

for the six related reactions which occur when *l*-bromosuccinic acid is treated with chloride ion in aqueous solution have been determined at temperatures ranging from 25 to 88°. No measurable trends of the heats of activation were found

for any of these reactions. The collision factors for the four bimolecular reactions are of the same order of magnitude as those calculated from kinetic theory.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

## Thermal Data on Organic Compounds. XVI. Some Heat Capacity, Entropy and Free Energy Data for Typical Benzene Derivatives and Heterocyclic Compounds

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This investigation was undertaken to obtain thermodynamic data for some typical benzene derivatives and heterocyclic compounds, and serves to supplement several previous studies by Parks and his collaborators.<sup>1</sup> In the present case we have measured the heat capacities of triphenylbenzene, nitrobenzene, thiophenol, benzyl alcohol, phthalic acid, phthalic anhydride, pyridine and quinoline.

### Materials

**Nitrobenzene** ( $C_6H_5NO_2$ ).—The sample of nitrobenzene employed was obtained from Eastman "highest purity" material by eight successive fractional crystallizations. Its melting point, determined by a mercury thermometer which had been calibrated by the United States Bureau of Standards, was 5.65° ( $\pm 0.05^\circ$ ), in good agreement with the "International Critical Tables" value of 5.7°.

**Thiophenol** ( $C_6H_5SH$ ).—Eastman "highest purity" thiophenol (b. p. 70–71° at 15 mm. pressure) was found to freeze sharply at –14.9°. Accordingly it was used without further purification.

**Benzyl Alcohol** ( $C_6H_5CH_2OH$ ).—Eastman "highest purity" benzyl alcohol was subjected to a careful fractional distillation at 86–88° with about 5 mm. pressure. The middle third of the distillate was selected for the present measurements. It melted at –15.5° ("I. C. T." value, –15.3°).

**Pyridine** ( $C_5H_5N$ ).—Dr. Poe Liang of this Laboratory had occasion to prepare some very pure pyridine for another investigation. He subjected a high-grade German material (boiling range about 0.5°) to a series of distillations over solid potassium permanganate, potassium hydroxide and barium oxide, and thus obtained a final product boiling within less than 0.1° and having a water content of about 0.02%. He kindly gave us some of this pyridine for our present study. Its melting point was –42.0°, which agrees exactly with the "I. C. T." value.

**Quinoline** ( $C_8H_7N$ ).—Eastman synthetic quinoline (b. p. 110–111° at 14 mm.) was subjected to a careful

fractional distillation at 78° and about 3 mm. pressure. The middle third of this distillate was then used in our measurements; it showed a sharp melting point at –14.7°, which is considerably above the "I. C. T." value (–19.5°).

**1,3,5-Triphenylbenzene** ( $C_{24}H_{18}$ ), ***o*-Phthalic Acid** [ $C_6H_4(CO_2H)_2$ ], and **Phthalic Anhydride** ( $C_8H_4O_3$ ).—These were Eastman "highest purity" materials with melting points at 170–171°, 206–208° (dec.) and 129–131°, respectively. All our specific heat measurements on these compounds were made at temperatures at least 100° below the melting points, where moderate amounts of organic impurities could not produce an appreciable effect on our results; hence, these materials were employed without further purification.

### Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.<sup>2</sup> In view of the accuracy of the various measurements involved, the absolute error in the experimental values thereby obtained is probably less than 0.7%, except in so far as impurities in a sample may cause premelting or otherwise influence the results. The fortuitous errors were ordinarily under 0.25%.

On an average about thirty-five specific heat determinations in the temperature interval between 90 and 300°K. were made upon each of the eight compounds investigated. These results were then plotted on a large scale, a smooth curve through the experimental data was drawn, and specific heat values were read off from this curve for various even temperatures. For the sake of spatial economy these derived values, rather than the more numerous experimental ones, are recorded in Table I. They and also the fusion data

(1) (a) Huffman, Parks and Daniels, *THIS JOURNAL*, **52**, 1547 (1930); (b) Huffman, Parks and Barmore, *ibid.*, **53**, 3876 (1931); (c) Parks, Huffman and Barmore, *ibid.*, **55**, 2733 (1933); (d) Parks and Light, *ibid.*, **56**, 1511 (1934); (e) Jacobs and Parks, *ibid.*, **56**, 1513 (1934).

