[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of *n*-Pentane

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Calculations of thermodynamic functions for the first four members of the normal paraffin series based on reliable third law data, had shown certain regularities[1] which could not further be examined because accurate data upon the higher members of the series were lacking. The heat capacity data of Parks and Huffman[2] on *n*-pentane extend only to 90°K. and the extrapolation to 0°K. introduces considerable uncertainty into the S°_{298} value. For this reason the investigation of *n*-pentane was undertaken. A preliminary value of S°_{298} based on the resulting data has already been used by Aston[1] to obtain preliminary thermodynamic functions.

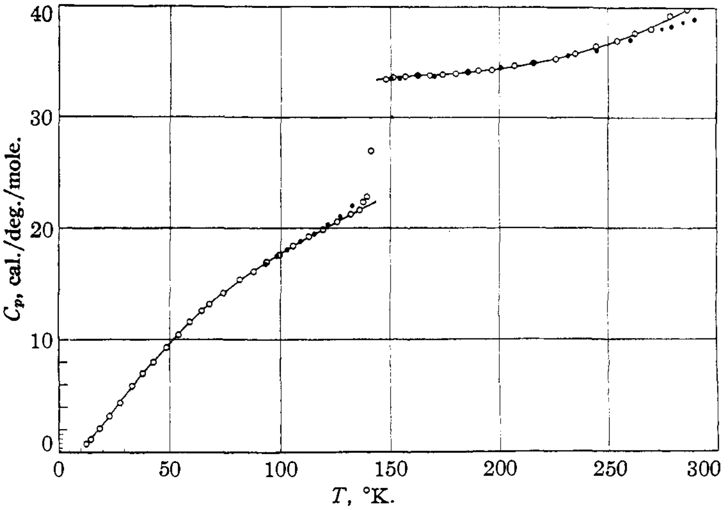

Fig. 1.—The molal heat capacity of *n*-pentane: this research, O; Parks and Huffman, ●.

Preparation and Purification of *n*-Pentane.—A sample of *n*-pentane was furnished us through the kindness of Professor M. R. Fenske of the Petroleum Refining Laboratory of this College. The material had been obtained by the careful fractionation of a Michigan "rubber solvent." After being dried over phosphorus pentoxide and freed of the last traces of air by repeated freezings and evacuations, about 45 cc. of the material was condensed in a weighed glass sample bulb.

The Heat Capacity Measurements.—The apparatus, methods, temperature scale and accuracy were as already described.[3] Gold calorimeter C was used for all measurements. The defined calorie was taken as 4.1833 international joules. The density of the liquid used in making a correction to the liquid heat capacities for vaporization into the filling line was obtained from the data of Timmermans.[4] The molal heat capacities are listed in Table I and graphed in Fig. 1, where also are plotted the heat capacity results of Parks and Huffman.[2] Below 220°K. the agreement of the data is well within the experimental error. Above this temperature the data of Parks and Huffman show deviation from the curve through our points which at the highest temperature becomes 2.0%. This agreement may be better than is indicated, however, from a statement of Parks, *et al.*,[5] that some of their earlier work was over-corrected for heat exchange at the higher temperatures. In Table II the molal heat capacity of *n*-pentane is listed at round values of the temperature.

The Vapor Pressure Measurements.—The method has been described already.[3] The results are given in Table III. Column one gives the absolute temperature as read by standard thermocouple S-7. Column two gives the observed pressure and column 3 the difference between the observed pressure and that calculated from the temperature by means of equation (1).

$$\text{Log}_{10} P_{\text{mm.}} = \frac{-2312.80}{T} - 10.18859 \log T + 0.0050000\, T + 8.75 \times 10^{-7} (260.0 - T)^2 + 34.18793 \quad (1)$$

Column four gives the temperature difference corresponding to column three. In view of the high purity of the sample, the accuracy except at the lowest pressure is determined solely by the temperature.

