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Thermodynamics of Cyclopentane, Methylcyclopentane and 1,*cis*-3-Dimethylcyclopentane: Verification of the Concept of Pseudorotation

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Cyclopentane, methylcyclopentane and 1,*cis*-3-dimethylcyclopentane were studied by vapor-flow calorimetry to obtain heat-of-vaporization, vapor-heat-capacity and gas-imperfection data. The accurate calorimetric and spectroscopic information now available for cyclopentane was used to demonstrate that one of the degrees of freedom of this puckered molecule is a "pseudorotation," as originally suggested by Kilpatrick, Pitzer and Spitzer. The chemical thermodynamic properties of cyclopentane, at selected temperatures from 0–1500°K., were calculated. Thermodynamic properties previously estimated for the methyl derivatives by approximate methods are in good agreement with the new experimental data. This finding shows that the incremental methods of calculating thermodynamic functions of related substances, developed in the last two decades, may be used with a high degree of confidence.

Cyclopentane has long been of interest to chemists because of the question of planarity or non-planarity of the molecule and to petroleum refiners because of the importance of cyclopentane and its derivatives in petroleum technology. For these reasons, the spectroscopic, thermodynamic and chemical properties and the molecular structure of cyclopentane have been the subject of many investigations. Kilpatrick, Pitzer and Spitzer,[1] Miller and Inskeep,[2] and Curnutte and Shaffer[3] have summarized most of the evidence that shows the cyclopentane ring to be non-planar. Kilpatrick, *et al.*,[1] introduced the concept of pseudorotation to account for the spectroscopic and thermodynamic properties of cyclopentane. They considered the ring puckering motions to be: "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." Other investigators[2,3] concluded later, on the basis of spectroscopic studies, that it is unnecessary to invoke pseudorotation to explain the various properties of cyclopentane. However, new thermal data obtained in this Laboratory provide conclusive evidence of the validity of the pseudorotation concept as originally proposed.[4]

This paper presents new values of the heat of vaporization and vapor heat capacity of cyclopentane, which were the basis for the conclusion reported in ref. 4, and detailed calculations of the thermodynamic properties. Also reported are experimental values of heat of vaporization and vapor heat capacity for methylcyclopentane and 1,*cis*-3-dimethylcyclopentane. (1,*cis*-3-Dimethylcyclopentane is the lower boiling (90.77°) isomer of 1,3-dimethylcyclopentane. This isomer was incorrectly labeled 1,*trans*-3-dimethylcyclopentane in literature before 1955.[5]) Details of the experiments and results are given in the Experimental section. For use in the discussion that follows, results needed in the calculation of thermodynamic properties from calorimetric, spectroscopic and molecular structure information are summarized in Table I.

TABLE I

OBSERVED AND CALCULATED MOLAL THERMODYNAMIC PROPERTIES IN THE IDEAL GASEOUS STATE

Entropy, S°, cal. deg.$^{-1}$			Heat capacity, C_p°, cal. deg.$^{-1}$		
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.	Calcd.
		Cyclopentane			
298.16	70.00	70.00	329.05	22.46	22.44
310.16	70.80	70.80	395.05	27.99	27.98
322.41	71.61	71.63	463.10	33.34	33.36
		Methylcyclopentane			
304.09	81.76	81.78[a]	333.20	29.70	29.70[a]
			362.55	32.55	32.54
			402.35	36.36	36.33
			436.25	39.49	39.44
			471.05	42.58	42.51
		1,*cis*-3-Dimethylcyclopentane			
322.62	90.19	90.33[a]	352.20	38.65	38.36[a]
			375.20	41.16	40.95
			415.20	45.55	45.40
			455.20	49.66	49.60
			500.20	54.04	54.05

[a] "Calculated" values for methylcyclopentane and 1,*cis*-3-dimethylcyclopentane obtained by interpolation in tables given in ref. 11 and 12.

