

sum $D(333/T) + 2E(494/T) + 2E(1058/T)$, which fits the data over the entire experimental range of temperature. In both instances only the Debye function is of importance in the extrapolation of entropy.

TABLE II
ENTROPIES AT 298.16°K. (CAL./DEG. MOL.)

	Mg ₂ SiO ₄	MgSiO ₃
0-50.12°K. (extrap.)	0.60	0.49
50.12-298.16°K. (graph)	22.15	15.73
$S_{298.16}$	22.7 ± 0.2	16.2 ± 0.2

Discussion

It is interesting to note that the entropy difference between these two magnesium silicates, 6.5 ± 0.4 , is virtually the same as the entropy of magnesium oxide,¹¹ 6.55 ± 0.15 . Analogous observations may be made from available data for sodium metasilicate and sodium disilicate³ and from available data for the basic carbonate and the basic sulfates of lead.¹¹ It would appear that

(11) Kelley, *Bureau of Mines Bull.*, 434, 1941, 115 pp.

if the entropy of one compound in a series of compounds formed from two oxides is known, then the others may be computed approximately merely by adding (or subtracting) the entropies of the oxides in accordance with the compositions of the compounds. This statement may be useful in estimating free energies of silicates, especially at the present time, as the available heat of formation data for silicates are generally so inaccurate that in comparison even appreciable errors in the assigned entropies cannot contribute much to the errors in free energies calculated from the relationship $\Delta F^\circ = \Delta H - T\Delta S$.

Summary

The specific heats of Mg₂SiO₄ and MgSiO₃ have been measured in the temperature range 51 to 298°K.

The corresponding entropies have been computed as $S_{298.16} = 22.7 \pm 0.2$ for Mg₂SiO₄ and $S_{298.16} = 16.2 \pm 0.2$ for MgSiO₃.

BERKELEY, CALIFORNIA RECEIVED DECEMBER 14, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Heat Capacity and Entropy, Heats of Transition, Fusion and Vaporization and the Vapor Pressures of Cyclopentane. Evidence for a Non-planar Structure

BY J. G. ASTON, HERMAN L. FINK AND S. C. SCHUMANN

A preliminary statement has been given already of evidence¹ which indicates that the cyclopentane ring is non-planar. The evidence consisted essentially of the results of a determination of the symmetry number of cyclopentane by a comparison, at three temperatures, of its entropy, as calculated from the spectroscopic and molecular data, with that obtained using the third law of thermodynamics and thermal data down to 11.8°K. The present paper presents the data on which the comparisons were based along with calorimetric determinations of the heat of vaporization of cyclopentane at 298.16°K.

Preparation and Purification of Cyclopentane.

—A highly purified sample of cyclopentane was furnished us through the kindness of Professor M. R. Fenske of the Petroleum Refining Laboratory of this college. The cyclopentane, prepared by Mr. R. B. Richards, had been obtained by decomposition of dicyclopentadiene and subsequent

hydrogenation of the cyclopentadiene formed, followed by fractionation through an eighty-plate column. After being dried over phosphorus pentoxide and freed from the last traces of air by repeated freezings and evacuations to 10^{-6} mm. of mercury, about 43 cc. of the material was condensed in a weighed glass sample bulb and then introduced into the calorimeter in the customary manner.² The sample bulb was of the type described already.² In addition to the sealed off side-tube through which it was filled this bulb had a main tube with an inner sealed capillary, which was broken open by moving a piece of iron sealed in glass along a side arm with the aid of a solenoid after sealing to the calorimeter filling line. The pure cyclopentane was thus distilled into the calorimeter without coming into contact with anything but glass (the manometric mercury excepted).

The Heat Capacity Measurements.—The apparatus, methods, accuracy and temperature

(1) Aston, Schumann, Fink and Doty, *THIS JOURNAL*, **63**, 2029 (1941).

(2) Aston and Eidinoff, *ibid.*, **61**, 1533 (1939).

parison of heat capacity values at rounded temperatures as obtained in this research and by Jacobs and Parks.⁴

TABLE II
THE MOLAL HEAT CAPACITY OF CYCLOPENTANE AT
ROUNDED TEMPERATURE VALUES

Mol. wt., 70.130. 0°C. = 273.16°K.

