Infrared Absorption Spectra, Structure and Thermodynamic Properties of Cyclobutane[1]

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Infrared and Raman measurements on cyclobutane are reported. The spectroscopic data, when used in conjunction with electron diffraction measurements and the measured entropy, suggest that the equilibrium configuration for cyclobutane is one with D_{2d} symmetry, but that the barrier hindering inversion of the molecule is sufficiently low so that even at ordinary temperatures an appreciable number of the molecules obey D_{4h} selection rules. A normal coördinate analysis for cyclobutane has been performed, and force constants compared with those of related molecules. A possible potential function for the out-of-plane bending motion of the ring has been suggested, and some of the thermodynamic properties of cyclobutane calculated.

Introduction

Cyclobutane and its derivatives have been the subjects of a number of recent investigations in molecular structure.[2-5] Strained CCC bonds in the ring suggest that the equilibrium configuration of the ring should be planar; on the other hand, torsional forces about the C–C bonds tend to cause a non-planar configuration. Previously, spectroscopic results have been interpreted as most consistent with a planar configuration for the skeleton (D_{4h} symmetry).[2] However, the entropy determination reported in the accompanying paper is in disagreement with the previous analyses. The investigations here reported were undertaken in an effort to supply further information about cyclobutane.

Apparatus and Sample.—Some of the spectroscopic observations were made by (N.K.F.) at the University of California using a Perkin–Elmer spectrometer that was converted from Model 12A to 12C during the course of the work. Potassium bromide, sodium chloride and lithium fluoride optics were used. Most of these measurements were repeated at Columbia University (by G. W. R.) using a Savitsky–Halford modified Perkin–Elmer 12 C spectrometer.[6] In addition, the spectrum of the liquid and the temperature dependence of certain vapor phase intensities were obtained. Sodium chloride and calcium fluoride optics were used. The published data represent what we regard as the best combination of the two sets of results.

The Raman measurements were made by Dr. J. T. Neu to whom we are indebted for his unpublished results. His measurements were made on a liquid sample using a Steinheil type GH three prism spectrograph.

The sample used was the same as reported in the accompanying article.[5]

Infrared Spectrum.—The infrared spectrum at room temperature is shown in Fig. 1. The optics used were as indicated in the figure, except for the liquid spectrum. In that case, sodium chloride optics were used below and calcium fluoride optics above 1400 cm.$^{-1}$.

With increasing temperature certain of the bands diminished in both peak and integrated intensity. The most noticeable case is the 750 cm.$^{-1}$ band. We have estimated $\int \ln(I/I_0)d\nu$ at 459°K. to be $73 \pm 5\%$ of the value at 299°K. Otherwise, with the exception of the 1889 cm.$^{-1}$ combination band,

(1) This work was assisted by the American Petroleum Institute through Research Project 50.

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

(3) H. Pajenkamp, Z. Elektrochem., 52, 104 (1948).

(4) J. D. Dunitz and V. Schomaker, J. Chem. Phys., 20, 1703 (1952).

(5) G. W. Rathjens and W. D. Gwinn, THIS JOURNAL, 75, 5629 (1953). Other references are also given in this article.

(6) A. Savitsky and R. S. Halford, Rev. Sci. Instruments, 21, 203 (1950).

it has generally not been possible to estimate quantitatively changes in intensity, and in some cases there is a question as to whether there actually was a change. Bands whose intensities were observed to decrease on heating are marked in Table II. In addition to the 750 cm.$^{-1}$ band, two other bands assigned as fundamentals, 1453 and 1261 cm.$^{-1}$, exhibited changes in structure on heating. These cases are discussed in the section on interpretation.

Comparison of the liquid spectrum with that of the gas has been of aid in making certain assignments; the single peak in the liquid at 750 cm.$^{-1}$ seems to indicate that the two observed peaks in the gas are part of the same band, and that the expected third branch does not appear; the pronounced shoulder on the 1261 cm.$^{-1}$ band seems to indicate definitely two assignments in that region; and the marked change in structure in the 2100 cm.$^{-1}$ region indicates that the very complex gas phase spectrum is in part probably due to rotational structure of the various combinations that occur in the region. In the assignment of combinations (Table II) this information has been used.

With minor exceptions, the spectra obtained by us are in agreement with that reported by Wilson.[2] Because of the accessibility to us of lithium fluoride optics, our spectrum shows better resolution in the higher frequency region, and it is in this region where our spectrum differs most significantly from that published by Wilson. We have also observed two weak bands in the gas phase, but not in the liquid, at 955 and 850 cm.$^{-1}$ which were not observed by Wilson. (These may be due to impurity.)

Raman Spectra.—Table II gives the Raman lines as observed by Neu, their estimated intensities, states of polarization and assignments. A comparison with Wilson's[2] data and that of Pajenkamp[3] shows certain differences. Wilson observed doubling of the lines at 1444, 1220 and 928 cm.$^{-1}$ while neither Pajenkamp's nor Neu's data show such doubling. The resolution available in the spectrum reported here seems to indicate that the doubling is not genuine. Three lines, 1148, 1515 and 634 cm.$^{-1}$ not reported by Wilson were observed by Neu.

