

The Thermodynamic Properties and Potential Energy of Solid Argon. II

O. K. Rice

Citation: [The Journal of Chemical Physics](#) **14**, 321 (1946); doi: 10.1063/1.1724139

View online: <http://dx.doi.org/10.1063/1.1724139>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/14/5?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Computational studies on thermodynamic properties, effective diameters, and free volume of argon using an ab initio potential](#)

J. Chem. Phys. **125**, 084510 (2006); 10.1063/1.2338310

[Ar n HF van der Waals clusters revisited: II. Energetics and HF vibrational frequency shifts from diffusion Monte Carlo calculations on additive and nonadditive potential-energy surfaces for n = 1 - 12](#)

J. Chem. Phys. **123**, 054305 (2005); 10.1063/1.1991856

[Spectroscopy of Ar-SH and Ar-SD. II. Determination of the three-dimensional intermolecular potential-energy surface](#)

J. Chem. Phys. **123**, 054325 (2005); 10.1063/1.1943968

[Line shape, transport and relaxation properties from intermolecular potential energy surfaces: The test case of CO₂-Ar](#)

J. Chem. Phys. **107**, 1824 (1997); 10.1063/1.474534

[The Thermodynamic Properties and Potential Energy of Solid Argon](#)

J. Chem. Phys. **12**, 289 (1944); 10.1063/1.1723941



The Thermodynamic Properties and Potential Energy of Solid Argon. II

O. K. RICE

University of North Carolina, Chapel Hill, North Carolina

(Received February 7, 1946)

In the first paper with this title, a relation was derived from the available experimental data giving the Debye characteristic temperature of solid argon as a function of a (the interatomic distance) or V (the molal volume of the solid). This relation was not consistent with the usual Grüneisen assumption, which for a small range of volumes may be written approximately $-\Theta^{-1}d\Theta/dV = \text{constant}$. In this paper it is shown that the Grüneisen assumption, with the constant set equal to 0.18 mole cc⁻¹ is reasonably consistent with the experimental data. On this basis a new relation between the potential energy E_p of solid argon and a is derived. Most of the earlier conclusions are unaltered, but the present basis seems more reasonable, and, as will be shown in the following paper, avoids difficulties when application is made to liquid argon.

IN a paper of the same title¹ (referred to herein after as I) we have used the available thermal and equation-of-state data on solid argon to determine the potential energy, E_p , and the Debye characteristic temperature, Θ , of the solid as functions of a , the equilibrium distance between nearest neighbors in the lattice. The relation thus obtained between Θ and a has the peculiarity that $d\Theta/da$ varies extremely rapidly with a . In fact, it gives $d\Theta/da = -211$ degree per angstrom at $a = 3.86\text{\AA}$ (with Θ itself, of the order of 80°), and $d\Theta/da = 0$ at $a = 3.924\text{\AA}$. This rapid variation seems extremely improbable, and when an attempt is made to apply such a function to a study of liquid argon it leads to difficulties. To be sure, the experimental data on which our expression for Θ was based extend only over a range of a from about 3.82 to 3.86\AA, so that anything outside this range may be said to be an extrapolation; however, even in this range, $-d\Theta/da$ varied from about 273 to 211. It appears quite possible that this apparent, rather violent variation of $d\Theta/da$ may be due to experimental error. In fact, as explained in the following article,² an examination of Bridgman's data³ indicates that they do not conform exactly to the values given by him for the volume of the liquid in equilibrium with the solid at various temperatures, and a new set of values has been estimated. These give rise to new values for the

volume of the solid in equilibrium with the liquid, which differ appreciably from those given by Bridgman.

Since our work was based on these volumes, some alteration in the results is obviously indicated, and it also appears that the margin of error may be somewhat greater than previously assumed. It, therefore, now appears reasonable to try the simple Grüneisen assumption,

$$d \ln \Theta / d \ln V = \text{constant},$$

where V is the molal volume; actually, since our range of V is small, and it is just as good theoretically and much more convenient, we set

$$-\Theta^{-1}d\Theta/dV = \Gamma, \quad (1)$$

where Γ is a constant. This is also nearly equivalent to setting $d\Theta/da$ constant, in view of the small range of a and Θ involved, and so in this respect the behavior of Θ is quite different from that supposed previously. The definition of the functional dependence of Θ is completed by setting

$$\Theta = 70.56^\circ \text{ at } V = 24.493 \text{ cc/mole} \\ (a = 3.8600\text{\AA}). \quad (2)$$

These equations replace Eq. (6) of I. Such a relationship must have an empirical basis, and can be considered as satisfactory only if it is consistent with the experimental data. To test this consistency we make use of Eq. (5) of I, which may be rewritten in the form

$$-P = \Theta^{-1}(d\Theta/dV)[(E_t + E_z) - (E_t + E_z)_{P=0}]. \quad (3)$$

¹ O. K. Rice, J. Chem. Phys. 12, 289 (1944). *Erratum*: Sign inside bracket on right-hand side of Eq. (4) should be + instead of -.

