crystalline precipitates removed by filtration. The first two crops consisted almost exclusively of the acid sodium salt of dimethylmaleic acid, and the third contained the remainder of this salt and some dimethylmaleic anhydride. These three fractions, combined and suspended in water, liberated dimethylmaleic anhydride upon addition of hydrochloric acid; yield 37%. The remaining three fractions from the original mixture consisted chiefly of dimethylfumaric acid; the first of these contained a small amount of dimethylmaleic anhydride which was removed by steam distillation. The yield of dimethylfumaric acid was 37%.

Repeated ether extraction of the filtrate from the above precipitations removed the methylitaconic acid which was obtained in a yield of 12%.

Summary

Sodium acid dimethylmaleate has been made by partial acidification of the disodium salt.

The precipitation of the monosodium salt has been used in the separation of products in the preparation of dimethylfumaric acid.

CHARLOTTESVILLE, VA. RECEIVED SEPTEMBER 27, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Interatomic Potential Curve and the Equation of State for Argon*

BY O. K. RICE

It has recently been stressed, that in order to obtain a good curve for the interatomic potential energy of a pair of atoms of a substance such as argon, it is necessary to take the properties of the solid into account. Buckingham[1] attempted to find a potential energy curve which would conform to a theoretical expression for large distances (obtained from refinement of London's theory of van der Waals forces), and would simultaneously correlate the heat of sublimation and lattice distance of the solid at 0°K. with the second virial coefficient for the gas. On the other hand, Herzfeld and Goeppert Mayer[2] and Kane[3] made calculations of the equation of state of the solid on the basis of preassumed potential curves. The potential curves used by them, however, were apparently not very satisfactory, since the calculated properties of the solid differed from the experimental in several important respects. A recently published calculation of a similar nature by Devonshire[4] did not take quantum effects into account.

As it appeared important, in connection with my recent studies on the fusion phenomena of argon, to have as accurate a potential energy curve as possible, it seemed that it would be worth while to construct a curve which would reproduce as well as possible the known properties of the solid from 0°K. to the melting point. At the same time it was desired that the curve pass into the theoretical expression of Buckingham for large distances, and also reproduce the second virial coefficient of the gas. This paper will present an attempt to construct such a curve, together with a discussion of the difficulties and uncertainties necessarily involved.

§1. Properties of the Solid in Terms of the Potential Energy Curve

We follow Buckingham in that we consider segments of the potential energy curve, assigning separate analytical expressions to the separate segments. We start by assuming Buckingham's form for the potential energy curve U at large interatomic distances, r, namely

$$U = -c_6 r^{-6} - c_8 r^{-8} \qquad (1)$$

with $c_6 = 60 \times 10^{-60}$ erg cm.^{6} and $c_8 = 180 \times 10^{-76}$ erg cm.^{8} for argon. These are slightly less than values, calculated by Buckingham,[5] which were stated to represent an upper limit. Reduced to more convenient units, we have

$$\begin{aligned} c_6 &= 8.64 \times 10^5 \text{ cal. mole}^{-1}\text{ Å.}^6 \\ c_8 &= 2.59 \times 10^6 \text{ cal. mole}^{-1}\text{ Å.}^8 \end{aligned} \qquad (2)$$

We assume that this potential can be used for all pairs of atoms which are not nearest neighbors.

For a short distance on either side of the minimum of the potential curve, we express U in the approximate form

$$U = U_0 + b_2(r - r_0)^2 - b_3(r - r_0)^3 + b_4(r - r_0)^4 \qquad (3)$$

where U_0 and r_0 are the respective values of U and

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(1) R. A. Buckingham, *Proc. Roy. Soc.* (London), **A168**, 264 (1938). See also J. Corner, *Trans. Faraday Soc.*, **35**, 711 (1939).

(2) K. F. Herzfeld and M. Goeppert Mayer, *Phys. Rev.*, **46**, 995 (1934).

(3) G. Kane, *J. Chem. Phys.*, **7**, 603 (1939).

(4) A. F. Devonshire. *Proc. Roy. Soc.* (London), **A174**, 102 (1940).

(5) R. A. Buckingham, *ibid.*, **A160**, 94 (1937).

r at the minimum, and b_2, b_3 and b_4 are constants. Although this form of potential has been much used in the discussion of band spectra, it has not recently, as far as I am aware, been applied to the problem at hand. It is very convenient because of its flexibility, and because of the fairly simple relation of the constants to the properties of the solid. The properties of the solid will be used to evaluate these constants. This done, we shall extend the curve smoothly through the intermediate region of r which lies between those regions for which Eqs. (1) and (3) hold. For evaluating the curve at very small values of r, the second virial coefficient will be used.

In considering the correlation of the constants, b_2, b_3 and b_4, with the properties of the solid, we shall first assume that the solid expands without introduction of any disorder[5a]; that is, we shall assume that, without exception, the positions of equilibrium about which the atoms vibrate remain in the relative positions proper to a face-centered cubic lattice, such as is characteristic of argon at the lowest temperatures. Later we shall consider the possibility that the beginning of disorder in the crystal—a phenomenon which could be described as premelting—plays a significant role, and shall see, roughly at least, how the potential energy curve must be altered in order to allow for it.

