

Equation-of-State Measurements in Compressed Argon*

R. K. CRAWFORD AND W. B. DANIELS

Department of Aerospace and Mechanical Sciences, Solid State and Materials Laboratory, Princeton University, Princeton, New Jersey 08540

(Received 4 December 1968)

A weighting technique used in obtaining experimental P - V - T data for argon at high pressures is described. The data for fluid argon at pressures from 0.2 to 6.3 kbar and temperatures from 95° to 210°K are presented, along with melting data for argon in this range. The entropy and energy of argon are derived from these data. Recent theoretical calculations are compared with the results, and a discrepancy between the calculated and experimental values for the energy is discussed.

INTRODUCTION

Probably the simplest fluids from the theoretical point of view are the noble gases, excluding helium, since these substances behave nearly classically in their fluid phases, and are thought to be describable in terms of relatively simple intermolecular forces. However, the theoretical treatment of the dense fluid phase and of the solid-fluid transition in these substances is still an extremely difficult task. The theoretical difficulties, coupled with the total lack of accurate experimental data over much of the temperature and pressure range of interest, have long discouraged any systematic study of the dense fluid phase or of the melting transition for these substances. Recently, the development of high-speed computers has made possible renewed theoretical efforts in these areas, but a thorough investigation over a wide range of temperatures and pressures has still been hindered by the lack of accurate experimental thermodynamic data for comparison with the theoretical calculations.

For this reason, an experimental method was developed to obtain such thermodynamic data for these substances over a wider pressure and temperature range than has previously been covered. This paper provides a description of this method and the results obtained for the fluid phase and the solid-fluid transition in argon at pressures from 0.2 to 6.3 kbar and temperatures from 95° to 210°K. Recent theoretical calculations agree reasonably well with these data although considerable room for improvement remains.

EXPERIMENTAL

In order to determine the molar volume of a fluid as a function of pressure and temperature, it is necessary to measure both the sample volume and the number of moles of the fluid present in the sample as functions of these variables. The measurement of the number of moles in the sample has caused difficulty in many of the previous P - V - T equation-of-state determinations for fluids at high pressures, so a somewhat different method for determining this quantity was employed in the present experiment.

In the method used for these measurements a pressure vessel is coupled to an external pressure system by means of very flexible pressure tubing, which in effect allows the vessel to be mechanically decoupled from the rest of the pressure system while still maintaining pressure communication with it. With the vessel thus mechanically decoupled, the weight of the fluid in it at various temperatures and pressures is determined by measuring the weight of the vessel and its contents, the weight of the empty vessel having been previously recorded. The number of moles in the sample is then obtained by dividing the weight of the fluid sample by the molecular weight of the fluid being studied. At the same time, the temperature of the vessel, and hence of the fluid sample, is controlled electronically and measured by sensors on the vessel, and the pressure is measured by means of a suitable pressure gauge at the other end of the flexible tubing.

Figure 1 shows the suspension system for coupling the pressure vessel to the analytical balance used in determining its weight. Details of this suspension system can be found elsewhere,¹ so only a few important features will be mentioned here. The electrical leads and the pressure tubing, which is hard-drawn stainless steel with 0.82-mm o.d. and 0.25-mm i.d., are brought to the vessel along the path ABCD in the figure. The sections AB and BC are each about 1.5 m long, so that the effect of the stiffness of the tubing upon the weight read at the balance is negligible. The portion BCD of the suspension is made rigid so that the vessel can be positioned directly beneath the balance by adjusting the movable support shown in the figure. This alignment, which is *essential* if the weight of the vessel and its contents is to be determined accurately, is checked by means of a calibrated weight which normally rests atop the vessel but which can be lifted free when desired.

Figure 2 shows details of the pressure vessel and the cryogenic apparatus. The pressure vessel itself is made of a hardened tool steel and has an estimated bursting pressure of about 10 kbar. It is about 15 cm long and 2.5 cm in diameter, with approximately 9-cm³

* Work supported by the National Science Foundation Grants GP-4916 and GP-7739.