² O. K. Rice, J. Chem. Phys. 14, 324 (1946).

³ P. W. Bridgman, Proc. Am. Acad. 70, 1 (1935).

TABLE I. Test of relation between Θ and V .

$T^\circ\text{K}$	P cal./cc	$V(\text{obs.})$, cc/mole Bridgman	V , cc/mole Revised	$\Theta(\text{calc.})$ $\Gamma=0.18$	$V(\text{calc.})$ $\Gamma=0.18$	$\Theta(\text{calc.})$ $\Gamma=0.195$	$V(\text{calc.})$ $\Gamma=0.195$
83.78	0	24.50†	24.50†	70.62*	24.489	70.62*	24.489
126.3	46.9	24.49	24.43	71.31	24.434	70.24	24.516
161.9	93.7	24.37	24.17	73.86	24.239	71.88	24.398
192.9	140.6	24.25	24.01	77.12	23.999	74.66	24.203

* Calculated from Table I of I.

† From Baly and Donnan; see reference 4.

In this equation P is the pressure at any given value of V and of the temperature, T , and E_t and E_z in the first parenthesis are the thermal and zero-point energies at this V and this temperature, while in the second parenthesis they are evaluated at the same value of V but at zero pressure and whatever temperature corresponds thereto.

To make use of Eq. (3) we note, first, that Table I of I gives an empirical relation between $(E_t + E_z)_{P=0}$ and Θ , both of which are determined there directly from the experimental data. On the other hand, the value of $E_t + E_z$ can be obtained from the Debye theory as a function of Θ/T . These two relations, together with Eq. (1), enable us to express the pressure P at any given T as a function of Θ , and, hence, through Eq. (1), as a function of V (or its equivalent a). The result of this procedure is thus to give a relationship between P , V , and T , which can be used to calculate V for the solid at values of P and T corresponding to various points along the melting curve. These calculated V 's can then be compared with those given by Bridgman or with our revised values. The results are given⁴ in Table I. It will be seen that calculations of V based on $\Gamma=0.195$ agree well with Bridgman's original estimates of V , while calculations based on $\Gamma=0.18$ agree well with my revised values.

⁴ The values of a given in Table II of I were slightly altered from those calculated directly from the values of V given by Bridgman, because the estimated value $V=0.616$ cc/g (see end p. 291 and top p. 292 of I) does not correspond exactly to the value of a at the melting point obtained from Table I of I. In Table I of the present paper the values of $V(\text{obs.})$, Bridgman, at the higher temperatures correspond exactly to those given by Bridgman, but the value at 83.78° is obtained from the measurements of the density of the liquid by E. C. C. Baly and F. G. Donnan (J. Chem. Soc. London **81**, 907 (1902)), and the measurement of ΔV of fusion by K. Clusius and K. Weigand (Zeits. f. physik. Chemie **B46**, 1 (1940)). Bridgman's value of ΔV of fusion at 83.78 is probably in error, but his value of the density of the liquid is close to that of Baly and Donnan.

Accepting the latter, it is clear that the results obtained by the use of $\Gamma=0.18$ are certainly well within the limits of experimental error. It may seem surprising that, by fitting Bridgman's V exactly as we did in I, we obtained results so different with respect to the behavior of $d\Theta/dV$, but this happens because all the other properties are very sensitive to small changes in the volume. On the other hand, experimental measurements of the volume are not correspondingly highly accurate, so that the representation given by Eq. (1) appears to be quite adequate.

The agreement with the measurement of $(\partial P/\partial T)_V$ at 73°K and zero pressure, made by Simon and Kippert⁵ is scarcely altered as compared with that in I. Calculating $(\partial P/\partial T)_V$ from the relation

$$(\partial P/\partial T)_V = -\Theta^{-1}(d\Theta/dV)C_v = \Gamma C_v, \quad (4)$$

(see Eq. (7) of I), using $\Gamma=0.18$, we find $(\partial P/\partial T)_V = 42$ atmos./deg.; in I it was evaluated as 43 atmos./deg. The experimental value is 38 atmos./deg.