Temp., °K.	C_p , cal./deg., this research	C_p , cal./deg., J. & P.	Dev., %
15 (solid)	0.90		
20	1.99		
25	3.19		
30	4.37		
40	6.68		
50	8.54		
60	10.07		
70	11.36		
80	12.40		
90	13.47	13.27	-1.4
100	14.48	14.07	-2.9
110	15.28	15.10	-1.2
120	15.93	16.07	+0.9
130	22.59	22.23	-1.6
140	21.49	21.23	-1.2
150	21.38	21.13	-1.2
160	21.30	21.07	-1.1
170	21.20	20.93	-1.3
180 (liquid)	23.79	23.57	-0.9
190	24.06	23.93	-0.4
200	24.42	24.27	-0.6
210	24.90	24.60	-1.2
220	25.38	25.07	-1.2
230	25.94	25.53	-1.6
240	26.53	26.10	-1.7
250	27.07	26.70	-1.4
260	27.66	27.40	-0.9
270	28.31	28.17	-0.9
280	29.10	29.00	-0.4
290	30.05	29.90	-0.5
300	30.96	30.87	-0.3

The Transition and Melting Points.—The procedure was the same as that described previously.⁵ The equilibrium temperatures during the lower and upper transitions are listed in Tables III and IV, respectively. The value ob-

TABLE III
EQUILIBRIUM TEMPERATURES OF LOWER TRANSITION OF
CYCLOPENTANE
0°C. = 273.16°K.

% in high temp. phase	Total time, min.	T , °K. Thermo- couple S-9	T , °K. Res. Th. R-200
8.1	120	122.335	122.375
23.1	175	122.354	122.393
38.1	245	122.363	122.402
53.1	355	122.370	122.397

Transition temperature 122.39 ±
0.05°K.

(5) Aston and Messerly, THIS JOURNAL, 58, 2354 (1936).

TABLE IV
EQUILIBRIUM TEMPERATURES OF UPPER TRANSITION OF
CYCLOPENTANE
0°C. = 273.16°K.

% in high temp. phase	Total time, min.	T , °K. Thermo- couple S-9	T , °K. Res. Th. R-200
20.2	115	138.025	138.068
38.6	185	138.033	138.076
58.4	245	138.037	138.080
83.1	320	138.029	138.072

Transition temperature 138.07 ±
0.05°K.

tained for the lower transition was 122.39 ± 0.05°K. (-150.77°C.). Other values reported for this are 121.6°K. (-151.6°C.),⁴ -151.5°C.,⁶ and -151.5°C.⁷ The value obtained for the upper transition was 138.07 ± 0.05°K. (-135.09°C.). The only other value reported is that of Jacobs and Parks, namely, 137.1°K. (-136.1°C.).

The equilibrium temperatures during fusion are reported in Table V. From the results of

TABLE V
EQUILIBRIUM TEMPERATURES OF FUSION OF CYCLOPEN-
TANE
0°C. = 273.16°K.

% Melted	Total time, min.	T , °K. Thermo- couple S-9	T , °K. Res. Th. R-200
11.1	125	179.650	179.637
33.5	210	179.692	179.671
48.3	295	179.687	179.683
64.7	420	179.694	179.687
78.5	545	179.696	179.689

Melting point of pure cyclopentane 179.69 ±
0.05°K.

Mole per cent. impurity 0.001

the determination of the melting point the impurity present in the sample was found to be 0.001 mole per cent., assuming no solid solution. The final value obtained for the melting point of pure cyclopentane is 179.69 ± 0.05°K. (-93.47°C.). Other values reported are 179.0°K. (-94.2°C.),⁴ -94.3°C.,^{3,6} -94.3°C.,^{3,7} -94.8°C.,^{3,8} and -95.0°C.⁹

The Heats of Transition and Fusion.—Tables VI, VII and VIII summarize the data for the heats of transition and fusion according to our usual methods of tabulation.⁵ The results of Jacobs and Parks⁴ are given for comparison.

The Vapor Pressures.—Vapor pressures were measured only below 20° to avoid condensation

(6) Wibaut, *et al.*, *Rec. trav. chim.*, 58, 329 (1939).

