nium ion containing 17 atoms other than hydrogen. These facts point to specific interactions which are dependent on constitutional and structural factors that cannot be elucidated without more extensive data than are presently available.

The dissociation constants of the quaternary onium salts are such as might be expected with a solvent of a dielectric constant of 12. With decreasing size of the negative ion, the dissociation constant diminishes. The high value of the dissociation constant for the two silver salts is puzzling. The silver ion is not an exceptionally slow ion when compared with the ethyltriphenylarsonium ion, for example. Yet the dissociation constant of silver perchlorate is practically the same as that of ethyltriphenylarsonium picrate. The conductance of the perchlorate ion is 47.3 and that of the silver ion is 34.1, while, in contrast, the conductance of the ethyltriphenylarsonium ion is 24.0 and that of the picrate ion is 33.7.

V. Summary

1. The conductance of the following salts has been measured in pyridine at 25°: silver nitrate and perchlorate, tetra-*n*-butylammonium picrate, bromide and iodide and ethyltriphenylarsonium picrate.

2. Values of Λ_0 and K for these salts have been derived by the method of Fuoss.

3. Ion conductances have been evaluated by the method of Fowler.

4. The dissociation constants of the silver salts are unexpectedly high.

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

The Thermodynamics and Molecular Structure of Cyclopentane[1]

BY JOHN E. KILPATRICK,[2] KENNETH S. PITZER[3] AND RALPH SPITZER[4]

The five-membered saturated ring is an important unit in organic chemistry. It is also particularly interesting because the torsional forces about the single bonds are in opposition to the forces tending to retain tetrahedral bond angles. Thus the latter forces tend to keep all five carbon atoms co-planar while the torsional forces tend to pucker the ring.

Aston, Schumann, Fink and Doty[5] have measured the entropy of gaseous cyclopentane and shown that it indicates a puckered ring, while one of us has found that calculations based on normal values of the force constants,[6] give lower energy to a puckered than to a planar ring. Douslin and Huffman[7] have also measured the entropy of cyclopentane and confirm the value of Aston and co-workers. Two of us[8] have recently measured the heat capacity of gaseous cyclopentane. It is the purpose of the present paper to analyze all of these and other data in order to give, if possible, a complete and reliable picture of the structure of the molecule and set of tables of thermodynamic properties.

Bond Distances and Angles.—Hassel and Viervoll[9] have recently reinvestigated cyclopentane by the electron diffraction method, using a rotating sector. They find C–C to be 1.54 Å. and C–H to be 1.09 Å. While they assumed a plane pentagonal model, the small puckering we shall find would have only a minor effect at this point. Indeed a study of their curves indicates that the fit at larger distances might be even more perfect if the slight changes due to puckering were taken into account. In any event this work gives us reliable distances; also it confirms approximate tetrahedral angles.

Vibration Frequencies.—The Raman spectrum of cyclopentane has been reported by Rosenbaum and Jacobson[10] who summarize earlier work. They remark about the unusual diffuseness of the lines. This we will find to be significant. The infrared spectrum has been reported by several laboratories.[11]

Since detailed and complete normal coördinate calculations would be excessively laborious for the puckered ring model, we first made calculations for the planar model which has the symmetry D_{5h}. At this point we are indebted to Dr. C. S. Lu and Dr. C. W. Beckett[12] who were studying certain features of the vibrational spectrum of the series cyclopropane through cyclohexane. Using force constants from this study, chiefly from cyclo-

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[1] This work was supported by Research Project 44 of the American Petroleum Institute with headquarters at the National Bureau of Standards.

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[4] National Research Fellow in Chemistry, 1945–46. Now at Department of Chemistry, Oregon State College, Corvallis, Oregon.

[5] J. G. Aston, S. C. Schumann, H. L. Fink and P. M. Doty, THIS JOURNAL, **63**, 2029 (1941); Aston, Fink and Schumann, *ibid.*, **65**, 341 (1943).