(2) Parks, *ibid.*, **47**, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

TABLE I  
SPECIFIC HEATS ( $C_p$ ) IN CALORIES PER GRAM OF SUBSTANCE  
( $s$  = crystalline;  $l$  = liquid)

$T$ , °K.	Triphenyl- benzene	Nitro- benzene	Thio- phenol	Benzyl alcohol	Phthalic acid	Phthalic anhydride	Pyridine	Quinoline
90	0.0969 <sub>s</sub>	0.1229 <sub>s</sub>	0.1271 <sub>s</sub>	0.1280 <sub>s</sub>	0.1035 <sub>s</sub> <sup>a</sup>	0.1010 <sub>s</sub>	0.1479 <sub>s</sub>	0.1068 <sub>s</sub>
100	.1044	.1303	.1363	.1373	.1117	.1091	.1542	.1136
110	.1119	.1373	.1488	.1467	.1197	.1167	.1610	.1209
120	.1191	.1443	.1691	.1561	.1275	.1236	.1678	.1283
130	.1266	.1516	.1831	.1673	.1351	.1302	.1754	.1360
140	.1342	.1588	.1843	.1791	.1430	.1372	.1830	.1440
150	.1420	.1664	.1912	.1922	.1511	.1446	.1911	.1520
160	.1499	.1744	.1987	.207	.1590	.1521	.1997	.1602
170	.1582	.1823	.2061	.228	.1669	.1595	.2094	.1688
180	.1668	.1903	.2138	.30	.1750	.1670	.2200	.1779
190	.1758	.1985	.2217	.27	.1830	.1747	.2318	.1876
200	.1849	.2078	.2306	.2410	.1912	.1824	.2463	.1975
210	.1940	.2171	.2403	.2520	.1994	.1902	.266	.2076
220	.2032	.2265	.2508	.2629	.2074	.1979	.323 <sub>s</sub>	.2185
230	.2125	.2357	.2622	.2740	.2155	.2055	.3670 <sub>l</sub>	.234
240	.2218	.2452	.2754	.293 <sub>s</sub>	.2236	.2131	.3716	.257 <sub>s</sub>
250	.2311	.2548	.305 <sub>s</sub>	...	.2315	.2211	.3763	...
260	.2405	.2650	.3653 <sub>l</sub>	.4246 <sub>l</sub>	.2396	.2294	.3809	.3388 <sub>l</sub>
270	.2501	.2770 <sub>s</sub>	.3699	.4395	.2478	.2376	.3873	.3466
280	.2602	.3506 <sub>l</sub>	.3745	.4545	.2559	.2459	.3946	.3544
290	.2705	.3571	.3792	.4694	.2640	.2543	.4018	.3622
300	.2816 <sub>s</sub>	.3637 <sub>l</sub>	.3838 <sub>l</sub>	.4843 <sub>l</sub>	.2722 <sub>s</sub>	.2627 <sub>s</sub>	.4091 <sub>l</sub>	.3701 <sub>l</sub>

<sup>a</sup>  $C_p = 0.0942$  at  $79.5^\circ$ .

TABLE II  
FUSION DATA<sup>a</sup>

Substance	M. p., °K.	Heat of fusion (cal. per g.)		
		I	II	Mean
Nitrobenzene	278.8	23.55	23.52	23.53
Thiophenol	258.2	24.91	24.89	24.90
Benzyl alcohol	257.6	19.84	19.82	19.83
Pyridine	231.1	24.90	25.08	24.99
Quinoline	258.4	20.00	19.95	19.98

<sup>a</sup> In the calculation of these fusion values, the marked rise in the specific heat of the crystals as the melting point is approached was attributed to premelting; and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point.

of Table II are expressed in terms of the calorie<sup>3</sup> (defined unit) and with all weights reduced to a vacuum basis.

The specific heat curves for the crystals of thiophenol and benzyl alcohol showed a distinct maximum or "hump." That for thiophenol appeared mainly between 120 and 130°K. and corresponded to an energy effect of 0.21 cal. per gram or 23 cal. per mole. The hump for benzyl alcohol was spread out to some extent over the temperature interval 150–200°K. It rose at 177° about 40% above the curve for the regular specific heat values and in all corresponded to an energy

(3) The factor 1.0004/4.185 has been used in converting the international joule to the calorie (defined unit).

effect of 1.48 cal. per gram or 160 cal. per mole. Before passing, it may be noted here that our detailed heat capacity data<sup>4</sup> for liquid nitrobenzene gave no evidence that this substance exists in two different liquid forms with a transition at about 282.7°K., as suggested by Mazur.<sup>5</sup>

For comparison with our heat capacity values the literature contains only very meager data.<sup>6</sup> Benzyl alcohol has been studied by Smith and Andrews over the temperature range 100–300°K. Their specific heats differ from ours by –2.8% at 100°, by –0.3% at 200° and by –0.9% at 300°. They also observed the "hump" which we have described in the preceding paragraph. Specific heat values for liquid nitrobenzene have been obtained by Regnault at 280, 285 and 290°, by Schulze at 283°, and by Timofejew at 293°. These differ from our curve by +0.3, –1.8, –2.0, +1.5 and –0.3%, respectively. The earlier determinations of the heat of fusion of this compound (22.3 cal./g. by Pettersson and Widman, 22.6 cal./g. by Tammann, and 22.46 cal./g. by

(4) Parks and Todd, *J. Chem. Physics*, **2**, 440 (1934).