(7) Smittenberg, Hoog and Henkes, THIS JOURNAL, 60, 17 (1938).

(8) Chavanne, *Bull. soc. chim. Belg.*, 31, 338 (1922).

(9) Timmermans and Hennaut-Roland, *J. Chim. Phys.*, 34, 693 (1937).

TABLE VI

MOLAL HEAT OF TRANSITION-I OF CYCLOPENTANE

Mol. wt. = 70.130; 0.46619 mole; transition point, 122.39 \pm 0.05 $^{\circ}$ K.; 0 $^{\circ}$ C. = 273.16 $^{\circ}$ K.

Temp. interval, $^{\circ}$ K.	Corrected heat input, cal./mole	$\int C_p dT$, cal./mole	ΔH transition, cal./mole
121.188-125.240	1282.9	117.8	1165.1
120.945-123.960	1249.8	83.9	1165.9
120.418-126.764	1348.0	183.7	1164.3

Mean 1165.1 \pm 0.8

Measured (Jacobs and Parks)⁴ 1134

TABLE VII

MOLAL HEAT OF TRANSITION-II OF CYCLOPENTANE

Mol. wt. = 70.130; 0.46619 mole; transition point, 138.07 \pm 0.05 $^{\circ}$ K.; 0 $^{\circ}$ C. = 273.16 $^{\circ}$ K.

Temp. interval, $^{\circ}$ K.	Corrected heat input, cal./mole	$\int C_p dT$, cal./mole	ΔH transition, cal./mole
137.928-139.993	145.720	62.994	82.726
137.850-139.539	134.489	51.624	82.865

Mean 82.80 \pm 0.08

Measured (Jacobs and Parks)⁴ 85.55

TABLE VIII

MOLAL HEAT OF FUSION OF CYCLOPENTANE

Mol. wt. = 70.130; 0.46619 mole; melting point, 179.69 \pm 0.05 $^{\circ}$ K.; 0 $^{\circ}$ C. = 273.16 $^{\circ}$ K.

Temp. interval, $^{\circ}$ K.	Corrected heat input, cal./mole	$\int C_p dT$, cal./mole	ΔH fusion, cal./mole
179.282-181.652	223.05	79.00	144.05
179.012-180.221	183.31	38.95	144.36
176.135-180.914	295.25	151.50	143.75

Mean 144.05 \pm 0.30

Measured (Jacobs and Parks)⁴ 144.5

in the connecting lines and manometer. The results are listed in Table IX. Column one gives

TABLE IX

THE VAPOR PRESSURES OF CYCLOPENTANE

0 $^{\circ}$ C. = 273.16 $^{\circ}$ K. g for State College, 980.124 ("I. C. T.")

T obs., $^{\circ}$ K.	P , obs., Int. mm.	$P_{obs.} - P_{calcd.}$, ^a Int. mm.	$T_{calcd.} - T_{obs.}$, $^{\circ}$ K.
225.91	6.23	-0.02	-0.031
234.80	11.78	0	0
241.52	18.35	0	0
248.45	28.15	-0.02	-0.010
254.55	40.20	-0.02	-0.009
260.25	55.13	0	0
265.86	74.07	-0.01	-0.002
271.22	96.99	0.01	0.001
277.62	131.78	0.01	0.002
282.48	164.63	-0.01	0.002
287.40	204.39	0	0

^a Calculated from equation (1).

the absolute temperature as read on the resistance thermometer. Column two gives the observed pressure and column three the difference between the observed pressure and that calculated from the temperature by means of the equation

$$\log_{10} P_{\text{mm.}} = -\frac{2298.386}{T} - 8.91170 \log_{10} T + 4.385677 \times 10^{-3}T - 1.054940 \times 10^{-5}T^2 + 30.957385 \quad (1)$$

Column four gives the temperature difference corresponding to the pressure difference. The normal boiling point of a portion of the sample which we used was measured in a modified Cottrell apparatus by Mr. R. B. Richards of the Petroleum Refining Laboratory. The value obtained for the boiling point was 49.20 \pm 0.05 $^{\circ}$ C. Other values reported are 49.20,^{6,3} 49.2,^{7,3} 49.30,^{3,9} 49.5,^{3,10} 49.4 to 49.5,^{8,11,12} 49.37,^{3,13} 49.35,^{3,14} and 49.0^{3,15} (all in $^{\circ}$ C.). For completeness the normal boiling point has been calculated from equation (1) to be 321.99 $^{\circ}$ K. (48.83 $^{\circ}$ C.). Needless to say, this value can be given no weight because of the long extrapolation.

