[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

The Thermodynamic Properties of the Three Monomethylcyclopentenes and Nine Dimethylcyclopentenes[1]

BY HENRY J. HROSTOWSKI AND GEORGE C. PIMENTEL

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The thermodynamic functions, C_p^0, $(H^0 - H_0^0)/T$, $-(F^0 - H_0^0)/T$, and S^0, have been calculated for the three monomethyl- and nine of the dimethylcyclopentenes in the ideal gaseous state from 298.16 to 1500°K. by the method of methyl increments.

At present the available spectral data for the methylcyclopentenes are not sufficiently complete to warrant detailed vibrational assignments for these molecules. Furthermore the complexity of most of these is such that spectral data alone may not result in satisfactory assignments. In the absence of calorimetric data the thermodynamic functions were obtained from those of cyclopentene[2] using the methyl increment from methylcyclohexane.[3]

For the monomethylcyclopentenes the method of calculation is illustrated by the equations

$$F(n\text{-methylcyclopentene}) = F'(\text{cyclopentene}) + F(\text{methyl}) + F_n(\text{ring puckering}) \quad (1)$$

$$F'(\text{cyclopentene}) = F(\text{cyclopentene}) - F_0(\text{ring puckering}) + (R \ln 2) \quad (2)$$

$$F(\text{methyl}) = F(\text{methylcyclohexane}) - F(\text{steric factor}) - F(\text{cyclohexane}) - (R \ln 6) \quad (3)$$

where F is a thermodynamic function of the indicated substance or the contribution of the indicated motion, and n is the position of substitution of the methyl group using the nomenclature of Fig. 1. The symmetry number corrections (parenthetical quantities) apply only to the entropy and free energy function. For 3-methylcyclopentene an additional $R \ln 2$ term is added to these functions to account for the mixing of identical d and l optical isomers. F(steric factor) is the contribution of the polar–equatorial tautomerism of methylcyclohexane. The potential barrier restricting rotation of the methyl group in the 3- and 4-methyl derivatives is assumed to be 3600 cal./mole as in methylcyclohexane. For the 1-methyl compound a restricting potential of 2350 cal./mole was taken from the analogy to isobutene[4] and a suitable correction[5] was applied to F(methyl).

The term F(ring puckering) is the contribution of an unusual ring puckering motion, the potential energy of which has been described for cyclopentene[2] in terms of the total strain energy as a function of the displacement, z, of atom 4 from the plane of the other atoms. It was assumed for simplicity of calculation that the effect of methyl substitution was alteration of the barriers opposing bond torsion and that the motion retained its plane of symmetry perpendicular to the molecule. The barriers used were assigned by analogy to simpler molecules and are listed in cal./mole in Table I. Potential curves for the monomethylcyclopentenes were calculated as for cyclopentene by minimizing the energy of bond twisting and bending within the geometrical constraints with constant bond lengths for each z value. These and the approximations thereof for the purpose of statistical mechanical calculation are shown in Fig. 2. The approximate curves have the form

$$V_n(z) = \begin{Bmatrix} 0 \\ b_n \quad (|z| - a_n)^2 \end{Bmatrix} \begin{matrix} |z| < a_n \\ |z| > a_n \end{matrix} \quad (4)$$

with coefficients a_n and b_n given in Table II.

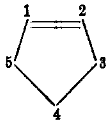

Fig. 1.—Nomenclature diagram of cyclopentene.

TABLE I

BOND TORSION BARRIERS IN THE MONOMETHYLCYCLOPENTENES IN CAL./MOLE

Compound	$V_{15}{}^a$	V_{23}	$V'_{\text{av.}}$	V_{34}	V_{45}	$V''_{\text{av.}}$
Cyclopentene[1]	1950[b]	1950	1950	2800[c]	2800	2800
1-Methylcyclopentene	2350[d]	1950	2150	2800	2800	2800
3-Methylcyclopentene	1950	2400[e]	2175	3400[f]	2800	3100
4-Methylcyclopentene	1950	1950	1950	3400	3400	3400

[a] By analogy to [b] propylene, [c] ethane, [d] isobutene, [e] 1-butene,[4] [f] propane.[6]

TABLE II

PARAMETERS FOR THE APPROXIMATE POTENTIAL CURVES OF THE MONOMETHYLCYCLOPENTENES

Compound	a_n, Å.	b_n, kcal./mole/Å.^{2}
1-Methylcyclopentene	0.270	15.75
3-Methylcyclopentene	.342	23.50
4-Methylcyclopentene	.410	30.50