[6] K. S. Pitzer, *Science*, **101**, 672 (1945).

[7] D. R. Douslin and H. M. Huffman, THIS JOURNAL, **68**, 173 (1946).

[8] R. Spitzer and K. S. Pitzer, *ibid.*, **68**, 2537 (1946).

[9] O. Hassel and H. Viervoll, *Tids. Kjemi Bergvesen*, **3**, 31 (1946).

[10] E. J. Rosenbaum and H. F. Jacobson, THIS JOURNAL, **63**, 2841 (1941).

[11] Spectrograms 343 and 446 distributed by Project 44 of the American Petroleum Institute, National Bureau of Standards. 343 is from the Radiometry section of the Bureau of Standards, which also supplied data at wave lengths greater than 15μ. 446 is from the Shell Development Company, Emeryville, Calif.

[12] These results including these force constants will be published separately.

hexane, one may calculate the frequencies shown in Table I. The methods of Wilson[13] were employed and C–H stretching motions were reduced out immediately. The highest order matrix remaining is then the fourth order E_2'. Table I also shows the selection rules and describes the principal coördinates involved.

TABLE I

CALCULATED VIBRATION FREQUENCIES OF CYCLOPENTANE BASED ON PLANAR MODEL OF SYMMETRY D_{5h}

	Raman active			Infrared active		Inactive		
Motion	A_1'	E_2'	E_1''	A_2''	E_1'	A_2'	A_1''	E_2''
CH_2 sym. bend.	1450	1452	..	..	1449	..	..	..
CH_2 twist	..	..	1348	..	..	..	1295	1327
CH_2 wag in plane	..	1207	..	..	1298	1231	..	..
CH_2 rock out of plane	..	..	905	896	..	..	..	1020
C–C stretch	838	1049	..	..	951	..	..	..
C–C–C bend	..	549	..	..	..	..	..	[a]

[a] This motion is the ring puckering; hence the calculated value for this model is meaningless.

In Table II are listed the observed frequencies below 1470 cm.$^{-1}$ which appear to us to be reasonably well established, together with their intensities and polarizations where available. These are compared with the active fundamentals calculated for the planar model.

TABLE II

COMPARISON OF OBSERVED SPECTRAL LINES OF CYCLOPENTANE BELOW 1470 CM.$^{-1}$ WITH VALUES CALCULATED ON THE PLANAR MODEL (D_{5h})

Infrared		Raman	
Obs.	Calcd.	Obs.	Calcd.
1462 (7)	1449 cm.$^{-1}$	1448 (5, dp)	1452 (dp)
1376 (1)	..		1450 (p)
1317 (1)	1298	..	1348 (dp)
1250	..	1298 (1)	..
950 (0)	951	1216 (?)	1207 (dp)
895 (4)	896	1032 (4, dp)	1049 (dp)
827 (1)	..	..	905 (dp)
769 (1)	..	888 (10, p)	838 (p)
616	..	..	595 (dp)
545	..	288 (1)	..

It will be noted that Table II shows relatively good agreement at the higher frequencies, while below 800 cm.$^{-1}$ there is no agreement at all. This is about what would be expected if cyclopentane is actually somewhat puckered. The high frequency vibrations are not closely related to the puckering motion, nor are their frequencies greatly affected. Consequently we would expect to find approximately the calculated frequencies, although there might be some breakdown of selection rules. The biggest frequency difference is on the symmetrical C–C stretching motion which is calculated at 838 and observed at 888 cm.$^{-1}$. However, as Rosenbaum and Jacobson[10] remark, the diffuseness of these higher frequency lines is probably associated with small effects of puckering. Indeed we shall find later that this puckering is of an indefinite character so that this diffuseness is most reasonable.

