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Citation: *The Journal of Chemical Physics* **16**, 303 (1948); doi: 10.1063/1.1746873

View online: <http://dx.doi.org/10.1063/1.1746873>

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Gas Heat Capacity and Internal Rotation in 1,2-Dichloroethane and 1,2-Dibromoethane

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(Received October 31, 1947)

The gas heat capacity of 1,2-dichloroethane was measured in the temperature interval from 356°K to 556°K. The gas heat capacity of 1,2-dibromoethane was measured in the temperature interval from 383°K to 473°K. A potential barrier to internal rotation for 1,2-dichloroethane was selected which is in agreement with all of the data on heat capacity, entropy, and dipole moment of the gaseous molecule. An approximate barrier to internal rotation was selected for 1,2-dibromoethane.

INTRODUCTION

THE problems of internal rotation in dichloroethane and dibromoethane have been studied by a number of investigators using various experimental methods. The dipole moment¹⁻⁷ has been measured and discussed. The electron diffraction data⁸⁻¹⁰ have shown that there must be a high barrier restricting internal rotation. The low temperature heat capacity and entropy¹¹ have been measured. The Raman spectrum¹²⁻¹⁴ has been studied in great detail. In the work about to be described, the gas heat capacities of the two compounds were measured and potential functions for internal rotation were selected which are in the best agreement with all of the experimental results.

EXPERIMENTAL METHOD AND RESULTS

The dichloroethane was purified by fractionation in a 25-plate column at atmospheric pressure. It was then dried with anhydrous calcium chloride in one sample and anhydrous magnesium sulfate in the other sample. The dibromoethane was fractionated in the same column at 16-cm pressure and then dried with anhydrous calcium chloride. The heat capacities of the two gases were measured in a flow calorimeter, which has been described by Pitzer.¹⁵

In Tables I and II the experimental heat capacities are given. In the last column the heat capacities of the hypothetical perfect gas are given. The corrections for the effect of gas imperfection were calculated from the critical constants of Nadejine¹⁶ and Vespignani.¹⁷ Berthelot's equation of state was assumed. In order to remove any uncertainties arising from this calculation, the heat capacity at 380°K was measured at two pressures and extrapolated to zero pressure. The resulting values of $\partial C_p / \partial p$ were 0.36 cal./mole deg. atmos., calculated from the experimental extrapolation, and 0.30 cal./mole deg. atmos. from Berthelot's equation.

THERMODYNAMIC PROPERTIES CONTRIBUTED BY INTERNAL ROTATION

The heat capacity contributed by internal rotation may be obtained by subtracting from the experimental heat capacity the heat capacity contributed by all other degrees of freedom.

¹ C. T. Zahn, *Phys. Rev.* **40**, 291 (1932); **38**, 521 (1931).

² J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.* **6**, 635 (1938).

³ W. Altar, *J. Chem. Phys.* **3**, 460 (1935).

⁴ J. E. Lennard Jones and H. H. M. Pike, *Trans. Faraday Soc.* **30**, 830 (1934).

⁵ C. P. Smyth, R. W. Dornste, and E. B. Wilson, Jr., *J. Am. Chem. Soc.* **53**, 4242 (1931).

⁶ I. Wantanabe, S. Mizushima, and Y. Morino, *Sci. Pap. I.P.C.R. (Tokyo)* **39**, 401 (1942).

⁷ E. W. Greene and J. W. Williams, *Phys. Rev.* **42**, 119 (1932).

⁸ J. Y. Beach and K. J. Palmer, *J. Chem. Phys.* **6**, 635 (1938).

⁹ J. Y. Beach and A. Turkevich, *J. Am. Chem. Soc.* **61**, 303 (1939).

¹⁰ S. Yamaguchi, Y. Morino, I. Watanabe, and S. Mizushima, *Sci. Pap. I.P.C.R. (Tokyo)* **40**, 417 (1943).

¹¹ K. S. Pitzer, *J. Am. Chem. Soc.* **62**, 331 (1940).

¹² Mizushima and Morino, *Bull. Chem. Soc. Japan* **17**, 94 (1942); Mizushima, Morino, and Simanouti, *Sci. Pap. I.P.C.R. (Tokyo)* **40**, 87 (1943).