The Heat of Vaporization.—The pressure was held constant during the vaporization by condensing the vapor into a weighed glass sample bulb, immersed in liquid air. The rate of distillation from the calorimeter was adjusted to keep the temperature constant by means of a stopcock with a groove cut part way around the barrel to give a finer adjustment. The material was condensed into a duplicate bulb while the stopcock was being set. When the pressure, as read on a G n voise Soci t  Cathetometer, remained constant, condensation into the weighed glass sample bulb was started by turning a three-way stopcock from the duplicate to the weighed sample bulb. After a measured time had elapsed, the three-way stopcock was turned again to the duplicate bulb whose contents were returned to the calorimeter after the measurements were complete. In this manner the pressure could be kept constant to better than 5 mm. over a period of forty-five minutes during which time energy was being supplied to the calorimeter. The average pressure during vaporization was obtained by plotting the pressure against the time, integrating and dividing by the total time. The value thus obtained corresponded to a temperature 0.7 $^{\circ}$ K. below that obtained by averaging the readings of thermocouple S-9 (soldered to the calorimeter bottom) in the same manner. The former temperature is calculated from a pressure

(10) Chavanne and Simon, *Compt. rend.*, **168**, 1111, 1324 (1919).

(11) Evans, *J. Inst. Petr. Tech.*, **24**, 321 (1938).

(12) Garner and Evans, *ibid.*, **18**, 751 (1932).

(13) Thery, Th se, Brussels, 1925.

(14) Chavanne and Van Risseghem, *Bull. soc. chim. Belg.*, **31**, 87 (1922).

(15) Eykman, *Chem. Weekblad*, **1**, 7 (1903).

which may be too low because of the pressure drop through the vaporization lines while the latter temperature may be too high due to superheating. The difference of 0.7°K., however, corresponds to but 11 cal./mole difference in the heat of vaporization so that it makes no great matter which temperature is chosen as representing that of the vaporization. The temperature as read by the thermocouple was finally chosen.

The results are given in Table X. In calculating the heat of vaporization of 298.16°K., the data used were (a) the heat content of the gas calculated from the spectroscopic data to be discussed, (b) the liquid heat capacities, (c) Berthelot's equation of state with $T_c = 520^\circ\text{K}$. and $P_c = 44.2$ atm.¹⁶

TABLE X
MOLAL HEAT OF VAPORIZATION OF CYCLOPENTANE

T , °K. vap.	Cor. heat input, cal./ mole	$\int C_p dT$, cal./ mole	Moles vap.	ΔH vap., cal./ mole at T , °K. ^a	ΔH vap. to ideal gas state at 298.16°K . ^b	ΔH vap. cal./ mole at 298.16°K . ^c
295.01	7121.6	113.0	0.050977	7009	7011	6974
295.03	7066.0	46.2	0.051703	7020	7023	6986
295.70	7218.0	206.3	0.050449	7012	7022	6985

Mean 6982 \pm 8

Calculated from equation (1) at 298.16°K. and critical data,¹⁶ $T_c = 520^\circ\text{K}$. $P_c = 44.2$ atm., Berthelot correction = 145 cal. 6859

Calculated from equation (1) and same critical data at 230°K., Berthelot correction = 8.4 cal. 7495

Calculated from equation (1) and same critical data at 260°K., Berthelot correction = 38.0 cal. 7225

^a Heat of vaporization to the real gas under the saturation pressure at the temperature given in column one.

^b Heat of vaporization to the ideal gas at 298.16°K. (any pressure). ^c Heat of vaporization to the real gas at 298.16°K. and the saturation pressure.

