[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Heat Capacities and Entropy of Cyclobutane[1]

BY G. W. RATHJENS, JR., AND WILLIAM D. GWINN

RECEIVED AUGUST 3, 1953

Heat capacities of cyclobutane solid and liquid have been obtained over the range 14°K. to its boiling point 285.67°K. A transition at about 145°K. has been investigated. The evidence is not conclusive, but is indicative of a λ-type transition. X-Ray diffraction photographs of the two solid phases have been obtained, and indicate both phases crystalline solids. The melting point of cyclobutane has been found to be 182.43°K. The heats of fusion and vaporization are 260.1 cal./mole and 5781 cal./mole, respectively. Vapor pressure measurements for the liquid have been obtained and represented by equation (1).

In recent years spectroscopic and electron diffraction measurements on cyclobutane and its derivatives have been made in attempts to elucidate structures and evaluate force constants.[2-12] These molecules are of particular interest because of the strained configuration of the carbon skeleton and because of the effect of such strain on the geometry and on the force constants. While these molecules may be expected to have planar carbon skeletons since CCC bond angles are a maximum for such configuration, torsional forces are present tending to cause pseudo-rotation about the C–C bonds thus resulting in non-planar configurations. Indications are that some of the derivatives of cyclobutane, octafluorocyclobutane[8,9] and octachlorocyclobutane,[6] probably have non-planar skeletons. The investigations here described were undertaken primarily as an attempt to throw light on the questions of the structure of cyclobutane and to remove certain other uncertainties in the spectroscopic interpretation.

Apparatus.—The calorimetric apparatus and methods used in this research were similar to those used in other investigations in the University of California's laboratories. A complete description of a similar apparatus has been given by Giauque and Egan.[13] Temperatures were measured with a standard thermocouple and with a gold resistance thermometer–heater which was calibrated against the thermocouple.

Preparation and Purity of the Cyclobutane.—The method of preparation of the cyclobutane has been described by Cason and Way.[14] The sample prepared by them was first used for infrared and Raman investigations before being used for the calorimetric work. Prior to the Raman investigation the purity of the sample was investigated by Dr. J. Y. Beach[3] with a mass spectrometer. He found less than 0.1% impurity with the possible exception of butenes. Because of the method of preparation used, the presence of butene impurity in the original sample was unlikely. However, to investigate this Dr. N. K. Freeman carefully checked the infrared spectra for bands characteristic of butenes; he found no evidence of their presence, and estimated that if present at all the amount was less than 1%. As a result of prolonged exposure in the Raman tube a white gelatinous precipitate, presumably a high polymer, was formed. It would seem likely that some less polymerized molecules also may have formed; however, no new Raman lines appeared after long exposure. The cyclobutane was separated from the polymer by distilling it into the calorimeter. During removal from the Raman tube the frozen cyclobutane was exposed to the air for a few seconds; it was, therefore, dried by passing it over anhydrous magnesium perchlorate. Dissolved atmospheric gases were removed by freezing several times and evacuating the space above the sample. Because of the size of the sample available, no further attempt at purification was made before undertaking the calorimetric investigations.

The premelting effect showed the sample to have approximately 0.19 mole % of liquid-soluble, solid-insoluble impurity. At high concentrations this impurity appeared not to obey Raoult's law, but did so quite well in more dilute solutions (see Table II). It was felt that this amount of impurity was undesirable particularly because of possible effects on the transition, and because it resulted in some uncertainty in the heat of fusion. Therefore, after the heat capacity, heats of transition, fusion and vaporization had been investigated, the material was fractionated by freezing and discarding the lowest melting fraction, and then by fractional distillation. Unfortunately, this only reduced the impurity to 0.14 mole %. This somewhat purified sample was used for the vapor pressure measurements and for a further investigation of the transition.

TABLE I

VAPOR PRESSURE OF LIQUID CYCLOBUTANE
(0°C. = 273.16°K.)