There are four modes of vibration expected to have frequencies less than 700 cm.$^{-1}$. On the planar model these are two degenerate modes; the higher is calculated at 595 cm.$^{-1}$ while no reasonable calculation can be made of the lower mode because it depends on twisting about the single bonds. In this range no credence can be given the selection rules for the planar model. Indeed the strict symmetry is so low that there will be no selection rules. Consequently it seems reasonable to select 616 and 545 cm.$^{-1}$ as the frequencies arising when the degenerate 595 frequency splits due to ring puckering. This leaves 288 cm.$^{-1}$ for one of the twisting modes. The other twisting mode will be discussed in the next section.

In Table III we summarize the complete vibration assignment used for thermodynamic calculations. It will be noted by comparison with Tables I and II that all values for hydrogen motions are well supported by calculated or observed results, usually both. However, average values are used for the groups of frequencies. The 2950 cm.$^{-1}$ value for C–H stretching is the average of closely spaced and largely unresolved lines in both spectra. For C–C stretching, 1032, 950 and 888 cm.$^{-1}$ are well substantiated. The selection of the observed lines at 827 and 769 cm.$^{-1}$ for the other two is quite arbitrary and was based largely on the gaseous heat capacity. The three low frequencies have been discussed already.

TABLE III

VIBRATING FREQUENCIES OF CYCLOPENTANE USED FOR THERMODYNAMIC CALCULATIONS

Motion	Frequency, cm.$^{-1}$	Degeneracy
C–H stretching	2950	10
CH_2 sym. bend.	1462	5
CH_2 twist	1376	2
	1298	3
CH_2 wag in plane	1250	5
CH_2 rock out of plane	950	3
	895	2
C–C stretching	1032	1
	950	1
	888	1
	827	1
	769	1
C–C–C bending	616	1
	545	1
C–C twisting	288	1

Pseudo-Rotation of Ring Puckering.—In order to analyze further the ring puckering motions we first calculated the potential energy. There are two ways a five-membered ring can pucker and still retain some symmetry. As is shown in Fig. 1, one atom can move out of the plane of the other

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[13] E. B. Wilson, Jr., *J. Chem. Phys.*, **9**, 76 (1941).

four giving the C_s mode or two atoms can twist relative to the others giving the C_2 mode. Calculations were made for these two modes in which the C–C bond lengths were kept at exactly their original value and the deviation of C–C–C bond angles from the tetrahedral value kept to a minimum. The potential energy of bond bending was evaluated by summing the squares of the deviations from tetrahedral angles together with the force constant $k = 0.8 \times 10^{-11}$ ergs/radian². The value of this constant is only approximate, but is consistent with the ring bending (616 and 545 cm.$^{-1}$) frequencies of cyclopentane, similar frequencies for cyclohexane and the skeletal bending frequency in propane. The potential energy associated with rotation or twist about the five C–C bonds was also included, using a cosine shape and the value from ethane,[14] 2800 cal. per mole, for the potential height, V_0.

The potential energy curve as a function of the deviation from planarity proved to be the same for the C_2 and C_s types of puckering as nearly as the two could be compared. This suggested that very probably intermediate types of puckering would also show the same potential curve. To investigate this we define the following coördinates. Let z_j be the displacement of jth carbon atom perpendicular to the plane of the unpuckered ring. Then write

$$z_j = \sqrt{\frac{2}{5}}\, q \cos 2\left(\frac{2\pi}{5} j + \varphi\right) \qquad (1)$$

where q is the amplitude of the puckering, φ is the phase angle of maximum amplitude (see Fig. 1) and j takes integral values from 1 to 5. Coördinates q and φ are orthogonal to each other and to translation and rotation of the whole molecule. The two symmetrical types of puckering are obtained by setting $\varphi = l\pi/10$ for C_s and $\varphi = (2l+1)\pi/20$ for C_2, where l is any integer. Figure 1 shows these two types of puckering, together with an intermediate position. This indicates how a rotation of the maximum amplitude of puckering gives successively the C_s and C_2 configurations.

