The molal free energies of formation from the elements appear in the last line of the table. The absolute error in these values may be as great as 700 calories, but for comparative purposes they are probably reliable to within 250 calories.

TABLE III

THERMAL DATA AT 298.1°K. FOR THE HYDROXYBENZOIC ACIDS

The 15° Cal. is used throughout and all weights have been reduced to a vacuum basis.

Compound	*Ortho*	*Meta*	*Para*
Heat of combustion at const. pressure	722,570	722,720	721,830
ΔH_{298}	−142,040	−141,890	−142,780
ΔS_{298} (in E. U.)	−134.2	−134.5	−134.8
ΔF°_{298}	−101,810	−101,570	−102,370

Our thermal data indicate that in the case of these benzenoid position isomers the heats of formation, entropies of formation and free energies lie very close together. While the apparent order of increasing thermodynamic stability (*i. e.*, decreasing ΔF°_{298}) is here (1) meta, (2) ortho and (3) para, the small difference between the values for the first two compounds is really within the experimental error.

Summary

1. The specific heats of *n*-tetradecane and of the ortho, meta and para hydroxybenzoic acids have been measured over a wide range of temperatures. The heat of fusion of *n*-tetradecane has also been determined.
2. The entropies of the four compounds have been calculated from these heat capacity data.
3. The free energies of formation of the three hydroxybenzoic acids have also been calculated and have been found to lie extremely close to one another.

STANFORD UNIVERSITY, CALIF. RECEIVED APRIL 17, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XIV. Some Heat Capacity, Entropy and Free Energy Data for Cyclic Substances

BY CHARLES J. JACOBS AND GEORGE S. PARKS

From *a priori* considerations as well as from the published experimental data it appears that a cyclic molecule possesses at ordinary temperatures considerably less intramolecular vibrational energy than the corresponding aliphatic or straight-chain molecule. As a consequence the molal entropy of the cyclic compound should be appreciably lower. This has been found true in the case of cyclohexane and *n*-hexane where S_{298} for the former is 49.2 E. U. per mole as against 70.8 E. U. for the latter.[1] In the past, however, the thermal data available for cyclic compounds outside of the class of the benzene derivatives have been quite scanty; and accordingly the present investigation was carried out to increase our information on ring compounds, both of the carbocyclic and heterocyclic types. In this connection we have studied cyclopentane, thiophene, dioxane, pyrene and graphite.

Materials

Cyclopentane (C_5H_{10}).—The cyclopentane was kindly prepared for us by Mr. Robert Kemp, working under the direction of Professor C. R. Noller. Commercial dicyclopentadiene was first purified by fractional distillation under reduced pressure at 85–87° and then depolymerized, by heating at 180–200°, to yield cyclopentadiene. The latter was immediately reduced by hydrogen with the aid of a platinum oxide catalyst. The resulting cyclopentane was then filtered to remove the catalyst, washed with sulfuric acid, dried with anhydrous potassium carbonate, and distilled twice through a 1-meter column packed with copper rings. The final product boiled sharply at 49.5° at 767 mm. It was extremely pure, as was proven by the sharpness of the melting process and transitions in the course of the ensuing heat capacity measurements.

Thiophene (C_4H_4S).—A 100-g. sample of Eastman synthetic thiophene was fractionally distilled in our laboratory, and the middle half of the resulting distillate was employed in the present measurements. This material in the crystalline condition at low temperatures showed a considerable premelting effect as the melting point was approached and its purity could hardly be adjudged as satisfactory.

1,4-Dioxane ($C_4H_8O_2$).—A high-grade Eastman material was subjected to eight fractional crystallizations. The final product had a sharp melting point at 11.1°, as measured with a mercury thermometer which had been calibrated by the United States Bureau of Standards.

Pyrene ($C_{16}H_{10}$).—Two samples of purified pyrene were employed in the present study. The first sample was prepared from a good German material by successive frac-

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(1) Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1038 (1930); Huffman, Parks and Barmore, *ibid.*, **53**, 3884 (1931).

tional crystallizations from petroleum ether and from benzene. The light yellow crystals thereby obtained were dried at 90° and kept in a vacuum for several days before use in the calorimeter. Their melting point, determined with a calibrated mercury thermometer, was 150.4°. The second sample was essentially the same material as the first but it had been subjected to three additional fractional crystallizations, once from methyl isobutyl ketone and twice from very pure benzene.

