The Thermodynamic Properties of Liquid Argon

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Equation (7) above gives a value of $-E_p$ about 2.2 calories per mole lower at 3.82A, about 0.7 calories lower at 3.83A, about 0.8 higher at 3.84A, about 1.4 calories higher at 3.85A, and about 0.2 calories higher at 3.86A. 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 0.01A 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 attempt[7] 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

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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 $(2^{\frac{1}{2}}V/N)^{\frac{1}{3}}$, 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 prefreezing 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

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

the thermal part of the energy of a monatomic liquid in a not too expanded state, and at a temperature such that classical considerations apply:

$$Q = Q_0{}^3$$
$$= [(2e)^{\frac{1}{3}}T/\Theta + (2\pi mkT/h^2)^{\frac{1}{2}}2^{-1/6}e(a-a_0)]^3. \quad (1)$$

In this equation Q is for one atom; Q_0, which is introduced here for convenience, is for one degree of freedom. The symbols used have the following significance:

T = absolute temperature,
Θ = Debye characteristic temperature of the *solid*, evaluated for such a degree of compression of the solid that the distance between nearest neighbors is a_0,
m = mass of an atom,
k = Boltzmann's constant,
h = Planck's constant,
a = the distance between neighbors which would be found if the liquid were a close-packed cubic lattice having the same density.

We have

$$a^3 = 2^{\frac{1}{2}}V/N, \quad (2)$$

where V is the molal volume and N is Avogadro's number. The quantity a_0 is a parameter; a_0 is always less than a. For the present purposes it is to be considered as a function of a (though when a more exact theory becomes possible, it may be found better to take it as a variable parameter to be found by minimizing the free energy).

The interpretation of a_0 and the justification for the use of Eq. (1) are explained in SML. It there appears that if we had a gas or liquid of hard elastic spheres of radius σ we could write

$$Q_0 = (2\pi mkT/h^2)^{\frac{1}{2}}2^{-\frac{1}{6}}e(a-\sigma). \quad (3)$$

In the case of the real liquid with a force field between the atoms, part of this quantity is replaced by the term $(2e)^{\frac{1}{3}}T/\Theta$. a_0 may, therefore, be described as a parameter which divides the space available to any degree of freedom into a part where the motion is translational and a part where it is vibrational. As pointed out in Section 4 of SML, we can consider two types of motion of atoms, one a long range motion in which the atoms move relatively great distances and exchange places, and one a short range motion. The first type is translational and the second type vibrational; any one degree of freedom, however, rapidly and frequently shifts

from one type to the other. Both types of motion are possible even in the case of hard elastic spheres, though in this case the "vibrational" type of motion is actually force-free. The vibrational motion is the short range type, one atom between its neighbors, not involving the longer motions involved in exchanges of position. It, therefore, seems reasonable to identify a_0, at least in simple cases, and at least approximately, with the actual average distance between centers of molecules which can be described as nearest neighbors in the liquid. Thus we understand that Θ is to be considered as a function of a_0, and we may expect the potential energy of the liquid to depend on a_0. This, of course, is not an exact statement; it may, however, be expected to contain a considerable element of truth, and does in fact lead to interesting correlations of the properties of the liquid with those of the solid, as we shall see.

We shall find it convenient to rewrite Eq. (1) in the form

$$Q_0 = LT/\Theta + MT^{\frac{1}{2}}(a-a_0), \quad (4)$$

where the meanings of L and M are defined by the equations. We can then concisely define certain useful quantities:

$$B = T(\partial Q_0/\partial T)_V = LT/\Theta + \tfrac{1}{2}MT^{\frac{1}{2}}(a-a_0), \quad (5a)$$

$$D = T(\partial B/\partial T)_V = LT/\Theta + \tfrac{1}{4}MT^{\frac{1}{2}}(a-a_0). \quad (5b)$$

Also we have

$$(\partial Q_0/\partial a)_T = -(LT/\Theta^2)(d\Theta/da_0)da_0/da$$
$$+ MT^{\frac{1}{2}}(1-da_0/da). \quad (6)$$

As noted above, the partition function takes into account only the thermal energy. The thermal energy, by the normal process of logarithmic differentiation of the partition function, is found to be, per mole (i.e., per $3N$ degrees of freedom),

$$E_t = 3RTB/Q_0. \quad (7)$$

The molal work function, A, is given by

$$A = -3RT \ln Q_0 + E_p, \quad (8)$$

where E_p is the potential energy per mole and is a function of a only. E_p is the energy the system would have if, without change of volume and without crystallization, it were reduced to absolute zero, and if there were no zero-point

TABLE I. Properties of liquid argon at its normal melting point.

Property	Source	Value
a	Baly and Donnan[a, b]	4.038A
a	Mathias et al.[c, d]	4.048A
a	Bridgman[e]	4.038A
a	Used in this paper[f]	4.037A
ΔV, fusion	Clusius and Weigand[g]	3.53 cc mole^{-1}
ΔV, fusion	Bridgman[c, e]	3.18 cc mole^{-1}
$\alpha [= V^{-1}(\partial V/\partial T)_P]$	Baly and Donnan[a, b]	0.0045 deg.$^{-1}$
α	Mathias et al.[c, d]	0.0042 deg.$^{-1}$
C_v	Eucken and Hauck[h, a]	5.5 cal. mole^{-1} deg.$^{-1}$
C_p	Eucken and Hauck[h, a]	10.5 cal. mole^{-1} deg.$^{-1}$
C_p	Clusius[a, i]	10.0 cal. mole^{-1} deg.$^{-1}$
$(\partial P/\partial T)_V$	Bridgman[e]	0.556 cal. deg.$^{-1}$ cc^{-1}
$(\partial P/\partial T)_V$	Simon and Kippert[j]	0.60 cal. deg.$^{-1}$ cc^{-1}
ΔS, fusion	Clusius and Weigand[g]	3.35 cal. mole^{-1} deg.$^{-1}$
ΔS, fusion	Bridgman[c, e]	3.12 cal. mole^{-1} deg.$^{-1}$

[a] Involves slight or quite certain extrapolation.
[b] See reference 8.
[c] Involves appreciable extrapolation.
[d] See reference 7.
[e] See reference 6.
[f] Consistent with V(calc.) of Table I of reference 9.

[g] See reference 11.
[h] A. Eucken and F. Hauck, Zeits. f. physik. Chemie 134, 161 (1928).
[i] See reference 10.
[j] F. Simon and F. Kippert, Zeits. f. physik. Chemie 135, 113 (1928).
For numbered references see citations in text.

energy. The zero-point energy does not need to be considered at all, in our case, since we deal only with temperatures sufficiently high so that the system may be thought of as classical. The energy E_t does actually include some potential energy in virtue of the vibrations of the atoms about their positions of equilibrium in the field of their neighbors. E_p might perhaps be more exactly defined as the lowest possible potential energy for the liquid at the molal volume V.