Contributions of these motions to the thermodynamic functions were calculated from the approximate potential curves using the relations given in reference 2. The effective mass which enters in these calculations was taken as 20.6 atomic mass units for the 1- and 3-methyl derivatives. This value (determined for cyclopentene[2]) was used since the form of the motion indicated little variation in the effective mass for methyl substitution in these positions. For 4-methylcyclopentene a much larger effective mass is required due to the long moment arm involved. An effective mass of 55 was considered to be a reasonable estimate of the influence of a methyl group in the 4-position for this motion. It should be noted that

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(1) This research was supported by the American Petroleum Institute Research Project 44.

(2) C. W. Beckett, N. K. Freeman and K. S. Pitzer, THIS JOURNAL, **70**, 4227 (1948).

(3) C. W. Beckett, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2488 (1947).

(4) J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **37**, 163 (1946).

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

(6) K. S. Pitzer, *ibid.*, **12**, 310 (1944).

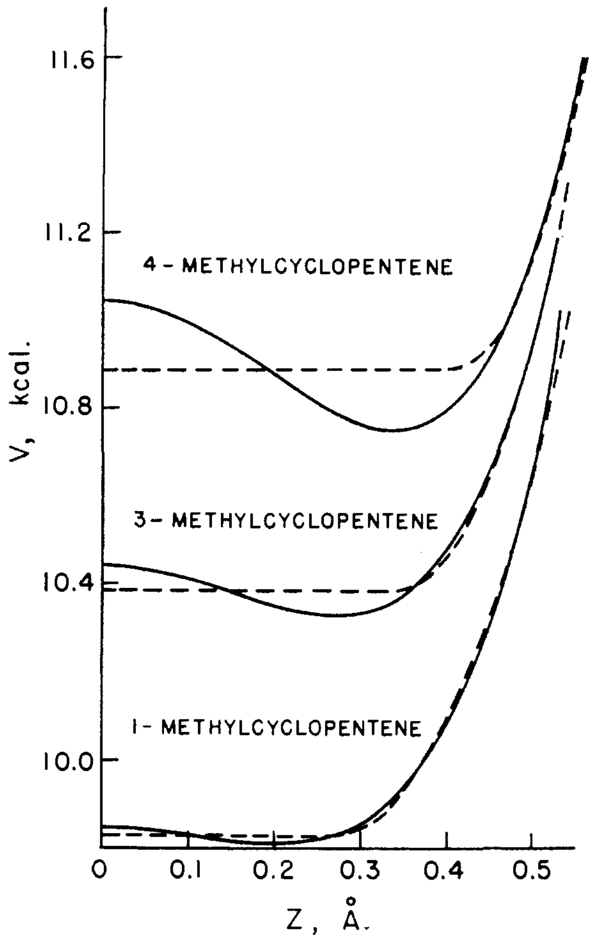

Fig. 2.

for constant mass the wide variation in the approximate potential curves yields a maximum difference of only 0.2 cal./deg. mole in the thermodynamic functions of the different compounds. However, a variation of 15 units in the mass leads to a difference of about 0.3 cal./deg. mole in the entropy and the free energy function.

The calculated thermodynamic properties of the monomethylcyclopentenes in the ideal gaseous state are given in Tables III–VI. Use of the cyclohexane methyl increment accounts for the contribution of a methyl group to these in all respects but the effect on the ring puckering motion. The error involved in this and subsequent approximations can be determined only when experimental thermal data are available.

TABLE III

HEAT CAPACITIES OF THE MONOMETHYLCYCLOPENTENES IN THE IDEAL GASEOUS STATE

Temp., °K.	C_p^0, cal./deg. mole		
	1-Methyl	3-Methyl	4-Methyl
298.16	24.1	23.9	23.9
300	24.3	24.1	24.1
400	32.5	32.6	32.6
500	40.2	40.5	40.4
600	46.8	47.1	47.0
700	52.3	52.6	52.5
800	57.0	57.2	57.1
900	60.9	61.1	61.1
1000	64.3	64.5	64.4
1100	67.2	67.4	67.3
1200	69.7	69.9	69.8
1300	71.9	72.0	71.9
1400	73.8	73.9	73.8
1500	75.4	75.5	75.4