T, °K.	$P_{\text{obsd.}}$, int. cm.	$P_{\text{obsd.}} - P_{\text{calcd.}}$, eq. 1
213.230	1.873	0.006
217.031	2.432	− .002
224.159	3.879	− .017
227.239	4.727	.003
239.301	9.534	.010
245.899	13.520	− .001
252.739	19.038	.016
257.343	23.658	.000
262.848	30.359	.002
270.103	41.425	− .005
278.460	57.931	− .001
285.358	75.122	.001

Vapor Pressure of Cyclobutane.—The vapor pressure was measured in a manometer, the arms of which had a diameter of 1.67 cm., using a standard meter bar and a Gaertner cathetometer as a comparison instrument. The pressure observations were corrected to international centimeters of mercury. In making the corrections the standard acceleration of gravity was taken as 980.665 cm./sec.^{2} and the gravitational acceleration[15] at Berkeley was taken as 979.973 cm./sec.^{2}. The data of Cawood and Patterson[16] were used for making meniscus corrections.

---

[1] Based on a dissertation submitted to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] T. P. Wilson, *J. Chem. Phys.*, **11**, 369 (1943).

[3] N. K. Freeman, Ph.D. dissertation, University of Calif. (Berkeley), 1949.

[4] J. O. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

[5] (a) J. D. Dunitz, *Acta Cryst.*, **2**, 1 (1949); (b) J. D. Dunitz and L. Weissman, *ibid.*, **2**, 62 (1949).

[6] T. B. Owen and J. L. Hoard, *ibid.*, **4**, 172 (1951).

[7] W. F. Edgell, THIS JOURNAL, **69**, 660 (1947).

[8] W. F. Edgell and D. G. Weiblen, *J. Chem. Phys.*, **18**, 571 (1950).

[9] H. P. Lemaire and R. L. Livingston, *ibid.*, **18**, 569 (1950).

[10] H. H. Claassen, *ibid.*, **18**, 543 (1950).

[11] H. Pajenkamp, *Z. Elektrochem.*, **52**, 104 (1948).

[12] G. W. Rathjens, N. K. Freeman, W. D. Gwinn and K. S. Pitzer, THIS JOURNAL, **75**, 5634 (1953).

[13] W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[14] J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949).

[15] Landolt, Börnstein and Roth, "Physikalische-chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

[16] W. Cawood and H. S. Patterson, *Trans. Faraday Soc.*, **29**, 522 (1933).

The vapor pressure may be represented by the equation

$$\log_{10} P = -1912.146/T + 24.66907 - 6.89257 \log_{10} T + 0.0029139T \quad (1)$$

The data are recorded and compared with equation 1 in Table I. Equation 1 was used to determine the normal boiling point, 285.67°K. Although the temperatures are given to 0.001°, the absolute error may be as large as several hundredths of a degree.

The vapor pressure of cyclobutane has been previously measured by Heisig[17] and by Benson.[18] The latter's results are admittedly of a lower order of precision; within the large limits of error, they agree with the results of this research. Most of the vapor pressure measurements of Heisig deviate from those calculated for the same temperature using equation 1 by 0.05–0.20 cm. This disagreement would seem to be more likely due to differences in purity than anything else. The heat of vaporization calculated using an equation fitted to Heisig's data and assuming a Berthelot gas agrees with the measured value of this research about as well as that obtained using equation 1.

Some of the thermodynamic properties of cyclobutane have recently been reported by Kaarsemaker and Coops.[19] Their reported boiling point is 285.7°K.

The Melting Point and the Heat of Fusion of Cyclobutane.—Table II summarizes the data obtained for the melting point of cyclobutane and Table III the data for the heat of fusion. In calculating the melting point of the completely melted samples a graphical plot of temperature *vs.* 1/fraction melted was used. At higher concentrations the data definitely deviate from Raoult's Law (see column 5, Table II).

