MELTING IN ARGON AT HIGH TEMPERATURES*

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Accurate measurements of the molar volume of argon in the fluid and solid phases along the melting curve have been made with a weighing technique and data obtained for melting temperatures and pressures up to 200°K and 6.3 kbar. A simple model for melting, which agrees reasonably well with these experimental data, indicates the correspondence between the details of the intermolecular pair potential and the quanlitative features evident in the transition.

Experimental.—In the method used a pressure vessel, which is connected to a pressure generating and measuring system by means of extremely flexible pressure tubing, is suspended beneath an analytical balance. The use of this flexible tubing, which has an o.d. of 0.82 mm and i.d. of 0.25 mm, enables the pressure vessel to be essentially mechanically decoupled from the external pressure system while maintaining pressure communication with it. Since the internal volume of the pressure vessel is known, the molar volume of the argon as a function of pressure and temperature can be determined by weighing the vessel at particular pressures and temperatures. Details of this method and its extension to p-V-T measurements in the fluid phase of argon will be reported in a future publication.[1]

The melting data obtained from these measurements are given in Table I. The values given for the latent heat of fusion were obtained from the pressure and volume data using Clapeyron's equation.

A similar technique, arrived at independently and applied to argon over a lower pressure and temperature range, has recently been reported by Van Witzenberg and Stryland[2] at Toronto. Their data agree with the fluid and solid molar volumes at melting shown in Table I to within about 0.3 % for melting temperatures and pressures up to 120°K and 1.7 kbar, the upper limit reported by that group. Both the Toronto data and the present data differ substantially from the argon solid and fluid molar volumes along the melting curve reported by Bridgman[3] and by Lahr and Eversole[4] as is shown in Fig. 1. However, Fig. 1 does indicate that the present data are consistent with the triple-point data obtained by Clusius and Weigand[5] and by Peterson, Batchelder, and Simmons.[6]

Melting model.—Previously, Longuet-Higgins and Widom[7] proposed a model for melting in systems characterized by weak long-range attractive forces and strong short-range repulsive forces, such as is the case for argon and the heavier rare gases. This model was based upon the phase transition which has been observed for systems of hard spheres.[8] It was assumed that the energy $U(V, T, N)$ and entropy $S(V, T, N)$ of a real system could be separated into "hard-sphere" and attractive parts given by

$$U(V, T, N) = U_{\mathrm{HS}}(T, N) + U_{\mathrm{ATT}}(V, T, N) \tag{1}$$

Table I. Experimental argon melting data.

Temperature (K)	Pressure (kilobars)	Molar Volume (cm^3/mole) Fluid	Solid	ΔV on Melting (cm^3/mole)	Latent Heat (joules/mole)
94.73±.02	0.451±.007	27.30±.02	24.34±.02	2.96±.02	1200 ± 50
94.74	0.459	27.31			
100.76	0.721	26.89			
108.12	1.051	26.52	24.02	2.50	1270
110.77	1.186	26.32			
120.85	1.674	25.85	23.65	2.20	1320
140.88	2.708	24.96	23.04	1.92	1460
160.40	3.805	24.26	22.54	1.72	1610
180.15	4.999	23.65	22.08	1.57	1760
180.20	5.003	23.66	22.11	1.55	1740
201.32	6.335	23.10	21.69	1.41	1780

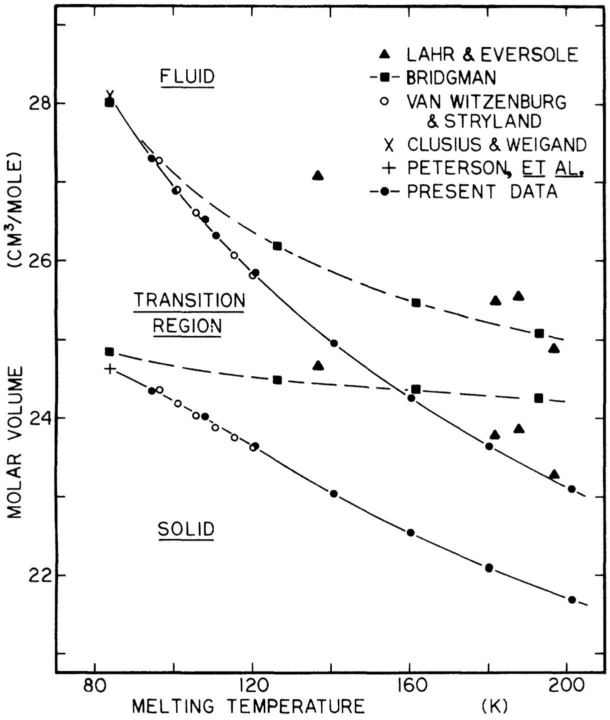

FIG. 1. Experimental molar volume of fluid and solid argon at melting as functions of melting temperature.

and

$$S(V,T,N)=S_{\mathrm{HS}}(V,T,N)+S_{\mathrm{ATT}}(V,T,N). \quad (2)$$

In this section V is the total volume, N is the number of particles, and T is the temperature. For the purpose of the model the further assumptions were made that

$$S_{\mathrm{ATT}}(V,T,N)=0 \quad (3)$$

and

$$U_{\mathrm{ATT}}(V,T,N)=aN^2/V, \quad (4)$$

where a is a multiplicative constant. With these assumptions the Helmholtz potential of the real system could be written as

$$F(V,T,N)=F_{\mathrm{HS}}(V,T,N)-aN^2/V, \quad (5)$$

so that the pressure was given by

$$p(V,T,N)\equiv-(\partial F/\partial V)_T$$
$$=p_{\mathrm{HS}}(V,T,N)-aN^2/V^2. \quad (6)$$

The hard-sphere pressure $p_{\mathrm{HS}}(V,T,N)$ has been calculated for a wide range of volumes, including the region of the solid-fluid phase transition, so Longuet-Higgins and Widom were able to use Eq. (6) to obtain a series of isotherms through the transition region for a system of particles having both hard-core and attractive interactions. With an appropriate choice for the constant a it was possible to obtain reasonably good values for the melting parameters of argon at the triple point, but the melting behavior predicted by this model for higher melting pressures and temperatures is not in accord with the data given in Table I above. Two changes in the model which yield improved agreement with the experimental data are described below.

