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Hindered Rotation of the Methyl Groups in Propane. The Heat Capacity, Vapor Pressure, Heats of Fusion and Vaporization of Propane. Entropy and Density of the Gas

BY J. D. KEMP* AND CLARK J. EGAN

Evidence proving the existence of a high potential barrier which hinders the rotation of the methyl groups about the single carbon–carbon bond in ethane[1–3] has made apparent the need for more experimental data on the hindering potentials in similar molecules. Accordingly, the entropy of propane gas has been obtained experimentally from calorimetric data with the aid of the third law of thermodynamics, and has also been calculated as a function of the height of the potential barrier by means of spectroscopic and molecular structure data. The contributions of a hindered rotator to the entropy, energy, and heat capacity have been given by Pitzer.[4] The height of the potential barrier was determined as that necessary to bring the spectroscopic entropy value into agreement with the experimental entropy value.

Purification of Propane.—C. P. propane, of 99.9% purity, from the Ohio Chemical Company, was bubbled through 12 *N* sodium hydroxide and 36 *N* sulfuric acid. It was then passed through a tube containing phosphorus pentoxide and condensed in a previously evacuated bulb. The liquid was subjected to two successive fractionations in a vacuum-jacketed fractionating column, the middle 30% being retained each time. From the course of the heat capacity curve just below the melting point, the amount of liquid-soluble solid-insoluble impurity was estimated to be less than 0.001 mole per cent. The method of making this calculation has been described previously.[5] A less accurate value of 0.002 mole per cent. impurity was calculated from the change of the melting point in heating from 5 to 20% melted.

Apparatus and Measurement of Amount. The Density of Propane at 1 Atmosphere and 298.10°K.—The calorimetric apparatus and procedure have been described previously.[6,7] Gold Calorimeter IV was used for the investigation. The volume of the propane was determined by means of the 5-liter measuring bulb described by Giauque and Johnston.[8]

A gas density determination was made after each of the three heats of vaporization. The volumetrically measured propane was condensed and weighed in a glass bulb containing pentane, which reduced the vapor pressure of the propane. The molal volume of propane, V, at T near 298°K. and P near 1 atm. was found to be

$$V = \frac{82.06T}{P} - 401 \pm 7 \text{ cc.} \qquad (1)$$

This gives 1.8325 ± 0.0007 g./liter for the density of propane gas at 298.10°K. and 1 atm.

(*) Present address: Standard Oil Co., Richmond, Calif.

[1] Kemp and Pitzer, *J. Chem. Phys.*, **4**, 749 (1936); THIS JOURNAL, **59**, 276 (1937).

[2] Howard, *Phys. Rev.*, **51**, 53 (1937).

[3] Kistiakowsky and Nazmi, *J. Chem. Phys.*, **6**, 18 (1938).

[4] Pitzer, *ibid.*, **5**, 469 (1937).

[5] Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

[6] Kemp and Giauque, *ibid.*, **59**, 79 (1937).

[7] Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[8] Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

Vapor Pressure.—The procedure used in the measurements of vapor pressure has been described previously.[6] The observations have been represented by the equation

liquid propane, 166 to 231°K., (0°C. = 273.10°K.)

$$\log_{10} P_{(\text{Int. cm. Hg})} = -(1325.358/T) + 9.64920 - 0.0118950T + 0.000013420T^2 \quad (2)$$

A summary of the measurements is presented in Table I. The calculated and observed values are compared in columns 3 and 4. Temperatures have been given to 0.001° because of the high relative accuracy. The absolute temperatures may be in error by several hundredths of a degree. Column 5 contains values of the rate of change of pressure with temperature calculated from equation (2).

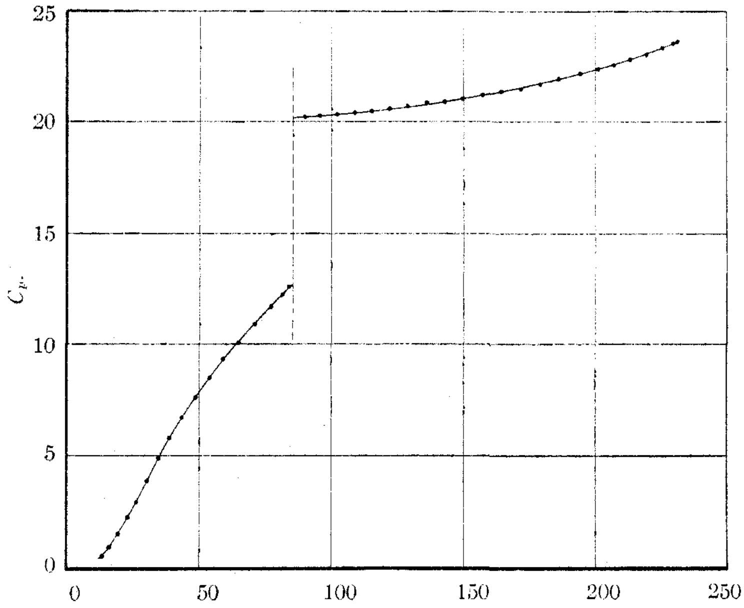

Fig. 1.—Heat capacity of propane in cal./deg. per mole.