¹³ Ta-You Wu, *Vibration Spectra and Structure of Polyatomic Molecules* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1946), second edition, pp. 306-312.

¹⁴ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., 1945), pp. 346-351.

¹⁵ K. S. Pitzer, *J. Am. Chem. Soc.* **63**, 2413 (1941). For later modifications see K. S. Pitzer and W. D. Gwinn, *J. Am. Chem. Soc.* **63**, 3313 (1941), and R. Spitzer and K. S. Pitzer, *J. Am. Chem. Soc.* **68**, 2537 (1946).

¹⁶ Nadejine, *Rep. de Phys.* **23**, 638 (1887).

¹⁷ Vespignani, *Gass. chimital* **33**, 73 (1903).

TABLE I. Heat capacity of 1,2-dichloroethane; units are calories/mole deg.

$T^{\circ}\text{K}$	P	C_p	$C_p - C_p^{\circ}$	C_p°
383	1 atmos.	21.82	0.30	21.52
399	1 atmos.	22.22	0.26	21.96
429	1 atmos.	22.90	0.21	22.69
463	1 atmos.	23.85	0.15	23.70
Same calorimeter with a floating heater in vaporizing unit.				
356	25 cm	20.47	0.10	20.37
380	25 cm	21.36	0.10	21.26
380	1 atmos.	21.60	0.30	21.30
556	1 atmos.	26.02	0.10	25.92
With an older calorimeter.				
383	1 atmos.	21.8	0.30	21.5
415	1 atmos.	22.5	0.24	22.3

TABLE II. Heat capacity of 1,2-dibromoethane; units are calories/mole deg.

$T^{\circ}\text{K}$	P	C_p	$C_p - C_p^{\circ}$	C_p°
383	16 cm	23.19	0.05	23.14
429	16 cm	24.61	0.04	24.57
473	16 cm	25.89	0.03	25.86

To obtain the vibrational heat capacity, the vibrational assignment of Wu¹³ was used. There are two sets of frequencies. One set corresponds to the *trans* configuration with C_{2h} symmetry, and the other set corresponds to the skew configuration with C_2 symmetry. The skew configuration is obtained from the *trans* configuration by an internal rotation of 120° , and has sometimes been called the *gauche* form or the 120° form. Wu assigns the two sets of frequencies on the basis of the C_{2h} and C_{2v} (*cis*) form. The same frequencies which Wu assigned on the basis of a C_{2v} model can be reassigned with little difficulty on the basis of a C_2 model. The only serious discrepancy arising from this reassignment is that the frequency at 124 cm^{-1} , which is listed as depolarized, should be polarized.

All of the frequencies of *trans*-dichloroethane are given except one, the unsymmetrical bending of the C—C—Cl bond angles. Recently Mizushima, Morino, and Simanouti¹² have observed a very weak Raman line at 223 cm^{-1} , which they interpret as a forbidden transition corresponding to the missing frequency. A normal coordinate analysis of the Cl—C—C—Cl skeleton confirms that the 223 cm^{-1} is a reasonable value for the unknown frequency. In any event the value should be lower than the corresponding symmetrical vibration at 300 cm^{-1} . Since the heat capacity associated with a vibrational frequency

TABLE III. Heat capacity contributed by internal rotation in 1,2-dichloroethane; units are cal./mole deg.

$T^{\circ}\text{K}$	356	383	428	473	556
C_p° (exp)	20.37	21.45	22.69	23.86	25.92
C (tran. + rot.) + R	7.948	7.948	7.948	7.948	7.948
$C_{\text{(vib)}}$	9.57	10.69	12.20	13.64	15.95
C (internal rotation)	2.85	2.86	2.54	2.27	2.02

TABLE IV. Heat capacity contributed by internal rotation in 1,2-dibromoethane; units are cal./mole deg.

$T^{\circ}\text{K}$	383	428	473
C_p° (exp)	23.14	24.57	25.86
C (tran. + rot.) + R	7.948	7.948	7.948
$C_{\text{(vib)}}$	11.35	12.85	14.24
C (internal rotation)	3.84	3.77	3.67

of 300 cm^{-1} is very close to the classical value of R at the temperature being considered, the lack of exact knowledge of this frequency introduces negligible uncertainty into the calculation of the gas heat capacity. However, the contribution to the entropy is quite sensitive to changes in frequency around 300 cm^{-1} . In the entropy calculations two values of this frequency will be considered: 223 cm^{-1} as the most probable value and 300 cm^{-1} as the upper limit.