The Melting Point of *n*-Pentane.—The equilibrium temperature of solid and liquid *n*-pentane was observed over a period of twelve hours with various fractions of the sample melted as estimated from the heat input. Table IV summarizes these data. From the change in the equilibrium temperature of the sample with fraction melted and the molal heat of fusion, the solid insoluble impurity present in the sample was found to be 0.039 ± 0.005 mole per cent.

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(1) Aston, *Chem. Rev.*, **27**, 59 (1940).

(2) Parks and Huffman, THIS JOURNAL, **52**, 4382 (1930).

(3) Aston and Messerly, *ibid.*, **58**, 2354 (1936); Messerly and Aston, *ibid.*, **62**, 886 (1940).

(4) Timmermans, *Sci. Proc. Roy. Dublin Soc.*, **13**, 310 (1912).

(5) Parks, Shomate, Kennedy and Crawford, *J. Chem. Phys.*, **5**, 359 (1937).

TABLE I

THE MOLAL HEAT CAPACITY OF *n*-PENTANE

Mol. wt., 72.147; 0.37631 mole in calorimeter; 0°C. = 273.16°K.

Temp., °K.	C_p, cal./°K.	ΔT, °K.
Series I		
58.99	11.591	5.8
68.02	13.183	5.3
74.09	14.164	5.1
81.22	15.192	5.9
87.77	16.14	6.2
93.57	16.96	5.7
99.49	17.62	6.0
105.77	18.41	6.1
112.74	19.23	6.1
119.13	19.87	6.2
125.64	20.58	5.8
131.83	21.23	6.0
137.62	22.34	5.2
143.47	melting point	
Series II		
151.32	33.62	5.1
156.97	33.69	5.6
162.77	33.81	5.4
168.38	33.83	5.3
174.20	33.89	5.7
180.07	33.95	5.5
185.71	34.11	5.4
190.53	34.24	5.7
196.67	34.31	5.6
207.05	34.71	5.3
215.84	34.96	5.0
226.16	35.31	4.6
234.81	35.90	4.6
244.55	36.54	4.4
254.22	37.00	4.2
262.56	37.66	4.2
270.01	38.02	4.4
279.08	39.26	4.1
286.41	39.85	4.0
Series III		
12.41	0.749	1.5
14.71	1.169	2.3
18.52	2.091	4.9
22.79	3.205	3.7
27.55	4.355	4.9
32.86	5.860	5.1
38.00	7.002	4.9
42.90	8.015	4.5
48.67	9.298	6.4
54.04	10.404	4.1
Series IV		
64.97	12.58	5.9
136.04	21.58	4.1
139.58	22.85	1.9
141.47	27.03	1.7
148.10	33.48	6.3

TABLE II

THE MOLAL HEAT CAPACITY OF *n*-PENTANE

T, °K.	C_p, cal./°K.	T, °K.	C_p, cal./°K.
Solid		Liquid	
10	0.47	150	33.61
15	1.22	160	33.75
20	2.45	170	33.87
25	3.74	180	33.99
30	5.06	190	34.19
40	7.41	200	34.46
50	9.36	210	34.77
60	11.73	220	35.15
70	13.50	230	35.60
80	15.02	240	36.16
90	16.40	250	36.77
100	17.72	260	37.32
110	18.90	270	38.17
120	20.01	280	39.13
130	21.03	290	40.15
140	21.99		

TABLE III

THE VAPOR PRESSURE OF *n*-PENTANE

0°C. = 273.16; *g* for State College, 980.124 ("I. C. T.")