Thermodynamic Properties and Pseudorotation

Vibrational Assignment.—Miller and Inskeep[2] and Curnutte and Shaffer[3] have reported detailed vibrational assignments for cyclopentane based on extensive spectroscopic information. In both of these assignments, the ring-puckering motion was treated as two genuine vibrational degrees of freedom. The assignment of Curnutte and Shaffer yields calculated values of heat capacity, C_p°, nearly 8% higher than the observed values in Table I. Even if the pseudorotation treatment of Kilpatrick, *et al.*,[1] is used with this assignment, the calculated values of C_p° are nearly 5% higher than observed. Because the accuracy of the experimental values is within 0.2%, the assignment of Curnutte and Shaffer evidently is incorrect. The results of these authors illustrate the unfortunate dependence on *input* data of normal coördinate analysis of vibrational degrees of freedom, which was the basis of their assignment. To fit the experimental entropy values and use a *degenerate* ring-puckering frequency, they had to choose other frequencies that, on the average, were too low. Also, Curnutte and Shaffer's use of D_{5h} symmetry in their analysis

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[1] J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2483 (1947).

[2] F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, **18**, 1519 (1950).

[3] B. Curnutte and W. H. Shaffer, *J. Mol. Spectra*, **1**, 239 (1957).

[4] J. P. McCullough, *J. Chem. Phys.*, **29**, 966 (1958).

[5] F. D. Rossini and Kun Li, *Science*, **122**, 513 (1955).

caused them to treat pairs of frequencies as degenerate that actually are non-degenerate. Thus, choice of wrong initial frequencies and use of an over-simplified model resulted in an incorrect assignment in spite of the excellent agreement they obtained between calculated and *assigned* frequencies.

The assignment of Miller and Inskeep[2] also is inconsistent with the experimental values of C_p°.[4] However, if the ring puckering is treated as suggested by Kilpatrick, *et al.*,[1] use of the assignment of Miller and Inskeep for all other vibrations yields excellent agreement between calculated and experimental values of both entropy, S°, and heat capacity, C_p°. Therefore, the following set of frequencies, taken from ref. 2, was used, with accidental multiplicities indicated by numbers in parentheses: 283, 545, 617, 769, 827, 886, 896, 949, 964(2), 1030(3), 1104(2), 1207(2), 1258(2), 1283(2), 1306, 1316, 1460(5) and 2920(10) cm.$^{-1}$. (Some of the multiple frequencies are averages of close-lying frequencies assigned individually in ref. 2.)

Pseudorotation in Cyclopentane and Related Molecules.—Kilpatrick, *et al.*,[1] gave a detailed treatment of the quantum and statistical mechanics of pseudorotation. Their separation of the Schroedinger equation involving the pseudorotation coördinates was admittedly inexact, but an exact separation is possible. Nevertheless, solution of the separated wave equation, with the usual approximations of an harmonic potential function and small amplitudes of vibration, leads to exactly the same result Kilpatrick, *et al.*, obtained.

If all configurations of the puckered cyclopentane molecule are energetically equivalent, that is, if pseudorotation is unhindered, the contributions of pseudorotation to C_p° and S° are $^1/_2R$ and $R[^1/_2 + {}^1/_2 \ln(8\pi^3 I_\mathrm{r} kT/h^2\sigma^2)]$, where I_r is the "reduced moment" of inertia for pseudorotation and $\sigma = 10$ is the symmetry number.[6] The value of I_r selected to fit the experimental entropy values is 10.59×10^{-40} g. cm.^{2}. After application of small anharmonicity corrections discussed in the next section, the calculated values of S° and C_p° given in Table I were obtained. The calculated and experimental results agree within 0.1% in the range of temperature of the experiments.

Such excellent agreement with the accurate calorimetric data for cyclopentane cannot be obtained unless the pseudorotation treatment of Kilpatrick, *et al.*, is invoked. Thus, the experimental and theoretical justification for this unusual concept is conclusive. The following paper on pyrrolidine[7] and an earlier paper on thiacyclopentane[8] provide additional evidence for the validity of the pseudorotation treatment. However, some puckered configurations of the heterocyclic compounds apparently are energetically favored, for it was necessary to assume that pseudorotation is hindered by barriers of 300 cal. mole^{-1} in pyrrolidine and 2800 cal. mole^{-1} in thiacyclopentane. These results are not surprising, and further information on barriers to pseudorotation may be obtained in a study of tetrahydrofuran now in progress in this Laboratory.