In the *trans*-dibromoethane there are two missing frequencies: the unsymmetrical bending of the C—C—Br bond angles, and the unsymmetrical stretching of the C—Br bond. The first frequency should be less than the corresponding symmetrical vibration at 180 cm^{-1} , and, by analogy with dichloroethane, it should be near 140 cm^{-1} . The C—X stretching frequency is observed in 1,2-dichloroethane, 1,2-chloriodoethane, 1,2-chlorobromoethane, and 1,2-diiodoethane to be 707, 655, 662, and 635 cm^{-1} , respectively. By analogy it is assumed to be 650 cm^{-1} in dibromoethane. The maximum possible error from this source is less than 0.1 calorie/mole deg.

In the skew configuration of both dichloroethane and dibromoethane there are two missing frequencies: a symmetrical CH_2 twisting frequency and an unsymmetrical CH_2 twisting frequency. Because of the method used in the following section to separate the partition function, the frequencies of the skew form are used only to calculate ω , which is defined in that section. The calculation of ω depends upon the

free energy contributed by these frequencies. Since the frequencies are approximately 1200 cm^{-1} , the free energy contributed is small. There will be negligible error in assuming that the free energy contributed by these two frequencies is the same as the free energy contributed by the corresponding two frequencies of the *trans* form.

Tables III and IV give the values of the heat capacity caused by internal rotation. These values are also plotted in Figs. 1, 3, and 4.

To obtain information from the entropy concerning the potential barrier to internal rotation the function $S_F - S$ is usually calculated and compared with the experimental values. The experimental $S_F - S$ is obtained by subtracting the experimental entropy of the gas from the statistical entropy calculated assuming free internal rotation. The entropy of the gas phase at 298.1°K was calculated by adding to the entropy of the liquid given by Pitzer,¹¹ the entropy of vaporization at its vapor pressure, a correction due to gas imperfection calculated from Berthelot's equation, and the entropy change when the perfect gas is compressed to 1 atmos. The heat of vaporization at 298.1°K was calculated from the value given by Mathews,¹⁸ by assuming ΔC_p to be constant. ΔC_p was calculated from the liquid and gas heat capacities at room temperature. The vapor pressure of dichloroethane was given by Pearce and Peters.¹⁹ The vapor pressure of dibromoethane was obtained from the International Critical Tables. In the calculation of the entropy at the normal boiling point, the heat capacity of the liquid was estimated from the heat capacity of the gas, assuming ΔC_p to be constant.

The calculation of the statistical entropy is complicated by the fact that the moments of inertia depend upon the angle of internal rotation. This problem will be discussed in a later section. The moments of inertia were calculated using the method described by Pitzer.²⁰ The calculations were made assuming tetrahedral angles, and the following bond distances^{8,9} C-H = 1.09Å, C-C = 1.54Å, C-Cl = 1.76Å, and C-Br = 1.92Å.

Since in dichloroethane the vibrational fre-

quency at 223 cm^{-1} is a little uncertain, the entropy is also calculated assuming the frequency has its maximum value of 300 cm^{-1} . In dibromoethane this frequency is unknown and the entropy is calculated on the basis of the frequency being 187 cm^{-1} (maximum value) and 139 cm^{-1} (estimate by analogy with dichloroethane). In dibromoethane the calculated entropy is quite uncertain and will be considered only as an order of magnitude. The results of the above calculations are summarized in Tables V and VI.

THE POTENTIAL BARRIER TO INTERNAL ROTATION

Qualitatively, the potential barrier would be expected to be similar to the threefold barrier of

TABLE V. Entropy of 1,2-dichloroethane.

