

The SolidLiquid Equilibrium in Argon

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approximately the same temperature range for both reactions. This would appear to constitute a further argument in favor of Bodenstein's mechanism.

The data for the entropy of activation given in Table VI covering the temperature range 150–300°C, the range covered by direct measurement of both the formation and decomposition, give by graphical interpolation a value of 6.1

for the entropy change of the reaction at 250°C. This may be compared with the value of 6.28 obtained by calculation from the entropies of nitric oxide,¹⁹ chlorine²⁰ and nitrosyl chloride.²¹ The agreement is very satisfactory.

¹⁹ H. L. Johnston and A. T. Chapman, J. Am. Chem. Soc. **55**, 153 (1933).

²⁰ W. F. Giaque and R. Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

²¹ F. P. Jahn, J. Chem. Phys. **6**, 335 (1938).

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The Solid-Liquid Equilibrium in Argon

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The method of investigating the equilibrium between solid and liquid phases, outlined in a previous paper, has been applied to argon. (In this method the intersections of the curves for the thermodynamic quantities $T(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T + P$, plotted as functions of the volume, are used to determine the conditions of equilibrium of the system.) Curves are found for the functions $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$, assumed dependent on volume and independent of temperature, which can reproduce with reasonable accuracy most of the melting parameters of argon at high pressures. The significance of these curves is discussed.

AS a preliminary to a theoretical study of the solid-liquid equilibrium, it seems desirable to make as complete an analysis as possible of the available experimental material for a substance in which the factors determining this equilibrium are as simple as possible. Argon seems to be a suitable substance for such a study, since the data available are fairly extensive, and since the intermolecular forces are of the pure van der Waals type.

The method we use is that presented in a previous paper,¹ and is based upon the thermodynamic equation

$$T(\partial S/\partial V)_T = (\partial E/\partial V)_T + P. \quad (1)$$

If the quantities $T(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T + P$ are plotted as functions of the volume, the points of intersection of these curves determine the volumes of phases which are in internal equilibrium at the given temperature and pressure. Such an equilibrium is a stable rather than an unstable one (i.e., corresponds to a minimum

rather than a maximum of free energy) if $(\partial E/\partial V)_T + P$ is greater than $T(\partial S/\partial V)_T$ for values of the volume greater than the equilibrium volume. Of course, if there are two or more stable equilibria indicated in this way, in general one of them is the most stable; the condition that two phases be equally stable, and hence capable of coexistence, is that the area under the $(\partial E/\partial V)_T + P$ curve between the volumes corresponding to the two phases should be equal to the similar area under the $T(\partial S/\partial V)_T$ curve.

If the functions $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ changed very greatly with the temperature, such a method of analysis would be of little assistance. However, it seems probable that $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ can be considered, as a first approximation, as functions of the volume which are independent of the temperature, provided the temperature is sufficiently high so that quantization is not important. Inasmuch as the Debye characteristic temperature for argon is approximately equal to its normal melting point, it

¹ Rice, J. Chem. Phys. **5**, 492 (1937).

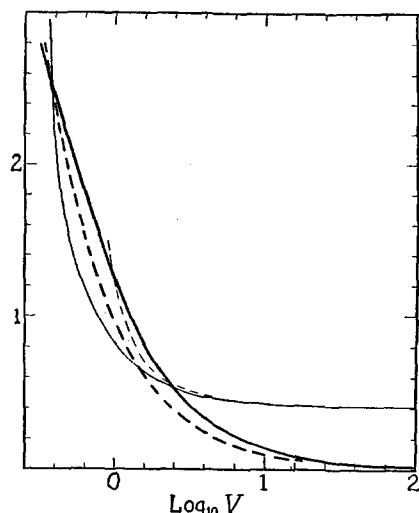


FIG. 1. Curves for large volumes. Heavy curve $(\partial E/\partial \log_{10} V)_T$; heavy broken curve approximation from Eq. (4) of Reference 1; light curve $T(\partial S/\partial \log_{10} V)_T$; light broken curve approximation from van der Waals equation, assuming b equals 1.5 times the critical volume. Energy and volume units as in Table I. Ordinates should be multiplied by 10^3 .

would seem that at temperatures equal to or above this melting point quantum effects can be neglected.²

In the cases of oxygen and nitrogen, the data on the transitions at normal pressures fix the $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ curves fairly well. This is largely because of the information furnished by the transitions between solid phases due to the setting in of molecular rotation in the solid state. In the case of argon there is no such transition point, so use has been made of Bridgman's data on the melting parameters at high pressures.³ Specifically, we have tried to see to what extent curves for $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$, which are assumed independent of the temperature, can be used to correlate Bridgman's data. First, of course, we have made use of the data on the equilibrium between liquid and gaseous argon to construct curves for volumes larger than the volume of the liquid at the boiling point, just as

² In reference 1 it was stated that the phenomenon of a transition point corresponding to fusion depended upon a characteristic decrease of the $(\partial S/\partial V)_T$ function at small volumes. It was suggested that this decrease was an effect of quantization. However, at the temperature of melting argon the entropy will have reached nearly its classical value, and it seems necessary to look for other causes for the decrease in the $(\partial S/\partial V)_T$ curve with decreasing volume.

