[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Thermodynamics of *n*-Heptane and 2,2,4-Trimethylpentane, Including Heat Capacities, Heats of Fusion and Vaporization and Entropies

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Thermodynamic functions for the saturated hydrocarbons through the butanes and tetramethylmethane were given by the writer in 1937.[1] More recent experimental work[2] has confirmed the general scheme used at that time, and the numerical values there listed within their respective limits of error. This paper represents the beginning of an attempt to extend this work through the octanes. The researches of Parks and co-workers[3] have included most of the hydrocarbons in this range; however, their entropies are based on long extrapolations of the heat capacity curve from 90°K. Thus, while accurate enough for their original purpose, these data are of doubtful value for the more precise work now at hand. It would be nice if lower temperature measurements on a few compounds should confirm the accuracy of Parks' extrapolations. The results presented below tend to support this hope for the normal paraffins but indicate that the branched chain compounds may deviate by large amounts.

Apparatus.—The calorimeter used for the condensed phases already has been described.[4] A calorimeter, somewhat similar to the one described by Bennewitz and Rossner[5] was used to measure the heats of vaporization. Data also were obtained on the heat capacity of the vapors. However, since work is continuing on certain aspects of the design and operation of the heat capacity calorimeter, a detailed description seems hardly worthwhile at present.

The parts used for heat of vaporization measurements may be described briefly as comprising a dewar with electrical heater inside in which the liquid is vaporized, and a condenser system in which the amount vaporized in a given time can be measured accurately. The dewar is rather tall and narrow (40 cm. long by 4.2 cm. diameter) with the heater near the bottom. During measurements a considerable height of liquid is present above the heater, tending to bring the vapor temperature to equilibrium and to prevent heat loss through the lead-in wires. The heater has a resistance of about 30 ohms and the lead wires are of no. 18 copper. A White potentiometer is used for measuring the heating energy, readings being taken across a 0.01-ohm standard resistance for the current, and across a suitable volt box for the potential. The error of these measurements is much less than 0.1%. The batteries supplying the heating current are steady within about 0.1% for the period of a measurement, which ranges from ten minutes to nearly an hour. The vaporizer dewar is jacketed with a bath of boiling liquid so as to maintain a temperature a few tenths of a degree higher outside than inside. The heat leak through the dewar is usually insignificant under these conditions, which further assure that no reflux can occur in the tube carrying vapor from the dewar. This tube of course passes through the jacket.

After leaving the vaporizer the gas passes through the specific heat calorimeter and then goes to the condensers. These comprise first a permanent condenser and reservoir and second a removable sample bulb. The latter is immersed in cold water, and the gas is condensed in a small tube before entering the bottom of the bulb. A second connection equalizes the pressure between the sample bulb and the reservoir so that practically no disturbance occurs when a change is made from one to the other. The sample bulb is connected with ground glass joints and has stopcocks on both openings.

A heat of vaporization measurement involves the following operations: 1. The jacket around the vaporizing dewar is adjusted to the proper temperature. 2. The current in the vaporizing heater is started and adjusted. 3. When a steady state has been attained, the flow is turned into the sample bulb for an accurately timed interval. 4. During this interval numerous precise readings are taken on the heater current and potential.

As a check on the accuracy of this calorimeter the heat of vaporization of water was measured. Three runs at different rates of heating gave 9730, 9740 and 9720 cal. per mole. In a recent paper Osborne, Stimson and Ginnings[6] report 9723 cal. per mole at the boiling point. The agreement is thus perfect, considering the experimental error of the present work.

Materials.—The 2,2,4-trimethylpentane had been recovered from other experiments in this University. The boiling point was remarkably constant and the heat capacity immediately below the melting point indicated less than 0.01% of solid insoluble, liquid soluble impurity. The *n*-heptane was obtained from the Eastman Kodak Co. After two fractionations its premelting heat capacity indicated 0.15% impurity. This impurity cannot have any large effect on the results reported below, and very probably is of no consequence at all. The melting point and heat of fusion were appropriately corrected assuming Raoult's law.