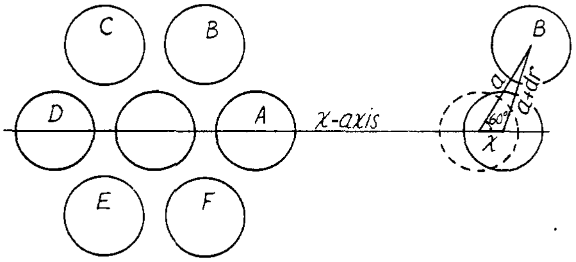

Fig. 1.—Surroundings of an atom. Figure at right indicates calculation for atom B.

We turn now to a consideration of the vibration of the atoms in the lattice. The usual procedure for exact calculations is to relate the force between atoms to the elastic constants of the crystal, and then relate the elastic constants to the Debye characteristic temperature.[6] I believe, however, that it is somewhat simpler to proceed in another way, which has also been applied in a rough calculation by Lennard-Jones and Devonshire (cited by Corner[1]) but which can be made exact.

Consider first the motion of a single atom in the field produced by its neighbors, assuming that all the neighbors remain fixed in their positions of equilibrium for the particular state of expansion of the lattice. We shall designate as x, y and z the coördinates of the displacement of the particular atom under consideration from its position of equilibrium. The potential energy of the single atom above its potential energy at its equilibrium position will, of course, be, in first approximation for small displacements, a quadratic function of x, y, z, and, in fact, on account of the cubic symmetry of the lattice, it will depend only on the combination $x^2 + y^2 + z^2$. This being the case, we may just as well consider displacements in the x-direction for which $y = z = 0$. Let the x-direction be defined as indicated in Fig. 1, which shows the atom under consideration surrounded by six others in a plane. We shall at first consider only nearest neighbors, so it will be necessary, in addition to those shown in the figure, to note that the central atom has three near neighbors in the plane above that shown and three in the plane below. A displacement of the central atom by a small amount x will produce an increase ϕ in potential energy, which is to be obtained by calculating

$$(\mathrm{d}U/\mathrm{d}r)\mathrm{d}r + \tfrac{1}{2}(\mathrm{d}^2U/\mathrm{d}r^2)\mathrm{d}r^2 \tag{4}$$

for each of the neighbor atoms, and adding together all the results, retaining only terms in x^2. The value of $\mathrm{d}r$ for any particular neighbor atom comes directly from the displacement x of the displaced atom. Turning to Fig. 1, we see that for atom A we have $\mathrm{d}r = -x$, and for atom D we have $\mathrm{d}r = x$. For the other atoms the situation is more complicated but $\mathrm{d}r$ can be obtained by use of the law of cosines for an oblique triangle. For atoms B and F we find $\mathrm{d}r = -\frac{1}{2}x + \frac{3}{8}x^2/a$, where a is the equilibrium distance for nearest neighbors; for atoms E and C we have $\mathrm{d}r = \frac{1}{2}x + \frac{3}{8}x^2/a$. Of the other six neighbors, not shown in Fig. 1, two have expressions like B and F, two like E and C, and for the other two, $\mathrm{d}r = \frac{1}{2}x^2/a$. This gives as a first approximation

$$\begin{aligned}\phi &= 4\{b_2 - (3b_3 - 2b_2a^{-1})(a - r_0) \\ &\quad + (6b_4 - 3b_3a^{-1})(a - r_0)^2 \\ &\quad + 4b_4a^{-1}(a - r_0)^3 - \beta\}x^2 \\ &= 4Bx^2\end{aligned} \tag{5}$$

The term β is inserted to take care of the more distant atoms. It may be evaluated by inserting Eq. (1) into expression (4) and adding over all

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[5a] For a discussion of disorder see O. K. Rice, *J. Chem. Phys.*, **7**, 883 (1939).

[6] See, *e. g.*, Herzfeld and Goeppert Mayer[3] or V. Deitz, *J. Franklin Inst.*, **219**, 459 (1935).

atoms which give appreciable contributions. Since β is relatively very small, it need be evaluated only roughly. B will be used hereafter as an abbreviation for the quantity in brackets.

Equation (5) may be generalized for any displacement of the atom by replacing x^2 by $x^2 + y^2 + z^2$, and is then the potential for a three-dimensional oscillator with frequency ν given by

$$\nu^2 = 2\pi^{-2}m^{-1}B \qquad (6)$$

where m is the mass of the atom.

Actually, of course, the energies of the various atoms are not independent, and the total potential energy will contain cross terms involving products such as x_1x_2, x_1y_2, etc., where the subscripts refer to different atoms. The introduction of such cross terms into the secular determinant of a classical perturbation problem gives the correct frequencies for the normal modes of vibration of the crystal, but it leaves the sum of the squares of the frequencies unaltered.[7] Equation (6), therefore, gives directly the average value of ν^2. If we assume the Debye distribution of frequencies in the crystal (an assumption which will be discussed in § 4) the average value of ν^2 is equal to $\frac{3}{5}\nu_m{}^2$, where $\nu_m = k\Theta/h$ is the Debye maximum frequency (Θ is the Debye characteristic temperature, k the Boltzmann constant, and h Planck's constant). We, therefore, have

$$\Theta^2 = (^{10}/_3)h^2\pi^{-2}m^{-1}k^{-2}B \qquad (7)$$

Θ is related to the zero-point energy E_z by the relation

$$E_z = (^9/_8)k\,\Theta \qquad (8)$$

We can now set up an expression for the total energy of the crystal, as follows

$$E = 6U_0 + 6b_2(a - r_0)^2 - 6b_3(a - r_0)^3 + 6b_4(a - r_0)^4 - 1.227c_6a^{-6} - 0.401c_8a^{-8} + E_z + E_t \qquad (9)$$

