The pressure dependence of the volume of solid argon up to 30 kbar at temperatures 77 and 201 K

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The *P*-*V* relation for 99.99% purity solid argon was measured at 77 and 201 K and pressures up to 30 kbar in a chamber of the piston and cylinder type supported on all sides by a hard-alloy cylinder. An equation for the volume dependence of the isothermal bulk modulus is proposed which agrees with experimental results obtained by various methods at various temperatures and pressures.

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Inert gases have a filled outer electron cloud and their condensation comes about as a result of the weak van der Waals attraction. Crystallized inert gases are the simplest solids. It is, therefore, not surprising that there have been a large number of both experimental and theoretical studies of the equation of state of solidified inert gases.[1]

The equation of state of solid argon has been studied at high pressures on isotherms at 4.2; 20; 40; 60 and 77 K at pressures up to 20 kbar (by the piston displacement method[2]) and on the 293 K isotherm to 80 kbar (by the x-ray method[3]). *T*-*P* measurements have also been made on several isochores ($V > 21.4\,\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$) at pressures up to 7 kbar (sealed bomb method[4]). The melting curve of argon has been studied up to 16 kbar (by various methods[5–8]).

In the present work experimental results are given of a study of the equation of state of solid argon up to 32 kbar at 77 K and up to 26 kbar at 201 K. The measurements were made by the piston displacement method. Unlike the earlier studies made on hydrogen,[9–11] a new high-pressure chamber, with a hydraulic holding clamp providing end support of the inner chamber cylinder,[12] was used in the present work. The pressure range could be extended and the accuracy of volume measurement increased by omnidirectional support of the high-pressure chamber, because high cylinder stiffness decreased the necessary corrections. In studying the volume dependence of the pressure at $T = 201$ K, the triple point was bypassed on the high pressure side of the argon *T*-*P* phase diagram, so that measurements could be carried out for the first time at a temperature above the triple point without crossing the melting curve. Since measurements were made only in the solid phase, there was no loss of accuracy which is inevitable when using a Bridgman unsupported packing, essential for maintaining the specimen when in the fluid phase.

METHOD OF MEASUREMENT

Measurements were carried out in three chambers with different channel diameters (Table I). The cylinders of chambers I and II were made of R 18 steel, while chamber III was made of hard alloy. The maximum pressure in chambers I and II was set by the allowable force of the low-temperature press (10 t), and in chamber III by the strength of the chamber (35 kbar). The use of chambers made of different materials and with different channel diameters enabled, first of all, systematic errors present in each individual chamber to be eliminated and, second, the range of pressures studied to be broadened without accuracy loss due to friction. In particular, the use of a chamber with large internal diameter allowed the value of the minimum pressure at which measurements could be made to be reduced, and consequently reduced the range over which the results obtained have to be extrapolated to $P = 0$. This extrapolation which is necessary for the determination of molar volume, is a weak point in the piston displacement method.

The solid sample was formed by condensing argon of 99.99% purity into the high-pressure chamber at liquid nitrogen temperature. The method of making the measurements, applying corrections, and evaluating specimen volumes and the pressure in it are in the main the same as described elsewhere.[9–12] The difference lay in the fact that when measuring on the 201 K isotherm (above the triple point), the specimen was first compressed at 77 K to a pressure of 10 kbar and then the liquid nitrogen refrigerant was replaced by a mixture of solid carbon dioxide and ethyl alcohol. At 77 K, 13 experiments were carried out on different chambers in the range 0.1–32 kbar; at 201 K, two experiments were carried out in chamber III at pressures from 7.5 to 26 kbar. The final uncertainty in the determination of

TABLE I. Characteristics of the high pressure chambers.

	I	II	III
Channel diameter, cm	2.405	1.222	0.568
Pressure range, kbar	0.1–2.2	0.4–8.4	1.5–32
Friction, % of max. force	1–2	2–3	2–4

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TABLE II. Values of the parameters for the Keane equation (1) and mean square error δ for 77 K and 201 K.