Thermodynamic Properties of Cyclopentane.—The molecular parameters discussed in the foregoing paragraphs were used in calculating the thermodynamic functions of cyclopentane. Values of the principal moments of inertia, $I_\mathrm{A} = I_\mathrm{B} = 13.028 \times 10^{-39}$ and $I_\mathrm{C} = 23.405 \times 10^{-39}$ g. cm.^{2}, were taken from ref. 1. The parameters, $\nu = 300$ cm.$^{-1}$ and $Z = 0.066$ cal. deg.$^{-1}$ mole^{-1}, of an empirical anharmonicity function[9] were evaluated from the vapor heat capacity data. This function is barely significant at 300°K. and increases to 0.46 and 0.39 cal. deg.$^{-1}$ mole^{-1} in C_p° and S° at 1500°K. The results of these calculations are given in columns 2–6, Table II.[10]

The values of thermodynamic functions in Table II, of the heat of formation of liquid cyclopentane, $\Delta Hf^\circ_{298.16} = -25.31$ kcal. mole^{-1}, reported by Prosen, *et al.*,[11] of the standard heat of vaporization, $\Delta Hv^\circ_{298.16} = 6.83$ kcal. mole^{-1}, derived from the results of this investigation, and of the thermodynamic functions of C(c, graphite)[12] and H_2(g)[12] were used to compute the values of standard heat, free energy and common logarithm of the equilibrium constant of formation given in columns 7–9, Table II.

The values of thermodynamic properties in Table II differ only slightly from those reported earlier by Kilpatrick, *et al.* However, because the calorimetric and spectroscopic data on which the results in Table II are based are more accurate than those available to Kilpatrick, *et al.*, they should be more reliable than the earlier results.

Methylcyclopentane and 1,*cis*-3-Dimethylcyclopentane.—Experimental values of C_p° for methylcyclopentane and 1,*cis*-3-dimethylcyclopentane are compared in Table I with calculated values reported by Pitzer, Rossini and co-workers.[13,14] These authors used incremental methods of calculation based on the thermodynamic properties of cyclopentane, cyclohexane and the methylcyclohexanes, with the barrier hindering pseudorotation in the substituted cyclopentanes taken to be 750 cal. mole^{-1}. For methylcyclopentane, the agreement between calculated and experimental values of C_p° is within the 0.2% accuracy uncertainty of the experimental data. The calculated results for 1,*cis*-3-dimethylcyclopentane are less accurate. Nevertheless, the agreement for both compounds is good enough that revision of the results of Pitzer, Rossini and coworkers[13,14] was not deemed necessary at this time.

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[6] According to communications from K. S. Pitzer and J. E. Kilpatrick, the use of a symmetry number of five in ref. 1 was incorrect.

[7] J. P. McCullough, D. R. Douslin, W. N. Hubbard, S. S. Todd, J. F. Messerly, I. A. Hossenlopp, F. R. Frow, J. P. Dawson and G. Waddington, This Journal, **81**, 5884 (1959).

[8] W. N. Hubbard, H. L. Finke, D. W. Scott, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington and Guy Waddington, *ibid.*, **74**, 6025 (1952).

[9] J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and G. Waddington, *ibid.*, **76**, 2661 (1954).

[10] Harmonic oscillator contributions and anharmonicity corrections were calculated in the Computation Laboratory, Bureau of Mines, Pittsburgh, Pa.

[11] E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 51 (1946).

[12] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *ibid.*, **34**, 143 (1945).

[13] J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer and F. D. Rossini, *ibid.*, **39**, 523 (1947).

[14] M. B. Epstein, G. M. Barrow, K. S. Pitzer and F. D. Rossini, *ibid.*, **43**, 245 (1949).

