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FROM LOW TEMPERATURE HEAT CAPACITY DATA

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A method by which barrier heights in potential functions hindering internal rotation in organic molecules can be obtained solely from thermal data for the solid phase is studied. The observed heat capacities are analyzed in terms of contributions from the lattice vibrations, the intramolecular vibrations, the expansion of the lattice, and the internal rotation.

Five compounds are treated. These are mesitylene, toluene, benzenethiol, methanethiol, and trifluoromethanethiol. Calculations show that the barrier values are 540, 340, 280, 1650, and 1630 cal/mole for the respective molecules.

It is shown that the potential barriers are in accord with barriers derived from gas phase entropy calculations and that the calculated and experimental heat capacities agree for the most part well within the expected limits. The precision of the low barriers is better than those determined from gas phase entropy calculations, while

the high barrier values have about the same precision as gas phase entropy values.

DETERMINATION OF BARRIERS TO INTERNAL ROTATION
FROM LOW TEMPERATURE HEAT CAPACITY DATA

by

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DETERMINATION OF BARRIERS TO INTERNAL ROTATION
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INTRODUCTION

The study of internal rotation and of the origin and magnitude of the forces interfering with free internal rotation has been of interest for many years. A molecule has internal rotation if one part of the molecule is able to rotate relative to the other about a single bond. A simple example is ethane, in which one methyl group can rotate with respect to the other about the carbon-carbon bond. At first, these rotations were thought to be essentially free since no isomers were found. However, by the 1930's it had been proven that barriers had to be surmounted in turning from one configuration to another.

A number of properties are markedly influenced by potential barriers. Some of these are heat capacity, entropy and chemical equilibrium constants. Since simpler molecules had been treated successfully by statistical mechanics combined with molecular structural data, it was only natural to try to extend the method to molecules with internal rotation. Much work has been done in this field, with the result that a large number of molecules can be treated, notably the simpler hydrocarbons. However, despite the extensive

work that has been done, the reliability of the results leaves much to be desired. The lack of reliability in barrier measurements has made it very difficult to evolve a satisfactory theory of barrier origin and is probably the most important reason for further study in this field.

There are many methods of measuring potential barriers. The three most commonly used methods are (1) the microwave method, (2) the infrared and Raman method, and (3) the thermodynamic method.

The microwave method is the newest and potentially the most accurate of the three methods. In this method, interaction of internal rotation with the overall rotation of the molecule affects the microwave spectrum. These effects can be measured; and by using various quantum mechanical methods, the barrier can be obtained. However, as this field is still relatively new, there is still much disagreement among the different spectroscopists.

The infrared and Raman methods are theoretically capable of giving accurate barriers to internal rotation. In this method the internal rotation appears as a peak in the spectrum either in combination with vibrations or alone. Unfortunately, these combinations are difficult to observe, and it is also very difficult to make a valid assignment, since there are many explanations for combination bands.

The thermodynamic method is one of the most successful

methods used. This method consists of a comparison of calculated and observed quantities such as heat capacity or entropy. Statistical mechanics is used for the calculation of a thermodynamic quantity of gaseous molecules. The potential barrier contribution is used as an adjustable parameter with which to secure agreement between calculated and observed data. Unfortunately, this method is very vulnerable to error either in the experimental measurements or particularly in the vibration frequency assignments, since the method is based on a small difference between two large numbers, and any errors at any point cause an error in the potential barrier value.

Wulff (26) proposed using solid phase heat capacity calculations instead of gas phase entropy calculations in order to permit more precise evaluation of barrier values. Wulff proposed that greater precision in the barrier would be obtained because solid phase heat capacity measurements are more precise and because any uncertainties in the vibrational assignments would be minimized because of their smaller contributions at low temperatures. For these reasons it was decided to apply Wulff's method to other compounds in order to confirm his method and if necessary, modify it to extend the number of molecules covered by this method.

THEORY

When thermal energy is absorbed at constant pressure by a crystalline solid such as toluene, this energy is distributed among: (1) the oscillations of the crystal lattice; (2) the internal vibrations of the molecules composing the lattice; (3) the work of expanding the lattice; and (4) the internal rotation of the molecules composing the lattice. There are $3N'$ possible motions per molecule, where N' is the number of atoms per molecule. Six of these are crystal lattice oscillations and the remaining $3N'-6$ are the internal vibrations of the molecule plus the internal rotation.

It can be shown, using quantum mechanics, that the various components of the heat capacity may be treated separately and then summed together as shown in Equation 1.

$$C_p = C_v^L + C_v^I + (C_p - C_v) + mC_v^{IR} \quad (1)$$

Each of the terms on the right side of Equation 1 corresponds respectively to the four modes of energy distribution to crystals mentioned above. Each of these terms will be explained more fully in the following sections.

The Crystal Oscillations Contribution, C_v^L

This is the contribution to the heat capacity from the oscillations of the crystal lattice. This contribution to the heat capacity

corresponds to the three degrees of rotational and the three degrees of translational freedom of a nonlinear polyatomic gas molecule. In a solid these translational and rotational degrees of freedom are not independent as in a gas, but are coupled throughout the crystal. The three translational degrees of freedom of a gas are replaced by three coupled oscillations of the atoms and the three rotational degrees of freedom of a gas are replaced by three motions which are some type of torsional oscillations. Unfortunately, even for simple atomic crystals, present day crystal lattice theory involving classical or quantum statistical mechanics is inadequate. Thus, it has been necessary to use the well-known theoretical treatments of Einstein and Debye, which were devised for atomic lattices, for molecular crystals. A brief review of the two methods follows.

Einstein proposed that the atoms in a crystal be treated as quantized, independent, harmonic oscillators each with the same frequency. Such oscillators can acquire energy only in definite amounts or quanta, $h\nu$, where h is Planck's constant and ν is the oscillator frequency. For a crystal the heat capacity is given by the following equation

$$C_v = 3R E(\theta_E/T) \quad (2)$$

$$\theta_E = h\nu c/k \text{ } ^\circ\text{K}$$

where $E(\theta_E/T)$ is the well-known Einstein function, h is Planck's constant, c is the velocity of light in centimeters per

second, k is Boltzmann's constant and ν is the harmonic oscillator frequency in reciprocal centimeters. Tables of these functions are available (8). This treatment does not give very good results even for very simple atomic lattices.

Debye assumed that the oscillations in a crystal were coupled, not independent, so that the frequencies range from very low to very high values. He assumed the crystal to be a continuous elastic medium and treated the oscillation frequencies of the atoms as acoustic waves, the nodes of which coincided with the boundaries of the crystal. There was an upper limit to the frequencies since the total allowed number of vibrations must be $3N$. With the further assumption that the velocity of propagation of the acoustic waves was independent of wave length and direction, Debye obtained an improved expression for the heat capacity of a solid which is used in most treatments of atomic solids today. Debye's expression is especially good at low temperatures where the theory gives a heat capacity proportional to T^3 which many atomic solids exhibit. The Debye expression for crystal heat capacity is given in the following equation

$$\begin{aligned} C_v &= 3R D(\theta_D/T) \\ &= h\nu_D c/k \text{ } ^\circ\text{K} \end{aligned} \quad (3)$$

where $D(\theta_D/T)$ is the well-known Debye function and ν_D is the maximum oscillation frequency of the atoms in the crystal. Tables

for this function are also available (5).

Neither of the two previous methods has been successful for molecular organic crystals. The main reason for their failure is that nonlinear, polyatomic molecules have a contribution from the torsional oscillations of the crystal molecules that replace the rotational mode in the gas state.

Lord (11) has discussed the methods which have been used for calculating molecular lattice heat capacity contributions. All of the methods are modifications of the theories of Debye and Einstein. They are as follows:

(1) The assumption was made, as did Einstein for atomic lattices, that all six frequencies were the same. The lattice heat capacity contribution (C_v^L) was then given by Equation 2 with $3R$ replaced by $6R$. The results obtained are no better than those obtained for atomic lattices.

(2) In the second method, the coupled oscillations of the atoms in the crystal were assumed to have frequencies distributed in the Debye fashion, and thus could be represented by Equation 3. The torsional oscillations or "rotation" of the crystal atoms were assumed to have frequencies nearly alike in the Einstein manner and thus could be represented by Equation 2. Since two frequencies were needed it was, of necessity, a trial and error method. However, it is found in practice that the answers obtained were often very good.