Symmetry Consideration and Selection Rules.—As previously indicated, the planarity or non-planarity of the carbon skeleton in cyclobutane is dependent on the balance of the forces tending to cause the two configurations. The most likely
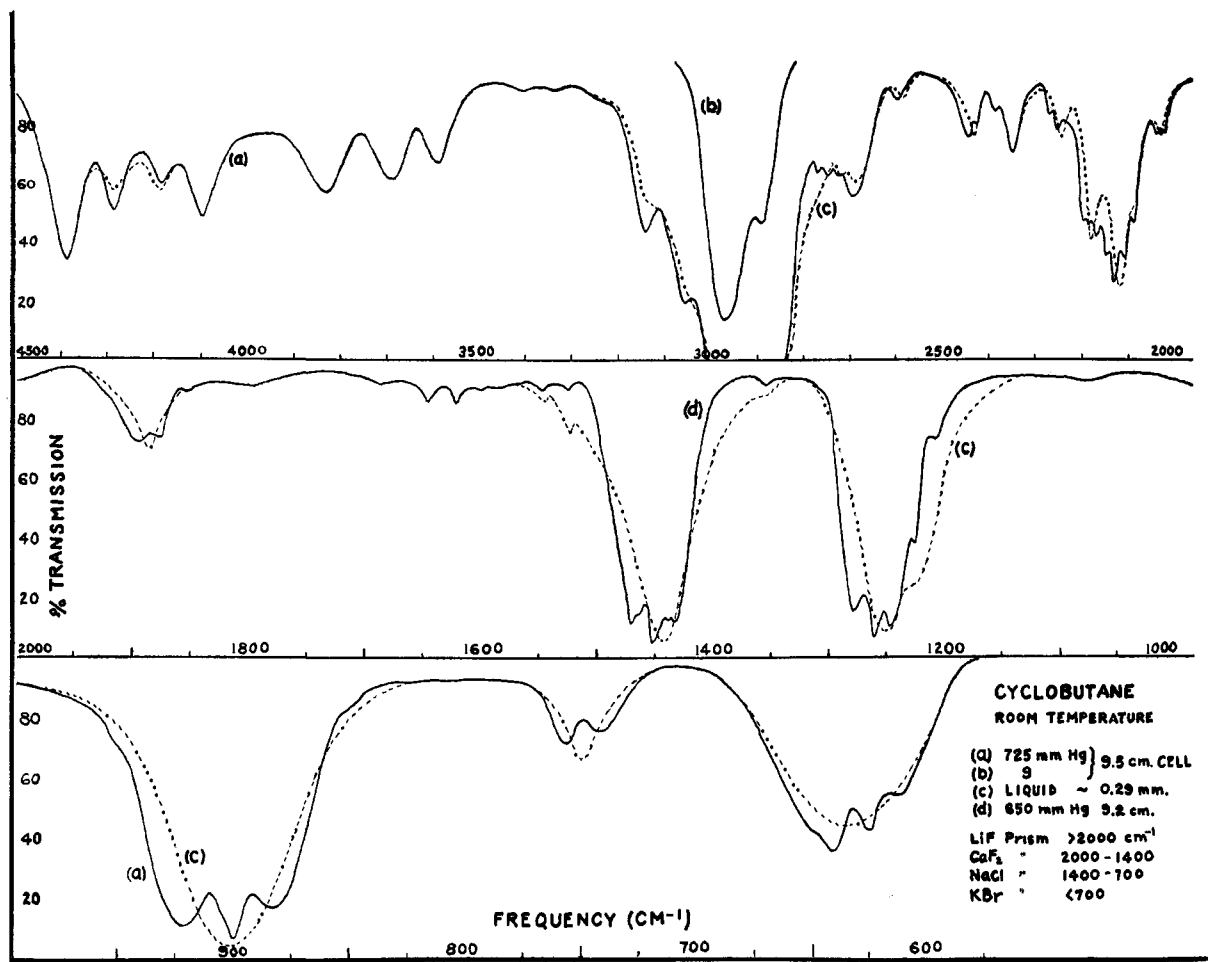
Fig. 1.—Infrared spectra of cyclobutane.

symmetries in the two cases are, respectively, D_{4h} and D_{2d}. Table I is a summary of the vibrations belonging to each class in the two symmetries, the selection rules, and the behavior of each class as the molecule goes from one symmetry to the other. From the table, it can be seen that B_{1u}, A_{1u}, A_{2u} and E_u vibrations become Raman active as the symmetry goes from D_{4h} to D_{2d}, and B_{2g} and E_g vibrations become infrared active as the symmetry goes to D_{2d}. It also can be seen that there are 23 fundamental vibrations and that for D_{4h} symmetry eleven fundamentals should be Raman active, and six infrared active with no coincidences. There are also six inactive fundamentals for this model. For D_{2d} symmetry nine vibrations are Raman active only, and twelve vibrations are active in both Raman and infrared. Two fundamentals remain inactive. Since the number of strong infrared bands and Raman bands actually observed is nearer the number predicted for D_{4h}, this is a factor in leading one tentatively to select D_{4h} symmetry. Wilson[2] interpreted his data on this model.

As a result of the discrepancy between the entropy measurement[6] and the value calculated from spectroscopic data with the assumption of a planar carbon skeleton, it has become necessary to consider more carefully the possibility of a non-planar skeleton, and to try to interpret the spectra in

terms of D_{2d} symmetry. If this model is assumed, not all of the allowed bands or coincidences between Raman and infrared are observed. This may be due to intrinsic weakness of the bands, especially inasmuch as the deviation from skeletal planarity is expected to be small. There are, however, three observed coincidences (630, 750 and 1220 cm.$^{-1}$) in the low frequency range, where accidental coincidences are less likely. Since these are observed in the liquid state, and might otherwise be interpreted as violations of (D_{4h}) selection rules, conclusions therefrom regarding symmetry are equivocal. Nevertheless, it seems unlikely that all three coincidences would arise from a planar molecule. The following section will clarify the point of view from which neither symmetry is strictly correct, and from which both must be considered.

Interpretation

From a thermodynamic point of view the most serious problem in the interpretation of the cyclobutane spectra has been in the assignment of the B_{1u} out-of-plane bending vibration (assuming for the time being D_{4h} symmetry) since this vibration is expected to be of very low frequency and extremely anharmonic. Wilson assigned a value of 145 cm.$^{-1}$ to it, and Cottrell[7] has used this assign-

(7) T. L. Cottrell, *Trans. Faraday Soc.*, **44**, 716 (1948).

TABLE I

FUNDAMENTAL VIBRATIONS,[a] SYMMETRY CLASSES AND SELECTION RULES

Vibration type	Cm.$^{-1}$	Symmetry class and selection rules D$_{4h}$	D$_{2d}$
CH stretching	2870		
CH$_2$ deformation	1444*	A$_{1g}$ R.(p.)	
CC stretching	1003*		
CH stretching	2921		A$_1$ R.(p.)
CH$_2$ rocking	(878)	B$_{1u}$ inactive	
Ring bend. (out-of-plane for D$_{4h}$)	b		
CH$_2$ wagging	(1299)	A$_{2g}$ inactive	A$_2$ inactive
CH$_2$ twisting	1104 (1155)	B$_{2u}$ inactive	
CH$_2$ wagging	(1286)		
CC stretching	928*	B$_{1g}$ R.(dp.)	B$_1$ R.(dp.)
CH$_2$ twisting	1148 (1155)	A$_{1u}$ inactive	
CH stretching	2981		
CH$_2$ deformation	1450*	B$_{2g}$ R.(dp.)	
Ring bend. (in-plane for D$_{4h}$)	730*		B$_2$ IR., R.(dp.)
CH stretching	2896		
CH$_2$ rocking	901*	A$_{2u}$ IR.	
CH stretching	2960		
CH$_2$ twisting	1220*	E$_g$ R.(dp.)	
CH$_2$ rocking	890^c*		
CH stretching	2974		E IR., R.(dp.)
CH$_2$ deformation	1453 (1420)	E$_u$ IR	
CH$_2$ wagging	1261*		
Ring deformation (stretch.-bend.)	625*		

[a] Frequencies used to evaluate force constants marked with an asterisk; calculated values in parentheses. [b] See text. [c] Assigned on the basis of combination bands.

ment to calculate thermodynamic properties for both harmonic and quartic potential functions. The measured entropy reported in the accompanying article is considerably greater than either of the values calculated. This suggests either that the frequency is even lower than 145 cm.$^{-1}$, or that the
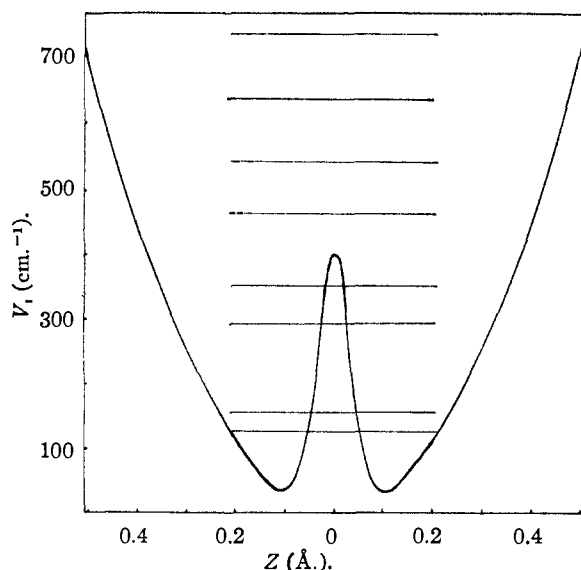

Fig. 2.—Potential function and vibrational levels for out-of-plane bending motion.

assumed shapes for potential functions are grossly in error, or both.

