 0.1%, and above 30°K. it is believed that the accuracy uncertainty should not be greater than 0.2%. The energy measurements were made in terms of the NBS international joule and were converted to calories by dividing by 4.1833.

Experimental

The Material.—The benzene used in this investigation was purified at the Laramie station of the Bureau of Mines[6] and supplied to this Laboratory for a check of its purity by a calorimetric melting point determination.

In July, 1944, a melting point study was made on this material but heat capacity measurements were not made at that time, since the laboratory hydrogen liquefier was not yet in operation. The material was left in the sealed calorimeter from July, 1944, until June, 1947, when the measurement of the heat capacity was undertaken. Due to a change in calorimetric technique it was necessary to

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[1] Published by permission of the Director, Bureau of Mines, U. S. Dept. of the Interior. Article not copyrighted.

[2] W. Nernst, *Ann. Physik*, **36**, 395 (1911).

[3] H. M. Huffman, G. S. Parks and A. C. Daniels, This Journal, **52**, 1547 (1930).

[4] J. E. Ahlberg, E. R. Blanchard and W. O. Lundberg, *J. Chem. Phys.*, **5**, 539 (1937).

[5] Ruehrwein and Huffman, This Journal, **65**, 1620 (1943).

[6] H. M. Thorne, W. Murphy and J. S. Ball, *Anal. Chem.*, **19**, 481 (1945).

