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

The Thermodynamics of Branched-Chain Paraffins. The Heat Capacity, Heat of Fusion and Vaporization, and Entropy of 2,3,4-Trimethylpentane

BY KENNETH S. PITZER AND DONALD W. SCOTT

This paper continues the program of developing general formulas for the thermodynamic properties of gaseous paraffin hydrocarbons. The experimental results are similar to those reported recently for *n*-heptane and 2,2,4-trimethylpentane.[1] It is found that the entropy of 2,3,4-trimethylpentane agrees quite well with the value calculated from the statistical formulas given previously.[2] These formulas are quite complex, however, and a more empirical formula is suggested which may be as accurate and is certainly much easier to apply.

Experimental Results

Sample.—The sample of 2,3,4-trimethylpentane was secured from Professor Boord of Ohio State University, through the coöperation of Dr. F. D. Rossini and others associated with the American Petroleum Institute Pure Hydrocarbon Project. The material received consisted of 500 cc. reported to be about 99.5% pure. It was used as received in the experiments on the heat of vaporization and the heat capacity of the gas. It was then subjected to several fractional crystallizations. The simple procedure employed was to place about 100 cc. in a large test-tube and freeze it partially onto the wall by dipping the test-tube into liquid air. The material was vigorously stirred. After 50 to 70% was frozen, the remaining liquid was poured out. This procedure was repeated many times, particularly on the poorer fractions, so that about 300 cc. of "best" material was finally obtained. After drying and a final fractional distillation, the freezing point behavior of this material indicated a purity of about 99.75%. It was employed in all measurements on the liquid and solid.

Melting and Boiling Points.—The melting point was observed as a function of fraction melted. The data are shown in Fig. 1 plotted against the reciprocal of the fraction melted. Assuming Raoult's law and observing that the liquid solutions are always dilute leads to the conclusion that all points should fall on a straight line. Extrapolation to zero (infinite fraction melted) gives the true melting point (163.63 ± 0.1°K.). The slope of the line gives the amount of impurity (0.25 mole %).

No precise observations of the boiling point were made. The value recommended by Egloff,[3] 113.4°C. or 386.5°K., appeared satisfactory and was used in all calculations.

Solid and Liquid Heat Capacities.—The apparatus and methods were the same as in the preceding work. No record was found in the literature of other measurements on this substance. All data are reported in terms of the defined calorie equal to 4.1833 Int. joules, and on the basis of 273.10°K. for the ice point. The error in these results should not exceed 0.2% except at the highest and lowest temperatures and just below the melting point. The results are listed in Table I and shown graphically in Fig. 2.

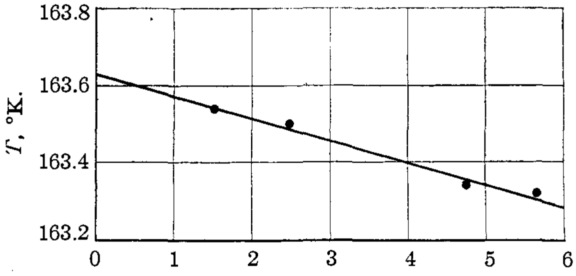

Fig. 1.—The melting point of 2,3,4-trimethylpentane as a function of the fraction melted.

TABLE I

THE MOLAL HEAT CAPACITY OF 2,3,4-TRIMETHYLPENTANE

T, °K.	C_p cal./deg.	T, °K.	C_p cal./deg.
14.68	1.946	127.70	27.95
16.84	2.647	139.82	30.06
18.83	3.290	142.77	30.47
21.22	4.216	146.98	31.01
23.54	5.116	149.18	31.53
25.95	5.942	Melting point	
28.58	6.761	172.76	45.66
35.93	9.007	181.51	46.50
40.87	10.34	196.38	47.93
46.13	11.56	200.79	48.30
51.94	12.94	212.80	49.61
58.08	14.27	212.88	49.57
64.33	15.65	223.71	50.61
65.70	15.96	227.10	50.86
71.24	17.06	245.27	53.08
73.50	17.57	266.79	55.59
82.46	19.43	279.58	57.07
86.32	20.17	293.79	58.85
95.51	22.13	310.69	61.15
105.53	24.02	323.59	62.64
114.27	25.61		

Heat of Fusion.—The results are presented in Table II. Although there appears to be a trend with time of heating, we believe this is spurious. The heat capacity measurements in the premelting region did not follow Raoult's law too well, nor did they seem completely reproducible. The last two measurements in Table II were made immediately following two series of heat capacity determinations, hence the premelting that had actually occurred was

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(1) K. S. Pitzer, THIS JOURNAL, **62**, 1224 (1940).

(2) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); *Chem. Rev.*, **27**, 39 (1940).

(3) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Pub. Corp., New York, N. Y., 1939.

