TABLE VIII

HEAT, FREE ENERGY AND LOGARITHM OF EQUILIBRIUM CONSTANT FOR FORMATION OF THIACYCLOPENTANE

| $T$, °K. | $\Delta H_f^0$, kcal. mole$^{-1}$ | $\Delta F_f^0$, kcal. mole | $\log_{10} K_f$ |
|---|---|---|---|
| $4C(\text{graphite}) + 4H_2(g) + S(\text{rhombic}) = C_4H_8S(\text{liq})$ | | | |
| 298.16 | −17.4 | +9.0 | −6.56 |
| $4C(\text{graphite}) + 4H_2(g) + \frac{1}{2}S_2(g) = C_4H_8S(g)$ | | | |
| 0 | −17.3 | −17.3 | Infinite |
| 298.16 | −23.5 | + 1.4 | − 1.05 |
| 300 | −23.5 | 1.6 | − 1.16 |
| 400 | −25.1 | 10.2 | − 5.58 |
| 500 | −26.4 | 19.2 | − 8.40 |
| 600 | −27.4 | 28.4 | −10.35 |
| 700 | −28.1 | 37.8 | −11.80 |
| 800 | −28.6 | 47.2 | −12.90 |
| 900 | −28.9 | 56.7 | −13.78 |
| 1000 | −29.1 | 66.3 | −14.48 |

reference 20. Diatomic sulfur gas was adopted as the reference state for elemental sulfur for temperatures other than 298.16°K. The computed values are presented in Table VIII.

[20] (a) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1949, *et seq.*, Series I, Tables 14-1 and Series III [$S_2(g)$]; (b) National Bureau of Standards Report No. 1037.

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# The Specific Heat of Small Particles at Low Temperatures

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The theory is developed for the specific heat of a very finely divided solid at low temperatures. Each particle is treated as if it were a separate molecule but the usual theory of vibrations of a solid is used to estimate the frequencies of the normal modes. Numerical values are given for 100 Å. cubes of aluminum in the range 1–6°K. At 1°K. the gross translation and rotation of whole particles make the principal contributions. It is concluded that the heat capacity of a finely divided solid will be higher than that of the infinite crystal up to the temperature at which the vibrations become classical.

To the temperature at which the internal vibrations of a solid become essentially classical, the heat capacity of a solid is a function of the particle size. The smaller the crystal size, the higher the heat capacity at a given temperature. Another parameter of importance is the shape of the crystal. Experimentally, this effect is illustrated by the heat capacity of MgO. Parks and Kelley[1] measured the heat capacity of very large crystals, while Giauque and Archibald[2] made similar measurements on a sample whose average cube size was 200 Å. The data of the latter authors are as much as 7% higher than for the large crystals. In this paper we treat the heat capacity only at very low temperatures, *i.e.*, up to a few degrees Kelvin.

Montroll[3] recently gave the first-order corrections to the Debye specific heat equation for small particles. We are taking a more drastic point of view in treating small particles essentially as molecules. This brings in detailed consideration of the translation and rotation of each particle. Also we avoid the assumption of a continuous distribution of vibration frequencies, although we retain the same equations that Debye used for the calculation of the frequencies of given modes of oscillation in terms of the macroscopic elastic constants.

The translation and rotation of particles in a powder will be limited by some restoring forces. There are certainly gravity and the ever present repulsive forces between atoms at small distances. Presumably there will also be attractive forces of an atomic character at slightly larger interatomic distances. For the usual reason, the net force is necessarily harmonic for very small amplitudes, and only such amplitudes will be involved at the very low temperatures where these translational and rotational modes make a substantial contribution. Thus we can use the harmonic oscillator formula for these heat capacity terms. However, the mass of even the smallest solid particle of interest will be several orders of magnitude larger than an atomic mass so that at presently attainable temperatures these motions can be regarded as classical.

