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Rotation in Molecular Crystals

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A postulate parallel to Boltzmann's postulate: log $W \propto S$, permits the estimation of heat capacity anomalies in substances for which data are published, and the prediction of anomalies in other crystals in which molecular rotation is possible. The dispersion relation relating excitation energy with frequency is derived from the data of molecular spectroscopy, based upon strong coupling between phonons and rotating molecules.

KEY WORDS Thermal entropy/Wave entropy/Disposal parameter/ Heat capacity/Molecular rotation/

INTRODUCTION

Boltzmann's postulate that the entropy of a gas was proportional to the log probability:

$$\log W \propto S$$

has been the cornerstone of equilibrium statistical mechanics, for from it, with the second law of thermodynamics, it is possible to define a thermodynamic temperature:

$$k\left(\frac{\partial \log W}{\partial U}\right)_V = \frac{1}{T}.$$

In the hands of later investigators, macroscopic quantities T, S, U and the other thermodynamic functions have been calculated from the quantum mechanical characteristics of a gas made of microscopic molecules.

A parallel postulate is proposed:

$$\left(\frac{\partial \log W}{\partial \varepsilon}\right)_V = \frac{1}{\nu}$$

where ν is the frequency of a wave, ε the energy of the wave and W is the probabiliy of this wave. With the aid of this postulate it is possible from quantum mechanics to calculate the energy of an excitation as a function of frequency: the dispersion relation.

Our principal quantum fluid, helium-4, has been described by Landau in terms of a dispersion relation.[1] At low frequency the excitations are phonons where $\varepsilon = h\nu$, at higher frequency there is a parabolic minimum which he named the roton. While many attempts have been made to describe these rotons in terms of microscopic states, no derivation has received unanimous acceptance.[2]

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TABLE I

THERMODYNAMICS Boltzmann's Postulate (Thermal Equilibrium)	WAVEDYNAMICS Wave Postulate (No Temperature)
$\log W \propto S$	$\log W \propto \frac{Q}{\nu}$
$k\left(\frac{\partial \log W}{\partial U}\right)_V = \frac{1}{T}$	$\left(\frac{\partial \log W}{\partial U}\right)_V \propto \frac{1}{\nu}$
Entropy	
$S = \frac{Q}{T}$	$\& = \frac{Q}{\nu}$
Free Expansion	
$\Delta S = \int_{V_i}^{V_f} \frac{dQ}{T}$	$\Delta \& = \int_{V_i}^{V_f} \frac{dQ}{\nu}$
Perfect Gas	Waves without Dispersion
$\Delta S \propto \log \frac{V_f}{V_i}$	$\Delta \& \propto \log \frac{V_f}{V_i}$
Carnot Cycle	
$\mathrm{Eff} = 1 - \frac{T_2}{T_1}$	$\mathrm{Eff} = 1 - \frac{\nu_2}{\nu_1}$
First Law	
$dU = TdS + \nu d\& - dW$ Temp. Waves	

We may in principle derive the thermodynamic character of an excitation gas such as the phonons or rotons in liquid helium using pistons and reservoirs in the traditional manner, and a comparison is made in Table I. The new quantity: wave entropy, &, has a definition entirely parallel to the entropy of a system in thermal equilibrium. Whereas temperature is that characteristic which has a common value for all systems in thermal equilibrium, frequency is that characteristic of a wave which remains constant as the wave passes from one medium to another. The wave-entropy must be carefully distinguished from thermal entropy for, as defined, it has the dimensions of action (erg sec.) and not energy (ergs). Rayleigh in 1902 discussed the vibrations of a string, and examined the analogy between frequency and temperature.[3] Each has only positive values and no upper bound. The zero of temperature and of frequency may be approached but not attained. Upon adiabatic expansion to lower temperature and frequency, and recompression, the original state is restored.

The significance of these formal statements resides in their utility. The purpose of the present study is to explore dispersion theory as it applies to molecular crystals and to identify its derivation from microscopic statistical mechanics, treating the molecule as an identifiable dynamical unit. A more complete statement of these proposals is to be found in reference 4.