Experimental	Calculation for 298°K	Calculation for 356°K
S liquid at 298.1°K (Pitzer ¹¹)	49.84 ± 0.15	49.84 ± 0.15
ΔS vaporization $\Delta H = 8438\text{ cal./mole}$ $T = 298.1^\circ\text{K}$ $P = 78.9\text{ mm}^{19}$	28.30	
ΔS (real gas \rightarrow perfect gas)	0.02	0.13
ΔS [gas ($P = 79.8\text{ mm}$) \rightarrow gas ($P = 760\text{ mm}$)]	4.50	
ΔS [liquid $298.1^\circ\text{K} \rightarrow$ liquid 356.8°K] (Graphical integration)		5.68
ΔS [vaporization $\Delta H = 7652$ (Mathews ¹⁸) $P = 1\text{ atmos.}$ $T = 356.8^\circ\text{K}$]		21.45
S° $P = 1\text{ atmos.}$ $T = 298.1^\circ\text{K}$	73.66	
S° $P = 1\text{ atmos.}$ $T = 356.8^\circ\text{K}$		77.10
Calculated		
S_F (free internal rotation)		
vib. $\alpha = 223\text{ cm}^{-1}$	76.24	79.33
vib. $\alpha = 300\text{ cm}^{-1}$	75.73	78.87
$S_F - S_{\text{exp.}}$ vib. $\alpha = 223\text{ cm}^{-1}$	2.58	2.23
vib. $\alpha = 300\text{ cm}^{-1}$	2.07	1.77

TABLE VI. Entropy of 1,2-dibromoethane.

Experimental	Calculation for 298°K	Calculation for 404.9°K
S liquid at 298.1°K (Pitzer ¹¹)	53.37 ± 0.15	53.37 ± 0.15
ΔS vaporization $\Delta H = 9975\text{ cal./mole}$ $T = 298.1^\circ\text{K}$ $P = 13.2\text{ mm}$	33.46	
ΔS (gas, $P = 13.2\text{ mm} \rightarrow$ gas, $P = 760\text{ mm}$)	8.06	
Gas imperfection	0.04	0.11
ΔS (liquid $298.1^\circ\text{K} \rightarrow$ liquid 404.9°K) Graphical integration		10.57
ΔS vaporization $\Delta H = 7688$ (Mathews ¹⁸) $P = 1\text{ atmos.}$ $T = 404.9^\circ\text{K}$		21.43
S° $P = 1\text{ atmos.}$ $T = 298.1^\circ\text{K}$	78.81	
$P = 1\text{ atmos.}$ $T = 404.9^\circ\text{K}$		85.98
Calculated		
S_F (free internal rotation)		
vib. $\alpha = 140\text{ cm}^{-1}$	82.29	88.10
vib. $\alpha = 187\text{ cm}^{-1}$	81.73	87.53
$S_F - S_{\text{exp.}}$ vib. $\alpha = 140\text{ cm}^{-1}$	3.48	2.62
vib. $\alpha = 187\text{ cm}^{-1}$	2.92	2.05

¹⁸ J. H. Mathews, J. Am. Chem. Soc. **48**, 562 (1926).

¹⁹ Pearce and Peters, J. Phys. Chem. **33**, 873 (1929).

²⁰ K. S. Pitzer, J. Chem. Phys. **14**, 239 (1939).

ethane with a superimposed onefold barrier caused by the additional interactions as a result of the halogen atoms. Initially, we will assume the barrier to have the mathematical form

$$V(\varphi) = V_1 \frac{(1 - \cos \varphi)}{2} + V_3 \frac{(1 - \cos 3\varphi)}{2}.$$

In most of the previous work^{2,4,5} on the interpretation of the dipole moment data, a simple cosine barrier ($V_3=0$) has been assumed. This interpretation can be definitely excluded because the heat capacity contributed by internal rotation is much larger than can be calculated on the basis of a simple cosine barrier. Alter³ has assumed a barrier to consist of the combination of a onefold and a twofold barrier. His work was completed before the barrier in ethane was studied. In view of the work on ethane, the twofold barrier is no longer reasonable, and it will not be considered in this work.

Quantitatively, the potential barrier will be found by calculating the thermodynamic functions and the dipole moment for the molecule, assuming various values of V_1 and V_3 . The values of V_1 and V_3 which give the best agreement between the calculated and the experimentally observed values will then be selected as best representing the potential barrier in the molecule.

In the calculation of the thermodynamic functions and the dipole moment, use will be made of the classical partition function for all degrees of freedom except vibration. Since the moments of inertia are large, this approximation will not introduce a serious error. In the case of the heat capacity calculated from a simple cosine barrier, this approximation introduces an error of less than 0.03 cal./mole deg.