Our temperature dependence measurements were initiated with the hope that increase in intensities on heating would locate definitely the difference bands involving the B$_{1u}$ vibration. No such increases have been observed, and we have been forced to conclude that no such differences are sufficiently intense to appear in our spectrum. (Possible exceptions are the 650 and 1355 cm.$^{-1}$ bands). However, a number of diminutions in intensity have been observed. Such behavior is consistent with a model in which the potential energy function for the puckering of the ring is of the form illustrated in Fig. 2. If the potential is of the illustrated shape and the barrier hindering inversion is sufficiently low, an appreciable fraction of the molecules will be in states whose energies lie above the barrier peak. These molecules and those slightly below the peak have effectively D$_{4h}$ symmetry while molecules whose energies lie well below the barrier peak will have D$_{2d}$ symmetry. On heating, the former population will be increased at the expense of the latter, and consequently there will be a decrease in intensity of all infrared bands that are allowed in D$_{2d}$ symmetry but are forbidden in D$_{4h}$ symmetry. This model is quite consistent with the observations, and also explains the weak Raman lines observed at 634 and 1148 cm.$^{-1}$.

The strength of the 750 cm.$^{-1}$ band, and the 1220 cm.$^{-1}$ shoulder in the liquid spectrum rather strongly suggest that an appreciable fraction of the molecules in the liquid obeys D$_{2d}$ selection rules.

In the discussion that follows we shall generally prefer to use the D$_{4h}$ nomenclature while keeping in mind the effects of D$_{2d}$ symmetry considerations.

From a consideration of the paraffins and particularly the other saturated rings, the C–H stretching frequencies for cyclobutane may be expected to fall in the range from 2900 to 3100 cm.$^{-1}$. We have assigned the strongly polarized Raman band at 2870 to the A$_{1g}$ vibration. No other polarized fundamentals should appear in this part of the spectrum for D$_{4h}$ symmetry, but for D$_{2d}$ symmetry the B$_{1u}$ vibrations become active. Also there are overtones of vibrations in the region of 1450 cm.$^{-1}$ which are totally symmetric and could yield polarized bands in the vicinity of 2900 cm.$^{-1}$. We have rather arbitrarily chosen to assign the 2921 cm.$^{-1}$ band to the B$_{1u}$ fundamental. All actual states in this region are presumably the resultants of the interaction of overtones and fundamentals, but we have no means to sort out the respective contributions.

Strong bands appear in the infrared at 2974 and 2896 cm.$^{-1}$. These have been assigned to vibrations of symmetry E$_u$ and A$_{2u}$, respectively, since both are allowed even in D$_{4h}$.

CH$_2$ deformation vibrations are expected to lie at approximately 1450 cm.$^{-1}$. In the infrared spectrum there is a strong band in this region. The band appears to be of somewhat complex structure, and changed qualitatively with increasing temperature. We have interpreted this band as being the superposition of an E$_u$ band at 1453 cm.$^{-1}$ and a B$_{2g}$ band at 1450 cm.$^{-1}$. The latter

TABLE II

SPECTRA AND ASSIGNMENTS

Gas Cm.⁻¹	Infrared I	Liquid Cm.⁻¹	I	Raman Cm.⁻¹	I	Pol.	Assignment	Class D_{2d}	D_{4h}	Selection rules D_{2d}	D_{4h}
611											
625	5	630	5	634 ± 5	0.5		Ring deformation	E	E_u	IR, R	IR
640											
650	0	648	0								
740	2^a	750	3	750 ± 5	1		Ring bending (in-plane for D_{4h})	B_2	B_{2g}	IR, R	R
758											
850	1										
885											
901	10	901	10				CH_2 rocking	B_2	A_{2u}	IR, R	IR
922											
				928 ± 1	8	dp.	CC stretching	B_1	B_{1g}	R	R
955	1										
				1002.6 ± 0.5	10	p.	CC stretching	A_1	A_{1g}	R	R
				1104 ± 5	0.5		CH_2 twisting	A_2	B_{2u}	ia.	ia.
		1147	1	1148 ± 5	2	dp.	CH_2 twisting	B_1	A_{1u}	R	ia.
1210	2^a	1220	3	1220 ± 1	5	dp.	CH_2 twisting	E	E_g	IR, R	R
1228	2										
1246											
1261	10	1253	10				CH_2 wagging	E	E_u	IR, R	IR
1277											
1355	1	1338	0?				$625 + 750 = 1375$	E	E_u	IR, R	IR
1433 ⎫											
1450 ⎬				1444 ± 1			CH_2 deformation	B_2	B_{2g}	IR, R	R
1471 ⎭	10	1445	10								
1433 ⎫											
1453 ⎬	b			1444 ± 1	7	p.?.	CH_2 deformation	E	E_u	IR, R	IR
1465 ⎭											
				1444 ± 1			CH_2 deformation	A_1	A_{1g}	R	R
1530	0			1515 ± 5	1		$625 + 890 = 1515$	E	E_u	IR, R	IR
							$625 + 901 = 1526$	E	E_g	IR, R	R
1550	1	1549	0				$625 + 928 = 1553$	E	E_u	IR, R	IR
1605	0	1605	0								
1630	1^a	1650	0				$750 + 890 = 1640$	E	E_g	IR, R	R
1650	1^a										
1683	0?										
1817	0?	1817	0				$890 + 928 = 1818$	E	E_g	IR, R	R
1879							$625 + 1261 = 1886$	E	E_g	IR, R	R
1898	3^a	1886	4				$890 + 1003 = 1893$	E	E_g	IR, R	R
2035	2^a	2039	2				$928 + 1104 = 2032$	B_2	A_{2u}	IR, R	IR
2047	1^a						$890 + 1148 = 2038$	E	E_u	IR, R	IR
2098	1	2098	2				$878 + 1220 = 2098$	E	E_u	IR, R	IR
2113	2										
2135	6	2123	7				$901 + 1220 = 2121$	E	E_u	IR, R	IR
2150	2						$890 + 1261 = 2151$	E	E_u	IR, R	IR
2176	1						$928 + 1261 = 2189$	E	E_u	IR, R	IR
2191	2^a	2183	4				$750 + 1444 = 2194$	B_2	B_{2g}	IR, R	R
2202	0						$750 + 1453 = 2203$	E	E_u	IR, R	IR
2264	2^a	2258	2				$1104 + 1148 = 2252$	B_2	B_{2g}	IR, R	R
2279	1^a						$1003 + 1261 = 2264$	E	E_u	IR, R	IR
2357	3	2358	3				$901 + 1444 = 2345$	B_2	A_{2u}	IR, R	IR
							$1148 + 1220 = 2368$	E	E_u	IR, R	IR
2404	0	2397	1				$1104 + 1286 = 2390$	B_2	A_{2u}	IR, R	IR
							$1148 + 1261 = 2409$	E	E_g	IR, R	R
2437	1	2441	3				$1148 + 1299 = 2447$	B_2	A_{2u}	IR, R	IR
2455	2	2467	0				$1003 + 1453 = 2456$	E	E_u	IR, R	IR
2603	1	2577	1				$1148 + 1453 = 2601$	E	E_g	IR, R	R
2675	0?										
2694	4	2680	3				$1220 + 1453 = 2673$	E	E_u	IR, R	IR
		2715	2				$1261 + 1444 = 2705$	E	E_u	IR, R	IR
2755	1	2760	1				$2 \times 928 + 901 = 2757$	B_2	A_{2u}	IR, R	IR
2775	1						$625 + 928 + 1220 = 2773$	E	E_u	IR, R	IR
				2870 ± 1	8	p.	CH stretching	A_1	A_{1g}	R	R