TABLE IV

HEAT CONTENT FUNCTIONS OF THE MONOMETHYLCYCLOPENTENES IN THE IDEAL GASEOUS STATE

Temp., °K.	$(H^0 - H_0^0)/T$, cal./deg. mole		
	1-Methyl	3-Methyl	4-Methyl
298.16	14.9	14.6	14.5
300	15.0	14.7	14.6
400	18.3	18.1	18.0
500	22.0	21.8	21.7
600	25.6	25.5	25.4
700	29.0	29.0	28.9
800	32.2	32.2	32.1
900	35.2	35.2	35.1
1000	37.9	38.0	37.9
1100	40.5	40.5	40.5
1200	42.8	42.8	42.8
1300	44.9	45.0	44.9
1400	46.9	47.0	46.9
1500	48.8	48.8	48.7

TABLE V

FREE ENERGY FUNCTIONS OF THE MONOMETHYLCYCLOPENTENES IN THE IDEAL GASEOUS STATE

Temp., °K.	$(F^0 - H_0^0)/T$, cal./deg. mole		
	1-Methyl	3-Methyl	4-Methyl
298.16	63.1	64.4	64.1
300	63.2	64.5	64.2
400	67.9	69.2	68.8
500	72.4	73.6	73.2
600	76.7	77.9	77.5
700	80.9	82.1	81.7
800	85.0	86.2	85.8
900	89.0	90.2	89.8
1000	92.8	94.0	93.6
1100	96.6	97.7	97.3
1200	100.2	101.4	100.9
1300	103.7	104.9	104.4
1400	107.1	108.3	107.8
1500	110.4	111.6	111.1

TABLE VI

ENTROPIES OF THE MONOMETHYLCYCLOPENTENES IN THE IDEAL GASEOUS STATE

Temp., °K.	S^0, cal./deg. mole		
	1-Methyl	3-Methyl	4-Methyl
298.16	78.0	79.0	78.6
300	78.2	79.2	78.8
400	86.2	87.3	86.8
500	94.4	95.4	94.9
600	102.3	103.4	102.9
700	109.9	111.1	110.6
800	117.2	118.4	117.9
900	124.2	125.4	124.9
1000	130.8	132.0	131.5
1100	137.1	138.2	137.8
1200	143.0	144.2	143.7
1300	148.6	149.9	149.3
1400	154.0	155.3	154.7
1500	159.2	160.4	159.8

Substitution of the methyl group on carbon 1 slightly flattens the bottom of the cyclopentene potential curve for ring puckering and has little effect on this motion. The potentials for 3- and especially 4-methylcyclopentene as calculated above show markedly the effect of methyl substitution. As a check of the validity of the statistical approximations each curve was expressed in the form

$$V = ax^4 - bx^2 - c \qquad (5)$$

and the disposition of the energy levels near the minima was investigated by the variation method with variation functions composed of harmonic oscillator wave functions. For the 4-methyl compound the six lowest calculated levels and the slope of the potential curve for large z were used to determine an approximate partition function from which thermodynamic functions were estimated at several temperatures. These results agreed within a few tenths of a unit with those calculated from the statistical curve.

When the methyl group is attached to carbon atoms 3 or 4, which are displaced most in the ring puckering, it is unlikely that this motion retains the simple form of equation 4 with both the carbon atom and methyl group moving as a rigid unit. In these cases it is more likely that the methyl group would effect some counter displacement of the cyclopentene ring. An expected result of this modification would be the smoothing out of the minima in the potential curve. Calculations of the detailed nature of such complex motions are unwarranted in view of the approximations already employed and the absence of experimental data.

In the light of the above considerations the calculated thermodynamic functions of 1-methylcyclopentene are most accurate, those of 4-methylcyclopentene least accurate. The error involved in the calculations presented in Tables III–VI should in no case be greater than 1 cal./deg. mole.