¹ R. K. Crawford, doctoral thesis, Princeton University, 1968 (unpublished).

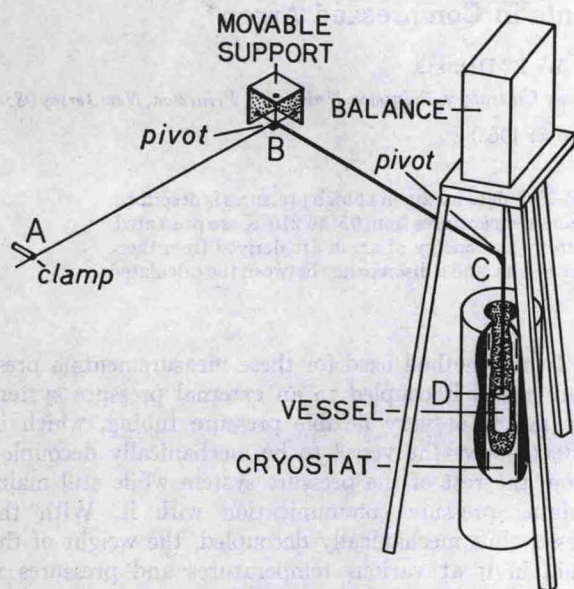


FIG. 1. Weighing apparatus.

internal volume. It is sealed by a standard Bridgman unsupported area seal using Teflon as the sealing gasket, with the pressure tubing silver-soldered into the "mushroom" part of the seal. A heater made of high-resistance wire is wound around the section of the pressure tubing which extends above the vessel

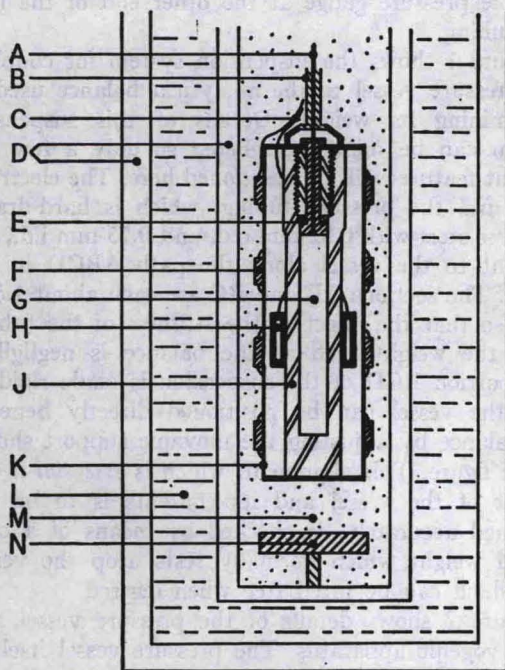


FIG. 2. Details of the pressure vessel and the cryogenic apparatus. A—pressure tubing; B—vertical portion of suspension (CD in Fig. 1); C—electrical leads; D—vacuum; E—Teflon high-pressure seal; F—heaters; G—sample volume; H—temperature sensor; J—pressure vessel; K—aluminum thermal enclosure for vessel; L—liquid nitrogen; M—dry nitrogen gas; N—heater for temperature gradient control.

and out of the cryostat. This heater serves to maintain the pressure tubing at a higher temperature than that of the vessel, thus preventing undesirable tubing blockage.

The temperature of the vessel is measured with small calibrated platinum resistance elements mounted in an aluminum collar which fits around the center of the vessel. The vessel temperature is controlled by adjusting the current through heaters mounted on the aluminum can which surrounds the vessel and is attached to it. The temperature gradient along the vessel is detected by means of a copper-constantan differential thermocouple between the ends of the vessel, and is controlled by adjusting the current through a heater mounted below the vessel.