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(1) Pitzer, *J. Chem. Phys.*, **5**, 473, 752 (1937).

(2) Kemp and Egan, THIS JOURNAL, **60**, 1521 (1938); Kistiakowsky and Nazmi, *J. Chem. Phys.*, **6**, 18 (1938); Kistiakowsky, Lacher and Ransom, *ibid.*, **6**, 900 (1938); Kistiakowsky and Rice, *ibid.*, **7**, 281 (1939); Kistiakowsky, Lacher and Stitt, *ibid.*, **7**, 289 (1939).

(3) Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1032, 3241 (1930); Parks and Huffman, *ibid.*, **52**, 4381 (1930); Parks, Huffman and Barmore, *ibid.*, **53**, 3876 (1931).

(4) Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928); Pitzer and Coulter, *ibid.*, **60**, 1310 (1938).

(5) Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 126 (1938).

(6) Osborne, Stimson and Ginnings, *J. Research Natl. Bur. Standards*, **23**, 197 (1939).

Melting and Boiling Points.—Since precise measurements of these physical constants have been reported by several workers, no attempt was made to obtain exact values in the course of this work. Approximate values were observed which are in agreement within 0.1° or less in each case. We shall adopt the results obtained by Smith and Matheson[7] and by Brooks,[8] which are for *n*-heptane, m. p. 182.52° and b. p. 371.51°, and for 2,2,4-trimethylpentane, m. p. 165.79° and b. p. 372.33°K. (273.10°K. = 0°C.).

TABLE I

THE MOLAL HEAT CAPACITY OF *n*-HEPTANE

$CH_3(CH_2)_5CH_3$ mol. wt. 100.19

T, °K.	C_p, cal./deg.	*T*, °K.	C_p, cal./deg.
15.14	1.500	79.18	18.53
17.52	2.110	86.56	19.83
19.74	2.730	96.20	21.58
21.80	3.403	106.25	23.22
24.00	4.122	118.55	25.09
26.68	4.935	134.28	27.15
30.44	6.078	151.11	29.54
34.34	7.370	167.38	31.96
38.43	8.731	Melting point	
42.96	10.02	194.60	48.07
47.87	11.36	218.73	48.49
53.18	12.80	243.25	49.77
58.96	14.27	268.40	51.71
65.25	15.69	296.51	53.68
71.86	17.04	317.65	55.72

TABLE II

THE MOLAL HEAT CAPACITY OF 2,2,4-TRIMETHYLPENTANE

(Iso-octane) $(CH_3)_3CCH_2CH(CH_3)_2$ mol. wt. 114.22

T, °K.	C_p, cal./deg.	*T*, °K.	C_p, cal./deg.
14.37	1.967	89.75	20.99
15.70	2.421	100.66	23.37
17.24	2.968	109.68	25.30
19.51	3.806	119.54	27.42
22.09	4.870	130.00	29.58
24.95	5.916	141.42	31.91
28.35	7.002	152.94	34.19
32.28	8.171	160.69	35.92
36.23	9.418	Melting point	
40.19	10.44	171.15	44.58
44.34	11.36	182.89	45.43
49.42	12.49	203.80	47.15
55.01	13.68	233.44	50.06
60.77	14.94	256.60	52.50
66.87	16.09	279.95	54.97
74.05	17.56	301.93	57.60
81.81	19.24	317.34	59.40

Solid and Liquid Heat Capacities.—The heat capacities were measured by the usual methods and are reported in Tables I and II. The unit is the defined calorie, equal to 4.1833 Int. joules, which is used throughout this paper. Above 90°K. the heat capacities of both substances were measured by Parks, Huffman and Thomas.[3] The agreement is reasonably satisfactory, and is better at the lower temperatures than near room temperature. The largest differences are about 1%, the values of Parks being lower in these cases. Over considerable regions the agreement is within 0.2%, which is approximately the accuracy claimed for the present investigation. The points at the highest and lowest temperatures are somewhat more uncertain than the others.

