Letters to the Editor

*T*HIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Vibrational Energy Levels and Specific Heat of Ethylene

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In a recent review of the experimental infra-red and Raman spectra of ethylene and tetradeuteroethylene,[1] Conn and Sutherland have succeeded in giving very reasonable estimates of the positions of the four fundamental levels associated with the "rocking frequencies" of the methylene groups in C_2H_4. They have at the same time revised the previous estimate of the position of the "torsional" level[2] to 700 cm^{-1}, for reasons which are in our opinion inadequate, and with results which prove to be unsatisfactory. In particular, as they themselves remark, the calculated heat capacities then become too large. We wish to point out that a return to the Bonner assignment of this level not only yields a more reasonable explanation of the intensities of the weak combination and harmonic lines in the Raman spectrum, but also leads to a theoretical heat capacity which is in good agreement with the existing measured values[3] and with new experimental values recently obtained in these Laboratories.

In the Conn and Sutherland analysis, the value 700 cm^{-1} for the fundamental A_{1u} level[4] was a consequence of three vibrational assignments. The upper state of the Raman line at 1656 cm^{-1} was assigned as the binary combination state $(700)+(950)B_{3g}$, that of the Raman line at 3272.3 cm^{-1} as $2(700)+2(950)A_{1g}$, and that of the rather doubtful prism infra-red band of Coblentz at about 1720 cm^{-1} as $(700)+(1030)B_{3u}$. We believe that it is equally satisfactory to assign these levels in terms of an A_{1u} fundamental at about 829 cm^{-1} as $2(829)A_{1g}$, $(1623)+2(829)A_{1g}$, and $(829)+(943)B_{1u}$, respectively. That the frequency agreement for the Coblentz band is less close with this assign-

ment seems of small importance, since neither its position nor its reality is certain. The intensity of the 1656-cm^{-1} Raman line may now be attributed to partial vibrational resonance of its upper state with the very strongly Raman active fundamental level $(1623.3)A_{1g}$, and the 3272.3 cm^{-1} line, while retaining its identity as a member of the 3272.3, 3240.3 cm^{-1} resonance doublet, is reduced from a quaternary to a ternary combination line.

The heat capacity of ethylene gas (Ohio Chemical Co., 99.5 percent C_2H_4) has been determined at three temperatures by the adiabatic expansion method of Lummer and Pringsheim, using pure nitrogen, whose heat capacity was calculated from spectroscopic data, as the standard comparison gas. In Table I are given average experimental values of C_p^0, the molal heat capacity at constant pressure corrected to infinite attenuation, together with the mean deviations of the individual determinations from the average. According to the experience of the authors in measurements on gases of known heat capacities these values may be expected to be accurate to within ±0.5 percent. It was assumed that the gas obeys the equation of state

$$P = RT/(V - B_0), \qquad (1)$$

where the coefficient B_0 is given by [5]

$$B_0 = 121.6 - 7.50 \times 10^4 (1/T) - 2.26 \times 10^8 (1/T^3). \qquad (2)$$

The experimental values presented in Table I, together with the older data,[3] are shown graphically in Fig. 1. The dotted curve presented in this figure shows the heat capacity of ethylene calculated to the harmonic oscillator approximation with the Conn and Sutherland vibrational assignments, while the solid curve shows the similarly calculated heat capacity with the "torsional" level placed at 828.5 cm^{-1}. Deviations of the experimental points from the dotted curve are clearly too large and too systematic to be the result of experimental error, while the solid curve is in excellent agreement with the measured values.
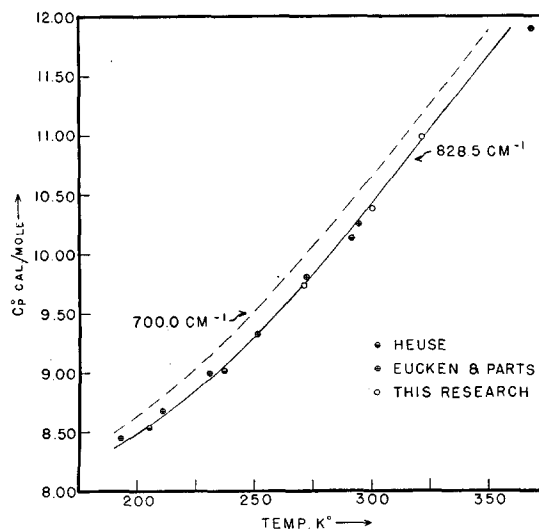

Fig. 1.

Table I. The heat capacity of ethylene gas.

TEMPERATURE (°K)	C_p^0 OBSERVED (CAL./MOLE-DEGREE)	MEAN DEVIATION (%)
270.7	9.74	0.1
300.0	10.39	0.4
320.7	10.99	0.2

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In the range $1F5–4F5°K$, these theoretical heat capacities in cal./mole-degree may be represented to within 0.02 by the following empirical equation:

$$C_p° = 9.638 - 3.109 \times 10^{-2}T + 1.551 \times 10^{-4}T^2 - 1.426 \times 10^{-7}T^3. \quad (3)$$

Until the details of the 10μ band in ethylene are completely understood, the following fundamental levels, used in calculating the full curve of Fig. 1, may be accepted as essentially correct:

A_{1g};	3019.3	B_{1u};	3105.7	B_{2u};	2988.2	B_{3g};	3075.0
	1623.3		1027.5		1443.9		1021.5
	1342.4						

B_{3u};	948.8	B_{1g};	943.0	A_{1u};	828.5.