The various thermodynamic quantities can now be obtained in terms of the quantities already defined. We have for the molal entropy,

$$S = -(\partial A/\partial T)_V = 3R \ln Q_0 + 3RB/Q_0, \quad (9)$$

and for the pressure

$$P = -(\partial A/\partial V)_T$$
$$= (3RT/Q_0)(\partial Q_0/\partial V)_T - dE_p/dV. \quad (10)$$

Also

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V$$
$$= (3R/Q_0)[(\partial Q_0/\partial V)_T + (\partial B/\partial V)_T$$
$$- (B/Q_0)(\partial Q_0/\partial V)_T], \quad (11)$$

and for the specific heat at constant volume

$$C_v = 3R[(B/Q_0) + (D/Q_0) - (B^2/Q_0^2)]. \quad (12)$$

Derivatives with respect to V may be replaced by derivatives with respect to a by means of Eq. (2), and Eq. (6) and a similar equation for $(\partial B/\partial a)_T$ may be used to get explicit expressions. For future reference we write down the expres-

sion for P:

$$P = \frac{2^{\frac{1}{3}}RT}{a^2 N Q_0}\left[-\frac{LT}{\Theta^2}\frac{d\Theta}{da_0}\frac{da_0}{da} + MT^{\frac{1}{2}}\left(1 - \frac{da_0}{da}\right)\right]$$
$$- \frac{2^{\frac{1}{3}}}{3a^2 N}\frac{dE_p}{da}. \quad (13)$$

It is now proposed to use the equations just developed as a guide in the study of the properties of liquid[2] argon. In doing this we shall adhere to the philosophy followed in a number of earlier papers[3] in which the approach was frankly semi-empirical. The equations do not suffice in themselves for a complete description of the liquid without reference to the experimental data, since we do not have sufficient information concerning some of the quantities involved in them. In particular, we do not know a_0 as a function of a, since we do not have a sufficiently detailed knowledge of the complicated geometry of a more or less random distribution of atoms. It does appear, nevertheless, that the equations offer a reasonably good guide for the handling of the experimental data, and for finding relations which might not otherwise be discovered.

It may be well to note that our method of handling the parameter a_0 is somewhat different from the procedure

[2] We use the term liquid to describe the amorphous phase if its density is greater than the critical density, regardless of the temperature. This is a consistent usage from our point of view since the properties are continuous at the critical temperature.
[3] O. K. Rice, J. Chem. Phys. 7, 136, 883 (1939).

used in the earlier work.[3] In this earlier study, instead of a_0, we used the concept of the average coordination number of the atoms in the liquid. This quantity was treated as though it were an extra variable of state, determined under any fixed set of conditions by the fact that the free energy of the system had to be a minimum. An attempt[3,4] was made to estimate the effect of this variable on the energy and entropy of the system, in order that the result of minimizing the free energy might be determined, and these attempts have been continued since. However, they were not entirely successful, and it became evident that the geometry of the system was too complicated to permit this program to be carried to completion. The later work indicated[5] that the approach outlined above might be more practicable and successful.

2. EXPERIMENTAL PROPERTIES OF ARGON

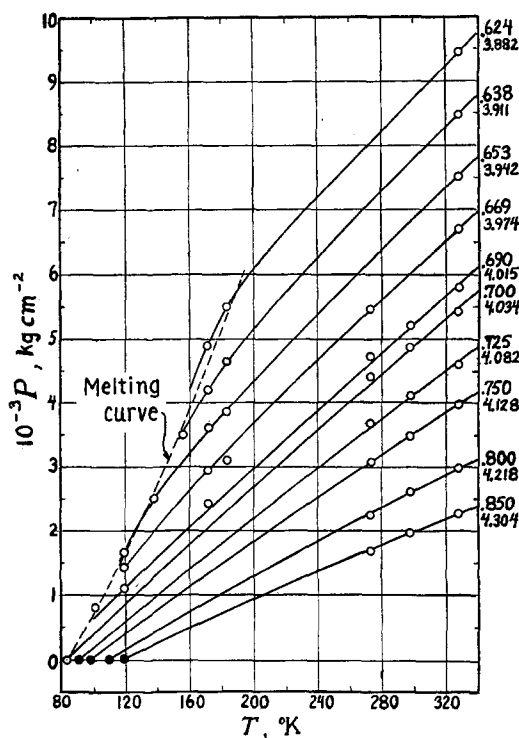It is convenient to start with a summary of the properties of argon at its normal melting

FIG. 1. Equation-of-state data for argon. The curves connect points for constant volume; the number at the right-hand end of each curve gives the volume in cc/g. The number just below the volume gives the value of a. Open circles are from Bridgman; black circles are from Mathias, Onnes, and Crommelin. The relation between the melting curve and the constant-volume curves is such as to indicate somewhat different values of the volume of the liquid along the melting curve than those given by Bridgman. At 2000, 4000, and 6000 kg/cm² we find, respectively, 0.654, 0.633, and 0.622 cc/g.

[4] O. K. Rice, J. Chem. Phys. 10, 654 (1942) (in this note the "number of holes" was used as a variable instead of the coordination number).
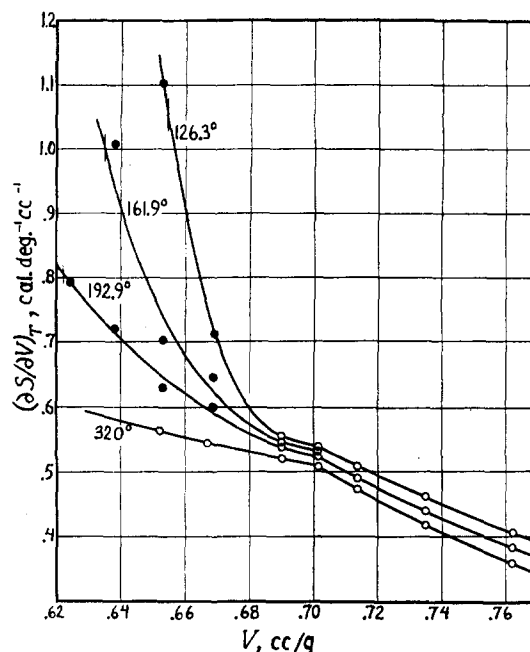[5] See reference 1, page 17.

FIG. 2. $(\partial S/\partial V)_T$ curves. The open circles are taken or interpolated directly from Table V (this table was also used to assist in construction of the curves of Fig. 1, as noted in text). The black circles are taken from measurements of slopes of curves in Fig. 1. Each circle in every case belongs to the curve nearest it.

point, 83.78°K, and atmospheric pressure; this is given in Table I where sources are indicated.

The other data which are available consist principally of equation-of-state data due to Bridgman[6] and to Mathias, Onnes, and Crommelin.[7] These are summarized in Fig. 1. The open circles are interpolated (in some cases there are slight extrapolations) from Bridgman's data, and give the variation of pressure with temperature for a number of constant volumes, as indicated. The points for a given volume are connected by curves, whose shapes are in part determined by theoretical considerations, as will be described below. The black circles are from Mathias, Onnes, and Crommelin's data. Their volumes have been corrected slightly so that they will be consistent with the specific volumes of Baly and Donnan[8] and of Bridgman, which agree well with each other (see note to Table V, below).

[6] P. W. Bridgman, Proc. Am. Acad. 70, 1 (1935).
[7] E. Mathias, H. K. Onnes, and C. A. Crommelin, Proc. Roy. Acad. Sci. Amsterdam, 15, 667, 960 (1912); C. A. Crommelin, ibid. 13, 54 (1910); 16, 477 (1913).
[8] E. C. C. Baly and F. G. Donnan, J. Chem. Soc. London 81, 907 (1902).

TABLE II. Entropies of solid and liquid argon at various temperatures in calories per mole per degree.

$T(°K)$	S_{solid}	ΔS_{fus}	ΔS_{expan}	S_{liquid} $(a=4.037)$
83.78	9.07*	3.35	0.00	12.42
126.3	11.39	2.07	1.28	14.74
161.9	12.65	1.59	1.78	16.02
192.9	13.43	1.34	2.01	16.78

* Though calculated from the same data, this is 0.05 lower than the value given by K. Clusius and A. Frank, Zeits. f. Elektrochemie 49, 308 (1943), which has recently come to my attention; the difference is not important.

