[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 Cyclohexane. The Vibrational Frequencies of Alicyclic Ring Systems[1]

BY J. G. ASTON, GEORGE J. SZASZ AND HERMAN L. FINK

The present paper presents measurements of complete thermal data from 10 to 294°K. and of heats of vaporization at 298.16°K. for cyclohexane from which the entropy of the ideal gas has been calculated at 298.16°K. The entropy thus obtained has been found to agree with the value calculated from the spectroscopic and molecular data using values for the γ frequencies (vibrations perpendicular to the ring) of $\gamma_1 = \gamma_2 = 210$ cm.$^{-1}$, $\gamma_3 = 377$ cm.$^{-1}$. Inasmuch as similar γ frequencies were assumed for cyclopentane[2,4] in an earlier paper pointing to a non-planar structure, this result can be taken as substantiating the results of that paper.

Preparation and Purification of Cyclohexane.—A purified sample of cyclohexane was furnished us through the kindness of Professor M. R. Fenske of the Petroleum Refining Laboratory of this College. The cyclohexane (from Röhm and Haas) was purified by Dr. W. R. Scott by acid extraction and fractionation through a glass 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 into a weighed glass sample bulb and then introduced into the calorimeter in the manner previously described.[3] The method used to distill the sample into the calorimeter without its coming into contact with anything but glass, was described recently.[4]

The Heat Capacity Measurements.—The apparatus, method, and temperature scale were as already described.[3] Calorimeter B was used for all measurements with resistance thermometers R-200 (platinum–rhodium) and R-102 (constantan). The indications of these thermometers were compared at ten-degree intervals with the standard thermocouple S-9 which was soldered to the calorimeter.[3] The maximum deviation noted was 0.05°. For reasons previously discussed,[4] the indications of R-200 and R-102 were considered more reliable than those of S-9.

A pressure of one third of an atmosphere of helium was introduced into the calorimeter while cooling for and during the heat capacity measurements on the solid but not on the liquid as this would have rendered corrections for vaporization into the filling line ambiguous. When the helium was present no effort was made to keep the inner block warmer as no appreciable quantity of solid could have collected in the time of the heat

TABLE I

THE MOLAL HEAT CAPACITY OF CYCLOHEXANE

Mol. wt. 84.156; 0.39651 mole in calorimeter; 0°C. = 273.16°K.

Temp., °K.	C_p, cal./deg./mole	ΔT, °K.
	Series III	
	Solid	
12.73	0.56	2.4
15.24	1.06	2.3
17.45	1.56	2.2
19.31	1.99	2.0
21.36	2.42	2.7
24.18	3.20	3.0
27.93	4.20	3.8
31.55	4.84	3.7
35.28	5.63	3.9
39.04	6.48	3.9
43.19	7.33	4.5
48.00	8.08	5.2
53.18	8.83	5.3
58.40	9.53	5.3
63.87	10.19	5.8
	Series II	
58.91	9.60	5.2
63.87	10.24	4.7
68.38	10.77	4.3
72.90	11.25	4.7
77.74	11.79	5.0
82.87	12.30	5.3
88.17	12.88	5.5
93.45	13.37	5.2
98.40	13.87	4.9
103.13	14.23	4.7
107.61	14.71	4.5
112.20	15.14	4.8
121.86	16.04	4.9
126.43	16.55	4.7
131.16	16.90	5.0
136.16	17.40	4.7
146.47	18.30	5.2
151.49	18.87	5.0
161.30	20.03	5.3
166.37	20.70	5.1
171.32	21.28	5.0
176.04	22.00	4.7
180.83	22.58	5.2
	Transition	
191.30	25.80	5.5
196.24	26.02	5.3
201.46	26.14	5.3
206.60	26.44	5.2
211.98	26.65	5.9
217.77	26.95	5.8
223.41	27.35	5.7
228.75	27.62	5.6
234.21	28.04	5.5
239.53	28.56	5.2
249.73	29.33	5.1
254.79	29.54	5.0
259.83	30.02	5.6
265.40	30.62	5.5
271.13	30.92	6.1
	Series I	
	Liquid	
281.63	36.11	2.8
284.89	36.48	3.7
288.79	36.88	4.0
292.46	37.12	3.3

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[1] The results of this paper have already been cited by J. G. Aston and R. M. Kennedy, Symposium on Low Temperature Phenomena, 104th meeting of the American Chemical Society, Buffalo, N. Y., Sept., 1942 (paper presented by S. C. Schumann).