Graphite.—The graphite was given to us for these measurements by the National Carbon Co. of Cleveland, Ohio. It was artificial (Acheson No. 38) graphite with a guaranteed purity of 99.9%. Ash and moisture tests which we made upon it corroborated this guarantee.

Experimental Results

As in the previous papers of this series,[2] the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and, in the necessary cases, the transition and fusion values. These heat capacity data (except the specific heats for crystalline thiophene), expressed in terms of the 15° calorie[3] and with all weights reduced to a vacuum basis, appear in Tables I, II and III. For the most part the errors in these values are probably less than 1%.

Crystalline cyclopentane showed two sharp transitions at 121.6° and 137.1°K., respectively. The heat effect accompanying the first of these transitions was much larger than the heat of fusion. A somewhat similar situation has been found previously in the case of cyclohexane.[1]

TABLE I

SPECIFIC HEATS PER GRAM OF SUBSTANCE

T, °K.	C_p	*T*, °K.	C_p	*T*, °K.	C_p
Cyclopentane: Crystals I					
93.0	0.193	106.3	0.210	114.1	0.219
99.0	.201				
Crystals II					
128.4	0.318	132.7	0.315		
Crystals III					
144.3	0.302	155.5	0.300	166.0	0.299
150.0	.300	160.9	.301	171.3	.299
Liquid					
186.0	0.339	214.1	0.353	275.4	0.407
191.7	.343	237.1	.370	282.9	.419
197.6	.344	242.3	.372	284.8	.419
203.1	.347	246.6	.378	288.8	.424
208.7	.351	251.6	.382	293.7	.429
Thiophene: Liquid					
237.8	0.320	255.6	0.332	280.1	0.344
243.8	.326	275.4	.341	283.8	.346
252.3	.330	277.5	.342	289.3	.350
1,4-Dioxane: Crystals I					
92.6	0.136	156.4	0.193	236.3	0.275
98.0	.142	162.8	.199	241.7	.281
104.8	.147	184.3	.219	247.0	.287
111.7	.153	190.1	.224	251.9	.294
118.6	.160	198.0	.233	257.2	.306
126.2	.167	224.6	.260		
Crystals II					
274.7	0.415	275.8	0.433		
Liquid					
288.7	0.408	293.7	0.410	298.2	0.415
Pyrene: Crystals					
94.2	0.0841	120.2	0.1079	204.5	0.178
96.4	.0855	126.2	.1067	210.7	.184
102.1	.0900	128.9	.1097	241.1	.214
104.7	.0924	135.9	.1160	246.4	.219
110.7	.1014	146.6	.1254	276.0	.251
112.2	.1060	154.9	.1322	281.1	.257
117.3	.1135	167.8	.1432	287.0	.263
118.4	.1113	190.0	.1641	291.1	.269
Graphite: Crystals					
93.3	0.0290	163.7	0.0734	227.2	0.1185
96.3	.0310	169.5	.0774	236.9	.1264
99.7	.0328	176.5	.0826	242.4	.1306
105.5	.0360	181.7	.0860	255.5	.1406
115.0	.0416	189.6	.0924	260.1	.1443
122.6	.0460	194.3	.0954	275.4	.1542
130.5	.0510	202.9	.1008	279.4	.1571
139.9	.0572	209.2	.1058	284.7	.1620
146.3	.0610	215.1	.1100	289.2	.1648
152.7	.0654	223.1	.1166	293.5	.1688

TABLE II

FUSION DATA

Substance	M. p., °K.	Heat of fusion (cal. per g.) I	II	Mean
Cyclopentane	179.0	2.07	2.06	2.06
Thiophene	233.7	14.11	...	14.11[a]
Dioxane	284.1	34.79	34.91	34.85[b]

[a] This fusion value for thiophene has been corrected for premelting.

[b] These fusion values for dioxane have been calculated on the assumption that C_p = 0.400 for the high temperature crystalline form.

TABLE III

TRANSITION DATA

Substance	Transition point, °K.	Heat of transition (cal. per g.) I	II	Mean
Cyclopentane I	121.6	16.17	..	16.17
Cyclopentane II	137.1	1.22	..	1.22
Thiophene	171.1	3.44	..	3.44
Dioxane	272.9	6.55	6.21	6.38

The results of the specific heat measurements on the thiophene crystals showed considerable premelting and some other irregularities which may have been due to impurities in the material. Consequently they do not possess the same degree of reliability as the values for the other four sub-

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(2) Parks, THIS JOURNAL, **47**, 338 (1925); Parks and Light, *ibid.*, **56**, 1511 (1934).