For the 1,n-dimethylcyclopentenes where n = 2, 3 or 4 the thermodynamic properties were calculated by the equation

$$F(1,n\text{-dimethylcyclopentene}) = F(1\text{-methylcyclopentene}) + F(n\text{-methylcyclopentene}) - F(\text{cyclopentene}) + (R \ln 2) \qquad (6)$$

A similar relationship was used for *cis*- and *trans*-3,5-dimethylcyclopentene. In the remaining cases the thermodynamic functions were approximated by adding appropriate methyl increments to F'(cyclopentene) and using the ring puckering contribution derived from the most nearly applicable potential curve of the monomethylcyclopentenes. The barrier potentials together with F_n(ring) designating the statistical curves used, are listed in Table VII. Terms accounting for the symmetry number of 1,2- and *trans*-3,5-dimethylcyclopentene and the identical *d*- and *l*-forms of (1,3), (1,4), (1,5), (*cis*-3,4) and (*trans*-3,5)-dimethylcyclopentene were included in the entropy and free energy functions. Cancellation of these factors makes the calculated functions for the *cis*-3,5 and *trans*-3,5 compounds identical. The barriers to internal rotation of the methyl group were taken to be the same as for the monomethyl derivatives except for *cis*-3,4- and 3,3-dimethylcyclopentene. Here 4300 and 6600 cal./mole, respectively, were used in analogy to the corresponding dimethylcyclohexanes.[8] In the case of the 1,2-derivative the restricting barrier may be somewhat lower than 2350 cal./mole[7] resulting in an entropy increase of perhaps 0.5 cal./deg. mole. However in the absence of experimental data there is no *ad hoc* reason for altering this barrier.

TABLE VII

BOND TORSION BARRIERS IN SOME DIMETHYLCYCLOPENTENES, CAL./MOLE

Dimethylcyclopentene	V_{15}[a]	V_{23}	V' av.	V_{34}	V_{45}	V''av.	Fn ring
1,5-	2400[b]	1950	2175	2800	3400	3100	F_3
3,3-	1950	2400[c]	2175	3600[d]	2800	3200	F_3
cis-3,4-	1950	2400	2175	4400[9]	3400	3900	F_4
trans-3,4-	1950	2400	2175	3600	3400	3500	F_4

[a] By analogy to [b] 2-methyl-2-pentene,[7] [c] 3-methyl-1-butene,[7] [d] isobutane.[8]

TABLE VIII

HEAT CAPACITIES OF NINE DIMETHYLCYCLOPENTENES IN THE IDEAL GASEOUS STATE

Temp, °K.	C_p^0, cal./deg. mole 1,2	1,3	1,4	1,5	*cis*-3,4	*trans*-3,4	*cis*- or *trans*-3,5	3,3
298.16	30.3	30.1	30.0	30.1	29.8	30.0	30.0	29.4
300	30.5	30.3	30.3	30.3	30.0	30.2	30.2	29.6
400	40.0	40.1	40.0	40.1	40.2	40.2	40.2	39.8
500	48.9	49.1	49.0	49.1	49.5	49.4	49.4	49.4
600	56.4	56.7	56.6	56.6	57.2	57.0	57.0	57.4
700	62.7	63.0	62.9	63.0	63.6	63.3	63.3	64.1
800	68.1	68.4	68.3	68.4	69.0	68.6	68.6	69.7
900	72.7	73.0	72.9	72.9	73.5	73.2	73.2	74.3
1000	76.7	76.9	76.8	76.8	77.4	77.1	77.1	78.5
1100	80.1	80.3	80.2	80.2	80.7	80.4	80.4	81.6
1200	83.1	83.2	83.1	83.2	83.6	83.3	83.3	84.3
1300	85.6	85.7	85.6	85.7	86.1	85.8	85.8	86.9
1400	87.9	87.9	87.8	87.9	88.2	88.0	88.0	89.0
1500	89.7	89.8	89.7	89.8	90.1	89.8	89.9	90.9