Temp., °K.	Pressure, Int. mm.	ΔP, mm. calcd. − obsd.	ΔT, °K. obsd. − calcd.
207.982	3.08	−0.030	−0.115
225.349	12.03	.000	.000
233.623	21.14	− .001	− .001
245.740	44.64	.000	.000
255.684	77.56	− .021	− .005
263.367	115.07	− .019	− .003
270.801	164.51	+ .004	+ .001
276.778	215.77	− .030	− .003
282.781	279.80	+ .083	+ .007
287.813	344.63	+ .158	+ .010
291.773	403.33	− .074	− .004
294.839	454.08	− .063	− .003
297.988	511.64	− .187	− .009

TABLE IV

THE MELTING POINT OF *n*-PENTANE

Date	% melted	T, °K. resistance thermometer	T, °K. thermocouple S-7	T, °K. thermocouple S-4
9/28/39				
11:00 A. M.	0.0	141.639	141.634	141.609
2:00 P. M.	1.1	142.983	142.963	142.933
4:15 P. M.	5.7	143.322	143.334	143.306
6:30 P. M.	20.0	143.419	143.435	143.408
8:30 P. M.	39.6	143.443	143.460	143.438
11:30 P. M.	70.8	143.446	143.471	143.446
	(100.0)		(143.476)	(143.451)
		Mean	143.46±0.05°K.	

Melting point of pure *n*-pentane 143.47±0.05° K.

Our value for the melting point of pure *n*-pentane is 143.47 ± 0.05°K. (−129.69°C.). Other values reported for this constant are 143.4°K.,[2] −129.93° C.,[6] −129.73°C.,[7] and 129.1°C.[8] The values reported by Shepard, *et al.*,[6] and by Mair[7] are given in terms of the International Temperature Scale. When converted to our temperature scale (0°C. = 273.16°K.) and corrected for the difference between the International and Kelvin scales at −130°C.,[9] these values become, respectively, 143.39°K. and 143.41°K. and are to be compared with our value of 143.47°K.

Because of condensation in lines we were unable to measure vapor pressures above 298°K. and consequently cannot report a boiling point of the material. The normal boiling point of a portion of the sample which we used was measured in a modified Cottrell apparatus by Mr. S. Lawroski of the Petroleum Refining Laboratory. The value obtained for the boiling point was 36.05 ± 0.05°C. Other values reported are 36.00,[6] 36.06,[7] 36.10,[8] 36.077[10] (all in °C.). For completeness it should be stated that the normal boiling point calculated from our vapor pressure equation is

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[6] Shepard, Henne and Midgley, THIS JOURNAL, **53**, 1948 (1931).

[7] Mair, *Bur. Standards J. Research*, **9**, 457 (1932).

[8] Timmermans and Hennaut-Roland, *J. chim. phys.*, **32**, 501, 589 (1935).

[9] $T_{\text{Kelvin}} - T_{\text{International}} = -0.015$°C. at −130°C. Keesom and Dammers, *Comm. Phys. Lab. Univ. Leiden*, #239e (1935).

[10] M. Wojciechowski, *J. Research Natl. Bur. Standards*, **17**, 453 (1936).

309.00°K. (35.84°C.) but in view of the extrapolation of our equation this value can be given no weight.

The Heats of Fusion and Vaporization.—The methods have been described before.[3] The results are given in Tables V and VI, along with values reported by other workers. During the vaporization, the temperature of the condensation bulb was held constant by immersing it in a small thermostat constant to ±0.01°. In calculating the heat of vaporization at 298.16°K., use was made of data on the heat capacity of the gas used by Sage, Webster and Lacey.[12] A value obtained by a small extrapolation of the heat of vaporization data of Sage, Evans and Lacey[13] is in good agreement with our experimental results. The heat of vaporization also has been calculated by thermodynamics using equation (1) and the modified Berthelot equation with $T_c = 197.2$°C. and $P_c = 33.0$ atm.[14] The deviation of the value obtained from the experimental value indicates that the later use of the modified Berthelot equation in correcting to the ideal gas state may produce an error of as much as 50% of the value of the correction.

TABLE V

MOLAL HEAT OF FUSION OF *n*-PENTANE

Melting point, 143.47 ± 0.05°K.; 0°C. = 273.16°K.; 0.37631 mole in calorimeter.

