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The Thermodynamic Properties of 1,1-Dichloroethane: Heat Capacities from 14 to 294°K., Heats of Fusion and Vaporization, Vapor Pressure and Entropy of the Ideal Gas. The Barrier to Internal Rotation[1]

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The heat capacity of 1,1-dichloroethane has been measured from 14 to 294°K. The melting point is found to be 176.18 ± 0.05°K. The heat of fusion is 1881 ± 2 cal./mole and the heat of vaporization 7409 ± 7 cal./mole at 293°K. The vapor pressure has been measured from 234 to 290°K. The entropy of the liquid and the ideal gas have been calculated to be 50.61 ± 0.10 and 72.89 ± 0.15 cal./mole deg., respectively, at 298.16°K. and 1 atm. The value for the ideal gas is compared with the result from molecular data. The thermodynamic properties of the ideal gas are tabulated from 200 to 1000°K. The barrier to internal rotation is found to be higher than that for either ethane or 1,1,1-trichloroethane.

This report presents the results of a low temperature calorimetric investigation on 1,1-dichloroethane. The purpose was to determine the entropy from the third law of thermodynamics and to compare this with the result from molecular data. Data for this compound complete the series: ethane, chloroethane, 1,1-dichloroethane and 1,1,1-trichloroethane and allows discussion of the trend in the potential barrier to internal rotation.

The results are presented in terms of the defined thermochemical calorie; the ice point is taken as 273.16°K.

The Purity and the Melting Point.—Commercially available 1,1-dichloroethane was purified first by fractional distillation and then by recrystallization three times. The purity achieved was calculated as 99.87% from the change in melting point as a function of the fraction melted. A plot of the temperature against the reciprocal of the fraction melted, using the data shown in Table I, showed conformity to Raoult's law. The true melting point was obtained by extrapolation to $1/F = 0$, and was found to be 176.18 ± 0.05°K. The impurity was probably methylchloroform, as found by Daasch, *et al.*,[2] and if this was so, the uncertainty introduced in the results was quite negligible.

TABLE I

MELTING POINT OF 1,1-DICHLOROETHANE

Fraction melted	Temp., °K.	Fraction melted	Temp., °K.
0.07	175.50	0.36	176.06
.10	175.74	.70	176.13
.13	175.84	.90	176.13
.18	175.93	∞ (extrapolation)	176.18

The Heat Capacities.—The measurement of heat capacities is a standard technique in this Laboratory. Detailed descriptions can be found in previous papers.[3] The calorimeter was made of gold and had a capacity of 100 ml. The thermocouple located at the bottom of the calorimeter was originally calibrated by gas thermometry and was checked at the triple and boiling points of both hydrogen and nitrogen in the present series of measurements. The resistance thermometer was then calibrated against the thermocouple. A new resistance–temperature table was made and smoothed to the second differences.

The observed heat capacities, with no correction for premelting, are listed in Table II and the smoothed values in Table III where a correction is made for premelting. The smoothed values are believed to represent the true heat capacity within 0.1–0.2% above 50°K., 0.5% from 20 to 50°K., and 1% below 20°K. The liquid heat capacities close to room temperature were corrected for the small heat effect due to vaporization into the space above the liquid. The temperature rise in each run can be judged from the spacing of the reported mean temperatures.

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[1] This research was assisted by the American Petroleum Institute through Research Project 50.

[2] L. W. Daasch, C. Y. Liang and J. R. Nielsen, *J. Chem. Phys.*, **22**, 1293 (1954).

[3] W. F. Giauque and C. J. Egan, *ibid.*, **5**, 45 (1937).