³ Bridgman, Proc. Am. Acad. 70, 1 (1935); Phys. Rev. 46, 930 (1934).

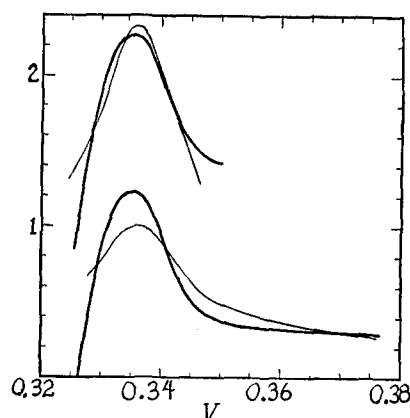


FIG. 2. Curves for small volumes. Heavy curves, $(\partial E/\partial V)_T + P$; light curves, $T(\partial S/\partial V)_T$. Units as in Table I. Ordinates should be multiplied by 10^4 .

was done with nitrogen and oxygen in our previous paper.⁴ The results are shown in Fig. 1. The curves for smaller volumes were then made to join smoothly to these.

Trials were made with a variety of curves for both $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$. Curves for $T(\partial S/\partial V)_T$ for various values of T were plotted on transparent coordinate paper, and these could be moved vertically over the $(\partial E/\partial V)_T$ curve until the relation between them was such as to indicate that the conditions were correct for the coexistence of two phases⁵ (assumed to be the liquid and solid phases). From the vertical displacement, the pressure at which the equilibrium between the two phases occurs could then be readily obtained. The temperature of the $T(\partial S/\partial V)_T$ curve then corresponds to the melting point at that pressure. The change of volume, ΔV , of fusion can also be readily obtained by noting the points of intersection of the $T(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T + P$ curves, and the change of energy, ΔE , on fusion can be obtained by measuring the area under the $(\partial E/\partial V)_T$ curve. The latter is not an entirely independent quantity, however.

In Fig. 2 we show the curves finally used. The $T(\partial S/\partial V)_T$ curve is shown for temperatures

⁴ See reference 1; the data used can be found in Landolt-Börnstein Tabellen. Most of it is collected in Rice, J. Chem. Phys. 5, 353 (1937).

⁵ The equality of the areas under the curves was first estimated by eye, with the aid, in the case of the curves finally used, of Dr. J. E. Magoffin. The final curves were then plotted on a larger scale and planimeted.

TABLE I. Calculated and experimental values of the melting parameters. (Energies in calories per mole. The volume of a mole at the critical point, 75 cc, is taken as unity. The pressure units are consistent with these energy and volume units. All observed values from Bridgman.)

TEMP. (°K)	V_s		ΔV		PRESSURE		ΔE	
	CALC.	OBS.	CALC.	OBS.	CALC.	OBS.	CALC.	OBS.
83.9	0.3293	0.331	0.0437	0.0423	0	0	248	262
106.3	.3296		.0279	.0295	1710	1762	200	211
126.4	.3296	.326	.0196	.0226	3500	3520	174	182
162.0	.3291	.324	.0154	.0149	7070	7040	152	153
193.1	.3285	.323	.0134	.0112	10430	10600	138	142

83.9°K and 193.1°K, the lowest and highest used, and the $(\partial E/\partial V)_T + P$ curve is also shown. Since the former temperature is the normal melting point, the corresponding value of P is equal to (practically) zero.

In Table I we present a comparison of the values of P , ΔV , ΔE , and V_s , the volume of the solid which is in equilibrium with the liquid, calculated from the curves, with the data obtained by Bridgman. (We use the term liquid to describe the amorphous phase produced by the melting of the solid, even though the critical temperature be exceeded.)

It is also possible to calculate the volume of the liquid which is in internal equilibrium at various pressures, and any given temperature. These can be compared with data for pressures below that which causes the liquid to freeze, and even at slightly higher pressures, due to "super-compression." Calculations for 183.0°K are compared with Bridgman's data at the same temperature in Table II.

DISCUSSION

It will be seen from Table I that the proposed $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ curves reproduce the experimental data for P , ΔV , and ΔE at the various temperatures, with reasonable accuracy. However, the values of V_s given by the curves do not show as much trend with the temperature as do the experimental values. Bridgman remarked on the approximate constancy of V_s ; however, actually it changes over the range considered, by some 2 percent, which can cause a relatively large change in the free or effective internal volume of a solid. It is possible that further experimentation with $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ would have produced a better fit; however, some effort failed to

TABLE II. Volume of the liquid at 183°K. (Critical volume of one mole of argon taken as unity. Pressure units as in Table I.)