Here, as before, a is the equilibrium distance between *nearest* neighbors; it, of course, depends on the degree of expansion of the lattice or the molal volume of the crystal. The first four terms on the right side of Eq. (9) take care of the potential energy contributions of nearest neighbors and come from Eq. (3). The factor 6 arises from the fact that there are twelve nearest neighbors, 12 being divided by 2 in order to avoid counting the potential of each atom twice. The next two terms give the potential due to all other than nearest neighbors.[8] E_t is the thermal energy, that is, it is the excess of energy over that which the system would have at 0°K. if the value of a remained the same. E_t/T is a function of Θ/T only, and has been tabulated for a Debye solid.[9]

Finally we turn to a consideration of the condition of equilibrium for the solid. This condition may be best obtained by use of the equation[10] for the pressure of any substance for which the thermodynamic quantities, E_t/T, S, etc., are determined in the usual manner as a function of Θ/T, only

$$P = -(E_t/\Theta)\mathrm{d}\Theta/\mathrm{d}V - \mathrm{d}E_z/\mathrm{d}V - \mathrm{d}E_p/\mathrm{d}V \qquad (10)$$

Here V is the molecular volume and E_p is the potential energy (first six terms on the right side of Eq. (9)). Atmospheric pressure is practically zero compared to the terms on the right in Eq. (10), so if P is set equal to zero Eq. (10) gives the condition for normal equilibrium (*i. e.*, it determines the value of V or a assumed by the crystal at any temperature). If we use a as the independent variable rather than V, the condition for equilibrium becomes

$$\mathrm{d}E_p/\mathrm{d}a + \mathrm{d}E_z/\mathrm{d}a + E_t\Theta^{-1}\,\mathrm{d}\Theta/\mathrm{d}a = 0 \qquad (11)$$

or, by Eq. (8)

$$\mathrm{d}E_p/\mathrm{d}a + \Theta^{-1}\,(\mathrm{d}\Theta/\mathrm{d}a)(E_z + E_t) = 0 \qquad (11a)$$

This equation may be written out in detail with the aid of Eqs. (7) and (9). To show how the above equations are applied it will be best to write them out in approximate forms. As a rough approximation we may set $B = b_2$ and write Eq. (7)

$$\Theta^2 = (^{10}/_3)h^2\pi^{-2}m^{-1}k^{-2}b_2 \qquad (12)$$

To this approximation Θ is constant, and since Θ is known from specific heat measurements, b_2 is determined.

In Eq. (9) the terms in $(a - r_0)^3$ and $(a - r_0)^4$ are small for values of a such as occur up to the melting point, while the terms for distant atoms and E_z have the effect chiefly of shifting the minimum of the potential energy curve without greatly changing its shape. If, therefore, we use the symbol Δ to denote the change in any quantity between 0°K. and some given higher temperature, T_0, Eq. (9) may be written roughly as

$$\Delta E - \Delta E_t = 6b_2(\Delta a)^2 \qquad (13)$$

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[7] See, *e. g.*, L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," McGraw-Hill Book Co., New York, N. Y., 1935, pp. 282 ff. The actual constancy of the sum of the squares of the frequencies is not proved there, but is a matter of simple algebra; see H. B. Fine, "College Algebra," Ginn and Co., Boston, Mass., 1901, p. 432.

[8] The numerical coefficient is derived from J. E. Jones (Lennard-Jones) and A. E. Ingham, *Proc. Roy. Soc.* (London), **A107**, 636 (1925).

[9] See Landolt–Börnstein, "Physikalisch-Chemische Tabellen," 1. Ergänzungsbd., 1927, pp. 702–707.

[10] This equation has appeared frequently in the literature, but a brief derivation is given in Appendix I.

The change in internal potential energy plus zero-point energy is given in terms of Δa, regardless of the cause of the expansion, by Eq. (13). This rough relation depends only on the gross features of the interatomic potential. The actual value of Δa, attained at different temperatures under conditions of equilibrium for zero pressure, will depend on the fine details of the potential curve, *i. e.*, chiefly on b_3, as shown below (see Eq. (14)). If b_3 (and b_4) were equal to zero there would be no expansion, the solid would follow, at least approximately, the Debye theory in its simplest form (*i. e.*, with constant Θ), and ΔE would be equal to ΔE_t. That this is not the case is indicated by the specific heat (C_p) values for argon, which run considerably higher than the Dulong–Petit value at the higher temperatures (nearly 8 cal. per mole per degree at the melting point). These specific heat data furnish a value for ΔE. ΔE_t may be calculated roughly at T_0 from the value of Θ used in Eq. (12), using the tabulated Debye functions. As b_2 is known from Eq. (12), Eq. (13) may then be used to get an approximate value of the actual expansion, Δa, of the lattice, provided the theory of this section (which says that the potential energy of the solid depends solely on the expansion of the lattice, without any effect of disorder) is correct.

