way.[13] The value of 1.09 Å. was used for the C–H distance and the H–C–H angle was taken as 116°56′ as suggested by Linnett.[11] From the data the moments of inertia times 10^{40} g. cm.^{2} were found to be $I_1 = I_2 = 42.3$ and $I_3 = 67.4$. The symmetry number is 6.

In these calculations the nuclear spin entropy, $6R \ln 2 = 8.263$ cal./deg. per mole, has been neglected. The values are compared in Table X. Those calculated from the molecular data may be in error by several hundredths of a unit.[14]

TABLE X

T, °K.	Calorimetric data Actual gas	 Ideal gas	Molecular data less nuclear spin entropy
240.30	54.04	54.17	54.26
298.10	...	56.75	56.84

The agreement of the two entropy values is within their limits of error and shows that cyclopropane approaches zero entropy as the absolute zero is approached.

The value of the entropy calculated from the molecular data is probably the more accurate of the two and this value, 56.84 cal./deg. per mole at 298.10°K., is the one to be used in thermodynamic calculations.

Summary

The heat capacity of solid and liquid cyclopropane has been measured from 15°K. to the boiling point.

The melting and boiling point temperatures were found to be 145.54 and 240.30°K., respectively (0°C. = 273.10°K.).

The heats of fusion and vaporization were determined by calorimetric observation to be 1301 and 4793 cal. mole^{-1}, respectively.

The vapor pressure of liquid cyclopropane was measured and the data has been represented by the equation

$$183 \text{ to } 241\text{°K.} \; \log_{10} P(\text{inter.cm.Hg.}) = 9.03877 - \frac{1348.2}{T} - 0.00823T + 7.45 \times 10^{-6}T^2$$

The density of cyclopropane gas at 298.10°K. and one atmosphere was found to be 1.7463 g./liter.

The calorimetric data have been used to calculate the entropy of cyclopropane gas and this value has been compared with one obtained from molecular data and it is found that the entropy of cyclopropane approaches zero near the absolute zero of temperature.

The most reliable value of the entropy is the one obtained from molecular data, 56.84 cal./deg. per mole at 298.1°K. and one atmosphere. This value does not include the nuclear spin entropy.

RECEIVED MARCH 7, 1946

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(13) Pauling and Brockway, THIS JOURNAL, 59, 1223 (1937).

(14) Note added in proof.—The modified frequency assignment of Smith, *Phys. Rev.*, [2] **59**, 924 (1941), and an H–C–H angle of 136° as suggested by his measurements of the rotational structure of the C–H vibration give 54.20 for the entropy at 240.30°K. which is in better agreement with calorimetric entropy. The corresponding value at 298.10°K. is 56.81 cal./deg. per mole.

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

The Thermodynamics of 2,2-Dimethylbutane, Including the Heat Capacity, Heats of Transitions, Fusion and Vaporization and the Entropy

BY JOHN E. KILPATRICK AND KENNETH S. PITZER

These measurements were made primarily to test the reliability of the general formulas[1,2] for the entropies of paraffin hydrocarbons proposed by one of us in 1940. As can be seen from Table X the agreement is excellent. In addition an interesting sequence of transitions was found in this substance, this sequence being very similar to that of cyclopentane.

Apparatus.—Three different calorimeters were used in this investigation. Hereafter they will be referred to as calorimeters I, II and III. The same numerals will be used to designate the three series of measurements performed, respectively, in the three calorimeters.

The basic apparatus, excluding the calorimeter, was essentially the same in all three series of measurements. This apparatus and calorimeter I have been described previously.[3]

In series I, measurements were made from 14° K. to above the triple point. At this time, it became obvious that a small leak had developed in the calorimeter. This series was terminated. Since it proved to be impractical to repair the leak a new calorimeter was constructed.

It was intended that calorimeter II should duplicate calorimeter I; however, certain changes were made inadvertently which caused it to be slow to reach equilibrium. Therefore, no heat capacity measurements with calorimeter II are reported. Calorimeter III was generally similar, but its platinum resistance thermometer was constructed with wire helices on a mica cross and extended to the top of the calorimeter.

The thermometers of calorimeters II and III were annealed in the usual manner and calibrated at the hydrogen triple point and at several vapor pressures of hydrogen, at the 43.76° K. transition of oxygen, its triple point and several vapor pres-

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(1) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).