(3) The third method assumed that the three "rotational" degrees of freedom were to have frequencies distributed in the Debye fashion. Here again a trial and error method was necessary since two arbitrary Debye functions with different θ_D 's were necessary. This representation usually gave answers as good as Method 2.

Lord (11) has indicated that the reason Methods 2 and 3 reproduced the lattice heat capacity so well could be attributed to two causes: (a) Since even if a frequency distribution was only approximately correct, the heat capacity contribution calculated from the distribution may be close to the true heat capacity because of the very good curve-fitting properties of the distribution functions used in Method 2 or 3. (b) The liberty of choice of two parameters (the two θ 's) clearly made possible better matching of calculation with observation.

However, Lord, Ahlbert and Andrews (13) and later Lord (11) made a further simplifying assumption. They assumed that the two θ_D 's of Method 3 be made equal. This simplification reduced to a minimum the number of parameters necessary to express the lattice heat capacity. When this method is used, the specific heat is expressed by a Debye equation (Equation 3) with $3R$ replaced by $6R$. Lord (12), Lord, Ahlberg and Andrews (13) and Brucksch and Ziegler (1) have shown that this method gave a good representation above 35 to 40° K and many times at lower temperatures provided the

two θ 's of Method 3 were not too far apart.

In this study the simplified single θ_D method of Lord was used whenever possible. If a good representation could not be obtained by this simpler method, then Method 2 which used a combination of Einstein and Debye functions were used.

The Intramolecular Contribution, C_v^I

This term corresponds to the contribution of the intramolecular vibrations of the molecules composing the lattice. There are $3N^1-6-m$ vibrations per molecule (m is the number of internal rotators per molecule). These contributions are calculated, using the harmonic oscillator approximation, by a combination of Einstein functions based on the observed vibrational spectrum. This contribution is given by the following equation.

$$C_v^I = R \sum_{i=1}^{3N^1-6-m} E(\theta_{Ei}/T) \quad (4)$$

The vibrational spectrum of the solid should be used whenever possible, but unfortunately, solid state studies have been made on only a few organic compounds. However, liquid or if necessary, gas vibrational assignments can be used in most cases without too much error (7, p. 534).

The Lattice Expansion Contribution, $C_p - C_v$

This term corresponds to the contribution made by the work of expanding the crystal lattice. This contribution is given by the following exact thermodynamic equation:

$$C_p - C_v = \alpha^2 TV / \beta \quad (5)$$

where V is the molar volume, T is the absolute temperature, α is the crystal's coefficient of thermal expansion and β is the coefficient of isothermal compressibility. Unfortunately, this equation cannot be used in practice because data on the coefficient of thermal expansion and the isothermal compressibility coefficient are not available for most organic solids. However, several approximation methods have been devised to treat this contribution. Two of these methods were used by this investigator and are explained below.

Nernst and Lindeman (14, p. 264) used the following semi-theoretical approximation:

$$C_p - C_v = 0.0214 C_p^2 T / T_{mp} \quad (6)$$

where T_{mp} is the melting point of the solid. This approximation is not usable at higher temperatures and works only moderately well at the lowest temperatures. Thus it was used only as an aid in making the first estimate of the lattice contribution.

A better approximation is that of Lord, Ahlberg and Andrews (13). They used the following equation.

$$C_p - C_v = [a \cdot C_v^L + b(C_v^I + mC_v^{IR})]^2 T \quad (7)$$

where a and b are empirical constants. The following derivation was given.

Starting with the exact equation (Equation 5)

$$C_p - C_v = a^2 TV/\beta \quad (5)$$

the right hand side could be changed to a more useful form by means of the following equation

$$a V/\beta = \text{constant} \times C_v \quad (8)$$

which Grüneisen (14, p. 345-356) had shown, by a combination of thermodynamic arguments with the results of lattice theory, should hold for atomic lattices. Lord et al. (13) extended Grüneisen's reasoning to molecular lattices which led to the expression

$$a V/\beta = \sum_i a_i (C_v)_i \quad (9)$$

in which the a_i 's are constants multiplying the several components of C_v , namely the contributions from the compressional and torsional vibrations (C_v^L) and the contributions from the various internal degrees of molecular freedom ($C_v^I + C_v^{IR}$). Equation 9 was

then simplified by making two assumptions about the coefficients a_i . The first assumption was that the coefficients of the compressional and the torsional oscillation contributions were the same. This assumption was in keeping with the use of the six degree Debye function to represent the lattice contribution. The assumption, while possibly not as good, was also used when it was necessary to use the Einstein plus Debye function instead. The second assumption assumes that the coefficients for the various components of the internal contributions ($C_v^I + C_v^{IR}$) could be combined together into one coefficient for the whole internal contribution. Thus Equation 9 is reduced to

$$aV/\beta = a' \cdot C_v^L + b'(C_v^I + mC_v^{IR}) \quad (10)$$

where a' and b' are constants. The empirically justifiable assumption was then made that the quotient V/β is temperature-independent. Combination of Equations 5 and 10 then gave Equation 7.

$$C_p - C_v = [a \cdot C_v^L + b(C_v^I + mC_v^{IR})]^2 T \quad (7)$$

The constants a and b must be evaluated empirically. However, several investigators (1, 12, 13) have found that in many cases a equals b or that b is zero, thus simplifying the calculations. Equation 7 was used as the final representation of the work of expansion contribution, because it is fairly simple and has been used quite successfully by other investigators of molecular solids.

The Internal Rotation Contribution, mC_v^{IR}

This term represents the contribution of the internal rotation to the heat capacity. C_v^{IR} is the internal rotation contribution per rotor and m is the number of rotors per molecule.

The principle problem involved in calculating contributions to thermodynamic properties from hindered internal rotation is the calculation of the quantum energy levels for the system. It is usually found to be more convenient to assume a form of potential function and then calculate energy levels than the reverse. What the actual form of this potential function should be is still uncertain because of the lack of knowledge as to barrier origins. Fortunately, an approximation has been found which in practice seems to be a very satisfactory representation of the actual potential curve. This potential function is

$$V = V_0(1 - \cos n\phi)/2 \quad (11)$$

where V_0 is the height of the potential barrier in calories per mole, n is the number of maxima encountered in one complete revolution of the internal rotation, and ϕ is the angle of rotation, measured from one of the minima.

The reasoning behind this choice of potential function can be illustrated by a simple example such as ethane. In ethane the

configurations in which the hydrogen atoms on opposite methyl groups are staggered, and hence as far away from one another as possible, would be expected to represent a minimum-energy configuration, while eclipsed or aligned configurations where the hydrogen atoms are as close together as possible would represent energy maxima. In this case there will be a periodic symmetry to the potential-energy curve representing internal rotation which is threefold (n equals three), each maximum and minimum having the same value each time. Thus, since we have a rotational coordinate, the potential energy must be a periodic function with period $2\pi/n$. Therefore, the potential can be expanded in a Fourier series, the first two terms of which are Equation 11. Further terms are usually found unnecessary.

$$V = c_0 + c_1 \cos n\phi + \dots \quad (12)$$

$$= \frac{1}{2}V_0 (1 - \cos n\phi) \quad (11)$$

Since Equation 11 has been proven to be a good representation of the actual potential function and is used by most investigators, it will be the potential function used in this study. One other obvious reason for using Equation 11 is that it contains only one adjustable parameter V_0 , the "potential barrier."

The contribution of the internal rotation to the heat capacity is very temperature dependent. Three temperature ranges give rise to

three different treatments for this internal rotation contribution.

Where the temperature is low or the barrier high, such that

$RT \ll V_o$ the contribution can be treated as that of a torsional oscillator with a harmonic frequency given by $\nu = (n/2\pi c)(V_o/4.7778 \times 10^{-8}NI_r)^{\frac{1}{2}}$ (2, p. 196), where I_r is the reduced moment of inertia.