We may now calculate the potential energy as a function of q and see if it is independent of φ. It proved too complicated mathematically to retain the condition of constant bond lengths at this stage since that introduces small motions in the x and y directions. Also we were unable to carry through the calculation with φ unspecified. However, it was possible to show that for various assumed values the C–C–C angle strain and the C–C twisting strain were each dependent on q and independent of φ. For example, calculations were made for $q = 0.308$ Å. and $\varphi = 0, \pi/40$ and $\pi/20$. The C–C–C angle strain was $1.445(k \times 10^{11})$ kcal./mole and the twisting strain $3.6036\ V_0$ kcal./mole, the same to four and five significant figures, respectively, for all three values of φ.

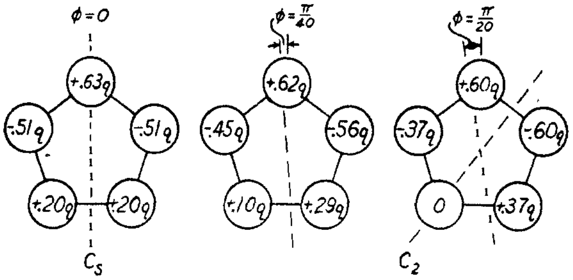

Fig. 1.—Pseudo-rotation of ring puckering in cyclopentane. Displacements perpendicular to the plane of the paper are given in the circles.

In the first method, where the bond distances were held constant, the following equations apply to the C_s mode. Let atom 1 be displaced from the plane of atoms 2, 3, 4 and 5. Ring angles $\omega_2 = \omega_5$ and $\omega_3 = \omega_4$. The following relations may be derived by the use of vector analysis

$$\cos \omega_3 = \frac{1}{2} - \sin \frac{1}{2}\omega_1$$

$$\cos \lambda = -\frac{\sin \frac{1}{2}\omega_1 \cos \omega_3 + \cos \omega_2}{\cos \frac{1}{2}\omega_1 \sin \omega_3}$$

$$\cos \theta_{12} = \frac{\cos \omega_2 (\cos \omega_1 - 1) - \sin \frac{1}{2}\omega_1 \left(1 - 2 \sin \frac{1}{2}\omega_1\right)}{\sin \omega_1 \sin \omega_2}$$

$$\cos \theta_{23} = \frac{\cos \omega_2 \cos \omega_3 + \sin \frac{1}{2}\omega_1}{\sin \omega_2 \sin \omega_3}$$

The angle θ_{mn} is the torsion of bond mn. By symmetry, $\cos \theta_{12} = \cos \theta_{51}$, and $\cos \theta_{23} = \cos \theta_{45}$. Torsion $\theta_{34} = 0$. The angle λ is the dihedral angle between the planes 251 and 2543. From λ the amplitude of the puckering can be calculated.

There are two independent variables in the above equations, which can be chosen as ω_1 and ω_2. It was found that the combination $\omega_1 = \omega_2$ gave substantially the lowest potential energy.

In the second method, with all displacements perpendicular to the ring, the following equations apply

$$\cos \omega_j = -\frac{\cos(2\pi/5) + (\Delta z_{j+1,j})(\Delta z_{j,j-1})}{(d_{j+1,j})\,(d_{j,j-1})}$$

$$\sin \theta_{j,j+1} = \frac{[\mathbf{r}_{j,j-1}\,\mathbf{r}_{j+1,j}\,\mathbf{r}_{j+2,j+1}]}{(d_{j,j-1})(d_{j+1,j})(d_{j+2,j+1}) \sin \omega_j \sin \omega_{j+1}}$$

$$d_{j+1,j} = (d_0^2 + \Delta z_{j+1,j}^2)^{1/2}$$

where Δz is the difference in the z coördinates indicated (from eq. 1), d is the absolute length of the bond indicated and in the second equation there is the triple vector product of the vectors, r, from atoms j − 1 to j, j to j + 1 and j + 1 to j + 2.

