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sufficient to rule out any nonlinear or asymmetric structure for carbon suboxide. It is disappointing that we cannot make a complete vibrational analysis of the absorption spectrum, but it appears quite probable that absorption studies made under higher resolution will enable the analysis to be completed. We are grateful to Professor Halford for his kindness in furnishing us with the carbon suboxide, to Professor Randall for placing the spectrometer at our disposal and particularly to Professor Dennison for helpful discussions.

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Calculation of the Heat Capacity Curves of Crystalline Benzene and Benzene-d_6

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The heat capacity curve for solid benzene has been computed with the help of the set of internal frequencies previously proposed by Lord and Andrews. The agreement with experiment is satisfactory over the entire temperature range in which the internal frequencies contribute, indicating that the frequency values are essentially correct. A prediction of the heat capacity of benzene-d_6 has also been made.

The existence of a complete set[1] of values for the internal frequencies of the benzene molecule makes it possible for the first time to calculate directly the contribution of these degrees of freedom to the heat capacity of crystalline benzene. Earlier attempts[2] to carry out computations of this sort involved empirical and rather rough estimates of these frequencies, and led only to qualitative information concerning the specific heat of the crystal. A precise calculation of the heat capacity of solid benzene is of interest, particularly in view of the experimental data obtained at "helium" temperatures recently by Ahlberg, Blanchard and Lundberg[3] and the other excellent values at higher temperatures which can be compared with calculated values. Our discussion will be concerned with this calculation and the conclusions to be drawn from such a comparison.

When thermal energy is absorbed at constant pressure by a crystalline solid such as benzene, this energy is distributed among: (1) the oscillations of the crystal lattice; (2) the internal vibrations of the molecules composing the lattice; and (3) the work of expanding the lattice. Before discussing these three components of the specific heat, we must emphasize that our ultimate interest lies in the contribution (2). Contributions (1) and (3) will be evaluated as accurately as possible by means of the traditional expressions for them, but it is not our purpose to improve these expressions or to criticize their theoretical origins.

Experience has shown that the share of the lattice vibrations in the specific heat of a crystal is ordinarily described rather accurately by the familiar Debye function $D(x)$:

$$C_v\,(\text{lattice}) = 3RD(x),$$

$$D(x) = \frac{12}{x^3}\int_0^x \frac{z^3dz}{e^z-1} - \frac{3x}{e^x-1}, \qquad (2)$$

in which x is the parameter $(h\nu_D/kT)$. ν_D is the well-known Debye characteristic frequency which must be determined in some way if we are to utilize the function $D(x)$.

The physical significance of ν_D has been the subject of much discussion. In a recent critique

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[1] Lord and Andrews, J. Phys. Chem. **41**, 149 (1937).
[2] D. H. Andrews, Proc. Roy. Soc. Amst. **29**, 744 (1926); Chem. Rev. **5**, 533 (1928); E. O. Salant, Proc. Nat. Acad. Sci. **12**, 334, 370 (1926).
[3] J. E. Ahlberg, E. R. Blanchard and W. O. Lundberg, J. Chem. Phys. **5**, 539 (1937).

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of the Debye theory, Blackman[4] points out that there is no theoretical justification for identifying ν_D with any of the actual vibrations of the crystal lattice. The assumption that ν_D is a residual ray frequency, for example, appears to be unwarranted despite the closeness of agreement between ν_D and reststrahlen frequencies for a number of crystals. For our purposes, however, the physical meaning of ν_D is of secondary importance. If a value of ν_D can be found by means of which $D(x)$ reproduces the lattice C_v, our requirements will be satisfied.

Before considering the method of evaluating ν_D, it is necessary to take up a question arising from the fact that the lattice of solid benzene is not an atomic lattice. Functions of the Debye type apply to crystal lattices made up of mass points having no moment of inertia. Each mass point possesses only three degrees of freedom and the compressional waves in the three dimensions of the space lattice are the crystalline analog of the three degrees of translational freedom allowed to the particles of a monatomic gas. Doubtless the molecules in a benzene crystal may be fairly considered as mass points insofar as the propagation of compressional waves is concerned. These compressional vibrations should therefore take up thermal energy in the manner described by the Debye function. In addition, however, the benzene molecule possesses three moments of inertia and correspondingly three degrees of rotational freedom. If the component molecules of the benzene lattice were rotating freely and independently of one another, the contribution of these rotational degrees of freedom to the heat capacity would be the same as their contribution to C_v of gaseous benzene. The benzene molecules do not rotate freely, of course, and therefore we have to determine what the nature of the rotatory motion is and what its effect on the specific heat will be.