Then for a gram atom of a solid, composed of $q$ particles, each particle containing $N/q$ atoms, the heat capacity is given by the expression

$$C = q\left[6k + \sum_{1}^{3N/q-6} g(u_v)\right] \qquad (1)$$

where $g(u)$ is the usual harmonic oscillator or Einstein function

$$g(u) = ku^2e^u/(e^u - 1)^2 \qquad (2)$$

$k$ is the Boltzmann constant and $u_v = h\nu_v/kT$ with $\nu_v$ the frequency of the $v$-th normal mode of vibration.

For convenience in evaluating $\nu_v$, we assume that the crystal is a rectangular parallelopiped. If $a_x$, $a_y$ and $a_z$ are the edges of this crystal, then, neglecting possible end corrections, the frequencies of the transverse normal modes are

$$\nu_t = (c_t/2)[(l/a_x)^2 + (m/a_y)^2 + (n/a_z)^2]^{1/2} \qquad (3)$$

where $l$, $m$ and $n$ are positive integers or zero. The corresponding expression is obtained for the longitudinal vibrations by substituting $c_l$ for $c_t$. At the low temperatures under discussion, the usual averaging of the transverse and longitudinal vibrations

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[1] G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[2] W. F. Giauque and R. C. Archibald, THIS JOURNAL, **59**, 561 (1937).

[3] E. W. Montroll, *J. Chem. Phys.*, **18**, 183 (1950).

leads to erroneous results. Consequently, any computations must be made considering each vibration independently. The heat capacity can now be written,

$$C = q[6k + 2\Sigma g(u_t) + \Sigma g(u_l)] \qquad (4)$$

where the two sums are the appropriate triple sums over $l$, $m$ and $n$.

Equation (3) for the frequencies of the various normal modes is subject to correction for both very low and very high frequencies. The high frequency corrections arise when the wave length is reduced to atomic dimensions. However, in the low temperature region of present interest, these corrections can be ignored if the particles have at least ten or twenty atoms on an edge.

The low frequency corrections apply only to transverse modes but are important at low temperatures. The lowest frequency modes are those with one of the indices $l$, $m$ or $n$ unity and the others zero. Also there are two transverse modes in each case, *i.e.*, for $l = 1, m = n = 0$, the displacements can be in either the $y$ or the $z$ direction. In Fig. 1 rough diagrams are given of the modes in the $x,y$-plane. These are first the mode with $l = 1$ and $y$ displacements and second the mode with $m = 1$ and $x$ displacements. It is seen that these two modes involve the same sort of distortion of the particle but include rotations in opposite directions. By taking proper linear combinations, one obtains a pure rotation and a single normal mode of vibration. The frequency of the true normal mode is approximately

$$\nu_t = (c_t/2)[(a_x^2 + a_y^2)/a^2 \; a \;]^{1/2} \qquad (5)$$

Corresponding expressions apply to the modes in the $y,z$- and $x,z$-planes. In each case the one frequency from equation (5) replaces the two lowest frequencies from equation (3).

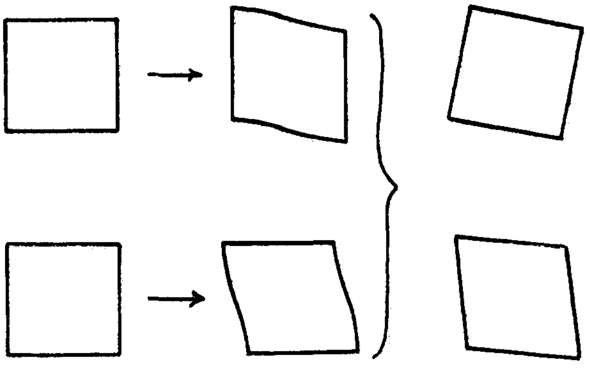

Fig. 1.—Transverse oscillations in the $x,y$-plane. The center column shows the displaced configurations implied by eq. (3), while the right-hand column shows the true motions: rotation above and a single vibration below.