(2) Pitzer, *Chem. Rev.*, **27**, 39 (1940).

(3) L. Guttman and K. S. Pitzer, THIS JOURNAL, **67**, 324 (1945).

sures and the ice and steam points. Also, the carbon dioxide sublimation point and sulfur boiling point were measured on II and the nitrous oxide triple point[4] on III. The ice point is taken as 273.16° K. The temperature scale was constructed with the aid of the international temperature scale formula and the data of Hoge and Brickwedde.[5]. The estimated error is a few hundreths of a degree except for a small region near 30° K. where it may be a tenth of a degree. Thermometer III was checked at the boiling point of oxygen after the completion of all measurements and was found not to have changed detectably.

Material.—Two highly purified samples of 2,2-dimethylbutane were furnished us by Dr. F. D. Rossini. One sample was used in series I and II and the other in series III. The samples appeared to be identical in all respects and each showed 0.005 mole per cent. of liquid soluble–solid insoluble impurity on the basis of melting point measurements. Pre-melting specific heat measurements indicating even smaller impurity.

Transition and Melting Points.—2,2-Dimethylbutane shows two transitions. So far as we are aware, the transition at 140.88° K. has not been reported previously. The temperature measurements on the transitions are given in Tables I and II, while those on the melting point (triple point) are in Table III. The rather large variation between series in the 140.88° transition is probably connected to its very small latent heat and consequent sensitivity to impurities or other disturbances.

The heat of fusion is so small that even the small impurity present affects the temperatures considerably. This situation, without doubt, is responsible for the large variation in literature values. Furthermore, in our work the variation with fraction melted does not follow the shape of curve predicted by Raoult's law.

TABLE I

TEMPERATURE OF THE LOWER TRANSITION OF 2,2-DIMETHYLBUTANE

% Tranformed	Temperature
Series I	
11	126.825° K.
19	126.837
82	126.862
	(126.86)
Series II	
5	126.740
27	126.767
48	126.775
70	126.783
	(126.79)
Series III	
18	126.762
48	126.777
81	126.785
	(126.79)
Accepted value, this research	126.81 ± 0.05° K.
Stull[6]	127.11°

TABLE II

TEMPERATURE OF THE UPPER TRANSITION OF 2,2-DIMETHYLBUTANE

% Transformed	Temperature
Series I	
41	140.781
72	140.785
	(140.79)
Series II	
23	140.916
41	140.921
	(140.93)
Series III	
27	140.899
54	140.911
82	140.920
	(140.93)
Accepted value, this research	140.88 ± 0.1° K.

TABLE III

THE MELTING POINT OF 2,2-DIMETHYLBUTANE

% Melted	Temperature
Series I	
23	174.076
59	174.145
	(174.19)
Series III	
18	174.010
39	174.059
60	174.089
	(174.12)
Accepted value, this research	174.16 ± 0.05° K.
Stull[6]	172.13
Hicks-Bruun[7]	174.46

We did not observe the peculiar behavior described by Hicks-Bruun, Bruun and Faulconer.[7] Possibly they obtained still another solid phase which never appeared in our experiments. Visual cooling experiments with the 2,2-dimethylbutane in a glass ampoule showed the formation of a clear solid, then a barely visible boundary surface as the 140° transition took place with solid II also transparent. At the 127° transition the material broke up into white crystals. On heating, the material remained white until it melted.

Vapor Pressures.—The mercury manometer was connected to the filling line of the calorimeter on one side and was continuously evacuated on the other. It consisted of a U-tube, 12.4 mm. i.d. The heights of the mercury columns were measured with a Gaertner cathetometer. The meniscus correction was made according to the

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[4] H. J. Hoge. *J. Research. Natl. Bur. Stds.*, **34**, 281 (1945).

[5] H. J. Hoge and F. G. Brickwedde. *ibid.*, **22**, 351 (1939).

[6] D. R. Stull. THIS JOURNAL. **59**, 2726 (1937).

[7] M. M. Hicks-Bruun. J. H. Bruun and W. B. M. Faulconer, THIS JOURNAL. **61**, 3099 (1939).

tables of Blaisdell.[8] The values listed are in international millimeters of mercury (0° C., g = 980.665). At the end of each heat capacity determination in series III above 210° K. the vapor pressure was measured. In addition, two determinations at the ice-point, with different ice-baths, were made of the vapor pressure of the sample from series I. The two readings agreed perfectly. All results are listed in Table IV.