TABLE II

EXPERIMENTAL HEAT CAPACITIES OF 1,1-DICHLOROETHANE

Temp., °K.	C_p, cal./deg. mole
Series I	
14.17	1.56
15.53	1.94
18.85	2.92
21.12	3.61
23.28	4.23
25.24	4.75
27.05	5.20
29.37	5.71
31.83	6.29
34.66	6.93
38.01	7.64
41.26	8.21
44.23	8.64
47.40	9.15
Series II	
41.04	8.19
42.48	8.40
44.62	8.70
47.14	9.06
49.70	9.37
53.30	9.77
56.59	10.10
59.55	10.40
62.31	10.68
64.91	10.94
67.47	11.20
70.51	11.51
74.61	11.87
78.90	12.27
83.63	12.66
89.21	13.12
95.42	13.59
102.66	14.13
110.18	14.75
117.39	15.33
124.62	15.92
131.91	16.48
138.59	16.98
144.82	17.51
150.63	18.00
156.89	18.58
163.48	19.71
170.02	22.96
Series III	
146.00	17.60
153.06	18.15
159.64	18.95
165.75	20.45
171.12	24.35
Series IV	
177.06	28.57
182.26	28.58
188.11	28.62
193.75	28.73
199.22	28.78
203.58	28.79
209.25	28.82
215.55	28.84
222.70	28.95
229.50	29.04
237.46	29.17
244.88	29.18
252.59	29.39
260.25	29.47
264.94	29.62
273.85	29.77
283.78	29.87
294.26	30.11

TABLE III

SMOOTHED HEAT CAPACITIES OF 1,1-DICHLOROETHANE

Temp., °K.	C_p, cal./deg. mole	Temp., °K.	C_p, cal./deg. mole
15	1.78	160	18.86[a]
20	3.27	170	19.77[a]
25	4.43	176.18	20.33[a]
30	5.90	(melting point)	
35	6.99	176.18	28.55
40	7.96	180	28.58
45	8.77	190	28.65
50	9.42	200	28.73
60	10.45	210	28.83
70	11.42	220	28.93
80	12.32	230	29.05
90	13.12	240	29.18
100	13.93	250	29.33
110	14.72	260	29.48
120	15.48	270	29.65
130	16.28	280	29.83
140	17.11	290	30.02
150	17.97	300	30.22

[a] Corrected for premelting.

The only heat capacity measurements for 1,1-dichloroethane in the literature are those of Kurbatov's.[4] His measurements were relatively crude and show deviations from our results by as much as 4%.

Vapor Pressure.—The vapor pressure was measured by means of a mercury manometer of 1.6 cm. inside diameter. A cathetometer with a precision of measurement of 0.002 cm. was used and calibrated against a standard meter bar suspended between the arms of the manometer. The results were reduced to international cm. of mercury at 0° and standard acceleration of gravity. An empirical equation was obtained from 15 measurements between 234 and 290°K. as

$$\log_{10} p_{\mathrm{cm}} = 6.1560 - 1258.1/(T - 36)$$

A comparison of the observed and calculated values is shown in Table IV.

TABLE IV

VAPOR PRESSURE OF 1,1-DICHLOROETHANE

Temp., °K.	$p_{\mathrm{obsd.}}$, cm.	$p_{\mathrm{obsd.}} - p_{\mathrm{calcd.}}$, cm.	Temp., °K.	$p_{\mathrm{obsd.}}$, cm.	$p_{\mathrm{obsd.}} - p_{\mathrm{calcd.}}$, cm.
234.38	0.644	−0.008	260.96	3.652	−0.008
243.55	1.237	− .006	270.93	6.319	.000
252.95	2.265	− .010	274.32	7.558	.025
253.98	2.426	.003	284.24	12.251	.007
254.30	2.476	.005	284.48	12.403	.020
255.47	2.638	− .014	290.64	16.408	− .009
256.34	2.787	− .007	290.76	16.502	− .003
260.55	3.579	.005			

There are two sets of vapor pressure data available in the literature covering the temperature range of our measurement. The older one is that of Rex[5] whose values are lower than ours by approximately 1% in the temperature range 273 to 303°K. The other set is that of Stull[6] whose values are based upon data from the literature and the Dow Chemical Company files and are lower than ours by 2 to 3% in the range 231 to 296°K. The disagreement may result from a much smaller percentage difference in the temperature scale, since Stull considered the possible error in his temperatures to be a few tenths of a degree.

Heat of Fusion and Vaporization.—The heat of fusion was measured in the usual manner. Correction was made for the heat of premelting. The results are shown in Table V, where the heat absorbed in heating the solid to the melting point and the liquid to the final temperature is not listed but can be obtained by difference.

TABLE V

HEAT OF FUSION OF 1,1-DICHLOROETHANE

Initial and final temp., °K.	Energy input, cal./mole	Heat of pre-melting, cal./mole	Heat of fusion, cal./mole
172.77 to 182.47	2207.2	28.43	1880
173.39 to 181.60	2150.6	32.98	1881
174.00 to 183.08	2186.4	37.89	1882
		Av.	1881 ± 2

The heat of vaporization was measured by vaporizing through a suitable capillary tube into a bulb

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[4] V. Ya. Kurbatov, *Zhur. Obshchei Khim* (*J. Gen. Chem.*), **18**, 372 (1948).