In the case of a symmetrical top attached to a rigid frame, the moments of inertia do not depend upon φ , the angle of internal rotation. The partition function may then be factored into a partition function for a molecule with free internal rotation multiplied by an integral over φ . However, in the case of both dichloroethane and dibromoethane, both groups are unsymmetrical, and it is not possible to factor rigorously the partition function. By integrating the classical partition function with respect to all

translational and rotational variables except φ , the partition function for this type of molecule may be written:

$$Q = \int_0^{2\pi} \frac{Q_F(\varphi)}{2\pi} \exp\left[\frac{-V(\varphi)}{RT}\right] d\varphi, \quad (2)$$

where $Q_F(\varphi)$ is identical in form to the partition function calculated for the molecule with free internal rotation. Q_F is a function of φ because the moments of inertia and vibrational frequencies depend upon φ . Q_F is not known at all values of φ , but it can be calculated at $\varphi=0^\circ$ (*trans*) and $\varphi=120^\circ$.

The problem of unsymmetrical tops attached to rigid frames has been discussed extensively by one of us.²⁰ It has been shown, by using the classical partition function for vibrational degrees of freedom, that the change in $Q_F(\varphi)$ caused by the change in vibrational frequencies cancels the change in $Q_F(\varphi)$ resulting from the change in moments of inertia, provided there are no cross terms in the potential energy between vibrational motion and internal rotation. This is easily verified in the case of dichloroethane. Using the classical partition functions for vibrational degrees of freedom, the two values of Q_F calculated at $\varphi=0^\circ$ and at $\varphi=120^\circ$ differ by only six percent. If the quantum-mechanical partition function is used, the two values differ by only one percent at 298.1°K and three percent at 555°K. In the above calculations the uncertain vibrational frequency was assumed to be 223 cm⁻¹. This calculation is uncertain in the case of dibromoethane because of the unknown low lying vibrational frequency. If this frequency is 140 cm⁻¹, the ratio of the two values of $Q_F(\varphi)$ (to be defined below as ω) is 0.654; and if the frequency is assumed to be 187 cm⁻¹ (maximum value), the ω is 0.901. This difference is too large to neglect.

As an approximation, Eq. (2) may be written:

$$Q = \frac{Q_F(\varphi=0^\circ)}{\pi} \int_0^{\pi/3} \exp\left[\frac{-V\varphi}{RT}\right] d\varphi + \frac{Q_F(\varphi=120^\circ)}{\pi} \int_{\pi/3}^{\pi} \exp\left[\frac{-V(\varphi)}{RT}\right] d\varphi \quad (3)$$

or,

$$Q = \frac{Q_F(\varphi=0^\circ)}{\pi} \left[\int_0^{\pi/3} \exp\left[\frac{-V(\varphi)}{RT}\right] d\varphi + \omega \int_{\pi/3}^{\pi} \exp\left[\frac{-V(\varphi)}{RT}\right] d\varphi \right], \quad (4)$$

where

$$\omega = \frac{Q_F(\varphi=120^\circ)}{Q_F(\varphi=0^\circ)}.$$

This approximation will introduce little error in the calculation of the entropy or dipole moment, since most molecules lie close to either the *trans* or skew form. It may introduce an error as large as several tenths of a calorie per mole in the heat capacity, since there is an appreciable contribution to the heat capacity from values of φ with high energy and low population. This approximation does make possible the factoring of the partition function and the calculation of the thermodynamic functions as the sum of two parts: the thermodynamic functions of the molecule assuming free rotation and using the moments of inertia and vibrational frequencies of the *trans* form, and the part contributed by the restriction of internal rotation, and, to a small extent, by ω .

In dichloroethane the effect of changing ω from 1.0 to 0.95, for example, would be approximately to lower the dipole moment by two percent, raise the entropy by 0.1 cal./mole deg. and lower the heat capacity by 0.03 cal./mole deg. Hence there is little error in assuming, for simplicity, $\omega=1$ in the following calculations.

The dipole moment will be calculated as the root mean square dipole moment from the partition function in the usual manner. Since the dipole moment of the C-Cl bond varies from one chlorinated ethane to another, the group moment of the $-\text{CH}_2\text{Cl}$ group will be considered as a variable. The group moment will be selected so that the calculated and experimental dipole moments are in agreement at 419°K.