In getting an approximation for Eq. (11) we note that $E_p + E_z = E - E_t$, so that, by Eq. (13), the first two terms of Eq. (11) become $12b_2\Delta a$. E_t is the same as ΔE_t of Eq. (13). $\Theta^{-1}\mathrm{d}\Theta/\mathrm{d}a$ is equal to $\frac{1}{2}B^{-1}\mathrm{d}B/\mathrm{d}a$, which is roughly (considering only the leading terms in evaluating both B and $\mathrm{d}B/\mathrm{d}a$) equal to $-\frac{3}{2}(b_3/b_2)$. Therefore, Eq. (11) takes the approximate form

$$12b_2\Delta a - (3/2)(b_3/b_2)\Delta E_t = 0 \tag{14}$$

It will be noted that, with b_2 and Δa found from Eqs. (12) and (13), Eq. (14) determines b_3. As stated above b_3 is intimately connected with the expansion of the lattice. The values of b_2 and b_3 obtained from Eqs. (12), (13) and (14) can be used as first approximations, which will then allow rough evaluation of the smaller terms in Eqs. (7), (9) and (11) or (11a) at the two different temperatures.

These approximate values of the small terms may then be used in the usual manner to get a second approximation for b_2, b_3 and Δa, and the process may be repeated as often as desired. At first we may set $b_4 = 0$; it requires data at a third temperature to get b_4. If b_4 is set equal to zero, and b_2 and b_3 are evaluated by using the data at 0°K. and at a temperature 10 or 20° below the melting point, it is found that the properties of the solid near the melting point are not reproduced at all. The theory makes the solid appear to expand excessively in the last few degrees below the melting point, and the calculated energy increases far too rapidly. According to the theory, the solid is evidently approaching a breakdown point, such as actually occurred below the experimental melting point in the calculations of Herzfeld and Goeppert Mayer[2] and of Kane.[3] This peculiar behavior is entirely eliminated by assigning the proper value of b_4. It thus appears that the properties of a substance may, under certain circumstances, become very sensitive to small changes in the potential energy curve.

In obtaining the second and higher approximations, it is necessary to know the actual value of a. This may be obtained with sufficient accuracy from the literature.

Once the other terms in Eq. (9) are known, U_0 may be determined if the absolute value of E, as well as its change with temperature, is known. E represents the difference between the energy of the solid at any given temperature and the energy of the infinitely dilute gas at 0°K. E may be calculated from available thermal data[11] (see Appendix II).

TABLE I[a]

RESULTS OF CALCULATIONS FOR ARGON NEGLECTING DISORDER

$b_2 = 769.1$, $b_3 = 968$, $b_4 = 294$, $r_0 = 3.8267$, $U_0 = -276.7$

T, °K.	Θ	ΔE (calcd.)	ΔE (exptl.)	a (calcd.)
16.0	82.00			3.794
51.1	78.24	158.0	157.3	3.824
69.6	74.60	275.6	276.4	3.852
82.2	70.63	371.5	370.2	3.882

[a] In this table ΔE is equal to the energy at the temperature noted minus the energy at 16.0°K. Units of length, Å.; units of energy, cal. per mole.

We give the results of our calculations in Table I. It will be noted that the values of b_2, b_3, b_4 and r_0 used reproduce the changes of energy with temperature almost within the limits of error over the whole range of temperatures. Θ at 16.0° has been made to agree with the value obtained by Clusius[11a] from specific heat data. The values of

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(11) Taken from (a) K. Clusius, *Z. physik. Chem.*, **B31**, 459 (1936); (b) A. Frank and K. Clusius, *ibid.*, **B42**, 395 (1939); and (c) K. Clusius and K. Weigand, *ibid.*, **B46**, 1 (1940). Values of physical constants taken from "Outline of Atomic Physics," 2d ed., by the University of Pittsburgh Physics Staff, John Wiley and Sons, Inc., New York, N. Y., 1937, Appendix II.

a will be discussed below, but it may be stated that they are approximately correct.

§2. Effect of Disorder in the Solid

All the above calculations were based upon the assumption that the effect of any disorder phenomenon in the solid is negligible. There are, however, data on another property of the solid which, if correct, indicate, when taken in conjunction with the above results, that disorder in the solid may play an important part in determining its properties.

Simon and Kippert[12] have measured $(\partial P/\partial T)_V$ for argon at 73°K. From this $(\partial E/\partial V)_T$ and hence $(\partial E/\partial a)_T$ can be calculated readily. The latter turns out to be about 1270 cal. per mole per Å., while calculations based on Table I give about 750. The experimental value of $(\partial E/\partial a)_T$ is thus nearly twice the theoretical. This suggests that actually a considerable amount of disorder is appearing in the solid even at 73°K., which is about 10° below the melting point. The actual value of $(\partial E/\partial a)_T$ is greater than the theoretical because at constant temperature the amount of disorder increases as the lattice distance increases.

Thus it appears that Simon and Kippert's data are not consistent with the assumption of §1 concerning the difference between ΔE and ΔE_t. We have overlooked a factor which makes expansion of the lattice almost twice as effective, as measured by $(\partial E/\partial a)_T$, as it is calculated to be in §1. This suggests that we ought to use a smaller value of b_3 than was used in §1, since obviously less expansion is required to take care of the difference between ΔE and ΔE_t. Also we must remember that the effect of disorder will itself be to make the expansion greater than calculated by the theory of §1. However, the best that can be done at present is to continue to use this theory, fixing the constants so as to give a fairly small expansion, thus making a rough allowance for the further expansion to be expected from disorder. Calculations made on this basis are shown in Table II. In this case the expansion is small enough so that we do not seem to be approaching a breakdown point, and for this reason it is satisfactory to set $b_4 = 0$. The difference between ΔE(obsd.) and ΔE(calcd.) may be considered to be a rough measure of the energy due to disorder.