[5] A. Rex, *Z. physik. Chem.*, **55**, 355 (1906).

[6] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

immersed in liquid nitrogen. The function of the capillary tube was to maintain a constant pressure difference at a constant flow rate. The temperature of vaporization and the rate of energy supply were so adjusted that the temperature of the calorimeter would change very little during measurement. The results are shown in Table VI; the average heat of vaporization was 7409 ± 7 cal./mole. The value calculated from vapor pressure data is also listed for comparison. In the calculation, the Clapeyron equation was used together with the Berthelot equation of state with critical constants given by Stull,[6] namely, $P_c = 50$ atm. and $T_c = 261.5°$. O'Hara and Fahien[7] have calculated the heat of vaporization from Stull's data. Their result is lower by about 50 cal./mole.

TABLE VI

HEAT OF VAPORIZATION OF 1,1-DICHLOROETHANE

Sample wt., g.	Av. temp., °K.	Max. temp. variation	Heat of vaporization,[a] cal./mole
4.961	293.00	0.08	7405
8.522	293.10	.10	7405
14.222	293.00	.18	7407
14.421	293.26	.83	7421
		Av.	7409 ± 7
Calcd. from vapor pressure of this work			7401

[a] Corrected to 293°K. on the basis of $\Delta C_p = -12$ cal./mole °K.

The Entropy from the Third Law of Thermodynamics.—The entropy was calculated from numerical integration of C_p/T against T using Simpson's rule. Two degree intervals were used for the solid and five degree intervals for the liquid. The entropy at 14°K. was calculated by extrapolating with the aid of a Debye function with six degrees of freedom. The resulting θ is nearly constant in the range 14–20°K. and a value of 116° was selected for the extrapolation. The calculation is summarized in Table VII. The difference in entropy from actual gas to ideal gas was calculated by assuming the Berthelot equation of state. The third law value of the entropy of the ideal gas at 298.16°K. and one atm. is 72.89 ± 0.15 cal./mole deg.

TABLE VII

ENTROPY OF 1,1-DICHLOROETHANE, CAL./DEG. MOLE

0 to 14°K. (extrapolation) ($\theta_D = 116°$)	0.531
14 to 176.18°K. (m.p.)	24.062
Fusion 1881/176.18	10.677
176.18 to 298.16°K. (liq.)	15.336
Liq. at 298.16°K.	50.606 ± 0.10
298.16 to 293°K.	−0.526
Vaporization 7409/293	25.287
Actual vapor at 293°K. and 18.20 cm.	75.367
$S^0 - S_{\text{actual}}$ (Berthelot eq.)	0.049
Compression (18.20 cm. to 1 atm.)	−2.841
294 to 298.16°K. ($C_p^0 = 18.05$)	0.314
Ideal gas at 298.16°K. and 1 atm.	72.89 ± 0.15

An interesting comparison of the entropy of ideal gaseous 1,1-dichloroethane with that of 1,2-dichloroethane was made by considering just the effect of the symmetry numbers of 3 and 2, respectively. This is equivalent to a consideration of the number of ways of arranging the two chlorine atoms. The entropy of ideal gaseous 1,2-dichloroethane given by Gwinn and Pitzer[8] is 73.66 cal./mole deg. at 298.1°K. and one atm. and is 0.77 higher than that of 1,1-dichloroethane. The calculated difference of $R \ln (3/2) = 0.81$ agrees well within the experimental error. This implies a precise cancellation of all other possible entropy differences between these isomers. Such precise cancellation is undoubtedly fortuitous.