TABLE II

THE MELTING POINT OF CYCLOBUTANE

M.p. pure cyclobutane 182.43°K.; series I–IV, 0.61416 mole; series V, 0.30344 mole.

Series	Fraction melted	T, °K.	Calcd. impurity in liq. assuming Raoult's law, mole %	Fraction melted × calcd. amt. of impurity, mole %
I	0.9285	181.891	0.212	0.197
II	0.0919	179.89	1.00	0.092
	.329	181.05	0.543	.179
	.617	181.64	.311	.192
III	0.0766	179.67	1.09	0.083
	.245	180.795	0.643	.157
	.479	181.393	.408	.195
	.930	181.929	.197	.183
IV	0.308	180.95	.582	0.179
Extrap.	1.000	181.942	0.192	0.192
Pure cyclobutane (calcd.)		182.458		
V	0.050	180.108	0.914	0.047
	.161	180.949	.583	.094
	.340	181.455	.384	.130
	.561	181.790	.252	.141
	.836	182.003	.168	.140
Extrap.	1.000	182.073	0.140	.140
Pure cyclobutane (calcd.)		182.420		

TABLE III

THE HEAT OF FUSION OF CYCLOBUTANE

(All energies in cal./mole).

Temp. interval, °K.	Energy supplied	$- \int C_p dT +$	Premelting corr. $=$	Heat of fusion
174.659–182.221	403.96	143.70	0.90	261.16
175.380–183.663	419.19	160.82	1.11	259.88
174.900–182.193	397.64	138.51	1.03	260.16
173.410–184.613	477.05	218.68	0.61	258.98
175.203–183.496	420.55	160.62	1.07	261.00
175.310–182.050	385.91	127.71	1.11	259.31
			Mean	260.1

The mean value for the heat of fusion (Table III) is somewhat uncertain (probably about 3 calories) because of uncertainties in the extrapolation of the heat capacities in the region where premelting is significant. However, any error introduced in the entropy of fusion by this uncertainty will be almost entirely compensated by an error in the opposite direction in the entropy resulting from integration of C_p d ln T in the premelting region. Kaarsemaker and Coops[19] give 183.0° as the melting point.

Heat of Vaporization of Cyclobutane.—The heat of vaporization was determined by adding measured amounts of energy to the calorimeter and by weighing the cyclobutane evaporated. The cyclobutane was condensed at the temperature of liquid nitrogen; a capillary system was used to maintain a vapor pressure of approximately 76.00 cm. Corrections were made for small deviations in pressure, for heat exchange between the calorimeter and its environment, and for change in temperature of the calorimeter and its contents between the beginning and end of vaporization measurements. The data are summarized in Table IV.

TABLE IV

HEAT OF VAPORIZATION OF CYCLOBUTANE AT THE NORMAL BOILING POINT

Estimated critical constants: T_c = 458°K., P_c = 49.8 atm.

Amt. evaporated, moles	Time of energy input, min.	ΔH, cal./mole
0.10348	30	5767
.13806	40	5769
.13592	40	5788
.13481	40	5796
	Mean	5781
From vapor press. eq. of this research		5714
From vapor press. eq. of Heisig[15]		5861

The heat of vaporization also has been calculated assuming the correction for gas imperfection can be made by using the Berthelot equation. In order to do this it has been necessary to estimate critical constants for cyclobutane. Heats of vaporization calculated using equation 1 and also the data of Heisig are included in Table IV. The disagreement between the values obtained in this research and the values calculated using equation 1 is greater than is to be expected. This possibly may be due to errors in estimating the critical constants and to the effect of impurity as well as to errors in the measured heats of vaporization.

---

(17) G. B. Heisig, THIS JOURNAL, **63**, 1698 (1941).

(18) S. W. Benson, *Ind. Eng. Chem., Anal. Ed.*, **14**, 189 (1942).

(19) S. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952).