TABLE IX

HEAT CONTENT FUNCTIONS OF NINE DIMETHYLCYCLOPENTENES IN THE IDEAL GASEOUS STATE

Temp., °K.	$(H^0 - H_0^0)/T$, cal./deg. mole 1,2	1,3	1,4	1,5	*cis*-3,4	*trans*-3,4	*cis*- or *trans*-3,5	3,3
298.16	18.2	17.9	17.8	17.9	17.4	17.6	17.6	17.0
300	18.3	18.0	18.0	18.0	17.5	17.7	17.7	17.1
400	22.5	22.3	22.2	22.3	21.9	22.1	22.1	21.5
500	27.0	26.8	26.7	26.8	26.5	26.7	26.7	26.2
600	31.3	31.2	31.1	31.1	31.0	31.1	31.1	30.7
700	35.3	35.3	35.2	35.2	35.2	35.2	35.2	35.0
800	39.1	39.1	39.0	39.1	39.1	39.0	39.0	39.0
900	42.6	42.6	42.5	42.6	42.7	42.6	42.6	42.7
1000	45.8	45.8	45.7	45.8	46.0	45.9	45.9	46.0
1100	48.8	48.8	48.7	48.8	49.0	48.9	48.9	49.1
1200	51.5	51.6	51.5	51.5	51.7	51.6	51.6	52.0
1300	54.0	54.1	54.0	54.0	54.2	54.1	54.1	54.6
1400	56.3	56.4	56.3	56.3	56.5	56.4	56.4	57.0
1500	58.4	58.5	58.4	58.5	58.7	58.6	58.6	59.1

The resulting thermodynamic functions of the dimethylcyclopentenes in the ideal gaseous state are given in Tables VIII–XI. The uncertainty is estimated to be about double that for the monomethyl compounds, less than 2 cal./deg. mole.

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(7) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

(8) K. S. Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39**, 435 (1946).

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

TABLE X

FREE ENERGY FUNCTIONS OF NINE DIMETHYLCYCLOPENTENES IN THE IDEAL GASEOUS STATE

Temp., °K.	$(F^0 - H_0^0)/T$, cal./deg. mole							
	1,2	1,3	1,4	1,5	*cis*-3,4	*trans*-3,4	*cis*- or *trans*-3,5	3,3
298.16	65.8	68.5	69.5	68.5	69.0	69.2	67.0	66.1
300	65.9	68.6	69.7	68.6	69.1	69.4	67.1	66.2
400	71.8	74.3	75.4	74.3	74.7	75.0	72.8	71.7
500	77.3	79.8	80.8	79.8	80.1	80.4	78.2	77.0
600	82.6	85.1	86.1	85.1	85.4	85.7	83.5	82.2
700	87.7	90.2	91.2	90.2	90.5	90.8	88.6	87.3
800	92.7	95.2	96.2	95.2	95.5	95.8	93.6	92.3
900	97.5	100.0	101.0	100.0	100.3	100.6	98.4	97.1
1000	102.1	104.6	105.6	104.6	104.9	105.2	103.0	101.7
1100	106.6	109.1	110.1	109.1	109.4	109.7	107.5	106.2
1200	110.9	113.5	114.4	113.4	113.8	114.1	111.9	110.6
1300	115.1	117.7	118.6	117.6	118.0	118.3	116.1	114.9
1400	119.2	121.8	122.7	121.7	122.1	122.4	120.2	119.0
1500	123.2	125.8	126.7	125.7	126.1	126.4	124.2	123.0

TABLE XI

ENTROPIES OF NINE DIMETHYLCYCLOPENTENES IN THE IDEAL GASEOUS STATE

Temp., °K.	S^0, cal./deg. mole							
	1,2	1,3	1,4	1,5	*cis*-3,4	*trans*-3,4	*cis*- or *trans*-3,5	3,3
298.16	84.0	86.4	87.4	86.4	86.4	86.8	84.6	83.2
300	84.3	86.6	87.6	86.6	86.6	87.1	84.8	83.4
400	94.3	96.7	97.6	96.6	96.6	97.1	94.9	93.3
500	104.2	106.6	107.6	106.6	106.6	107.1	104.8	103.2
600	113.8	116.2	117.2	116.2	116.3	116.7	114.5	112.9
700	123.0	125.5	126.4	125.4	125.7	126.0	123.8	122.3
800	131.8	134.3	135.2	134.2	134.6	134.9	132.7	131.3
900	140.1	142.6	143.5	142.5	143.0	143.2	141.0	139.7
1000	147.9	150.4	151.3	150.4	150.9	151.1	148.9	147.7
1100	155.3	157.9	158.8	157.9	158.4	158.6	156.4	155.3
1200	162.4	165.0	165.9	165.0	165.5	165.7	163.5	162.5
1300	169.1	171.7	172.6	171.7	172.2	172.4	170.3	169.4
1400	175.5	178.2	179.0	178.1	178.6	178.8	176.7	175.9
1500	181.6	184.3	185.1	184.2	184.8	185.0	182.8	182.1

Since for 4,4-dimethylcyclopentene there is great uncertainty in the form of the ring puckering motion and the estimation of an appropriate reduced mass, the thermodynamic functions were not calculated for this compound.

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