In each method, after the values of all ω's and θ's are obtained, the potential energy is calculated from the standard equations.

While the two calculations mentioned above can not be expected to agree quantitatively, they indicate clearly that the potential energy is at maximum in the planar configuration and falls to a minimum about 4 kcal./mole lower at q approximately 0.3 Å. Near this minimum the curve is roughly parabolic with a curvature corresponding to a force constant of about 10^5 dynes per cm.

We may now introduce the Schrödinger equation and calculate the energy levels for this system.

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[14] K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).

$$\frac{-h^2}{8\pi^2 m}\sum_{j=1}^{5}\frac{\partial^2\psi}{\partial z_j^2} + V\psi = E\psi \qquad (2)$$

where m is the mass of a carbon atom, V is the potential energy and E the total energy for wave function ψ. In addition to the coördinates q and φ defined in equation (1) we have translation in the z direction and rotation about two axes. Equations for all of these coördinates may be written as

$$z_j = \sqrt{\frac{2}{5}}\left[q \cos 2\left(\frac{2\pi}{5}\,j + \varphi\right) + \alpha \cos \frac{2\pi}{5}\,j + \beta \sin \frac{2\pi}{5}\,j + \frac{t}{\sqrt{2}}\right] \qquad (3)$$

where α, β and t describe the two rotations and the translations, respectively. Following the usual procedure for the separation of variables, one obtains

$$\begin{aligned}
-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi_t}{\partial t^2} &= E_t\,\psi_t \\
-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi_\alpha}{\partial \alpha^2} &= E_\alpha\,\psi_\alpha \\
-\frac{h^2}{8\psi^2 m}\frac{\partial^2\psi_\beta}{\partial \beta^2} &= E_\beta\,\psi_\beta \\
-\frac{h^2}{32\pi^2 m q_0^2}\frac{\partial^2\psi_\varphi}{\partial \varphi^2} &= E_\varphi\,\psi_\varphi \\
-\frac{h^2}{8\pi^2 m q}\frac{\partial}{\partial q}\left(q\,\frac{\partial\psi_q}{\partial q}\right) + V(q)\,\psi_q &= E_q\,\psi_q \qquad (4) \\
E &= E_t + E_\alpha + E_\beta + E_\varphi + E_q \\
\psi &= \psi_t\,\psi_\alpha\,\psi_\beta\,\psi_\varphi\,\psi_q
\end{aligned}$$

The validity of the equations for α, β and q is limited to small values of these variables. The equations in α and β can be rearranged, when the x and y coördinates are also considered, to give the usual equations for rotation; however, the limitation of q to small values (as compared to the distance between atoms) remains. Since the puckering of the cyclopentane ring is small, this restriction is not serious. The separation of the q and φ equations is based on q remaining near an equilibrium value, q_0.

We may now proceed to solve the equations for q and φ. The latter yields the usual energy levels for a free, one dimensional rotation, however, the boundary condition is $\psi(\varphi) = \psi(\varphi + \pi)$ because there are two regions of positive amplitude around the ring (or because eq. 1 contains essentially cos 2 φ). Then

$$E_\varphi = n^2h^2/8\pi^2 m q_0^2 \qquad (5)$$

in which mq_0^2 is essentially a moment of inertia and n takes integral values both positive and negative including zero.

The effect of symmetry is to eliminate four-fifths of the values of the quantum number, n, for any given over-all rotational state. In particular if nuclear spins are such that symmetric states are allowed, then $K + n$ must be an integral multiple of five. Here K is the quantum number for the rotation about the five-fold axis.[15] Since the energy levels for successive multiples of five for n would be separated by approximately kT at the temperature of interest, it is important to note that all values of n are allowed for any nuclear spin species. For a given value of n, only one-fifth of the values of K are allowed, but since the energy level spacing even for increase of K by five is close compared to kT, the classical formulas with symmetry number are still valid for statistical calculations. In order to solve the equation in q, some assumption must be made about the nature of $V(q)$. As a first approximation we assume a harmonic oscillator potential about the equilibrium position q_0. Then the substitution $\psi_q = q^{-1/2}f(q)$ gives substantially the harmonic oscillator energy levels