The pressure vessel and attached devices are suspended in an atmosphere of dry nitrogen gas which is separated from the reservoir of liquid nitrogen by a partial vacuum. The dry nitrogen gas flows slowly into the bottom of the inner chamber of the cryostat

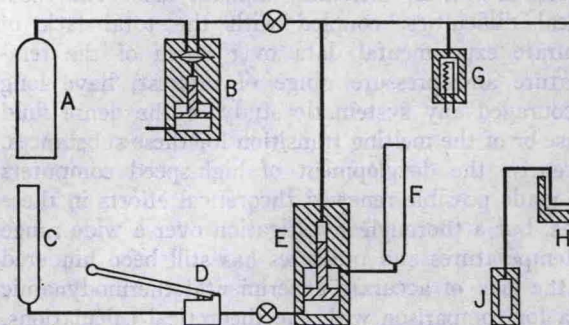


FIG. 3. Pressure system. A—argon supply; B—diaphragm gas pump; C—oil supply; D—oil pump; E—15:1 intensifier; F—oil reservoir used to indicate piston position; G—pressure gauge; H—cold trap; J—pressure vessel.

and out the top. This flow prevents any moisture which may be in the air in the room from entering the cryostat and condensing on the pressure vessel and the suspension. The flow is interrupted briefly whenever the weight of the vessel is to be determined, as otherwise the viscous drag of the gas flowing past the vessel would introduce a small error in the measured weight.

The pressure generating and measuring system is indicated schematically in Fig. 3. This system is leak free and reliable for gases at pressures of at least 7 kbar. A manganin resistance pressure gauge with a precision better than ± 0.5 bar was used to measure pressure in all the data runs in the fluid phase of argon. This gauge was calibrated at the freezing pressure of mercury at 273.15°K (7.5662 kbar²) and at the freezing pressure of argon at 113.648°K (1.32384 kbar³), with an accuracy estimated to be better than

² D. H. Newhall, L. H. Abbot, and R. A. Dunn, in *High Pressure Measurement*, A. A. Giardini and E. C. Lloyd, Eds. (Butterworths, Inc., Washington, D.C., 1963).

³ A. Michels and C. Prins, *Physica* **28**, 101 (1962).

TABLE I. Experimental argon melting data.

Temperature (°K)	Pressure (kilobars)	Molar volume (cm ³ /mole)		ΔV on melting (cm ³ /mole)
		Fluid	Solid	
94.73±0.02	0.451±0.007	27.30±0.02	24.34±0.02	2.96±0.02
94.74	0.459	27.31		
100.76	0.721	26.89		
108.12	1.051	26.52	24.02	2.50
110.77	1.186	26.32		
120.85	1.674	25.85	23.65	2.20
140.88	2.708	24.96	23.04	1.92
160.40	3.805	24.26	22.54	1.72
180.15	4.999	23.65	22.08	1.57
180.20	5.003	23.66	22.11	1.55
201.32	6.335	23.10	21.69	1.41

±1 bar at the lower pressures and ±4 bar at the higher pressures. Construction of this gauge had not been completed at the time the measurements on the solid-fluid phase transition in argon were made, so a Heise Bourdon-tube pressure gauge with somewhat lower sensitivity and accuracy was used in these measurements. The resulting lower accuracy in the determination of the melting pressures will soon be rectified by high-precision measurements of pressure versus temperature along the melting curve for argon and other substances, which are in progress in this laboratory.

The volume of the argon sample was determined by a method not commonly used, but which has several desirable features. In the "normal" data runs the weight of the fluid occupying the entire vessel was measured as a function of pressure and tem-

perature. In addition to these data runs another set of runs was made spanning the same pressure and temperature range, but this time with a solid iron cylinder filling most of the internal volume of the vessel. The difference between the weights of the fluid in the vessel at a given pressure and temperature with and without the iron cylinder in place is just the weight of a volume of the fluid equal to the volume of the iron cylinder at this pressure and temperature. Since this cylinder was subjected only to hydrostatic pressure, the small changes in its volume with pressure and temperature could be calculated accurately from the known equation of state of iron. Such a method for volume determination eliminates the need for assumptions concerning the behavior of a pressure vessel and its closure seals when the vessel is subjected to internal pressure. This is desirable since it was shown, at least for the pressure vessel being used in the present experiment, that the internal volume did *not* behave according to the usual assumptions.¹