Heat Capacities of Cyclobutane.—The heat capacity results are tabulated in Table V and plotted in Fig. 1. Values taken from smooth curves are tabulated in Table VI. Most of the measurements were made in three series: VII, XI and XII. Several shorter series and some isolated points were also obtained particularly in the temperature ranges just below and above the transition, fusion and vaporization temperatures. Unsuccessful attempts were made to supercool the high temperature solid phase, designated solid I, in the hope that measurements could be made on both solids and the entropies compared. It was found that on slow cooling the solid I phase could be slightly supercooled (about 2°). However, in each of the several experiments when this was tried it was found impossible to further supercool solid I without sudden transformation into solid II (the low-temperature form). (Very rapid cooling was not tried.) One heat capacity determination was made on the slightly supercooled solid I (first run, series V) and heat capacity determined in this experiment is in agreement with others for solid I indicating that little if any of the solid had been transformed into solid II. In order to determine whether or not all of the solid had been transformed into solid I in the various experiments, several different cooling conditions were used. The agreement of the heat capacities obtained in each of the several series, the smooth character of both the heat capacity curve and the cooling curves, and the agreement of the heat of transition measurements are indications that the transition was completed.

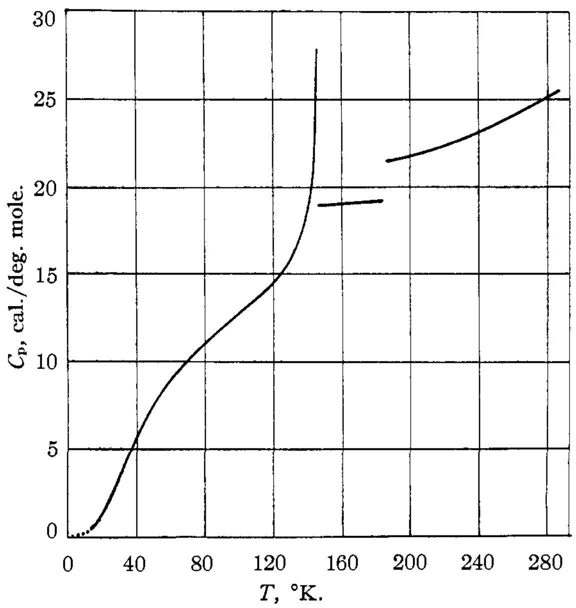

Fig. 1.—Heat capacity of cyclobutane.