[2] Aston, Schumann, Fink and Doty, THIS JOURNAL, **63**, 2029 (1941).

[3] Aston and Eidinoff, *ibid.*, **61**, 1533 (1939).

[4] Aston, Fink and Schumann, *ibid.*, **65**, 341. (1943).

capacity measurements, as demonstrated experimentally.

One defined calorie was taken equal to 4.1833 international joules. Corrections to the heat capacities for vaporization into the filling line were made using the values for the density given by Egloff.[5] The molal heat capacities are listed in Table I and plotted in Fig. 1, where are also plotted the measurements of Parks, Huffman and Thomas.[6] Table II contains a comparison of heat capacity values at rounded temperatures as obtained in this research and by Parks, Huffman and Thomas.[6]

TABLE II

THE MOLAL HEAT CAPACITY OF CYCLOHEXANE AT ROUNDED TEMPERATURE VALUES

Mol. wt., 84.156; 0°C. = 273.16°K.

Temp., °K.	C_p, cal./deg./mole This Research	P., H. and T.	Dev., %
12 (solid I)	0.54		
15	1.02		
20	2.17		
25	3.37		
30	4.50		
40	6.72		
50	8.38		
60	9.74		
70	10.93		
80	12.02		
90	13.04	13.02	−0.15
100	14.01	14.04	+0.21
110	14.95	14.99	+0.27
120	15.88	15.97	+0.60
130	16.80	16.88	+0.48
140	17.73	17.79	+0.32
150	18.73	18.73	0.00
160	19.87	19.78	+0.46
170	21.15	21.00	−0.71
180	22.50	22.48	−0.09
190 (solid II)	25.77	25.93	+0.62
200	26.16	26.40	+0.92
210	26.61	26.73	+0.45
220	27.13	27.21	+0.29
230	27.75	27.76	+0.04
240	28.48	28.40	−0.28
250	29.29	29.14	−0.51
260	30.18	29.98	−0.66
270	31.08	30.88	−0.64
280 (liquid)	35.89	35.32	−1.58
290	36.97	36.11	−2.33
295	37.25	36.70	−1.48

The Transition and Melting Points.—The procedure was the same as that described previously.[7] The equilibrium temperatures during transition and fusion are listed in Tables III and IV, respectively. The value obtained for the transition point was 186.09 ± 0.05°K. (−87.07°C.). The only other value reported for this is 185.9°K. (−87.3°C.).[6] From the results of the determination of the melting point the impurity in the sample was found to be 0.095 mole per cent. assuming no solid solution. The final value obtained for the melting point of pure cyclohexane is 279.84 ± 0.05°K. (6.68°C.). All other reported values are summarized by Egloff.[5] They range from 4.5°C.[8,5] through 279.3°K. (6.1°C.)[6] and 6.40°C.[9] to 6.7°C.[10]

TABLE III

EQUILIBRIUM TEMPERATURES OF TRANSITION OF CYCLOHEXANE (DATE 4/9/42)

% in high temp. phase	Total time, min.	T, °K. Thermocouple S-9	T, °K. Res. Th. R-200
2.12	60	186.063	186.026
21.10	135	186.104	186.082
40.08	225	186.112	186.062
59.14	315	186.114	186.086
78.23	405	186.122	186.097

Transition temperature 186.09 ± 0.05°K.