DISPERSION RELATION

The dispersion relation: $\varepsilon = f(\nu)$ is a relation between the energy, ε, of an excitation

and its frequency, ν. In Landau's theory of liquid helium[1] there is no temperature dependence. In fact the dispersion relation can be measured at essentially zero temperature.[5] This dispersion relation allowed him to account for the deviation of the thermodynamic properties of liquid helium from those of the Debye theory. His dispersion curve was synthesized to fit the data, and no clear picture emerged of the excitation which he named the roton. Efforts have been made over the last decades to find a microscopic origin for the roton, but no identification has been generally accepted.[2,4]

In Planck's radiation theory, he is dealing with a wave of constant velocity so that $\varepsilon = h\nu$. His derivation can be extended to waves with variable velocity, such as are observed in liquid helium and other systems, by substituting $\varepsilon = (1-m)\, h\nu$, where m is initially considered a disposable parameter.[4] The energy of the excitation then becomes

$$U = \frac{(1-m)\, h\nu}{e^{(1-m)h\nu/kT} - 1} \qquad (1)$$

Analytically m must be a pure number which can take any value between zero and unity $(0<m<1)$. In statistical mechanics such parameters are usually related to concentrations. For example the concentration of ortho-hydrogen ranges from zero at low temperature to 0.75 for the high temperature mixture, and a statistical definition is used.[6] m, however, must be a function only of frequency, and not of temperature, for the dispersion relation is thought to apply to systems in the absence of temperature. It is then outside the realm of equilibrium thermal statistical mechanics, and the postulate $\log W \propto Q/\nu$ is introduced.

The present study extends the author's work on liquid helium to a class of compounds characterized by strong bonding between atoms of a small molecule and weak bonding between molecules. In such solids the molecular approximation may be expected to have utility.

The overwhelming success of traditional statistical mechanics is largely a consequence of the study of gases. In such systems there are strong forces between atoms of a molecule and very weak forces between molecules. The heat capacity, internal energy and free energy can be separated, and the total is the sum of the (a) translational contribution of the molecules and the (b) internal motions within the molecule. In the simplest case this is rotation of the molecule as a whole. At higher temperatures vibrational and other modes are excited.

In the study of absolute entropy there have been many attempts to correlate the thermodynamic properties of the molecular gas with those of the solid. While a superficial correlation may exist, it is not strong nor compelling. The heat capacity in a few cases may be the sum of the T^3 low temperature Debye term and an anomaly of the variety proposed by Schottky.[7] Yet a substance such as elementary oxygen, O_2, is surely a molecular solid in which a single molecule may occupy a lattice cell. In it the two atoms are strongly bonded, and the van der Waal forces between molecules are comparatively weak. The separation between atoms is 1.2Å whereas the separation between molecules is 4.1Å. There should, therefore, be an analogy between the thermodynamics of the solid and of the gas.[8] Experimentally an anomaly is found in O_2 beginning near 3°K, with a maximum near 10°K. The maximum for the gas should occur near 5°K.

The usual assumption of lattice theorists is that molecular rotation does not occur in solids. Yet solid hydrogen exists in ortho and para forms and the transformation rate

has been measured.[6] Methane has been extensively studied by Yamamoto upon the basis of the existence of spin states.[9] Pitzer has catalyzed spin transformation by adding molecular O_2 to his sample.[10] We have previously observed spin transformation in C_2H_2, H_2O, CH_4, and CH_2O.[4]

Oxygen is a particularly simple system, for it is homonuclear with zero nuclear spin, so rotational quantum numbers are restricted to $J=0, 2, 4\ldots$ We shall use this molecule as an example to reduce the complexity of the mathematics. The full expressions for other molecules will be included in a later section.