TABLE I

VAPOR PRESSURE OF LIQUID PROPANE

(0°C. = 273.10°K.)

T, °K.	$P_{\text{int. cm.}}$ obsd.	$P_{\text{obsd.}} - P_{\text{calcd.}}$	$T_{\text{obsd.}} - T_{\text{calcd.}}$	$\frac{dP}{dT}\frac{\text{cm.}}{\text{deg.}}$
166.140	1.161	−0.003	+0.028	0.108
173.270	2.200	+ .002	− .011	.187
179.792	3.739	.000	.000	.292
187.297	6.544	.000	.000	.466
195.081	11.103	− .002	+ .003	.720
202.860	17.992	.000	.000	1.067
209.876	26.833	− .013	+ .009	1.472
214.932	35.166	.000	.000	1.827
220.209	45.913	+ .001	− .000	2.257
225.048	57.889	− .015	+ .006	2.708
228.756	68.619	− .032	+ .010	3.092
231.412	77.271	+ .014	− .004	3.392

TABLE II

MELTING POINT OF PROPANE

(0°C. = 273.10°K.)

Time	% melted	T, °K., resistance thermometer	T, °K. thermocouple
0:00		Stopped supply of heat	
0:55	5	85.428	85.43
1:27	5	85.424	85.43
2:00	5	85.426	85.43
2:15		Stopped supply of heat	
3:40	20	85.434	85.43
4:15	20	85.430	85.45
5:15	20	85.430	85.44
5:30		Stopped supply of heat	
7:00	40	85.436	85.45
7:30		Stopped supply of heat	
9:00	65	85.439	85.46
	Accepted value	85.45 ± 0.05°K.	

The boiling point calculated from equation (2) is 231.04 ± 0.05°K. (0°C. = 273.10°K.).

Melting Point.—The melting point was observed with various percentages of the propane melted. The results are summarized in Table II. Table III contains a summary of the melting and boiling point temperatures observed by other experimenters.

Heat Capacity of Propane.—No measured values of the heat capacity of condensed propane below the boiling point could be found in the literature.

The heat capacity measurements are given in Table IV. 1.0004 absolute joules was taken equal to 1 International joule and 4.185 absolute joules equal to 1 calorie. A graphical

TABLE III

MELTING AND BOILING POINT TEMPERATURES OF PROPANE

M. p., T, °K.	B. p., T, °K.	Observer
	228.1	Olszewski[9] (1894)
	229.0	Burrell and Robertson[10] (1915)
83.2	228.6	Maass and Wright[11] (1921)
	230.98	Dana, Jenkins, Burdick and Timm[12] (1926)
	230.8	Francis and Robbins[13] (1933)
86.0	230.93	Hicks-Bruun and Bruun[14] (1936)
85.45	231.04	This research

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(9) Olszewski, *Ber.*, **27**, 3305 (1894).

(10) Burrell and Robertson, THIS JOURNAL, **37**, 2188 (1915).

(11) Maass and Wright, *ibid.*, **43**, 1098 (1921).

(12) Dana, Jenkins, Burdick and Timm, *Refrig. Eng.*, **12**, 387 (1926).

(13) Francis and Robbins, THIS JOURNAL, **55**, 4339 (1933).

(14) Hicks-Bruun and Bruun, *ibid.*, **58**, 810 (1936).

representation is shown in Fig. 1. Table V contains values of the heat capacity taken from a smooth curve through the data.

TABLE IV

HEAT CAPACITY OF PROPANE

Molecular weight, 44.092;[15] 1.6779 moles in calorimeter.