Figure 2 gives the value of $(\partial P/\partial T)_V$ or $(\partial S/\partial V)_T$, converted to cal. cc^{-1} deg.$^{-1}$, for several selected temperatures, as obtained from the curves of Fig. 1. Figure 2 will be discussed in detail in a later section, but will be found useful here in enabling us to determine the entropy of the liquid at its normal volume, where $a=4.037$, at various temperatures. For this purpose it is necessary to find first the entropy of the solid in equilibrium with the liquid at various temperatures. This is obtained from the values of Θ found for $\Gamma=0.18$ in Table I of the preceding article.[9] We then obtain the change of entropy on fusion (ΔS_{fus}) from the heat of fusion as given by Clusius[10,11] at the normal melting point of 83.78°K and by Bridgman at the higher temperatures. Finally, for the higher temperatures, we obtain the entropy of expansion (ΔS_{expan}) of the liquid from its volume when in equilibrium with the solid to its "normal" volume, for which $a=4.037$, by integrating the $(\partial S/\partial V)_T$ values. The limits of integration are shown on the curves in Fig. 2 by short vertical lines. For consistency these volumes are adjusted

to conform to the calculated V's for the solid given for $\Gamma=0.18$ in Table I of the preceding article, using Bridgman's values of ΔV of fusion. The results are given in Table II.

3. APPLICATION OF THE EQUATIONS TO ARGON AT ITS "NORMAL" VOLUME

In attempting to apply the equations, we come at once to a difficulty, since, as noted above, we do not have any theoretical way to find a_0 as a function of a. However, the considerations of Section 1 do indicate that a_0 may be approximated by the average distance between nearest neighbors. The atomic distribution in argon has been studied by Lark-Horovitz and Miller[12] and by Eisenstein and Gingrich,[13] who agree that near the freezing point the first maximum in the distribution curve of liquid argon occurs at 3.79 or 3.80A, within about 1 percent. The average distance of nearest neighbors is slightly displaced toward greater distances, though it is not too exactly defined because of the broadness of the maximum. We have, therefore, carried out computations of a number of the thermodynamic quantities for $a=4.037A$ and $a_0=3.82A$, 3.85A, and 3.88A. These are given in Table III. In this table S and C_v are calculated directly from Eq. (9) and Eq. (12) from the value of a_0 given, determining Θ from a_0 by use of the preceding article. L and M are evaluated as indicated by comparison of Eqs. (4) and (1) using Birge's values of the constants.[14] We have evaluated da_0/da and dE_p/da empirically by using two experimental values of the pressure (given in

TABLE III. Calculated thermodynamic properties of liquid argon at $a=4.037A$, $L=1.7584$, $M=0.8769A^{-1}$ deg.$^{-1}$.

a_0	3.82			3.85				3.88		
da_0/da	0.487			0.441				0.411		
dE_p/da	993			1067				1128		
T	83.78	192.9	320	83.78	126.3	192.9	320	83.78	192.9	320
S	12.08	16.27	18.92	12.19	14.29	16.51	19.23	12.35	16.80	19.59
C_v	4.88	5.17	5.31	5.05	5.19	5.31	5.43	5.23	5.45	5.54
P	(0)	58.1	(123.9)	(0)	23.3	58.7	(123.9)	(0)	59.2	(123.9)
$(\partial S/\partial V)_T$	0.544	0.524	0.514	0.562	0.540	0.523	0.505	0.571	0.523	0.499

Units: a_0 and a in A; E_p in cal. mole^{-1}; T in °K; S and C_v in cal. mole^{-1}deg.$^{-1}$; P in cal. cm^{-3}; V in cm^3 mole^{-1}. To convert P to kg/cm^2 divide by 0.02343.

[9] O. K. Rice, J. Chem. Phys. 14, 321 (1946).
[10] K. Clusius, Zeits. f. physik. Chemie B31, 459 (1936).
[11] K. Clusius and K. Weigand, Zeits. f. physik. Chemie B46, 1 (1940).

[12] K. Lark-Horovitz and E. P. Miller, Nature 146, 459 (1940).
[13] A. Eisenstein and N. S. Gingrich, Phys. Rev. 62, 261 (1942).
[14] R. T. Birge, Rev. Mod. Phys. 13, 233 (1941).

TABLE IV. Calculated thermodynamic properties of liquid argon at $a = 4.037A$, $L = 1.9$, $M = 0.8769A^{-1}$ deg.$^{-1}$.

a_0	3.82			3.85				3.88		
da_0/da	0.494			0.453				0.425		
dE_p/da	984			1050				1109		
T	83.78	192.9	320	83.78	126.3	192.9	320	83.78	192.9	320
S	12.38	16.61	19.29	12.51	14.63	16.87	19.61	12.70	17.19	19.99
A				(0)	−580.0	−1634.2				
C_v	4.93	5.20	5.35	5.10	5.24	5.35	5.47	5.28	5.47	5.58
P	(0)	58.0	(123.9)	(0)	23.3	58.6	(123.9)	(0)	58.9	(123.9)
$(\partial S/\partial V)_T$	0.542	0.526	0.514	0.556	0.538	0.524	0.507	0.565	0.522	0.502

Units: A in cal. mole^{-1}; for the others see Table III.

parentheses) in Eq. (13), thus setting up two simultaneous equations of the form of Eq. (13). Since Θ and $d\Theta/da_0$ are known from the preceding article, and all other quantities are also known except da_0/da and dE_p/da (which are the same in the two simultaneous equations, since they depend only on a, not on T), we can solve for the latter two quantities. Having done this, the values of P not enclosed in parentheses are obtained from Eq. (13), and the values of $(\partial S/\partial V)_T$ from Eq. (11).

It will be observed that none of the thermodynamic quantities depend strongly on the value chosen for a_0. However, the values of S are a little low as compared to those given in Table II. Since S does show a slight increase with a_0, this discrepancy could be lessened by going to larger values of a_0, but it is felt that a value of a_0 too much larger than that for the maximum in the atomic distribution curve should not be used.

On page 16 of SML the value of L was determined by certain considerations concerning the relaxation of the effect of "side-atoms" on going from the solid to the liquid state. If we imagine an atom vibrating in a crystal lattice directly toward one nearest neighbor and directly away from the opposite one, the field of force in which it moves is also influenced by the atoms off at an angle, these being fixed in their positions in a lattice. This means that Θ for the solid is roughly $2^{\frac{1}{2}}$ times as great[15] as it would be if these side-atoms did not exist. In the liquid it is assumed that these side-atoms, not being fixed in position, but being free to move, on the average adjust themselves about an atom which happens to be displaced toward one of its neighbors and away from the opposite one. Thus, since we use Θ for

the solid in our partition function, we should divide Θ by $2^{\frac{1}{2}}$. Actually, however, the side-atoms do have space-filling properties, which reduces the free space available to the vibrating atoms, and the net result is that Θ should be divided by $2^{\frac{1}{2}}/2^{\frac{1}{2}}$ or $2^{\frac{1}{2}}$. Now since there are fewer nearest neighbors in the liquid than in the cubic close-packed solid argon, the space-filling properties of the neighbors may not be quite so great as for the solid; furthermore, if an atom in a liquid is displaced toward one neighbor, there will not in general be another neighbor *exactly* opposite. This suggests that there may be a little greater relaxation in the liquid than is given by dividing Θ by $2^{\frac{1}{2}}$, and that, therefore, we should take a slightly larger value for L than that given[16] in Table III. We have, therefore, tried $L = 1.9$, and have obtained the results shown in Table IV. To this table we have, for reasons which will appear later, added, in one case, values of the molal work function A, taken arbitrarily zero at the normal melting point.

It is seen that with $a_0 = 3.85$ we have achieved quite satisfactory agreement with the entropy values given in Table II. It may, of course, be

[15] Exactly, if only nearest neighbors are effective, and the lattice is cubic close-packed.