TABLE V

HEAT CAPACITIES OF CYCLOBUTANE

Series	T, °K.	Approx. ΔT	C_p, cal./deg. mole	Series	T, °K.	Approx. ΔT	C_p, cal./deg. mole
			Solid II				
XII	13.88	1.16	0.531	VII	107.47	5.3	13.389
XII	17.97	1.29	1.120	I	107.71	5.9	13.423
XII	19.85	2.08	1.451	VII	113.05	5.4	13.845
XII	22.07	2.49	1.734	I	113.79	5.8	13.893
XII	24.89	2.85	2.345	VII	118.73	5.6	14.359
XII	28.54	3.73	3.282	I	119.70	5.4	14.481
XII	32.67	4.46	4.118	VII	124.47	5.7	15.031
XII	36.49	3.55	5.091	I	125.54	5.9	15.184
XII	39.76	3.09	5.490	VII	130.06	5.3	15.94
XII	43.51	4.21	6.173	I	131.52	5.9	16.26
XII	47.40	3.46	6.946	II	133.96	4.5	16.76
XII	52.31	3.2	7.770	VII	135.43	5.3	17.14
XII	55.55	2.9	8.325	I	137.55	5.4	17.84
XII	59.09	4.1	8.729	III	138.69	3.6	18.62
XII	63.50	4.8	9.297	II	138.92	4.8	18.39
VII	66.58	3.4	9.606	VII	140.58	4.7	19.37
XII	68.32	4.8	9.880	III	141.60	2.1	20.48
VII	71.71	6.5	10.315	XIII	142.16	2.2	20.79
XII	73.44	5.3	10.518	II	142.74	2.6	21.51
VII	77.60	4.8	10.901	I	142.77	4.3	29
XII	78.54	4.8	10.928	III	143.55	1.8	22.75
VII	82.36	4.5	11.134	XIII	144.23	1.5	25.4
VII	86.72	4.1	11.546	III	144.98	0.50	49
VII	91.54	5.3	12.028	III	145.11	.13	311
VII	96.83	4.9	12.461	IV	145.11	.16	409
I	96.95	5.3	12.514	IV	145.32	.23	459
VII	102.06	5.2	12.957	III	145.32	.20	392
I	102.13	4.8	12.965	III	145.46	.23	565
				IV	145.54	.20	876
			Solid I				
V	145.82	1.0	18.867	VII	165.37	4.3	18.866
V	147.53	2.3	18.899	IX	166.83	5.3	19.050
VII	148.47	4.4	18.942	VII	169.42	3.3	19.051
VII	153.44	5.3	18.897	XI	170.61	5.6	19.094
IX	155.71	4.1	16.616	IX	172.71	5.1	19.172
VII	159.67	6.4	18.938	VII	173.05	3.3	19.198
IX	160.93	5.5	18.991	X	173.18	2.9	19.190
				VIII	176.84	2.8	19.913
			Liquid				
IX	184.79	4.5	21.406	XI	235.13	5.9	22.989
VII	185.80	3.6	21.455	XI	242.28	5.7	23.243
XI	187.87	5.6	21.445	XI	249.24	5.5	23.471
XI	193.87	5.6	21.679	XI	256.97	6.2	23.952
XI	199.80	5.1	21.664	XI	265.34	6.0	24.313
XI	206.31	6.2	21.988	XI	273.07	5.8	24.716
XI	213.16	5.9	22.119	XV	275.91	9.8	24.961
XI	220.44	6.5	22.422	XI	281.15	5.8	25.237
XI	227.88	6.2	22.560	XIV	283.57	2.6	25.116
				XV	284.57	4.7	25.246

TABLE VI

HEAT CAPACITIES OF CYCLOBUTANE FROM SMOOTH CURVE

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
	Solid II		
15	0.66	70	10.05
20	1.45	80	11.01
25	2.44	90	11.90
30	3.53	100	12.76
35	4.60	110	13.58
40	5.58	120	14.48
45	6.52	130	15.95
50	7.37	140	19.1
60	8.88	143	21.8
	Solid I		
150	18.91	170	19.03[a]
160	18.97	180	19.09[a]
	Liquid		
190	21.56	240	23.14
200	21.78	250	23.57
210	22.06	260	24.04
220	22.39	270	24.54
230	22.75	280	25.10
		285	25.41

[a] Extrapolated values

TABLE VII

TRANSITION TEMPERATURE *vs.* ENERGY TO BE SUPPLIED TO COMPLETE TRANSITION

	Cal./mole required to complete trans.	*T*, °K.
Series I	1369	144.984
0.61416 mole	1325	145.111
	1238	145.321
	1093	145.561
	731	145.752
	476	145.798
	207	145.842
Series II	1352	145.030
0.61416 mole	1287	145.194
	1181	145.433
	1003	145.646
	802	145.744
Series III	1254	145.297
0.30344 mole	892	145.707
	595	145.786
Point IV	249	145.633
0.61416 mole		
Point V	306	145.666
0.61416 mole		

Over most of the temperature range 40 to 265°K. the error in the heat capacity measurements is probably not more than 0.2%. Below 40°K. the error is larger, at 14°K. it may be as large as 5%. In the temperature range below the melting point the heat capacities are in error due to the premelting effect. In making the entropy calculation, extrapolated values were used. The heat capacities of the liquid have been corrected for vaporization. Because of uncertainties in this correction and because of the increasingly large correction for heat exchange between the calorimeter and its surroundings, the error in the heat capacities may be as large as 0.4% from 265°K. to the boiling point. Measurements in the transition region are discussed in the next section.