Table II (Continued)

Infrared Gas Cm.$^{-1}$	I	Liquid Cm.$^{-1}$	I	Raman Cm.$^{-1}$	I	Pol.	Assignment	Class D2d	D4h	Selection rules D2d	D4h
2896	20	c					CH stretching	B$_2$	A$_{2u}$	IR, R	IR
				2921 ± 3	7	p.	CH stretching	A$_1$	B$_{1u}$	R	ia.
				2960 ± 3	7	dp.	CH stretching	E	E$_g$	IR, R	R
2974	20						CH stretching	E	E$_u$	IR, R	IR
				2981 ± 3	2	p.?	CH stretching	B$_2$	B$_{2g}$	IR, R	R
3058	3						901 + 928 + 1220 = 3049	E	E$_u$	IR, R	IR
3145	4^a	3130	2				928 + 1003 + 1220 = 3151	E	E$_g$	IR, R	R
3238	0						750 + 1220 + 1261 = 3231	E	E$_u$	IR, R	IR
3341	0	d					2 × 1220 + 901 = 3341	E	E$_u$	IR, R	IR
3401	0						928 + 1220 + 1261 = 3409	E	E$_u$	IR, R	IR
							625 + 2960 = 3585	E	E$_u$	IR, R	IR
3585	3^a?						625 + 2974 = 3599	E	E$_g$	IR, R	R
							625 + 2981 = 3606	E	E$_u$	IR, R	IR
3690	4						750 + 2921 = 3671	B$_2$	A$_{2u}$	IR, R	IR
							890 + 2921 = 3811	E	E$_u$	IR, R	IR
3832	4^a?						878 + 2960 = 3838	E	E$_u$	IR, R	IR
4100	5						1148 + 2960 = 4108	E	E$_u$	IR, R	IR
4190	3^a?						1220 + 2981 = 4201	E	E$_g$	IR, R	R
							1220 + 2974 = 4194	E	E$_u$	IR, R	IR
4290	3						1299 + 2974 = 4273	E	E$_u$	IR, R	IR
4390	6						1450 + 2921 = 4371	B$_2$	A$_{2u}$	IR, R	IR
							1453 + 2960 = 4413	E	E$_u$	IR, R	IR

^{a} Diminishes in intensity on heating. ^{b} See text. ^{c} The CH stretching region was not investigated in the liquid. ^{d} No calibration was made on the liquid spectrum above 3300 cm.$^{-1}$. The 4190 cm.$^{-1}$ band appears slightly stronger in the liquid than in the gas, and the 4290 cm.$^{-1}$ band perhaps slightly weaker; otherwise, there is no apparent difference.

vibration should be infrared active in D$_{2d}$ symmetry, but not for D$_{4h}$; therefore, a change in observed band structure on heating is to be expected though the intensity change might not be marked if the E$_u$ absorption is much stronger than that of the B$_{2g}$ vibration. The B$_{2g}$ vibration should be Raman active for both symmetries, and we believe the 1444 cm.$^{-1}$ line observed in the Raman must be assigned B$_{2g}$. It is also necessary to assign 1444 cm.$^{-1}$ to the expected A$_{1g}$ vibration since no other line appearing in the Raman spectra can reasonably be assigned to it. The 1515 cm.$^{-1}$ band is at a higher frequency than would be expected. The questionable state of polarization of the 1444 cm.$^{-1}$ line is consistent with the possibility that it is actually two lines.

CH$_2$ twisting and wagging frequencies may be expected to lie in the region 1100 to 1400 cm.$^{-1}$. The E$_g$ twisting vibration should appear in both Raman and infrared if the symmetry is D$_{2d}$; for D$_{4h}$ symmetry it is Raman active only. A Raman line is observed at 1220 cm.$^{-1}$ and a pronounced shoulder appears in the infrared spectrum of the liquid at the same value. In the gas phase two shoulders appear at 1228 and 1210 cm.$^{-1}$; because of the changing rotational structure of the 1261 cm.$^{-1}$ band, it is not possible to decide whether there is any variation in intensity of the 1228 cm.$^{-1}$ shoulder; however, the shoulder at 1210 cm.$^{-1}$ does appear to diminish in intensity on heating. We believe these two to be branches of the E$_g$ twisting vibration. In view of the uncertainty in locating the peaks and the absence or obscuration of the third branch we have used the 1220 cm.$^{-1}$ observed in the liquid phase in our assignment. The 1261 cm.$^{-1}$ infrared band can only be the E$_u$ wagging vibration (allowed in infrared, for D$_4$ symmetry). The B$_1$ wagging vibration should be Raman active

only, regardless of symmetry. The observed 1148 cm.$^{-1}$ Raman band may be that of this vibration; however, correlation with the 1261 cm.$^{-1}$ E$_u$ wagging vibration is not very satisfactory. A large interaction constant is required in the normal coördinate analysis, and the resulting calculated value for the A$_{2g}$ wagging vibration is well above the expected value. We, therefore, have assumed that the B$_{1g}$ wagging vibration did not appear in Neu's spectrum, and have assigned the observed 1148 cm^{-1} line to the A$_1$ twisting vibration (allowed in the Raman for D$_{2d}$ symmetry but not for D$_{4h}$.) The B$_{2u}$ twisting vibration is forbidden in Raman and infrared for both symmetries. However, we have tentatively attributed the very weak Raman band at 1104 cm.$^{-1}$ to it assuming a selection rule violation in the liquid.