PRESSURE	VOLUME	
	CALC.	EXP.
5280	0.3572	0.357
6160	.3520	.352
7050	.3479	.346
7930	.3460	.3415
8800	.3440	.336
9680	.341	.332

produce an improvement. The discrepancy would be removed if both $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ curves moved bodily to the left on the diagram at higher temperatures, but a shift sufficient to reproduce the observed trend seems rather unreasonable.⁶ Table II also shows a discrepancy between observed and calculated values; this, however, is closely related to the discrepancies in the values of V_s , for it is clear that if there is a discrepancy in the volumes of the solid, without a corresponding discrepancy in ΔV , the discrepancy must reappear with the liquid. More disturbing is the discrepancy in the compressibility; this could probably be explained, however, by relatively slight trends in the $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ curves with temperature.

At certain pressures where the $T(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T + P$ curves nearly coincide over considerable ranges of the volume the calculated values of ΔV are very sensitive to small changes in the curves. Such small changes could readily occur with changing temperature, and could easily account for all the disagreement between experimental and calculated values in Table I, except for the case of V_s .

In spite of the difficulties discussed above, I believe that the $(\partial S/\partial V)_T$ and $(\partial E/\partial V)_T$ curves given in Fig. 2 cannot be far wrong. They present several features of interest, which, pending a complete theoretical treatment of the phenomena involved, seem worthy of some discussion.

⁶ Professor Bridgman has very kindly communicated on this matter, and has stated that it is not impossible that the trend in his results is within experimental error. In this connection it should, however, be remarked that the volume of solid argon at around 20°K is given in the Strukturbericht as about 0.317 in our units, considerably too small to be accounted for by our curve, but the discrepancy is probably within the limits of experimental error.

In the first place we may make a comparison with the similar curves for nitrogen and oxygen. Of course, on account of the complications involved in the setting in of rotation in nitrogen and oxygen no direct comparison can be made of the $(\partial S/\partial V)_T$ curves. In the case of the $(\partial E/\partial V)_T$ curves it is of interest to note that the maximum is much broader in the case of nitrogen and oxygen than it is in the case of argon. It is not excluded that that may be to some extent due to inaccuracy in drawing the curves, but it hardly seems probable that it can be entirely due to this cause. Rather, it seems likely that the difference is associated with the fact that nitrogen and oxygen are diatomic while argon is monatomic. In the usual theory of van der Waals forces the attractive potential between molecules depends only on the distance between them and follows an inverse sixth power law. This theory, however, needs modification when the molecules are very close together. Corrections have been introduced which take the form of an eighth power attractive potential, but probably something more radical than that is needed. We might make the speculation that, with matter in bulk and very close packed, the correction depends upon the area of the surface of the molecule exposed to its neighbors. A diatomic molecule has more exposed surface than a monatomic molecule in comparison to the volume it occupies. A diatomic molecule should, therefore, have a relatively greater interaction with its neighbors; furthermore, as the substance expands the distance between the surfaces of neighboring molecules will increase less uniformly in the case of the diatomic molecule. Thus the force due to the pulling away of the molecules should be large over a greater range

of volumes in the case of a diatomic molecule, and the maximum in the $(\partial E/\partial V)_T$ curve should be broader.

In agreement with these general ideas it may be mentioned that an attempt to account for the increase of energy of argon in the volume range between that of the solid and the liquid assuming an inverse sixth power attractive potential with coefficients of the right magnitude to give the correct energy of sublimation, was entirely unsuccessful no matter what repulsive potential was used.* The increase in the energy of the system at small volumes is entirely too great to be accounted for in this way, and would appear to indicate that the attractive force increases very rapidly at very small distances.⁷ It should be possible, from the $(\partial E/\partial V)_T$ curve found here, to obtain the potential curve for a pair of molecules. Also, knowing the nature of the potential function for any molecule in the field of its neighbors, it should be possible to estimate its available free volume, and thus find the $(\partial S/\partial V)_T$ curve. The result could then be compared with the $(\partial S/\partial V)_T$ curve used here to reproduce the experimental data, and the comparison may throw some light on the question as to whether or not the excitation of "communal" entropy plays any appreciable role in the process of fusion.⁸ It is proposed to continue the investigation along these lines in the near future.

* Powers for the repulsive potential as high as the 36th were considered.

⁷ It should be noted that these calculations depend upon the assumption that corresponding to an increase is a uniform expansion of the lattice, an assumption which may need some further scrutiny, in view of the recent theories of holes.

⁸ See the accompanying paper, J. Chem. Phys. 6, 476 (1938).