T, °K.	C_p cal./deg. per mole	ΔT	Series
13.29	0.514	3.375	II
16.36	.865	2.795	II
19.60	1.504	3.705	II
23.11	2.257	3.315	II
26.57	2.970	3.609	II
30.51	3.864	4.221	II
34.58	4.870	3.915	II
38.85	5.785	4.590	II
43.68	6.682	5.132	II
48.91	7.593	5.219	II
54.48	8.471	4.899	II
59.10	9.328	5.447	II
64.87	10.08	5.947	II
70.96	10.87	6.373	II
77.05	11.69	5.733	II
81.32	12.21	2.673	II
83.60	12.42	1.851	III
83.84	12.60	2.551	II
84.75	12.70	0.438	III
85.14	13.14	.343	III
85.45	Melting point		
89.67	20.20	5.339	I
95.48	20.25	6.134	I
101.91	20.33	6.642	I
108.45	20.41	6.326	I
115.11	20.50	6.879	I
121.92	20.59	6.600	I
128.85	20.68	7.119	I
135.90	20.84	6.827	I
142.74	20.89	6.578	I
149.69	21.06	7.089	I
156.80	21.19	6.840	I
164.34	21.35	7.910	I
171.97	21.47	7.031	I
179.04	21.68	6.769	I
185.85	21.90	6.547	I
194.23	22.17	6.243	I
200.89	22.42	6.041	I
207.04	22.52	5.885	I
213.05	22.80	5.707	I
219.20	23.00	5.539	I
224.91	23.29	5.401	I
229.76	23.48	3.941	I
231.04	Boiling point		

Heat of Fusion.—No measured values of the heat of fusion were found in the literature. The present measurements of the heat of fusion of propane are summarized in Table VI.

TABLE V

HEAT CAPACITY OF PROPANE

Molecular weight, 44,092. Values taken from smooth curve through observations.

T, °K.	C_p cal./deg. per mole	T, °K.	C_p cal./deg. per mole
15	0.662	90	20.20
20	1.592	100	20.31
25	2.635	110	20.42
30	3.765	120	20.55
35	4.960	130	20.71
40	5.995	140	20.87
45	6.923	150	21.05
50	7.765	160	21.25
55	8.570	170	21.47
60	9.342	180	21.73
65	10.08	190	22.03
70	10.77	200	22.35
75	11.42	210	22.70
80	12.04	220	23.07
85	12.64	230	23.49
85.45	Melting point	231.04	Boiling point

TABLE VI

HEAT OF FUSION OF PROPANE

Molecular weight, 44.092

Temp. interval, °K.	Corr. heat input per mole	$\int C_p dT$	ΔH cal./mole
81.974–87.775	972.5	130.4	842.1
82.208–87.423	958.3	116.3	842.0
85.082–87.952	917.7	75.1	842.6

Average value = 842.2 ± 0.8 cal./mole

Heat of Vaporization.—The propane was vaporized from the calorimeter into the 5-liter measuring bulb mentioned previously. A constant pressure regulating device described by Giauque and Johnston[8] was used. The individual measurements are summarized in Table VII, and are compared with the value calculated from equation (2) and Berthelot's equation.[7] The value measured by Dana and co-workers[12] is also included.

TABLE VII

HEAT OF VAPORIZATION OF PROPANE

Boiling point, 231.04°K.; molecular weight, 44.092.

No. moles vaporized	Time of energy input, min.	ΔH at 760 mm. cal./mole
0.21634	38	4488
.21871	39	4487
.21865	39	4485

Average value = 4487 ± 4

From vapor pressure equation 2. This includes a Berthelot correction of −180 cal./mole	4475
Value of Dana, Jenkins, Burdick and Timm	4475 ± 45

Entropy from Calorimetric Data.—The calculation of the entropy of propane at the boiling point, 231.04°K., from the calorimetric data is summarized in Table VIII.

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(15) Int. At. Wt. Committee, THIS JOURNAL, 59, 219 (1937).

TABLE VIII

ENTROPY OF PROPANE FROM CALORIMETRIC DATA

0–15°K., Debye extrapolation, ($h c \nu / k$ = 128)	0.25
Solid, 15–85.45°K., graphical	9.702
Fusion, 842.2/85.45	9.856
Liquid, 85.45–231.04°K., graphical	21.063
Vaporization, 4487/231.04	19.421
Entropy of actual gas at boiling point	60.29 ± 0.1
Correction for gas imperfection	0.16
Entropy of ideal gas at 1 atm. and 231.04°K.	60.45 cal./deg. per mole

The correction for gas imperfection was obtained from the expression[7]

$$S_{\text{ideal}} - S_{\text{actual}} = (27RT_c^3P)/32T^3P_c$$

The values of the critical pressure and temperature were taken as T_c = 369.9°K. P_c = 42.01 atm.[16]

Magnitude of the Potential Barrier.—Although it would be more logical to evaluate the entropy due to the two degrees of freedom concerned with the internal rotation of the methyl groups and thereby estimate the magnitude of the potential barrier, it is more convenient to calculate an entropy value with the assumption of free internal rotation and evaluate $S_{\text{free}} - S_{\text{experimental}}$. With this quantity and a table of $S_{\text{free}} - S_{\text{hindered}}$ as a function of the potential barrier, the magnitude of the barrier may be obtained.