Temp. interval, °K.	Total input, cal./mole	$\int C_p \, dT$ cal./mole	Premelting correction, cal./mole	ΔH fusion, cal./mole
139.420–145.354	2254.5	245.8	2.3	2011.0
140.877–143.470	2233.8	228.4	5.6	2011.0
140.450–146.027	2247.3	240.3	4.5	2011.5
			Mean	2011.2 ± 1
	Parks and Huffman[2] (1930)			2002
	Timmermans[11] (1934)			2000

TABLE VI

MOLAL HEAT OF VAPORIZATION OF *n*-PENTANE

Mol. wt., 72.147; 0°C. = 273.16°K.

Moles vaporized	Mean temp. of vapn., °K.	Total input, cal./mole	$\int C_p \, dT$ cal./mole	ΔH at 298.16°K.[a] cal./mole
0.05095	293.46	6832	503	6268
.05021	293.46	6829	514	6254
.05097	293.47	6748	424	6263
			Mean	6262 ± 15
Measured, Sage, Evans and Lacey[13] (1939)				6270 ± 50
Calculated from eqn. (1) and modified Berthelot eqn. $T_c = 197.2$°C., $P_c = 33.0$ atm., correction = −204 cal./mole				6375

[a] C_p gas − C_p liquid = −13.1 cal./mole/deg.

The Entropy from Thermal Data.—The calculation is summarized in Table VII. The correction for gas imperfection is based on the modified Berthelot equation of state with critical constants cited above.[14]

TABLE VII

THE MOLAL ENTROPY OF *n*-PENTANE

Mol. wt., 72.147; 0°C. = 273.16°K.

	E. u.
0–11.68°K. Debye extrapolation	0.200
11.68–143.47°K. graphical	22.566
143.47°K., 2011/143.47 fusion	14.016
143.47–298.16°K., graphical	26.000
298.16°K., 6262/298.16, vaporization	20.99
Entropy of real gas, 298.16°K., 0.67783 atm.	83.772
Correction for gas imperfection[a]	0.135
Entropy of ideal gas, 298.16°K., 0.67783 atm.	83.907
Compression to one atmosphere	0.773
Entropy of ideal gas, 298.16°K., one atmosphere	83.13 ± 0.2

[a] $S_{\text{ideal}} - S_{\text{real}} = 27\,RT_c^3P/32T^3P_c$; $P_c = 33.0$ atm.; $T_c = 197.2$°C.

The Thermodynamic Functions from Thermal and Molecular Data.—Following the method discussed for the case of *n*-butane,[15] the experimental entropy value was used to estimate the frequency formally associated with the two modes of torsional motion about the middle C–C bonds. In calculating the translational and rotational entropy, the *n*-pentane molecule was assumed to exist in the four pseudo-rigid forms obtained by rotation of the terminal ethyl groups. The potential minima were assumed to be equivalent to a D_{3d} symmetry for the stable ethane molecule. The vibrational frequency assignment was based in part on the work of Kohlrausch and Köppl[16]: C-chain, 250 (1), 326 (2), 835 (1), 898 (1), 954 (1), 1068 (1) cm.$^{-1}$; H bending and stretching, 950 (13), 1455 (9), 3000 (12) cm.$^{-1}$. The rotation of the methyl groups is restricted by a potential of 3300 cal./mole in accord with the result of Kemp and Egan for propane.[17,18] When the entropy of mixing of the four forms of the *n*-pentane molecule,

$$S_{\text{mixing}} = R\left(\frac{1}{9}\ln 9 + \frac{4}{9}\ln\frac{9}{2} + \frac{4}{9}\ln\frac{9}{4}\right)$$

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(11) Timmermans, *Bull. soc. chim. Belg.*, **43**, 626 (1934).

(12) Sage, Webster and Lacey, *Ind. Eng. Chem.*, **29**, 1309 (1937).