TABLE IV

THE VAPOR PRESSURE OF 2,2-DIMETHYLBUTANE, 0° C. = 273.16° K.

T, °K.	$P_{\text{obs.}}$, mm.	$P_{\text{obs.}} - P_{\text{calcd.}}$	$T_{\text{obs.}} - T_{\text{calcd.}}$
211.00	1.91	−0.04	+0.24
219.75	4.05	− .04	+ .13
229.91	8.90	+ .04	− .07
240.70	18.52	+ .09	− .08
250.29	33.11	− .03	+ .01
258.32	52.05	+ .04	− .02
266.98	81.45	− .08	+ .02
275.30	121.60	− .06	+ .01
282.87	170.85	− .05	+ .01
289.39	225.33	+ .14	− .01
273.16	110.12	+ .05	− .01

The following equation was selected as best representing the main series of measurements (excluding the ice-point readings)

$$\log P_{\text{mm.}} = 6.7329 - 1072.7/(T - 44.50) \quad (1)$$

Deviations between calculated and observed pressures and temperatures are shown in Table IV, each on the basis that there is no deviation in the other. These deviations may be explained as the combined effect of errors of 0.01° in temperature and 0.05 mm. in pressure with a single exception at 240.70° K. where 0.08 mm. must be assumed. The ice-point reading agrees well within these limits, serving as a check on the thermometer.

The vapor pressure of 2,2-dimethylbutane has been measured by Willingham, Taylor, Pignocco and Rossini[9] over the range from 288.5° K. to the boiling point and thus just joins our data. Their equation is

$$\log P_{\text{mm.}} = 6.75483 - 1081.176/(T - 43.817) \quad (2)$$

At 289° K. equation (1) gives a pressure 0.2 mm. higher than (2) and a slope 0.2% lower. While better agreement would be desirable, this is reasonably satisfactory.

Heat Capacity.—The heat capacity measurements of series I and series III overlap for 80° and agree well within experimental error. Series II was discarded for reasons already given. Measurements are reported on the basis of the defined calorie equal to 4.1833 international joules. The correction for sample vaporized into the filling line amounted to 1.50 cal. per degree at the highest temperature, but is quite accurate and decreases rapidly at lower temperatures. Thermal equilibrium was attained only very slowly with solid II, which accounts for the appreciable scatter of the heat capacities on this phase.

Under optimum conditions, the experimental error should be considerably less than 0.2%. However, in the regions already mentioned and below 40° K. (the latter because of thermometer uncertainty) the errors are larger and may reach 1%. The original measurements are given in Table V with smoothed values at rounded temperatures in Table VI and Fig. 1. The curve of Stull,[6] also shown in Fig. 1, deviates in places by 5%. Considering also his failure to observe the 140° transition, it seems doubtful whether the type of calorimeter used in that research is suitable for accurate measurements.[10]

TABLE V

THE MOLAL HEAT CAPACITY OF 2,2-DIMETHYLBUTANE

Temp., °K.	C_p, cal./deg. mole
Series Ia	
15.52	1.700
16.54	1.971
17.96	2.416
19.67	2.979
21.10	3.443
22.56	3.909
24.58	4.607
26.93	5.380
34.94	7.583
38.77	8.419
43.28	9.351
48.85	10.472
57.21	11.962
63.32	12.892
Series Ib	
28.67	5.882
31.78	6.770
34.67	7.498
45.23	9.758
51.86	11.033
Series Ic	
85.97	16.46
92.32	17.47
99.49	18.58
107.07	19.71
115.87	21.11
Series Id	
64.32	13.02
68.80	13.77
73.48	14.48
79.02	15.33
85.07	16.35
90.35	17.16
98.40	18.42
123.73	22.45
Series IIIa	
89.28	16.96
96.77	18.17
103.71	19.26
110.69	20.35
118.45	21.58
Series Ie	
132.90	30.57
135.00	30.75
137.48	31.11
Series If	
131.85	30.54
134.17	30.75
Series IIIb	
132.16	30.30
137.15	30.93
Series Ig	
146.10	32.16
152.05	32.39
158.60	32.59
165.71	32.88
Series Ih	
143.95	32.17
149.02	32.32
162.50	32.79
169.90	33.16
Series Ii	
147.00	32.38
154.61	32.53
161.80	32.78
166.86	32.93
168.77	33.03
Series IIIc	
146.41	32.23
154.19	32.44
163.10	32.73
Series IIId	
157.80	32.59
164.83	32.85
169.71	33.04
Series IIIe	
178.73	36.00
187.51	36.56
197.11	37.22
206.62	37.78
215.72	38.38
225.24	39.12
236.65	40.00
246.07	40.72
254.86	41.49
263.15	42.16
271.71	42.95
279.57	43.69