Potential Barrier Hindering Internal Rotation and the Thermodynamic Properties of Ideal Gas.—From the third law of entropy, it is possible to calculate the contribution due to the internal rotation. The potential barrier can then be estimated by assuming a 3-fold cosine potential energy function using the table of Pitzer and Gwinn.[9]

The assignments of the vibrational frequencies by Daasch, Liang and Nielsen[2] were examined with the substitution product rule as shown in Table VIII for the series: CH_3CH_3, CH_3CH_2Cl, CH_3CHCl_2 and CH_3CCl_3. The calculation was based on the reduced moments of inertia for internal rotation in order to avoid possible uncertainties in torsional frequencies. The product ratios[10] for the substitution of Cl for H in methane derivatives are also listed for comparison. While the ratios show greater variation than might be expected, it was concluded that the assignments were consistent with respect to the four molecules. The calculations[11] for vibrational contributions were therefore based on the assignment of Daasch, Liang and Nielsen,[2] namely, 277, 317, 405, 651, 705, 982, 1058, 1094, 1239, 1282, 1383, 1445, 1445, 2873, 2941, 2986 and 3012 cm.$^{-1}$. The vibrational contribution to the entropy at 298.16°K. was calculated to be 4.845 cal./mole deg., which differs slightly from the value 4.802 of Daasch, *et al.*,[2] for some unknown reason.

TABLE VIII

PRODUCT RATIOS FOR THE SUBSTITUTION PRODUCT RULE

Substitution	One bending motion	Sym.	One bending and one stretching motion	Sym.
CH_3CH_3[12] to CH_3CH_2Cl[2]	0.114	A″	0.0167	A′
CH_3CH_2Cl to CH_3CHCl_2[2]	.178	A′	.0168	A″
CH_3CHCl_2 to CH_3CCl_3[13]	.147	A″	.0200	A′
CH_3CH_3 to CH_3CCl_3	.109	A_2	.0232	A_1
Methane derivatives[10]	0.11 to 0.16	..	0.015 to 0.020	..

The moments of inertia for external rotation were calculated from the interatomic distances and the bond angles given by Daasch, *et al.*[2] The average chemical atomic weight was used for each atom. For the axis perpendicular to the plane of symme-

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(7) (a) J. B. O'Hara and R. W. Fahien, *Ind. Eng. Chem.*, **43**, 2924 (1951); (b) Document 3327, Am. Doc. Inst., Washington, D. C.

(8) W. D. Gwinn and K. S. Pitzer, *J. Chem. Phys.*, **16**, 303 (1948).

(9) K. S. Pitzer and W. D. Gwinn, *ibid.*, **10**, 428 (1942).

(10) K. S. Pitzer and E. Gelles, *ibid.*, **21**, 855 (1953).

(11) The calculations were performed with the aid of the Table of Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom published by the Office of Naval Research, Department of the Navy, Washington, D. C.

(12) G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952).

(13) K. S. Pitzer and J. L. Hollenberg, THIS JOURNAL, **75**, 2219 (1953).

try, the moment of inertia was calculated to be 128.9 × 10^{-40} g. cm.^{2}. The other two principal moments of inertia were 264.5 and 371.1 × 10^{-40} g. cm.^{2}, respectively. The axis for the intermediate moment makes an angle with the C–C bond of 22° 19′. The results were again slightly different from those of Daasch, *et al.*[2] The contribution to entropy for translation and external rotation was then calculated to be 66.022 cal./mole deg. at 298.16°K. and 1 atm.

Using the third law entropy, 72.89 ± 0.15, obtained from this work, the contribution due to internal rotation is 2.02 ± 0.15 cal./mole deg. The reduced moment of inertia for internal rotation is 5.20 × 10^{-40} g. cm.^{2}. From these values, the height of the potential barrier is calculated to be 3550 ± 450 cal./mole from the table of Pitzer and Gwinn.[9] The tentative value of 3750 cal./mole of Daasch, *et al.*, which is based on a faint Raman line of 239 cm.$^{-1}$, lies within the experimental error of our result. Furthermore, an unpublished infrared spectrum of liquid 1,1-dichloroethane measured in this Laboratory by Mr. Roger C. Millikan shows a weak band at 240 cm.$^{-1}$. The spectrum of the gas failed to show this band; possibly the intensity arises chiefly from liquid state perturbations. In any event we believe that the internal rotation fundamental should be assigned to the 239 cm.$^{-1}$ frequency.

The thermodynamic properties of ideal gaseous 1,1-dichloroethane are tabulated in Table IX using 3750 cal./mole for the potential barrier for internal rotation. The values differ slightly from the table of Daasch, Liang and Nielsen[2] because of the differences already mentioned.