TABLE II[a]

RESULTS OF CALCULATIONS FOR ARGON CONSIDERING DISORDER

$b_2 = 781.5, b_3 = 703, b_4 = 0, r_0 = 3.8608, U_0 = -279.9$

T, °K.	Θ	ΔE (calcd.)	ΔE (obsd.)	a(calcd.)
11.0	82.00			3.820
54.4	80.31	178.6	185.7	3.841
81.2	78.49	336.0	370.5	3.863

[a] In this table ΔE is equal to the energy at the temperature noted minus the energy at 11.0°K. Units of length, Å.; units of energy, cal. per mole.

We may now make a brief statement about the lattice constants. The tables have been made to conform as closely as possible with available data. X-Ray measurements at 20°K.[13] and 40°K.[14] give about 3.82 ± 0.04 Å. and 3.83 ± 0.015 Å., respectively, while at the melting point the density of the liquid and the change of volume on melting give[11c] about 3.86 Å. In view of the possibility of error in the individual measurements, and the fact that they are not strictly comparable, having been done by different investigators and by different methods, it seems probable that no conclusion as to the actual expansion of the solid up to its melting point is justified. Table II looks much better in this respect than Table I, but the difference is not conclusive. Further experimental data on this point are very much to be desired.

§3. The Potential Energy Curves

The question now arises as to how to construct the complete potential curve from Eqs. (1) and (2) combined with Eq. (3) as evaluated from either Table I or Table II. We wish to know first how far from r_0 we should use Eq. (3). In order for Eq. (7) to have much significance[15] it would seem that Eq. (3) should hold at least somewhat beyond distances corresponding to the actual displacement of an atom with average energy. It is seen from Eq. (5) and from Table I or Table II that an atom vibrating with an energy of about kT near the melting point will have a maximum displacement of about 0.25 Å. The curve should, therefore, follow Eq. (3) to a distance $r - r_0$ equal to 0.4 or 0.5 Å.

We have made the assumption that Eq. (1)

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[12] F. Simon and F. Kippert, *Z. physik. Chem.*, **135**, 113 (1928).

[13] J. de Smedt and W. H. Keesom, *Comm. Phys. Lab. Leiden*, **178**, 19–21 (1926).

[14] F. Simon and C. v. Simson, *Z. Physik*, **25**, 160 (1924).

[15] It should be noted that Eq. (7) depends on the assumption that the motion of an individual atom is harmonic, *i. e.*, all higher terms in Eq. (5) must be truly negligible. There will be no term in the third degree in x, y, and z, on account of the symmetry, and the term in the fourth degree will actually be not more than a few per cent. of the term in the second degree for displacements of the magnitude which we shall need to consider.

holds for all but nearest neighbors. To be consistent our potential energy curve should coincide with Eq. (1) for all distances beyond that of the next nearest neighbors, or approximately 5.4 Å.

The curves actually constructed are shown, plotted against r^3, in Fig. 2. They are compared with the curve given by Buckingham,[1] and with Lennard-Jones's curve[16] of the form $-\mu r^{-6} + \lambda r^{-s}$ with $s = 12$. The latter coincides fairly closely with the curve recommended by Corner[1] and is the type of curve used by Devonshire[4] in his calculations.

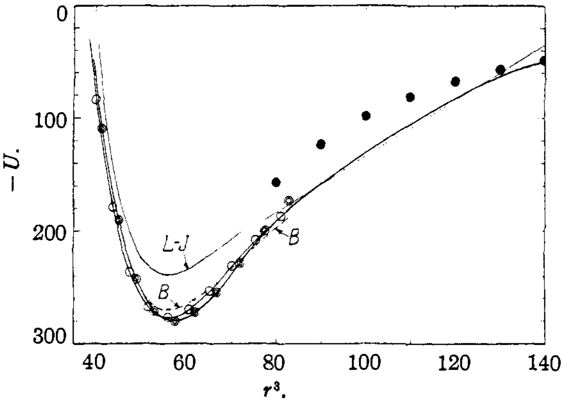

Fig. 2.—Interatomic potential curves for argon: U in cal. per mole, r in Å.; ○ from Eq. (3) and Table I; ◉ from Eq. (3) and Table II (the curves from Table I and Table II are assumed to coincide beyond $r^3 = 80$); ● from Eqs. (1) and (2); L-J from Lennard-Jones; B from Buckingham. Straight line, see §5.

It is seen that both of the curves obtained in the present paper rise more steeply to the right of the minimum than either of the other curves. I am inclined to believe that the curve derived from Table II, which rises the most steeply of them all, is to be preferred, and I feel that the true curve cannot vary from it very much, especially in the important region between $r^3 = 60$ and $r^3 = 75$. It may seem a little flat beyond $r^3 = 80$, though it joins fairly well with the curve from Eq. (1) at large distances. It was given this shape to make it conform reasonably well with the second virial coefficient of the gas (see §5). Of course, some change in this region is not out of the question.

§4. Discussion of Errors and Deviations from the Debye Theory

It will be well to discuss the possibility of error in the potential energy curve caused by any error in Θ. This is the least certain quantity both from the experimental and theoretical point of view, and is also the one most likely to affect the potential energy curve.

