

[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 Pressures of Isopentane

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Thermal data on isopentane from 10°K. to the vapor at the normal boiling point, are required to complete the thermal data on the pentanes within the accuracy obtainable by modern methods. Data from 80 to 298°K. have been obtained by Parks, Huffmann and Thomas¹ who used them to calculate the entropy of the liquid at 298°K. The present investigation extends down to 11.6°K. and includes measurements of the heat of vaporization.

In the previous paper² hysteresis in the liquid below -40° has been demonstrated. Hysteresis was found in the heat capacities of solid methylamine, and seemed to be associated with a transition of very low energy change.³ A similar hysteresis has been found in solid isopentane which seems to be of the same type. The heat capacity values graphed in Fig. 1 show the phenomenon clearly. The small peak at 70°K. is perhaps comparable with the one at 101.5°K. in methylamine. It is possible, in isopentane, that the hystereses on solid and liquid are related, but not very likely since no experimental connection could be found between them.

The Heat Capacity Measurements.—The material used, method and accuracy were the same as in the measurements of the previous paper,² of which this work is a continuation. Calorimeter B was used in all measurements. One defined calorie was taken equal to 4.1833 international joules. The molal heat capacities of the solid, and those on the liquid from 113.39 to 180°K. and from 240 to 298°K. are graphed in Fig. 1. Those in the range 180 to 240°K. have been discussed in the previous paper.² The legend to the points given below Fig. 1 includes a brief cooling history. Series VIII is, on an average, 4% below the curve which can be drawn satisfactorily through the points of all the other series except those of series XV which are on the average 0.2 per cent. low. Series VIII was taken immediately after repetition of a number of heat capacity measurements on the empty calorimeter had shown the apparatus to be functioning properly,²

and, since then, heat capacity measurements on dimethyl ether⁴ have checked satisfactorily those obtained with calorimeter C. This point is important as low measurements have never been obtained since. In view of the unexplained low points, it has seemed best to give a table (Table I) of rounded values of the heat capacity of the solid instead of the actual data. The values of the molal heat capacity in Table I were read from the best curve through the points excluding those of Series VIII and XV. This curve is shown in Fig. 1. For the sake of uniformity the liquid values are treated similarly over the range not given in the previous paper, although all the different series were concordant as shown in Fig. 1. They

TABLE I
THE MOLAL HEAT CAPACITY OF ISOPENTANE AT ROUNDED TEMPERATURE VALUES

Mol. wt. = 72.146. 0°C. = 273.16°K.		
Temp., °K.	C_p , cal./deg., this research	C_p , cal./deg., P., H. and T
20 (Solid)	3.25	
25	4.82	
30	6.00	
35	7.24	
40	8.41	
45	9.46	
50	10.41	
55	11.37	
60	12.38	
70	15.00	
80	15.19	15.60
90	16.96	17.13
100	18.81	19.53
110	20.75	
120 (Liquid)	29.68	29.50
130	29.99	29.95
140	30.38	30.42
150	30.72	30.77
160	31.06	31.12
170	31.48	31.56
186	31.95	32.00
...
240	35.20	35.20
250	35.89	35.90
260	36.59	36.63
270	37.37	37.36
280	38.31	37.95
290	40.49	

(1) Parks, Huffmann and Thomas, *THIS JOURNAL*, **52**, 1032 (1930).(2) Aston and Schumann, *ibid.*, **64**, 1034 (1942).(3) Aston, Siller and Messerly, *ibid.*, **59**, 1743 (1937).(4) Kennedy, Sagenkahn and Aston, *ibid.*, **63**, 2267 (1941).