For the case of coaxial symmetrical tops, such as $\text{CH}_3\text{-CCl}_3$,

$$I_r = \frac{I_A I_B}{I_A + I_B}$$

where I_A and I_B are the moments of inertia of the respective tops (the methyl or the trichloromethyl group) about the common axis of internal rotation. For other structures I_r is more complicated (15). Where the temperature is high or the barrier low, such that $RT \gg V_o$, the heat capacity contribution approaches that of a free rotor (2, p. 199-200) where V_o is independent of the angle of rotation. The value of C_v^{IR} for free rotation is $C_v^{IR} = 0.994$ cal/mole per rotor. The heat capacity contributions at intermediate temperatures can be treated using the tables of Pitzer and Gwinn (15) and the extended tables of Li and Pitzer (10).

The two sets of tables of internal rotation contributions for intermediate temperatures were calculated by substituting Equation 11 for the potential function into the Schrödinger equation for a one dimensional rotation and solving for the energy levels. From these energy levels the contribution of a single restricted rotor to the

partition function and to the thermodynamic functions was calculated. The tables were tabulated as functions of the dimensionless quantities V_o/RT and $1/Q_f$ which is the reciprocal of the partition function for free rotation $[Q_f = (8\pi^3 I_r kT)^{1/2}/nh]$.

It was found that the $1/Q_f$ values for several of the solids treated were larger than the values on the tables of Li and Pitzer (10), thus making an extension of the tables necessary. It was felt safe to do this, as the only restriction to using the tables was that the external rotations be separated from the internal rotations, and for solids the two do not interact appreciably, if at all (4, p. 633).

The following method of extending the tables was used. First, the heat capacity contributions of the extended table of Li and Pitzer (10) were plotted on a large graph as a function of $1/Q_f$ at constant V_o/RT 's. The table was then extended graphically from $1/Q_f = 1$ to $1/Q_f = 2$. The graph was plotted to three decimal places to make the second decimal place as accurate as possible.

A method devised by Halford (6) to approximate Pitzer and Gwinn's tables was used to give a second extrapolation. Halford's method approximated Pitzer and Gwinn's tables by using the contribution of a harmonic oscillator approximation with $\theta_E/T = (1.74/Q_f)(V/RT)^{1/2}$ plus an additive constant. This constant which was a function of V_o/RT but independent of $1/Q_f$ was necessary to obtain agreement between the approximation and Pitzer and

Gwinn's tables. Although Halford's approximation was used only for the original tables of Pitzer and Gwinn's, it was found that the method could be used on the tables of Li and Pitzer which are an extension to higher $1/Q_f$ values of the original tables. A slight modification was necessary because the constant which was added to the harmonic oscillator approximation was found to be slightly dependent upon $1/Q_f$ also. The dependence was calculated as accurately as possible for Li and Pitzer's table and then used to extrapolate the table to $1/Q_f = 2$.

There was good agreement between the two methods for all V_o/RT 's in the region between $1/Q_f$ equal to 1 and 1.4. For V_o/RT greater than 12 and less than 7 for all $1/Q_f$ agreement was good. However, for the region between V_o/RT of 7 and 12 for $1/Q_f$ greater than 1.4 the two methods deviated rapidly from each other. An average of the two methods was used for the actual calculations since it was not known which was the best extrapolation. Fortunately whenever $1/Q_f$ was high, V_o/RT was also high, thus the extrapolation was used where the two methods were in fairly close agreement and the contribution small. Figures 1 and 2 show "average" curves which were derived from the two extrapolations.

Summary of the Theory

As stated at the beginning of this section, the heat capacity of

a solid can be divided into: (1) a lattice contribution; (2) an internal vibration contribution; (3) the contribution of the work of expanding the lattice; and (4) the internal rotation contribution. These terms were represented by Equation 1

$$C_p = C_v^L + C_v^I + (C_p - C_v) + mC_v^{IR} \quad (1)$$

where the terms on the right respectively represent the four contributions mentioned above.

The contributions in Equation 1 are given by the following equations. The lattice contribution is given by either

$$C_v^L = 6R D(\theta_D/T) \quad (13)$$

or

$$C_v^L = 3R D(\theta_D/T) + 3R E(\theta_E/T) \quad (14)$$

whichever is necessary, but using Equation 13 whenever possible.

The contribution of intramolecular vibrations of the lattice molecules is given by

$$C_v^I = R \sum_{i=1}^{3N^l - 6 - m} E(\theta_{Ei}/T) \quad (4)$$

where $3N^l - 6 - m$ is the number of different vibrations of each molecule. The work of expanding the lattice contribution is given by

$$C_p - C_v = [a \cdot C_v^L + b(C_v^I + mC_v^{IR})]^2 T \quad (7)$$

where C_v^L and C_v^I are given by Equations 13 or 14 and 4, and the internal rotation contribution, C_v^{IR} , is given by the tables of Pitzer and Gwinn (15) and Li and Pitzer (10) and by Figures 1 and 2. The method of applying these equations to fitting the observed data, the results obtained from these equations and the parameters used in the equations are given in the following sections.

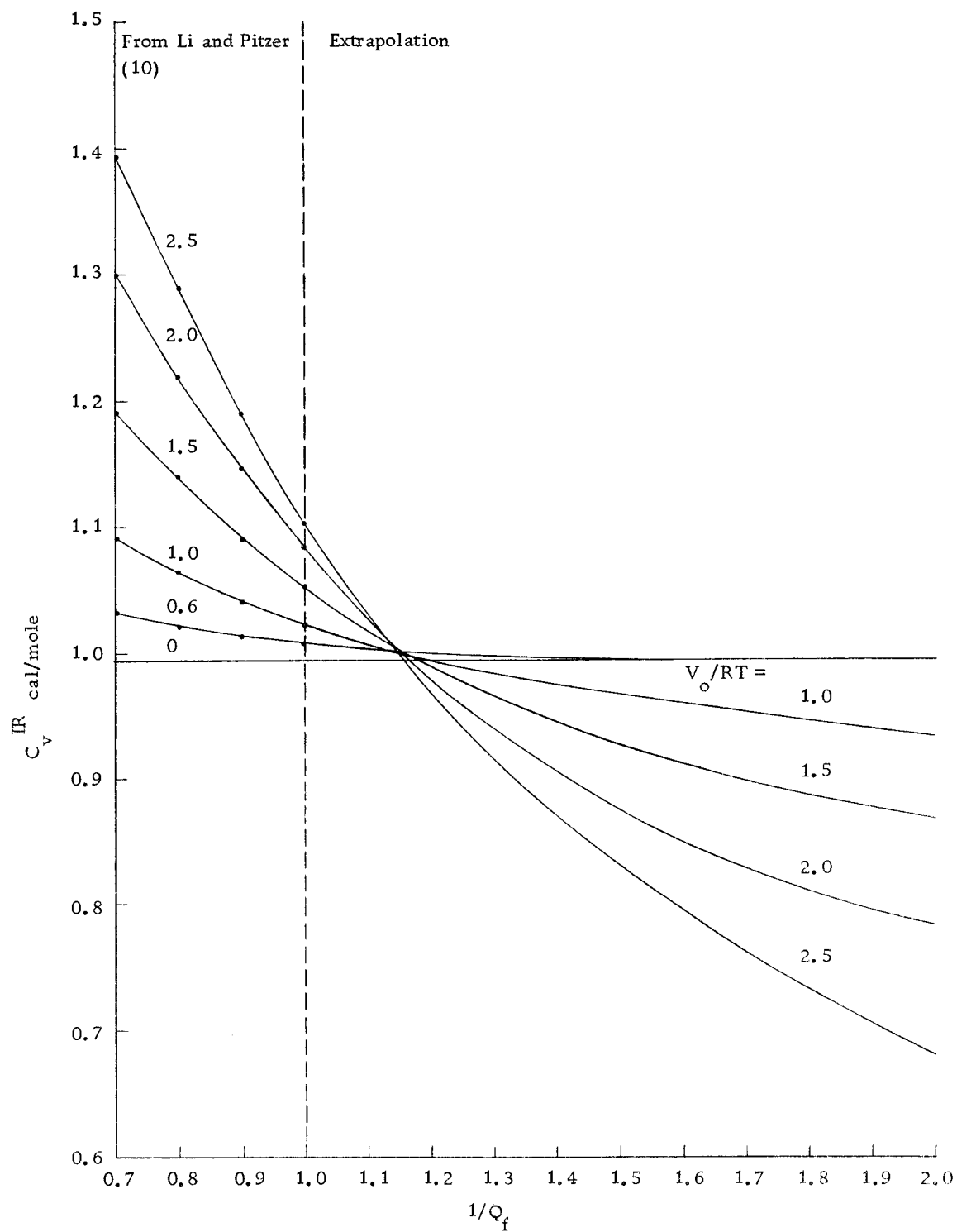


Figure 1. An extension of the table by Li and Pitzer for the internal rotation contribution to the heat capacity for $V_o/RT = 0.6$ to $V_o/RT = 2.5$.