$$E_q = \left(n' + \frac{1}{2}\right)h\nu_q - h^2/32\pi^2 m q_0^2 \qquad (6)$$

with

$$\nu_q = (1/2\pi)(k/m)^{1/2},\ V = (k/2)(q - q_0)^2$$

We now identify ν_q with the observed Raman line at 288 cm.$^{-1}$. The very small, constant second term in (6) is considered part of the vibrational zero point energy.

Consideration of the hydrogen atoms complicates the mathematics considerably but the only change in the essential results is to give the mass of the single atom, m, the value 28.1 on the atomic weight scale. This figure was calculated from the inverse kinetic energy matrix, G, for E_2'' (planar D_{5h} model) by making all of the coördinates except q rigid. This of course assumes that the CH_2 group is a rigid unit which should be a good approximation for such low frequency motion. Although we have assumed a puckered form for the equilibrium configuration of the ring, the reduced mass for the CH_2 group for the puckering motion should still be about this magnitude. In any event, a slight error in this reduced CH_2 mass is absorbed in the value of q_0 determined from the experimental entropy.

The essential result of this section has been to show that for the potential energy function expected for cyclopentane, the ring puckering motions are: first, an ordinary vibration in which the amount of puckering oscillates about a most stable value and second, a pseudo one-dimensional rotation in which the phase of the puckering rotates around the ring. This is not a real rotation since the actual motion of the atoms is perpendicular to the direction of rotation and there is no angular momentum about the axis of rotation. Since the higher vibration frequencies must be at least slightly affected by the coördinate φ, the observed diffuseness of the spectral lines is most reasonable. The 288 cm.$^{-1}$ frequency corresponds to a force constant of 1.4×10^5 dynes per cm. on the coördinate q. This agrees with our calculations within their accuracy, which is not very high because of uncertainties in the potential constants. Likewise our calculated value of the position of minimum potential energy, q_0, is not very accurate. Consequently we shall use the observed 288 cm.$^{-1}$ frequency and shall evaluate the exact value of q_0 later from the entropy value.

Experimental Entropy Value.—Before proceeding to the final calculations, a few words must be said about the selection of a best value of the entropy of cyclopentane from the experimental "Third Law" method. Although the heat capacity curves of Aston, Fink and Schumann[5] and of Douslin and Huffman[7] do not agree too well, their final values of the entropy of the liquid differ by only 0.08 cal. per degree. This is within the limit of error assigned by Douslin and Huffman and just outside the optimistically small limit assigned by Aston. However, the value given by Aston, Fink and Schumann for the heat of vaporization at 298.16° K. is unacceptable because it is in serious disagreement with their own vapor pressure curve and with that of Willingham, Taylor, Pignocco and Rossini.[16]

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[15] L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," McGraw-Hill Co., New York, N. Y., 1935, pp. 275–280.

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

The use of the vapor pressure data above to calculate the heat of vaporization at 298.16° K. is not very satisfactory since gas imperfection effects are considerable and may not be estimated accurately by available equations of state. We can avoid this difficulty by making the calculation at a lower temperature and pressure where the gas is nearly perfect. Table IV summarizes these calculations. We have used the vapor pressure equation selected by Project 44 of the American Petroleum Institute[17] from both sets of data mentioned above. In both cases the effect of gas imperfection was calculated with the Berthelot equation with critical constants[5] $T_c = 520°$ K. and $P_c = 44.2$ atm.