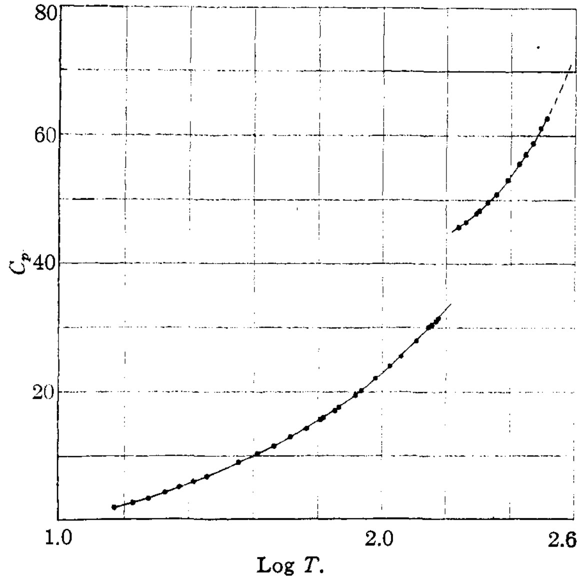

Fig. 2.—The molal heat capacity of 2,3,4-trimethylpentane in calories per degree.

known. This was not true for the first two measurements. The first two were given less weight in the average, since their deviation from the others may have arisen in this way.

TABLE II

THE HEAT OF FUSION OF 2,3,4-TRIMETHYLPENTANE

Temp. interval, °K.	Time of energy input, min.	ΔH^0 fusion, cal./mole deg.
155.68–166.42	22	2221
157.24–164.56	42	2207
158.34–168.03	29	2216
160.29–168.35	35	2215
	Weighted average	2215 ± 5

Heat of Vaporization.—The results are shown in Fig. 3. The relatively large change in apparent heat of vaporization with rate of flow was caused by the use of *n*-butyl alcohol in the jacket around the vaporizing dewar. Its boiling point, 117.7°C., is 4.3° above that of 2,3,4-trimethylpentane. The scarcity of the trimethylpentane itself prevented its use in the jacket. The extrapolated value for the true heat of vaporization is 7810 ± 30 cal. per mole.

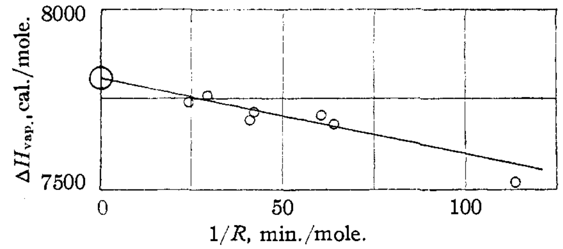

Fig. 3.—The apparent heat of vaporization of 2,3,4-trimethylpentane at various rates of evaporation.

Heat Capacity of the Gas.—These measurements were made in the calorimeter mentioned but not described previously.[1] In view of the fact that an improved calorimeter is now in use and is described in a paper accompanying this one, it does not seem worth while to give the details of the preliminary apparatus. The result obtained for the heat capacity of 2,3,4-trimethylpentane gas at 417°K. is 60.1 ± 0.6 cal. per degree mole. Correcting with the Berthelot equation of state and estimated critical constants to the perfect gas yields 59.6 cal. per degree.

Entropy.—The entropy was calculated by the usual graphical integrations and Debye extrapolation. The best fit was obtained by using twice the Debye function with θ equal to 110°. It was necessary to make a short extrapolation of the liquid heat capacity just below the boiling point. This is shown dotted on Fig. 2. Table III lists the resulting values.

TABLE III

THE ENTROPY OF 2,3,4-TRIMETHYLPENTANE

0.00–14.13°K.	Debye extrapolation	0.63
14.13–163.63	Graphical, solid	33.96
163.63	Fusion (2215/163.63)	13.54
163.63–298.1	Graphical, liquid	30.58
	Entropy of liquid at 298.1°K.	78.71 ± 0.2
298.1–386.5	Graphical, liquid	16.86
386.5	Vaporization (7810/386.5)	20.21
	Entropy of real gas at 386.5°K.	115.78 ± 0.3
	Correction to perfect gas	0.21
	Entropy of perfect gas at 386.5°K.	115.99

Discussion

Comparison of 2,3,4-Trimethylpentane Entropy.—Applying the formulas given previously[2] to 2,3,4-trimethylpentane yields the entropy value[4] 116.7 cal. per degree at the boiling point, to be compared with the experimental value 115.99 ± 0.3. This agreement is quite satisfactory, considering the complexity of the molecule, and increases confidence in the other values calculated by this method.

Simplified Equations for All Branched Paraffins.—While this approximate statistical method appears to be satisfactory, it becomes quite laborious and in one aspect rather arbitrary in more complex molecules. A compromise between this statistical method and the simple empirical procedure of Parks and Huffman[5] has been developed. It retains those features of the statistical method which are simple and certainly correct, and makes simple empirical correction for all other factors.