(5) Mazur, *Nature*, **126**, 993 (1930); **127**, 893 (1931); *Acta Phys. Pol.*, **1**, 53 (1932); also Wolfke and Mazur, *Z. Physik*, **74**, 110 (1932); *Acta Phys. Pol.*, **1**, 71 (1932).

(6) (a) Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, pp. 1265–1278 and 1474, and 1st Ergänzungsband, 1927, p. 695; (b) Bramley, *J. Chem. Soc.*, **109**, 496 (1916); (c) Smith and Andrews, *THIS JOURNAL*, **53**, 3656 (1931).

TABLE III

	ENTROPIES OF THE COMPOUNDS PER MOLE							
	Triphenyl- benzene	Nitro- benzene	Thio- phenol	Benzyl alcohol	Phthalic acid	Phthalic anhydride	Pyridine	Quinoline
Crystals (0-90°)	27.40	14.85	13.07	12.92	15.82	13.89	11.96	13.13
Crystals (above 90°)	60.41	25.46	23.04	23.47	33.90	29.02	14.58	22.32
Fusion	...	10.39	10.62	8.32	...	...	8.55	9.98
Liquid (m. p. to 298°)	...	2.94	5.91	7.11	...	...	7.74	6.51
$S_{298}^{\circ}$ (experimental)	87.8	53.6	52.6	51.8	49.7	42.9	42.8	51.9
$S_{298}^{\circ}$ (predicted)	86.0	52.5	46.5	50.7	46.6	41.9	41.9	51.7

Julius Meyer) are all considerably lower than our result in Table II, probably due in part to the use of a higher value for the heat capacity of the crystals just below the melting point than that employed in the present study. In the case of pyridine Timofejew's specific heat value at 293° is only 0.2% above our curve and that of Bramley at 283° is 0.5% below. For quinoline the latter's corresponding value lies 1.4% below our data.

#### Entropy Data

Using the heat capacity data contained in the preceding section in conjunction with the third law of thermodynamics, we have calculated the entropies at 298.1°K. for these eight substances. The detailed entropy values are given in Table III. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman<sup>7</sup> for estimating the entropy increases for the crystals (line 1 in the data) from 0 to 90°K. The various increments from 90 to 298.1°K. which appear in the succeeding lines, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree per mole are then given in the line for " $S_{298}^{\circ}$  experimental"; they are probably reliable to about 1%.

It is also possible to predict values for  $S_{298}^{\circ}$  for these compounds from the results of previous studies and without recourse to the present experimental data. Parks and Huffman<sup>8</sup> have correlated the changes in molal entropy with various structural modifications in the organic molecule and have assigned definite amounts of entropy for the introduction of particular atoms or groups. Using their empirical data, we have obtained the " $S_{298}^{\circ}$  predicted" values in the last line of Table III for the first five compounds of this study. They did not derive data for heterocyclic rings, but in the present case we have assumed that the entropies of pyridine and quino-

line would be the same, respectively, as those found previously by Huffman, Parks and Daniels<sup>1a</sup> for benzene and for naphthalene (calculated to the liquid state). For the bicyclic phthalic anhydride we have also made a prediction by taking the entropy of solid naphthalene and increasing it by 2.0 E. U., which is Parks and Huffman's estimate for the effect of two ketone oxygen atoms in a crystalline compound.

A comparison of the  $S_{298}^{\circ}$  values in Table III shows that these "predictions" are in reasonably satisfactory agreement with the experimental results except in the cases of thiophenol and, perhaps, phthalic acid. For sulfur compounds Parks and Huffman suggested that 2.0 E. U. be added to the entropy value for the corresponding oxygen compound. This suggestion, however, represented merely a guess, in the absence of experimental data; and the recent study of Huffman and Ellis<sup>9</sup> and our present experimental value for thiophenol indicate that the substitution of a SH for a hydrogen atom in an organic molecule actually produces an entropy increase of 8.6 ( $\approx 1.0$ ) E. U. With phthalic acid the discrepancy of 6% between the experimental and predicted values of  $S_{298}^{\circ}$  is a little more obscure. Possibly the proximity of two carboxyl groups in one molecule leads to this deviation from the empirical rules for entropy which have been found to hold fairly well with other organic acids.