Heats of Transition and Fusion.—The heats of transition and fusion were measured in the usual

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[8] B. E. Blaisdell. *J. Math. and Phy.*, **XIX3**, 226 (1940).

[9] C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research, Natl. Bur. Stds.*, **35**, 219 (1945).

[10] Very recently Dr. H. M. Huffman has also made measurements on this substance which agree satisfactorily with those of the present research.

TABLE VI

THE MOLAL HEAT CAPACITY OF 2,2-DIMETHYLBUTANE AT ROUNDED TEMPERATURES

Temp., °K.	C_p, cal./deg. mole	Temp., °K.	C_p, cal./deg. mole
Solid III		Solid I	
20	3.08	150	32.35
25	4.76	160	32.67
30	6.28	170	33.01
40	8.69	Liquid	
50	10.67	180	36.08
60	12.41	190	36.72
70	13.95	200	37.35
80	15.49	210	37.99
90	17.09	220	38.71
100	18.67	230	39.49
110	20.24	240	40.25
120	21.83	250	41.05
Solid II		260	41.91
130	30.36	270	42.81
140	31.18	280	43.73
		290	44.67

manner and are reported in Tables VII, VIII and IX. Values obtained in series II are included. Apparently, the slowness in attaining equilibrium had little effect. The resistance thermometer on the outside of the calorimeter was used to measure the temperature of the radiating surface for heat exchange corrections.

TABLE VII

THE HEAT OF THE LOWER TRANSITION OF 2,2-DIMETHYLBUTANE

$T = 126.81°$ K.

Series	Temp. interval, °K.	Heat input, cal./mole	$\int C_p dT$, cal./mole	ΔH, cal./mole
I	124.33-128.23	1458.4	162.8	1295.6
I	126.40-131.62	1508.8	221.7	1287.1
II	124.61-129.88	1492.2	206.1	1286.1
II	125.24-129.38	1451.4	163.5	1287.9
III	122.66-129.58	1553.6	264.1	1289.5

Accepted value, this research 1289.2 ± 3
Stull[6] 1095

TABLE VIII

HEAT OF THE UPPER TRANSITION OF 2,2-DIMETHYLBUTANE

$T = 140.88°$ K.

Series	Temp. interval, °K.	Cor. heat input, cal./mole	$\int C_p dT$, cal./mole	ΔH, cal./mole
I	138.85-141.61	192.29	124.77	67.52
I	139.68-141.11	131.81	64.56	67.25
I	140.02-141.38	129.33	62.10	67.23
II	140.43-141.14	99.53	31.48	68.05
II	140.46-141.41	110.64	41.99	68.65
III	140.82-141.75	110.77	42.76	68.01
III	140.47-141.71	123.88	56.34	67.54
III	139.59-142.13	182.39	114.13	68.26

Accepted value, this research 67.7 ± 1

Heat of Vaporization.—Calorimeter III was not well suited for heat of vaporization measurements because the heater extended above the liquid level. Then the gas may be superheated before leaving the calorimeter. Indeed the results show a progressive rise in apparent heat of vaporization as the liquid level dropped. Consequently, we can only report the apparent heat of vaporization, with the highest level of liquid, 6819 cal. per mole at 282.6° K., and conclude that the true value is lower by not more than about 20 cal.