TABLE II

THE MOLAL THERMODYNAMIC PROPERTIES OF CYCLOPENTANE[a]

T, °K.	$(F° - H°_0)/T$, cal. deg.$^{-1}$	$(H° - H°_0)/T$, cal. deg.$^{-1}$	$H° - H°_0$, kcal.	$S°$, cal. deg.$^{-1}$	$C_p°$, cal. deg.$^{-1}$	$\Delta Hf°$,[b] kcal.	$\Delta Ff°$,[b] kcal.	log Kf[b]
0	0	0	0	0	0	−10.70	−10.70	Infinite
273.16	−56.92	11.43	3.122	68.35	17.84	−17.86	+6.91	− 5.53
298.16	−57.94	12.06	3.596	70.00	19.84	−18.48	9.21	− 6.75
300.00	−58.02	12.10	3.630	70.12	19.99	−18.53	9.37	− 6.83
400	−61.89	15.13	6.052	77.02	28.38	−20.82	19.04	−10.40
500	−65.64	18.56	9.280	84.20	36.07	−22.67	29.22	−12.77
600	−69.33	22.04	13.224	91.37	42.57	−24.11	39.74	−14.48
700	−72.99	25.37	17.76	98.36	48.01	−25.21	50.47	−15.76
800	−76.57	28.50	22.80	105.07	52.60	−25.99	61.35	−16.76
900	−80.10	31.40	28.26	111.50	56.50	−26.53	72.29	−17.55
1000	−83.55	34.08	34.08	117.63	59.84	−26.82	83.30	−18.21
1100	−86.92	36.55	40.20	123.47	62.70	−26.94	94.30	−18.74
1200	−90.20	38.84	46.61	129.04	65.17	−26.88	105.31	−19.18
1300	−93.39	40.95	53.24	134.34	67.30	−26.72	116.33	−19.56
1400	−96.50	42.90	60.06	139.40	69.14	−26.49	127.31	−19.87
1500	−99.52	44.70	67.05	144.22	70.74	−26.19	138.30	−20.15

[a] To retain internal consistency, some values are given to one more decimal place than is justified by the absolute accuracy. [b] For the reaction 5C(c, graphite) + $5H_2(g) = C_5H_{10}(g)$.

The reliability of the approximate methods of calculation for these two compounds provides evidence of the accuracy of thermodynamic property values calculated for related compounds by similar methods.

NOTE ADDED IN PROOF.—In a recent article [THIS JOURNAL, 81, 3213 (1959)] Pitzer and Donath gave a detailed discussion of the conformations and strain energy of cyclopentane and its derivatives. Some of their conclusions should be compared with those presented herein and in the following paper on pyrrolidine.

Experimental

The vapor-flow calorimeter system used in measurements of the heat of vaporization and vapor heat capacity of cyclopentane, methylcyclopentane and 1,*cis*-3-dimethylcyclopentane was that described by Waddington, Todd and Huffman[15] with, in some of the experiments, the modifications and improvements made later.[16] The 1951 International Atomic Weights,[17] the 1951 values of fundamental physical constants[18] and the relations, 0°C. = 273.16°K. and 1 cal. = 4.1833 int. j., were used. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale.[19] All electrical and mass measurements were referred to standard devices calibrated at the National Bureau of Standards.

TABLE III

MOLAL HEAT OF VAPORIZATION AND SECOND VIRIAL COEFFICIENT

T, °K.	P, atm.	ΔHv, cal.	B, cc.	
			Obsd.	Calcd.[a]
		Cyclopentane		
298.16	0.4176	6818 ± 6[b]	−1066	−1064
310.16	0.6560	6677 ± 1	− 972	− 978
322.42	1.0000	6524 ± 2	− 907	− 904
		Methylcyclopentane		
304.09	0.2325	7487 ± 4	−1456	−1466
325.98	0.5354	7206 ± 5	−1263	−1255
344.97	1.0000	6949 ± 4	−1118	−1122
		1,*cis*-3-Dimethylcyclopentane		
322.62	0.2500	7846 ± 1	−1826	−1792
341.82	0.5000	7582 ± 1	−1590	−1570
363.93	1.0000	7265 ± 0	−1351	−1370

[a] Calculated by use of equations in Table V. [b] Indicated uncertainty interval is the maximum deviation from the mean of replicate determinations.