TABLE IV

THE ENTROPY OF CYCLOPENTANE

T, °K.	260°K.		298.16°K.	
Source	A., F., S.[5]	D. and H.[7]	A., F., S.[5]	D. and H[7]
Liquid at melting point	35.533	35.493	35.533	35.493
M. p. to *T*° K.	9.403	9.342	13.388	13.293
Vaporization to real gas	27.94	27.94	22.84	22.84
Gas imperfection	0.020	0.020	0.084	0.084
Correction to 1 atm.	−5.244	−5.244	−1.725	−1.725
Entropy of ideal gas, *T*° K. and 1 atm.	67.65	67.55	70.12	69.99
Calculated	67.54		70.00	

Thermodynamic Functions and Final Molecular Model.—We are now ready to make the final calculations of the entropy, heat capacity and other functions. The moments of inertia calculated on the planar model with the distances given above are $I_x = I_y = 13.028$ and $I_z = 23.405$ each $\times 10^{-39}$ g. cm^2. The vibration frequencies are given above. The effective symmetry number for over-all rotation of the puckered ring is one. (Aston, *et al.*[5] give $\sigma = 2$ for the C_2 model but they have neglected the fact that it has *d* and *l* forms which cancels the effect of the symmetry number.) When the pseudo rotation is added a symmetry number of five is introduced as explained above. In order to fit the entropy closely, the value of 0.236 Å. was selected for q_0. This is reasonably close to the rough value calculated above. Also in order to fit the heat capacity values more closely, an anharmonicity coefficient of 0.03 was assumed for the 288 cm.$^{-1}$ vibration. Since it is a double minimum vibration with the central peak only about 4 kcal. above the minima, this is quite reasonable. In any case the effect of the anharmonicity is quite small.

Table IV compares the calculated entropy of the gas with the experimental values while Table V similarly compares values for the heat capacity of gaseous cyclopentane. The experimental values of the gas heat capacity are from Spitzer and Pitzer.[8] The values of physical constants and working formulas for the calculations are given by Wagman, Kilpatrick, Taylor, Pitzer, and Rossini.[18]

TABLE V

THE HEAT CAPACITY OF CYCLOPENTANE IN THE IDEAL GAS STATE

T, °K.	C_P^0 exptl.[8]	C_P^0 calcd.
353	24.38 ± .2 24.45 ± .3	24.37
372	25.85 ± .2	25.94
395	28.03 ± .3	27.83
424	30.19 ± .3	30.16
463	33.16 ± .3	33.16
503	36.02 ± .4	36.07
539	38.26 ± .4	38.52

Using the formulas and parameters already mentioned, values were calculated for the functions $-(F_T^0 - H_0^0)/T$, $(H_T^0 - H_0^0)/T$, S^0 and C_P^0 over a range of temperatures. These are given in Table VI.

TABLE VI

THE THERMODYNAMIC FUNCTIONS OF CYCLOPENTANE (CAL./DEG. MOLE FOR THE IDEAL GAS STATE)

T, °K.	$-(F_T^0 - H_0^0)/T$	$(H_T^0 - H_0^0)/T$	S^0	C_P^0
298.16	57.93	12.07	70.00	19.82
300	58.00	12.12	70.12	19.98
400	61.88	15.12	77.00	28.24
500	65.62	18.52	84.14	35.86
600	69.30	21.98	91.28	42.36
700	72.95	25.29	98.24	47.81
800	76.52	28.40	104.92	52.44
900	80.04	31.29	111.33	56.37
1000	83.48	33.97	117.45	59.75
1100	86.84	36.46	123.30	62.68
1200	90.13	38.75	128.88	65.18
1300	93.31	40.87	134.18	67.36
1400	96.40	42.83	139.23	69.24
1500	99.42	44.65	144.07	70.89

Discussion.—Initially we had hoped that it would be possible to correlate a number of quantities which depend on the bond twisting and bending forces in the cyclanes. These include the heats of formation per CH_2 group of cyclopentane, cyclohexane and cyclooöctane,[19] the energy difference of chair and boat forms of cyclohexane and the detailed nature of the puckering of cyclopentane. While the use of the ethane potential for twisting gives rough agreement,[6] some of these relationships indicate a lower value while others indicate a higher value of this twisting potential. Numerous plausible assumptions are involved in these relationships at least one of which apparently must be in error but we are not prepared to say which it is. As an example, the intrinsic C–C bond energy might not be exactly the same for five- and six-membered rings although we are inclined to believe that it should be. Further study appears to be needed before these various relationships can be put on a quantitative basis. Nevertheless we believe the analysis given

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[17] American Petroleum Institute Research Project 44: selected values of properties of hydrocarbons, Table 7k (part 2), 8/31/44.

