[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF CALIFORNIA]

The Heat Capacity of Gaseous Cyclopentane, Cyclohexane and Methylcyclohexane

BY RALPH SPITZER[1] AND KENNETH S. PITZER

The cycloparaffins are of interest because their geometry restricts internal rotation about the carbon–carbon single bonds. Therefore, a study of the thermodynamics and molecular structure of these hydrocarbons should lead to some increased knowledge about the form and nature of the potential hindering rotation in hydrocarbons. Cyclopentane is of particular interest because it has been shown[2] that the classic planar model for this molecule is incorrect and the interaction between angle strain and restricted rotation leads to a puckered ring. In cyclohexane, the isomerism between chair and boat forms should lead to a contribution to the heat capacity of the gas from which some information about the restricting potential should be derived.

Although reliable measurements have previously been made on cyclohexane and methylcyclohexane[3] the temperature range used was too small to be useful in deciding questions of molecular structure. Our temperature range was from about 25° above the boiling point to 250°.

Experimental

Apparatus.—The apparatus used for measuring the heat capacities was essentially that described by Pitzer.[4]

One major change in design was the substitution of a floating heater for the fixed heater which had previously been used in the vaporization unit. The use of this heater led to much steadier boiling rates resulting in steadier temperatures and more reproducible results. The heater was a Chromel helix fastened to a thin-walled glass cylinder by glass rods. Very flexible leads made of four strands of 36 gage Formex coated copper wire were used.

Materials.—Two samples of cyclopentane were used, both originally from the Tidewater Associated Oil Company. One contained 1.3% neohexane (analyzed by mass spectrometer) for which correction was made. The second sample, which was received only after some measurements were completed, was very pure, having been finally fractionated at the National Bureau of Standards. The cyclohexane was prepared from Eastman technical cyclohexane by treating with fuming sulfuric acid for a week to remove benzene, washing, fractionally crystallizing three times and finally distilling from sodium in a 25-plate column. The National Bureau of Standards supplied a sample of methylcyclohexane whose purity they had determined by freezing point depression to be 99 mole per cent.

Corrections for Gas Imperfection.—In order to check the validity of the Berthelot correction for gas imperfection, the heat capacities of cyclopentane and cyclohexane were measured at reduced pressure.[5] Even at the lowest temperatures used, extrapolation to zero pressure gave results that were indistinguishable from the Berthelot corrections within experimental error; therefore, the Berthelot correction has been used in reducing the results to the ideal gas state. The critical temperatures and pressures used were: 520° K. and 44.2 atm. for cyclopentane, 554° K. and 40.4 atm. for cyclohexane and 572° K. and 34.6 atm. for methylcyclohexane.

Experimental Heat Capacities.—Table I presents the results of the measurements, the Berthelot corrections and the heat capacities of the ideal gases. The latter are presented to facilitate comparison with theory which we hope to publish later.

Figure 1 presents these results graphically. For the results of other investigators, see ref. (3). The curves drawn in Fig. 1 are empirical. The size of the symbols is equal to the experimental error of approximately 1%.

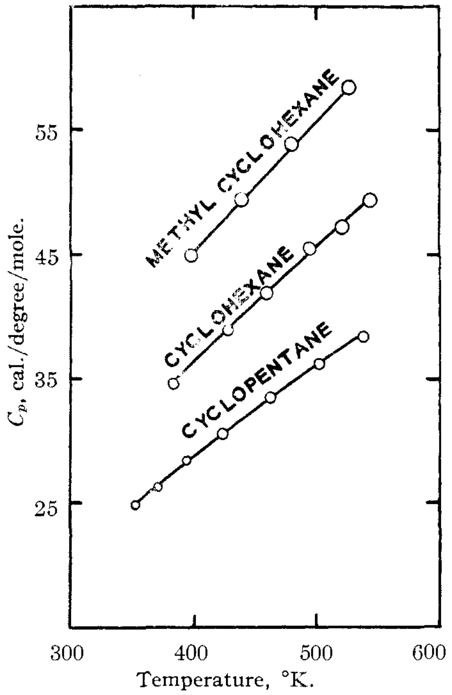

Fig. 1.—Experimental heat capacities at one atmosphere.

Heats of Vaporization.—The present vaporization unit was constructed too tall and was not completely immersed in the thermostat; the resulting heat leak led to heats of vaporization which varied with the rate of flow. The values obtained by extrapolating to infinite rate of flow, however, agree fairly well with the heats of vaporization measured with other apparatus. The best values obtained for the heats of vaporization at their boiling points of cyclopentane, cyclohexane and methylcyclohexane, respectively, are: 6570 ± 40, 7185 ± 30 and 7600 ± 50 calories Mathews[6] obtained 7205 and 7545 for the latter two.

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(2) Aston, Schumann, Fink and Doty, THIS JOURNAL, **63**, 2029 (1941); Pitzer, *Science*, **101**, 672 (1945).