[16] The considerations of SML dealing with the gas of hard elastic spheres (before the effect of interatomic forces was taken into account at all) indicate the possibility that the partition function in Eq. (3) above may be an underestimate from another cause (see p. 13, especially Fig. 5, of SML). This would mean that Q_0 in Eq. (1) would also be an underestimate. This would cause an increase in the whole expression in brackets in Eq. (1), rather than just in the first term, but would have about the same effect. On the other hand, the communal entropy was handled in such a way as to make the equations give an overestimate for Q_0 (see Section 1 of SML), so these effects counterbalance each other to a greater or less degree. It may be remarked, however, that the relaxation of the effect of the side-atoms could possibly cause some increase in the communal entropy carried by the vibrational term in Q_0 over that characteristic of a Debye solid, especially since in the latter the communal entropy is not fully excited (see page 7 of SLM).

TABLE V. Calculated thermodynamic properties of argon at various volumes, $L=1.9$, $M=0.8769$.

a	4.15	4.10	4.06	4.037	4.015	3.97	3.94
a_0	3.8912	3.8753	3.8600	3.85	3.8400	3.8195	3.8058
da_0/da	0.287	0.351	0.415	0.453	0.456	0.456	0.456
dE_p/da	1057	1070	1065	1050	962	740	547
T_{sat}*	101.58	94.24	87.75	83.78	100		
P at T_{sat}	(0.1)	(0.0)	(0.0)	(0.0)	15.1		
P at 192.9°	36.5	44.9	53.2	58.6	66.2		
P at 320°	(83.6)	(99.3)	(114.4)	(123.9)	(133.2)	(155.4)	(173.8)
$(\partial P/\partial T)_V$ at T_{sat}	0.416	0.474	0.525	0.556	0.565		
$(\partial P/\partial T)_V$ at 192.9°	0.384	0.440	0.489	0.524	0.538		
$(\partial P/\partial T)_V$ at 320°	0.361	0.419	0.473	0.507	0.520	0.544	0.563
$(10.5/12)(da_0/da)(dE_{p,s}/da_0)$†	536	610	645	639	565	360	190

* T_{sat} is the temperature at which the liquid having the given value of a is in equilibrium with its vapor (except for $a=4.015$, where the lower temperature was taken arbitrarily). These temperatures were obtained from the data of Mathias, Onnes, and Crommelin (see reference 7), their values being slightly corrected so as to conform to Baly and Donnan's value (see reference 8) at the melting point, but so as to be consistent with their own values of α, as given in Table VI.
† See Section 7, subsection, "Potential Energy of Liquid Argon."

said that this is obtained only by the use of two adjustable constants, a_0 and L. However, the adjustment of L is really quite small, it being increased over the originally estimated value by only 8 percent, while the value of a_0 used is entirely reasonable, and the results are not extremely sensitive to it. In any event, we have matched three values of S reasonably well with the value of a_0 used, and the only slightly adjusted value of L. Furthermore, the curve for P against T comes out to be almost a straight line, which is obviously correct as indicated in Fig. 1, though too much stress on this point must not be laid, since presumably any reasonably sensible theory would give this result.

TABLE VI. Specific heats of saturated liquid (calories per mole per degree).

T(°K)	83.78	87.75	94.24	101.58
a(A)	4.037	4.06	4.10	4.15
α(deg.$^{-1}$)$\times 10^3$*	4.20	4.38	4.74	5.23
C_v(obs.)**		5.50	5.50	5.50
C_p(obs.)**		10.5	10.72	11.04
C_p(obs.)†		10.06		
C_v(calc.)	5.10	5.10	5.08	5.04
C_p-C_v(calc.)	5.49	5.75	6.20	6.73
C_p(calc.)	10.59	10.85	11.28	11.77

* Mathias, Onnes, and Crommelin, reference 7 (values at 83.8 and 87.75 obtained by extrapolation).
** Eucken and Hauck, reference h, Table I. (Actually the specific heat at saturation was measured, but over the range involved this is essentially C_p.)
† Clusius, reference 10.

TABLE VII. Entropies and specific heats at $a=4.037$A (calories per mole per degree).

T(°K)	83.78	126.3	161.9	192.9
S (Table II)	12.42	14.74	16.02	16.78
S (Table IV)	12.51	14.63	15.94	16.87
$C_{v, Av.}$ (Table II)		5.63	5.1	4.3
$C_{v, Av.}$ (Table IV)		5.17	5.3	5.3

We shall return to a discussion of the specific heat values in Section 5.

4. APPLICATION OF THE EQUATIONS TO ARGON AT VARIOUS VOLUMES

By combining the results of Bridgman and Mathias, Onnes, and Crommelin, as presented in Fig. 1, we have a series of data at high temperatures and at one much lower temperature for each of a number of volumes greater than the "normal" volume of melting argon; i.e., values of a greater than 4.037A. These data can be used in the same way as the data at $a=4.037$A to obtain values of da_0/da and dE_p/da, as well as the various thermodynamic quantities. Starting with $a_0=3.85$A at $a=4.037$A, a_0 at any other value of a will be determined by integration of da_0/da; on the other hand, da_0/da at any given a itself depends upon the corresponding value of a_0. It is, therefore, obvious that it is necessary to make successive adjustments to assure consistency in this matter. This, however, is relatively easy, because the dependence of da_0/da on a_0 at a given a is slight.

For values of a less than 4.015, we see from Fig. 1 that the slopes of the P vs. T curves change sharply at the lower temperatures. On the basis of Eq. (13) this is a distinctly "abnormal" behavior. This "abnormal" behavior will be discussed later; we believe that the high temperature ends of these curves are "normal." Unfortunately, there is in each of these cases only one experimental point at a high temperature, so the slope in this region can only be inferred. The curves for $a \leq 4.015$ shown in Fig. 1 are drawn

with slopes (for the high temperature ends of the curves) calculated from Eq. (11) on the assumption that as a goes below 4.037 the value of da_0/da reaches a limit of 0.456. It is obvious that the slopes shown in Fig. 1 cannot be greatly in error, but some more experimental work in this region would be most welcome.

The calculations mentioned in the above two paragraphs are summarized in Table V. Again pressures which are obtained directly or by interpolation from the experimental data are given in parentheses. It was these which were used for $a \geq 4.037$ to calculate da_0/da and dE_p/da. (For $a = 4.015$ it was assumed, as noted above, that $da_0/da = 0.456$ and P at 100° was then calculated). In all cases the values of Θ necessary for the calculations were obtained from a_0, using Eqs. (1) and (2) of the preceding article, taking $\Gamma = 0.18$.

The curves given in Fig. 1 were all drawn with the aid of the values of P and $(\partial P/\partial T)_V$ given in Table V (except for the low temperature ends of those with $a < 4.015$). Since the values of a in Table V and Fig. 1 do not all coincide, interpolation, or, in some cases, extrapolation, was necessary in order to construct the curves.

5. THE SPECIFIC HEATS

The data on the specific heat of the liquid are summarized in Tables VI and VII. The data in Table VI refer to liquid in equilibrium with its vapor. C_v(calc.) comes directly from Eqs. (5) and (12) using Table V. $C_p - C_v$(calc.) is obtained from the formula

$$C_p - C_v = \alpha V T (\partial P/\partial T)_V, \qquad (14)$$

α is obtained from the density measurements of Mathias, Onnes, and Crommelin[7] (these all being made at what amounts essentially to zero pressure). $(\partial P/\partial T)_V = (\partial S/\partial V)_T$ is taken from Table V, or, what is the same thing, from Fig. 1.

In Table VII the average C_v's were calculated from the changes in entropy with temperature; the values from Table II are essentially the "experimental" values, though some calculation is involved in them, also, since they depend on the entropy of the solid, which has not been measured directly. To the values of Table IV one at 161.9° has been added.