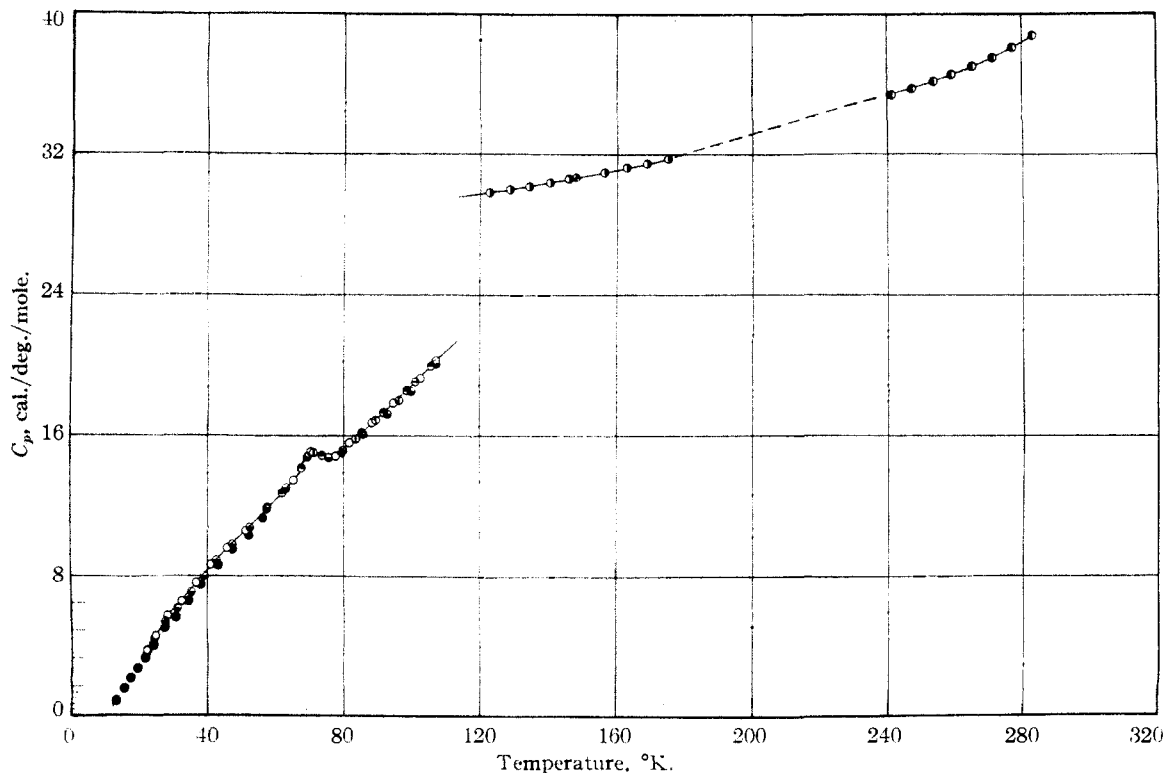


Fig. 1.—The heat capacity of isopentane (data arranged according to temperature): ●, series VIII, sample distilled into calorimeter at 200–210°K. and frozen. sample held at 90–110°K. for fourteen days, before being cooled to 60°K. over 2 hours, after standing at 60°K. for twelve hours was slowly cooled to 20°K. (three hours); ●, series XV, sample held between 60–110°K. for twenty-one days, heated to 200°K. and stood between 200–230°K. for one week, slowly frozen, melted, refrozen and then kept between 100–120°K. for twenty-four days, calorimeter now cooled from 82 to 20°K. in twenty-five minutes, heat capacities taken continuously till 60°K., seven hours then elapsing before the remaining heat capacities and heat of fusion were taken; ●, series XVI, sample held for twenty-three days between 100–120°K. (the history of cooling of the sample to 20°K., and the method of taking the heat capacities were practically the same as for series XV); ○, series XVII, after standing sixteen days at 100–120°K. the sample was slowly cooled to 20°K. as in series VIII, heat capacities were then taken continuously till 60°K., eighty-four hours then elapsing before the measurements to 113°K. and the heat of fusion were completed; ●, series II, sample had been frozen and melted twice during four days before the points of this series were taken; ●, series IV, after series II, the sample was heated to room temperature, cooled rapidly to 260°K., and then slowly to the melting point and frozen, then melted, warmed to 200°K., refrozen and remelted over twenty-four hours, taking eight hours to heat to the initial temperature of the series, after which points were taken continuously over eighteen hours; ⊕, series (A), as in previous paper; ●, series (I), as in previous paper; ⊖, series (M) and (N), as in previous paper.