(13) Sage, Evans and Lacey, *ibid.*, **31**, 763 (1939).

(14) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, 1928, p. 244.

(15) Aston and Messerly, THIS JOURNAL, **62**, 1917 (1940).

(16) Kohlrausch and Köppl, *Z. physik. Chem.*, **B26**, 209 (1934).

(17) Kemp and Egan, THIS JOURNAL, **60**, 1521 (1938).

(18) For methods of calculation see Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

is added to the rotational and vibrational entropy, the result at 298.2°K. is 4.61 e. u. less than the experimental entropy. This difference is equivalent to a torsional frequency of 185 (2) cm.$^{-1}$, or to a restricting potential of the order of 16,000 cal./mole.

Considerable doubt is cast on the practical significance of this calculation when an attempt is made to reproduce the heat capacity curve of gaseous *n*-pentane measured[12] over the range 310–440°K. Using the vibrational frequency assignment given above, the slope of the calculated C_p–T curve is greater than that of the measured values. Table VIII illustrates this for four different values of the uncertain averaged "waving" frequency $\tilde{\nu}'$ (taken as 950 cm.$^{-1}$ in the above assignment) for the methyl and methylene groups.

TABLE VIII

THE HEAT CAPACITY OF GASEOUS *n*-PENTANE

COMPARISON OF MEASURED AND CALCULATED VALUES

T, °K.	311.0	344.3	377.6	411.0
C_p exptl.	29.2	30.6	32.3	34.1
C_p calcd.[a]				
$\tilde{\nu}' = 950$	31.0	33.8	36.7	39.5
$= 1050$	29.3	32.1	35.0	37.7
$= 1150$	28.2	30.8	33.4	36.2
$= 1250$	27.2	29.7	32.3	34.8

[a] $C_{p\ \text{real}} - C_{p\ \text{ideal}} = 81/32\ RT_c^3/P_c\ P/T^3 = 5/33 \times (470/T)^3$.

Similar discrepancies between measured and calculated gaseous C_p values have been attributed for the case of *i*-butane,[19] and methylamine[20] to inaccurate experimental values. In view of the fact that a measurement by a different method of the heat capacity of gaseous *n*-pentane at 410°K.[21] is in good agreement with the results of Sage, *et al.*, it appears that the theoretical treatment is in error in this case.

Acknowledgment.—We are indebted to Professor M. R. Fenske for supplying us with an exceptionally pure sample of *n*-pentane. We wish also to thank Mr. M. L. Sagenkahn and Dr. S. C. Schumann for help with the experimental work.

Summary

The heat capacity of *n*-pentane has been determined from 12 to 288°K.

The melting point of *n*-pentane is 143.47°K. (−129.69°C.).

The heat of fusion, and the heat of vaporization of *n*-pentane at 298°K., are 2011.2 ± 1 and 6262 ± 15 cal./mole, respectively.

The vapor pressure of *n*-pentane over the range 208–298°K. is represented by the equation

$$\text{Log}_{10} P_{\text{mm.}} = \frac{-2312.80}{T} - 10.18859 \log T + 0.0050000\,T + 8.75 \times 10^{-7}(260.0 - T)^2 + 34.18793$$

The molal entropy of liquid *n*-pentane at 298.16°K. is 62.78 ± 0.2 e. u. The entropy of the ideal gas at 298.16°K. and one atmosphere is 83.13 ± 0.2 e. u.

The torsion of the ethyl *vs.* propyl groups in *n*-pentane is hindered by a potential of the order of 16,000 cal., equivalent to a torsional frequency of 185 cm.$^{-1}$.

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RECEIVED AUGUST 14, 1940

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(19) Aston, Kennedy and Schumann, THIS JOURNAL, **62**, 2059 (1940).

(20) Aston, Messerly and Siller, *ibid.*, **59**, 1743 (1937).

(21) Bennewitz and Rosser, *Z. physik. Chem.*, **B39**, 126 (1938).