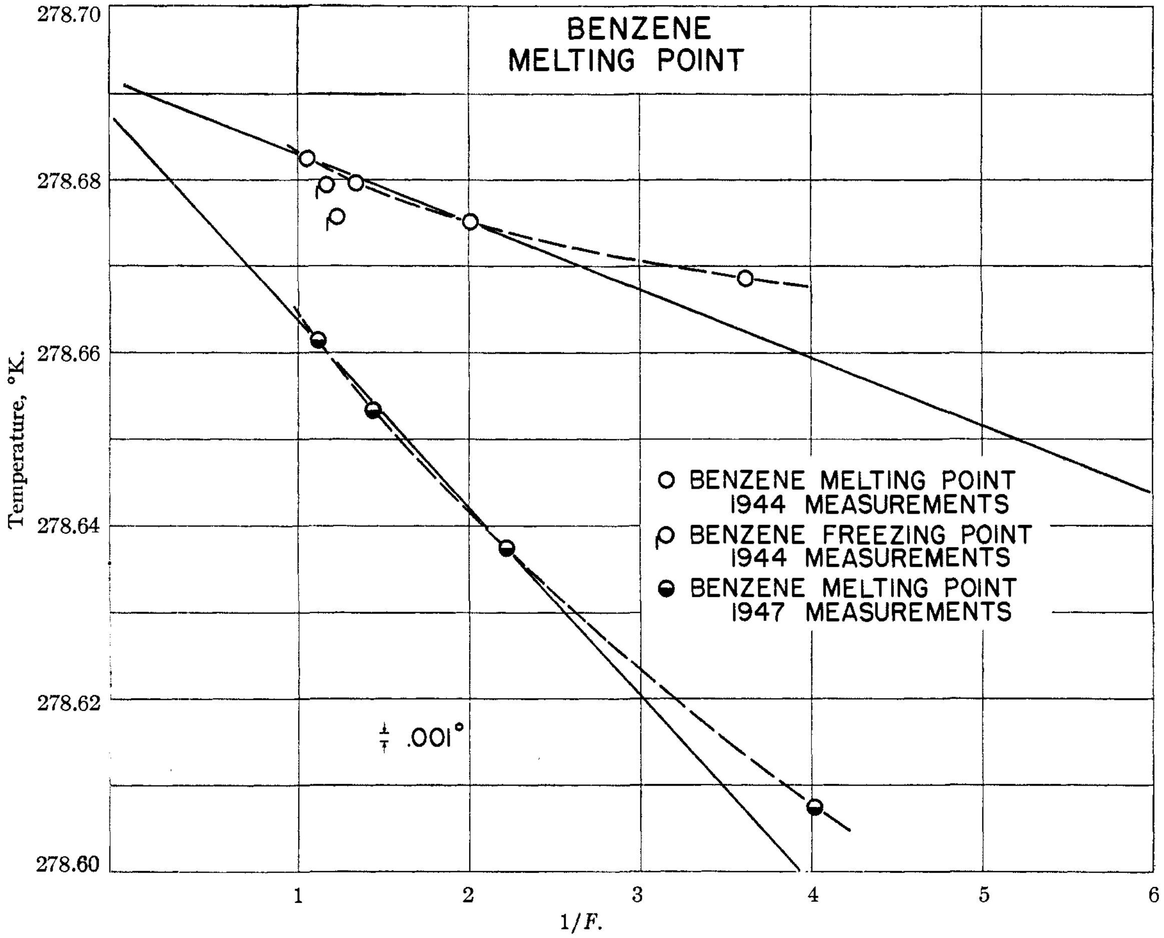

Fig. 1.—Benzene melting point.

transfer the benzene to another calorimeter. The transfer was made by distillation at room temperature in an air-free glass system.

During the heat capacity measurements, a second study of the melting point was made, and the amount of impurity found was approximately three times as great as in the original investigation. This finding suggests that benzene stored in copper is not stable, although it is possible that the benzene may have been contaminated in the transfer process.

TABLE I

BENZENE MELTING POINT SUMMARY

0°C. = 273.16°K. $N_2/F = 0.0153\Delta T$

1944 Expt.			1947 Expt.		
% Melted	T, °K. Obsd.	T, °K. Calcd.	% Melted	T, °K. Obsd.	T, °K. Calcd.
5.3	278.5882	278.5436	24.9	278.6067	278.5974
27.6	.6686	.6626	45.1[a]	.6367	.6367
49.7[a]	.6751	.6751	69.3	.6526	.6537
74.4	.6796	.6804	89.5[a]	.6606	.6606
81.0[b]	.6757	.6812	100%		.6633
85.3[b]	.6794	.6817	Pure		.6850
94.1[a]	.6825	.6825			
100%		.6830			
Pure		.6908			

Triple point = 278.691 ± 0.010 Triple point = 278.685 ± 0.010

Impurity = 0.012 mole % Impurity = 0.033 mole %

[a] These points used to obtain calculated values. [b] These points obtained from freezing expt.

The melting point studies were made in the way described by Todd, Oliver and Huffman.[7] The results of the investigations are summarized in Table I. As discussed in the above reference,[7] a plot of the melting point against the reciprocal of the fraction melted should yield a straight line if Raoult's law is obeyed. The data are plotted in Fig. 1, and it is apparent that the observed points do not follow the theoretical linear relationship. It may be argued that the departure from linearity is due to experimental error. This is quite possible, but it is believed that it is not due to the thermometry, as in general the thermometry is precise to a few ten thousandths of a degree. The fact that the departure from linearity is qualitatively the same in both sets of measurements is a substantial argument in favor of the observations being characteristic of the benzene solution. If the observed curvature is not characteristic of the benzene solution under equilibrium conditions, it is a resultant of the combination of benzene, the calorimetric system, and the method employed. This latter statement is made because, in similar studies of other compounds using the same calorimetric system, a linear relation, within the thermometric error, has been found.

The data have been used in the usual way to obtain the melting point of the pure material by an extrapolation of the straight line, through the points at approximately 90 and 50% melted, to $1/F$ equals zero. The slope of this line times the cryoscopic constant gives the mole fraction of impurity.

It is obvious that, in this case, the above procedure is

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[7] S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947).

arbitrary, since the data do not show conclusively that Raoult's law is obeyed. These observations will emphasize the conclusion of Todd, Oliver and Huffman[7] that the interpretation of melting point data obtained in the ordinary specific heat calorimeter should be made with caution.

Results

In Table II are given the results of the experimental heat capacities and in Table III are listed the values of the molal heat capacity at integral temperatures as selected from a smooth curve drawn through the experimental data. The smoothed heat capacity data of Ahlberg, Blanchard and Lundberg[4] and of Huffman, Parks and Daniels[3] have also been listed in Table III for comparison.