are included in Table I with the values on the solid. Column 3 gives the values of Parks, Huffman and Thomas.⁴

The Vapor Pressure Measurements.—The measurements over the complete pressure range were taken on a sample of uncertain thermal history. The results are given in Table II. Column one gives the absolute temperature as read on the resistance thermometer. Column two gives the observed pressure and column three the difference between the observed pressure and that calculated from the temperature by means of the equation

$$\log_{10} P_{\text{mm.}} = -9170.850/T - 194.4680 \log_{10} T + 0.3108920T - 1.936031 \times 10^{-4}T^2 + 439.3143 \quad (1)$$

Column four gives the temperature difference corresponding to the pressure difference. In view of the hysteresis demonstrated in the previous paper² the points in the low pressure range obviously have no meaning to better than one mm. Since no hysteresis is observed above 50 mm., the data obtained above this pressure are of the usual accuracy.³

The Melting Point and Normal Boiling Point.—The method of determination of the melting point was that described before.⁵ From the results, the solid-insoluble, liquid-soluble impurity present in the sample was found to be 0.005 mole

⁽⁵⁾ Aston and Messerly, *THIS JOURNAL*, **58**, 2354 (1936)

TABLE II

THE VAPOR PRESSURE OF ISOPENTANE

0°C. = 273.16°K.; b. p. = 300.90°K.; (g for State College = 980.124, "I. C. T.")

T obsd.	P obsd. Int. mm. Hg	P obsd. - P calcd. Int. mm. Hg	T calcd. - T obsd., °K.
217.206	10.95	-0.001	-0.001
231.421	29.08	+ .017	+ .009
238.811	45.67	+ .007	+ .002
245.332	66.28	+ .038	+ .010
250.394	87.14	- .030	- .006
255.761	114.89	- .012	- .002
263.604	168.56	- .018	- .002
270.597	231.49	- .027	- .002
276.940	304.43	- .104	- .008
281.631	369.37	- .130	- .009
286.987	456.51	+ .053	+ .003
292.208	556.43	+ .318	+ .016
295.196	620.98	- .072	- .003

per cent. Three determinations of the melting point were made under different conditions. No detectable difference in the melting point could be determined between samples which gave different liquid heat capacities. The final value obtained for the melting point of pure isopentane is $113.39 \pm 0.05^\circ\text{K}$. (-159.77°C). Other values reported are -159.6°C ,⁶ -160.6°C ,⁷ -160.0°C ,⁸ -159.6°C ,⁹ and -159.65°C .¹⁰ The normal boiling point of isopentane as calculated from Eq. (1) is $300.90 \pm 0.05^\circ\text{K}$. (27.74°C). The normal boiling point of a portion of the sample which we used, measured in a modified Cottrell apparatus by Dr. Dorothy Quiggle and Mr. R. H. McCormick of the Petroleum Refining Laboratory, was $27.78 \pm 0.05^\circ\text{C}$. The check thus obtained is additional confirmation of the validity of our vapor pressures above 50 mm. Other values reported for the normal boiling point are 27.8°C ,⁷ 28.0°C ,¹ 29.7°C ,¹¹ 30.55°C ,¹² 28.05°C .¹³ and 27.95°C .¹⁴

The Heats of Fusion and Vaporization.—The methods have been described before.^{5,15} The results are given in Tables III and IV. In calculating the heat of vaporization at 298.16°K , use was made of the data on the heat content of

(6) Hoog, Smittenberg and Visser, in Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939.