TABLE IV

MOLAL VAPOR HEAT CAPACITY IN CAL. DEG.$^{-1}$

Cyclopentane

T, °K.	329.05	395.05	463.10
C_p (0.9989 atm.)	23.032	28.215	33.457
C_p (0.4180 atm.)	22.688	28.080	33.385
$C_p°$ (obsd.)	22.458	27.986	33.335
$-TB''$ (obsd.)[a]	0.537	0.220	0.118
$-TB''$ (calcd.)[b]	0.537	0.226	0.113

Methylcyclopentane

T, °K.	333.20	362.55	402.35	436.25	471.05
C_p (1.0000 atm.)		33.128	36.705	39.728	42.730
C_p (0.5354 atm.)	30.188	32.847			
C_p (0.2325 atm.)	29.903	32.683	36.441	39.540	42.617
$C_p°$ (obsd.)	29.695	32.554	36.365	39.486	42.584
$-TB''$ (obsd.)[a]	0.875	0.533	0.322	0.232	0.141
$-TB''$ (calcd.)[b]	0.871	0.549	0.320	0.215	0.149

1,*cis*-3-Dimethylcyclopentane

T, °K.	352.20	375.20	415.20	455.20	500.20
C_p (1.0000 atm.)		41.955	45.977	49.974	54.255
C_p (0.5000 atm.)	39.095	41.518			
C_p (0.3232 atm.)				49.757	54.111
C_p (0.2500 atm.)	38.864	41.356	45.651		
$C_p°$ (obsd.)	38.646	41.164	45.548	49.659	54.045
$-TB''$ (obsd.)[a]	0.844	0.703	0.397	0.297	0.201
$-TB''$ (calcd.)[b]	0.877	0.663	0.431	0.297	0.206

[a] $-TB'' = -T(d^2B/dT^2)$; units are cal. deg.$^{-1}$ atm.$^{-1}$. [b] Calculated from equations for B, Table V.

The Materials.—The sample of cyclopentane was obtained through the courtesy of Dr. F. D. Rossini[20]; the purity was reported to be 99.96 mole %. The sample of methylcyclopentane was prepared by H. J. Coleman and B. H. Eccleston of this Station: A commercial sample was percolated through silica gel and distilled in an efficient fractionating column to yield a final sample with purity of 99.92 mole %. The sample of 1,*cis*-3-dimethylcyclopen-

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(15) G. Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947).

(16) J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and G. Waddington, *ibid.*, **76**, 4791 (1954).

(17) E. Wichers, *ibid.*, **74**, 2447 (1952).

(18) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

(19) H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

(20) The sample of cyclopentane was prepared by the American Petroleum Institute Research Project 6 at the Carnegie Institute of Technology from material supplied by Tidewater Oil Company.

TABLE V

EMPIRICAL EQUATIONS FOR HEAT OF VAPORIZATION, HEAT CAPACITY AND SECOND VIRIAL COEFFICIENT

	$\Delta Hv = a + bT + cT^2$, cal. mole^{-1}			$C_p° = a + bT + cT^2$, cal. deg.$^{-1}$ mole^{-1}			$B = b + c \exp(a/T)$, cc. mole^{-1}		
Compound	a	b	$-c \times 10^3$	$-a$	b	$-c \times 10^5$	b	$-c$	a
Cyclopentane	7556	6.439	2.990	10.158	0.11189	3.881	−192	59.59	800
Methylcyclopentane	9701	−2.100	1.704	8.096	.12743	4.211	−402	39.69	1000
1,*cis*-3-Dimethylcyclopentane	10679	−4.079	1.457	9.388	.15882	6.398	139	220.5	700

TABLE VI

MOLAL ENTROPY IN CAL. DEG.$^{-1}$

Compound	T, °K.	$S_{\text{satd.}}$[a]	$\Delta Hv/T$	S(ideal) − S(real)[b]	$R \ln P$[c]	$S°$(obsd.)
Cyclopentane	298.16	48.786	22.867	0.084	−1.735	70.00 ± 0.15
	310.16	50.000[d]	21.528	.114	−0.838	70.80 ± .15
	322.41	51.227[d]	20.234	.150	0	71.61 ± .15
Methylcyclopentane	304.09	59.974[d]	24.621	.066	−2.899	81.76 ± .20
1,*cis*-3-Dimethylcyclopentane	322.62	68.544[d]	24.320	.080	−2.755	90.19 ± .20