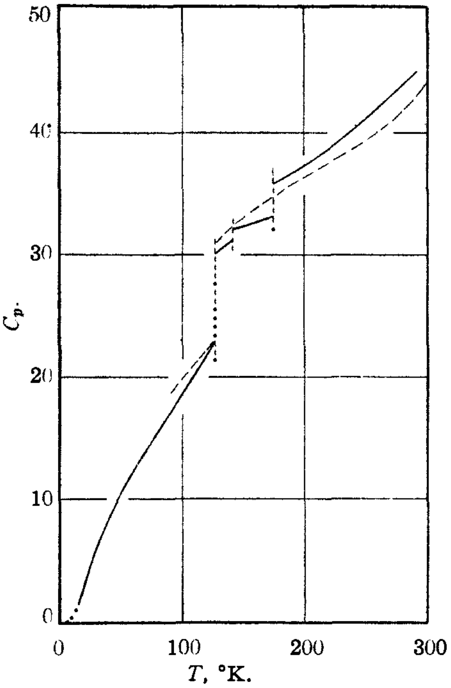

Fig. 1.—The molal heat capacity of solid and liquid 2,2-dimethylbutane: solid line, this research; dashed line, Stull.

TABLE IX

HEAT OF FUSION OF 2,2-DIMETHYLBUTANE

$T = 174.16°$ K.

Series	Temp. interval, °K.	Cor. heat input, cal./mole	$\int C_p dT$, cal./mole	ΔH fusion, cal./mole
I	171.50-175.10	315.0	176.4	138.6
I	173.02-174.90	231.3	92.8	138.5
I	168.42-177.55	588.9	450.1	138.8
III	168.31-176.94	554.3	416.7	137.6
III	168.49-176.79	539.7	401.0	138.7

Accepted value, this research 138.5 ± 0.5
Stull[6] 111

Fortunately we have available an accurate measurement by Osborne and Ginnings,[11] 6617.4 ± 6 cal. at 298.16° K., together with a value measured by one of us,[12] 6355 ± 20 cal. at 322.9° K. The heat capacity data on gas (discussed below) and liquid indicate that $\Delta C_p = -11.5$ for vapori-

[11] N. S. Osborne and D. C. Ginnings, Natl. Bur. Stds., unpublished data.

[12] K. S. Pitzer, THIS JOURNAL, 63, 2413 (1941).

zation. Combining all these values one obtains as an equation

$$\Delta H_{\text{vap.}} = 10051 - 11.5T \text{ cal. per mole} \quad (3)$$

which should be accurate to 10 cal. in the range 270–340° K.

The correlation between equation (3) and the vapor pressure equations was studied. However, until more is known concerning the imperfection of the gas, the only conclusion is that there is no conflict between calorimetric and vapor pressure data.

Entropy from Calorimetric Data.—The entropy was calculated by the usual integration methods. The extrapolation below 15° K. was made on the basis of a Debye function for six degrees of freedom with a value of 123° for Θ.

Statistical Thermodynamic Data.—The entropy calculated[1] in 1940 by relatively crude methods is compared with the experimental value in Table X. The exactness of agreement is probably fortuitous, but in any event increases our confidence in the general method employed. As has been noted elsewhere,[13] the hydrogen bending frequencies assigned in 1940 were too low, giving too great a heat capacity for the gas at ordinary temperatures. There is not yet enough more data to make a thorough revision at this point. However, this matter is not important for the calculation of entropies at room temperature nor does it seriously affect differences in various functions between hydrocarbon isomers.

TABLE X

THE ENTROPY OF 2,2-DIMETHYLBUTANE

0.00–15.00°K.	Debye extrapolation	0.546
15.00–126.81	Integration—Solid III	21.644
126.81	Transition (1289.2/126.81)	10.166
126.81–140.88	Integration—Solid II	3.227
140.88	Transition (67.7/140.88)	0.480
140.88–174.16	Integration—Solid I	6.907
174.16	Fusion (138.5/174.16)	0.795
174.16–298.16	Integration—Liquid	21.365
Entropy of liquid at 298.16° K.		65.13 ± 0.15
298.16	Vaporization (6622/298.16)	22.21
298.16	Gas imperfection[a]	0.10
298.16	Compression to 1 atm.	−1.72
Entropy of ideal gas at 298.16° K. and 1 atm.		85.72 ± 0.2
Calculated Pitzer[1] (1940)		85.7

[a] Calculated from Berthelot equation with $P_c = 30$ atm., $T_c = 490$°K.

Nevertheless, in order to make progress along these lines it seems worthwhile to attempt detailed statistical thermodynamic calculations for this molecule.