If free molecular rotation is assumed, we must seek a method of coupling these states to the Debye or phonon states. This is accomplished using the dispersion relation, and deriving the heat capacity from this dispersion relation. The form of the dispersion curve will be less extreme than that of liquid helium (Fig. 3). The expression $\varepsilon=(1-m)h\nu=(1-m)/h\omega$ permits us to represent a wave with velocity dependent upon frequency. The character of m is, therefore, central to the discussion. When $m=0$, the dispersion relation is that of phonons: $\varepsilon=h\nu$, and the Debye low temperature heat capacity is obtained: $C\infty T$.[3] As m becomes finite, the dispersion curve will deviate from the phonon line, resulting in excess heat capacity and an anomaly. m is not a function of temperature and can not therefore obtained from the traditional equilibrium theory of statistical mechanics. m is a function of frequency only. If we are to obtain a microscopic theory for m it must start from a new principle. A postulate equivalent to Boltzmann's postulate has been proposed:

$$\frac{\partial \log W}{\partial \varepsilon}\infty\frac{1}{\nu} \tag{2}$$

This permits us to define a partition function equivalent to the usual one but with kT replaced by $f(\nu)$.

$$Z=(2J+1)\,e^{-J(J+1)B/\varsigma\nu} \tag{3}$$

where J is the rotational quantum number, B, the rotational constant $B=h^2/8\pi^2I$ (with I the moment of inertia of the molecule), ν, the frequency and ς, a constant. From this partition function we can obtain the internal energy, entropy and heat capacity for a gas of quanta (or their equivalent waves) for which $\varepsilon=f(\nu)$, with energy a function of frequency and the velocity of the wave, frequency dependent.

Since the range of m is from zero to unity, it has the character of a concentration. At zero temperature, at equilibrium, all molecules will be in their lowest available state. For oxygen, this will be $J=0$. A low frequency wave will not produce molecular transitions and will be a phonon. $m=0$ would characterize this condition. As the wave frequency is increased (still at zero temperature) molecules can be rotationally excited by the passing wave and the concentration of excited molecules will depend upon frequency. $m>0$ would characterize this situation. For oxygen, $J=0, 2$, is sufficient to account for the observed anomaly. The concentration of excited molecules, in analogy with equilibrium statistics, will be $m=(Z-1)/Z$ and for oxygen will be:

$$m=\frac{\sum_{J=2,4\ldots}(2J+1)\,e^{-J(J+1)B/\varsigma\nu}}{\sum_{J=0,2,4\ldots}(2J+1)\,e^{-J(J+1)B/\varsigma\nu}} \tag{4}$$

The value of ç, empirically required, is $h/4\pi$ (to be compared with k for an equilibrium system). With this substitution, and $\omega=\nu/2\pi$ we obtain:

$$m=\frac{5e^{-6h/I\omega}}{1+5e^{-6h/I\omega}} \tag{5}$$

Figure 1 shows m as a function of circular frequency, ω, for O_2, N_2, CO, and F_2.

The rigorous derivation of these expressions is given in reference 4.

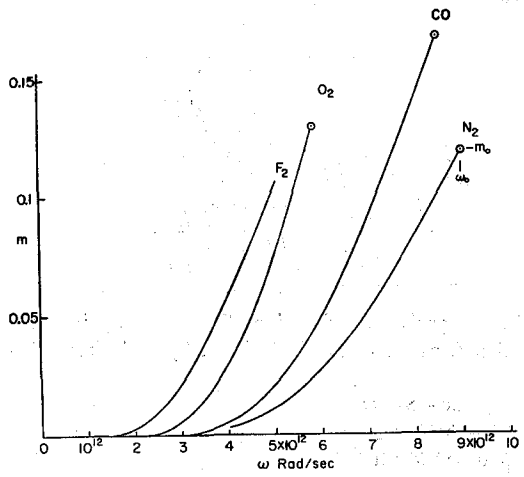

Fig. 1. Calculated values of m as a function of frequency ω.