TABLE IX

THERMODYNAMIC PROPERTIES OF IDEAL GASEOUS 1,1-DICHLOROETHANE

Temp., °K.	$C_p°$, cal./deg. mole	$H° - H_0°$, cal./mole	$-(F° - H_0°)/T$, cal./deg. mole	$S°$, cal./deg. mole
200	14.45	2,078	55.95	66.34
250	16.37	2,847	58.38	69.77
273.16	17.27	3,238	59.41	71.26
298.16	18.22	3,682	60.47	72.82
300	18.29	3,716	60.54	72.93
400	21.85	5,727	64.37	78.69
500	24.82	8,066	67.76	83.89
600	27.24	10,672	70.85	88.64
700	29.21	13,497	73.71	92.99
800	30.85	16,503	76.37	97.00
900	32.25	19,657	78.87	100.72
1000	33.45	22,945	81.23	104.18

We turn now to the comparison of potential barriers for similar compounds. First let us consider the situation for ethyl chloride. Gordon and Giauque[14] report a barrier of 3700 cal./mole from their experimental entropy value; Wagner and Dailey[15] find 3000 cal./mole from the relative intensities of microwave lines; Daasch, Liang and Nielsen[2] interpret a very weak infrared band at 276 cm.$^{-1}$ to be the internal rotation frequency and calculate a barrier of 4470 cal./mole. In addition Eucken and Franck[16] measured the heat capacity of ethyl chloride gas and interpreted their data in terms of a 2700 cal. barrier. Their interpretation must be revised in view of more recent spectroscopic studies, but their heat capacity data cannot be reconciled with the vibrational assignment of Daasch, *et al.*[2] However, the recent spectra can be interpreted with somewhat higher C–H wagging and rocking frequencies than were chosen by Daasch, *et al.* Then one can obtain agreement, within experimental error, with the data of Eucken and Franck, provided the potential barrier is in the range 3600 to 4000 cal./mole. While considerable uncertainty still remains, it seems to us most likely that the potential barrier for ethyl chloride is near the value 3700 cal./mole given by Gordon and Giauque.

We are now in a position to compare the potential barriers for the series of chloroethanes as follows: CH_3–CH_3, 2875 ± 125[17]; CH_3–CH_2Cl, 3700; CH_3–$CHCl_2$, 3750; and CH_3CCl_3, 2950.[13] The surprising maximum in the middle of this sequence appears to be outside of experimental error although one cannot be certain. Simple theories[18] which consider the total barrier as a sum of terms for bond or atom interactions necessarily yield a linear sequence of values and cannot explain this maximum. We believe that the explanation probably lies in the crowding of the chlorine atoms at the C–Cl bond distance around a single carbon atom. Urey and Bradley[19] showed that the vibrational spectrum of carbon tetrachloride indicated large Cl–Cl forces. If this crowding forces the electron clouds of the chlorine atoms in the CCl_3 group to fill more uniformly the space between atoms, then the torsional interaction with the CH_3 group would be lessened because the electron cloud repulsions would vary less with internal rotation than would have been expected from the uncrowded chlorine atom in ethyl chloride.

The available values for the potential barriers in the series CH_3CH_3, CH_3CH_2F, CH_3CHF_2 and CH_3CF_3 are 2875 ± 125, 4260 ± 150, 3700 ± 600 and 3700 ± 450 cal./mole, where the last three values are from the summary of Kraitchman and Dailey.[20] Again the substitution of the first halogen causes a large increase in barrier while further additions cause little change or even a decrease.

This peculiar trend of barrier heights deserves further attention, both to confirm its reality and to understand its cause.

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[14] J. Gordon and W. F. Giauque, THIS JOURNAL, **70**, 1506, 4277 (1948).

[15] R. S. Wagner and B. P. Dailey, *J. Chem. Phys.*, **22**, 1459 (1954).

[16] A. Eucken and E. U. Franck, *Z. Elektrochem.*, **52**, 195 (1948).

[17] K. S. Pitzer, *Disc. Faraday Soc.*, **10**, 66 (1951).

[18] For example, N. W. Luft, *J. Chem. Phys.*, **22**, 1814 (1954).

[19] H. C. Urey and C. A. Bradley, *Phys. Rev.*, **38**, 1969 (1931); see also Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

[20] J. Kraitchman and B. P. Dailey, *J. Chem. Phys.*, **23**, 184 (1955).