A comparison between the experimental data and calculations is shown in Fig. 1. The points represent the experimental heat capacity from Table III, the values of $S_F - S_{\text{exp}}$ from Table V, and the dipole moment data of Zahn.¹ It is impossible to find a potential barrier of the type given in Eq. (1), for which the calculated values

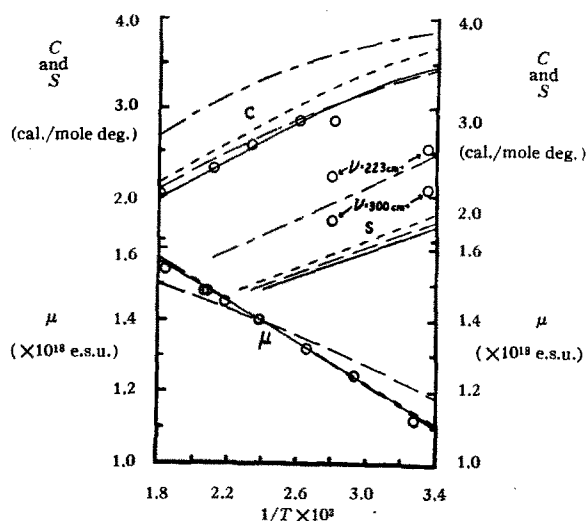


FIG. 1. A comparison between the calculated curves and the experimental points in 1,2-dichloroethane.

Curves	Code	V_1	V_3	μ_0
1	—	2030	1200	1.59
2	---	1780	1780	1.51
3	----	1330	2210	1.37
4	-.-.-	1170	2880	1.56

are in agreement with all of the experimental values of the dipole moment, entropy, and gas heat capacity. However, it is possible to select values of V_1 and V_3 so that there is good agreement in gas heat capacity and dipole moment (set of curves No. 1) or entropy and dipole moment (set No. 4). It is impossible to bring both the entropy and gas heat capacity into agreement with the same potential barrier of the type given in Eq. (1).

The dipole moment is dependent primarily upon the value of V_1 . If V_3 is selected as any value within several kilocalories/mole, then a V_1 may be found which will give good agreement in the dipole moment data. The value of V_1 will be very close to 1900 calories/mole and will deviate by not more than a few hundred calories for various choices of V_3 . The curves numbered 3 in Fig. 1 show the effect on the dipole moment of varying V_1 , and changing V_3 to preserve the agreement in gas heat capacity. The curves numbered 2 show the effect on the gas heat capacity of varying V_3 and changing V_1 to preserve the agreement in dipole moment.

It can be seen in Fig. 1 that, when a barrier is selected so that the gas heat capacity and dipole moment are in agreement, the calculated value

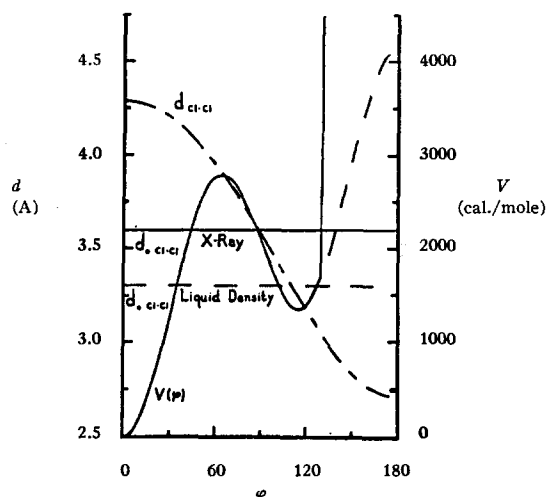


FIG. 2. The distance between the two chlorine atoms and the final potential energy as a function of the angle of internal rotation in 1,2-dichloroethane.