Each molecule in the benzene lattice is situated at an equilibrium position in the field of force resulting from the presence of the neighboring molecules. If one molecule be somewhat displaced from this position by a translation or by rotation through some small angle about its center of gravity, it will tend to return to the equilibrium position. The displacement will, however, affect the neighboring molecules, since the force field acting on each of them is partly due to the displaced molecule. This interaction of molecules undergoing translational displacement leads to the compressional waves mentioned above. Similarly *angular displacement* results in the production of *torsional waves*, in which the molecules in the crystal lattice execute rotatory oscillation through small angles. The oscillations of each molecule bear definite phase relationships to the oscillations of the others, and the oscillational waves are propagated in all three dimensions of the space lattice. It is our assumption that these torsional waves contribute to the specific heat in the same manner as the compressional waves, and that this contribution is accordingly described by a Debye function $D(x)$. The maximum frequency ν_D for the torsional waves will of course differ in general from ν_D for the compressional vibrations. The expression for the heat capacity of the benzene lattice will be therefore

$$C_v \text{ (lattice)} = 3R[D(x_1)+D(x_2)]. \qquad (3)$$

To evaluate the two ν_D's required by Eq. (3), we use the following procedure. At low temperatures, say below 50°K, the internal vibrations and work of expansion make only trifling contributions to the specific heat of benzene. Consequently, the experimentally observed heat capacity corresponds to that given by Eq. (3). Hence, if we select values for ν_{D_1} and ν_{D_2} which reproduce the heat capacity curve over the range 0°–50°K, we can feel confident that these values are the correct ones for use at higher temperatures.

When the two values of ν_D are not widely different, we may say

$$D(x_1)+D(x_2)=2D\left(\frac{x_1+x_2}{2}\right). \qquad (4)$$

Or, setting $h\nu_{D_1}/k=\theta$, $h\nu_{D_2}/k=\theta_2$ and $(\theta_1+\theta_2)/2=\theta$,

$$D(\theta_1/T)+D(\theta_2/T)=2D(\theta/T). \qquad (5)$$

From unpublished calculations by Dr. V. Deitz and Mr. C. F. Squire, extending the former's investigations of crystal lattices[5] it appears that θ_1 (for compressional oscillations) in benzene is about 25 percent smaller than θ_2 (for torsional

[4] Blackman, Proc. Roy. Soc. **A148**, 365, 384 (1935).

[5] V. Deitz, J. Frank. Inst. **219**, 459, 565, 703 (1935).

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oscillations). When the θ's considered lie in the range 100–200 and differ by 25 percent, the approximation (5) holds to within experimental error at temperatures above 35°–40°K. Even at temperatures considerably lower the approximation is valid to better than 5 percent. Accordingly we may obtain from the heat capacity data at low temperature the value of a single θ and in terms of this θ express the heat capacity due to the lattice of crystalline benzene over the entire temperature range of the solid. The equation will be:

$$C_v \text{ (lattice)} = 6RD(\theta/T). \tag{6}$$

The question of the accuracy of Eq. (6) and of possible variatons in θ will be considered later.

The contribution made by the internal frequencies in the benzene molecule to the specific heat of the crystal is readily calculable. The heat capacity arising from one degree of internal freedom of frequency ν_i is

$$C_v = RE(x_i),$$

where $x_i = h\nu_i/kT$, and the Einstein function $E(x) = x^2e^x/(e^x-1)^2$. Hence the total internal heat capacity will be

$$C_v \text{ (internal)} = R\cdot\sum_{i=1}^{n} E(x_i). \tag{7}$$

The summation extends over the n internal degrees of freedom. n for benzene is thirty.

The addition of Eqs. (6) and (7) yields the heat capacity of the crystal at constant volume. To convert this into the experimentally measurable heat capacity at constant pressure, C_p, use is made of the standard thermodynamic formula

$$C_p - C_v = \alpha^2 VT/\beta, \tag{8}$$

where α is the crystal's coefficient of thermal expansion, β the coefficient of compressibility and V the molar volume of the crystal. Eq. (8) expresses the contribution made to C_p by the work required to expand the lattice.

The right-hand member of (8) can be changed to a more useful form by means of Mie's[6] relation:

$$\alpha V/\beta = \text{const.} \times C_v. \tag{9}$$

[6] Mie, Ann. d. Physik **11**, 657 (1903).