LOW TEMPERATURE HEAT CAPACITY

The internal energy of a system for a single mode of oscillation, *e. g.* compressional, giving rise to longitudinal waves, is obtained from the dispersion relation:

$$u=\frac{V}{2\pi^2k^3}\int\frac{\varepsilon\omega^2d\omega}{e^{\varepsilon/kT}-1}. \tag{6}$$

From this the heat capacity is obtained by differentiation with respect to temperature, $\varepsilon=(1-m)/h\omega$ taken as temperature independent,

$$C_v=\frac{V}{2\pi^2c^3kT^2}\int\frac{\varepsilon^2e^{\varepsilon/kT}\omega^2d\omega}{(e^{\varepsilon/kT}-1)^2} \tag{7}$$

In the low temperature region, where $\varepsilon=/h\omega$, and the upper limit of integration may be replaced by infinity, we obtain

$$C_\varphi=\frac{16\pi^5Vk^4T^3}{15c^3h^3} \tag{8}$$

This means that there can be no significant contribution from excitations in oxygen with ω greater than 2×10^{12} rad/sec (Fig. 1), and corresponds to temperatures for oxygen less than 3° K. It is the Debye low temperature approximation: $C_\varphi\infty T^3$.

A second low temperature approximation is possible where the range of the integral extends beyond the phonon region into the region where m is small but not zero. This is the region where the theory is expected to be most reliable, for the excitations should be phonon-like ($1-m\cong1$). This region will then define the departure from phonon

heat capacity, attributed to molecular excitations (in the cases considered, the excitation of molecular rotation). It then is a predictable departure from T^3 heat capacity based only upon the moment of inertia of the molecule and the quantum rules familiar in molecular spectroscopy. It is a predictable correction to the "smooth extrapolation" used in absolute entropy studies.

The ratio of heat capacities with and without dispersion is evaluated by numerical integration, and $(C-C_\varphi)/C_\varphi$ is plotted against temperature in a log-log plot in Fig. 2.

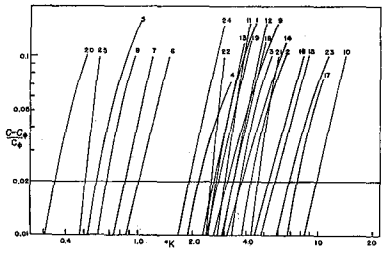

Fig. 2. Relative heat capacity as a function of temperature in the low temperature approximation for substances of Table II. Symbols from Table II.

$$\frac{C}{C_\varphi}=\frac{\int\frac{(1-m)^2 e^{(1-m)/h\omega/kT}\omega^4 d\omega}{(e^{(1-m)/h\omega/kT}-1)^2}}{\int\frac{e^{(1-m)/h\omega/kT}\omega^4 d\omega}{(e^{(1-m)/h\omega/kT}-1)^2}} \qquad (9)$$

Table II shows the result of calculation. The second column gives the moment of inertia, I, of the molecule; column three, the nuclear spin, S, of the pertinent atoms; column four, the quantization; column five, the calculated temperature for $(C-C_\varphi)/C_\varphi=0.02$, near the beginning of the anomaly; column six, the observed temperature. Column seven gives the calculated slope $d\ln(C-C_\varphi/C_\varphi)/d\ln T$ at $(C-C_\varphi)/C_\varphi=0.02$, which measures the strength of the anomaly: column eight gives the equivalent slope for the materials studied to sufficiently low temperatures. Column nine gives the value of m_0, empirically required to fit the maximum of the anomaly.

Where heat capacity measurements extend to the phonon region, the calculated threshold temperature corresponds reasonably well to that measured. The strength of the anomaly also corresponds to that measured, with one notable exception (CD_4). For the systems for which measurements have not been made, the predictions of the theory are given. In nearly every case the high temperature mixture has been used, for uncatalyzed nuclear spin transformations are slow. In the case of H_2O and H_2S, observers have seen slow release of heat in the calorimeter, and the equilibrium heat capacity has therefore been calculated.[11]

Not every one of the substances studied will necessarily show the effect. Formaldehyde (H_2CO) has a strong tendency to polymerize, and free rotation cannot be expected in the polymer. Hydrogen bonds may inhibit molecular rotation in H_2O and NH_3, but the excellence of the fit suggests that these bonds do not prevent rotation of the molecule.

One of the most interesting aspects of the theory is that internal rotation can be estimated. The rotation of the methyl radical $-CH_3$ has been extensively studied.