(3) The factor 0.2390 has been used in converting the joule to the 15° calorie.

stances and we have not included them in the data of Table I. The values for the heat of transition in crystalline thiophene and its heat of fusion may also be somewhat uncertain for the same reasons but the specific heat data for the liquid state are probably quite reliable, as the impurities in the material were undoubtedly related organic compounds with approximately the same heat capacities for the liquid state.

Crystalline dioxane exhibited a transition point at 272.9°K., just about 11° below its melting point. The two specific heat values obtained for the crystals of this substance above the transition are probably too high, due to the complication of some premelting; it is likely that a value of about 0.40 cal. per g. at 276°K. would be nearer the truth. Our curve for the liquid is 1.5% below the specific heat value found by Roth and Meyer[4] at 291° and 1.7% below that of Herz and Lorentz[5] at 296°K. On the other hand, the mean of our fusion values is almost 3% higher than that of Roth and Meyer, due largely to the lower C_p value which we have employed for the "Crystals II."

In the case of pyrene our measurements made with the first sample exhibited a distinct maximum or "hump" in the heat capacity curve around 116°K. Fearing that this effect might be attributable to impurities, we then prepared the second sample by further purifications and repeated the measurements. The second set of data checked the first within 0.5%, an indication that this "hump" is a real phenomenon pertaining to pyrene. In magnitude it represents a heat effect of 0.12 cal. per g., or 24 cal. per mole, in excess of a smooth heat capacity curve.

Our measurements on the heat capacity of graphitic carbon at low temperatures are apparently the first since the early work of Nernst[6] and of Koref.[7] In Fig. 1 we have plotted our results in comparison with the preceding values. The curve through our data lies 4.8% below Nernst's value at liquid air temperatures, 3.6 and 1.5%, respectively, below Koref's "average" specific heats at 137 and 232°, and just 0.2% above Weber's value at 284°K.

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 five substances. The detailed data for cyclopentane, dioxane and pyrene are given in Table IV. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[8] for estimating the entropy increases for the crystals (Line 1 in the data) from 0 to 90°K. The various entropy 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 last line of the table; they are probably reliable to within 1%.

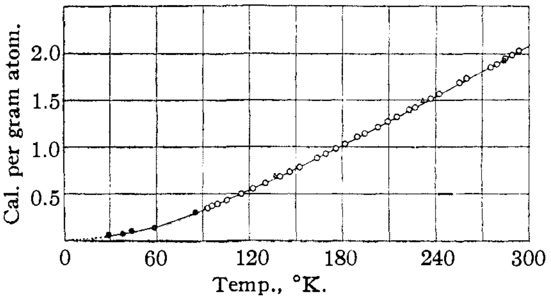

Fig. 1.—The atomic heat capacity of graphite plotted against the absolute temperature. The normal circles represent the present determinations, the heavy circles those of Nernst, the triangles the values of Koref, and the square that of Weber.

For liquid thiophene we have estimated by a similar procedure S_{298} = 42.2 E. U. per mole. In spite of the uncertainties in our specific heat data for the thiophene crystals, this result is probably good to ±1.0 E. U.

Our new heat capacity data also serve as a basis for a recalculation of the entropy of graphitic carbon. Between 90 and 298.1° they yield, by graphical integration, an entropy increment of 1.182 E. U. per gram atom. With the aid of Nernst's specific heats at lower temperatures and the Debye T^3 law we then estimate the increment between 0 and 90°K. to be 0.182 E. U.[9] Accordingly the new value for the atomic entropy of graphite at 298.1°K. is 1.36 E. U. Previously Lewis and Gibson[10] by application of their "*n* formula" to the scanty data of Nernst, Koref, etc., deduced the value 1.27 E. U., while Rodebush and

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(4) Roth and Meyer, *Z. Elektrochem.*, **39**, 35 (1933).

(5) Herz and Lorentz, *Z. physik. Chem.*, **A140**, 406 (1929).

(6) Nernst, *Ann. Physik*, **36**, 395 (1911).

(7) Koref, *ibid.*, **36**, 49 (1911).