Grüneisen[7] has shown, by a combination of thermodynamic argument with the results of lattice theory, that such a relation should hold for atomic lattices whose C_v is given by Eq. (1). Extension of Grüneisen's reasoning to molecular lattices leads to the expression

$$\alpha V/\beta = \sum_i a_i (C_v)_i, \tag{10}$$

in which the a_i's are constants multiplying the several components of C_v, namely C_v due to compressional and to torsional lattice vibrations, and due to the various internal degrees of molecular freedom. Eq. (10) may be simplified by making two reasonable assumptions about the coefficients a_i. In the first place we assume, in keeping with our discussion of the relative magnitudes of the ν_D's of compression and of torsion, that the coefficient of C_v due to compressional oscillations is the same as that for C_v due to torsional oscillations. Secondly, we suppose that the coefficients for the various components of the internal C_v may be lumped together into one coefficient for the whole internal C_v. Thus we reduce (10) to

$$\alpha V/\beta = a'C_v \text{ (lattice)} + b'C_v \text{ (internal)}. \tag{11}$$

a' and b' are constants. If we make the empirically justifiable[8] assumption that the quotient V/β is temperature-independent, combination of (8) and (11) gives

$$C_p - C_v = [a\cdot C_v \text{ (lattice)} + b\cdot C_v \text{ (internal)}]^2 T. \tag{12}$$

The evaluation of the constants a and b is essential for our calculation of C_p, but unfortunately there is at present no independent way of determining them. We should expect the constant a to have a value of the order of magnitude of similar constants for atomic lattices, but no precedent exists for estimating b. We therefore resort to an empirical procedure for finding a and b.

The difference between observed C_p and calculated C_v above 50°K is ascribed to work of expansion. With the help of this difference at

[7] Grüneisen, *Handbuch der Physik*, Vol. X, p. 22 ff. See also Eucken, *Handbuch der Experimentalphysik*, Vol. VIII, part 1, p. 281.

[8] Cf. Eucken, reference 7, p. 282; cf. Grüneisen, Ann. d. Physik **26**, 211 (1908).

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any two temperatures, we can calculate a and b from Eq. (12). When such a calculation is carried out,[9] a and b are found to have the same value within about 5 percent. We may therefore set $a=b$, and reduce Eq. (12) to:

$$C_p - C_v = kC_v^2T. \tag{13}$$

TABLE I. *Heat capacity of benzene and benzene-d_6.*

Temperature °K	Lattice C_v	Internal C_v	C_p-C_v	Calc. C_p	Observed C_p	Calc. C_p ($\nu_{16}=160$ cm^{-1})	Calc. C_p C_6D_6
4	0.018			0.018	0.0195	.018	.024
6	.060			.060	.065	.060	.074
8	.144			.144	.147	.144	.173
10	.270			.270	.346	.270	.336
15	.908			.908	.920	.91	1.10
20	1.932			1.932	1.84	1.94	2.29
25	3.18		0.02	3.20	3.00	3.24	3.66
30	4.41		.04	4.45	4.24	4.57	4.94
40	6.45		.11	6.56	6.47	7.06	7.04
50	7.90		.20	8.10	8.14	9.20	8.56
60	8.90	0.02	.31	9.23	9.32	10.98	9.72
70	9.60	.07	.42	10.09	10.16	12.48	10.62
80	10.07	.17	.54	10.78	10.85	13.69	11.47
90	10.42	.31	.67	11.40	11.44	14.73	12.29
100	10.70	.51	.81	12.02	11.99	15.67	13.12
110	10.89	.79	.97	12.65	12.59	16.50	13.94
120	11.02	1.09	1.13	13.24	13.24	17.21	14.82
130	11.14	1.45	1.33	13.92	13.96	17.96	15.75
140	11.24	1.84	1.55	14.63	14.71	18.66	16.73
150	11.32	2.31	1.80	15.43	15.49	19.46	17.78
160	11.38	2.77	2.07	16.22	16.26	20.19	18.91
170	11.43	3.26	2.37	17.06	17.10	20.97	20.13
180	11.48	3.80	2.71	17.99	18.02	21.80	21.39
190	11.53	4.31	3.08	18.92	19.00	22.62	22.76
200	11.58	4.95	3.53	20.06	20.02	23.66	24.17
210	11.62	5.53	3.98	21.13	21.11	24.68	25.65
220	11.65	6.16	4.50	22.31	22.24	25.80	27.20
230	11.68	6.80	5.07	23.55	23.45	26.88	28.85
240	11.70	7.47	5.69	24.86	24.75	28.11	30.51
250	11.72	8.13	6.35	26.20	26.09	29.38	32.28
260	11.73	8.77	7.05	27.55	27.75	30.67	34.12
270	11.74	9.46	7.83	29.03	29.70	32.09	35.98