	77 K	201 K
V_0, cm^3/mol	24.3098	27.4256
B_0, kbar	13.9104	11.1553
B_0'	9.9576	6.2426
B_∞'	5.3765	5.4734
δ, cm^3/mol	0.021	0.024

volume, in which the error in pressure determination is included, was ± 0.5% at 77 K and ± 1% for 201 K.

RESULTS AND DISCUSSION

All the results obtained on any isotherm were normalized to a volume corresponding to some normalization pressure. The normalized results of all the experiments at a given temperature were treated together by the method of least squares. The Keane equation[13] was used

$$P=B_0\left[\frac{B_0'}{B'^2_\infty}\left(y^{B'_\infty}-1\right)-\left(\frac{B_0'}{B'_\infty}-1\right)\ln y\right], \tag{1}$$

where

$$y=V_0/V,\quad B_0=-V(\partial P/\partial V)_T,\quad B_0'=(\partial B_T/\partial P)_T$$

for $V=V_0$; $B'_\infty=B'_0$ for $P\to\infty$ $(V\to 0)$. The parameters for Eq. (1) are shown in Table II with the mean square uncertainty δ for the 77 and 201 K isotherms. The values $V_0=24.309$ cm$^3\cdot$mol^{-1} at $T=77$ K, $P=0.277$ kbar (Ref. 14) and $V_0=21.38$ cm$^3\cdot$mol^{-1} at 201 K, $P=6.362$ kbar (Ref. 7) were used.

Our results at 77 K are in good agreement (no worse than 0.3% in volume) with similar measurements up to 20 kbar.[2] These are the first results for the 201 K isotherm. There has recently been an x-ray study[3] of the compression of argon up to 80 kbar at 293 K in a diamond cell and the equation of state was calculated on the Debye approximation, taking account of zero-point vibrations. Comparison of this equation[1)] with high-accuracy results[2] and with our results shows a systematic disagreement outside the limits of experimental errors.

Figure 1 shows the P-T phase diagram of argon, on which are inserted the results[2] of isothermal experiments at 4.2; 20; 40 and 60 K, results of the present work at 77 and 201 K, the results[3] at 293 K for several fixed values of volume, and also isochore measurements at 22.11 cm$^3\cdot$mol^{-1}.[4] Results of work on the melting curve of argon[7,8,16] are also shown. It can be seen that our results at 201 K lie on straight lines joining points on the melting curve and on the 77 K isotherm with the same values of volume, while the results[3] at 293 K are shifted to smaller pressures relative to these straight lines. The inset to Fig. 1 shows the volume dependences of the slope of these lines $D=(\partial P/\partial T)_V$. Curve 1 is derived using results of Stishov and Fedosimov,[7] while curve 2 uses the results[8,16] for values of volume V_m along the melting curve. The existing results are insufficient for drawing definite conclusions about the temperature and volume dependence of the quantity D. Evidently, however, D is not a constant for $T>\Theta$ as has been indicated.[2,4,17]