CH$_2$ rocking frequencies may be expected at from 900 to 1000 cm.$^{-1}$. The 901 cm.$^{-1}$ infrared band is almost certainly the A$_{2u}$ vibration; it is quite clearly a parallel type band, and the P–R splitting is as predicted using the formula of Gerhard and Dennison.[8] Both the B$_{1g}$ stretching and E$_g$ rocking vibrations should appear in the same region of the Raman spectra as depolarized lines. Since only one line was observed, 928 cm.$^{-1}$, we have chosen to assign it to the stretching vibration, and to believe the rocking vibration was not observed. We have assigned a value of 890 cm.$^{-1}$ to the latter. Such an assignment is certainly a weak point in our analysis, but it is the only assignment we can advance consistent with the observed diminution in intensity of the 1630 and 1650 cm.$^{-1}$ combinations on heating.

The polarized Raman line at 1003 cm.$^{-1}$ is clearly the A$_{1g}$ C–C stretching vibration. The E$_u$ stretching-bending vibration should be active in infrared

(8) S. L. Gerhard and D. M. Dennison, Phys. Rev., 43, 197 (1933).

for D_{4h} symmetry, and both infrared and Raman active for D_{2d} symmetry. We believe that the infrared band at 625 cm.$^{-1}$ and the Raman line at 634 cm.$^{-1}$ correspond to it. The expected value of the frequency is much higher, but we can offer no other explanation for the observed infrared band and Raman line. Our interpretation requires a rather large interaction constant in the normal coördinate analysis. In hope of support for our assignment we have studied the published spectra of cyclobutane derivatives. Because of the removal of degeneracy, these should exhibit pairs of corresponding frequencies. Unfortunately, infrared investigations on derivatives seem to have been confined to the region above 700 cm.$^{-1}$. Kohlrausch and co-workers[9] have, however, obtained the Raman spectra of a large number of derivatives, and that of methylenecyclobutane is also available.[10] The corresponding lines are not found in cyclobutanone or methylenecyclobutane but, in general, lines that may correspond to this vibration are found for the derivatives of lower symmetry.

We have assigned the B_{2g} ring bending vibration as 750 cm.$^{-1}$. This vibration should be only Raman active for D_{4h} symmetry, but also infrared active for D_{2d}. This assignment (compared with Wilson's value of 595 cm.$^{-1}$)[2] is supported by the observance of the corresponding lines in the Raman spectra of methylenecyclobutane (657 cm.$^{-1}$)[9] and cyclobutanone (674 cm.$^{-1}$),[9] and also in other derivatives.[9] The observed diminution in intensity on heating of the infrared band at 750 cm.$^{-1}$ is perhaps the strongest single point supporting a low-barrier double minimum potential function for the out-of-plane bending.

The Assignment of Inactive Vibrations.—In order to calculate most of the frequencies of the inactive vibrations and also the force constants, we have resorted to a normal coördinate analysis, using Wilson's F and G matrices and the CH stretching frequencies have been factored out by his method.[11] The analysis has been made on the basis of D_4 symmetry. Since the deviation from planarity in going to D_2 symmetry is small, this is permissible. The fact that frequency shifts are not observed on heating may be taken as support for this procedure. The B_{1u} out-of-plane bending vibration has such a low frequency that interaction between this and other B_{1u} vibrations can be neglected. This has been done in our calculations, and the out-of-plane bending treated separately. The symmetry coördinates have been obtained in terms of the internal coördinates defined below

ξ = change in C–C bond length
α = change in CCC bond angle
β = change in HCH bond angle
χ = change in HCC bond angle
η = change in C–H bond length (above plane)
ρ = change in C–H bond length (below plane)

(9) K. W. F. Kohlrausch and R. Skrabel, *Z. Elektrochem.*, **43**, 282 (1937); *Monatsh.*, **70**, 44 (1937); A. W. Reitz and R. Skrabel, *ibid.*, **70**, 398 (1937); R. Skrabel, *ibid.*, **70**, 420 (1937).

(10) F. F. Cleveland, M. J. Murray and W. S. Gallaway, *J. Chem. Phys.*, **15**, 742 (1947).

(11) E. B. Wilson, Jr., *ibid.*, **9**, 76 (1941). We acknowledge also the aid of some preliminary calculation of C. S. Lu on cyclic molecules.

ψ = change in angle between Z and Y (see Fig. 3) where Z is fixed in the plane of the CH_2 group and Y in the plane of the carbon skeleton. This is the coördinate for CH_2 twisting motion.

ϕ = change in angle between Y and X (see Fig. 3), where Y is fixed in the plane of the carbon skeleton and X is the bisector of the CH_2 angle. This is the coördinate for the CH_2 wagging motion.

θ = change in angle between X and Z where Z is fixed perpendicular to the skeletal plane and X is the bisector of the CH_2 angle. The coördinate corresponds to the CH_2 rocking motion.
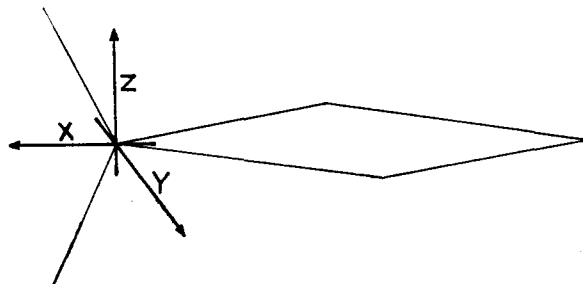

Fig. 3.—Vectors for describing CH_2 motions.

A redundancy relationship about each C atom exists between α, β and χ

$$\left(\sin\frac{\alpha_0}{2}\cos\frac{\beta_0}{2}\right)\alpha + \left(\cos\frac{\alpha_0}{2}\sin\frac{\beta_0}{2}\right)\beta + (\sin\chi_0)\chi_0 = 0$$

where the zero subscripts refer to equilibrium angles, and χ_0 is the normalized sum of the four HCC bond angles, $\chi_c = \frac{1}{2}(\chi_i + \chi_j + \chi_k + \chi_l)$. This redundancy relationship has been used to reduce the three coördinates α, β and χ to a new mutually orthogonal pair α' and β' where

$$\alpha' = \frac{\left(\sin^2\chi_0 + \cos^2\frac{\alpha_0}{2}\sin^2\frac{\beta_0}{2}\right)\alpha - \sin\frac{\alpha_0}{2}\cos\frac{\beta_0}{2}\left[\left(\cos\frac{\alpha_0}{2}\sin\frac{\beta_0}{2}\right)\beta + (\sin\chi_0)\chi\right]}{\sin^2\chi_0 + \cos^2\frac{\alpha_0}{2}\sin^2\frac{\beta_0}{2} + \sin^2\frac{\alpha_0}{2}\cos^2\frac{\beta_0}{2}}$$

$$\beta' = \frac{\sin\chi_0\left[(\sin\chi_0)\beta - \left(\cos\frac{\alpha_0}{2}\sin\frac{\beta_0}{2}\right)\chi\right]}{\sin^2\chi_0 + \cos^2\frac{\alpha_0}{2}\sin^2\frac{\beta_0}{2}}$$