TABLE IV

EQUILIBRIUM TEMPERATURES OF FUSION OF CYCLOHEXANE (DATE 3/17/42)

% melted	Total time, min.	T, °K. Thermocouple S-9	T, °K. Res. Th. R-200
0.8	60	278.908	278.953
16.9	110	279.173	279.214
33.1	160	279.317	279.358
49.2	270	279.324	279.358
65.2	350	279.424	279.453
78.6	440	279.482	279.515
97.6	495	279.556	279.589

Melting point of pure cyclohexane, 279.84 ± 0.05°K.
Mole per cent. impurity 0.095

The Heats of Transition and Fusion.—Tables V and VI summarize the data for the heats of transition and fusion according to our usual methods of tabulation.[7]

The Vapor Pressures.—Vapor pressures were measured only below 22°C. to avoid condensation in the connecting line and manometer. The results are listed in Table IX. Column 1 gives the absolute temperature as read on resistance thermometer R-200, column 2 gives the corresponding pressure and column 3 gives the pressure calculated from

$$\log_{10} P_{\text{mm.}} = (19.889412/T) + 36.878414 \log_{10} T - 0.0680782287T + 0.0000582352947T^2 - 74.204387 \quad (1)$$

The normal boiling point of a portion of our

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[5] Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Company, New York, N. Y., 1940.

[6] Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1035 (1930).

[7] Aston and Messerly, *ibid.*, **58**, 2354 (1936).

[8] Garner and Evans, *J. Inst. Petroleum Tech.*, **18**, 751 (1932).

[9] Timmermans and Martin, *J. chim. phys.*, **23**, 760 (1926).

[10] Rotinjanz and Nagornow, *Z. physik. Chem.*, **169A**, 20 (1934).

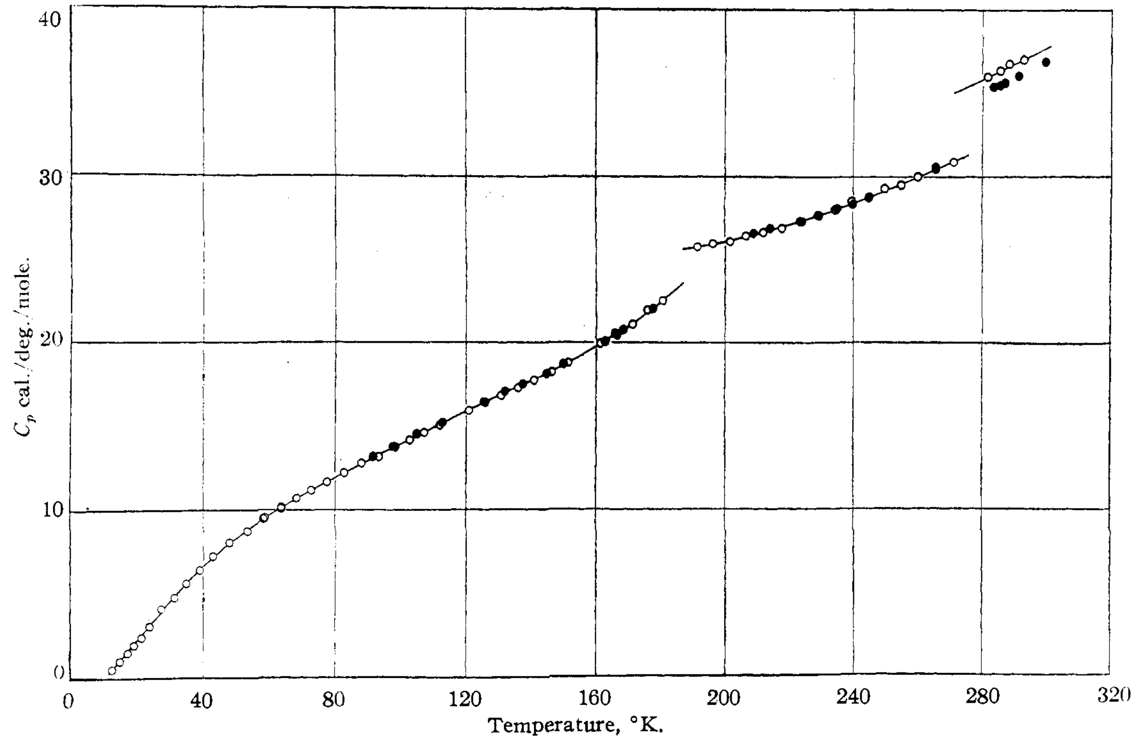

Fig. 1.—The molal heat capacity of cyclohexane: This Research ○; Parks, *et al.*, ●.