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(4) The numbers of minima of various energies for internal rotation were taken as follows: 2 at 0, 2 at 3a, and 5 at ∞. Previously a was assigned the value 800 cal. per mole.

(5) G. S. Parks and H. M. Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Co., Inc., New York, N. Y., 1932.

Symmetry numbers for both external and internal rotation and the isomer factor are retained from statistical equations. The empirical correction is a constant value to be subtracted from the entropy for each branching. More specifically the equation is

$$S = S_n + R \ln 2 + R \ln (I/\sigma_e\sigma_i) - 3.5B \qquad (1)$$

where S_n is the entropy of the normal paraffin isomer at the temperature desired, I, σ_e, and σ_i are, respectively, the number of isomers included (2 for a racemic mixture), the symmetry number for external rotation, and the symmetry number for internal rotation in the carbon skeleton; and B is the number of chain branchings. The factor $R \ln 2$ arises because the normal paraffins all have the external symmetry number two.

This equation implies that all paraffin isomers have the same gaseous heat capacity. Within the accuracy of present experiments or calculations, this is true for paraffins with six or more carbon atoms. Figure 5 of the accompanying paper shows the experimental data.

Table IV shows the calculations by this method on all branched-chain paraffins through the octanes, and lists for comparison the entropies calculated by the more complex statistical method. The agreement is within about 1 cal. per degree except on very highly branched compounds. Also listed in Table IV are the experimental entropies in so far as they are available. In calculating these values to 298.1°K. it was assumed that ($C_{p\ \mathrm{gas}} - C_{p\ \mathrm{liquid}}$) was −11 cal. per degree, a value which appears to be in agreement with the available data. Entropies of vaporization, where not known experimentally, were estimates made by Dr. F. D. Rossini. The entropies of the branched-chain heptanes, which are from the work of Parks, Huffman and co-workers, are based on extrapolations from 90°K. These extra-

TABLE IV

ENTROPIES OF BRANCHED CHAIN PARAFFINS CALCULATED BY THE SIMPLIFIED METHOD

Substance	B	σ_e	σ_i	I	$-3.5B$	$R \ln (I/\sigma_i\sigma_e)$	S_{298} simplified	S_{298} statis.	S_{298} exptl.
2-Methylpropane	1	3	1	1	− 3.5	−2.2	69.9	70.5	70.4 ± 0.2
2-Methylbutane	1	1	1	1	− 3.5	0.0	81.2	82.0	
2,2-Dimethylpropane	2	12	1	1	− 7.0	−4.9	71.8	73.2	73.2 ± .3
2-Methylpentane	1	1	1	1	− 3.5	0.0	90.3	90.1	
3-Methylpentane	1	1	1	1	− 3.5	0.0	90.3	90.0	
2,2-Dimethylbutane	2	1	3	1	− 7.0	−2.2	84.6	85.7	
2,3-Dimethylbutane	2	2	1	1	− 7.0	−1.4	85.4	86.5	
2-Methylhexane	1	1	1	1	− 3.5	0.0	99.4	99.5	98.1 ± 1
3-Methylhexane	1	1	1	2	− 3.5	+1.4	100.8	101.3	
3-Ethylpentane	1	3	1	1	− 3.5	−2.2	97.2	98.3	97.3 ± 1
2,2-Dimethylpentane	2	1	3	1	− 7.0	−2.2	93.7	93.4	92.3 ± 1
2,3-Dimethylpentane	2	1	1	2	− 7.0	+1.4	97.3	98.8	
2,4-Dimethylpentane	2	2	1	1	− 7.0	−1.4	94.5	94.7	94.2 ± 1
3,3-Dimethylpentane	2	2	1	1	− 7.0	−1.4	94.5	95.4	94.5 ± 1
2,2,3-Trimethylbutane	3	1	3	1	−10.5	−2.2	90.2	92.3	90.4 ± 1
2-Methylheptane	1	1	1	1	− 3.5	0.0	108.5	108.6	
3-Methylheptane	1	1	1	2	− 3.5	+1.4	109.9	110.1	
4-Methylheptane	1	1	1	1	− 3.5	0.0	108.5	108.1	
3-Ethylhexane	1	1	1	1	− 3.5	0.0	108.5	109.3	
2,2-Dimethylhexane	2	1	3	1	− 7.0	−2.2	102.8	102.9	
2,3-Dimethylhexane	2	1	1	2	− 7.0	+1.4	106.4	105.9	
2,4-Dimethylhexane	2	1	1	2	− 7.0	+1.4	106.4	106.3	
2,5-Dimethylhexane	2	2	1	1	− 7.0	−1.4	103.6	104.7	
3,3-Dimethylhexane	2	1	1	1	− 7.0	0.0	105.0	104.5	
3,4-Dimethylhexane (meso)	2	1	1	1	− 7.0	.0	105.0	105.5	
3,4-Dimethylhexane (racemic)	2	2	1	2	− 7.0	.0	105.0	104.2	
2-Methyl-3-ethylpentane	2	1	1	1	− 7.0	.0	105.0	105.2	
3-Methyl-3-ethylpentane	2	3	1	1	− 7.0	−2.2	102.8	103.3	
2,2,3-Trimethylpentane	3	1	3	2	−10.5	−0.8	100.7	101.4	
2,2,4-Trimethylpentane	3	1	3	1	−10.5	−2.2	99.3	101.4	100.9 ± .3
2,3,4-Trimethylpentane	3	1	1	1	−10.5	0.0	101.5	102.8	102.1 ± .3
2,3,3-Trimethylpentane	3	1	1	1	−10.5	0.0	101.5	102.9	
2,2,3,3-Trimethylbutane	4	6	3	1	−14.0	−5.7	92.3	94.1	