Clusius[11a] has calculated the value of Θ corresponding to his measured specific heat (corrected to give C_v) over a range of temperatures from 10.5° to 17.6°K., C_v varying from 0.95 to 2.34 calories per mole per degree. The value of Θ shows a trend, increasing from 79.3° at the lowest temperature to 83.7° at the highest. If anything, one would expect a decrease due to expansion of the lattice, but the expansion over this temperature range is negligible, so that actually constancy should be expected, as is, indeed, observed in the case of krypton.

There is, therefore, an uncertainty in Θ of perhaps 3%. By Eq. (12) this will produce approximately a 6% error in b_2. But by Eq. (14) we see that, roughly, b_3 is proportional to b_2^2 and to Δa. If Eq. (13) is to be maintained, as in the calculations for Table I, Δa is proportional to $b_2^{-\frac{1}{2}}$, which would make b_3 proportional to $b_2^{3/2}$. In any event, b_3 will increase somewhat more than b_2, and the result is that the changes in U for the important region to the right of the minimum partially cancel. A 3% error in Θ is not likely to produce more than a 2- or 3-calorie error in the curve at $r - r_0 = 0.4$ Å.

There is another possible difficulty, which has to do with the fundamental definition of Θ. The Debye theory of the solid state assumes a definite and rather arbitrary distribution of frequencies, and it has recently been suggested that considerable deviations from the Debye assumption are to be expected. It, therefore, seems desirable to compare the physical properties of a solid which would follow from some radically different assumptions as to the distribution of frequencies. We shall consider the Einstein theory, in which all the frequencies have the same value, and the approximation, suggested by the recent work of Fine[17] that two-thirds of the frequencies have a definite value, and the other third has a frequency 1.5 times as great. The latter we shall designate as the simplified Fine theory.

It is seen from Eq. (6) and the discussion following it, that it is the root-mean-square frequency, $\bar{\nu}$, which is of direct physical significance. In the Debye theory we have

$$\Theta = (5/3)^{1/2} h\bar{\nu}/k \qquad (15)$$

In the Einstein theory the characteristic tempera-

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[16] See R. H. Fowler, "Statistical Mechanics," 2d ed., The Macmillan Company, New York, N. Y., 1936, Chapter X.

[17] P. C. Fine, *Phys. Rev.*, **56**, 355 (1939).

ture is ordinarily defined differently (as $h\nu/k$); however, it is practically necessary for our present purposes to have characteristic temperatures which are directly comparable, and we shall use Eq. (15) to define our Θ for all the theories.

In Eqs. (9) and (11a) the important quantity $E_z + E_t$ depends on Θ. A comparison of $E_z + E_t$ as calculated for the different theories using the same value of Θ is given in Table III. It is seen that there is very good agreement between the theories, especially between the Debye theory and the simplified Fine theory. As is to be expected, the agreement is best at high temperatures.

TABLE III

VALUES OF $(E_z + E_t)/T$

Θ/T	Debye	Einstein	Fine
1	6.252	6.253	6.252
2	7.097	7.105	7.097
4	10.021	10.104	10.034

TABLE IV

VALUES OF Θ/T

C_v	Debye	Einstein	Fine
1.0	7.39	6.50	6.97
2.0	5.29	4.92	5.17
3.0	4.00	3.84	3.96
4.0	2.95	2.88	2.94

However, the actual determination of Θ is effected by means of the specific heat, C_v. In Table IV, therefore, we give values of Θ/T corresponding to different values of C_v, according to the different theories. Here there is a greater discrepancy between the theories. However, the Einstein theory is known to be far from correct, and in the simplified Fine theory, we neglect the continuous character of the frequency distribution, altogether. Actually, the distribution is continuous, even though it shows distinct maxima at certain frequencies. It, therefore, is probable that the error in Θ caused by using the Debye theory is considerably less than the difference between the Debye theory and the simplified Fine theory shown in Table IV. Use of the Debye theory, therefore, seems to be justified.

Incidentally it may be remarked that there appears to be no possibility of explaining the variation in Θ found by Clusius on the basis of a different frequency distribution, and it seems to me to be likely that this variation is due to experimental error.

§5. The Virial Coefficient

If we write the equation of the gas in the form

$$pV = kT + B_p p + C_p p^2 + \dots \qquad (16)$$

where p is the pressure, V the volume per molecule, k the Boltzmann constant, and B_p, C_p, . . . constants, B_p is what we shall call the second virial coefficient. It is given in terms of the interatomic potential, U, by the relation[16]

$$\begin{aligned} B_p &= 2\pi \int_0^\infty r^2(1 - e^{-U/kT})\mathrm{d}r \\ &= \tfrac{2}{3}\pi \int_0^\infty (1 - e^{-U/kT})\,\mathrm{d}w = \tfrac{2}{3}\pi I \qquad (17) \end{aligned}$$

where $w = r^3$ and I is defined by the equation. We divide the integral into parts, writing

$$I = I_1 + I_2 + I_3 + I_4 \qquad (18)$$

where I_1 is the integral taken between limits such that Eq. (1) holds (in this case we assume it holds for $w > 140$ Å.^{3}), I_3 is the part for which Eq. (3) holds (as an approximation for the purpose of calculating I, we assume it holds if -0.5 Å. $< r - r_0 < 0.5$ Å.), I_2 is the part between I_1 and I_3, and I_4 is the part for small values of r and w.