In spite of the differences between Eq. (1) of the present article and Eq. (6) of I, the conclusions drawn in the earlier work are not substantially modified. In the experimental range of volumes involved in Bridgman's measurements of the solid, $-\Theta^{-1}d\Theta/dV$ as calculated from I, ranges from 0.157 to 0.193, of the same order of magnitude as the 0.18 found here.⁶ On the other hand, the calculations of my earlier article⁷ in which an attempt was made to establish a theoretical connection between Θ and E_p , made it appear that $-\Theta^{-1}d\Theta/dV$ could

⁵ F. Simon and F. Kippert, Zeits. f. physik. Chemie **135**, 113 (1928).

⁶ This means that the total expansion of the solid between 0°K and the melting point is scarcely changed from that shown in Table I of I.

⁷ O. K. Rice, J. Am. Chem. Soc. **63**, 3 (1941).

not be greater than about 0.10 in the experimental range, which is a very significant difference. It was already pointed out in this earlier article that these results were not consistent with the work of Simon and Kippert, nor are they consistent with Bridgman's data.

In I it was concluded that the previously derived⁷ theoretical relation between Θ and E_p probably was not valid because the vibration of an atom in the fields of its neighbors would be markedly anharmonic, even when only zero-point vibrations were involved. This situation arose because the curvature of the E_p vs. a curve changed rapidly. This conclusion is not invalidated by the results of the present paper, when they are combined with Table I of I, to give a new relation between E_p and a .

The direct method of getting this relationship would be to use Eqs. (1) and (2) above to get V , and hence a , as a function of Θ . In this way we could assign new values for a for the temperatures in Table I of I, and so obtain a new relation between E_p and a . However, in the course of some other calculations being made in collaboration with Mr. G. W. Murphy, it appeared that a much more accurate relation could be obtained by an indirect method, using the Grüneisen equation for the pressure [Eq. (3) of I]. For the special case of zero pressure, this equation becomes

$$0 = \Gamma(E_t + E_z) - dE_p/dV. \quad (5)$$

From Table I of I, we can find $E_t + E_z$ as a function of Θ . The following empirical equation expresses this relationship quite well:

$$E_z + E_t = 296.7 + 29.5(80 - \Theta) - 0.643(80 - \Theta)^2. \quad (6)$$

Eq. (6) comes directly from the experimental data and the Debye theory, and is not affected by the dependence of Θ on a . With any given value of Γ , however, it can be changed into a relation between $E_z + E_t$ and a , and inserted into Eq. (5); at the same time dV may be expressed in terms of da . We then obtain dE_p/da as a function of a . It is convenient to set up a new empirical expression for dE_p/da . This has been done, and it has been integrated to give

$$-E_p = 2007.6 - 1410.0x - 10,710x^2 + 53,947x^3 - 76,500x^4, \quad (7)$$

where $x = a - 3.84$. The greater accuracy of this method of obtaining the expression for E_p arises because the absolute error of $E_z + E_t$ in Table I of I is about the same as that of E_p . Small but changing errors in E_p can make appreciable differences in dE_p/da ; on the other hand, such small errors are a very small percentage of $E_z + E_t$ which can, therefore, be used in Eq. (5) to get a much more accurate value of dE_p/da . This, when integrated, using an integration constant to match E_p in Table I of I at one value of Θ (correlated with x from Eqs. (1) and (2)), should give a better expression for E_p than that obtained directly.

We may now compare Eq. (7) above with Eq. (8) of I. The coefficients of x^3 and x^4 in Eq. (7) are much smaller than the corresponding ones of Eq. (8) of I, while the coefficient of x^2 , with which the other coefficients must be compared, is larger. Nevertheless, the rate of change of curvature of Eq. (7) is still quite substantial. Thus the value of d^2E_p/da^2 obtained from Eq. (7) changes by about 150 percent in a range of a of about 0.1A. However, this estimate is based on the third-degree term in the expression for E_p , and when we consider the motion of an atom surrounded by a highly symmetrical distribution of neighbors, the effects of any term of odd order, in causing anharmonicities in the effective field in which the atom vibrates, tend to cancel out in first approximation. It is, therefore, desirable to consider the fourth-degree term as well. This is also considerably less than the fourth-degree term in Eq. (8) of I, but by no means negligible. In fact, the fourth-degree term is itself sufficient to cause a change of more than 40 percent in d^2E_p/da^2 over a range of a of 0.1A. It is, of course, true that the fourth-degree term can be determined only roughly. But, since greater displacements than 0.1A may be expected, even for the zero-point vibrations, there seems to be no reason to doubt that the reasons given in I for the breakdown of the previously derived⁷ relation between Θ and E_p are substantially correct as there given.