(7) Smittenberg, Hoog and Henkes, ref. 6.

(8) Timmermans, *Comm. Phys. Lab. Univ. Leiden Suppl.*, No. 64, 3 (1929).

(9) Timmermans and Martin, *J. chim. phys.*, **23**, 747 (1926).

(10) Timmermans, Horst and Onnes, *Chem. Zentr.*, IV, 377 (1923).

(11) Fischer and Klemm, *Z. physik. Chem.*, **147A**, 275 (1930).

(12) Brown and Carr, *Ind. Eng. Chem.*, **18**, 718 (1926).

(13) Anderson and Erskine, *ibid.*, **16**, 263 (1924).

(14) Young and Thomas, *J. Chem. Soc.*, **71**, 440 (1897).

(15) Messerly and Kennedy, *THIS JOURNAL*, **62**, 2988 (1940).

TABLE III

HEAT OF FUSION OF ISOPENTANE

Cor. heat input, cal./mole	$\int C_p dT$, cal./mole	Premelting, cal./mole	ΔH fusion, cal./mole
1460.6	235.1	0.3	1225.8
1430.2	204.7	.6	1226.1
1441.1	218.3	.0	1225.8
1444.3	217.3	.0	1227.0
1438.3	211.6	.0	1226.7

Average = 1226.3 ± 0.5

Measured (Parks, *et al.*) = 1222

TABLE IV

MOLAL HEAT OF VAPORIZATION OF ISOPENTANE

T , °K. vap.	Cor. heat input, cal./mole	$\int C_p dT$, cal./mole	Moles vap.	ΔH vap., cal./mole	ΔH vap., cal./mole 298.16°K.
293.92	7746.6	1809.7	0.04970	5937	5880
293.98	6249.9	317.8	.04434	5932	5875
Average					5878 ± 5

Calculated from Eq. (1) and the modified Berthelot equation at 298.16°K . with $T_c = 461^\circ\text{K}$. and $P_c = 32.9$ atm. (Berthelot correction = 336 cal.)

5850

Calculated from Eq. (1) and the modified Berthelot equation at 240.00°K . (Berthelot correction = 37 cal.)

6617

the gas calculated from the spectroscopic data to be discussed. The heat of vaporization also has been calculated at 298.16°K . by thermodynamics using Eq. (1) and the modified Berthelot equation with $T_c = 461.0^\circ\text{K}$. and $P_c = 32.9$ atm.¹⁶ This result is also given in Table IV, along with the value calculated similarly at 240.0°K .

The Entropy from Thermal Data.—The calculation at 240°K . and at 298.16°K . is summarized in Table V. The correction for gas imperfection is based on the modified Berthelot equation of state with critical constants cited above. The area between 180 and 240°K . was taken simply by averaging arithmetically the highest and lowest curves obtained in the previous paper.² For the solid and the rest of the liquid range, the heat capacities in Table I and shown in Fig. 1 determined the area. The difference in area between the highest and lowest curve for the liquid is 0.18 E. u. and this uncertainty, together with the uncertainty in the rather large Debye extrapolation, mainly determines the error assigned to the entropy values.

The Entropy from Thermal and Molecular Data.—Table VI summarizes the calculation of the frequency formally associated with the mode of torsional motion between the ethyl and iso-

(16) "International Critical Tables," Vol. 3, McGraw-Hill Book Company, New York, N. Y., 1928, p. 248.

TABLE V
THE MOLAL ENTROPY OF ISOPENTANE
Mol. wt., 72.146; 0°C. = 273.16°K.