PROCEDURE AND RESULTS

Using the apparatus and techniques described above, P - V - T data were obtained for argon (99.995% pure). These data consist of several isotherms, each of which is made up of a number of equilibrium P - V - T points. The procedure for each isotherm, after the system had been initially pressurized, was first to pump a small amount of argon into the vessel or to release a small amount from it. The system was then allowed to equilibrate before the values of the pressure in the system and the temperature and weight of the vessel were recorded. This process was then repeated to obtain a series of points along the isotherm. Immediately after all the points for a particular isotherm

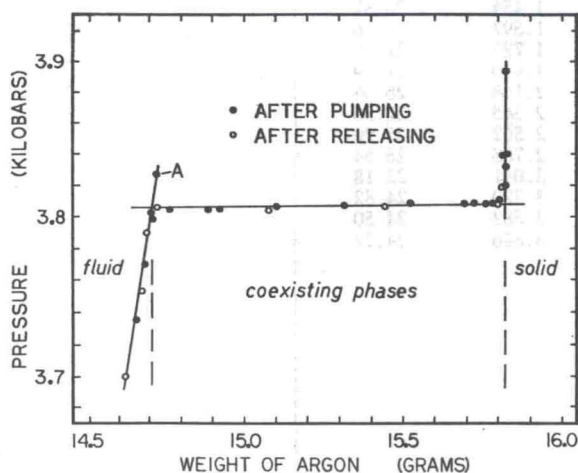


FIG. 4. Isotherm through the solid-fluid phase transition in argon. Point A indicates a pressurization into the supercooled region before the argon began freezing in the vessel.

TABLE II. Experimental P - V - T data for fluid argon (P is in kilobars; V is in cubic centimeters per mole).