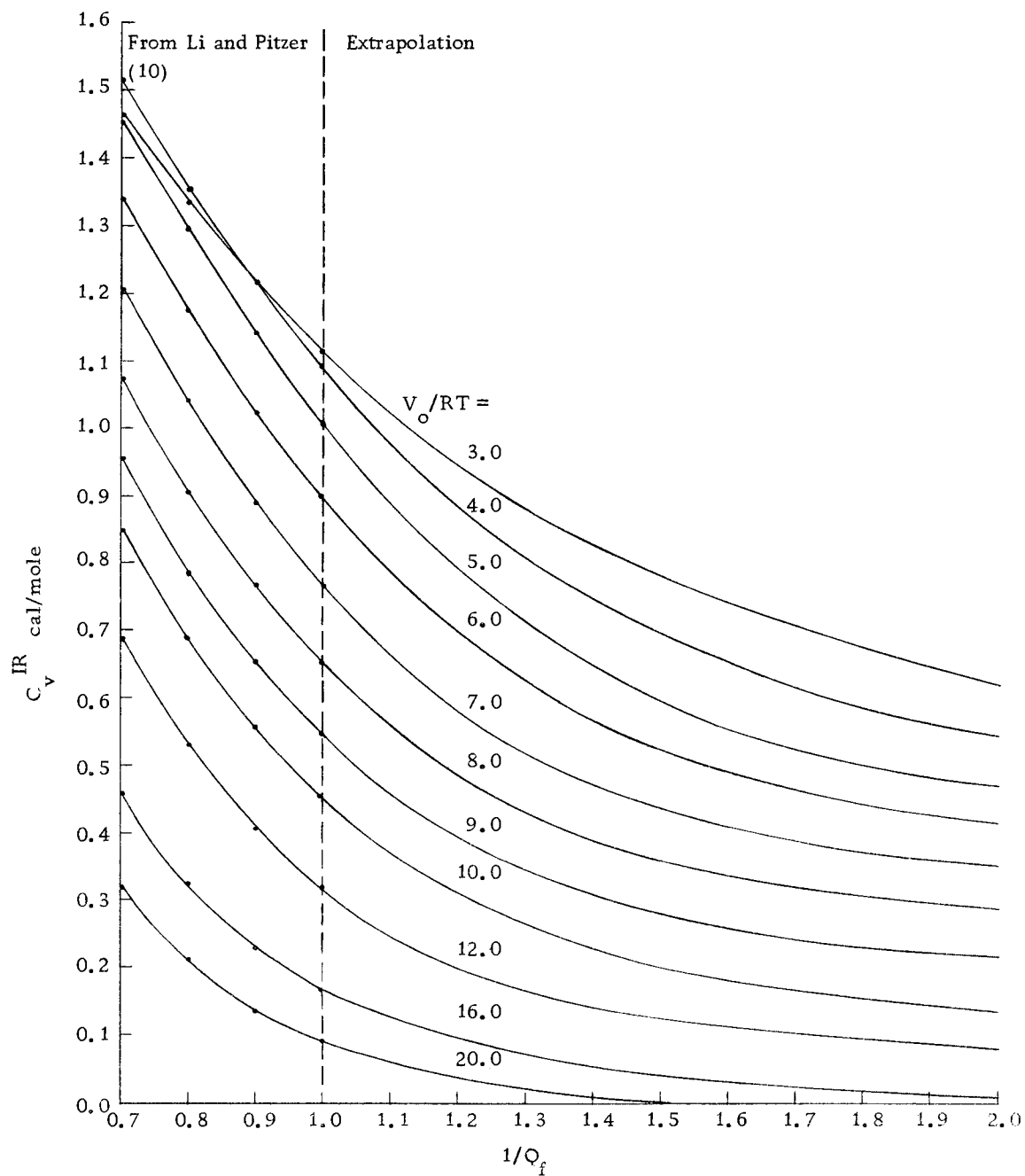


Figure 2. An extension of the table of Li and Pitzer for the internal rotation contribution to the heat capacity for $V_o/RT = 3.0$ to $V_o/RT = 20.0$.

PROCEDURE

The application of Equation 1 to fitting the actual heat capacity data was as follows:

(1) The best vibrational assignment was determined from the literature and the contribution (C_v^I) at each temperature was calculated using Equation 4. C_v^I was then subtracted from the experimental heat capacity.

(2) The work of expansion contribution $(C_p - C_v)$ was then estimated at the lower temperatures by the Nernst and Lindeman equation (Equation 6) and subtracted from the remainder of Step 1.

(3) If V_o was known to be high then the remainder from Step 2 was approximately the lattice contribution C_v^L , and thus was used to deduce an approximate θ_D (Equation 13) or if necessary $\theta_D + \theta_E$ (Equation 14). However, if the barrier was low or unknown the internal rotation contribution was not negligible and had to be included. Therefore the remainder from Step 2 was fitted by trial and error to a C_v^L plus C_v^{IR} form to estimate θ_D or θ_D and θ_E .

(4) Using the θ_D or θ_D and θ_E from Step 3, the lattice contribution, C_v^L , was calculated for each temperature.

This contribution was then subtracted from the remainder of Step 1.

(5) The remainder from Step 4 was then fitted by trial and

error with the more accurate work of expansion term $[(C_p - C_v)$, Equation 7] and a hindered rotor contribution (C_v^{IR}) . The best fit to the experimental data was found by plotting the sum of the squares of the deviations of the calculated heat capacities from the experimental heat capacities versus the barrier height, V_o , and finding the minimum.

(6) The procedure in Step 5 was then repeated for slightly larger and slightly smaller lattice contributions (C_v^L) to determine if a better fit could be obtained (see Appendix A).

(7) The uncertainty in the parameters of Equation 12 was then calculated. This was done by seeing how much the parameters could be changed in either direction from the chosen best value without the sum of the squares of the deviations exceeding twice the value of the minimum value. This criterion for determining the uncertainty was chosen since it was found that when the value of the sum of the squares of the deviations was doubled, many of the deviations changed by 0.05 cal/(mole °K) or more and became unacceptable. Calculated values were unacceptable when they deviated more than ± 0.08 cal/(mole °K) from the experimental values. Also it was felt that this uncertainty assignment would take into account the uncertainties in the method.

PRESENTATION OF RESULTS

The five compounds treated in this study were mesitylene, toluene, benzenethiol, methanethiol, and trifluoromethanethiol. The results of the calculations on these five compounds are given in the seven tables which follow. Tables 1 and 2 give the general information required for the calculations, while Tables 3-7 show the calculations on the specific compounds.

Table 1 gives the parameters for Equations 4, 7, and 13 or 14 whichever was used (see theory section). These equations were then used in Equation 1. Table 1 also gives the number of rotors per molecule as well as the source of the heat capacity and spectral data.

Table 2 gives the barrier heights calculated through the use of Equation 1. For comparison the table gives the "best" values for the barriers from the literature. The parameters necessary to calculate the internal rotation contribution to the heat capacity from Figures 1 and 2 and from the tables of Li and Pitzer (10) and of Pitzer and Gwinn (15) are also given.

Tables 3 through 7 give the calculated and the experimental heat capacities for each compound. They also give the calculated values of the individual components of Equation 1 which make up the total calculated heat capacity. The differences between the observed and the calculated heat capacities are also tabulated.

Table 1. The parameters for equation 1.

Substance	θ_D	θ_E	a	b	m	Source of C_p (obs)	Source of spectral data
	$^{\circ}K$						
mesitylene	113 ± 3	-	0.0154 ± 0.0004	0	3	21	16
toluene	128 ± 3	-	0.0101 ± 0.0006	0	1	20	20, 24
benzenethiol	275 ± 15	72 ± 3	0.0115 ± 0.0005	0	1	19	19
methanethiol	248 ± 3	95 ± 1	0.0097 ± 0.0007	0	1	18	18
trifluoromethanethiol	102 ± 1	-	0.0102 ± 0.0015	0	1	3	3

Table 2. Barrier heights derived from thermal data.