TABLE II

Molecule	I x10^{-32} (gm cm^2)	S	Quantization	T(Calc.) $\frac{C-C_\varphi}{C_\varphi}=0.02$	T(Obs.)	$\frac{d}{d\ln T}\left(\ln\frac{C-C_\varphi}{C_\varphi}\right)$ (Calc.)	(Obs.)	m_φ
DIATOMIC								
1 Oxygen	1.93	0	J=0, 2	2.7	3.5	5.9	6	0.13
2 Nitrogen	1.38	1	2/3 J=0, 2 1/3 J=1, 3	4.2	5.0	5.7	6	0.12
3 C=O	1.45	0	J=0, 2	3.7	4.0	5.9	7	0.17
4 F_2	3.26	1/2	1/4 J=0, 2 3/4 J=1, 3	2.2		4.3		
5 Cl_2	11.48	3/2	3/8 J=0, 2 5/8 J=1, 3	0.6		5.7		
LINEAR								
6 HCN	1.89		J=0, 1	1.0		4.3		
7 DCN	2.31		J=0, 1	0.8		4.7		
8 HC≡CD	2.82		J=0, 1	0.7		5.7		
9 HC≡CH	2.37	1/2	1/4 J=0, 2 3/4 J=1, 3	3.1		3.9		
METHANE etc.								
10 C H_4	0.533	1/2	A, E, F	9.8		4.7		0.65
11 CH_3D	0.722	1/2, 1	A, E	3.0		6.8		0.42
12 CH_2D_2	0.792	1/2, 1	"A, E"	3.3		4.9		0.4
13 CHD_3	0.854	1/2, 1	A, E	2.6		4.8		0.42
14 CD_4	1.057	1	A, E, F	3.8		3.7		
15 SiH_4	0.946	1/2	A, E, F	5.7		4.0		
16 GeH_4	0.97(?)	1/2	A, E, F	5.3		4.0		
SYMM. ROTOR								
17 NH_3	0.45	1/2	2/3 J=0, 1 ; k=0 1/3 J=1, 2 ; k=1	7.6	6.6	5.0	4	0.12
18 PH_3	0.628	1/2	〃 〃	3.4		4.7		
19 AsH_3	0.752	1/2	〃 〃	2.8		4.7		
20 CH_3Cl	6.315	1/2	〃 〃	0.25		5.0		
ASYMM. ROTOR								
21 H_2O(Eq.)	0.33	1/2	J=0, 1	4.6	4.5	7.6	7	0.22
22 H_2S(Eq.)	0.59	1/2	J=0, 1	2.5		10.4		
23 $H_2C=O$ (H. T. Mx)	2.31	1/2	1/4 J=0, 2 3/4 J=1, 3	3.1		4.2		
INTERNAL ROTOR								
24 -CH_3	0.588	Planar Rotor	2/3 J=0, 1 ; k=0 1/3 J=1, 2 ; k=1	2.0		4.9		
LIQUID								
25 He-He	4.7	0	J=0, 2, 4	0.51	0.5	10	10	0.75

There appears to be universal agreement that in dimethylacetylene there is little or no restriction.[12] Unfortunately, heat capacity measurements do not extend to the necessary low temperature. We have not found data to check the theory for any compound with internal rotation.

If the anomalies predicted are found in the laboratory, absolute entropies based upon "smooth extrapolation" of the measured heat capacties have systematic errors, and

must be revised following further measurements.

COMPLETE REPRESENTATION

Dispersion theory in the form described appears to be successful in predicting the departure from T^3 heat capacity, in position and in form. Even in the hands of Landau, dispersion theory cannot describe the lambda point for liquid helium. His best dispersion curve accounts for the data only to 1.6°K, well below $T_\lambda=2.17$°K. He suggests that roton-roton interactions may account for the data at higher temperatures.[1] Yarnell *et al.* introduce temperature dependence in the parameters of the dispersion curve, and with these three additional disposable functions can account for the data to nearly T_λ[7].