	E. u.	
0-21.00°K. Debye extrapolation (6 degrees of freedom, $\theta = 122$)	1.334	
21.00°K.-113.39°K., graphical	18.293	
Fusion, 1226.3/113.39-113.39-240.00°K., graphical	10.814	
	23.824	
Entropy of liquid at 240.00°K.	54.265 ± 0.4	54.265 ± 0.4
Vaporization 6616.6/240.00		27.569
Entropy real gas at 0.06446 atm.		81.834
Gas imperfection ^a		0.023
Entropy ideal gas at 0.06446 atm.		81.857
Compression to 1 atm.		- 5.447
Entropy ideal gas at 240.00°K. and 1 atm.		76.41 ± 0.5
240.00-298.16, graphical		8.123
Entropy of liquid at 298.16°K.	62.388 ± 0.5	
Vaporization 5878/298.16		19.714
Entropy real gas at 298.16°K.		82.102
Gas imperfection ^a		0.097
Entropy ideal gas at 298.16°K.		82.199
Compression to 1 atm.		- 0.190
Entropy ideal gas at 298.16°K. and 1 atm.		82.01 ± 0.55

^a $S_{\text{ideal}} - S_{\text{real}} = 27RT_0^3P/32T^3P_0; P_0 = 32.9 \text{ atm.}, T_0 = 461^\circ\text{K.}$

propyl groups. The constants used were $N = 6.06 \times 10^{-23}$, $R = 1.9869 \text{ cal./deg.}$ and $hc/k = 1.4325 \text{ cm. deg.}$ For the calculation of the translational and rotational entropy the method is exactly the same as that used for *n*-butane,¹⁷ except that for isopentane, the symmetry number of each of the three forms is unity. The vibrational frequency assignment was based on the work of Kohlrausch and Köppl¹⁸ and of Mecke:¹⁹ C-chain; (250 (1)), 366 (1), 469 (2), 796 (1),

(17) Aston and Messerly, *THIS JOURNAL*, **62**, 1919 (1940).

(18) Kohlrausch and Köppl, *Z. Physik. Chem.*, **B26**, 209 (1934).

(19) Mecke, *ibid.*, **B36**, 347 (1937).

TABLE VI
THE ENTROPY OF ISOPENTANE IN THE IDEAL GAS STATE
FROM MOLECULAR AND SPECTROSCOPIC DATA

	Entropy, cal./deg./mole	
	$T = 240.00^\circ\text{K.}$	$T = 298.16^\circ\text{K.}$
Translation and external rotation of rigid molecule ($N_{\text{asym.}} = 0.6817$, $N_{\text{sym.}} = 0.3183$) ^a	65.101	66.829
Vibrational	3.913	6.351
Total	69.014	73.180
Calorimetric	76.410 ± 0.5	82.009 ± 0.55
S_{rr}	7.396	8.829
S_{rr} 3CH ₃ , $V = 3700 \pm 200$, $I = 5.2 \times 10^{-40}$	4.665	5.972
S_{rr} C ₂ H ₅ (exptl.)	2.73	2.86
S_{rr} C ₂ H ₅ 116 cm. ⁻¹	2.73	3.16
Pitzer ²⁰ S_{total}		82.0

^a The quantities in parentheses are the respective mole fractions of the asymmetrical and symmetrical forms used in calculating the entropy of mixing. They were calculated assuming no heat of transition and an entropy difference equal to that in their rotational entropy.

906 (1), 948 (1), 979 (1). Hydrogen bending and stretching; 950 (11), 1327 (4), 1448 (6), 2900 (12) cm.⁻¹. The lowest skeletal bending mode is missing from all spectral data and has been chosen at 250 cm.⁻¹ by analogy with *n*-butane. The rotation of the three methyl groups is assumed to be restricted by a potential of 3700 cal./mole.

Solution at the lower temperature indicates a torsional frequency of 116° cm.⁻¹ corresponding to a restricting potential of the order of 8000 cal./mole. Using this frequency, comparison of the entropies of the gas at 298.16° gives results which are not entirely satisfactory. That the thermal data may be in error by an amount considerably more than usual is probable.