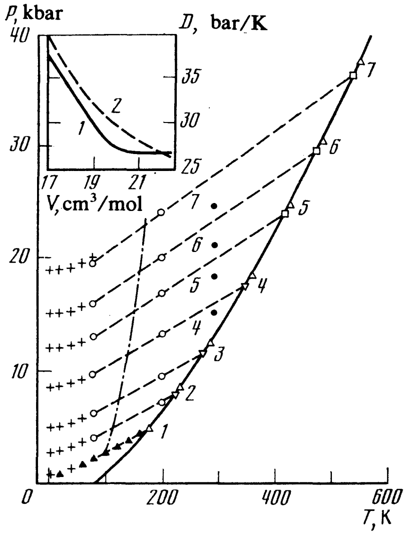

FIG. 1. Phase diagram of solid argon. The numbers 1 to 7 correspond to isochores at 22.11, 20.99, 20.14, 19.19, 18.5, 18.0 and 17.5 cm$^3\cdot$mol^{-1}. The melting curve is computed from the Simon formula.[15] The symbols correspond to experimental results: +) Anderson and Swenson,[2] ○) present work, ●) Finger *et al.*,[3] ▲) Lewis *et al.*[4]; results on the melting curve: △) Cheng *et al.*,[8] ▽) Stishov and Fedosimov,[7] □) Kechin[16] (extrapolation of Ref. 7). The dashed straight lines connect points on the melting curve with those on the 77 K isotherm at the same molar volume. The dash-dot line corresponds to the Debye temperature Θ. The inset shows the dependences of $D=(\partial P/\partial T)_V$, bar$\cdot$K^{-1}, on volume V, cm$^3\cdot$mol^{-1}; 1,2 results of the present work, see text.

It was established earlier[4] that the isothermal bulk modulus B_T of argon depended neither on temperature nor on pressure, but only on volume. This was later generalized to the other heavy inert gases krypton and xenon[3] in which the zero-point vibrations have, as in argon, little effect. The relation

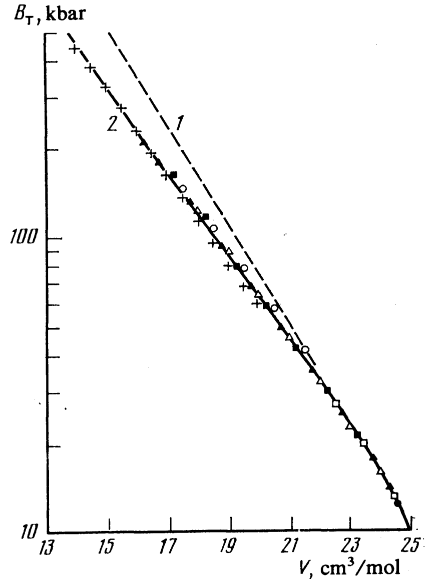

FIG. 2. Volume dependence of the isothermal bulk modulus B_T of solid argon. □) ultrasonic, $P=0$;[18] ●) Brillouin scattering, $P=0$;[19] ○,△) piston displacement, P up to 20 kbar, $T=4.2$ K and 77 K respectively[2]; ▲,■) piston displacement, P up to 30 kbar, $T=77$ K and 201 K respectively (present work); +) x-ray, P up to 80 kbar, $T=293$ K.[3] The dashed line 1 is drawn according to Eq. (2), the solid line 2 according to Eq. (3).

$$B_T = B_0 \exp(-AV), \tag{2}$$

has been proposed for argon,[4] with $B_0 = 1.852 \times 10^5$ kbar, $A = 0.391\ \mathrm{mol} \cdot \mathrm{cm}^{-3}$.

Results for the isothermal modulus $B_T(V)$ of argon obtained by various methods and under different conditions are collected together in Fig. 2. The results included here are: results of the present work up to 30 kbar and results up to 20 kbar for various temperatures, obtained by the piston displacement method; x-ray results[3] up to 80 kbar; ultrasonic measurements[18] and measurements using Brillouin scattering.[19] It can be seen from the figure that the experimental values of B_T obtained by different methods, at different temperatures and pressures, lie on one curve, confirming the conclusion that B_T depends to a first approximation only on volume. It can also be seen from Fig. 2 that Eq. (2) (the straight line in Fig. 2) is only satisfied over a narrow volume range. We propose instead of Eq. (2) an equation which describes the whole set of existing results:

$$B_T = B_0 \left[\frac{B_0'}{B'_\infty} \left(y^{B'_\infty} - 1 \right) + 1 \right], \tag{3}$$

where $V_0 = 22.557\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, $B_0 = 26.81$ kbar, $y = V_0/V$, $B'_0 = 7.92$, $B'_\infty = 5.1$ (curve 2 of Fig. 2).

[1)] We note that Finger *et al.*[3] used the value $B_0 = 23.701$ kbar for $V_0 = 22.557\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, in their calculations, quoting Peterson *et al.*,[14] although the latter give for B_0 the value 26.7 kbar.

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