The infrared absorption spectrum has been given by Avery and Ellis[14] and the Raman spectrum by several workers.[15] A unique assignment of vibration frequencies cannot be made from these data alone and normal vibration calculations are hardly feasible for a molecule of this complexity and low symmetry. A tentative assignment has been made by analogy from related molecules, together with a knowledge of the expected number of frequencies in each general range. For example, tetramethylmethane has skeletal bending frequencies at 335 (double) and 415 (triple). One motion each of the pair and triplet should be substantially unchanged in 2,2-dimethylbutane because they allow the additional carbon atom to remain stationary. Indeed we find Raman lines at 339 and 411 and an infrared band at 418 cm.$^{-1}$ in 2,2-dimethylbutane. Similar arguments indicate that the remaining four skeletal bending modes should be distributed with one below 335, two below 415 (and possibly below 335), and one probably above 415. If we take all the remaining Raman lines in this region we have 260, 276, 362 and 485 cm.$^{-1}$, which are the correct number and in reasonable positions. Table XI gives the complete assignment.

TABLE XI

TENTATIVE ASSIGNMENT OF VIBRATION FREQUENCIES OF 2,2-DIMETHYLBUTANE

Skeletal bending	260, 276, 339, 362, 418, 485
C–C stretching	710, 1020, 1251 (3)
CH_2 and CH_3 rocking	782, 870, 930 (2), 995, 1073 (2), 1217 (2), 1340
CH_2 twisting	1304
CH_3 sym. bending	1376 (4)
CH_2 sym. bending	1439
CH_3 unsym. bending	1475 (8)
C–H stretching	2950 (14)

Certain of the higher frequencies in Table XI are quite arbitrary, but certainly near the correct values. The greatest uncertainty is in the CH_2 and CH_3 rocking frequencies, which are low enough to be of some importance thermodynamically yet not definitely assignable from the spectra.

The entropy of translation and over-all rotation is readily calculated by the usual methods. Using tetrahedral angles, 1.54 Å. for the C–C distance and 1.09 Å. for the C–H distance one obtains 32.467, 32.385, and 19.324 (each $\times 10^{-39}$ g. sq. cm.) for the three principal moments of inertia. The axis of least inertia makes an angle of 36° 8.6′ with the ethyl–tertiary-butyl bond.

The class of molecules for which Pitzer and Gwinn[16] gave formulas for internal rotation are those composed of symmetrical tops attached to a rigid frame. In 2,2-dimethylbutane, we have methyl groups rotating on the tertiary butyl skeleton which in turn rotates with respect to the ethyl group. Consequently, this molecule does not fall in the class treated previously. However, the moment of inertia of the skeletal rotation is an order of magnitude larger than that of the methyl groups. Consequently, the coupling is very small

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(13) K. S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944).

(14) W. H. Avery and C. F. Ellis, *J. Chem. Phys.*, **10**, 10 (1942).

(15) E. J. Rosenbaum, A. V. Grosse and H. F. Jacobson, THIS JOURNAL, **61**, 689 (1939); P. A. Bazhulin, *et al.*, *Bull. acad. Sci. U. R. S. S., Classe Sci. Chim.*, 198 (1943).

(16) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

and one may treat the motions separately with good approximation.

The more involved methods appropriate to this type of molecule have been worked out and will be published elsewhere; however, for reasons given in the next paragraph, the refinements would be quite insignificant.

Using the distances given above, the reduced moment of the skeletal rotation is 33.8×10^{-40} g. sq. cm. and the methyl group moment is 5.30×10^{-40}. However, the value 5.50×10^{-40} has been found recently for the methyl group in ethane and the methyl halides.[17] The spectrum of methane,[17] on the other hand, gives 5.33×10^{-40} and the spectra of various deuteromethanes[17] confirm this value. Consequently, one cannot assign a methyl group moment more accurately than $(5.4 \pm 0.1) \times 10^{-40}$.

While the exact value of the reduced moment of inertia for the various methyl groups depends on the assumptions concerning skeletal rotation, the differences are insignificant and the rounded average value $(5.3 \pm 0.1) \times 10^{-40}$ will be used for all methyl rotations.