Over the range of a from 3.82A to 3.86A, which about covers the expansion of the solid from 0°K to the melting point, the appearance of the E_p vs. a curve is not greatly changed from that given by Eq. (8) of I. (See Fig. 1 of I.)

Equation (7) above gives a value of $-E_p$ about 2.2 calories per mole lower at 3.82Å, about 0.7 calories lower at 3.83Å, about 0.8 higher at 3.84Å, about 1.4 calories higher at 3.85Å, and about 0.2 calories higher at 3.86Å. Outside this range, where the E_p vs. a curves represent extrapolations, the differences are naturally greater. In particular, the minimum of E_p (and correspondingly the minimum of the interatomic potential curve) given by Eq. (7) is displaced by approximately 0.01Å toward smaller values of a as compared to that given by Eq. (8) of I. However, these differences can hardly affect the qualitative relationship between the curves shown in Fig. 2 of I. It should be emphasized that the

most important difference between the two curves shown in Fig. 2 of I is their difference in slope in the experimental range of a . It will be clear that this difference is scarcely altered by the present work. We, therefore, conclude here, as in I, that the slope of the E_p vs. a curve in the experimental range, obtained by direct application of the Debye theory to the experimental data, is much greater than that expected from the attempt⁷ to derive a relation between E_p and Θ ; and, as stated above, that the attempted derivation fails because of the extreme anharmonicity of the interatomic potential curve, which means that the theory of small vibrations cannot be applied.

The Thermodynamic Properties of Liquid Argon

O. K. RICE

University of North Carolina, Chapel Hill, North Carolina

(Received February 7, 1946)

The thermodynamic properties and equation-of-state data of liquid argon are interpreted in terms of a partition function previously derived. This partition function has a part due to vibratory motion of the atoms in the liquid and a part due to translational motion. The vibratory part contains the Debye characteristic temperature Θ for the solid, evaluated for a certain interatomic distance a_0 which appears as a parameter in the partition function. a_0 is interpreted as the average interatomic distance between nearest neighbors in the liquid, and is a function of a , the latter being defined as $(2V/N)^{1/3}$, where V is the molal volume and N Avogadro's number. With V set equal to the molal volume of the liquid at its normal melting point, a_0 is assigned a value which appears reasonable from the atomic distribution curves obtained by x-ray studies of the liquid. With this value of a_0 , the partition function for this fixed value of V gives reasonably good values of the entropy over a large range of temperatures. A small, entirely reasonable change in the partition function improves the agreement with the experimental data. The parameters in the partition function have been evaluated for other values of V by using equation-of-state data. This leads to a calculation of the specific heats of saturated liquid argon over a range of temperatures. The agreement with experimental data is not exceedingly close, but is probably within experimental error. A calculation

is also made of the free energies of the solid and liquid phases along the melting curve. They are found to be equal to within reasonably close limits. The application to various values of V leads to the evaluation of a_0 as a function of a . The experimental curve for $(\partial S/\partial V)_T$ plotted against V appears to show a change of slope near the value of V characteristic of the liquid at its normal melting point. There is also a change in slope of the curve for da_0/da vs. a , at the corresponding value of a . These facts are interpreted in terms of the atomic distribution curves, which appear to indicate a change in structure of the liquid which starts near the same value of V or a . The liquid appears to change from a distorted face-centered structure to a distorted body-centered structure as the volume increases. Information about the potential energy of liquid argon is obtained from the experimental data by application of the partition function. It is found that the potential energy of the liquid can be rather effectively correlated with the potential energy of the solid. Finally, certain peculiarities of the equation-of-state data are believed to indicate a pre-freezing phenomenon, in which particles containing appreciable numbers of atoms and having the structure of the solid, appear in the liquid. A state of this sort can be stabilized by the entropy of mixing of the solid particles with the liquid.

1. THE GENERAL THEORETICAL EQUATIONS.

IN a paper entitled "On the Statistical Mechanics of Liquids, and the Gas of Hard

Elastic Spheres"¹ (referred to hereafter as SML) I proposed the following partition function for

¹O. K. Rice, J. Chem. Phys. 12, 1 (1944).