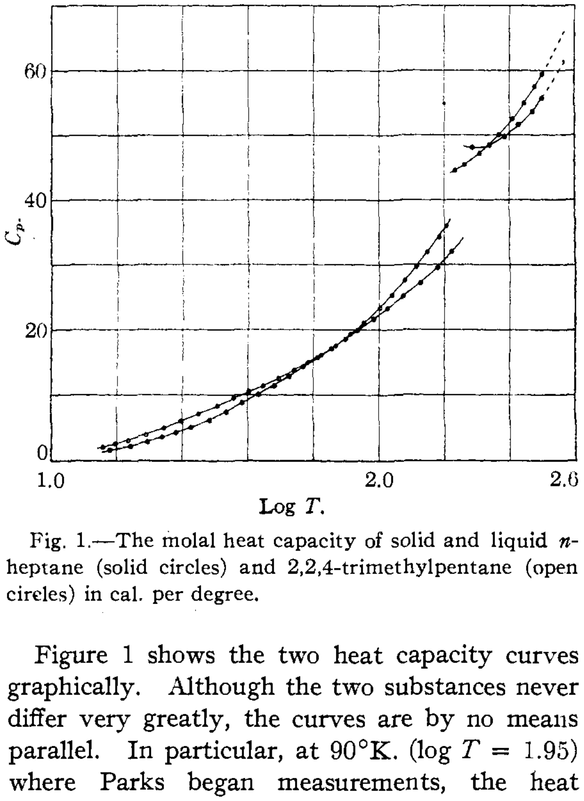

Fig. 1.—The molal heat capacity of solid and liquid *n*-heptane (solid circles) and 2,2,4-trimethylpentane (open circles) in cal. per degree.

Figure 1 shows the two heat capacity curves graphically. Although the two substances never differ very greatly, the curves are by no means parallel. In particular, at 90°K. (log T = 1.95) where Parks began measurements, the heat capacities are almost equal and the 2,2,4-trimethylpentane has the greater slope. Thus almost any reasonable extrapolation would have the curves cross, and give the heptane the larger entropy at 90°K. However, this is not correct, and it illustrates the danger of heat capacity extrapolations from such a high temperature.

Heats of Fusion.—Table III presents the heat of fusion results. The agreement between the individual results is remarkable, particularly when one considers that the temperature intervals and rates of heating were varied considerably. The

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(7) Smith and Matheson, *Natl. Bur. Standards J. Research*, **20**, 641 (1938).

(8) Brooks, *ibid.*, **21**, 847 (1938); for earlier work see Egloff, "Physical Constants of Hydrocarbons," Reinhold Pub. Corp., New York, N. Y., 1939.

TABLE III

THE HEATS OF FUSION OF *n*-HEPTANE AND 2,2,4-TRIMETHYLPENTANE

Temperature interval, °K.	Time of energy imput, min.	$\Delta H°_{\text{Fusion}}$, cal./mole deg.
n-Heptane, m. p. = 182.52°K.		
175.80–184.24	24	3356.0
173.95–184.61	20	3355.6
	Average	3355.8 ± 4
(Parks, Huffman and Thomas[3]		3385)
2,2,4-Trimethylpentane, m. p. = 165.79		
163.13–168.45	22	2201.7
162.93–168.36	33	2201.4
	Average	2201.6 ± 2
(Parks, Huffman and Thomas[3]		2160)

uncertainties given are based on estimates of the various constant errors.

It is quite possible that the heats of fusion reported by Parks, Huffman and Thomas[3] are calorimetrically in better agreement than would appear from Table III. The differences may arise from their treatment of the premelting heat for the less pure samples that they had available. The lack of any appreciable impurity precludes such an error in the 2,2,4-trimethylpentane value from this research. If Raoult's law is not even approximately followed the *n*-heptane result may be in error by somewhat more than the uncertainty listed. Any error of this nature will, however, be approximately compensated in the heat capacities just below the melting point and therefore does not appreciably affect the final entropy value.