polations have been revised by Dr. Parks and Dr. K. K. Kelley in view of recent data to lower temperatures, including those of this paper. Thus these somewhat arbitrary steps in the calculations have been carried out in a completely impartial manner. At best, however, these values are still uncertain and have been arbitrarily assigned the error of 1 cal. per degree. The other experimental values are from this and the preceding research for the two trimethylpentanes, and from the work of Aston and associates for isobutane[6] and tetramethylmethane.[7] It appears that in the heptane–octane range equation (1) gives as good results as the more complex statistical equations, although possibly the average of the two results would be better. The accuracy seems to be to about 1 cal. per degree. For the simpler molecules the statistical treatment is to be preferred.

In connection with equation (1) it may be convenient to note that the entropies at 298.1°K. of the gaseous normal paraffins above butane can be represented by the simple equation

$$S_n = 9.13n + 37.62 \text{ cal. per degree mole} \quad (2)$$

where n is the number of carbon atoms. This equation fits both the experimental entropies and the statistical formulas within about 0.1 cal. per degree.

The combination of these two equations for entropies and the equation given in the accompanying paper for heat capacities should make possible very convenient and reasonably accurate calculations of the various thermodynamic properties of the paraffins in the perfect gas stage, provided of course that heat of formation values are available where needed. Although experimental data on additional substances are desirable, it appears that considerable confidence can be placed in these results.

Summary

The following results were obtained for 2,3,4-trimethylpentane: melting point, 163.63 ± 0.1°K.; heat of fusion, 2215 ± 5 cal. per mole; heat of vaporization, 7810 ± 30 cal. per mole; entropy of liquid at 298.1°K., 78.71 ± 0.2 cal. per degree mole; entropy of the real gas at the boiling point 386.5°K., 115.78 ± 0.3 cal. per degree mole. Heat capacities of the solid, liquid, or gas are given covering most of the range 15 to 417°K. This entropy is shown to be in reasonable agreement with a value calculated from approximate statistical formulas.

A simple semi-empirical formula is suggested for calculating entropies of the heavier branched-chain paraffins. It is shown to give results in agreement with the available experimental data, and with the values calculated from the more complex statistical formulas. The combination of this formula for entropies with the simple formula for heat capacities, given in the accompanying paper, should constitute a convenient method for thermodynamic calculations.

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[6] J. G. Aston, R. M. Kennedy and S. C. Schumann, THIS JOURNAL, **62**, 2059 (1940).

[7] J. G. Aston and G. H. Messerly, *ibid.*, **58**, 2354 (1936).

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

Vapor Pressure Studies. II. Chlorobenzene–1-Nitropropane[1]

BY J. R. LACHER, W. B. BUCK AND W. H. PARRY

The present paper reports on vapor pressure measurements of chlorobenzene–1-nitropropane mixtures. It also includes some data on the heats of mixing of ethylene bromide, chlorobenzene and 1-nitropropane. The results make possible a fairly accurate comparison of the thermodynamic properties of the three possible binary mixtures of these liquids.

Experimental Details.—The apparatus employed in the vapor pressure measurements was practically identical to that designed by Sameshima[2] and differs from that used in the previous research[1] in that the liquid was boiled directly by means of an electrically heated wire. The experimental procedure was the same in both cases. The composition of the liquid and condensed vapor was determined by measuring densities at 30°. The densities of known mixtures could be fitted to the equation

$$d_m = 0.9901 + 0.1058N_C + [0.0192 - 0.0040N_C]N_CN_N \quad (1)$$

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[1] Paper I appeared in THIS JOURNAL, **63**, 1752 (1941).

[2] J. Sameshima, *ibid.*, **40**, 734 (1918).