I_1 is found by expressing U as a function of w, expanding the exponential and integrating the series term by term. I_2 is found by approximating U by the straight line shown in Fig. 2; this should be sufficiently accurate and makes possible immediate evaluation of the integral. I_3 is found by using the form of the integral with r rather than w as the variable of integration, then changing the variable to $y = r - r_0$. The exponential then takes the form

$$e^{-U_0/kT} e^{-b_2y^2/kT} e^{(b_3y^3 - b_4y^4)/kT}$$

The first factor is constant, and the last factor can be expanded as a series. The exponential part of the integrand can be written as a sum of terms of the form $y^n e^{-b_2y^2/kT}$, and these can be integrated term by term with the aid of tables of the incomplete moment integral.[18]

I_4 requires special consideration. The lower limit of I_3 is already in the steep part of the potential curve, where the repulsive forces are of paramount importance. It should not introduce too much error into the virial to assume that U is a linear function of w for these small values of r or w, even though it is clear that this cannot be by any means an exact expression. If we designate the value of w corresponding to the lower limit of I_3 as w_1, this means that for $w < w_1$

$$U = U_1 + \alpha(w_1 - w) \qquad (19)$$

where U_1 is the value of U for $w = w_1$, and α is another constant. We then have

[18] K. Pearson, "Tables for Statisticians and Biometricians," Part I, 3d ed., Biometric Laboratory, University College, London, 1930, pp. xxiv, 22–23.

$$I_4 = \int_0^{w_1} (1 - e^{-U/kT})\mathrm{d}w \cong w_1 - \frac{kT}{\alpha} e^{-U_1/kT} \qquad (20)$$

since U is very large at $w = 0$. If the potential energy curve went up infinitely steeply from the point where $w = w_1$, then α would be infinite and we would have simply $I_4 = w_1$. With α finite, we see by comparing Eqs. (19) and (20), that I_4 is equal to that value of w for which U is equal to $U_1 + kTe^{-U_1/kT}$. This suggests that we use the experimental values of I (*i. e.*, the values calculated from the experimentally determined values of the second virial coefficient, B_p) for a range of temperatures together with the calculated values of I_1, I_2 and I_3, in order to obtain I_4 from Eq. (18). This being simply the value of w for which U has the value noted, we can calculate U as a function of w for the small values of w. Since Eq. (19) is only an approximation, we would not expect these values of U and w all to correspond to exactly the same value of α, but the curve obtained should be a fairly good one, and if all the data are mutually consistent it should fit on well to the part of the curve for U obtained in §3.

The experimental values of I are obtained from the work of Holborn and Otto[19] and Cath and Onnes.[20] These are shown plotted in Fig. 3. Where the two sets of data do not agree, values from the curve have been used.

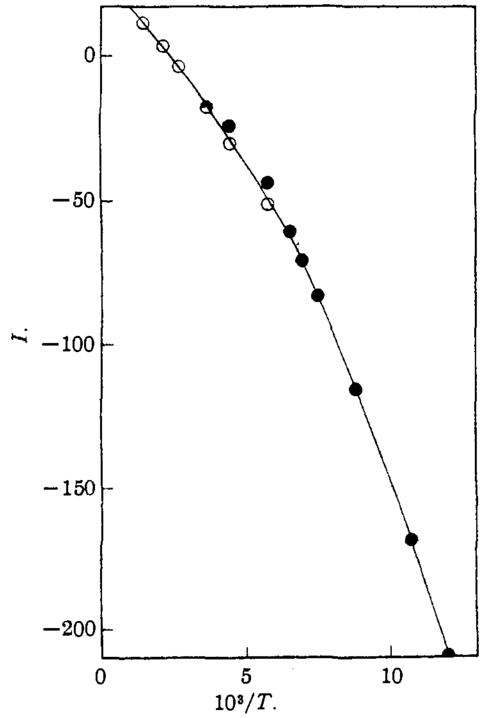

Fig. 3.—Values of I; ○ from Holborn and Otto; ● from Cath and Onnes.

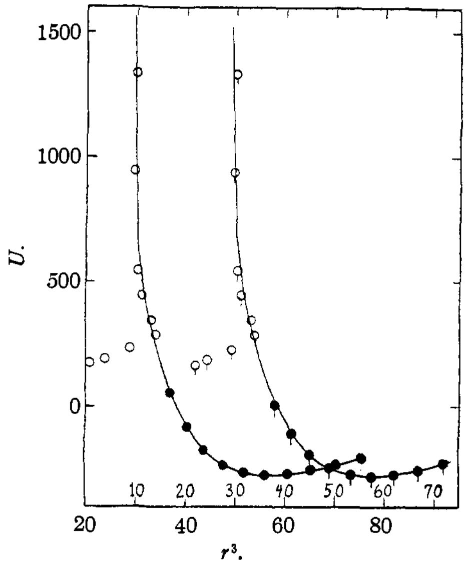

Fig. 4.—Interatomic potential curves for argon: U, in cal. per mole, r in Å.; ● from Eq. (3) and Table I; ○ from virial coefficient and Table I; ● from Eq. (3) and Table II; ○ from virial coefficient and Table II. Upper abscissas for right-hand curve and points; lower abscissas for left-hand curve and points.