TABLE IV

THE HEATS OF VAPORIZATION OF *n*-HEPTANE AND 2,2,4-TRIMETHYLPENTANE

Average $E \times I$ for heater, watts	Rate of flow, moles per min.	$\Delta H°$ vap. cal. per mole
n-Heptane, b. p. = 371.51°K.		
14.80	0.02776	7650
7.81	0.01458	7680
This research, weighted average		7660 ± 20
Mathews[9]		7649
Bennewitz and Rossner[5]		7850
2,2,4-Trimethylpentane, b. p. = 372.33°K.		
15.01	0.02899	7420
14.89	.02886	7410
9.96	.01936	7380
6.06	.01166	7450
	Weighted average	7410 ± 20

Heats of Vaporization.—The apparatus and procedure in measuring heats of vaporization were described above, where the check measurements with water were also mentioned. The results for the hydrocarbons are given in Table IV, together with those from other observers. The result for *n*-heptane reported by Mathews[9] is in excellent agreement with the value obtained in this research. Bennewitz and Rossner's result differs, however, by about 3%.

Smith and Matheson[7] have reported accurate vapor pressure–temperature curves for both of these substances. If the true molal volumes of the saturated vapors were known, good heats of vaporization could be calculated. Careful measurements of these volumes were carried out, using the Dumas method. While these results were not as accurate as the calorimetric values, they agree within the 1% uncertainty to be assigned to the former. The volumes at the boiling points for both substances are approximately 4.5% lower than would be calculated from the perfect gas law.

Gas Heat Capacities.—Measurements of the heat capacity of these hydrocarbons as gases were made in connection with the heat of vaporization work. The calorimeter was mentioned above, but, as was stated there, a complete description will be postponed until developments now in progress have been more nearly completed. The present results are to be regarded as less accurate than results to be obtained in the near future. The values obtained are for 423°K. except in the case of steam which was measured at 432°K. All are at a constant pressure of one atmosphere. The results are: for H_2O, 8.4; for CCl_4, 22.7; for *n*-heptane, 53.9; and for 2,2,4-trimethylpentane, 61.6 cal. per degree per mole.

From the work of Gordon,[10] Wilson,[11] and Keyes and co-workers,[12] one may calculate an accurate heat capacity for steam to compare with that obtained in this work. The value obtained is 8.49 cal. per degree. For carbon tetrachloride a complete calculation is not possible, but using the approximate (rigid rotator–harmonic oscillator) spectroscopic calculations of Vold[13] and assuming the Berthelot equation of state one obtains 22.5 cal. per degree. The true value would be expected to be a little larger. The agreement on the two "knowns" is thus to within about 1%. Probably the values for the hydrocarbons are not in error

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(9) Mathews, THIS JOURNAL, **48**, 562 (1926).

(10) Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(11) Wilson, *ibid.*, **4**, 526 (1936).

(12) Collins and Keyes, *Proc. Am. Acad. Arts and Sci.*, **72**, 283 (1938); and earlier papers.

(13) Vold, THIS JOURNAL, **57**, 1192 (1935).

by much more than this amount. The value for *n*-heptane (45.1 cal. per degree at 410°K.) reported by Bennewitz and Rossner[5] seems definitely too low.

For thermodynamic calculations it would be desirable at least to estimate the temperature variation of the heat capacity. On the basis of statistical calculations to be published soon, the following equations are suggested. They should not err grossly in the range 300–600°K.

$$n\text{-heptane};\ C_p = -235.0 + 110 \log T$$
$$2,2,4\text{-Trimethylpentane};\ C_p = -227.3 + 110 \log T$$

It is suggested that these equations be used in preference to constant heat capacities for these gases until accurate data are available. They agree with the experiments at 423°K., of course.