In this molecule there are, strictly, four different potential barriers to internal rotation. However, the differences are probably small and less significant than possible interactions which must also be neglected. Assuming then the same value for all potential barrier heights, one can determine this value to be 4375 cal. per mole in order to fit the entropy at 298.16° K. as shown in Table X. This value may be compared with 4300 cal. per mole for tetramethylmethane.[18]

It may be noted from Table XII that the reasonably certain skeletal bending frequencies contribute most of the vibrational entropy and that those above 1350 cm.$^{-1}$, labeled "all others" contribute very little. Thus, the average potential barrier calculated is certain enough to be significant.

TABLE XII

STATISTICAL ENTROPY OF 2,2-DIMETHYLBUTANE

Potential barrier chosen to fit experimental value

Translation + over-all rotation	66.081
Skeletal internal rotation	3.658
Methyl internal rotation (4)	7.160
Vibration:	
Skeletal bending (6)	7.149
C–C stretching (5)	0.479
Rocking + twisting (11)	.990
All others (28)	.200
Total	85.72

The heat capacity of 2,2-dimethylbutane was calculated from these same data and is shown as the curve in Fig. 2 in comparison with experimental points from several sources.[12,19,20] The slope of the calculated curve is a little too great although the height is about correct at the lower temperatures. Probably the oversimplified treatment of internal rotation accounts for most of the difference.

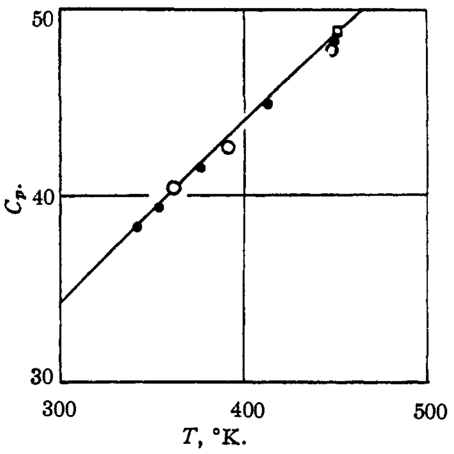

Fig. 2.—The molal heat capacity of gaseous 2,2-dimethylbutane in cal. per degree. Curve is calculated; points are experimental from the following authors: solid circles, Waddington and Huffman[19]; open circles, Pitzer[12]; square, Eucken and Sarstedt.[20]

Discussion.—Probably the most interesting result of this investigation is the pattern of transitions observed, see Fig. 1. Turkevich and Smyth[21] observed the lower transition with the polarizing microscope and reported that 2,2-dimethylbutane is anisotropic below and isotropic above. This combined with the large entropy of transition and small entropy of fusion suggested that molecular rotation begins at the lower transition. However, the existence of the upper transition suggests that this rotation (or randomness of orientation) is somewhat limited in the region 127–140°K. The 2,2-dimethylbutane molecule is very compact but not spherical. The description as trimethyl ethyl methane illustrates this point. Thus it is not unreasonable that there is some preferred relative orientation of ethyl groups in the 127–140° range which is lost at the 140°K. transition.

The very considerable increase in heat capacity at the 127° transition supports the picture of disorder and increased freedom or torsional oscillation above this temperature. If the rotation of the molecules became relatively free a drop, or at least no increase, in heat capacity would be expected.

It is interesting to note that a very similar thermal pattern has been reported for cyclopentane[22] which is likewise very compact but not closely spherical.

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(17) G. Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, pp. 437 ff.

(18) Unpublished calculations of the present authors. Values in this range have been given previously,[1] the differences arising from changes in the vibration frequency assignment.

(19) G. Waddington and H. M. Huffman, private communication.

(20) A. Eucken and B. Sarstedt, *Z. physik. Chem.*, B50, 143 (1941).

(21) A. Turkevich and C. P. Smyth, THIS JOURNAL, **64**, 737 (1942).

(22) J. G. Aston, H. L. Fink and S. C. Schumann, *ibid.*, **65**, 341 (1943).

By comparison, closely spherical molecules such as tetramethylmethane and hexamethylethane show a single large transition well below the melting point, a relatively high melting point and a very short liquid range.

We wish to thank Dr. F. D. Rossini for furnishing the extremely pure samples of 2,2-dimethylbutane and Drs. Waddington and Huffman for giving us the results of their calorimetric measurements in advance of publication.