It will be seen from Table VI that our cal-

culated values of C_v are somewhat lower than the experimental values of Eucken and Hauck. This discrepancy seems to be confirmed by Table VII in view of the difference between the experimental and calculated C_v's for the range between 83.78° and 126.3°. On the other hand if the calculated value of C_v at 83.8°, given in Table VI, is too small, then the calculated $C_p - C_v$ must be too large; otherwise, C_p would considerably exceed the experimental value. However, $C_p - C_v$ is actually pretty well tied to the experiments. The value of $(\partial P/\partial T)_V$ used in Eq. (14), from which $C_p - C_v$ is calculated, is one which fits Bridgman's data as shown in Fig. 1; in fact, the only role of the theory here is to indicate the variation of $(\partial P/\partial T)_V$ with the temperature. The data do not definitely exclude a slightly different curvature of the P vs. T curve. $(\partial P/\partial T)_V$ might have a lower value than that given in Table V, at the lower end of the curve, and a higher value at the upper end; the theory may be wrong in this respect, though it seems unlikely.[17] Furthermore, the independent direct measurement by Simon and Kippert of $(\partial P/\partial T)_V$ for the normal liquid gives a value *greater* than that inferred from Bridgman's data (see Table I). Also, in applying Eq. (14) we have used the smaller of the two values of α, a value which was in fact obtained by extrapolation. In other words, our estimate of $C_p - C_v$ appears to be about the least possible. It, therefore, seems justifiable to say that there are inconsistencies between various sets of experimental data as great as any errors in the theory. We may note further that, while we have no direct check on the C_v values of Eucken and Hauck, disagreements appear in other thermal measurements. Thus the C_p values of these authors do not agree exactly with

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[17] A slight decrease in $(\partial P/\partial T)_V$, that is $(\partial S/\partial V)_T$, with increasing temperature seems normal from general considerations. In contrast to a liquid composed of hard elastic spheres, which would, at any given total volume, have a free volume independent of temperature, the free volume of a real liquid increases with temperature. Hence a given increase in total volume should have a smaller *relative* effect on the free volume at a higher temperature, so that $(\partial S/\partial V)_T$ should be smaller.

We may look at this matter in another way. We have

$$[\partial(\partial S/\partial V)_T/\partial T]_V = [\partial(\partial S/\partial T)_V/\partial V]_T = T^{-1}(\partial C_v/\partial V)_T.$$

But as the liquid expands and becomes more gas-like, C_v should decrease, and $(\partial C_v/\partial V)_T$ should be negative, which means, then, that $(\partial S/\partial V)_T$ decreases with increasing temperature.

Clusius. Clusius has noted that his C_p's for solid argon are 1 to 6 percent lower than earlier values of Eucken, while his value of the heat of fusion is considerably higher than that of Eucken.

Turning to Table VII, we see that the calculated trend of C_v values is upward with increasing temperature, while the experimental values appear to decrease. Here, again, the theory reflects the normal expectation. A slight rise of C_v with temperature is to be expected because the vibratory motion, as compared to the translational, should become relatively more prominent at the higher temperatures where its amplitude increases.

We note that if the entropies at 126.3° and 161.9° from Table II were lower by about 0.2 entropy units, the discrepancy in the C_v values would be removed. An error of this magnitude is perhaps not beyond the limits of experimental inaccuracy, since it would be only 6 percent of the entropy change of about 3.35 units which occurs in going from melting solid to liquid with $a = 4.037$A.

Since the relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ holds, whether the system is undergoing a change of phase or not, the discrepancy would be removed if Bridgman's dP/dT for the melting curve, and the average ordinates of the curves for 126.3° and 161.9° in Fig. 2 above, were all too high by 6 percent. The curves of Fig. 2 certainly may well be in error by this amount. And there is some suggestion from the more recent though less extended melting curve of Clusius and Weigand[11] that Bridgman's melting curve may be this much in error. At 0° and the normal melting point, Clusius and Weigand found $dP/dT = 40.5$ kg/cm^{-2} deg.$^{-1}$, while Bridgman's value is 42.0. (The discrepancy is not so great as indicated by Clusius and Weigand, who must have made an incorrect conversion of units.) However, the curvature of Clusius and Weigand's P vs. T curve is very much greater than that of Bridgman's, so that already at about $P = 200$ kg/cm^2, the limit of Clusius and Weigand's pressure range, the two slopes become equal. Assuming the careful measurements of Clusius and Weigand to be correct over their limited range of pressures, the question arises as to whether, with rising pressure, the slope is correctly given by Bridgman's data, or whether it continues to increase. If the latter occurs, the true pressures, which (assuming them to be given by Clusius and Weigand's data) at temperatures very close to the normal melting point lie below Bridgman's curve, would soon cross it. If the true pressures again crossed Bridgman's curve around 135°K, there would be a region where the slope was a little less than that given by Bridgman. This could happen without any of Bridgman's temperatures being in error by more than about ±1 to 1.5°, but there would be a slight inflection in the P vs. T curve. Such an

inflection would not be surprising if it were associated with the prefreezing phenomenon mentioned later in the paper. However, as noted in Section 6, there is a small discrepancy between the free energies of the liquid and solid along the melting curve, which would be somewhat increased if new experiments should confirm changes such as are suggested. Furthermore, it is difficult to make a complete analysis of the situation because of the way various experimental errors may interact with each other.[18] So the above analysis is not to be taken too literally, but it does suggest that the calculated values in Table VII are correct to within experimental error. Complete consistency between all possible data analyzed on the basis of our theory, is perhaps too much to hope for, in view of our rather bold use of the Debye theory of the solid, when there are strong indications[19] that it may need some modification on account of anharmonicities in the vibrations of the atoms.

The calculated value of $C_p - C_v$, as presented in Table VI, rises much more rapidly with temperature than the experimental values of Eucken and Hauck. We again recall that the calculated value of $C_p - C_v$ is closely tied to experimental data, but it is again true that the data of Fig. 1 do not exclude somewhat smaller values of $(\partial P/\partial T)_V$ at the lower end of the curves. Any change in curvature of the P vs. T curves sufficient to make $(\partial P/\partial T)_V$ increase with increasing temperature has the same objections as those previously noted.[17] Even if we assume that $(\partial P/\partial T)_V$ is independent of temperature at $a = 4.15$, say, C_p(calc.) for 101.58° is reduced only to 11.20 cal. mole^{-1} deg.$^{-1}$, and this value is based on the calculated C_v of 5.04, which is much lower than Eucken and Hauck's experimental value. I believe, however, that while the decrease in $(\partial P/\partial T)_V$ may not be as great as given in Table V, $(\partial P/\partial T)_V$ certainly will decrease with temperature to some extent. This, therefore, is further indication of error in some, at least, of the experimental results. The work of three sets of investigators enters into the comparison of values of C_p in Table VI, namely, that of Bridgman, that of Mathias, Onnes, and Crommelin, and that of Eucken and Hauck. While it seems unlikely that any one of these

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[18] An error in the melting curve would not itself be without other complicating effects. A change would have to be made in the calculations of Table I of the preceding paper. These changes would be rather small, and the effect on the estimated entropy of the liquid (aside from that caused directly by changes in the slopes of the curves) could be neglected; but other changes in the experimental results might well result in unforeseen complications.

[19] O. K. Rice, J. Chem. Phys. 12, 289 (1944); and see the preceding paper (reference 9).

pieces of work is sufficiently in error to account for the discrepancies involved, it may well be that the combined errors in all of them are great enough.

That this is a possibility is also suggested by some experiments on the velocity of sound in liquid argon made by Liepmann.[20] A slight extrapolation of his results gives a velocity of 8.30×10^4 cm/sec. at 87.75°K. The velocity of sound is given in terms of thermodynamic quantities by $(C_p - C_v)^{\frac{1}{2}}(C_p/C_v\alpha^2 T)^{\frac{1}{2}}$ (see Liepmann's Eq. (5)). Using the values of α from Table VI and our calculated values of the specific heats (converted to ergs per gram) we obtain 8.73×10^4 cm/sec., about 5 percent too high. If we use, instead, the specific heats of Eucken and Hauck, the velocity is calculated at 7.73×10^4 cm/sec., about 7 percent too low.