TABLE V

THE MOLAL ENTROPY OF *n*-HEPTANE

0–15.14°K.	Debye extrapolation	0.535 cal./deg.
15.14–182.52	Graphical–solid	35.186
182.52	Fusion (3355.8/182.52)	18.386
182.52–298.10	Graphical–liquid	24.488
	Entropy at 298.10°K. (liquid)	78.60 ± 0.2
298.10–371.51	Graphical–liquid	12.55
371.51	Vaporization (7660/371.51)	20.62
	Entropy at 371.51°K. (gas)	111.77 ± 0.3

TABLE VI

THE MOLAL ENTROPY OF 2,2,4-TRIMETHYLPENTANE

0–14.13°K.	Debye extrapolation	0.683
14.13–165.79	Graphical–solid	35.309
165.79	Fusion (2201.6/165.79)	13.279
165.79–298.10	Graphical–liquid	29.132
	Entropy at 298.10°K. (liquid)	78.40 ± 0.2
298.10–372.33	Graphical–liquid	13.75
372.33	Vaporization (7410/372.33)	19.90
	Entropy at 372.33°K. (gas)	112.05 ± 0.3

Entropies.—The entropy calculations are summarized in Tables V and VI. The Debye extrapolations are for six degrees of freedom to include torsional as well as compressional waves in the crystal, and to obtain better agreement with the first few experimental points.[14] All the other contributions are based on experimental data of this research except for short ranges of the liquids just below their boiling points. These regions are shown dotted in Fig. 1. The uncertainty from this source can hardly be very large considering the regularity of heat capacity curves for liquid substances of this type.

It already has been mentioned that any reasonable extrapolation method starting from 90°K. cannot give the correct answer for both of these compounds. Thus the results of Parks, Huffman, and Thomas[3] can at best agree in only one case. Actually their *n*-heptane value agrees very well (78.9 cal. per degree at 298.1°K.) while their result for 2,2,4-trimethylpentane is too small (75.2 cal. per degree at 298.1°K.). When one considers that the crystals of all normal paraffins must be very similar it seems likely that a method of extrapolation from 90°K. may have a fair accuracy for this limited group of compounds. Since Parks' original[15] values for *n*-butane and *n*-heptane appear to be nearly correct,[16] the corresponding values for other normal paraffins can be used with some confidence. On the other hand it seems that crystals of branch chain compounds will possess no such similarity and that in consequence entropies based on long extrapolations may be considerably in error in these cases.

Statistical calculations in terms of molecular structure data will be presented elsewhere. It suffices to say here that these experimental entropies and gas heat capacities are consistent with internal rotation potential barriers of the same order of magnitude as have been found for simpler molecules.[1]

Summary

The thermal behavior of *n*-heptane and of 2,2,4-trimethylpentane has been investigated from 15 to 423°K. for which range heat capacities of the solid, liquid or gas are given. The following heats of fusion and vaporization were obtained: *n*-heptane, 3355.8 ± 4 and 7660 ± 20; 2,2,4-trimethylpentane, 2201.6 ± 2, 7410 ± 20 cal. per mole. The entropies were calculated for the liquid at 298.1°K. and for the gas at the boiling point respectively to be: *n*-heptane 78.60 ± 0.2 and 111.77 ± 0.3 and 2,2,4-trimethylpentane 78.40 ± 0.2 and 112.05 ± 0.3. A discussion of these results in terms of statistically calculated entropies will be presented elsewhere.

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(14) See Lord, Ahlberg and Andrews, *J. Chem. Phys.*, **5**, 649 (1937), for a fuller discussion of this matter.

(15) Those given in ref. 3 not the revised values given or suggested by Parks, Shomate, Kennedy and Crawford, *ibid.*, **5**, 359 (1937).

(16) For *n*-butane at its b. p. Parks obtained originally 72.5 but revision of his entropy of vaporization data will lower this a few tenths. Aston (personal communication) has recently obtained 72.0 cal. per degree.