In Fig. 4 we give the results of the above indicated calculation, *i. e.*, the values of U as a function of w. It is seen that in both cases the points derived from virial coefficients at the higher temperatures (*i. e.*, the higher points) fit in well with the curve for larger values of w, while the points derived from the lower temperatures fall sharply toward the left. It does not seem likely that any change in the potential energy curve could improve the situation with respect to these points without worsening it with respect to the points which now fit. I am inclined to believe that the virial coefficients at the lowest temperatures are somewhat in error. Even at the lowest temperature the error would need to be only 6 or 8% to explain the discrepancy, and since the virial coefficient is in itself a correction term this does not seem unreasonable. I believe, therefore, that we may conclude that, within experimental error, the equation of state for gaseous argon is consistent with the equation of state for the solid. The virial coefficient does not assist us in deciding between the two sets of assumptions regarding the solid.

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(19) L. Holborn and J. Otto, *Z. Physik*, **33**, 1 (1925).

(20) P. G. Cath and H. K. Onnes, *Arch. Neërland. Sci.*, **6**, 26 (1923).

I wish to thank Professor R. H. Lyddane for some very helpful suggestions and discussion.

Appendix I

Derivation of Eq. 10.—Since no heat is lost or gained by a system in an adiabatic expansion, we may write

$$P = -(\partial E/\partial V)_S = -(\partial E_t/\partial V)_S - \mathrm{d}E_s/\mathrm{d}V - \mathrm{d}E_p/\mathrm{d}V$$

But as S is a function only of Θ/T, the latter does not change in an adiabatic process. And since E_t/T depends only on Θ/T, it is also true that $E_t/\Theta = (E_t/T)(T/\Theta)$ does not change in an adiabatic process. Hence

$$\left(\frac{\partial E_t}{\partial V}\right)_S = \left(\frac{\partial \Theta(E_t/\Theta)}{\partial V}\right)_S = \frac{E_t}{\Theta}\frac{\mathrm{d}\Theta}{\mathrm{d}V}$$

so that Eq. (10) follows immediately.

Appendix II

Calculation of Heat of Sublimation of Solid.—This calculation proceeds in a straightforward manner from the specific heats of solid, liquid, and vapor (assumed a perfect gas), the heat of fusion and the heat of vaporization of the liquid[11]; but the latter must be corrected to give the heat of vaporization to form a perfect gas. This correction was made as follows. We assume all terms in Eq. (16) in p^2, or higher powers, to be negligible, and then apply the thermodynamic equation

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

Integrating $(\partial H/\partial p)_T$ from 1 atmosphere to zero pressure we find

$$\Delta H = -\left(B_p - T\frac{\mathrm{d}B_p}{\mathrm{d}T}\right)\frac{RT}{V}$$

where V is the volume of one mole of gas at T (the boiling point) and 1 atmosphere. We then use the data of Cath and Onnes to evaluate B_p and $\mathrm{d}B_p/\mathrm{d}T$. This gives ΔH = 17.7 cal.

For the heat of sublimation of the solid at 16.0°K. to give vapor at 0°K., we find 1840.6 cal. per mole; if the solid is at 11.0° it is 1848.9 cal. per mole.

§6. Summary

A detailed investigation has been made of the relation between the interatomic potential energy curve and the properties of solid argon. The characteristic temperature and the total energy of the solid have been expressed in a simple way in terms of the constants of the potential energy expression, and the condition for equilibrium has been set up and applied in the determination of the potential energy curve for argon from the experimental data. The effect of the setting in of disorder (premelting) in the solid has been considered. What is believed to be a good potential energy curve for argon has been found, and compared with some others which have been previously used. The effect of the distribution of the frequencies of the normal modes of vibration of the solid upon its physical properties has been considered, and the effect of possible deviations from the Debye theory estimated. Finally, it has been shown that the potential curve obtained reproduces, probably within the limits of error, the experimental values of the second virial coefficient of the gas.

CHAPEL HILL, N. CAROLINA RECEIVED OCTOBER 8, 1940

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Structures of Complex Fluorides.[1] The Stereochemistry of Some Fluocolumbate and Oxyfluocolumbate Complexes. The Crystal Structure of Potassium Oxyfluocolumbate-Potassium Bifluoride, $K_2CbOF_5 \cdot KHF_2$*

BY J. L. HOARD AND W. J. MARTIN

When columbium fluoride, potassium fluoride, and hydrofluoric acid are mixed in varying proportions in aqueous solution, six distinct crystalline compounds can be prepared.[2] Two of these, obtainable when columbium fluoride is added in excess, will not be discussed in detail. Empirical formulas of the remaining four compounds are $K_2CbOF_5 \cdot H_2O$, K_3CbOF_6, K_3HCbOF_7, and K_2CbF_7. An X-ray study of potassium heptafluocolumbate, K_2CbF_7, demonstrating that it contains the seven-coördination complex, $CbF_7^{=}$, has been reported.[1a] The purpose of the present paper is twofold: first, to point out the remarkable fact that three stereochemically distinct types of complex columbate ions are represented among the four compounds for which formulas are given above, and, secondly, to report in detail the determination from X-ray diffraction data of the crystal structure of potassium oxyfluocolumbate-

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[1] For earlier papers in this series see (a), THIS JOURNAL, **61**, 1252 (1939); (b), *ibid.*, **61**, 2849 (1939); (c), *ibid.*, **62**, 3126 (1940).

[2] C. W. Balke and E. F. Smith, *ibid.*, **30**, 1637 (1908).