While in principle there are similar corrections for rotation to all the odd overtones of transverse oscillations, these are found to be negligible except in the case discussed above.

To illustrate the conclusions of the previous paragraphs, we have computed the specific heat of aluminum to 6°K. Aluminum was chosen because of the close agreement between the Debye temperatures obtained from the specific heat and from elastic constant data. The data which were used were taken from the tabulation in Fowler and Guggenheim.[4] In these computations it was assumed that these constants were independent of size.

Figure 2 shows the calculated heat capacity of (1) the infinite crystal, (2) cubes of volume $10^{-18}$ cm.$^3$ each, *i.e.*, 100 Å. on an edge, and (3) rectangular parallelopipeds of the same volume with dimensions of 79.37, 79.37 and 158.74 Å. The data for the infinite crystal were computed from the $T^3$ law, and for the two small crystals by the summation of the series as given by equation (4). The necessary end corrections were made for the transverse vibrations as given in equation (5). Possible electronic contributions to the heat capacity have been neglected.

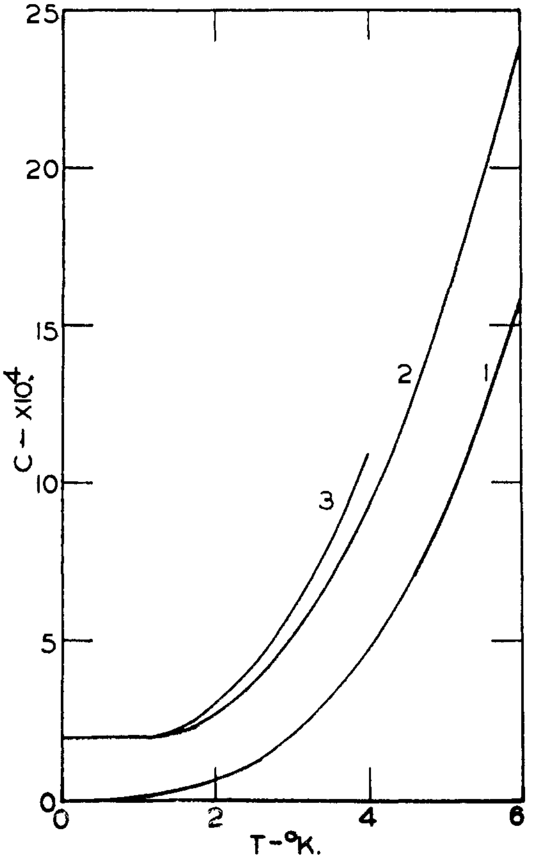

Fig. 2.—Effect of size and shape on the heat capacity of aluminum: (1) infinite crystal; (2) cube of volume $10^{-18}$ cm.$^3$; (3) rectangular parallelopiped of same volume, edges of 79.4, 79.4, and 159.8 A.

As expected, the heat capacity of the small crystals is larger than that of the infinite crystal. The heat capacity is larger for two reasons. The contribution of the gross motion of the particle is surprisingly large. Its contribution to the heat capacity is $1.95 \times 10^{-4}$ cal. deg.$^{-1}$. This quantity is constant and extends almost certainly to $10^{-3}$ °K. The contribution of the internal vibrations does not reach this value until nearly 3°K.

Not enough is known concerning the potential

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[4] R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," University Press, Cambridge, 1939, p. 148.

energy and distribution of these small particles to compute with any certainty the constants for the gross translational and rotational motion of these particles. The translational vibrational frequency can be estimated in the following manner. The most unfavorable system would be that in which the particle is completely surrounded by other particles at the normal interatomic distance. Essentially what we treat is the motion of a block of the proper size in an infinite crystal. Let us make the nearest neighbor approximation and consider the potential to be given by the Lennard-Jones potential for argon. If we compute the force constant in this manner it is found that $h\nu/k$ = 1.7 × $10^{-7}$ °K. Since the forces which we normally would need consider are either of the ionic or metallic type, it seems reasonable that if we multiplied this result by $10^3$, we would fix an upper limit to the frequency of vibration of the particle. Thus, neglecting the gravitational field, it seems safe to assume that the vibration of the particle is essentially classical at temperatures above $10^{-3}$ °K. The rotational oscillation would give a similar result.