210.16°K ^a		190.73°K		170.36°K		150.73°K	
P	V	P	V	P	V	P	V
0.209	61.45	0.203	51.55	0.209	42.37	0.212	36.79
0.277	51.60	0.277	44.99	0.280	39.30	0.274	35.44
0.360	45.77	0.348	41.66	0.347	37.50	0.341	34.35
0.437	42.71	0.418	39.49	0.422	36.02	0.416	33.38
0.515	40.43	0.483	38.02	0.489	35.00	0.489	32.62
0.598	38.68	0.559	36.72	0.560	34.14	0.573	31.91
0.702	37.04	0.633	35.67	0.634	33.39	0.664	31.25
0.782	36.03	0.729	34.56	0.719	32.67	0.753	30.68
0.884	34.98	0.824	33.68	0.820	31.93	0.854	30.12
0.977	34.15	0.938	32.79	0.930	31.23	0.984	29.50
1.072	33.43	1.044	32.08	1.051	30.57	1.112	28.96
1.195	32.61	1.174	31.33	1.178	29.96	1.255	28.45
1.315	31.92	1.299	30.72	1.311	29.42	1.412	27.95
1.420	31.41	1.432	30.14	1.458	28.88	1.575	27.50
1.552	30.78	1.565	29.63	1.634	28.33	1.754	27.05
1.734	30.06	1.728	29.07	1.829	27.78	1.958	26.63
1.939	29.38	1.935	28.46	2.015	27.33	2.153	26.25
2.146	28.75	2.136	27.93	2.220	26.89	2.369	25.86
2.355	28.22	2.346	27.45	2.434	26.50	2.605	25.48
2.530	27.81	2.552	27.03	2.648	26.10	2.840	25.14
2.759	27.33	2.776	26.61	2.914	25.69	3.115	24.77
3.035	26.83	3.026	26.18	3.179	25.31	140.94°K	
3.306	26.37	3.261	25.83	3.450	24.94		
3.577	25.99	3.554	25.42	3.726	24.62	P	V
3.839	25.61	3.835	25.07	4.000	24.31		
4.123	25.26	4.139	24.72	4.301	24.01		
4.462	24.88	4.478	24.37	160.47°K			
4.806	24.53	4.797	24.07				
5.143	24.22	5.134	23.78	P	V	0.208	34.84
5.484	23.95	5.486	23.50			0.291	33.53
5.823	23.67	5.561	23.43			0.380	32.47
6.160	23.42					0.459	31.75
6.464	23.20					0.537	31.14
201.29°K		180.21°K				0.632	30.52
						0.725	29.97
P	V	P	V			0.823	29.48
						0.924	29.05
0.205	57.20	0.203	46.62	0.203	39.60	1.059	28.53
0.275	48.50	0.275	42.05	0.263	37.63	1.173	28.13
0.348	44.12	0.352	39.29	0.346	35.81	1.308	27.71
0.416	41.55	0.424	37.52	0.409	34.79	1.445	27.33
0.493	39.48	0.487	36.39	0.469	34.01	1.589	26.98
0.554	38.24	0.553	35.40	0.540	33.24	1.756	26.58
0.624	37.08	0.634	34.45	0.626	32.47	1.939	26.21
0.731	35.69	0.724	33.55	0.728	31.69	2.114	25.88
0.838	34.58	0.831	32.67	0.833	31.02	2.310	25.55
0.941	33.68	0.935	31.95	0.939	30.42	2.524	25.22
1.041	32.95	1.053	31.23	1.053	29.88	2.720	24.95
1.163	32.18	1.160	30.67	1.184	29.30		
1.266	31.59	1.282	30.10	1.317	28.82		
1.401	30.93	1.406	29.60	1.454	28.37		
1.550	30.28	1.554	29.08	1.597	27.96		
1.716	29.66	1.749	28.46	1.728	27.59		
1.938	28.95	1.949	27.92	1.940	27.09		
2.355	27.86	2.152	27.43	2.148	26.64		
2.566	27.40	2.355	27.00	2.345	26.26		
2.768	27.01	2.558	26.61	2.562	25.90		
3.002	26.60	2.787	26.22	2.788	25.54		
3.249	26.20	3.038	25.81	3.041	25.18		
3.517	25.80	3.316	25.42	3.320	24.82		
3.791	25.44	3.573	25.09	3.582	24.50		
4.130	25.03	3.871	24.74	3.846	24.22		
4.458	24.67	4.136	24.44				
4.806	24.33	4.444	24.14				
5.150	24.03	4.738	23.86				
5.488	23.74	4.916	23.71				
5.824	23.47						
6.203	23.20						