Substance	$I_r \times 10^{40}$ $g\ cm^2$	Source of I_r	n	V_o	V_o (lit)	Source of V_o (lit)*
				cal/mole		
mesitylene	5.46	16	6	540 ± 40	0-900 190 ± 25	22 (S) 26 (C)
toluene	5.008	20	6	340 ± 200	500 ± 500 200 ± 25	20 (S) 26 (C)
benzenethiol	2.741	19	2	280 ± 70	<500	19 (S)
methanethiol	1.853	18	3	1650 ± 200	1460 ± 270 1270 ± 30	18 (S) 9 (M)
trifluoromethanethiol	2.821	3	3	1630 ± 180	1540 ± 260 1215	3 (S) 17 (I)

* S - From gas phase entropy data.

C - From low temperature heat capacity data.

M - From microwave measurements.

I - From infrared measurements.

Table 3. Contributions to the heat capacity of mesitylene.

T °K	C_v^L	C_v^I	$C_p - C_v$	C_v^{IR}	$C_p^{(cal)}$	$C_p^{(obs)}$	Δ
	cal/(mole °K)						
20	3.56	0.00	0.06	0.15	3.77	3.77	0.00
25	5.12	0.01	0.16	0.38	5.67	5.67	0.00
30	6.42	0.02	0.29	0.74	7.47	7.48	0.01
35	7.45	0.07	0.46	1.11	9.09	9.09	0.00
40	8.25	0.17	0.65	1.45	10.52	10.49	-0.03
45	8.87	0.29	0.84	1.76	11.76	11.77	0.01
50	9.36	0.45	1.04	2.05	12.90	12.97	0.07
60	10.05	0.89	1.44	2.58	14.96	15.16	0.20
70	10.50	1.38	1.83	2.97	16.68	16.59	-0.09
80	10.81	1.92	2.22	3.26	18.21	18.18	-0.03
90	11.03	2.52	2.60	3.45	19.60	19.55	-0.05
100	11.20	3.01	2.97	3.57	20.75	20.76	0.01
120	11.41	4.32	3.71	3.67	23.11	23.12	0.01
140	11.54	5.52	4.42	3.69	25.17	25.39	0.22

Table 4. Contributions to the heat capacity of toluene.

T °K	C_v^L	C_v^I	$C_p - C_v$	C_v^{IR} cal/(mole °K)	C_p (cal)	C_p (obs)	Δ
25	4.23	0.00	0.05	0.37	4.65	4.60	-0.05
30	5.54	0.01	0.09	0.47	6.11	6.00	-0.11
35	6.63	0.02	0.16	0.56	7.37	7.28	-0.09
40	7.51	0.05	0.23	0.67	8.46	8.40	-0.06
45	8.21	0.10	0.31	0.75	9.37	9.38	0.01
50	8.78	0.17	0.39	0.82	10.16	10.23	0.07
60	9.60	0.35	0.56	0.93	11.44	11.64	0.20
70	10.15	0.61	0.74	1.00	12.50	12.73	0.23
80	10.53	0.92	0.90	1.05	13.40	13.60	0.20
90	10.80	1.29	1.07	1.07	14.23	14.35	0.12
100	11.00	1.70	1.23	1.08	15.01	15.01	0.00
120	11.27	2.65	1.55	1.09	16.56	16.40	-0.16
140	11.44	3.73	1.87	1.09	18.13	17.91	-0.22

Table 5. Contributions to the heat capacity of benzenethiol.

T °K	C_v^L	C_v^I	$C_p - C_v$	C_v^{IR} cal/(mole °K)	C_p (cal)	C_p (obs)	Δ
30	4.35	0.02	0.08	1.34	5.79	5.73	-0.06
35	5.10	0.06	0.12	1.47	6.75	6.75	0.00
40	5.77	0.12	0.18	1.53	7.60	7.64	0.04
45	6.37	0.21	0.24	1.55	8.37	8.41	0.04
50	6.90	0.32	0.31	1.55	9.08	9.10	0.02
60	7.80	0.61	0.48	1.51	10.40	10.37	-0.03
70	8.52	0.96	0.67	1.45	11.60	11.53	-0.07
80	9.09	1.29	0.87	1.39	12.64	12.64	0.00
90	9.55	1.80	1.09	1.34	13.78	13.80	0.02
100	9.91	2.28	1.30	1.30	14.79	14.97	0.18

Table 6. Contributions to the heat capacity of methanethiol.

T °K	C_v^L	C_v^I	$C_p - C_v$	C_v^{IR} cal/(mole °K)	C_p (cal)	C_p (obs)	Δ
30	3.50	0.00	0.03	0.00	3.53	3.52	-0.01
35	4.45	0.00	0.06	0.00	4.51	4.51	0.00
40	5.28	0.00	0.10	0.02	5.40	5.43	0.03
45	6.03	0.00	0.15	0.06	6.24	6.27	0.03
50	6.68	0.00	0.20	0.11	6.99	7.05	0.06
60	7.74	0.00	0.34	0.23	8.31	8.33	0.02
70	8.55	0.00	0.48	0.38	9.41	9.41	0.00
80	9.16	0.00	0.63	0.56	10.35	10.30	-0.05
90	9.63	0.00	0.78	0.73	11.14	11.08	-0.06
100	10.00	0.01	0.94	0.90	11.85	11.79	-0.06
110	10.28	0.02	1.09	1.05	12.44	12.44	0.00
120	10.52	0.05	1.25	1.19	13.01	13.08	0.07
130	10.70	0.08	1.40	1.33	13.51	13.74	0.23

Table 7. Contributions to the heat capacity of trifluoromethanethiol.

$^{\circ}\text{K}$	C_v^L	C_v^I	$C_p - C_v$	C_v^{IR} cal/(mole $^{\circ}\text{K}$)	C_p (cal)	C_p (obs)	Δ
30	7.12	0.00	0.16	0.00	7.28	7.32	0.04
35	8.07	0.00	0.24	0.03	8.34	8.35	0.01
40	8.80	0.00	0.32	0.08	9.20	9.19	-0.01
45	9.35	0.01	0.41	0.14	9.91	9.89	-0.02
50	9.77	0.02	0.50	0.22	10.51	10.48	-0.03
55	10.10	0.04	0.58	0.31	11.03	10.99	-0.04
60	10.36	0.08	0.67	0.40	11.51	11.48	-0.03
65	10.58	0.13	0.76	0.51	11.98	11.96	-0.02
70	10.75	0.20	0.84	0.61	12.40	12.41	0.01
75	10.89	0.29	0.93	0.71	12.82	12.84	0.02
80	11.01	0.40	1.01	0.81	13.23	13.26	0.03
85	11.11	0.52	1.09	0.91	13.63	13.65	0.02
90	11.19	0.67	1.17	1.00	14.03	14.22	0.19

DISCUSSION OF RESULTS

In general the calculated and the experimental heat capacities of the compounds treated in this investigation agreed within the expected limits. The results obtained for molecular solids by other investigators (13, 26) led to the conclusion that the calculated heat capacities should not deviate, for the most part, more than ± 0.08 cal/(mole $^{\circ}$ K) from the experimental heat capacities and in most instances even less.

It was found, however, that for some temperatures the deviations between the calculated and observed heat capacities were of the order of 0.20 cal/(mole $^{\circ}$ K) or greater. With the exception of mesitylene and toluene, these larger deviations occurred at the upper-most temperature which were near the melting point or near an anomaly in the heat capacity curves. The divergence between theory and experiment close to the melting point may be due either to inaccuracy of Equation 13 or 7 where melting is imminent, or to a slight uncorrected increase in the observed heat capacity near the melting point because of the presence of a trace of impurity in the sample under observation. The most probable reason is the failure of the six degree Debye function, since spectroscopic studies have shown that the torsional or "rotational" energy levels are discrete instead of continuous and that they are functions of temperature. In

fact, evidence shows that the molecules of some crystals actually undergo restricted rotation of lattice sites well below the melting point (23, p. 61-62) thus making the calculated values low. Therefore, the increasing contributions of torsional oscillations near the melting point, which are not considered by six degree Debye function, probably account for the increased discrepancy between the calculated and experimental heat capacity values.