The coördinates η and ρ have been transformed to a mutually orthogonal pair

$$\eta' = 1/\sqrt{2}\,(\eta + \rho) \text{ and } \rho' = 1/\sqrt{2}(\eta - \rho)$$

The definition of the $\bar{s}$ vectors is straightforward except in the case of that associated with the carbon atom for a β' vibration. In this case there is an α component as well as a β one; thus

$$\bar{S}_{\beta'_0} = \bar{S}_{\beta_0} + \frac{\sin\alpha_0\sin\beta_0}{4\left(\sin^2\chi_0 + \cos^2\frac{\alpha_0}{2}\sin^2\frac{\beta_0}{2}\right)}\bar{S}_{\alpha_0}$$

Symmetry coördinates are defined in Table III. The choice for the E_u skeletal deformation was particularly made so that a stretching–bending interaction term would occur in the potential energy function. In evaluating the elements of the G matrix, we have used the following parameters: C–C bond length 1.568 Å., C–H bond length 1.096 Å., HCH bond <114°.[4]

Force constants obtained are given in Table IV. The frequencies used for evaluating force constants, and the calculated frequencies are given in Table I. K's are principal force constants, L's are interac-

<div align="center">TABLE III</div>

<div align="center">SYMMETRY COÖRDINATES</div>

i, j, k, l refer to the four vertices of the carbon skeleton, with i opposite k.

A_{1g}	$R_1 = \frac{1}{2}(\eta'_i + \eta'_j + \eta'_k + \eta'_l)$	$R_2 = \frac{1}{2}(\beta'_i + \beta'_j + \beta'_k + \beta'_l)$
	$R_3 = \frac{1}{2}(\xi_i + \xi_j + \xi_k + \xi_l)$	
A_{1u}	$R = \frac{1}{2}(\psi_i + \psi_j + \psi_k + \psi_l)$	
A_{2g}	$R = \frac{1}{2}(\phi_i + \phi_j + \phi_k + \phi_l)$	
A_{2u}	$R_1 = \frac{1}{2}(\rho'_i + \rho'_j + \rho'_k + \rho'_l)$	$R_2 = \frac{1}{2}(\theta_i + \theta_j + \theta_k + \theta_l)$
B_{1g}	$R_1 = \frac{1}{2}(\phi_i - \phi_j + \phi_k - \phi_l)$	$R_2 = \frac{1}{2}(\xi_i - \xi_j + \xi_k - \xi_l)$
B_{1u}	$R_1 = \frac{1}{2}(\rho'_i - \rho'_j + \rho'_k - \rho'_l)$	$R_2 = \frac{1}{2}(\theta_i - \theta_j + \theta_k - \theta_l)$
	$R_3 = \frac{1}{2}(\gamma_i - \gamma_j + \gamma_k - \gamma_l)^a$	
B_{2g}	$R_1 = \frac{1}{2}(\eta'_i - \eta'_j + \eta'_k - \eta'_l)$	$R_2 = \frac{1}{2}(\beta'_i - \beta'_j + \beta'_k - \beta'_l)$
	$R_3 = \frac{1}{2}(\alpha'_i - \alpha'_j + \alpha'_k - \alpha'_l)$	
B_{2u}	$R = \frac{1}{2}(\psi_i - \psi_j + \psi_k - \psi_l)$	
E_g	$R_{1a} = \frac{1}{2}(\rho'_i + \rho'_j - \rho'_k - \rho'_l)$	$R_{1b} = \frac{1}{2}(\rho'_i - \rho'_j - \rho'_k + \rho'_l)$
	$R_{2a} = \frac{1}{2}(\theta_i + \theta_j - \theta_k - \theta_l)$	$R_{2b} = \frac{1}{2}(\theta_i - \theta_j - \theta_k + \theta_l)$
	$R_{3a} = \frac{1}{2}(\psi_i + \psi_j - \psi_k - \psi_l)$	$R_{3b} = \frac{1}{2}(\psi_i - \psi_j - \psi_k + \psi_l)$
E_u	$R_{1a} = \frac{1}{2}(\eta'_i + \eta'_j - \eta'_k - \gamma'_l)$	$R_{1b} = \frac{1}{2}(\eta'_i - \eta'_j - \eta'_k + \eta'_l)$
	$R_{2a} = \frac{1}{2}(\beta'_i + \beta'_j - \beta'_k - \beta'_l)$	$R_{2b} = \frac{1}{2}(\beta'_i - \beta'_j - \beta'_k + \beta'_l)$
	$R_{3a} = \frac{1}{2}(\phi_i + \phi_j - \phi_k - \phi_l)$	$R_{3b} = \frac{1}{2}(\phi_i - \phi_j - \phi_k + \phi_l)$
	$R_{4a} = 1/\sqrt{6}[(\xi_i - \xi_k) - \tau^{-1}(\alpha'_i + \alpha'_j - \alpha'_k - \alpha'_l)]^b$	
	$R_{4b} = 1/\sqrt{6}[(\xi_j - \xi_l) + \tau^{-1}(\alpha'_i - \alpha'_j - \alpha'_k + \alpha'_l)]$	

^{a} Coördinate for the out-of-plane skeletal vibration. ^{b} τ = reciprocal of the C–C distance.

<div align="center">TABLE IV</div>

FORCE CONSTANTS FOR CYCLIC HYDROCARBONS COMPARED^a

	Cyclobutane K	Cyclobutane L	Cyclopropane[13] K	Cyclopropane L	Cyclohexane[14] K	Cyclohexane L
$\theta\theta$	1.418	0.232	1.145	0.286	1.502	0.166
$\phi\phi$	0.868	0	0.506	0	0.920	– .017
$\psi\psi$	2.273	0	1.778	−0.034	2.703	– .046
$\alpha'\alpha'$	2.457	0			1.966	.129
$\beta'\beta$	1.130	0	1.096	0	1.176	0
$\xi\xi$	7.141	0			6.791	0.170

	(K + 2L)	(K + 2L)	(K + 2L)
$\xi\xi$	7.141	7.251	7.131

	F	F	F
$\xi\alpha'\xi\alpha'^b$	1.044	1.823	4.3

	A
$\xi\beta'$	−0.119
$\xi\phi$	−0.107
$\xi\alpha'$	2.495

	K	L
$\alpha\beta'$	0	0
$\theta\psi$		0
$\phi\alpha'$	0	
$\beta\phi$		0

^{a} In atomic weight, ångström units. For conversion to cgs. units divide by the factors below:[12]

Force constant	Factor
$K_{\theta\theta}, K_{\phi\phi}, K_{\psi\psi}, K_{\alpha'\alpha'}, K_{\beta'\beta'}, L_{\theta\theta}$	1.69765×10^{11}
$K_{\xi\xi}, K_{\xi\alpha'\xi\alpha'}$	1.69765×10^{-5}
$A_{\xi\beta'}, A_{\xi\theta}, A_{\xi\alpha'}$	1.69765×10^{3}

^{b} This force constant is for the stretching-bending skeletal deformation; it includes $\xi\xi$, $\xi\alpha'$ and $\alpha'\alpha'$ terms. It is not possible to evaluate these terms separately for cyclopropane.

