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THE HEAT CAPACITY AND THE FREE ENERGY FORMATION OF NAPHTHALENE

J. N. PEARCE AND W. B. TANNER

Because of work in project it became necessary to determine the heat capacity of compounds and solutions at low temperatures. To test the apparatus and method we have determined the heat capacity of naphthalene at temperatures from liquid air to 25°.

With slight alterations the apparatus and technique employed are essentially that described by Gibson, Latimer and Parks¹ and later modified by Parks.² A statement of a few of the important features may not be amiss. The solid material was placed in a hollow brass cylinder, 9.5 cm. long by 2.5 cm. in diameter. The top and bottom of the cylinder were sealed by two tight fitting screw caps. To the bottom cap was attached a slender brass rod bearing ten radial metal vanes to facilitate the attainment of thermal equilibrium. When filled the calorimeter was effectively sealed by a thin film of bakelite varnish. The calorimeter was carefully shielded and suspended in a closed polished silver can by means of a heavy silk thread to further prevent heat conduction.

The heating coil surrounding the calorimeter consisted of two double-silk-wound heating wires, B, and S., No. 36, each exactly 130 cm. in length and wound in parallel. The parallel winding reduced the voltage required for heating the calorimeter and made it possible to read both the voltage and the current through the coil by a single adjustment of the "Super K" potentiometer.

Temperature changes were determined by means of a two-junction copper-constantan thermocouple which had been calibrated for the whole temperature range against a Bureau of Standards platinum resistance thermometer. One junction of the thermocouple was sealed to the top of the calorimeter by means of a mixture of shellac and powdered copper. The polished silver can which served as a shield was also equipped with a thermocouple and heating coil. By means of these the shield was maintained at the same temperature as the calorimeter. The temperature of the calorimeter and the shield never differed by more than 0.3°. The whole calorimeter system was suspended in a large pyrex glass vessel which was immersed in a large Dewar flask containing the

refrigerant. The degree of vacuum was determined by means of a spark tube.

Chemically pure naphthalene was twice recrystallized from alcohol and then resublimed.

The results obtained are given in Table I. The molal heat capacity data, C_p , represent several independent runs over the same temperature range. When plotted against $\ln T$, the molal heat capacities, C_p , fall very closely upon a smooth curve. Only in a very few cases do the heat capacities deviate by as much as five-tenths percent. Since approximately sixty heat capacity determinations were made, the influence of the opposing deviations upon the area under the curve cancel each other to a large degree.

Table I—Molal Heat Capacities of Naphthalene

(15° - calorie, M. Wt. = 128.064. All weights reduced to vacuum.)							
°K	C_p	°K	C_p	°K	C_p	°K	C_p
	cal.		cal.		cal.		cal.
93.5	13.91	141.1	18.39	189.7	24.01	255.7	32.75
96.1	14.53	144.1	18.81	192.2	25.52	256.3	33.02
96.7	14.68	147.2	19.41	209.9	25.98	259.1	33.35
97.9	14.67	150.3	19.73	215.3	26.88	262.6	33.81
103.4	15.13	156.1	20.56	216.0	26.79	263.4	33.85
106.5	15.17	159.2	20.71	216.3	26.84	270.8	35.44
110.6	15.39	164.8	21.20	217.4	27.25	286.6	37.46
114.5	15.78	167.4	21.82	221.2	27.40	288.2	37.99
121.1	16.37	169.7	21.98	227.1	28.04	291.4	38.44
124.7	16.58	172.9	22.41	231.2	28.37	292.9	38.58
130.7	17.58	179.6	22.77	231.4	28.96	294.4	38.77
134.3	17.70	183.5	23.33	236.2	29.24	295.3	39.36
137.4	18.36	185.1	23.64	249.5	31.25	296.0	39.26
140.4	18.47	187.3	23.67	252.5	31.92	297.6	40.17

The entropy of naphthalene at 298.1°K may be calculated by means of the relation,

$$S_{298.1} = \int_0^{298.1} C_p d \ln T.$$

The value of ΔS for the interval from 90°K to 298.1°K was obtained by plotting the experimental values of C_p against those of $\ln T$ and determining the area under the curve by means of a polar planimeter. To obtain the change in entropy between 0°K and 90°K use was made of the extrapolation equation deduced by Kelley, Parks and Huffman⁸:

$$S_{90} = \int_0^{90} C_p dT/T = A \int_0^{90} C_p^0 dT/T + B \int_0^{90} C_p^0 dT = AS_{90}^0 + B \int_0^{90} C_p^0 dT.$$

Here, S_{90} is the entropy of the experimental substance at 90° K, and S_{90}^0 that of the standard substance at 90° K. C_p^0 is the molal heat capacity of the standard substance. For ring compounds $S_{90}^0 = 13.7$ E.U. and $\int_0^{90} C_p^0 dT = 697$ cal. The values of A and B

calculated from our data are 0.93227 and 0.000251, respectively. By these methods we find for the entropy of the solid naphthalene: $S_{90} = 13.94$ E.U., $S_{298.1} - S_{90} = 26.94$ E.U. and $S_{298.1} = 39.88$ E.U.

Taking the entropy of C as 1.39 E.U. per mole,⁴ and of H₂ as 31.23 E.U. per mole,⁵ the change in entropy accompanying the formation of naphthalene from its elements at 298.1° K is, $\Delta S_{298.1} = -98.94$ E.U.

The heat of combustion of naphthalene is 1231600 cal.⁶ Taking the heat of combustion of C as 94240 cal.⁷ and that of H₂ as 68310 cal.⁸, we obtain for the heat of formation of naphthalene, $\Delta H_{298.1} = +15960$ cal.

Employing the fundamental thermodynamic equation, $\Delta F = \Delta H - T\Delta S$, we calculate the free energy of formation of naphthalene to be, $\Delta F_{298.1} = +45494$ cal.

The final thermodynamic data for naphthalene are collected in Table II. In this we have included the data of Parks⁹ and Huffman, Parks and Daniels,¹⁰ and the very accurate data recently obtained by Southard and Brickwedde.¹¹

Table II — Thermal Data for Naphthalene at 298.1° K

AUTHORS	$S_{298.1}$	HEAT OF COMBUSTION	$\Delta H_{298.1}$	$\Delta S_{298.1}$	$\Delta F_{298.1}$
	E.U.	AT COAST PRESSURE	CAL.	E.U.	CAL.
P. and T.	39.88	1231600	+ 15960	- 98.94	+ 45490
P ⁹	39.9	—	+ 15960	- 98.0	+ 45200
H. P. D. ¹⁰	39.9	—	+ 15600	- 91.5	+ 42900
S. B. ¹¹	39.89				

The identical agreement in the values of $S_{298.1}$ is very striking. The difference between our values and those of Parks and his co-workers for $\Delta S_{298.1}$ and for $\Delta F_{298.1}$ lies largely in their choice of the entropy of carbon, viz., 1.3 E.U.

SUMMARY

The heat capacity of naphthalene has been determined for temperatures between that of liquid air and 298.1° K. From this data has been calculated the changes in heat content, entropy and free energy accompanying its formation from its elements.

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