of S_F-S is too low. This indicates that the actual internal rotation is more restricted than the assumed model. The reason for this becomes apparent when the Cl-Cl distance is calculated and compared with the van der Waals radius. The Cl-Cl distance is plotted against φ in Fig. 2. The solid horizontal line represents the van der Waals diameter of 3.6 Å found by the x-ray studies of Dickinson²¹ on benzenehexachloride. The dotted horizontal line represents the value of 3.3 Å found by Smyth²² from the measurement of the density of liquid chlorine. For reference, the potential barrier which was finally selected is also included in Fig. 2. The van der Waals radius of two chlorine atoms in the same molecule might be different from the radius of two chlorine atoms in different molecules, but the chlorines in dichloroethane probably come in contact at some value of φ less than 180°. As φ becomes greater than this value, the potential energy will rise rapidly because of the compression of the chlorine atoms and the distortion of the C-C-Cl bond angle. As an approximation to this situation, the potential energy is assumed to become infinite at some value of φ intermediate between the angle of contact and 180°.

If the angle at which the potential energy is

²¹ R. C. Dickinson and Bilicke, *J. Am. Chem. Soc.* **50**, 764 (1928).

²² C. P. Smyth and K. B. McAlpine, *J. Am. Chem. Soc.* **57**, 979 (1935).

assumed to become infinite is taken to be 130°, it is then possible to bring the calculated curves into agreement with the experimental points. Figure 3 shows the results of the best choice of V_1 and V_3 . The agreement between the calculated curves and experimental points is within the experimental error, except for the gas heat capacity point and the dipole moment point at the lowest temperature. The potential barrier finally selected is:

$$V = 1830 \left(\frac{1 - \cos \varphi}{2} \right) + 2300 \left(\frac{1 - \cos 3\varphi}{2} \right) \frac{\text{cal.}}{\text{mole}}, \quad 0^\circ < \varphi \leq 130^\circ$$

$$V = \infty, \quad \varphi > 130^\circ.$$

The agreement in the dipole moment at low temperature could be improved by increasing V_1 by approximately 150 calories/mole, but this would increase the error in gas heat capacity.

The value of the dipole moment of the $-\text{CH}_2\text{Cl}$ group was found to be 1.69×10^{-18} e.s.u. Now, considering the recent measurements of Dr. J. R. Thomas²³ in this laboratory, and the values in the literature,²⁴ the dipole moments of

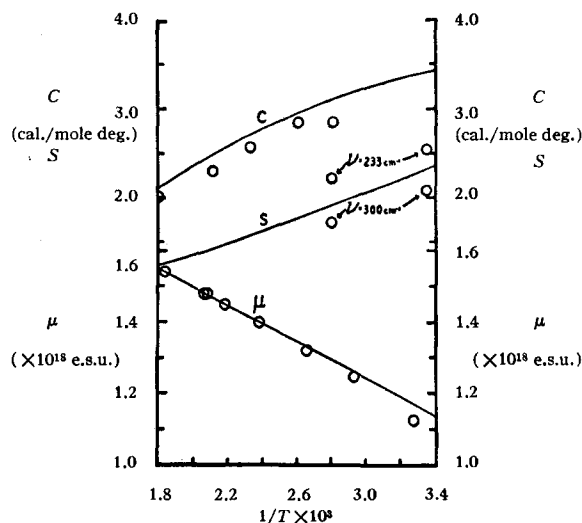


FIG. 3. A comparison of the experimental points for 1,2-dichloroethane with the curves calculated, assuming the following barrier

$$V(\varphi) = 1830 \left(\frac{1 - \cos \varphi}{2} \right) + 2300 \left(\frac{1 - \cos 3\varphi}{2} \right), \quad 0^\circ < \varphi < 130^\circ$$

$$V(\varphi) = \infty, \quad \varphi > 130^\circ.$$

²³ J. R. Thomas, Ph.D. Thesis, University of California (1947).

²⁴ R. Sanger, *Physik. Zeits.* **27**, 556 (1926); **32**, 20 (1931); P. M. Ghosh, P. C. Mahanti, and D. N. Sen Gupta,

the entire series of chlorinated ethanes are known. This value of μ for the $-\text{CH}_2\text{Cl}$ group falls in line with the trend of the C-Cl bond moment, as the number of chlorine atoms in the molecule is varied. This will be explained in detail in a later publication.

The height of the threefold barrier, V_3 , should approximate the barrier in ethane²⁵ ($V_3=2700$ cal./mole) and methyl chloroform²⁶ ($V_3=2700$ cal./mole). The value of 2300 cal./mole agrees within the various uncertainties involved.