The values of the natural constants used were those given in the "International Critical Tables." The following data from the electron diffraction measurements of Bauer[17] were used to calculate the rotational contribution to the entropy.

$$\begin{aligned} \text{C–C} &= 1.50_3 \pm 0.02\ \text{Å}. \\ \text{C–H} &= 1.08_1 \pm 0.02\ \text{Å}. \\ \text{C–C–C} &= 114\overset{\circ}{1}2' \end{aligned}$$

The remaining H–C–H angles were assumed to be tetrahedral, namely, 109°28′. Kassel[18] has derived the partition function for freely rotating propane. The expression for the rotational entropy

$$S_{\text{free rotation}} = R/2 \ln (I_x - 2K \sin^2\alpha)(I_y - 2K \cos^2\alpha)(I_z)(K)^2 + 5/2\, R \ln T - R \ln \sigma + 447.599$$

may be separated into the usual expression

$$S_{\text{external rotation}} = R/2 \ln I_xI_yI_z + 3/2\, R \ln T - R \ln 2 + 267.649$$

plus

$$S_{\text{free internal rotation}} = R/2 \ln (I_r)^2 + R \ln T - R \ln 9 + 179.950$$

where the reduced moment

$$(I_r)^2 = (K)^2 \left(1 - \frac{2K \sin^2\alpha}{I_x}\right)\left(1 - \frac{2K \cos^2\alpha}{I_y}\right)$$

K = moment of inertia of a methyl group. α = one-half of the C–C–C angle. I_z = moment of inertia about the axis through the center of gravity and perpendicular to the carbon plane. I_y = moment of inertia about the axis which bisects the C–C–C angle in the carbon plane. I_x = moment of inertia about the axis through the center of gravity and perpendicular to both y and z axes.

From the above data the moments of inertia times 10^{40} g. cm.^{2} were found to be I_x = 26.9; I_y = 96.8; I_z = 108.2; K = 5.18; I_r^2 = 18.93. The symmetry number σ was taken equal to 18.

Kohlrausch and Köppl[19] have summarized the Raman data on propane. They have also included the results of Bartholomé[20] on the infrared spectrum of propane. The three vibrations of the carbon skeleton have been identified at 373, 867 and 1053 cm.$^{-1}$. For the calculation of the vibrational contribution to the entropy, the remaining frequencies were estimated as follows: seven at 950 cm.$^{-1}$, seven at 1440 cm.$^{-1}$ and eight at 3000 cm.$^{-1}$.[21]

The sum of the translational, rotational and vibrational entropies of freely rotating propane was calculated to be 63.85 ± 0.25 cal./deg. per mole at one atmosphere at the boiling point, 231.04°K. The disagreement of this value with the experimental value, 60.45 ± 0.10 cal./deg. per mole, indicates that the rotation of the methyl groups in propane is hindered rather than free. Although lack of equilibrium in the crystal at low temperatures has caused discrepancies in the experimental and spectroscopic entropy values of several molecules, the reasons for this lack of equilibrium are known and such an explanation for the disagreement in the case of propane as in the cases of ethane,[1] tetramethylmethane[22] and methylamine[23] seems very improbable. Pitzer,[21] by interpolating the values of the barriers present in similar molecules, has predicted a hindering potential of 3400 cal./mole for propane.

The difference, $S_{\text{free}} - S_{\text{experimental}}$, was found to be 3.40 ± 0.3 cal./deg. per mole at the boiling point. This amount of entropy corresponds to a

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(16) Beattie, Poffenberger and Hadlock, *J. Chem. Phys.*, **3**, 96 (1935).

(17) Bauer, *ibid.*, **4**, 406 (1936).

(18) Kassel, *ibid.*, **4**, 276 (1936).

(19) Kohlrausch and Köppl, *Z. physik. Chem.*, **B26**, 209 (1934).

(20) Bartholomé, *ibid.*, **B23**, 152 (1933).