The equation also predicts that, at the very lowest temperatures, the contribution from the internal vibrations is less for the small crystal than the large. This is due to the absence of very low frequencies in the crystallite. Thus at 1°K. the comparative figures are 7.42 and 1.08 × $10^6$ cal. deg.$^{-1}$ for the large and small crystals, respectively. At 2°K. and higher, the reverse is true. The reason for this has been pointed out by Montroll.

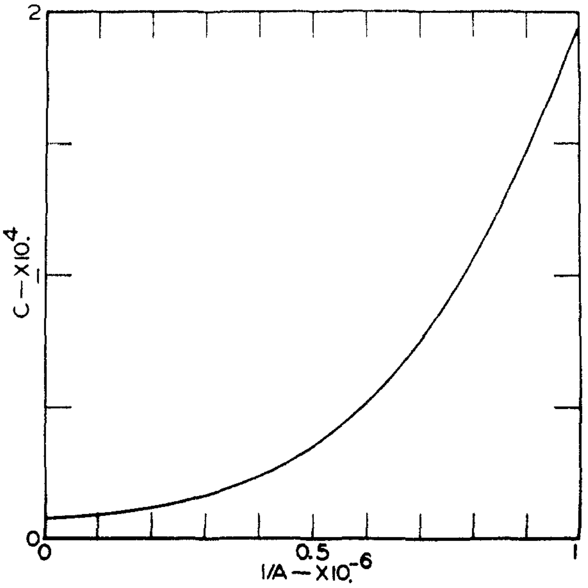

Fig. 3.—Effect of length of cube edge, A, on heat capacity of aluminum at 1 °K.

A comparison of these results with those obtained by the method of Montroll shows similar discrepancies. Montroll retains the continuous distribution of frequencies. Thus the contribution from the usual crystal vibrations is even higher. At 1°K. his computed heat capacity would be 19.7 × $10^{-6}$ cal. deg.$^{-1}$, whereas, the more refined computation gives 1.08 × $10^{-6}$ cal. deg.$^{-1}$ for the internal vibrations and 1.96 × $10^{-4}$ cal. deg.$^{-1}$ for the total heat capacity. At temperatures of 3° and higher, the computation of Montroll gives a lower contribution than the method of the present paper for even the internal vibrations alone. This decrease is due to the fact that Montroll has made only the first-order correction in the distribution function. If the edges of the $l$, $m$, $n$ space are counted in the same manner as Montroll, then the present computation is less than that which is obtained by Montroll's equation, as would be expected.

The change of shape of the particle also leads to an expected result, an increase in the heat capacity with an increase in area at constant volume. This change in heat capacity is not proportional to the area in this low temperature region but will become so in the region where Montroll's equations apply.

The entropy is given, of course, by the usual integral of the equation for the heat capacity. At these low temperatures the major contribution to the entropy is from the motion of the entire particle. Its exact value depends upon the force constants for the motion, these in turn depend on the shape and size. Thus the entropy cannot be precisely determined. The entropy of a gram atomic weight of aluminum cubes 100 Å. on edge is approximately 0.001 e.u., at 1°K. At ordinary temperatures, this is not important. The inability to compute the exact value of this quantity at these low temperatures precludes the possibility of comparing the entropy as a function of area.

Figure 3 shows the behavior of the heat capacity at 1°K. as a function of cube size. As the particle becomes larger, the contribution of the gross motion becomes smaller. There is an appreciable effect of particle size up to cubes 600 Å. on edge. The effect becomes especially marked as the cube edge becomes less than 200 Å.

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