The simple theory described is therefore an induction theory. If m is calculated to high values of ω it will approach unity. The dispersion curve will then have a maximum but no minimum and the heat capacity will diverge and become infinite. (Landau's dispersion curve avoids this catastrophy by using a parabola for the roton.) Experimental studies of helium suggest that a better representation is a "second phonon" line, parallel to the phonon line.[5] The heat capacity then has a maximum and the anomaly diminishes slowly with higher temperatures. The same "second phonon" region is assumed for the molecular solids of Table II, equivalent to introducing a disposable constant m_0: the terminus of the calculated dispersion curve (Fig. 3). For many substances the limiting value of m_0 is near 0.1 and the maximum ratio of heat capacities $(C/C_\varphi)_{\max}$ is less than 2. Liquid helium has an extreme minimum with $m_0=0.75$ and methane has nearly as high a value.

Figure 4 shows the experimental data plotted in the same fashion as Fig. 2, with the theoretical line represented. These curves necessarily converge on the low temperature approximation of Fig. 2.

Oxygen is particularly simple for the molecule is homonuclear with zero spin.[13] Odd

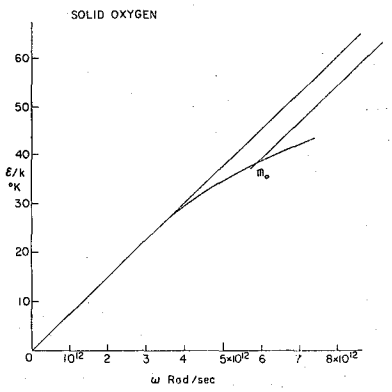

Fig. 3. Excitation energy of oxygen as a function of frequency. m_0 at w_0 defines the end of the low temperature approximation and the beginning of the "second phonon" line.

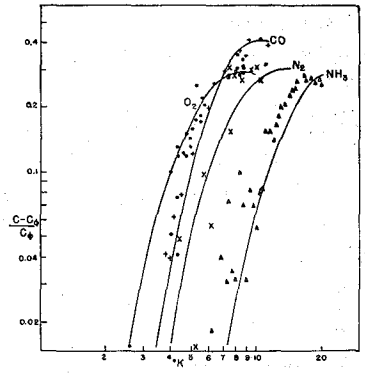

Fig. 4. Relative heat capacity of oxygen, •; carbon monoxide, +; nitrogen, ×; and ammonia, △; compared to theory in high temperature form. Curves must necessarily converge upon low temperature approximation.

values of J are missing, and the partition function is:

$$Z=\sum_{J=0,2,4\ldots}(2J+1)\,e^{-J(J+1)h/I\omega} \tag{10}$$

Only two states are needed, J=0, 2 for $m\leq 0.12$.

Nitrogen has ortho and para forms and unit nuclear spin (S) so the partition function for the high temperature mixture is

$$Z=\frac{2}{3}(2S+1)\sum_{J=0,2,4\ldots}(2J+1)\,e^{-J(J+1)h/I\omega}+\frac{1}{3}(2S+1)\sum_{J=1,3\ldots}(2J+1)\,e^{-J(J+1)h/I\omega} \tag{11}$$

A dilemma appears in connection with the para contribution. In our previous studies, $J\neq 0$ molecules were assumed to be locally defined and therefore not part of the ground state continuum. If J=1 molecules, locally defined, are counted as excited, then phonons at low temperatures are cooperative modes among only two-thirds of the molecules. If pure para nitrogen were prepared (by means not identified) then presumably there would be no phonon excitations at low temperature and no T^3 low temperature heat capacity. The assumption, subject to modification, has therefore been made that cells with J=1 are to be counted with J=0 molecules as the ground state and m then becomes the population of excited states.

$$m=\frac{2}{3}\frac{\sum_{J=2,4\ldots}(2J+1)\,e^{-J(J+1)h/I\omega}}{\sum_{J=0,2,4\ldots}(2J+1)\,e^{-J(J+1)h/I\omega}}+\frac{1}{3}\frac{\sum_{J=3,5\ldots}(2J+1)\,e^{-J(J+1)h/I\omega}}{\sum_{J=1,3,5\ldots}(2J+1)\,e^{-J(J+1)h/I\omega}} \tag{12}$$

The principal contribution is from J=0, 2, and only near m_0 does J=1, 3 become significant. The low temperature measurements of Burford and Graham do not join well with those of Bagatskii *et al.*[14] The latter more complete data have been used.