TABLE II

THE MOLAL HEAT CAPACITY OF BENZENE

0°C. = 273.16°K., mol. wt. 78.108
0.60020 mole in calorimeter

T, °K.	ΔT	$C_{\text{satd.}}$ cal./deg.	T, °K.	ΔT	$C_{\text{satd.}}$ cal./deg.
12.97	1.502	0.687	156.08	8.996	15.943
14.25	1.765	.870	157.46	8.151	16.045
14.77	2.142	.957	164.90	8.645	16.646
16.52	2.802	1.270	173.39	8.323	17.393
16.95	2.259	1.350	181.56	8.018	18.154
19.64	3.142	1.913	189.92	8.694	18.979
19.93	4.037	1.981	198.90	9.281	19.895
23.04	3.666	2.689	207.99	8.903	20.916
23.67	3.463	2.837	216.73	8.560	21.921
26.77	3.794	3.570	225.53	9.048	23.002
27.47	4.141	3.717	234.19	8.268	24.072
30.59	3.841	4.427	235.10	10.145	24.200
31.77	4.466	4.698	242.79	8.945	25.285
36.51	5.026	5.691	245.02	9.691	25.583
41.68	5.318	6.631	252.03	9.529	26.583
47.09	5.498	7.482	254.51	9.282	26.948
52.68	5.673	8.232	261.36	9.129	27.972
54.07	4.743	8.404	261.41	8.192	27.896
58.09	5.151	8.860	263.16	8.029	28.249
59.33	5.780	8.999	269.42	7.834	29.427
65.52	6.616	9.607	270.28	8.709	29.592
71.72	5.762	10.100	270.61	6.862	29.612
78.20	7.196	10.602		Liquid	
85.58	7.569	11.151	286.90	8.108	31.930
93.35	7.943	11.646	289.37	8.124	32.063
101.65	8.682	12.151	294.96	8.012	32.343
110.12	8.257	12.681	300.41	9.389	32.629
118.19	7.885	13.194	309.73	9.255	33.104
125.92	7.572	13.712	318.92	9.119	33.614
133.80	8.188	14.262	327.97	8.986	34.160
141.84	7.887	14.835	336.89	8.856	34.670
149.59	7.603	15.425			

Two measurements of the heat of fusion were made. The values found were 2357.6 and 2358.6 calories per mole, mean 2358.1 ± 0.5 calories per mole. The uncertainty given is the precision uncertainty; the accuracy uncertainty may be considerably greater than this due to lack of knowledge of the exact amount of premelting, of the exact composition, and of the behavior of the impurity when the material was crystallized.

TABLE III

MOLAL HEAT CAPACITY OF BENZENE AT INTEGRAL TEMPERATURES

T, °K.	This research	$C_{\text{satd.}}$ cal./degree	
		A, B & L	H, P & D
13	0.685		
14	.830		
15	.995	0.920	
20	2.000	1.84	
25	3.145	3.00	
30	4.300	4.24	
35	5.385		
40	6.340	6.47	
45	7.165		
50	7.885	8.14	
55	8.505		
60	9.065	9.32	
65	9.540		
70	9.975	10.16	
75	10.375		
80	10.750	10.85	
85	11.105		
90	11.430	11.44	11.40
95	11.745		11.70
100	12.050	11.99	12.01
110	12.670		12.65
120	13.310		13.34
130	14.000		14.07
140	14.700		14.80
150	15.450		15.56
160	16.230		16.34
170	17.090		17.16
180	18.020		18.06
190	18.980		19.03
200	20.010		20.06
210	21.140		21.17
220	22.320		22.32
230	23.550		23.55
240	24.880		24.83
250	26.300		26.21
260	27.760		27.77
270	29.310		
278.69	30.760		
....	....		
278.69	31.52		
280	31.59		31.46
290	32.10		31.87
298.16	32.52		32.22
300	32.62		32.30
310	33.16		
320	33.69		
330	34.26		
340	34.87		
350	35.50		
353.26	35.70		

The heat capacity data have been utilized to calculate the entropy of benzene. The results of these calculations are summarized in Table IV.