[9] The numerical determination of the two constants is made most reliably by utilizing the C_p-C_v difference at two rather widely different temperatures, e.g. at 150° and 250°. The constants found at these two temperatures may be used in turn to calculate the expansion term for all other temperatures. The constants may also be evaluated separately. In the region 60°–100°, C_v (internal) makes no appreciable contribution to the C_p-C_v difference. Hence the constant a may be determined independently of b at any temperature in this region. The evaluation of b is then possible at a single temperature above 100°, preferably at a temperature high enough so that the C_v (internal) term is relatively large. The a and b values found in this way agree well with those found by simultaneous solution of two numerical equations obtained from Eq. (12). It is of interest to note that the value of the constant a, 8.3×10^{-3} reciprocal calories, agrees reasonably well with the value one would compute from the formula proposed by Nernst and Lindemann (Zeits. f. Elektrochem. **17**, 817 (1911)) for this constant, namely $a^2=0.0214/T_m$, where T_m is the fusion temperature of the crystal. The value of a calculated from this expression is 8.77×10^{-3}.

The constant $k(k\cong a^2\cong b^2)$ has the value of 6.45×10^{-5} reciprocal calories for crystalline benzene.

Calculation of C_p for Benzene

With the help of Eqs. (6), (7) and (13) we have calculated C_p for crystalline benzene over its entire temperature range. The value of θ used in (6), namely $\theta=150$, was obtained in the manner we have described. (See the discussion of Eqs. (3)–(6).) The internal frequencies for Eq. (7) have been taken from our previous paper.[1] The results of the calculation are listed in Table I together with values obtained by interpolating at a regular series of temperatures between the experimental results of Ahlberg, Blanchard and Lundberg[3] and Nernst[10] below 90°K, and of Huffman, Parks and Daniels[11] above 90°.

It will be seen from Table I that the agreement between calculation and experiment is remarkably good except for several points in the neighborhood of 25°K. These rather small discrepancies are probably to be ascribed to some fluctuation in the value of θ. Such fluctuations have been discussed by Blackman.[4] He points out that θ should fluctuate somewhat at low temperatures but should tend to remain constant at higher values of T. (For "higher values" one might say "values of T larger than $\theta/2$." Compare, for example, Blackman's Fig. 3, page 375, for one-dimensional lattices.)

For our purposes it is sufficient if θ remains reasonably near to 150 in the range above 80°K, for in that range the lattice C_v has very nearly attained its classical value and is not very sensitive to moderate changes in θ. The temperature region above 80° is of primary interest because in this region the internal vibrations make their contribution to C_p. It will be noticed that from 50° to 250° the agreement of theory with observation is quite satisfactory. This close check may be regarded as an excellent confirmation of the values of the internal frequencies used in Eq. (7). The slight divergence of theory and experiment close to the melting point may be due on the one hand to inaccuracy of Eq. (6)

[10] W. Nernst, Ann. d. Physik **36**, 395 (1911).

[11] Huffman, Parks and Daniels, J. Am. Chem. Soc. **52**, 1547 (1930).