Most of the deviations, however, were near an anomaly in the heat capacity curve. These anomalies which take the form of a "hump," sharp peak, or a discontinuity in the heat capacity curve can be caused by any one of a great variety of phase transitions. These phase transitions are a change in crystal structure or arrangement of molecules in a lattice, changes in the orientation or conformation of molecules at lattice sites or both. This investigation was confined to the region below the anomaly since in most cases the parameters needed to fit the experimental heat capacity curve above the anomaly changed. The only exception to this was the mesitylene heat capacity curve which exhibited a small "hump" at 60 °K. In this case the same equation parameters could be applied both above and below the anomalies. The reason then for the deviation of calculated and experimental values can then be attributed to being in the region affected by the anomaly or possibly even the beginning of the change in the parameter values to the new values above the anomaly.

The calculated and literature values for the barriers to internal rotation are given in Table 2. The barrier values obtained by this investigation are in accord with gas phase entropy calculations and are more precise especially for the lower barriers. This greater precision was expected since the experimental uncertainty of a typical organic substance, including those of this investigation, is about 0.02 cal/(mole °K) at 100 °K. This uncertainty corresponds to an uncertainty of only 10 cal/mole for a barrier of approximately 500 cal/mole. On the other hand, the uncertainty in gas phase entropy calculations is about 0.15 to 0.30 cal/(mole °K). The tables of Pitzer and Gwinn (15) indicate that an uncertainty of 0.2 cal/(mole °K) in the entropy due to internal rotation would encompass values of the potential barrier between 0 and 900 cal/mole for a methyl group affected by a low-potential barrier, at 300 °K. For higher barriers, the same uncertainty would be consistent with potential barriers between 2600 and 3600 cal/mole.

However, there are other factors with respect to the method itself which cause the uncertainty to be higher, especially with relatively high barriers. One of these factors is the use of gas-phase spectral data, where the frequencies may be shifted somewhat on transition to the solid phase. However, Wulff (26) states that a discrepancy of five cm^{-1} in a frequency of 146 cm^{-1} , which is somewhat lower than the lowest frequency encountered in this investigation,

would change the heat capacity contribution by only 0.03 cal/(mole °K) at 100 °K and by 0.04 cal/(mole °K) at 50 °K.

Another factor that introduces some uncertainty is that Equations 13, 14 and 7 are approximations to the actual lattice and work of expansion terms. As mentioned earlier it has been shown that the "rotational" contributions are discrete instead of continuous and are temperature dependent. It was also stated that molecules of some crystals actually undergo restricted rotation at temperatures well below the melting point. These are not taken into account by the simple six degree Debye function or even by the Einstein and Debye function which assumes all the "rotational" vibrations to be equal which probably is not true. Also as a crystal expands with increasing temperature its elastic constants change, causing θ_D to be a function of temperature instead of a constant.

The foregoing considerations show that the work of lattice expansion term, Equation 7, may not be a good measure of the actual quantity. This term may absorb all of the error resulting from the first two factors above. However, it is found that the combination of Equations 13, or 14, 4, and 7 give good quantitative results for molecules without internal rotation. Therefore it was the conclusion of Wulff (26) and of this investigator that while the representation of the individual components may be somewhat in error their sum does give a fairly accurate representation of the combined contributions and

thus should not unduly affect the accuracy of the barrier value when internal rotation is added.

The greatest source of uncertainty to the barrier value is in the extrapolation of the tables of Li and Pitzer (10) for the internal rotation contribution. Fortunately in the region of high $1/Q_f$ numbers (> 1.5) where the extrapolation was the most uncertain, high V_0/RT numbers (> 16) were used and thus were in the region of small contributions. Also the two extrapolation methods agreed fairly well in this region leading to the belief that the results were roughly correct.

The criterion used to determine the uncertainty in the barrier was the ability of the parameters of Equation 1 (see theory section) to give a unique fit to the experimental heat capacity curve within the limits assigned. As mentioned in the theory section the best fit was found by minimizing the sum of the squares of the deviations and then finding out how far the parameters of Equation 1 could be varied on each side of the minimum sum of the squares value and still stay within twice this sum of the squares value. This criterion for determining the error was chosen since it was found that when the value of the sum of the squares of the deviation was doubled, many of the deviations changed by $0.05 \text{ cal}/(\text{mole } ^\circ\text{K})$ or more and became unacceptable. Calculated values were unacceptable when they deviated more than $\pm 0.08 \text{ cal}/(\text{mole } ^\circ\text{K})$ from the experimental values. Also

it was felt that this uncertainty assignment would take into account the uncertainties in the method previously mentioned. A discussion of the individual molecules follows.

The calculated and observed heat capacities of mesitylene are given in Table 3, and the differences, Δ , between the two are shown in the last column. With the exception of the points at 60° and 140 °K, the calculated values of the heat capacity agree within the expected limits. The deviation at 60 °K is caused by a "hump" in the heat capacity curve which was discussed earlier. The deviation at 140 °K is probably caused by the failure of the six degree Debye function representing the lattice contribution. This failure is possibly caused either by the effects of the phase transition which occurred at 60 °K or more probably by the increased contribution of the "rotational" contribution as the melting point of 228.3 °K is neared. Restricted rotation of the molecules might even be taking place although there is no evidence to support this hypothesis. The barrier for mesitylene as given in Table 2 falls near the center of the range of barrier values obtained from gas phase entropy data. The barrier value, however, does not agree very well with the value obtained by Wulff (26). However, it was felt that Wulff's representation of the internal rotation contribution using a harmonic oscillator approximation was not appropriate for these lower barriers.

It was found that θ_D , a , and V_o could not be varied too

much without the heat capacity exceeding the acceptable variations of twice the minimum sum of the squares of the deviations. Thus Equation 1 provided a fairly unique fit to the heat capacity curve and the uncertainty in the barrier value was very much smaller than for the gas phase entropy calculations.

The calculated and observed heat capacities of toluene as shown in Table 4 do not agree within the accepted limits of ± 0.08 cal/(mole °K). No reason is known why it was impossible to obtain better agreement. One possibility is that there might be a misassignment of one or more of the vibrational frequencies though it is unlikely that this would account for all the error. However, even with the poor agreement between the calculated and experimental values of the heat capacity, the calculated barrier is still in the range of values indicated by Scott et al. (20) and Wulff (26). Unfortunately, the inability of Equation 1 to provide acceptable agreement between the calculated and observed values causes a correspondingly large uncertainty in the barrier value.

The deviations between the calculated and observed heat capacity values for benzenethiol as shown in Table 5 are, for the most part, well within the expected deviation. The large deviation at 100 °K is probably caused by the nearness of a phase transition anomaly at 128 °K as discussed earlier. From Table 2 the calculated barrier is seen to be in accord with the barrier from gas phase

entropy calculations. The value of the barrier is more precise than the gas phase entropy value. From Table 1 it is seen that the parameters of Equation 1 were unable to provide a unique fit within the accepted error. The reason for this is that approximately the same lattice contribution curve could be obtained over the range of θ_D and θ_E indicated, because a 1 °K change in θ_E could almost offset a 5 °K change in θ_D . Therefore the reason the barrier uncertainty is still low is that Equation 1 actually did give a fairly unique fit of the parameters if the fact is considered that the lattice contribution was much more constant than the θ_D and θ_E values would lead one to believe.

The agreement between the calculated and observed heat capacities of methanethiol as shown in Table 6 are also within the expected limits. The exception at 130 °K is again probably caused by an anomaly in the heat capacity curve at 137.6 °K which was discussed previously. The barrier of 1460 cal/mole obtained by Russell et al. (18) from gas phase entropy data and the barrier of 1650 cal/mole obtained from this investigation are in agreement within their uncertainties. Neither barrier value agrees very well with the barrier obtained by Kojima and Nishikawa (9) from microwave spectra. Microwave methods yield much more precise potential barriers than do thermodynamic methods, provided assignment of microwave lines are correct. The uncertainties of the parameters

of Equation 1 are low with the exception of the barrier uncertainty. This large uncertainty is inherent at these higher barrier values because the contribution does not change rapidly with barrier height.