The Transition and the Properties of the Two Solid Phases of Cyclobutane.—Transitions are quite common in cyclic hydrocarbons; both cyclopentane and cyclohexane exhibit sharp transitions with no region of high heat capacity; in the case of cyclopentene there is an indication that the transition is preceded by a range of a high heat capacity.[20] In this connection it is possibly significant that the forces tending to result in a planar skeleton are greater in the cases of cyclobutane and cyclopentene than in the cases of cyclopentane and cyclohexane. In undertaking the present investigation it was considered desirable to establish, if possible, whether or not the λ-type transition is characteristic of pure cyclobutane. The presence of impurity or failure to obtain equilibrium during the heat capacity measurements might lead to the appearance of the same type of curve.

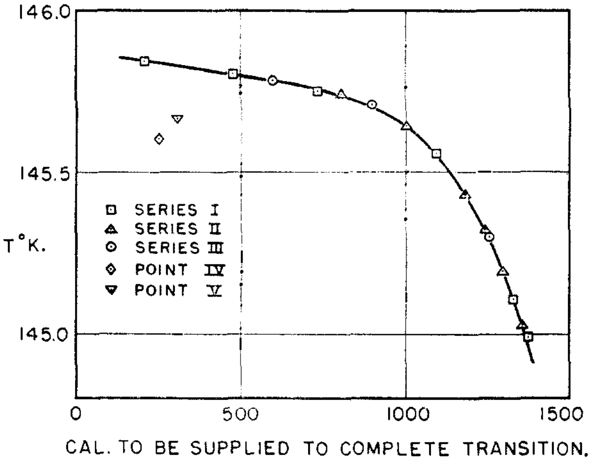

Fig. 2.—Transition temperature of cyclobutane.

In order to investigate these possibilities, experiments were performed to determine the temperatures *vs.* the extent of completion of the transition on both the sample with 0.19% impurity (series I, II, IV and V, Table VII and Fig. 2) and on the sample with 0.14% impurity (series III). Most of the measurements were made by warming the sample into the transition region but to determine whether equilibrium was obtained points IV and V were obtained by cooling the solid I. The measurements represented by these points are definite evidence that equilibrium was not obtained in series I, II and III, and it is likely, therefore, that heat capacity measurements between 145°K. and the temperature at which the transition is completed are in error as a result. The measurements represented by points IV and V indicate the heat capacity curve is somewhat steeper than that indicated by the heat capacity measurements; however, the closeness of approach to equilibrium in series I, II and III (to within about 0.2°) indicates that there is definitely a region of high heat capacity in the case of cyclobutane—at least in the case of the somewhat impure sample on which these measurements were made. A comparison of the results of series III with those of series I and II indicates that the effect probably cannot be attributed to impurity although this evidence is not as conclusive as it might be because of the slight difference in purity of the samples and because of the failure to obtain equilibrium. The measurements made in the transition region and on solid II definitely seem to indicate a discontinuous drop in the heat capacity; apparently the transition has a sharp end-point or the heat capacity curve drops over a very narrow temperature interval. The temperature at which the transition was completed (145.7°K.) was determined by extrapolation (Fig. 2) with consideration of data obtained in cooling as well as heating.

Our experimental evidence seems to indicate a gradual transition starting at approximately 120°K. and ending abruptly at 145.7°K. The possibility of a transition occurring at one definite temperature (approximately 145.7°K.) preceded by a very sharp rise in the heat capacity curve (C_p at least 25 cal./deg. mole at 145.7°K.) is not excluded. There appears to be better evidence for the latter type of behavior in the case of cyclopentene, and Huffman and co-workers[20] have so interpreted their data.