(3) Montgomery and De Vries, THIS JOURNAL, **64**, 2375 (1942).

(4) Pitzer, *ibid.*, **63**, 2413 (1941).

(5) Pitzer and Gwinn, *ibid.*, **63**, 3313 (1941).

(6) Mathews, *ibid.*, **48**, 562 (1926).

TABLE I

EXPERIMENTAL HEAT CAPACITIES OF GASEOUS CYCLOPENTANE, CYCLOHEXANE AND METHYLCYCLOHEXANE

Calories per degree per mole

Substance	Press., atm.	T, °K.	C_p	$C_p - C_p°$	$C_p°$
Cyclopentane	1	353	24.74 ± 0.2	0.36	24.38
		372	26.16 ± .2	.31	25.85
		395	28.29 ± .3	.26	28.03
		424	30.40 ± .3	.21	30.19
		463	33.32 ± .3	.16	33.16
		503	36.14 ± .4	.12	36.02
		539	38.36 ± .4	.10	38.26
	0.6	353	24.67 ± .3	.22	24.45
Cyclohexane	1	384	34.59 ± .3	.38	34.21
		428	38.94 ± .4	.27	38.67
		460	41.9 ± .4	.22	41.7
		495	45.5 ± .5	.18	45.3
		521	47.2 ± .5	.15	47.0
		544	49.4 ± .5	.13	49.3
	0.46	384	34.31 ± .3	.17	34.14
	0.30	384	34.35 ± .3	.11	34.24
Methylcyclohexane	1	398	44.58 ± .4	.45	44.13
		439	49.00 ± .5	.38	48.62
		480	53.48 ± .5	.24	53.24
		527	58.06 ± .6	.18	57.82

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Summary

The heat capacities of gaseous cyclopentane, cyclohexane and methylcyclohexane have been measured from slightly above the boiling point to about 250°. A few measurements made at reduced pressures indicated that the heat capacities of the ideal gas are given to good approximation by the Berthelot correction.

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Amphiprotic Substances. II.[1] The System Formamide–Ammonia

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The fact that amides of the carboxylic acids stand at a point intermediate between ammonia and carboxylic acids in the Brönsted scale of acidities has already been discussed. Likewise, experimental evidence for the basic properties of these amides in anhydrous acetic acid and for their acidic properties in liquid ammonia has been cited. Compound formation was shown to take place in the systems acetamide–ammonia and acetamide–acetic acid. The systems formamide–acetic acid, formamide–formic acid, formamide–*n*-butyric acid, and formamide–water also have been studied.[2] The system formamide–ammonia remained, however, to be investigated. The investigation of this system was therefore undertaken as the second step in the present series of experiments.

Experimental

Materials.—The formamide was obtained from the Eastman Kodak Co. It was dried by allowing it to stand over drierite for one week, and was purified by distillation under vacuum, a middle fraction boiling from 107 to 109° under 15 mm. pressure being retained. The substance thus obtained melted at 2.2 ± 0.2°, in good agreement with the values of 2.0 to 2.55° given in the literature.[3]

The ammonia used was synthetic anhydrous ammonia

TABLE I

S	T	S	T
(a) Solid phase, $HCONH_2$			
0	2.2	35.5	−36.3
1.9	1.0	39.7	−44.0
5.7	−2.3	44.0	−50.9
7.3	−3.7	46.8	−55.2
11.5	−8.5	49.2	−62.5
14.0	−10.4	49.9	−75.1*
15.9	−12.0	50.3	−67.7
22.6	−19.8	51.1	−75.4*
30.3	−29.8	52.1	−72.7
33.5	−33.9	53.4	−74.0
(b) Solid phase, $NH_3 \cdot HCONH_2$			
53.5	−75.1	65.1	−83.0
54.9	−75.5	67.3	−90.5*
56.6	−76.0		−85.4
58.9	−77.6	68.5	−86.6
60.8	−77.6	69.6	−89.5
(c) Solid phase, $2NH_3 \cdot HCONH_2$?			
71.1	−91.9	77.5	−97.5*
71.6	−91.5		−95.0
	−94.0*	77.9	−94.8
73.5	−92.3	79.2	−96.0
75.4	−93.0		
(d) Solid phase, NH_3			
80.2	−94.0	91.9	−83.2
82.2	−91.4	94.3	−80.9
83.4	−90.6	100.0	−77.5
86.9	−85.8		

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[1] The first paper in this series: Sisler, Davidson, Stoenner and Lyon, THIS JOURNAL, **66**, 1888 (1944).

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[2] English and Turner, *J. Chem. Soc.*, **107**, 774 (1915).

[3] *E. g.* English and Turner, ref. 2; Lowry and Cutter, *J. Chem. Soc.*, **125**, 1469 (1933); Taylor and Davis, *J. Phys. Chem.*, **32**, 1469 (1928).