As far as experiment is concerned, the agreement between the barriers found at two temperatures is affected only by the thermal data between the two temperatures, and the heats of vaporization. It is doubtful if an appreciable error could be made in these quantities. On the other hand, the uncertainties in the calculation from the molecular and spectroscopic data could well account for the lack of agreement (0.3 E. u.) at the two temperatures. However, a value of the entropy of the gas at 298°K. in exact agreement with our experimental value has been calculated by Pitzer²⁰ using a method different from

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

his original one. Pitzer has discussed his second method as compared to the one used here (Pitzer's first method) in the case of *n*-butane and *n*-pentane.²¹ His second method separates "steric" effects hindering rotation from those of the type which occur in ethane (probably due to hydrogen repulsions). The steric effects are allowed for in a separate factor in the partition function. This factor allows for the fact that the energy due to steric hindrance is not the same in each of the positions of minimum (or of maximum) energy. On the other hand, the method used here combines the two effects and assumes that all minima (and maxima) are equal. The error produced in such a procedure is less than in the cases of *n*-butane and *n*-pentane because two of the minima (and maxima) have the same steric effects. If *all* the minima had the same steric effects, our procedure would be correct and the potential barrier would be the sum of the two effects. Taking the value of Pitzer's parameter *a* as 800 cal. and assuming 3600 cal. for the part of the barrier height due to ethane type interaction, the total barrier height would be 4400 cal., aside from slight differences in the vibrational spectrum. The difference between this value and the 8000 cal. obtained by the method of this paper is due to the fact that, by Pitzer's second method, the entropy of mixing of the "forms" of minimum energy is lowered. This is due to the fact that an exponential factor reduces the amounts of all those forms of higher steric energy, and therefore agreement is obtained with the experimental value of the entropy without *having to* make as large a reduction for "hindered rotation." While Pitzer's second method seems to afford a way out of most difficulties,²¹ it does not predict a barrier or steric effect which is large enough to explain the hysteresis in the specific heats of the liquid.

The Free Energy Relations among the Pentanes.—The entropies of neopentane and *n*-pentane for the gases at 298.16°K. have previously been determined experimentally in this Laboratory^{5,15} from third law data down to 10°K. Heats of formation for the three pentanes have been determined by Rossini and Knowl-

ton.^{22,23} Using these experimental values and the experimental results of this research on isopentane, free energies of formation may be calculated. Table VII summarizes the results. Column 1

TABLE VII
FREE ENERGY OF FORMATION OF THE PENTANES AT
298.16°K.

	ΔF_{298} calories	% in equilibrium mixture	% if no neopentane
Neopentane	-5349 ± 320	97.0	...
Isopentane	-3243 ± 300	2.8	93.7
<i>n</i> -Pentane	-1647 ± 270	0.2	6.3

gives values of the free energy of formation for each of the pentanes. Column 2 gives the percentage of each isomer which should exist in an equilibrium distribution of the three pentanes. Column 3 gives similar data for *n*-pentane and isopentane if the formation of neopentane is in some way prohibited.

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Summary

1. The heat capacity from 12–290°K., the vapor pressure from 240–290°K., the melting point, the boiling point, and the heats of fusion and vaporization have been directly determined.
2. An empirical formula has been derived for the vapor pressure over the observed range of temperature and from it values of the boiling point and the heat of vaporization have been calculated.
3. The molal entropies of the gas and liquid, as well as the potential of the torsional motion between the ethyl and isopropyl groups in isopentane, have been calculated from the above data.
4. The free energies of neopentane, isopentane and *n*-pentane at 298°K. have also been calculated from these and previously obtained data.

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(22) Rossini, *Bur. Sids. J. Research*, **12**, 735 (1934).

(23) Knowlton and Rossini, *J. Res. Natl. Bur. Sids.*, **22**, 415 (1939).

(21) Pitzer, *THIS JOURNAL*, **63**, 2413 (1941).