(12) J. E. Kilpatrick and K. S. Pitzer, J. Research Natl. Bur. Standards, **38**, 191 (1947).

(13) The force constants for cyclopropane were obtained from an analysis using the assignments given in Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945, except that we have interchanged the E" rocking and twisting assignments. The following parameters were used: C–C distance 1.525 Å., C–H distance 1.08 Å., and HCH angle 117°.

(14) From unpublished calculations by C. S. Lu, C. W. Beckett and K. S. Pitzer.

tion constants for adjacent vertices or bonds, and A's are interaction constants for bond stretching and the bending of an adjacent angle. Other interaction constants have been taken equal to zero.

The B_{1u} ring bending vibration is inactive except that it should be Raman active for D_{2d} symmetry. As was previously pointed out, it was hoped that an assignment could be made on the basis of difference bands. Since the line was neither observed in the Raman nor definitely assignable on the basis of combination and difference bands, we have had to assign it indirectly.

The calculation of a potential function for this vibration using the potential constants for the B_{2g} ring bending vibration and accepted values for the torsional interaction about C–C bonds is unsatisfactory because of uncertainties in the magnitude and the form of the two terms. The interaction of nonbonded carbon atoms introduces a further complication.

We have finally calculated a potential function that is in reasonable agreement with the measured entropy, the observed diminution in intensity of the 750 cm.$^{-1}$ band on heating, and the dihedral angle reported by Dunitz and Schomaker from their election diffraction work.[4] As all of this information, and particularly the last two pieces, is quite uncertain, our potential function must at best be regarded as a crude approximation. Because of the mathematical simplicity we have assumed a perturbed harmonic oscillator function of the form $V = 2800 z^2 + 400e^{-500z^2}$ where z is the distance (in Å.) of alternate carbon atoms above and below the average plane, V is in cm.$^{-1}$, and an effective reduced mass of 20.7 mass units for the vibrations has been assumed.[15] We realize that probably

(15) The value 20.7 for μ, the effective reduced mass, is obtained using the molecular constants of Dunitz and Schomaker.

$$\mu = M_0 + 2M_H \left(1 + \frac{2\sqrt{2}\epsilon}{\delta} \cos \beta/2\right)^2$$

where M_0 = mass of C, M_H = mass of H, δ = C–C bond distance ϵ = C–H bond distance, β = HCH bond angle.

other terms, particularly a quartic term, should be added, but feel that refinement is not worthwhile in view of the several uncertainties and lack of more data. For the lower two states the effect of the perturbation is quite large so we have used simple variation functions $\psi = qe^{-as^2/2} + re^{-as^2}$ and $\psi = sze^{-as^2/2} + tze^{-as^2}$ to calculate the values 128 and 155 cm.$^{-1}$ for these two states. The next four levels we have calculated using the perturbation method: 292, 351, 464 and 542 cm.$^{-1}$. For still higher levels we have assumed the spacing to be constant and equal to 95 cm.$^{-1}$. Correlation with observed diminution in intensity is satisfactory if it is assumed that molecules in all of the above states except the two lowest have transition probabilities for D_{2d} allowed, D_{4h} forbidden transitions that are negligible when compared with those for these two states. Actual calculation of transition probabilities may indicate some modification of the potential function. Because of centrifugal effects, the barrier height will be reduced for molecules having high rotational quantum numbers. However, a simple calculation suggests that this effect will not be pronounced at temperatures at which we have worked, and while it may be a contributing cause in the diminution in intensity on heating, we believe the effect is principally the result of depopulation of the lowest two vibrational levels.

Combination Bands.—Observed infrared bands are listed in Table II with possible assignments for most of the combinations. Since no bands were observed to increase in intensity on heating, we have avoided any difference assignments. Most of the bands observed to decrease in intensity on heating are satisfactorily explained on the basis of our model. Several bands, notably those at 650, 850 and 955 cm.$^{-1}$ are not explained in Table II. We think it likely that these (and also probably those at 2755, 2775, 3058 and 3145 cm.$^{-1}$) may be combinations involving the B_{1u} out-of-plane bending motion. Because of uncertainties in the shape of the out-of-plane bending potential, we have not attempted to assign these bands. Those at 850 cm.$^{-1}$ and 650 cm.$^{-1}$ might well be sum and difference bands with the 750 cm.$^{-1}$ vibration. It is unfortunate that these bands are so weak since the behavior of their shapes and intensities with temperature could conceivably throw light on the out-of-plane bending potential function. In spite of the simplification that results in going to the liquid, the region around 2100 cm.$^{-1}$ is still fraught with uncertainties. A number of combinations besides those listed are allowed in this region; with this large number of combinations some cases of Fermi resonance are likely and the assignments given are most uncertain. Because of these complications, our failure to explain diminutions in intensity with increase in temperature for the bands at 2035 and 2047 cm.$^{-1}$ cannot be regarded as serious evidence against our analysis.

Force Constants.—Values of principal force constants for cyclobutane are compared with those for cyclohexane and cyclopropane in Table IV. The methylene constants for cyclobutane, as expected, generally have values intermediate between those for the other two compounds. The values ob-

tained for $L_{\psi\psi}$ for cyclohexane and cyclopropane suggest that a small negative value be used also in the case of cyclobutane. The introduction of such a constant results in an increased value for the B_{2u} twisting vibration. It may be that the 1104 cm.$^{-1}$ Raman band has been erroneously assigned; a possible combination assignment could be skeletal $B_{1u} + 1003$ cm.$^{-1}$, $A_{1g} = 1104$ cm.$^{-1}$ (combination allowed for D_{2d} symmetry, but not for D_{4h}.)

Correlation of the skeletal force constants is necessarily less complete because of the limited information available from cyclopropane. That the value for $K_{\alpha'\alpha'}$ for cyclobutane is appreciably greater than for cyclohexane is not surprising. Because of the rather small diagonal distance across the ring, interaction between the opposite carbons may be very much greater in cyclobutane than in strain-free cases. (Dunitz and Schomaker[4] have estimated the magnitude of the effect from a consideration of lengthening of C–C bonds in cyclobutane.) Our failure to include an interaction term between opposite angles may well account for the large value for $K_{\alpha'\alpha'}$. A similar difficulty is implicit in our failure to include stretching interaction terms. The value obtained for $F_{\xi\alpha'\xi\alpha'}$ is unusually small, and we have assigned a large stretching–bending interaction term to explain this (see Table IV). The value of this interaction term will be reduced, but probably not greatly so, if the aforementioned α' and ξ interaction terms are included.

The observed strain energy[16] in cyclobutane, when taken in conjunction with our value for $K_{\alpha'\alpha'}$ requires that either the large value of $K_{\alpha'\alpha'}$ be in part due to an interaction term, or that C–C bonds be very much bent[17,18] or (more likely) both.[19]

Thermodynamic Functions

Thermodynamic functions based on our analysis are tabulated in Table V. The data cannot be regarded as being as reliable as is usual, particularly in view of the uncertainty in the potential function for the out-of-plane bending motion.