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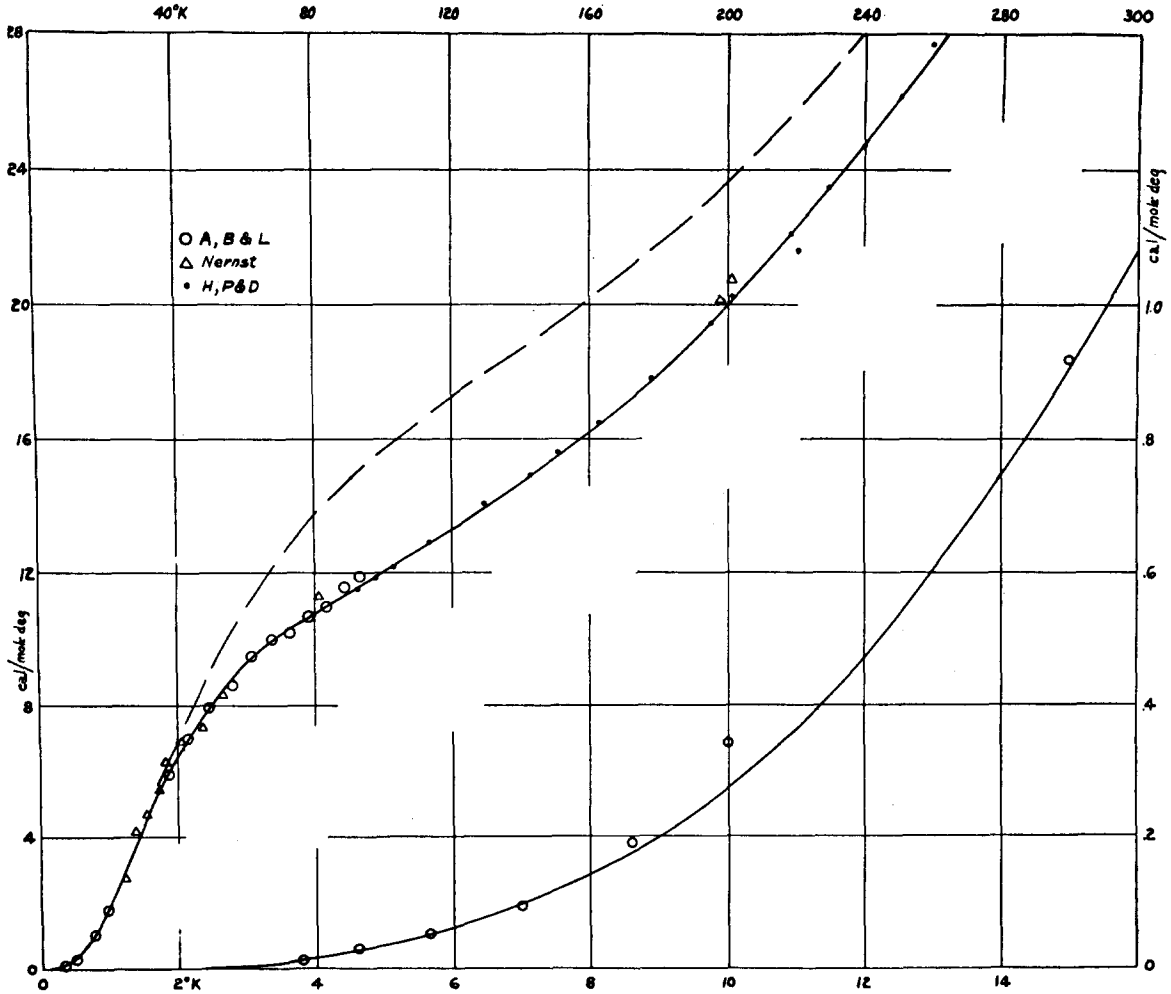

FIG. 1. The calculated values of the heat capacity of benzene with $\nu_{16}=406$ cm^{-1} and $\nu_4=538$ cm^{-1} (solid line); with $\nu_{16}=160$ cm^{-1} and $\nu_4=212$ cm^{-1} (dashed line). The experimental observations are taken from Ahlberg, Blanchard and Lundberg,[3] Nernst,[10] and Huffman, Parks and Daniels.[11]

or (13) when fusion is imminent, or on the other to slight increase in observed C_p near the melting point because of the presence of a trace of impurity in the sample under observation.

The exactness with which the theoretical and experimental C_p's coincide indicates that fundamental frequencies below 400 cm^{-1} can hardly be present in benzene. Evidence from the band spectra of benzene, however, has often been interpreted as demonstrating the presence of a fundamental frequency of 160 cm^{-1}. If such a fundamental were to exist in benzene, it would perforce belong to vibrational modes 4 or 16 (Wilson's notation[12]). The reasons for this assignment have been previously discussed.[1, 13] If we assume that ν_{16} has a value of 160 cm^{-1}, then ν_4 must lie somewhere in the neighborhood of 212 cm^{-1}. Column 7, Table I, gives C_p for benzene calculated on the assumption that ν_{16} and ν_4 have the respective values 160 cm^{-1} and 212 cm^{-1}, rather than 406 cm^{-1} and 538 cm^{-1}. The latter values (see reference 1) were used in obtaining the values of "calculated C_p" in the fifth column. The C_v portion of the values in column 7 has been obtained as before from Eqs. (6) and (7). To find the C_p-C_v term, we have used Eq. (13), in which the constant k has

[12] Wilson, Phys. Rev. **45**, 706 (1934).