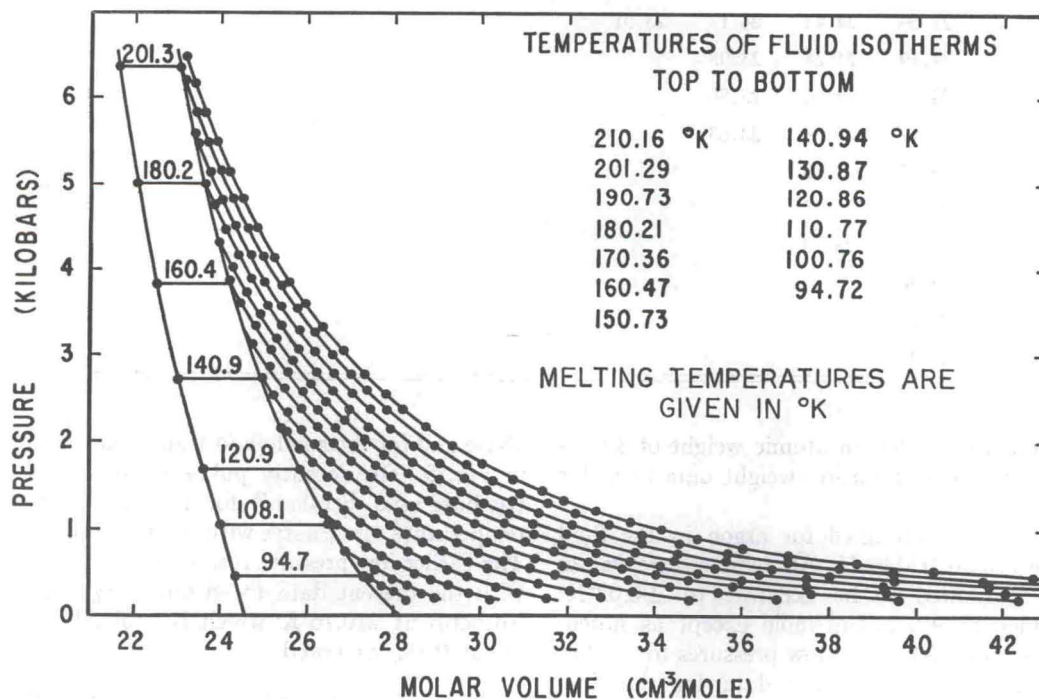
TABLE II (Continued)

130.87°K		120.86°K		110.77°K		100.76°K	
P	V	P	V	P	V	P	V
0.229	32.78	0.205	31.55	0.198	30.26	0.208	28.97
0.290	32.08	0.273	30.91	0.263	29.78	0.267	28.67
0.365	31.38	0.346	30.35	0.341	29.30	0.339	28.32
0.447	30.74	0.443	29.72	0.418	28.88	0.412	28.00
0.530	30.18	0.534	29.23	0.493	28.52	0.505	27.60
0.612	29.71	0.630	28.77	0.585	28.12	0.593	27.30
0.724	29.16	0.726	28.37	0.685	27.75	0.693	26.98
0.827	28.71	0.834	27.97	0.792	27.39	0.720	26.89
0.928	28.32	0.930	27.65	0.914	27.02		
1.038	27.94	1.059	27.25	1.031	26.70	94.72°K	
1.157	27.56	1.201	26.87	1.147	26.42	P	V
1.272	27.24	1.360	26.48				
1.442	26.80	1.662	25.85				
1.589	26.47						
1.740	26.15					0.211	28.32
1.909	25.84					0.273	28.03
2.083	25.52					0.345	27.74
2.133	25.45					0.426	27.43

^a Molar volume data for the isotherm at 210.16°K may be in error by as much as 0.3%.

had been obtained, the pressure was released to atmospheric pressure and the weight of the "empty" vessel at the temperature of the isotherm was recorded. After a small correction for the amount of argon in the vessel at atmospheric pressure this weight was then subtracted from the other total weights to give the weight of the argon in the vessel at each point.

The data for a typical isotherm through the solid-fluid phase transition are shown in Fig. 4. It can be seen that the transition is quite sharply defined so that it is possible to obtain accurate values for the molar volumes of the solid and fluid phases at melting. The values obtained for these quantities have been previously reported,⁴ but are repeated here in Table I

FIG. 5. P - V - T data for argon.

⁴ R. K. Crawford and W. B. Daniels, Phys. Rev. Letters **21**, 367 (1968).

TABLE III. Molar volume (in cubic centimeters per mole) of argon at round values of pressure and temperature.