The heat of vaporization has also been calculated at 298.16°K. by thermodynamics using equation (1) and the modified Berthelot equation. The value is 1.8% low. This large error may be due, in part, to use of equation (1) beyond the range of the measurements.

For use in entropy calculations, values of the heat of vaporization have also been calculated from equation (1) in the same way at 230.00°K. and 260.00°K. These values can be expected to be more reliable as the deviation of the vapor from that of a perfect gas is much less.

(16) The critical constants for cyclopentane were obtained from those for *n*-pentane, isopentane, *n*-hexane, diisopropyl and cyclohexane using the following relation applied to T_c/T_B and to P_c . The average of *n*-pentane and isopentane + cyclopentane = the average of *n*-hexane and diisopropyl + cyclohexane. The ratios of the critical temperature to the boiling temperature (T_c/T_B) were fairly constant for the isomeric compounds (Aston and Messerly, THIS JOURNAL, 58, 2354 (1936)).

The Entropy from the Calorimetric Data.—The calculation for the liquid at the melting point and at 298.16°K. is summarized in Table XIa

TABLE XIa
THE MOLAL ENTROPY OF LIQUID CYCLOPENTANE AT
179.69 AND 298.16°K.
Mol. wt., 70.130. 0°C. = 273.16°K.
E. u.

0–12.59°K. Debye extrapolation ($\theta = 149.7$, 6 degrees of freedom)	0.184
12.59–122.39°K., graphical $\int C_p d \ln T$	16.072
122.39°K., (1165.1/122.36) transition	9.520
122.39–138.07°K., graphical $\int C_p d \ln T$	2.722
138.07°K., (82.796/138.03) transition	0.600
138.07–179.69°K., graphical $\int C_p d \ln T$	5.633
179.69°K., (143.05/179.70) fusion	0.802
Entropy of liquid at the melting point	35.533 \pm 0.04
179.70–298.16°K., graphical $\int C_p d \ln T$	13.338
Entropy of liquid at 298.16°K.	48.87 \pm 0.05

while the calculations at 230, 260, and 298.16°K. for the liquid, the saturated vapor and the ideal gas at one atmosphere are given in Table XIb.

TABLE XIb
THE MOLAL ENTROPY OF GASEOUS CYCLOPENTANE AT
CERTAIN TEMPERATURES
Mol. wt., 70.130. 0°C. = 273.16°K.

	E. u.		
	230.00°K.	260.00°K.	298.16°K.
Liquid at melting point	35.533	35.533	35.533
179.69 — T °K. graphical	6.110	9.403	13.388
Vaporization at T °K.	32.587 ^b	27.790 ^b	23.416 ^c
Gas imperfection correction ^a	0.005	0.020	0.084
Correction to 1 atm.	-8.945	-5.240	-1.725
Entropy ideal gas at T °K., 1 atm.	65.27 \pm 0.15	67.51 \pm 0.15	70.70 \pm 0.07

^a $S_{\text{ideal}} - S_{\text{real}} = 27RT_c^3 P / 32T^3 P_c$; $P_c = 44.2$ atm.; $T_c = 520^\circ\text{K}$. ^b These values were calculated from the vapor pressure equation. ^c The value at 298.16°K. is the measured value.

The Entropy from the Spectroscopic Data.—Table XII contains a summary of the calculation of the entropy from molecular and spectroscopic data at 230.00, 260.00 and 298.16°K. and a comparison with the calorimetric values. The atomic distances used were C-C, 1.54 Å. and C-H, 1.09 Å. The moments were calculated on the basis of a planar ring (D_{5h}). They are: $A = 227.2 \times 10^{-40}$; $B = C = 129.6 \times 10^{-40}$ gm. cm.² These gave for the translational and external rotational entropy

$$S_{T+R} = 18.488 + 4 R \ln T - R \ln \sigma \quad (2)$$

The frequency assignment was that given in the previous communication.¹

The best fit with the experimental data results by taking σ in equation (2) equal to unity corresponding to the configuration C_3 (one atom out of the plane). In the last two lines of Table XII