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

(9) A rough check on this estimate between 0 and 90° has been secured by applying the extrapolation method of Kelley, Parks and Huffman for cyclic organic compounds. By such a procedure 0.16 E. U. was obtained for this increment.

(10) Lewis and Gibson, THIS JOURNAL, **39**, 2554 (1917).

Rodebush[11] from the same experimental quantities found 1.39 E. U.

TABLE IV

ENTROPIES OF THE COMPOUNDS PER MOLE

Compound	C_5H_{10}(l)	$C_4H_8O_2$(l)	$C_{16}H_{10}$(s)
Crystals (0 to 90°)	12.69	11.12	14.29
Crystals (above 90°)	22.61[a]	23.41[b]	37.16
Fusion	0.81	10.77	...
Liquid	13.30	1.72	...
S_{298}	49.4	47.0	51.4

[a] This value includes the entropy effects (9.32 and 0.62 E. U.) for the two transitions in the crystals.

[b] This value includes the entropy effect (2.06 E. U.) for the transition in the crystals at 272.9°K.

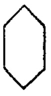
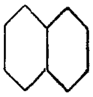
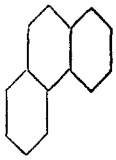
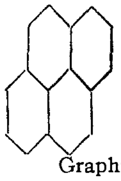
With the aid of these newly found entropies several interesting comparisons pertaining to cyclic compounds can now be made. The molal entropy of liquid cyclopentane at 298.1°K. is 49.4 E. U. as against 49.2 E. U.[1] found previously for cyclohexane. Similarly, earlier studies[12] have yielded 59.2 E. U. for methylcyclopentane and 59.3 E. U. for methylcyclohexane. Thus it is evident that the contributions of the cyclopentane and cyclohexane rings to the molal entropy are equal within the limits of experimental error. Furthermore, it is probable that all saturated heterocyclic five- and six-membered rings also possess approximately the same entropy effect. Thus, if two of the CH_2 groups in cyclohexane are replaced by oxygen atoms, we obtain dioxane with a molal entropy only 2.2 E. U. lower. This relatively small difference is undoubtedly due to the inherently lower entropy contribution of oxygen as compared with CH_2 rather than to a specific effect of the particular ring, since a parallel relationship has been found between diethyl ether and *n*-pentane where S_{298} for the former is 60.5 E. U. as compared with a value of 62.0 E. U. for the latter.[12b,13]

The marked similarity of thiophene to benzene in many of its physical and chemical properties appears again in connection with the molal entropies at 298.1°K. The value just found for liquid thiophene is only 0.7% above that (41.9 E. U.) found previously by Huffman, Parks and Daniels[14] for liquid benzene. On the other hand, the entropies associated with these two aromatic (or unsaturated) rings fall about 7 E. U. below those of cyclopentane and cyclohexane.

The results for pyrene and graphite enable us now to represent, in Table V, an interesting series of substances involving an increasing number of aromatic rings. In Column 3 appear the molal entropies for benzene, naphthalene, phenanthrene, pyrene and graphite, all calculated for the crystalline state at 298°K., although, of course, in the case of benzene this value,[14] calculated by extrapolation above the melting point, is purely hypothetical. Then the last column contains the average entropy effect per carbon atom, obtained by considering the entropy contributions of the hydrogens as negligible. These data serve to bring out emphatically the marked effect of the additional benzenoid rings in tightening up the molecule. Graphite can quite logically be regarded as the limiting term in such a series.

TABLE V

ENTROPY DATA FOR AN AROMATIC SERIES

Formula			
Condensed	Structural	S_{298}, E. U.	S_{298}/n, E. U.
C_6H_6		32.9	5.48
$C_{10}H_8$		39.9	3.99
$C_{14}H_{10}$		50.6	3.61
$C_{16}H_{10}$		51.4	3.21
C_nH_0	Graphite	*n* (1.36)	1.36

Free Energies of Cyclopentane, Thiophene and Dioxane

We have also calculated the free energies of liquid cyclopentane, thiophene and dioxane by means of the third law of thermodynamics and the fundamental equation, $\Delta F = \Delta H - T\Delta S$. The essential thermal data are given in Table VI. For the heat of combustion of cyclopentane we have used the "I. C. T." value[15] and for dioxane we have selected the recent result of Roth and Meyer.[4] Both these data have been converted to 298.1°K. for our present purposes. In the

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(11) Rodebush and Rodebush, "International Critical Tables," Vol. V, p. 87.