TABLE V

MOLAL HEAT OF TRANSITION OF CYCLOHEXANE

Mol. wt., 84.156; 0.39651 mole; transition point, 186.09 ± 0.05°K.; 0°C. = 273.16°K.

Temp. interval, °K	Corrected heat input, cal./mole	$\int C_p\,dT$, cal./mole	ΔH transition, cal./mole
185.522-189.956	1757.78	164.98	1592.8
183.293-188.751	1794.44	197.63	1596.8
178.976-188.705	1944.15	344.43	1599.7
		Mean[a]	1598.3 ± 1.5
Measured (Parks, Huffman and Thomas)[5]			1605

[a] Only the last two values were averaged as some transition may have occurred prior to energy input in the first run.

TABLE VI

MOLAL HEAT OF FUSION OF CYCLOHEXANE

Mol. wt. 84.156; 0.39651 mole; melting point, 279.84 ± 0.05°K.; 0°C. = 273.16°K.

Temp. interval, °K.	Corrected heat input, cal./mole	$\int C_p\,dT$, cal./mole	ΔH fusion, cal./mole
276.498-282.137	892.42	263.44	628.98
274.791-283.908	1055.99	427.57	628.42
275.453-281.745	916.96	290.93	626.03
		Mean	627.8 ± 1.8
Measured (Parks, Huffman and Thomas)[5]			623.6

TABLE VII

THE VAPOR PRESSURES OF CYCLOHEXANE (LIQUID)

0°C. = 273.16°K.; *g* for State College, 980.124 ("I. C. T.")

T obs., °K.	*P* obs., Int. mm. Hg	*P* calcd. from equation (1)
279.48 (triple point)	40.41	40.41
283.04	48.16	48.16
286.78	57.73	57.73
290.80	69.96	69.96
294.12	81.83	81.83

sample was measured in a modified Cottrell apparatus by Dr. R. W. Scott of the Petroleum Refining Laboratory. The value obtained for the boiling point was 80.8°C. Other reported values have been summarized by Egloff,[5] who chooses 80.79°C. as the most probable one. Other vapor pressures reported in the literature are those of Rotinjanz and Nagornow.[10]

The Heat of Vaporization.—The method and accuracy were exactly as described before.[4] The

TABLE VIII

MOLAL HEAT OF VAPORIZATION OF CYCLOHEXANE

T, °K. vap.	Corrd. heat input, cal./mole	$\int C_p\,dT$, cal./mole	Moles vap.	ΔH vap., cal./mole, to real gas at *T* °K. and saturation pressure	ΔH vap., cal./mole, to ideal gas at 298.16°K.	ΔH vap., cal./mole to real gas to 298.16°K. and saturation pressure
291.73	7578.5	480.5	0.048250	8059	7981	7965
292.36	7699.6	386.4	.047587	8086	7989	7974
292.94	7900.7	146.1	.046070	8047	7978	7963
					Mean	7967 ± 8
Calculated from equation (1) at 298.16°K. Berthelot correction = 66 cal./mole						7940
Calculated from equation (2) at 298.16°K.						7860

results are given in Table VIII. In calculating the heat of vaporization at 298.16°K. from the measured heats of vaporization, the data used were (a) the heat content of the gas from spectroscopic data, (b) the liquid heat capacities, (c) Berthelot's equation of state, with $T_c = 554.2$°K. and $P_c = 40.57$ atm.[10] The method of calculation has been given already.[3,4]

The heat of vaporization has also been calculated at 298.16°K. by thermodynamics using equation (1) and the modified Berthelot equation. For comparison the table also includes the value calculated using equation (2)

$$\Delta H_T = 8861 + 3.16057T - 0.0219T^2 \qquad (2)$$

derived by Kolossowsky and Alimow from their[11] experimental data.

The Entropy from the Calorimetric Data.—The calculation for the ideal gas at 298.16°K. is summarized in Table IX.