In whatever way the questions raised in this section are ultimately settled, they do indicate one thing which is most important for the present; namely, there is a great need of new, highly accurate experimental work both on the thermal properties and the equation of state. The data now at hand represent excellent and beautiful pioneer work; but it is pioneer work and does not give a sufficiently detailed account of liquid argon to furnish a satisfactory basis for the theory. New measurements, using the best modern techniques, are urgently required.

In the meantime, since the theory seems to represent the various sets of experimental results within approximately the limits indicated by their mutual inconsistencies, it seems worth

TABLE VIII. Free energy changes along the melting curve (calories per mole.)

$T(°K)$	$\Delta A_{t,s}$	$P_m V_s$	ΔE_p	ΔF_s	$\Delta A_{V,l}$	$P_V V$	I	ΔF_l
126.3	−432	1145	−5	708	−580	652	639	711
192.9	−1190	3374	−40	2144	−1634	1642	2145	2153

[20] H. W. Liepmann, Helv. Phys. Acta 12, 421 (1939). Liepmann has noted the inconsistencies between his values and the thermal data. The inconsistency between his results and Eucken and Hauck's specific heat data would not appear to be quite so great had he used the values of α given in Table VI instead of the values given by Donnan and Baly; however they would still exist. It seems to me unlikely that the possible explanation offered by Liepmann, namely, that the sound wave is too fast to allow internal equilibrium to be established in the liquid, can be correct, since $\Theta = 80$ corresponds to a frequency of about 1.7×10^{12}, far higher than the frequency of the sound wave used by him.
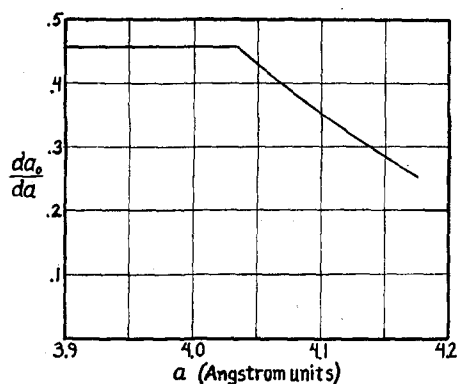

FIG. 3.

while to use it to make some calculations and deductions.

6. THE FREE ENERGY ALONG THE MELTING CURVE

Let us write ΔF_s for the free energy of the solid at any temperature and pressure, minus its free energy at zero pressure and its normal melting point at zero pressure; and let us write ΔF_l for the similar quantity for the liquid. Then at any point along the melting curve we should have

$$\Delta F_s = \Delta F_l. \qquad (15)$$

We write

$$\Delta F_s = \Delta A_{t,s} + P_m V_s + \Delta E_p. \qquad (16)$$

Here $\Delta A_{t,s}$ is the change in $A_{t,s}$, the thermal part of the work function of the solid, along the melting curve; it is readily computed, using the Debye theory, from the Θ's given in the preceding paper. P_m is the pressure along the melting curve, at the temperature of interest, and is known from Bridgman's work. V_s is the volume of the solid at the same temperature obtained from the V(calc.) of Table I of the preceding paper. The change in potential energy ΔE_p can be readily calculated, since E_p is known as a function of Θ from Eqs. (7), (1), and (2) of the preceding paper. As always, we use $\Gamma = 0.18$.

For ΔF_l we write

$$\Delta F_l = \Delta A_{V,l} + P_V V + \int_{P_V}^{P_m} V dP. \qquad (17)$$

Here $\Delta A_{V,l}$ is the change in work function at constant volume ($a = 4.037$) (the A of Table IV). P_V is the pressure reached at the temperature of

interest at the constant volume V (with $a = 4.037$); the values given in Table IV are used. The integral takes care of the change in F when the liquid is now compressed at constant temperature until solid begins to form, and can be evaluated from Bridgman's equation-of-state data (Fig. 1).

ΔF_s and ΔF_l and the other quantities in Eqs. (16) and (17) are given in Table VIII. The integral in ΔF_l is designated as I. Equation (15) is reasonably well satisfied.

We have noted that $\Delta A_{V,l}$ is calculated from the theoretical results of Table IV. Since some of the entropies in this table are higher than the experimental values and some lower, the average which goes into the equation $(\partial A/\partial T)_V = -S$ is about the same as if the experimental values had been used. However, if the experimental values in the middle temperature range were adjusted downward, as proposed in the preceding section, the discrepancy in Table VIII would be increased by use of the experimental values. This suggests that possibly the value of S at the normal melting point should be adjusted upward. This would have to represent a change in the ΔS of fusion, because if the entropy of the solid were also changed no net effect would result on the difference between ΔF_s and ΔF_l, since solid and liquid would be affected similarly. It seems unlikely, however, that there is any appreciable error in Clusius' value of the heat of fusion, so the normal ΔS of fusion should be well known. Although the difference between ΔF_l and ΔF_s is small, it seems more difficult to account for the discrepancy as experimental error than it does to account for the discrepancies involving the specific heats discussed in Section 5. The difficulty may be connected with the possible breakdown of the Debye theory of the solid, discussed in previous work,[19] and mentioned in Section 5. At the same time, it may be emphasized again that a complete reworking of the data on argon would be of the utmost value.

7. DISCUSSION

Behavior of da_0/da

In Fig. 3, we have plotted da_0/da against a. It will be noticed that there is a sharp break in the slope of this curve between $a = 4.03A$ and $a = 4.04A$. This break corresponds to the break in $(\partial S/\partial V)_T$ for 320°K, coming at the same place as shown in Fig. 2. Though we cannot exclude the possibility that this break in the slope of the curves should be rounded off somewhat, there seems to be no doubt that the break in $(\partial S/\partial V)_T$ is real in the sense that there is a fairly marked change of slope in the region shown; the interpretation of it in terms of da_0/da depends upon

our acceptance of the behavior of Θ with a_0 described in the preceding article.[21]

It might be possible to suppose that the break in the slope of the $(\partial S/\partial V)_T$ curve results from a change in the nature of the dependence of $d\Theta/da_0$, rather than of da_0/da on a_0. Especially might we consider this to be a possibility if the parameters were chosen (as is not excluded) in such a way that the value of a_0 involved was outside the experimental range of lattice distances in the solid where we have direct knowledge of the behavior of Θ. This would mean that we refer the break in slope of $(\partial S/\partial V)_T$ to a property of the solid rather than to a special property of the liquid. Aside from the inherent improbability of such an assumption, I believe that we can find some circumstantial evidence that the break is a distinct property of the liquid.

This rests on an examination[22] of the atomic distribution curves found by Eisenstein and Gingrich,[13] and by Lark-Horovitz and Miller.[12] Eisenstein and Gingrich found curves for liquid argon at 84.35°K and 91.8°K which differed very noticeably from each other. Each of these curves showed a maximum just below 3.8A, but there were 10.2 to 10.9 atoms under the first peak at 84.35°K and only 6.8 to 7.2 at 91.8°K, and the maximum was much lower in the latter case. Furthermore, at 91.8° there was a second peak at 4.7A, but at 84.35° there was a rather sharp minimum near this distance. Lark-Horovitz and Miller found a distribution curve at 89.2°K which appeared to be much more like the distribution curve at 84.35°K than that at 91.8°,

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[21] The calculations of the earlier article (see reference 19), which the preceding paper modifies, led to a very radical variation of $d\Theta/da_0$ with a_0. Applied to the liquid, this made da_0/da increase rapidly with a, so that da_0/da became greater than 1 when the liquid was expanded somewhat beyond $a = 4.037A$. This seemed very unreasonable because it meant that the compressibility of the individual atoms was greater than that of the liquid as a whole. At large values of a, we may, in fact, expect a_0 to approach a constant value, determined by the "size" of a single atom; da/da_0, then, should decrease asymptotically to zero. It was these considerations which led us to make the recalculation for the solid.