Carbon monoxide has been a cause celebre in absolute entropy studies, for a difference between spectroscopic calculations and heat capacity observations persist.[15] The atoms of the molecule have zero nuclear spin, the atoms are of similar size, but the center of gravity is not midway between nuclei. In the gas, odd and even values of J are observed. In the solid, if the ends are not identical, an ordered state of COCOCOC will be the ground state. If there is little difference between the ends of the molecule then a disordered state COOCOCCO will be possible and a maximum entropy of mixing of $R\ln 2=1.38$ cal/mol deg will remain. The entropy difference of 1.1 cal/mol deg is attributed to this source. Even in lattice calculations the molecule is commonly treated as symmetrical.[16]

In our calculations the differences are crucial. If the ends are distinguishable, all values of J will be found. The deviation calculated then occurs at much too low a temperature. If the ends are indistinguishable, then J=1, 3 will be missing and the calculation will be the same as in oxygen. Both curves are plotted in Fig. 5. It is evident that the observations conform to the symmetrical hypothesis.[17] Carbon monoxide then becomes a most intriguing example of the Gibbs Paradox. The molecule appears to rotate in its cell about an axis midway between nuclei, and the electron clouds would appear to be indistinguishable.

Methane is a particularly interesting case for measurements are available for the deuterium derivatives to temperatures of 1−2°K.[18] While the structure and molecular weight (and hence the molecular volume and velocity of sound) are only slightly

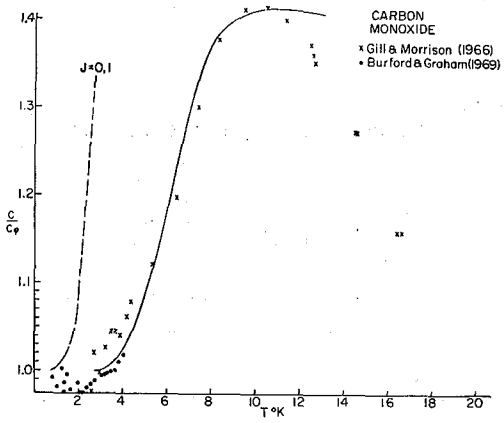

Fig. 5. Comparison of heat capacity of carbon monoxide with theory. Curve for J=0, 1 represents unsymmetrical molecule.

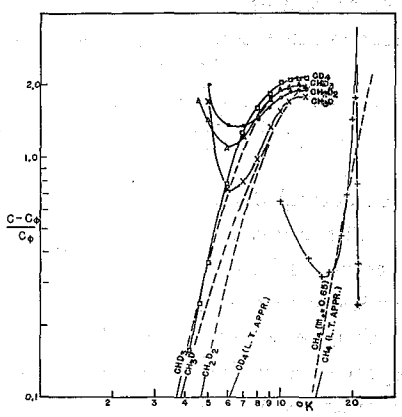

Fig. 6. Relative heat capacity for methane and its deuterium derivatives. Broken curves, theory.

changed, the quantum character is radically changed, for CH_4 and CD_4 are spherical tops, CH_3D and CHD_3 are respectively prolate and oblate symmetrical tops and CH_2D_2 is an asymmetric top. Early studies of Maue[19] and his partition functions have been the basis of out calculations. Because of the four identical nuclei in CH_4 and CD_4 there are three spin states A. E. F, singlet, triplet and quintet, named by Maue, ortho, meta and para. CH_4, having the smallest moment of inertia, shows an anomaly beginning at 10°K which accurately approximates the approach to the 20.6° lambda point (Fig. 6). (The deviation of the data from the calculation below 16° is due to the effect of the strong anomaly near 1°K.) The C_φ contribution is interpolated between the heat capacity above and below the lambda transition.

In the deuterium derivatives the anomaly appears at much lower temperatures, 2.5-3°K (calc), and the strongest contribution occurs near 10°K. The observed heat capacity curves are complex since the weak rotational anomaly falls between large anomalies ~1° and ~20° (which are not predicted by this theory). We have taken the data corrected for isotopic impurities given by Colwell *et al.*[18(b)] We have assumed the molecular volumes and velocities of sound to be the same for the deuterium derivatives; we have used the C_φ of CD_4.