Summary

The heat capacity of 2,2-dimethylbutane has been measured from 15 to 280° K. and the vapor pressure from 211 to 290° K. The following values were obtained: heats of transition, 1289.2 ± 3 cal./mole at 126.81° K.; 67.7 ± 1 cal./mole at 140.88° K.; heat of fusion 138.5 ± 0.5 cal./mole at 174.16° K.; entropy at 298.16° K., 65.13 ± 0.15 for the liquid and 85.72 ± 0.2 cal./degree mole for the ideal gas.

A vibrational assignment is made and the average potential barrier to internal rotation calculated to be 4375 cal./mole. The experimental entropy agrees very satisfactorily with the value calculated by one of us in 1940, which supports the general method employed then.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF MONTANA STATE COLLEGE]

Heats of Formation of Liquid Methyl Sulfoxide and Crystalline Methyl Sulfone at 18°

BY THOMAS B. DOUGLAS*

The properties of coördinate and of d-orbital bonds are of considerable interest, not only in the theory of molecular structure but by virtue of their occurrence in many well-known compounds. Although thermochemical studies have provided the energies of such bonds in many inorganic compounds, this information is lacking for the majority of the corresponding simple organic compounds, whose study seems particularly inviting because of the relative stability and apparent electromeric simplicity of the bonds attaching the aliphatic radicals.

Both of these bond types probably make major contributions to the structures of the sulfur–oxygen bonds in sulfoxides and sulfones. The heats of formation of methyl sulfoxide and methyl sulfone, hitherto unreported but given in this paper, can later be combined with their heats of vaporization, now being determined by the author, to give what may be formally designated as the sulfur–oxygen bond energies of these two compounds. These values may throw light on the large dipole moment[1] and the unusually short sulfur–oxygen bonds[2] of methyl sulfone.

Because the molar heats of combustion of even such simple organic compounds as these are large, it was thought that more accurate values of their heats of formation from methyl sulfide could be calculated from heats of oxidation by suitable reactions in solution, provided there were employed in each case one oxidant or reductant whose heat of formation had previously been determined accurately by two or more independent workers. This paper reports the results of measuring (1) the heat of oxidation of methyl sulfide to methyl sulfoxide by hydrogen peroxide, and (2) the heat of oxidation of methyl sulfoxide to methyl sulfone by permanganate. The accuracy of the measurements was checked by determining the heat of neutralization of hydrochloric acid by sodium hydroxide.

Experimental

Methyl Sulfide.—Eastman Kodak Co. methyl sulfide was allowed to stand over sodium metal for several days. On distilling, a large middle fraction was collected, b. p. (637 mm.) 32.30–32.32°.

Methyl Sulfoxide.—A small excess of methyl sulfide, mixed with an equal volume of glacial acetic acid, was treated at 0–10° with 30% hydrogen peroxide. The solution was made alkaline and extracted with chloroform. A product was obtained which was 99.8% pure as determined from freezing point measurements and oxidation with permanganate, and showed no appreciable tendency to decompose. Cooling curves indicated 18.5° to be the m. p. of the pure compound.

Methyl Sulfone.—Methyl sulfide was treated with an excess of a 6% solution of potassium permanganate. After separation from the salts by solution in chloroform, the product was recrystallized twice from water. Only one crystalline form appeared, m. p. 108.1–108.5° (cor.).

Apparatus and Calorimetric Method.—Solutions of the required molalities were prepared and standardized using the usual methods and precautions. All weights were corrected to a vacuum basis.

A non-adiabatic calorimetric method was employed, the calorimeter vessel being a closed silvered dewar flask. In each run the reacting solutions other than the first were introduced from the jacket water-bath, which was thermostated to ±0.001° when necessary. Small unavoidable differences in temperature were properly corrected for. Temperatures were measured by Beckmann thermometers, and the temperature rise was corrected by use of the Regnault–Pfaundler equation,[3] the thermal leakage modulus being redetermined in each run. The electrical calibrations were so conducted as to make the calorimetric method a substitution one. All measuring instruments were accurately calibrated, and each standard of potential and resistance was believed to be accurate to ±0.01%. The time of electrical heating was automatically measured to 0.1 second.

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[1] Coop and Sutton, *Trans. Faraday Soc.*, **35**, 507 (1939).

[2] Lister and Sutton, *ibid.*, **35**, 497 (1939).

[3] White, "The Modern Calorimeter," Chemical Catalog Co., Inc., (Reinhold Publ. Corp.), New York, N. Y., 1928, p. 41, equation (13).