The agreement between the calculated and observed heat capacities of trifluoromethanethiol as shown in Table 3 is also well within the expected limits. The exception at 90 °K is caused by the nearness of the melting point of 116 °K. From Table 2 the potential barrier obtained by this investigator and that obtained by Dininny and Pace (3) from gas phase entropy calculations are in good agreement. Neither of the barrier values agreed with the value found by Redington (17) from infrared techniques. Infrared methods are capable of giving precise potential barriers provided the assignment of the infrared lines are correct and the band center can be determined. The uncertainty in the barrier found in this investigation is caused mainly by the insensitivity of the contribution to a change in the barrier value.

CONCLUSIONS AND RECOMMENDATIONS

It is evident that the barrier heights obtained in this study are in accord with those obtained from gas phase entropy data. Also, the precision is substantially greater for low barriers and about the same or slightly better for high barriers. The ability of the combination of functions to represent the experimental heat capacities is also very good. The agreement was generally well within the accepted limits set.

Improvement in the method could probably be obtained through the use of a computer since the time needed for the calculations could be shortened considerably. This would be especially true of compounds with unknown or very uncertain barrier values, since a large number of barrier and parameter values could be covered in minutes rather than days.

Some uncertainty caused by the method itself could be made by finding, if possible, a better method for extending the tables of Li and Pitzer (10). A possible solution is an extension of Pitzer and Gwinn's (15) original calculations into the region of interest.

Any other improvements in the method would have to be with respect to previously discussed problems in the lattice motion contribution and the expansion of the lattice contribution and would be of an experimental nature.

NOMENCLATURE

- a = Constant in Equation 7.
- b = Constant in Equation 7.
- c = Velocity of light = 2.998×10^{10} cm/sec.
- C_p = Constant pressure heat capacity.
- C_v = Constant volume heat capacity.
- C_v^I = Contribution to the heat capacity from intramolecular vibrations.
- C_v^{IR} = Contribution to the heat capacity from each internal rotation.
- C_v^L = Contribution to the heat capacity from lattice motions.
- $D(\theta_D/T)$ = Debye function.
- $E(\theta_E/T)$ = Einstein function.
- h = Planck constant = 6.6252×10^{-27} erg sec.
- I_r = Reduced moment of inertia.
- k = Boltzmann constant = 1.380×10^{-16} erg/sec.
- m = Number of internal rotors in molecule.
- N = Avagadro's number = 6.023×10^{23} molecules/g-mole.
- N' = Number of atoms per molecule.
- n = Number of potential maxima encountered in one revolution of internal rotor.
- Q_f = Free rotation partition function = $(8\pi^3 I_r kT)^{\frac{1}{2}}/nh$.

R	= Ideal gas constant = 1.98717 cal/g mole deg.
T	= Temperature, °K.
T_{mp}	= Melting point temperature, °K.
V_o	= Barrier to internal rotation, cal/g-mole.
α	= Coefficient of thermal expansion.
β	= Isothermal compression coefficient.
θ_D	= Debye characteristic temperature = $hc\nu_D/k$ °K.
θ_E	= Einstein characteristic temperature = $hc\nu/k$ °K.
ν	= Frequency in cm^{-1} of a harmonic oscillator.
ν_D	= Debye frequency, cm^{-1} .
ϕ	= Angle of revolution of internal rotor.

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APPENDICES

APPENDIX A

SAMPLE CALCULATIONS

The calculations can be divided into two main categories, those for molecules having a relatively high barrier (>1000 cal/mole) and those having a low barrier. In addition, two compounds presented an extra calculation because the lattice contribution had to be calculated from Equation 14 involving a Debye and an Einstein function. The remaining compounds could be treated with the simple six degree Debye function. A sample calculation for a compound with a high barrier and with a lattice contribution given by the Debye and Einstein equation will be shown. A second calculation for a compound having a low barrier and a lattice contribution given by the simpler six degree Debye function (Equation 13) is shown for completeness.

Methanethiol: A High Barrier Case

The calculations will be done by the steps listed in the procedure section. The compound treated is methanethiol.

Step 1: The intramolecular vibration contribution was calculated at each temperature in the following manner.

At 100°K the frequencies making a contribution to the heat capacity of methanethiol were 704cm^{-1} , 803cm^{-1} , 957cm^{-1} and

1060cm^{-1} . All other fundamental vibrations involved higher energies and made no contribution at this temperature. This contribution was calculated from Equation 4 in the following manner.

$$C_v^I = R \sum_{i=1}^{3N'-6-m} E(\theta_{E_i}/T)$$

where $\theta_E/T = hc\nu/kT = 1.4388\nu/T$

$$\begin{aligned} C_v^I &= R [E(10.13) + E(11.55) + E(13.77) + E(15.25)] \\ &= R (0.0041 + 0.0013 + 0.0006) \\ &= 0.01 \text{ cal/mole} \end{aligned}$$

The contribution at each temperature was then subtracted from the experimental heat capacity.

Step 2: The contribution of the work of expanding the lattice was then approximated at the lowest temperatures by the Nernst and Lindeman equation. As an example, the contribution at 35°K for methanethiol was as follows:

$$\begin{aligned} C_p - C_v &= 0.0214 C_p^2 T/T_{mp} \\ &= 0.0214 (4.51)^2 (35^\circ\text{K})/150.2^\circ\text{K} \\ &= 0.10 \text{ cal/mole} \end{aligned}$$

These contributions were then subtracted from the remainder in Step 1.

Step 3: The barrier for methanethiol was known to be fairly high. Therefore the internal rotation contribution of lower temperatures was quite small and the remainder from Step 2 was approximately the contribution of the lattice motions. It was found that it

was necessary to use the Einstein and Debye function (Equation 14) to represent the lattice contribution for methanethiol. Through a trial and error calculation a θ_E and θ_D were found for Equation 14

$$C_v^L = 3R E(\theta_E/T) + 3R D(\theta_D/T) \quad (14)$$

by choosing a value for one of the θ 's, say θ_D , finding the contributions for the low temperatures used in Step 2 and subtracting the contribution from the remainder in Step 2. This remainder was used to calculate θ_E at each temperature. Different θ_D 's were chosen until the calculated θ_E was as close as possible to being temperature independent. An initial try and the final try are shown below for methanethiol.

Initial try with $\theta_D = 260^\circ\text{K}$ (all units are cal/(mole $^\circ\text{K}$) unless otherwise stated).

$T^\circ\text{K}$	C_p	C_v^I	$C_p - C_v$ Eq. 6	Step 2 remainder	$C_v(\theta_D)$	Remainder	$\theta_E^\circ\text{K}$
25	2.52	0.00	0.02	2.50	0.40	2.10	93.0
30	3.52	0.00	0.05	3.47	0.67	2.80	93.7
35	4.51	0.00	0.10	4.41	0.99	3.42	92.9
40	5.43	0.00	0.17	5.26	1.34	3.92	91.5
45	6.27	0.00	0.25	6.02	1.70	4.32	89.9

Final try with $\theta_D = 250^\circ\text{K}$.

$T^\circ\text{K}$	Step 2	$C_v(\theta_D)$	remainder	$\theta_E^\circ\text{K}$
25	2.50	0.45	2.05	94
30	3.47	0.74	2.73	95.4
35	4.41	1.09	3.32	95.4
40	5.26	1.46	3.80	95.0
45	6.02	1.83	4.19	94.0

The values chosen for the initial values of θ_D and θ_E were 250°K and 95°K respectively.