[a] Entropy in the saturated liquid state; from data given in ref. 27. [b] Calculated from equation of state $PV = RT(1 + B/V)$ and equations for B in Table V. [c] Calculated from data in ref. 25. [d] Extrapolated values.

tane[5] was obtained through the courtesy of Dr. K. W. Greenlee[21]; the purity was reported to be 98.5 mole %. The effect of this much impurity on the measured properties of the last compound probably was not significant because the impurities would be expected to be isomeric substances.

Heat of Vaporization.—Replicate determinations of the heat of vaporization of each hydrocarbon were made at each of three temperatures corresponding to vapor pressures between 1/4 and 1 atm. The results are listed in Table III. The estimated accuracy uncertainty of these data is 0.1%. Table V contains constants of empirical equations that represent the heat-of-vaporization data; these equations may be used for interpolation in the range of temperature of the experiments and for short extrapolation.

The value for the heat of vaporization of cyclopentane at 298.16°K. reported by Aston, Finke and Schumann[22] differs grossly from that listed in Table III. In a recent communication to the authors, Professor Aston stated that the value reported in ref. 22 was probably in error for unknown reasons. The value in Table III is in excellent agreement with that calculated by Kilpatrick, *et al.*[1]

The value of $\Delta Hv_{298.16}$ for methylcyclopentane calculated from the equation in Table V is in exact agreement with that reported by Osborne and Ginnings,[23] 375.78 int. j.g.$^{-1}$ (7560 cal. mole^{-1}).

Vapor Heat Capacity.—For each compound, experimental values of the vapor heat capacity as a function of temperature and pressure and derived values of the heat capacity in the ideal gaseous state, $C_p°$, are listed in Table IV. The estimated accuracy uncertainty of these heat capacity data is 0.2%. The results for $C_p°$ are represented accurately by the empirical equations whose constants are given in Table V.

The values of $C_p°$ for cyclopentane in Table IV agree with those reported by Spitzer and Pitzer[24] well within the 1% accuracy uncertainty claimed by these authors.

Effect of Gas Imperfection.—Values of the second virial coefficient, B, in the equation of state, $PV = RT(1 + B/V)$, were calculated from the heat of vaporization data, vapor pressure data[25] and the Clapeyron equation; the results are given in Table III. Values of $-T(\mathrm{d}^2B/\mathrm{d}T^2) = \lim_{P \to 0} (\partial C_p/\partial P)_T$ were derived from the heat capacity data and are included in Table IV. These effects of gas imperfection were correlated by the procedure described in an earlier publication from this Laboratory.[26] Constants for empirical representations of the second virial coefficient are given in Table V. Values of B and $-T(\mathrm{d}^2B/\mathrm{d}T^2)$ calculated from these equations are compared with "observed" values in Tables III and IV.

Entropy in the Ideal Gaseous State.—Values of entropy in the liquid state reported previously from this Laboratory,[27] vapor pressure data,[25] and the results reported herein were used in calculating values of entropy in the ideal gaseous state, as shown in Table VI.

Acknowledgments.—The authors gratefully acknowledge the assistance of Mrs. M. E. Gross and W. Roberts in some of the experiments reported.

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(21) The sample of 1,*cis*-3-dimethylcyclopentane was provided by the American Petroleum Institute Research Project 45 at the Ohio State University.

(22) J. G. Aston, H. L. Finke and S. C. Schumann, THIS JOURNAL, **65**, 341 (1943).

(23) N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947).

(24) R. Spitzer and K. S. Pitzer, THIS JOURNAL, **68**, 2537 (1946).

(25) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Substances," American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Table 6k.

(26) J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and G. Waddington, THIS JOURNAL, **58**, 142 (1954).

(27) (a) D. R. Douslin and H. M. Huffman, *ibid.*, **68**, 173 (1946); (b) M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, **75**, 2801 (1953).