P (kilobars)	T										
	200°K	190°K	180°K	170°K	160°K	150°K	140°K	130°K	120°K	110°K	100°K
0.20	57.15	51.68	46.80	42.81	39.55	36.93	34.78	33.01	31.47	30.13	28.94
0.40	41.83	39.84	38.02	36.36	34.85	33.46	32.17	30.98	29.90	28.91	27.99
0.60	37.28	36.01	34.81	33.68	32.64	31.62	30.63	29.70	28.83	28.00	27.21
0.80	34.80	33.82	32.90	32.03	31.19	30.34	29.53	28.76	28.02	27.31	
1.00	33.11	32.30	31.53	30.80	30.09	29.38	28.68	28.01	27.37	26.74	
1.20	31.85	31.15	30.47	29.83	29.21	28.59	27.98	27.39	26.82	26.26	
1.40	30.84	30.22	29.62	29.06	28.51	27.95	27.40	26.86	26.35		
1.60	30.01	29.46	28.92	28.41	27.91	27.41	26.90	26.41	25.93		
1.80	29.31	28.81	28.31	27.84	27.38	26.91	26.45	25.99			
2.00	28.70	28.24	27.79	27.35	26.94	26.50	26.06	25.62			
2.20	28.17	27.74	27.32	26.91	26.52	26.11	25.71	25.31			
2.40	27.70	27.30	26.91	26.52	26.15	25.77	25.37				
2.60	27.28	26.90	26.53	26.17	25.82	25.46	25.07				
2.80	26.89	26.54	26.19	25.85	25.51	25.17	24.81				
3.00	26.54	26.20	25.87	25.54	25.22	24.89					
3.20	26.22	25.90	25.57	25.27	24.96	24.64					
3.40	25.92	25.61	25.30	25.00	24.71						
3.60	25.64	25.34	25.04	24.75	24.47						
3.80	25.38	25.10	24.81	24.53	24.25						
4.00	25.14	24.86	24.58	24.31							
4.20	24.91	24.64	24.37	24.10							
4.40	24.69	24.43	24.17	23.91							
4.60	24.49	24.24	23.98								
4.80	24.30	24.06	23.80								
5.00	24.12	23.88	23.63								
5.20	23.95	23.70									
5.40	23.79	23.55									
5.60	23.62	23.38									
5.80	23.46										
6.00	23.32										
6.20	23.18										

for easy reference. (Note: An atomic weight of 39.944 for argon⁵ was used in reducing weight data to molar volumes.)

The P - V - T data obtained for argon in the fluid region are given in Table II. All temperature values quoted are estimated to be accurate to $\pm 0.02^\circ\text{K}$; molar volumes to $\pm 0.02 \text{ cm}^3/\text{mole}$ except as noted; and pressures from ± 1 bar at low pressures to ± 4 bar at the highest pressures. These data for the fluid

phase and for the solid-fluid transition are summarized in Fig. 5. The recently published results of van Witenburg and Stryland⁶ for a smaller pressure and temperature range agree with these data to about 0.4%. The earlier low-pressure results of Michels *et al.*⁷ agree with the present data to within 0.1% except for our isotherm at 210.16°K which is probably in error by about 0.3% as noted.

⁶ W. van Witenburg and J. C. Stryland, Can. J. Phys. **46**, 811 (1968).

⁷ A. Michels, J. M. H. Levelt, and W. de Graaf, Physica **24**, 659 (1958).

⁵ Handbook of Chemistry and Physics, C. D. Hodgman *et al.*, Eds. (Chemical Rubber Co., Cleveland, Ohio, 1964), 45th ed.

TABLE IV. Molar entropy (in joules per mole·°K) of argon at round values of pressure and temperature.