[1] Conn and Sutherland, Proc. Roy. Soc. **A172**, 172 (1939).
[2] Bonner, J. Am. Chem. Soc. **58**, 34 (1936).
[3] Eucken and Parts, Zeits. f. physik. Chemie **B20**, 184 (1933); Heuse, Ann. d. Physik **59**, 86 (1919).
[4] These group-theoretical designations are uniquely defined by the standard tables of irreducible representations of the crystallographic point groups and the assertion that the z axis has been chosen to lie along the carbon-carbon bond, and the x axis to lie in the plane of the molecule.
[5] Keyes, J. Am. Chem. Soc. **60**, 1761 (1938).

Simultaneous Determination of Adiabatic and Isothermal Elasticities

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Simultaneous measurement of the temperature curve of an isothermal and a corresponding adiabatic elastic modulus through the temperature region of phase transitions of higher order seems possible by any dynamical method using a proper frequency system, one part of which consists of isothermal, the other part of adiabatic proper vibrations. To determine appropriate conditions for such a method, the following problem has been investigated:

How does the adiabatic or isothermal character of a proper vibration depend on the frequency range, the vibrational type and the form of the sample?

From the investigations of Herzfeld and Rice[1] one can conclude that also in solids, plane sound waves above about 10^{11} cycles/sec. are to be considered as isothermal, while waves of lower frequency should be adiabatic.

However, consideration of proper vibrations of solids shows that somewhere in the low frequency range a change must occur, since for frequency 0, i.e., under static conditions, isothermal behavior is to be expected again. It is rather evident that the temperature distribution existing in a plane wave will be changed, when the boundary conditions begin to play a part. This is the case, when the distance between temperature maxima and minima becomes comparable with one of the dimensions of the sample. That again depends on the type of the excited vibration: For longitudinal vibrations this distance is characterized by the wave-length; for transverse vibrations successive regions of compression can only occur normally to the "direction of propagation." In the case of bending vibrations of plates, reeds, rods and circular wire loops the
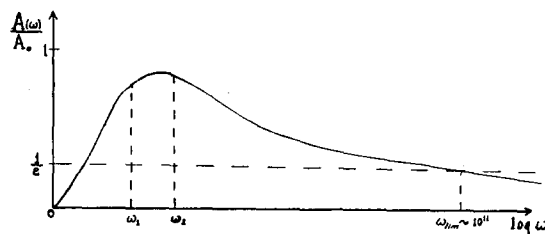

FIG. 1. Case A: all three dimensions of the sample of the same order. The $A(\omega)$ curve refers to longitudinal, transverse and surface vibrations, which in a finite solid occur combined.

temperature gradient across the thickness is the only important one.

The temperature distribution in a vibrating sample can be expressed by:

$$T = T_0 + (A_1(\omega) + iA_2(\omega)) \cdot f(xyz) \cdot e^{i\omega t}.$$

The function T is characterized by two temperature vibrations, one of which is in phase, the other out of phase with the elastic vibrations. If the absolute value of the temperature amplitude $|A_1 + iA_2| = A(\omega)$ is small, the vibration is isothermal, otherwise it is adiabatic. $A(\omega)$ has to be normalized by the "perfectly adiabatic" amplitude A_0.

Taking into account the processes of heat conduction and heat production or absorption, and inserting the boundary conditions imposed by the size of the sample, we computed $A(\omega)$ for the different types of vibrations and found the following results:

(a) If the three dimensions of the sample are all of the same order, $A(\omega)$ turns out to be of the form given in Fig. 1. The $A(\omega)$ curve refers to longitudinal, transverse and surface vibrations, which in a finite solid occur combined. One sees that isothermal conditions (below the dotted line) exist above 10^{11} cycles/sec. and in the low frequency range only below the first proper frequency. There are no isothermal proper vibrations here, only forced isothermal vibrations.

(b) If one of the sample dimensions is small compared to the other two (plates, reeds, rods, loops), one has the situation given in Fig. 2. The $A(\omega)$ curve of Fig. 1 splits into two $A(\omega)$ curves characterizing vibrations, which are symmetrical or antisymmetrical with respect to the longitudinal mid-plane of the sample; finally the symmetrical vibrations are shown to pass over into compressional ones, the antisymmetrical ones pass over into bending vibrations. All of the symmetrical vibrations are adiabatic, as in the
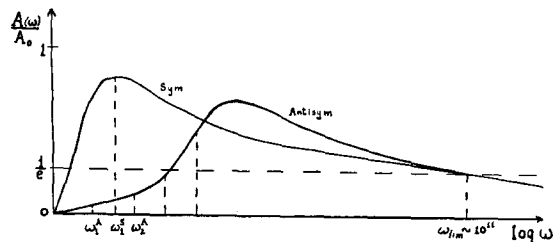

FIG. 2. Case B: one of the sample dimensions small compared to the other two. The $A(\omega)$ curves refer to symmetrical and to antisymmetrical vibrations.