TABLE XII

THE ENTROPY OF CYCLOPENTANE IN THE IDEAL GAS STATE FROM MOLECULAR AND SPECTROSCOPIC DATA AT CERTAIN TEMPERATURES

	230.00°K.	260.00°K. cal./deg./mole	298.16°K.
Translational + Rotational ($\sigma = 1$)	61.75	62.72	63.77
Vibrational ($\gamma_1 = 165$, $\gamma_2 = 285$ cm. ⁻¹)	3.90	4.89	6.39
Total, C_3 ($\sigma = 1$)	65.65	67.61	70.16
Total, C_2 ($\sigma = 2$)	64.27	66.23	68.78
Total, D_{3h} ($\sigma = 10$)	61.08	63.04	65.59
Calorimetric	65.27 \pm 0.15	67.51 \pm 0.15	70.70 \pm 0.07
Total vibrational with γ_1 changed to 56 and γ_2 to 88 cm. ⁻¹	8.08	9.13	10.69
Total, D_{3h} ($\sigma = 10$) $\gamma_1 = 56$, $\gamma_2 = 88$ cm. ⁻¹	65.26	67.28	69.89

we have compared the experimental values with those calculated using the same frequency assignment except with $\gamma_1 = 56$ cm.⁻¹ and $\gamma_2 = 88$ cm.⁻¹ and taking $\sigma = 10$ to get an idea of what revision in the frequency assignment would be necessary to get agreement for $\sigma = 10$. These frequencies were chosen to give agreement at the lowest temperatures. For reasons already given¹ such values of γ are unlikely. Recent measurements of the entropy for cyclohexane down to 10°K. made in this laboratory compared with the "spectroscopic" value calculated using values of the γ frequencies of roughly the same magnitude and estimated in the same way as the preferred values of the γ frequencies for cyclopentane are consistent with only the chair form of the ring. This speaks against low γ frequencies in rings of this type.

We have already pointed out elsewhere¹ that these results indicate a non-planar ring (C_2) caused by hydrogen repulsions. Thus there is little doubt that the potential barriers hindering internal rotation are due to hydrogen repulsions as opposed to attractions as has already been suggested on the basis of other evidence.¹⁷

It should be pointed out that in the solid there can be no random orientation of the non-planar rings about an axis perpendicular to a plane containing four (or three) of the carbon atoms. If there were undetected complete randomness, the

calorimetric entropies would have been too low by $R \ln 10$ and would have pointed to a value of σ equal to ten. Whether the order is achieved by orientation of the rings or by a process involving a double potential energy minimum as occurs in the ammonia molecule in the gas state is not known although the latter alternative seems the more plausible.

Since our first communication on this subject, Rosenbaum and Jacobson¹⁸ found that the Raman lines of cyclopentane were extraordinarily diffuse. This diffuseness was greatly in contrast to the sharpness of the lines of benzene and cyclohexane. They attributed this diffuseness to the non-planarity of the cyclopentane ring.

Acknowledgment.—We wish to thank Professor M. R. Fenske for supplying us with an extremely pure sample of cyclopentane, Mr. P. M. Doty and Mr. G. J. Szasz for assisting with the experimental measurements and calculations and Mr. M. L. Sagenkahn for preparing the liquid hydrogen. The Grants-in-Aid of the National Research Council with which much of the apparatus was purchased and financial aid from the Standard Oil Development Company and the Research Corporation made this work possible.

Summary

1. The heat capacity of solid and liquid cyclopentane has been measured from 11.8° to 293.82°K.
2. The equilibrium temperatures of the lower transition, the upper transition and the fusion, together with their heats have been determined.
3. The heat of vaporization has been determined at 298.16°K. The experimental vapor pressure equation over the range 220° to 287°K. has been used to calculate values of the heat of vaporization at 230°, 260° and 298.16°K.
4. Comparisons of the experimental entropy with that calculated from statistical and molecular data at 230 and 298.16°K. indicate a symmetry number of one and that the cyclopentane ring is non-planar, one carbon atom being out of the plane. This effect is attributed to hydrogen interactions of the type hindering internal rotation which must therefore be repulsions.

STATE COLLEGE, PA.

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(17) Aston and Kennedy, *THIS JOURNAL*, **62**, 2567 (1940).

(18) Rosenbaum and Jacobson, *ibid.*, **63**, 2841 (1941).