TABLE V

THERMODYNAMIC FUNCTIONS OF CYCLOBUTANE (IN CAL./ DEG. MOLE)

T (°K.)	$\dfrac{H_0 - H_0^0}{T}$	$\dfrac{F_0 - H_0^0}{T}$	S^0	C_p^0
285.67	10.81	51.91	62.72	16.46
298.16	11.07	52.37	63.43	17.26
300	11.11	52.44	63.55	17.37
400	13.49	55.95	69.44	23.89
500	16.18	59.25	75.42	29.86
600	18.88	62.43	81.31	34.76
700	21.45	65.54	86.99	38.89
800	23.86	68.56	92.42	42.42
900	26.09	71.50	97.59	45.41
1000	28.15	74.36	102.51	47.96
1500	36.32	87.43	123.75	56.34

The entropy given in Table V may be combined with the measured heat of combustion for cyclobu-

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

(17) J. E. Kilpatrick and R. Spitzer, *J. Chem. Phys.*, **14**, 463 (1946).

(18) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(19) If our $K_{\alpha'\alpha'}$ is used, and the bonds are assumed to be distorted from 109° 28′ to 90°, the strain resulting from the distortion alone is much larger than is actually observed.

tane, 2774.1 kj./mole.[16] and other data[20] to obtain the free energy of formation. Free energy of isomerization to isobutene may also be calculated. These values together with the corresponding values for cyclopropane and cyclopentane are given in Table VI. The values given are consistent with the observation that synthesis of cyclobutane has been difficult.

Our analysis of cyclobutane suggests that some other strained cyclic compounds may also have double minimum potential functions with barriers sufficiently low so that similar effects might be observed. Spectroscopic investigation has confirmed this expectation in the cases of cyclopentene and cyclopentane. Preliminary spectroscopic investi-

(20) "Properties of Hydrocarbons," Project #44, American Petroleum Institute.

TABLE VI

FREE ENERGY OF FORMATION ($\Delta F^0_{f\,298°}$) AND ISOMERIZATION ($\Delta F^0_{i\,298°}$) OF CYCLIC HYDROCARBONS

Hydrocarbon	$\Delta F^0_{f\,298°}$, kcal./mole	$\Delta F^0_{i\,298°}$ (to most stable alkene), kcal./mole
Cyclopropane[13]	24.98	− 9.99
Cyclobutane	26.31	−11.73
Cyclopentane	9.23	5.04

gation of octafluorocyclobutane has yielded negative results.

We are indebted to Professor R. S. Halford for helfpul suggestsions and advice in connection with this problem.

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Condensed Gas Calorimetry. V. Heat Capacities, Latent Heats and Entropies of Fluorine from 13 to 85°K.; Heats of Transition, Fusion, Vaporization and Vapor Pressures of the Liquid[1]

By Jih-Heng Hu, David White and Herrick L. Johnston

Heat capacities of fluorine were measured from 14 to 85°K. A first-order transition was found at 45.55°K. with heat of transition equal to 173.90 ± 0.04 cal./mole. The melting point of pure fluorine was found to be 53.54°K. and the heat of fusion, 121.98 ± 0.5 cal./mole. The heat of vaporization at 84.71°K. and 738 mm. was found to be 1563.98 ± 3 cal./mole. The vapor pressure of liquid fluorine was measured between the melting point and 90°K., and the data were fitted to the equation: $\log P_{mm} = 7.08718 - \dfrac{357.258}{T} - \dfrac{1.3155 \times 10^{13}}{T^8}$. The normal boiling point, calculated from this equation, is 85.02 ± 0.02°K. Thermodynamic functions of fluorine have been computed from 0 to 85°K. The entropy in the ideal gas state at 85.02°K., from the calorimetric measurements, is 39.58 ± 0.16 e.u. Values calculated from spectroscopic data by Haar and Beckett, and by Cole, Farber and Elverum (39.56 ± 0.01 and 39.62 ± 0.02 e.u., respectively) are in good agreement with the calorimetric value.

Introduction

At present there are very few accurate measurements of the physical properties of fluorine at low temperatures. The calorimetric measurements by Kanda[2] show considerable uncertainties and do not agree with the results obtained from spectroscopic data. Furthermore, Murphy and Rubin[3] have pointed out, from a careful examination of these

data, that a transition in the solid may have been overlooked.

Because of a variety of important commercial uses for fluorine, considerable interest in accurate thermal properties of this molecule has been evident recently. We therefore deemed it desirable to reinvestigate the thermal properties of F_2 with our improved instruments and techniques which were not available to the earlier investigators.

Materials

The fluorine used in our calorimetric study was produced by a Harshaw laboratory-size fluorine cell. Its electrolyte was a mixture of KF, 2HF and 1.0–1.5% LiF. The cell was allowed to operate several hours before F_2 was allowed to collect in the purification system. The procedure for purifying the material and filling the calorimeter is shown schematically in Fig. 1. All tubings and valves in this system were made of Monel or nickel, the valves were packed with Teflon, and all joints were silver-soldered.

The system was first evacuated and flushed with fluorine several times before use. After leaving the Harshaw electrolytic cell (1) and passing through a dry ice trap (2) to remove most of the HF vapor, 100 cc. of liquid fluorine was condensed into a Monel cylinder (3). The greatest part of the remaining HF was removed from the material by an NaF absorption train before it was further purified by repeated bulb to bulb distillations, (3) to (5), (5) to (6), and finally from bulb (6) to the high-pressure Monel bomb (7) in which the material was carefully weighed at room temperature before condensing into the calorimeter. The amount of F_2 condensed in the calorimeter, determined by weighing the bomb (7) before and after filling the calorime-
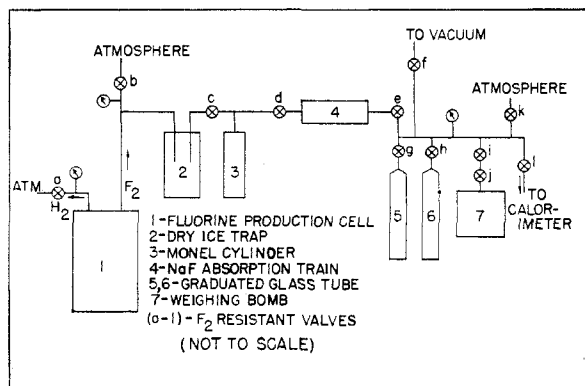

Fig. 1.—Purification system.

ATMOSPHERE

TO VACUUM

ATMOSPHERE

ATM

F_2

H_2

1-FLUORINE PRODUCTION CELL
2-DRY ICE TRAP
3-MONEL CYLINDER
4-NaF ABSORPTION TRAIN
5,6-GRADUATED GLASS TUBE
7-WEIGHING BOMB
(o-l)-F_2 RESISTANT VALVES
(NOT TO SCALE)

TO CALOR-IMETER

(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) E. Kanda, Bull. Chem. Soc. Japan, 12, 473 (1937).

(3) G. M. Murphy and E. Rubin, J. Chem. Phys., 20, 1179 (1952).