A still earlier paper (O. K. Rice, J. Am. Chem. Soc. **63**, 3 (1941)) gave $d \ln \Theta/dV = 0.10$ instead of the 0.18 used here. The low value of $d \ln \Theta/dV$ gives a value of da_0/da equal to about 1.9. This is obviously ridiculous, and may be added to the reasons already discussed for discarding these calculations.

[22] This examination was greatly facilitated by more detailed data very kindly sent me both by Dr. Gingrich and Dr. Lark-Horovitz. I wish to thank these investigators for their assistance in this matter.

and which had about 10.0 atoms under the first peak. One thus gets the impression that there is a sharp change between 89.2° and 91.8°, amounting almost to a transition. It seems very natural to suppose that this change in the atomic distribution would be associated with a change in the behavior of da_0/da with a. But if the transition takes place between 89.2° and 91.8° one would expect the break in the curve in Fig. 2 or Fig. 3 to take place at $a = 4.07$ or 4.08 instead of around $a = 4.04$. However, a closer examination shows that the change in the atomic distribution curve is actually more gradual than appears on the surface. A close scrutiny of Eisenstein and Gingrich's Fig. 10, and Lark-Horovitz and Miller's Fig. 2, allows us to make the following estimates of the density function $4\pi r^2\rho(r)$ at the maximum (that is, the height of the maximum) at the various temperatures: 84.35°K, 12.7; 89.2°K, 10.5; 91.8°K, 9.3. Also, we make the following estimate of the value of this function at the first minimum (first two temperatures), or the second maximum (last temperature): 84.35°K, 2.5; 89.2°K, 3.9; 91.8°K, 5.9. Thus, certainly within the limits of error, we can say that we have a gradual decrease of density at the first maximum, and at the next position, around 4.7A, a gradual increase in density. Just how suddenly the minimum appears to change into a maximum only a more closely spaced and very accurate series of experiments by a single investigator could show. It may be that the second peak, which at 84.35°K is around 5.3A, slides with increasing temperature into the position at 4.7A. In any event, at present the process looks like a gradual shift from a distribution resembling a distorted face-centered cubic lattice to one resembling a body-centered cubic lattice. This goes on all through the temperature range from near the normal freezing point of argon to 91.8° and beyond (from the work of Eisenstein and Gingrich it appears to continue on into the high temperature range), which means that the change starts when a is in the neighborhood of 4.03 or 4.04A. (It could start at a slightly higher, but presumably does not start at a much lower value of a, for the distribution at 84.35° resembles a face-centered cubic distribution about as closely as would
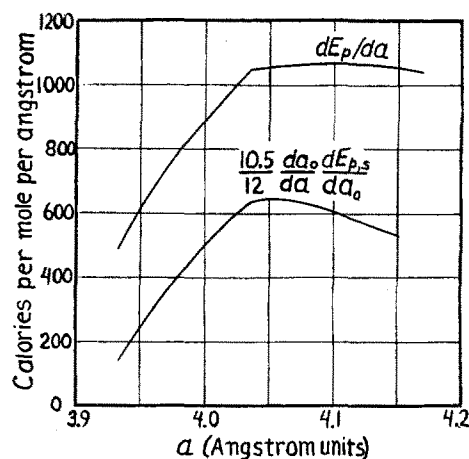

FIG. 4.

seem to be possible without having a definite lattice of that form). The apparently sudden change in coordination number between 89.2° and 91.8° is a psychological rather than a physical phenomenon. As soon as the minimum turns into a maximum, one divides the space around the central atom in a different way and relegates some of what were "nearest neighbors" to the class of "next-nearest neighbors."

If this interpretation of the atomic distribution curves is correct, it seems natural to associate the change in the slope of the curve da_0/da vs. a between $a = 4.03$ and $a = 4.04$ with the beginning of the appearance of traces of the distorted body-centered lattice at about the same value of a. In fact, off hand, one would not be surprised to see a discontinuity in da_0/da, but, according to the present picture, such a discontinuity would be associated with a discontinuity of $(\partial S/\partial V)_T$ or $(\partial P/\partial T)_V$, which would then occur at a definite volume independent of temperature, and this would be impossible by the theory of second-order transitions.

The Potential Energy of Liquid Argon

In Table V we have tabulated calculated values of dE_p/da. These can be correlated with the potential curve of the solid, as given in the preceding article. Since we believe that a_0 is to be identified fairly closely with the actual average interatomic distance of nearest neighbors in the liquid, we expect E_p to be related to the E_p for the solid at the given value of a_0. In fact, we

should be able to write, at least roughly,

$$E_p = (N/12)E_{p,s}(a_0) + E_d, \qquad (18)$$

where E_d is a constant, $E_{p,s}(a_0)$ is the potential energy of the solid at lattice distance a_0, and N is the average coordination number in the liquid.[23] If there is a "mixture" of face-centered and body-centered lattices in the liquid, we should perhaps add another adjective, and say that N is the effective average coordination number, as the next nearest neighbors in a body-centered lattice are close enough to have quite an influence on the central atom. If we differentiate Eq. (18) we obtain

$$dE_p/da = \tfrac{1}{12}(dN/da)E_{p,s}(a_0) + (N/12)(dE_{p,s}/da_0)(da_0/da). \quad (19)$$

We may suppose that the greater portion of the variation of dE_p/da is in the last term of Eq. (19). Also the variation of N is probably not too large. Therefore, in the last term of Eq. (19) we have assumed N constant at 10.5. In Fig. 4 we have plotted dE_p/da from Table V and $(10.5/12) \times (dE_{p,s}/da_0)(da_0/da)$, taking $dE_{p,s}/da_0$ from the preceding article and da_0/da from Table V. It is seen that the two curves parallel each other in the region of small values of a, which may, at least for this region of a, be taken as confirmation of our point of view that information about the energy of the liquid may be obtained in a simple manner from the solid. It must be granted that we can only make this correlation because the somewhat arbitrarily chosen parameter a_0 lies within the range for which we have experimental data on the solid. In spite of this, we believe that the result must have at least qualitative significance.

The difference at small values of a between the two curves in Fig. 4, about 400 cal. mole^{-1} A^{-1}, gives the first term on the right-hand side of Eq. (19) and, since $E_{p,s}(a_0)$ is near 2000 cal. mole^{-1}, we find $dN/da = 2.4A^{-1}$. This rate of change of N is small enough to justify our taking N constant[24] in the last term of Eq. (19); it may seem a little smaller than expected, but it is insensitive to the parameters. In any

[23] Except for the constant E_d, which will be discussed later, this is essentially the assumption we have made previously (see reference 3).

[24] A correction would decrease the parallelism of the curves, but only slightly.

event, it can have a really objective significance in terms of the pictorial theory of the liquid only below a equal to 4.03 or 4.04A, where the lattice change begins to come in. For a greater than about 4.03A, it is seen that dE_p/da appears to be approximately constant, more so than $(N/12)(dE_{p,s}/da_0)(da_0/da)$. While we cannot ignore that the determination of $dE_{p,s}/da_0$ involves an extrapolation in this region, the greater degree of constancy of dE_p/da may be significant and explainable in the following way. Since the position of the first maximum of the distribution curve remains almost fixed,[13] the "percentage of body-centered structure," which must thus determine E_p, would be expected to be a linear function of a, at least over a small range. It is then not surprising if E_p is similar in this respect, and dE_p/da consequently nearly constant.