Although Eq. (6) probably gives the pressure of a real fluid reasonably well, it is not a particularly good approximation to the pressure of a solid. A much better expression for the pressure in a solid can be obtained by assuming $U_{\mathrm{ATT}}(V,T,N)$ to be given by a lattice sum over particles interacting with a Lennard-Jones potential:

$$U_{\mathrm{ATT}}^{S}(V,T,N)$$
$$=2N\epsilon[A(V_0/V)^4-B(V_0/V)^2]. \quad (7)$$

Here V_0 stands for $N\sigma^3/\sqrt{2}$ with σ and ϵ being the usual Lennard-Jones potential parameters. The constants A and B result from the lattice sum and are, respectively, 12.132 and 14.454.[9] This gives for the solid pressure

$$p^{S}(V,T,N)=p_{\mathrm{HS}}(V,T,N)$$
$$+\frac{2N\epsilon}{V_0}\left[4A\left\{\frac{V_0}{V}\right\}^5-2B\left\{\frac{V_0}{V}\right\}^3\right]. \quad (8)$$

The hard-sphere isotherm calculated by molecular-dynamics methods[8] for a particular temperature is shown in Fig. 2(a). The hard-sphere phase-transition pressure has beem taken to be the value used by Longuet-Higgins and Widom since this pressure cannot be determined accurately from the molecular-dynamics calculations. The isotherm for the system with attractive forces is obtained from this hard-sphere isotherm by using Eq. (8) for volumes less than V_B and Eq. (6) for volumes greater than V_B. The constant a in Eq. (6) is determined by requiring that the isotherm be continuous at V_B. This choice of V_B as the dividing point between the use of Eq. (6) and Eq. (8) is made for convenience rather than for any fundamental reason. The isotherm so obtained exhibits a Van der

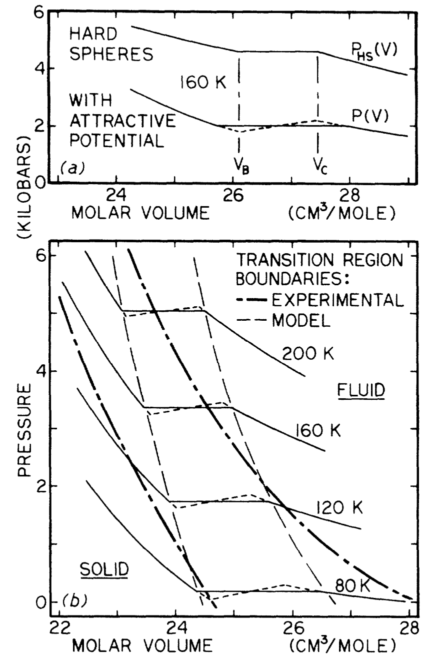

Fig. 2. (a) Hard-sphere isotherm through the solid-fluid transition and the corresponding isotherm obtained when an attractive potential is included (see text). (b) Solid-fluid phase transition calculated from the model, compared with the experimentally determined transition region.

Waals-type loop in the transition region, which is eliminated by the usual Maxwell "equal-areas" construction. From the figure it can be seen that the effect of the attractive potential has been to lower the pressure in both phases. The pressure is lowered by less in the liquid than in the solid, causing a broadening of the transition region.

The second improvement suggested for the model is the use of a "temperature-dependent hard-sphere diameter." Barker and Henderson[10] have recently shown that the use of a hard-sphere diameter d given by

$$d = \int \{1 - \exp[-u(r)/kT]\} dr \qquad (9)$$

can account quite well for the effects of the "softness" of the intermolecular potential $u(r)$ on the thermodynamic properties of simple liquids at moderate densities. Application of Eq. (9) at densities appropriate to the solid-fluid transition causes the calculated transition region to be shifted to smaller molar volumes at higher temperatures and pressures, which is in accord with the experimental data for agron.

A series of isotherms through the transition region obtained by this procedure are shown in Fig. 2(b) along with the experimental data from Table I. It is seen that this improved model reproduces all the qualitative features of the experimental data and gives reasonably good quantitative agreement, even though it has not been fitted to these data in any way. This good agreement suggests several tentative conclusions about melting in simple substances:

(1) The solid-fluid transition in simple substances with weak attractive potentials is fundamentally related to geometrical packing of the hard cores of the molecules.

(2) The attractive part of the intermolecular potential serves mainly to lower the pressure and is responsible for the large change of volume on melting which is observed at lower temperatures.

(3) The shift of the transition region to smaller molar volumes as the melting temperature and pressure are increased is due to the "softness" of the repulsive part of the potential.

(4) As the temperature and pressure are increased, the transition approaches that of a system of hard spheres with temperature-dependent diameters. Conclusion 4 above may be useful for extrapolation of the solid-fluid transition to high temperatures and pressures, and so may be useful in geophysical applications. However, it must be cautioned that the model, as outlined above, is directly applicable only to substances which solidify in close-packed structures.

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[1] For additional details see also R. K. Crawford, thesis, Princeton University, 1968 (unpublished).

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