(12) (a) Huffman, Parks and Barmore, THIS JOURNAL, **53**, 3884 (1931); (b) Parks and Huffman, *ibid.*, **52**, 4387 (1930).

(13) Parks, Kelley and Huffman, *ibid.*, **51**, 1971 (1929).

(14) Huffman, Parks and Daniels, *ibid.*, **52**, 1554 (1930).

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

case of thiophene an approximate combustion value for the liquid was obtained by subtracting the heat of vaporization of benzene (8100 cal./mole at 298°K.[16]) from Thomsen's result for the heat of combustion of gaseous thiophene as recently revised by Parks and Huffman.[16] The figures for the ΔH_{298} and ΔS_{298} of formation of each compound were then derived with the aid of the atomic heats of combustion and entropies used in the preceding paper of Parks and Light[2] together with the values $S_{298} = 7.6$ E. U.[10] per atom for rhombic sulfur and $\Delta H_{298} = -70{,}940$ cal.[17] for its combustion to $SO_2(g)$.

TABLE VI

THERMAL DATA AT 298.1°K.

The 15° cal. is used throughout and all weights have been reduced to a vacuum basis.

Substance	$C_5H_{10}(l)$	$C_4H_4S(l)$	$C_4H_8O_2(l)$
Heat of combustion at const. pressure	783,300	600,100	554,400
ΔH_{298}	−29,450	+16,400	−95,800
ΔS_{298} (in E. U.)	−113.5	−33.3	−132.4
ΔF°_{298}	+4,400	+26,300	−56,300

The molal free energies of formation of the three compounds from their elements appear in the last line of the table. These results, while they may easily involve absolute errors of the order of one or two thousand calories, show clearly that the ring compound, at least in some cases, possesses an appreciably higher free energy than comparable aliphatic substances. Thus the value for cyclopentane is 13,000 calories above that ($\Delta F^{\circ}_{298} = -8600$ cal.[18]) found previously for *n*-pentane. Similarly we may compare dioxane with butyric acid ($\Delta F^{\circ}_{298} = -91{,}500$ cal.[18]) and ethyl acetate ($\Delta F^{\circ}_{298} = -77{,}600$ cal.[18]), since these three compounds, though different in type, possess the same empirical formula; and again we find that the ring structure has definitely the highest free energy.

Summary

1. The specific heats of cyclopentane, thiophene, 1,4-dioxane, pyrene and graphite have been measured from the temperature of liquid air up to that of the room. Heats of fusion and of transition have also been determined for the first three substances.

2. The entropies of the four ring compounds and that of graphite have been calculated from these heat capacity data and the results have been correlated with entropy data found in previous investigations.

3. The free energies of cyclopentane, thiophene and dioxane have also been calculated.

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(16) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932, pp. 93, 207.

(17) Eckman and Rossini, *Bur. Standards J. Research*, **3**, 597 (1929).

(18) Reference 16, p. 232.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Equilibria in Aqueous Solutions of Bromine and Potassium Bromide

BY GRINNELL JONES AND SVEN BAECKSTRÖM

Introduction.—The evaluation of the standard potential of the bromine electrode from measurements of the potential of cells containing bromine and bromides requires a knowledge of the various equilibria present in such solutions. This paper records the results of an experimental investigation of these equilibria at 25° as a part of the determination of the standard potential of the bromine electrode.

A summary of the numerous earlier investigations of this problem is given in another paper.[1]

The equilibria which are generally believed to be present in aqueous bromine solutions (with or without added bromides) are hydrolysis, $Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HBrO$; and complex formation, $Br_2 + Br^- \rightleftharpoons Br_3^-$ and $2Br_2 + Br^- \rightleftharpoons Br_5^-$. For the first two reactions there is abundant evidence in the literature. Neither is there any doubt that a complex exists which is richer in bromine than the tribromide because the solubility of bromine in potassium bromide solutions of 0.1 *N* and above is greater than can be accounted for as Br_2, HBrO and Br_3^-. The evidence that this high complex has the formula, Br_5^-, as suggested by Jakowkin,[2] is, however, not conclusive. On the other hand, no one

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(1) Grinnell Jones and M. L. Hartmann, *Trans. Am. Electrochem. Soc.*, **30**, 295 (1916).

(2) A. A. Jakowkin, *Z. physik. Chem.*, **20**, 38 (1896).