TABLE IX

THE MOLAL ENTROPY OF CYCLOHEXANE AT 279.84°K. AND 298.16°K.

Mol. wt., 84.156; 0°C. = 273.16°K.

	E. u.
0–12.59°K. Debye extrapolation (θ = 143.5, 6 degrees of freedom)	0.208
12.59–186.09°K., graphical $\int C_p\, d \ln T$	23.898
186.09°K., (1598.3/186.09) transition	8.589
186.09–279.84°K., graphical $\int C_p\, d \ln T$	11.436
279.84°K., (627.8/279.84) fusion	2.243
Entropy of liquid at the melting point	46.374
279.84–298.16°K., graphical $\int C_p\, d \ln T$	2.355
Entropy of liquid at 298.16°K.	48.729 ± 0.15
298.16°K., (7967/298.16) vaporization	26.720
Gas imperfection correction	0.014
Correction to 1 atm. $R \ln 98.85/760$	−4.053
Entropy of ideal gas at 298.16°K. 1 atm.	71.41 ± 0.18

The Entropy from Spectroscopic and Molecular Data and the Structure of Cyclohexane.—The assignment of the vibration frequencies and symmetry number was based on the work of Kohlrausch and his collaborators.[12] The following frequencies were used

Ring: $\omega_{1,2} = 425$, $\omega_3 = 801$, $\omega_4 = 750$, $\omega_{5,6} = 1050$, $\omega_{7,8} = 1266$, $\omega_9 = 1370$, $\gamma_1 = \gamma_2 = 210$, $\gamma_3 = 377$

CH_2 internal: ${}^{12}\nu = 2770$, ${}^{6}\gamma = 1300$

CH_2 waving and torsion: ${}^{6}\delta_1 = 885$, ${}^{6}\delta_2 = 1028$, ${}^{6}\delta_3 = 1345$

It was assumed that all the molecules were in the "chair" form in accord with the vibration spectrum.[12c] The symmetry number is six for the "chair" form. The ${}^{6}\delta_1$ frequencies were assigned by considerations based on analogous cases and thus by solving for $\gamma_1 = \gamma_2$, the value obtained is 210 cm.$^{-1}$. These assignments give a satisfactory check with the available gaseous heat capacity data.[13] The comparison is summarized in Table X. Column 1 is the value calculated from our frequency assignment, column 2 is the single experimental result of Bennewitz and Rossner and column 3 lists the results of Montgomery and DeVries. The atomic distances used were, C–C 1.54 Å., and C–H 1.09 Å. The product of the moments of the "chair" form was found to be (A B C) = 12.39 × 10^{-114} (g. cm.^{2}).[3] The results are summarized in Table XI.

TABLE X

COMPARISON OF GASEOUS HEAT CAPACITIES FOR CYCLOHEXANE

C_p in cal./deg./mole at	Calcd.	Found (a)	Found (b)
370°K.	32.91		33.0
390°K.	35.00		35.0
410°K.	37.04	37.0	36.8

TABLE XI

THE ENTROPY OF CYCLOHEXANE IN THE IDEAL GAS STATE AT 298.16°K. FROM MOLECULAR AND SPECTROSCOPIC DATA

	"Chair" form of cyclohexane. Symmetry group, D_{3d}. Symmetry number, $\sigma = 6$
Translational and rotational	61.95
Vibrational ($\gamma_1 = \gamma_2 = 210$ cm.$^{-1}$)	9.28
Total	71.23
Calorimetric	71.41 ± 0.18

The data in this paper were taken in greater haste than those on dimethylamine.[3] Below the transition the accuracy is reduced to about 0.2% above 30°K. and to about 2% below 30°K. Due to unusual slowness of reaching equilibrium, the heat capacity measurements on this compound above the transition point are not as precise as the usual measurements in this calorimeter. The accuracy of the heat capacities above 186°K. is estimated to be 0.5% on this account. Before the proof of this paper was corrected we had the privilege of reading a manuscript by R. A. Ruehrwein and H. M. Huffman describing heat capacity measurements on this compound over essentially the same range as those herein. As a result certain small errors in the first values have been corrected and this Note added (May 12, 1943); however, differences in the heats of transition and fusion cannot be reconciled.