CD_4 is quite different from the other methanes for the ~1°K anomaly is absent, and the heat capacity becomes $C_\varphi \propto T^3$ below 3°K. The position of the rotational anomaly is well predicted, but the strength is quite inadequate. The assumption of spin equilibrium, however, gives a threshold temperature much too low and a strength much too high. No satisfactory model has been found to represent CD_4. Yamamoto[20] believes that the lattice for CD_4 is quite different from that of CH_4.

The rotational spectrum of ammonia has been analyzed using the mathematical model of the oblate symmetrical top. The moment of inertia about the axis of symmetry (I_A), is greater that the other two identical moments of inertia (I_B). An additional quantum number, k, appears and again there is slow conversion between nuclear spin states, designated A and E (analogous to ortho and para forms). The high temperature

mixture consists of 2/3 A and 1/3 E. The analytical character of the dispersion relation becomes more complex.

$$m=\frac{2}{3}\frac{\sum_{J=1,2;k=0}(2J+1)\,e^{-J(J+1)h/I_B\omega}}{\sum_{J=0,1,2;k=0}(2J+1)\,e^{-J(J+1)h/I_B\omega}}+\frac{1}{3}\frac{\sum_{J=2;k=1}2(2J+1)\,e^{-J(J+1)h/I_B\omega-(h/I_A\omega-h/I_B\omega)k^2}}{\sum_{J=1,2;k=1}2(2J+1)\,e^{-J(J+1)h/I_B\omega-(h/I_A\omega-h/I_B\omega)k^2}} \tag{13}$$

Experimental data are from reference 21.

The asymmetric rotor has been previously discussed for the case of water.[4] Some investigators have found slow response in the calorimeter, thought to be caused by spin conversion in the solid.[11] Flubather *et al.* found one sample, which they designated IIa, which gave a curve 9% above their other samples.[22] We have measured the time dependence of the neutron cross section for two samples of water which gave widely disparate results.[4] These questions have been resolved by Pitzer for methane.[10] A highly purified sample in the calorimeter gave sluggish response to the addition of heat, whereas a sample containing 0.8% of molecular oxygen, O_2, gave rapid response. This elegant work explains the difficulties with water, for small concentrations of oxygen are not easily identified. In our work the sample with rapid response ($T_{1/2}\cong 100$ minutes) contained an unknown amount of oxygen. The single crystal sample, at 4°K, ($T_{1/2}>100$ hours) contained little distributed oxygen. We also confirm Pitzer's studies in the case of methane, for again, an impure sample showed spin transformation ($T_{1/2}\cong 20$ minutes) whereas a carefully purified sample gave slow response ($T_{1/2}>100$ hours).[23]

Flubacher's data are well represented if we assume spin equilibrium in the calorimeter. No useful results are obtained for the high temperature mixture. This assumption is also applied to H_2S. Further heat capacity measurements will be required to resolve this problem.

LIQUIDS

Three quantum liquids have been discussed previously: helium-4, SiO_2 and GeO_2.[4] In helium, the departure from the phonon line is well represented. However, the $J=4$ rotational state must be artificially strengthened to obtain the deep minimum of the dispersion curve. Liquid helium is included in Fig. 2 and Table II for comparison. In the glasses, adequate representation is achieved using adjusted moments of inertia 0.37×10^{-39} for SiO_2 and 0.42×10^{-39} for GeO_2. These values correspond to Si-O-Si and Ge-O-Ge bond angles of 153° and 152°.

SUMMARY

The assumption of a postulate parallel to Boltzmann's postulate permits the calculation of dispersion relations for molecular crystals where molecular rotation within the cell is plausible. Heat capacity anomalies are calculated which correspond in position to observed anomalies for systems with adequate data. The strength of the measured anomaly, near threshold, corresponds to the strength calculated except for the single case of CD_4. Estimation of the maximum relative strength (C/C_φ) requires the inclusion of an empirical cutoff, m_0.

Predictions have been made which are subject to experimental verification for sys-

tems with no adequate data.

Catalysis of spin transformations by molecular oxygen appears to be a controlling factor in the study of molecular systems.

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