[18] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research, Natl. Bur. Standards*, **34**, 143 (1945).

[19] R. Spitzer and H. M. Huffman, THIS JOURNAL, **69**, 211 (1947).

in this paper for cyclopentane brings into agreement a number of previously unrelated facts, and that a final understanding of the broader problems will not essentially change this analysis.

Summary

The published data from electron diffraction, Raman and infrared spectra, entropy and specific heat measurements have been combined to develop as complete a picture of structure of the cyclopentane molecule as possible. Most striking is the result that the puckering of the ring is not of a definite type but that the angle of maximum puckering rotates around the ring. Other properties prove to be consistent with this conclusion. Among the results obtained are an assignment of vibration frequencies and tables of the thermodynamic functions, $-(F - H_0)/T$, S, $(H - H_0)/T$ and C_P for the range 298.16 to 1500° K.

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

The Thermodynamic Properties and Molecular Structure of Cyclohexane, Methylcyclohexane, Ethylcyclohexane and the Seven Dimethylcyclohexanes[1]

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This paper is a continuation of studies on the structural and thermodynamic properties of hydrocarbons. As compared to cyclopentane,[5] in which a large number of configurations with nearly equal stability result from the opposition of torsional forces about single bonds against forces tending to maintain tetrahedral angles, cyclohexane has one predominant stable configuration, the chair form, since it lies at the minimum in potential energy of each type. Other, higher energy tautomers exist in quite small amounts at room temperature. The energies of these, however, are low enough so that they may contribute to thermal properties. We[6] have recently measured the heat capacity of gaseous cyclohexane and methylcyclohexane and these data are compared with calculated values in the present paper.

In the course of our study very interesting effects of geometrical tautomerism in disubstituted cyclohexanes became apparent. These have been mentioned briefly in a communication to the editor,[6a] but further details are given in this paper.

These compounds are important as constituents of petroleum hence their properties should have considerable practical interest.

We shall first discuss the work on cyclohexane in some detail and then briefly describe the less detailed calculations on its derivatives.

Cyclohexane

Equilibrium Configuration.—Hassel and collaborators[7] have made an extensive study of cyclohexane by the electron diffraction method. They find that substantially all of it is in the more symmetrical chair (D_{3d}) form with a carbon–carbon distance of 1.54 Å. and approximately tetrahedral bond angles. They do not exclude a small percentage of the less symmetrical, boat form. If the staggered position is the potential minimum for the rotation about single bonds, then the chair form would be expected to have a lower energy since it maintains the staggered position throughout while the boat form twists two C–C bonds into an opposed configuration.[8]

Spectra and Vibration Frequencies.—Rasmussen[9] has very adequately summarized his own and previous spectroscopic work on cyclohexane and has shown that all lines can be explained on the chair (D_{3d}) model. This confirms the conclusion drawn from electron diffraction results. Since Rasmussen's work, the infrared spectrum has been investigated[10] further in the range 15–25μ. This later work shows that the frequency reported by Kettering and Sleator[11] at 673 cm.$^{-1}$ is spurious and that instead a band exists at 522 cm.$^{-1}$. Another weaker band at 459 cm.$^{-1}$ is also suggested.

A normal coördinate analysis has been carried out for the series of molecules cyclopropane, cyclobutane, cyclopentane and cyclohexane by Dr. C. S. Lu and certain of the present authors which will be published separately.[12] This analysis,

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