We now return to a discussion of the constant, or approximately constant, quantity E_d. The long range or translational type of motion, discussed in Section 1 above, in which the atoms slip around and exchange places, could not take place without changes in the distances between neighboring atoms. Thus the potential energy of the system cannot be the same as it would be if there were no such translational motion, and all neighboring atoms were at the same distance from each other. Even the translational motion will involve exchange of potential energy of certain pairs of molecules with other pairs, though the total potential energy in the entire large assemblage must always remain the same for any given a, and independent of temperature, if the motion is, in fact, to be properly described as translational. The energy E_d is the extra potential energy associated with the fluctuation in interatomic distances necessary for the translational motion to occur. E_d is always positive because the atoms are near a minimum of the mutual potential energy curve, i.e., in a region where it is concave upward.

From the available thermochemical energy we can estimate the total energy E of argon liquid at its freezing point. (This is reckoned on the basis of perfect gas at absolute zero having zero energy.) We can estimate E_t from Eq. (7). The difference $E - E_t$ is E_p; since we are dealing with the classical case we do not need to consider the

zero-point energy. E_d can then be estimated from Eq. (18). We find for argon liquid at its normal freezing point:

$$E = -1177 \text{ cal./mole,}$$
$$E_t = 398 \text{ cal./mole,}$$
$$E_p = -1575 \text{ cal./mole,}$$
$$E_d = 167 \text{ cal./mole,}$$

(assuming $N = 10.5$, $a_0 = 3.85$, and $L = 1.9$). It will be recalled that E_t itself contains some potential energy. The kinetic energy is equal to $\frac{3}{2}RT$ or 250 cal./mole, so the potential energy contributes 148 cal./mole to E_t, a quantity of the same order of magnitude as E_d.

Prefreezing Phenomenon

In Section 4 we have noted that the curves in Fig. 1 corresponding to low molal volumes have an "abnormal" slope at the low temperature end. This is reflected in Fig. 2, where it is seen that $(\partial S/\partial V)_T$ is "abnormally" great at low temperatures and small values of a. An indication of the reason for this apparent abnormality is found when we plot

$$(\partial E/\partial V)_T = T(\partial S/\partial V)_T - P$$

against a, as in Fig. 5. The curve for dE_p/dV is included for comparison, and it is seen that at 320°K the $(\partial E/\partial V)_T$ curve parallels it reasonably well, but at lower temperatures $(\partial E/\partial V)_T$ becomes very great at small values of a. The values of $(\partial E/\partial V)_T$ are subject to considerable uncertainty, because they are calculated as a relatively small difference, but the qualitative trend is unmistakeable.

The trend of the curves in Figs. 2 and 5 can be explained if we suppose that at the lower temperatures the system tends on compression to go to some special state of low entropy and, simultaneously, low energy. This leads one to speculate that we are dealing here with a prefreezing phenomenon, in which submicroscopic particles or crystalloids, having essentially the crystal structure of the solid, are formed in the liquid.

Such a phenomenon can, of course, occur only if the free energy of the entire system is thereby lowered. One might wonder why, if formation of what are essentially small particles of solid lowers the free energy, the system does not go the whole way, and form a large crystal. The answer is, of course, the entropy of mixing of the solid par-
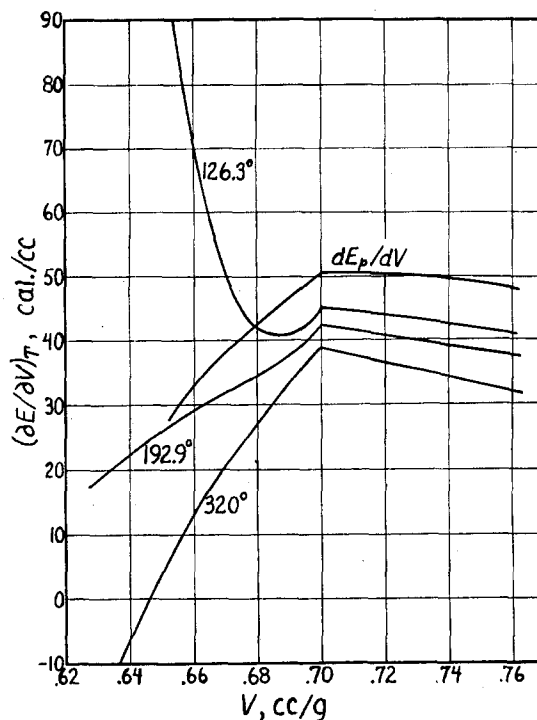

FIG. 5.

ticles with the molecules of liquid. When the liquid (without crystalloids) and the solid have very closely similar free energies, this may be sufficient to turn the balance and stabilize the mixture. One would not expect such a system to be stable over a very extended range. In Figs. 1 and 2, curves are shown[25] which indicate the points at which solid and liquid are in equilibrium. It will be seen that the abnormal values of $(\partial S/\partial V)_T$ actually occur to a considerable extent in the metastable region, where the solid has a lower free energy than the liquid. Only over a rather small range is our hypothetical mixture important and stable. It is hoped that it may be possible in subsequent work to give a more quantitative discussion of these phenomena. In our earlier discussion of the gas of hard elastic spheres we noted the possibility that such a gas on compression would form regions in which the "atoms" are in a cubic-close-packed structure (see SLM, p. 14). In this case, however, the "atoms" do not have an attractive force field, and, furthermore, these groupings are associated with an increase in the entropy of the

[25] In Fig. 2 the curve is merely indicated by the short vertical lines.

system. It appears, therefore, that this is not the same phenomenon as the "prefreezing" phenomenon we are discussing here. We may speculate that both types of grouping can occur in an actual liquid, the prefreezing phenomenon involving larger groups and being characterized also by a change in the interatomic distance to that of the solid, which is probably considerably larger than the average distance between closest neighbors in the liquid in the range in which prefreezing occurs.

The phenomena that we have here described as prefreezing were already noted in our earlier work.[3] The explanation given there, namely, that the decrease in entropy as the volume is decreased is associated with an increase in the average coordination number of the atoms of the liquid toward the coordinate number characteristic of solid argon, has some resemblances to and some points of difference from the explanation offered here. The process of prefreezing described in the above paragraphs will obviously be associated with an increase in average coordination number, but of a somewhat more specialized type than that envisaged in the earlier work. In particular, in the present discussion we conceive of the coordination number as varying appreciably in different regions which may be of appreciable size, whereas in the earlier work it was supposed that the average coordination number changed gradually with no appreciable local variations extending over considerable regions.

Conclusion

In concluding we may point out that perhaps the greatest advance recorded in this paper is the rather good correlation of the properties of the liquid with those of the solid. The attempt to use values of Θ taken directly from the solid appears to be successful. It is particularly interesting that it is absolutely essential to take into account the relaxation of the forces of the side-atoms in the liquid, and, in fact, as we have noted in Section 3, the liquid appears to be slightly more relaxed than our first estimate indicated. The correlation with the solid appears not only in the fact that the values of Θ for the solid give a good description of the properties of the liquid when proper account is taken of the interatomic distance, but also in the examination of the potential energy of the liquid and its comparison with that of the solid. Considerable uncertainty, unfortunately, still remains in the interpretation of the properties of the solid, since it does not appear to be possible to correlate Θ theoretically with the lattice distance. In the liquid we have a somewhat similar difficulty, since it requires recourse to the experimental data to correlate a_0 with a. Further progress in the understanding of the liquid will require solution of both problems. Since only one of them is actually characteristic of the liquid, the other belonging to the domain of the theory of the solid state, it now seems fair to say that our present understanding of the liquid has advanced to a point not too far behind our understanding of the solid.