#### Free Energy Data for Seven Compounds

We have also calculated the free energies of formation of seven of these compounds by means of the fundamental thermodynamic relationship,  $\Delta F = \Delta H - T\Delta S$ . The absence of any combustion value for thiophenol precludes such a calculation in its case at the present time.

The essential thermal data are given in Table IV. For obtaining the values of  $\Delta H_{298}$  we have used 68,310 and 94,240 cal.<sup>10</sup> for the heats of combustion of hydrogen and graphitic carbon, re-

(7) Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

(8) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932, p. 209.

(9) Huffman and Ellis, *THIS JOURNAL*, **57**, 46 (1935).

(10) Reference 8, pp. 44 and 46.

spectively, in conjunction with the combustion value of the particular compound. For the heats of combustion of triphenylbenzene and phthalic anhydride we have chosen the accurate values obtained recently by Mr. J. W. Richardson<sup>11</sup> in this Laboratory and for phthalic acid we have employed a mean of Richardson's result and that of Verkade and Hartman.<sup>12</sup> For the other four compounds we have had to rely on the values selected for the "International Critical Tables"<sup>13</sup> from a survey of earlier, and presumably much less reliable, data. These respective molal combustion values, calculated for constant pressure at 298.1°K. and with the Washburn<sup>14</sup> correction to 1 atm. in the case of the first three substances, are: triphenylbenzene, 2,924,300 cal.; phthalic acid, 769,700 cal.; phthalic anhydride, 779,700 cal.; nitrobenzene, 738,900 cal.; benzyl alcohol, 892,900 cal.; pyridine, 659,900 cal.; and quinoline 1,122,900 cal. The tabulated  $\Delta S_{298}^{\circ}$  values, which simply represent the differences between

the  $S_{298}^{\circ}$  for each compound and the corresponding values for the entropies of the elements contained therein, were calculated with the following atomic entropies: C (graph.), 1.36<sup>16</sup> E. U.;  $\frac{1}{2}$ H<sub>2</sub>, 15.615<sup>10</sup> E. U.;  $\frac{1}{2}$ O<sub>2</sub>, 24.52<sup>10</sup> E. U.; and  $\frac{1}{2}$ N<sub>2</sub>, 22.89<sup>10</sup> E. U.

The molal free energies of formation of these compounds from their elements appear in the last column of the table. For the most part the accuracy of the values is limited by the accuracy of the combustion data employed. In the cases of phthalic acid and the anhydride the error in the free energy is probably less than 1000 cal.; for benzyl alcohol and triphenylbenzene it should be within 3000 cal.; while for nitrobenzene, pyridine and quinoline it may easily be as great as 5000 cal. Although the values for these last three compounds have mainly qualitative significance at the present time, they do serve to indicate the approximate free energy level for a mono-nitro compound and for the two heterocyclic rings containing nitrogen.

TABLE IV

## THERMAL DATA AT 298.1°K.

In calories per mole with all weights reduced to a vacuum basis

Substance	$\Delta H_{298}^{\circ}$ (cal.)	$\Delta S_{298}^{\circ}$ (E. U.)	$\Delta F_{298}^{\circ}$ (cal.)
Triphenylbenzene (s)	47,750	-225.9	115,100
Nitrobenzene (l)	2,680	-104.6	33,900
Benzyl alcohol (l)	-40,020	-107.2	-8,100
Phthalic acid (s)	-189,150	-152.9	-143,600
Phthalic anhydride (s)	-110,840	-104.0	-79,800
Pyridine (l)	17,920	-65.0	37,300
Quinoline (l)	35,650	-92.5	63,200

(11) Richardson, private communication to the authors prior to publication. His combustion value for phthalic acid is 769,400 cal. per mole (in vacuum) at 1 atm. constant pressure and 25°.

(12) Reference 6a, 1st *Ergänzungsband*, p. 874.

(13) "International Critical Tables," Vol. V, p. 163.

(14) Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

## Summary

1. The specific heats of six typical benzene derivatives and of pyridine and quinoline have been measured between liquid air temperatures and that of the room. Heats of fusion have also been determined in five cases.

2. The entropies of the eight compounds have been calculated from these heat capacity data. In general, the results are in good agreement with the corresponding values predicted by the use of some empirical entropy regularities, but a revision of the entropy contribution of the SH group is necessary.

3. The corresponding free energies for seven of these compounds have also been calculated.

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