Kaarsemaker and Coops[19] report a simple first-

---

(20) H. M. Huffman, M. Eaton and G. D. Oliver, THIS JOURNAL, **70**, 2911 (1948).

order transition with a transition temperature of 146.37°K.

In an effort to further elucidate the nature of the transition, samples of cyclobutane were submitted to Carter and Templeton[21] for X-ray diffraction photographs of the two solid phases. They report, "Single crystal X-ray diffraction studies at about −100° show that the crystal structure of the high temperature form of cyclobutane is body-centered cubic with $a = 6.06 \pm 0.03$ Å. and two molecules per unit cell. The molecules have rotational disorder, either static or dynamic, corresponding to octahedral symmetry. Powder patterns show the low temperature form to be of lower symmetry." A model with dynamical rotational disorder in the high temperature form is consistent with other observations: small heat of fusion, large heat of transition and poor thermal conductivity of solid I.

In the temperature range just below the transition peak the curvature of the heat capacity curve is so great that some of the temperature increments used do not adequately approximate differentials. Corrections have been made where necessary.

For the purpose of calculating the entropy of the transition, the calorimeter and its contents were brought to a temperature sufficiently below that of the transition peak so that heat capacity measurements were still deemed reliable. Sufficient energy was then supplied to complete the transition. For the purposes of comparing the several measurements, the energy required to heat cyclobutane from 143.36°K. to just through the transition, 145.74°K., was arbitrarily chosen—see Table VIII.

TABLE VIII

HEAT OF TRANSITION OF CYCLOBUTANE

Temp. interval, °K.	Energy supplied, cal./mole	$-\int C_p\,dT$, cal./mole	Heat absorbed 143.36–145.74°, cal./mole
143.406–147.450	1444.59	31.29	1413.30
143.478–146.564	1425.96	12.96	1413.00
143.339–146.185	1422.31	8.89	1413.42
		Mean	1413.24

The Entropy of Cyclobutane from Calorimetric Data.—In making the entropy calculation, graphical integration was used up to 145.06°K. and above 145.74°K. For the entropy calculation in the region 145.06 to 145.74°K., the value $1413.24 - \int C_p\,dT$ was simply divided by 145.7. Any error introduced by this approximation is negligible. The entropy calculation from calorimetric data is summarized in Table IX. Previous calculations of the entropy of cyclobutane using molecular data have given values appreciably lower than that in Table IX.[2,22] The discrepancies led to a reinvestigation of the vibrations of cyclobutane, the results of which are reported in an accompanying paper.[12] The ring puckering motion has such a low frequency that even at liquid hydrogen temperatures there is appreciable excitation. The characteristic temperature given in Table IX has been calculated using Debye functions with six degrees of freedom.

TABLE IX

ENTROPY FROM CALORIMETRIC DATA

0–14°	Debye function $\theta = 168°$	0.178 cal./mole deg.
14–145.06°	Graphical integration	16.853
145.7°	Transition $\frac{1363.50\text{ cal.}}{145\ 7}$	9.358
145.74–182.43°	Graphical integration	4.250
182.43°	Fusion $\frac{260.1\text{ cal.}}{182.43°}$	1.426
182.43–285.67°	Graphical integration	10.275
285.67°	Vaporization $\frac{5781\text{ cal.}}{285.67°}$	20.237
	Entropy of actual gas at its normal b.p.	62.54
	Cor. for gas imperfection	0.14
	Entropy of ideal gas at its normal b.p.	62.72 ± 0.2 cal./mole deg.

We are indebted to Professor K. S. Pitzer for suggesting this problem, to Professor W. F. Giauque for helpful suggestions, to Dr. Chi-ho Chu for assistance in the experimental work and to Drs. Carter and Templeton for supplying us with the results of their investigations in advance of publication.

BERKELEY, CALIF.

---

[21] G. Carter and D. H. Templeton, private communication, Feb. 20, 1953.

[22] T. H. Cottrell, *Trans. Faraday Soc.*, **4**, 716 (1948).