(21) Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

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

(23) Aston, Siller and Messerly, *ibid.*, **59**, 1743 (1937).

barrier of 3300 ± 400 cal./mole,[24] which is in excellent agreement with the predicted value mentioned above. The entropy at 298.10°K. has been calculated to be 64.7 ± 0.3 cal./deg. per mole from molecular and spectroscopic data, the experimental value of the potential barrier and the experimental value of the entropy at the boiling point. This value at 298.10°K. is the entropy to be used in thermodynamic calculations.

In these calculations the nuclear spin entropy, $8 R \ln 2 = 11.015$ cal./deg. per mole, has been neglected. Table IX contains a summary of the calculations.

TABLE IX

CALCULATION OF THE MAGNITUDE OF THE POTENTIAL BARRIER IN PROPANE

	$T = 231.04°$K. $P = 1$ atm. cal./deg. per mole	$T = 298.10°$K. $P = 1$ atm.
$S_{\text{trans.}} = 3/2\ R \ln M + 5/2\ R \ln T - R \ln P - 2.300$	36.02	37.28
$S_{\text{external rotation}} = R/2 \ln I_x I_y I_z \times 10^{120} + 3/2\ R \ln T - R \ln 2 - 6.851$	20.46	21.22
$S_{\text{free internal rotation}} = R/2 \ln I_r^2 \times 10^{80} + R \ln T - R \ln 9 - 3.050$	6.32	6.83
$S_{\text{vibrat.}} = \Sigma_{\nu_1 \text{ to } \nu_{25}} S_{\text{Einstein}}$	1.05	2.22
	63.85 ± 0.25	67.55
Calorimetric entropy	60.45 ± 0.10	
$S_{\text{free}} - S_{\text{hindered}}$	3.40 ± 0.3	2.86
Entropy of propane with a potential barrier of 3300 cal./mole (nuclear spin entropy not included)		64.7 ± 0.3

Summary

The heat capacity of condensed propane has been measured from 15°K. to the boiling point. The melting point was found to be 85.45 ± 0.05°K., the boiling point 231.04 ± 0.05°K., the heat of fusion 842.2 ± 0.8 cal./mole and the heat of vaporization 4487 ± 4 cal./mole.

Vapor pressure measurements have been made on liquid propane and the results have been represented by the equation (liquid propane, 166 to 231°K. (0°C. = 273.10°K.))

$$\log_{10} P_{(\text{Int. cm. Hg})} = -(1325.358/T) + 9.64920 - 0.0118950T + 0.000013420T^2$$

The density of propane gas at 298.10°K. and one atmosphere was found to be 1.8325 ± 0.0007 g./liter.

At one atmosphere at the boiling point the experimental entropy of propane (ideal gas) was evaluated as 60.45 ± 0.10 cal./deg. per mole.

The entropy of propane calculated with the assumption of free internal rotation minus the experimental entropy, $S_{\text{free}} - S_{\text{experimental}}$ (at the boiling point), was found to be 3.40 ± 0.3 cal./deg. per mole, which corresponds to a potential barrier of 3300 ± 400 cal./mole hindering the internal rotation of the methyl groups.

The entropy of propane (ideal gas, with a 3300 cal./mole barrier) at one atmosphere and 298.10°K. was found to be 64.7 ± 0.3 cal./deg. per mole (nuclear spin entropy not included). This is the entropy value to be used in thermodynamic calculations.

BERKELEY, CALIF.

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[24] Refer to Table I of ref. 4.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Vapor Pressure Studies. I. Evidence for the Validity of Raoult's Law. The Systems Benzene–Diphenyl, Benzene–Benzyl Benzoate, Ethyl Acetate–Benzyl Benzoate

BY H. H. GILMANN[1] AND PAUL GROSS

Attention recently has been drawn[2] to the paucity of direct experimental evidence which is available in support of Raoult's law. In view of its importance for modern solution theory and because of the difficulty of giving a general theoretical foundation to the law, the desirability[3] of adding to this evidence has been emphasized.

In connection with a study of the stability of addition compounds in non-aqueous systems as indicated by partial pressure determinations, partial pressure data were also obtained for certain binary systems consisting of a volatile and a non-volatile component. Some of these cases furnish evidence bearing on the validity of Raoult's law.

The systems in question are benzene–diphenyl, benzene–benzyl benzoate and ethyl acetate–benzyl benzoate. Benzyl benzoate boils at 324°

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[1] Part of a thesis of H. H. Gilmann submitted in partial fulfilment of the requirements for the Ph.D. in Chemistry.

[2] Guggenheim, *Trans. Faraday Soc.*, **33**, 161 (1937).

[3] Hildebrand, THIS JOURNAL, **59**, 794 (1937).