Acknowledgment.—We wish to thank Professor M. R. Fenske for supplying us with the pure sample of cyclohexane, Messrs. E. L. Pace and C. W. Ziemer for assisting with the experi-

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[11] Kolossowsky and Alimow, *Bull. soc. chim.*, (5) **1**, 879 (1934).

[12] (a) Kohlrausch and Stockmair, *Z. physik. Chem.*, **B31**, 382 (1936); (b) Kahovec and Kohlrausch, *ibid.*, **B35**, 29 (1937); (c) Kohlrausch and Wittek, *ibid.*, **B48**, 177 (1941).

[13] (a) Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 137 (1938); (b) Montgomery and DeVries, THIS JOURNAL, **64**, 2376 (1942).

mental 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 cyclohexane has been measured from 12.6 to 293.8°K.

2. The equilibrium temperatures of the 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 280 to 294°K. has been used to calculate the value of the heat of vaporization at 298.10°K.

4. Comparisons of the experimental entropy with that calculated from statistical and molecular data afford a means to assign the lowest vibration frequencies. The result which was based on a "chair" configuration for the cyclohexane molecule is in good agreement with previous assignments on similar molecules.

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[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. XVI. The Heat Capacity and Entropy of Isopentane. The Absence of a Reported Anomaly

BY GEORGE B. GUTHRIE, JR., AND HUGH M. HUFFMAN

In two recent papers[1] Aston and co-workers have reported the results of their low temperature studies on isopentane. During this investigation they obtained certain anomalous results in their heat capacity and vapor pressure measurements. These anomalous results were especially evident in the temperature interval 180 to 240°K. Aston has attempted to account for these results on the basis of a hysteresis in the establishment of equilibrium between isomeric forms due to hindered rotation. The heat capacity of isopentane was also measured in 1930 by Parks, Huffman and Thomas,[2] who did not observe any irregularities in the heat capacity.

Because of the great importance of such a phenomenon and the great effect its existence would have upon similar experimental and theoretical studies on other hydrocarbon molecules, it is of paramount importance that its actual existence be established beyond any reasonable doubt.

We have accordingly reinvestigated the heat capacity of isopentane over the temperature range 13 to 300°K. Unfortunately, the design of our apparatus did not permit the simultaneous observation of the vapor pressure.

Experimental

The Material.—Measurements were made on two different samples of isopentane. The first was purified for us by the Shell Development Company, who state that the entire sample, 300 cc., boiled at 27.92 ± 0.01°C. The second sample was the isopentane that Aston, *et al.*,[1] had used in their calorimeter and was kindly sent to us by Professor Aston. From data obtained during the melting point determinations we have calculated that the liquid-soluble, solid-insoluble impurity in the first (Shell) sample was 0.013 mole per cent. and that in the second (Aston) sample was 0.008 mole per cent.

The Apparatus.—Our heat capacity measurements were carried out in an adiabatic calorimetric system which will be described in detail in a later publication. The calorimeter proper was of copper and had an internal volume of approximately 60 cc.

The isopentane was transferred to the calorimeter by distillation through a glass system to which the calorimeter was connected by a glass to metal seal. This system was connected to the high vacuum line and to the source of helium by means of stopcocks, which were greased with Apiezon grease M. The stopcocks were so placed as to be out of the direct distillation path. In transferring the first sample (Shell) to the calorimeter it was necessary to expose the isopentane to the air for a short time hence precautions were taken to remove any water, which might have gotten into the sample, by several distillations from phosphorus pentoxide in the closed system. The second sample (Aston) was received in a container that could be sealed directly into the transfer system before opening. In both cases the system and the sample were carefully outgassed by pumping with an oil diffusion pump while the isopentane was frozen in liquid air. After outgassing the

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[1] (a) Aston and Schumann, THIS JOURNAL, **64**, 1034 (1942); (b) Schumann, Aston and Sagenkahn, *ibid.*, **64**, 1039 (1942).

[2] Parks, Huffman and Thomas, *ibid.*, **52**, 1032 (1930).