The 124 cm^{-1} Raman line has been interpreted as the torsional vibration in the skew form of dichloroethane. Using the curvature of the potential barrier of Eq. (6) and the moment of inertia, this frequency is calculated to be 79 cm^{-1} . However, the actual barrier, instead of becoming infinite at $\varphi=130^\circ$, will gradually increase, and the curvature will be increased considerably at 120° . This can easily increase the calculated value of the frequency so that it agrees with the observed value.

Using the above potential function, it is now possible to calculate the thermodynamic functions for 1,2-dichloroethane. The results are tabulated in Table VII.

TABLE VII. Table of thermodynamic functions of 1,2-dichloroethane.

T	$C\left(\frac{\text{cal.}}{\text{mole deg.}}\right)$	$S\left(\frac{\text{cal.}}{\text{mole deg.}}\right)$	$\frac{H^0-H^0}{T}\left(\frac{\text{cal.}}{\text{mole deg.}}\right)$	$\mu(\text{e.s.u.})$
250°K	17.2	70.7	12.9	0.98×10^{-18}
298.1°K	18.8	73.9	13.7	1.14×10^{-18}
500°K	24.7	85.1	17.0	1.49×10^{-18}
750°K	29.6	96.1	20.4	1.65×10^{-18}
1000°K	33.0	105.0	23.1	1.71×10^{-18}
1250°K	35.5	112.8	24.9	1.74×10^{-18}

In dibromoethane it is impossible to get satisfactory agreement between the calculated curves and the experimental points. If the unknown frequency is taken to be 140 cm^{-1} , the calculated heat capacity is about 0.4 of a calorie/mole deg. low, and the entropy is too high by 0.3 cal./mole deg. If the frequency is taken to be 187 cm^{-1} , then the calculated entropy is too high by 0.8 cal./mole deg. If ω were unity,

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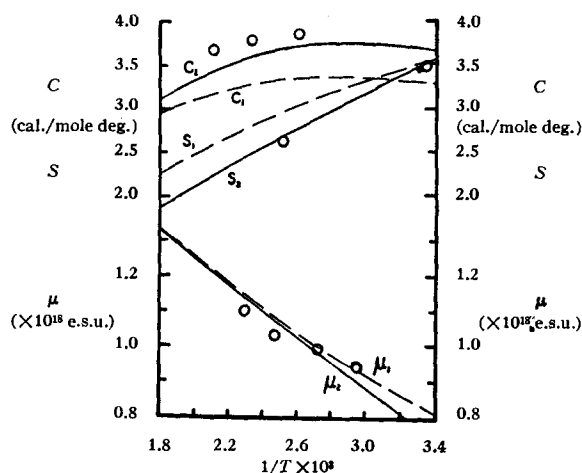


FIG. 4. A comparison of the calculated curves and the experimental points for 1,2-dibromoethane. V is assumed to become infinite at $\varphi=140^\circ$.

	V_1	V_3	ω	μ_0
Curve 1	2450	4100	0.654	1.65×10^{-18} e.s.u.
Curve 2	2500	4170	1.0	1.57×10^{-18} e.s.u.

then it would be possible to bring everything into agreement. However, this would require an extensive reassignment of vibrational frequencies, which we are not prepared to advocate at this time. It would be necessary to lower the low lying vibrational frequencies of the 120° form, and this does not appear possible without an entirely different assignment of the low frequencies. The dipole moment does require that V_1 must be within a few hundred calories of 2100 cal./mole. To come close to the heat capacity or entropy, V_3 must be 4000 ± 1000 cal. For reference, Fig. 4 shows the agreement between the experimental points and the calculated curves, using the 140 cm^{-1} frequency, and assuming that the potential energy becomes infinite at $\varphi=140^\circ$. The curves numbered 1 are calculated with $\omega=0.654$, and the curves numbered 2 are calculated on the assumption that ω is unity. In the calculations assuming ω as unity the vibrational assignment of the *trans* form was used and the detailed vibrational assignment of the skew form was ignored.

It may be possible to obtain better agreement with the experimental results by using a potential function in which the onefold term is some function other than $\cos\varphi$. In the near future we hope to publish tables of thermodynamic functions for internal rotation using the potential function given in Eq. (1).