Step 4: The lattice contribution was then subtracted from the remainder in Step 1 using the following equation for C_v^L .

$$C_v^L = 3R E(95/T) + 3R D(250/T)$$

Step 5: The remainder from Step 4 was then fitted over the entire temperature range by trial and error to an internal rotation contribution plus the more accurate work of expansion term as shown by the following equation.

$$\text{Remainder Step 4} = mC_v^{\text{IR}} + [a \cdot C_v^L + b(C_v^L + C_v^{\text{IR}})^2] T$$

In order to compute C_v^{IR} it was necessary to calculate the reciprocal of the partition function for free rotation at each temperature. For example, the value of the partition function at 50°K for methanethiol was calculated in the following manner.

$$\begin{aligned} 1/Q_f &= nh / (8\pi^3 I_r kT)^{\frac{1}{2}} \\ &= n / 2.73935 (10^{38} I_r T)^{\frac{1}{2}} \end{aligned}$$

For methanethiol, n , the number of maxima encountered by the rotor in one complete revolution equals three and I_r , the reduced moment of inertia, equals $1.853 \times 10^{-40} \text{ g cm}^2$ (18). Therefore, for $T = 50^\circ\text{K}$

$$\begin{aligned} 1/Q_f &= 3 / (2.7935 (1.853 \cdot 10^{-40} \cdot 10^{38} \cdot 50)^{\frac{1}{2}}) \\ &= 1.116 \end{aligned}$$

Then a barrier was chosen, V_0/RT calculated, and the

contribution found from Figures 1 or 2 or the tables of Li and Pitzer (10) or Pitzer and Gwinn (15) using the appropriate $1/Q_f$ and V_o/RT values. The contributions were then subtracted from the remainder in Step 1. This remainder was then fitted as closely as possible by the lattice expansion term.

$$C_p - C_v = [a \cdot C_v^L + b(C_v^I + mC_v^{IR})^2] T \quad (7)$$

The deviation of the expansion contribution from the last remainder was then calculated and the sum of the squares of the deviations was found. The barrier and the expansion term were then changed until the sum of the squares was minimized.

Steps 4 and 5 are shown below for methanethiol for only a few of the temperatures. The initial parameters used were $\theta_D = 250^\circ K$, $\theta_E = 95K$, an initial barrier of 1500 cal/mole, $a = 0.0097$ and $b = 0.0$.

T °K	$C_p - C_v^I$	$C_v^L(\theta_E)$	$C_v^L(\theta_D)$	C_v^L	$C_p - C_v^I - C_v^L$	C_v^{IR}	Re-main-der	$C_p - C_v$	Δ^*
30	3.52	2.75	0.74	3.49	0.03	0.00	0.03	0.03	0.00
50	7.05	4.45	2.20	6.65	0.40	0.14	0.26	0.20	0.06
80	10.30	5.31	3.83	9.14	1.16	0.64	0.52	0.63	-0.11
100	11.78	5.53	4.45	9.98	1.80	0.99	0.81	0.94	-0.13
120	13.03	5.66	4.85	10.51	2.52	1.27	1.25	1.25	0.00

$$*\sum\Delta^2 = 3.26 \times 10^{-2}$$

However upon changing the barrier and the parameter, a , it was found that a better fit existed at $V_o = 1700$ cal/mole and a unchanged, all other parameters being the same. This is shown below.

T ^o K	C _p - C _v ^I - C _v ^L	C _v ^{IR}	Remainder	C _p - C _v	Δ*
30	0.03	0.00	0.03	0.03	0.00
50	0.40	0.10	0.30	0.20	0.10
80	1.16	0.53	0.63	0.63	0.00
100	1.80	0.87	0.93	0.94	-0.01
120	2.52	1.16	1.36	1.25	0.11

$$*\sum\Delta^2 = 2.22 \times 10^{-2}$$

Step 6: The values of θ_D and θ_E were then varied slightly one at a time and the procedure in Step 5 repeated to try to find a better fit. The final parameters for methanethiol were then $\theta_D = 248^\circ \text{K}$, $\theta_E = 95^\circ \text{K}$, $a = 0.0097$, $b = 0.0$, and a barrier of 1650 cal/mole. The contributions are shown below.

T ^o K	C _v ^L	C _p - C _v ^I - C _v ^L	C _v ^{IR}	Remainder	C _p - C _v	Δ*
30	3.50	0.02	0.00	0.02	0.03	-0.01
50	6.68	0.37	0.11	0.26	0.20	+0.06
80	9.16	1.14	0.56	0.58	0.63	-0.05
100	10.00	1.78	0.90	0.88	0.94	-0.06
120	10.52	2.51	1.19	1.32	1.25	+0.07

$$*\sum\Delta^2 = 1.47 \times 10^{-2}$$

Step 7: The uncertainty of the method was found by finding the maximum amount the parameters could be varied and still keep within twice the minimum value of the sum of the squares of the deviations.

Mesitylene: A Low Barrier Case

The only difference between the low and the high barrier calculation occurred in Step 3. This step had to be modified because the barrier was low, and thus the contribution was no longer negligible.

The remainder from Step 2 must be fitted by trial and error to the following equation.

$$\text{Step 2 remainder} = C_v^L + C_v^{IR}$$

The calculation for mesitylene was further simplified because the lattice contribution could be represented by the simpler six degree Debye equation (Equation 13).

In this calculation a barrier was chosen and its contribution calculated and subtracted from remainder in Step 2. This remainder was then used to calculate a θ_D from Equation 13 at several temperatures.

$$C_v^L = 6R D(\theta_D/T)$$

The barrier was changed until the calculated θ_D 's were approximately independent of the temperature used. This is shown below for an initial trial and for the final trial for mesitylene.

Initial trial with $V_o = 600$ cal/mole

T °K	Step 2 remainder	$3C_v^{IR}$	Remainder	θ_D °K
20	3.72	0.06	3.66	111.3
45	10.37	1.56	8.81	114.4

Final try with $V_o = 640$ cal/mole

T °K	$3C_v^{IR}$	Remainder	θ_D °K
20	0.02	3.70	110.6
45	1.41	8.96	110.9

The θ_D then chosen was 111 °K. The remaining calculations were the same as in the high barrier case.

APPENDIX B. Supplementary chart to aid in drawing figures 1 and 2.

V_o/RT	$1/Q_f$											
	1.00	1.10	1.20	1.30	1.40	1.50	1.60	1.70	1.80	1.90	2.00	
0.6	1.008	1.004	1.001	0.998	0.996	0.994	0.994	0.994	0.994	0.994	0.994	0.994
0.8	1.015	1.006	0.999	0.993	0.988	0.984	0.980	0.977	0.974	0.971	0.968	0.968
1.0	1.022	1.008	0.992	0.981	0.972	0.964	0.957	0.950	0.944	0.939	0.934	0.934
1.5	1.053	1.019	0.990	0.966	0.945	0.927	0.911	0.897	0.886	0.875	0.867	0.867
2.0	1.084	1.028	0.978	0.937	0.904	0.875	0.850	0.829	0.811	0.795	0.782	0.782
2.5	1.104	1.030	0.968	0.914	0.869	0.830	0.795	0.763	0.733	0.704	0.680	0.680
3.0	1.113	1.019	0.942	0.879	0.826	0.780	0.742	0.706	0.674	0.644	0.616	0.616
3.5	1.108	1.003	0.920	0.850	0.792	0.743	0.699	0.660	0.627	0.587	0.580	0.580
4.0	1.085	0.969	0.879	0.806	0.748	0.699	0.653	0.612	0.586	0.560	0.545	0.545
4.5	1.051	0.932	0.839	0.764	0.703	0.650	0.605	0.566	0.542	0.526	0.513	0.513
5.0	1.006	0.886	0.790	0.715	0.650	0.591	0.554	0.524	0.500	0.485	0.475	0.475
6.0	0.893	0.783	0.693	0.624	0.565	0.522	0.490	0.464	0.443	0.426	0.413	0.413
7.0	0.767	0.660	0.582	0.521	0.474	0.438	0.411	0.392	0.374	0.362	0.352	0.352
8.0	0.647	0.555	0.484	0.428	0.387	0.358	0.336	0.319	0.305	0.294	0.287	0.287
9.0	0.542	0.456	0.391	0.342	0.306	0.279	0.258	0.244	0.232	0.222	0.213	0.213
10.0	0.451	0.365	0.307	0.262	0.228	0.201	0.181	0.165	0.152	0.142	0.136	0.136
12.0	0.315	0.248	0.198	0.165	0.140	0.124	0.111	0.101	0.093	0.086	0.083	0.083
14.0	0.228	0.174	0.138	0.110	0.089	0.074	0.063	0.055	0.048	0.043	0.040	0.040
16.0	0.165	0.122	0.092	0.070	0.054	0.041	0.032	0.024	0.019	0.014	0.010	0.010
18.0	0.120	0.082	0.055	0.037	0.025	0.016	0.008	0.003	0.000	0.000	0.000	0.000
20.0	0.089	0.058	0.036	0.020	0.009	0.002	0.000	0.000	0.000	0.000	0.000	0.000

Note: For internal consistency more digits are retained in this table than are justified.