Discussion

Heat capacity measurements on liquid benzene were made to within about 12° of the normal boil-

TABLE IV

ENTROPY OF BENZENE IN CAL./DEG./MOLE

$S_{13°}$ (Debye, 4.5° freedom, $\theta = 130.5$)	= 0.228
$\Delta S_{13-278.69}$ (graphical)	= 30.560
$\Delta S_{278.69}$ (2358.1/278.69)	= 8.461
$\Delta S_{278.69-298.16}$ (graphical)	= 2.162
$S_{298.16}{}^a$ liquid	= 41.411 ± 0.08
$\Delta S_{\text{vap., }298.16}$ (8090[12]/298.16)	= 27.133
$\Delta S_{\text{compression,}}$ ($R \ln 95.13$[13]/760)	= −4.129
$\Delta S_{\text{gas imperfection}}{}^b$	= 0.042
S^0, ideal gas at 1 atm.	= 64.457 ± 0.12
$\Delta S_{278.69-353.26}$ (liq.) graphical	= 7.928
$S_{\text{liq.}}{}^a{}_{353.26}$	= 47.177
$\Delta S_{\text{vap., }353.26}$ (7349[14]/353.26)	= 20.803
$\Delta S_{\text{gas imperfection}}{}^b$	= 0.145
S, ideal gas at b. p. 353.26	= 68.125 ± 0.12

[a] Entropy of saturated liquid. [b] From equation of state of reference.[11]

ing point. Hence it should be noted that the values listed in the tables are for the saturated liquid. The difference between C_p and $C_{\text{satd.}}$ may become barely significant at the higher temperatures.

The heat capacity measurements of Ahlberg, Blanchard and Lundberg[4] showed no regular deviation from those of this research but were both lower and higher in the temperature range 15 to 90°K. The differences ranged from −8.7 to +3.2%. They calculated a value of 10.89 cal./degree for the molal entropy at 90° compared with 10.82 cal./degree obtained in this research.

The entropy of gaseous benzene has been calculated by Taylor, Wagman, Williams, Pitzer and Rossini,[8] who used the vibrational assignment of Pitzer and Scott.[9] They calculated $S_{\text{gas }298.16°} = 64.34$ and $S_{\text{gas }353.26°} = 67.98$ cal./degree/mole. A similar calculation using the more recent vibrational assignment of Herzfeld, Ingold and Poole[10] and the same values for the moments of inertia and fundamental constants used by Taylor, *et al.*,[8] gives values of 64.33 and 67.97 cal./degree/mole. The vapor heat-capacity data of Scott, Waddington, Smith and Huffman[11] indicate significant anharmonicity in the vibrations of the benzene molecule. The correction for anharmonicity increases the calculated entropy by 0.02 and 0.04 cal./degree/mole at 298.16° and 353.26°K., respectively. These calculated values are shown in Table V. The agreement between the experimental and calculated values is within the estimated experimental error.

TABLE V

COMPARISON OF CALCULATED AND EXPERIMENTAL ENTROPIES OF BENZENE GAS

	298.16°K.	353.26°K.
S^0, ideal gas at 1 atm. (calcd.)[a]	64.33	67.97
Correction for anharmonicity[b]	0.02	0.04
	64.35	68.01
S^0, ideal gas at 1 atm. (exptl.)	64.46 ± 0.12	68.12 ± 0.12

[a] Harmonic oscillator–rigid rotator approximation, using vibrational assignment of Herzfeld, Ingold and Poole.[10] [b] See ref. 11.

Summary

The heat capacity of benzene has been measured over the temperature range 12 to 341°K. From these and other data the entropy of the liquid and vapor at 298.16 and 353.26°K. were calculated. The experimental values of the entropy were found to be in good agreement with those calculated from spectroscopic and molecular data.

BARTLESVILLE, OKLA. RECEIVED DECEMBER 5, 1947

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(8) Taylor, Wagman, Williams, Pitzer and Rossini, *J. Research, Natl. Bur. Standards*, **37**, 95 (1946).

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(10) Herzfeld, Ingold and Poole, *J. Chem. Soc.*, 316 (1946).

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(12) Osborne and Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947).

(13) American Petroleum Institute Research Project 44 at the National Bureau of Standards, Selected Values of Properties of Hydrocarbons, Table No. 5k (Part 1).

(14) Waddington and Douslin, THIS JOURNAL, **69**, 2275 (1947).