[13] Angus, Bailey, Hale, Ingold, Leckie, Raisin, Thompson and Wilson, J. Chem. Soc. (London) 984 (1936).

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been assigned the empirically determined value 6.45×10^{-5} cal^{-1}.[14] For comparative purposes these results have been plotted in Fig. 1. It will be seen from this plot that a fundamental frequency of 160 cm^{-1} is incompatible with the heat capacity curve over the whole range 50°–250°K.

Prediction of C_p for Benzene-d_6

A calculation of the heat capacity of benzene-d_6 seemed desirable because comparison of theoretical and experimental C_p's should indicate just how accurate are the low internal frequencies which have been worked out for that molecule.

The lattice C_v for benzene-d_6 is assumed to be given by Eq. (6). The shift in θ was estimated by presuming that

$$\begin{aligned}\theta_1' &= \theta_1(M/M')^{\frac{1}{2}},\\ \theta_2' &= \theta_2(I/I')^{\frac{1}{2}},\end{aligned} \tag{14}$$

where θ_1 and θ_2 are the compressional and torsional θ's, respectively (see Eq. (5)). M is the molecular weight and I *any* moment of inertia of benzene. The primes refer to the corresponding quantities in benzene-d_6. (There is no ambiguity in regard to the moments of inertia, for the ratio I/I' is the same for all three moments in benzene.) From (14) and the assumption that $\theta_1 \cong \theta_2$, we find that

$$\theta' = (\theta/2)[(M/M')^{\frac{1}{2}} + (I/I')^{\frac{1}{2}}]. \tag{15}$$

(15) yields the value $\theta' = 140$.

The vibrational frequencies of benzene-d_6 as given in reference 1 were used in Eq. (7) to compute the internal C_v. The constant k in Eq. (13) was taken as 6.45×10^{-5} reciprocal calories. Column 8, Table I, gives C_p for benzene-d_6.

Despite the rough nature of the method of finding θ', it is likely that our estimate of the $\theta-\theta'$ shift is fairly good, so that the contribution of the lattice C_v to the net specific heat has been pretty closely estimated. Presumably the expansion formula is as valid as it proved to be for benzene. The accuracy of our prediction, then, depends upon the accuracy with which the internal frequencies are known. Excepting ν_4 and ν_{16}, the important (i.e., low) frequencies in benzene-d_6 have been observed spectroscopically and are known with a precision adequate for our purposes. The calculation of C_p therefore hinges to a large extent on the correctness of our estimate of ν_4 and ν_{16}.

The assignment of ν_{16} in benzene to the faint Raman frequency at 406 cm^{-1} is apparently substantiated by the excellence of agreement between theoretical and observed C_p's. It is to be remarked, however, the doubt here lies not in the value of the Raman line in question but in the assignment of ν_{16} to it. If the assignment is correct, we know the value of ν_{16} to within two or three cm^{-1}. Unfortunately, the corresponding line has not been observed for benzene-d_6, so that it is necessary to calculate the frequency at ν_{16} in the latter. There is some considerable degree of doubt about the accuracy of such a calculation and therefore we can scarcely expect to find the same excellence of agreement between theoretical and experimental C_p's for benzene-d_6 as was obtained for benzene. The measurement of C_p for crystalline benzene-d_6, which will be undertaken in the immediate future, is awaited therefore with considerable interest, for if such measurement agrees closely with our calculation, the frequencies of the distortion vibrations 4 and 16 have been correctly estimated. The extent of any discrepancy between theory and observation, on the other hand, will indicate the size and direction of the error in our estimate of ν_4 and ν_{16}.

[14] One might object, with considerable reason, that it is hardly legitimate to use here a constant found empirically under the assumption of different values for certain of the internal frequencies. This objection may be answered in part by remarking that the value of the constant used is close to that given by the independent formula of Nernst and Lindemann (reference 9). In addition it should be remembered that we are attaching no particular theoretical significance to the hypothetical C_p curve other than its utility in demonstrating the improbability of the presence of the very low frequencies in benzene. Even if the expansion term is disregarded entirely, the low frequencies still cause some contradiction with experiment, for in the region 80°–140°K the calculated C_v is *larger* than observed C_p by 1–2 percent.

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