P (kilobars)	T										
	200°K	190°K	180°K	170°K	160°K	150°K	140°K	130°K	120°K	110°K	100°K
0.20	75.9 ^a	72.8 ^a	69.4 ^b	65.8 ^b	61.9 ^b	57.7 ^b
0.40	84.1 ^a	82.0 ^a	79.9 ^a	77.5 ^a	75.1 ^a	72.4	69.7	66.6	63.3	59.7	55.7
0.60	80.9	79.0	77.0	74.9	72.7	70.1	67.5	64.6	61.5	58.0	54.0
0.80	78.6	76.8	75.0	73.0	70.8	68.3	65.8	63.0	59.9	56.4	
1.00	76.8	75.1	73.4	71.4	69.3	66.8	64.3	61.6	58.5	55.1	
1.20	75.2	73.6	71.9	70.1	67.9	65.5	63.0	60.3	57.3	54.0	
1.40	73.9	72.4	70.7	68.9	66.8	64.3	61.9	59.2	56.3		
1.60	72.7	71.2	69.6	67.8	65.7	63.2	60.9	58.2	55.3		
1.80	71.7	70.2	68.6	66.8	64.7	62.3	59.9	57.3			
2.00	70.7	69.2	67.7	65.9	63.8	61.4	59.0	56.4			
2.20	69.8	68.4	66.8	65.1	63.0	60.5	58.1	55.6			
2.40	68.9	67.5	66.0	64.3	62.2	59.7	57.3				
2.60	68.2	66.8	65.3	63.5	61.5	59.0	56.5				
2.80	67.4	66.0	64.5	62.8	60.8	58.2	55.8				
3.00	66.7	65.4	63.9	62.2	60.1	57.6					
3.20	66.1	64.7	63.2	61.6	59.5	56.9					
3.40	65.4	64.1	62.6	60.9	58.9						
3.60	64.8	63.5	62.0	60.4	58.3						
3.80	64.2	62.9	61.4	59.8	57.8						
4.00	63.7	62.3	60.9	59.2							
4.20	63.1	61.8	60.3	58.7							
4.40	62.6	61.2	59.8	58.2							
4.60	62.1	60.7	59.3								
4.80	61.6	60.2	58.7								
5.00	61.2	59.7	58.2								
5.20	60.7	59.2									
5.40	60.2	58.7									
5.60	59.8	58.2									
5.80	59.3										
6.00	58.9										
6.20	58.4										

^a Obtained from Ref. 8.^b Obtained from Ref. 9.

THERMODYNAMIC ANALYSIS

Since the present results overlap with the lower pressure results of other workers, it is possible to use standard thermodynamic methods to calculate the entropy and energy of argon in the range covered by the present P - V - T data. The entropy can be calculated from the formula

$$S = S_0 - \int_{P_0}^P \left. \frac{\partial V}{\partial T} \right|_P dP \quad (1)$$

or from

$$S = S_0 + \int_{V_0}^V \left. \frac{\partial P}{\partial T} \right|_V dV, \quad (2)$$

while the energy can be calculated from the equation

$$U = U_0 + \int_{V_0}^V \left[T \left. \frac{\partial P}{\partial T} \right|_V - P \right] dV. \quad (3)$$

The derivatives and integrals can be evaluated by standard numerical procedures, and the low-pressure values S_0 and U_0 can be obtained from earlier low-

TABLE V. Molar energy (in joules per mole) of argon at round values of pressure and temperature.

P (kilobars)	T										
	200°K	190°K	180°K	170°K	160°K	150°K	140°K	130°K	120°K	110°K	100°K
0.20	-2334 ^a	-2748 ^a	-3128 ^b	-3549 ^b	-3970 ^b	-4387 ^b
0.40	-1055 ^a	-1383 ^a	-1716 ^a	-2055 ^a	-2398 ^a	-2760	-3105	-3426	-3796	-4173	-4558
0.60	-1483	-1772	-2066	-2366	-2676	-3014	-3332	-3624	-3968	-4323	-4685
0.80	-1766	-2031	-2301	-2578	-2874	-3197	-3499	-3771	-4099	-4441	
1.00	-1977	-2223	-2476	-2739	-3023	-3339	-3627	-3887	-4202	-4534	
1.20	-2146	-2377	-2614	-2864	-3141	-3450	-3730	-3980	-4286	-4610	
1.40	-2284	-2500	-2727	-2968	-3237	-3541	-3814	-4056	-4353		
1.60	-2397	-2603	-2820	-3054	-3317	-3618	-3884	-4118	-4408		
1.80	-2491	-2689	-2897	-3124	-3383	-3680	-3942	-4169			
2.00	-2572	-2762	-2964	-3184	-3440	-3736	-3994	-4213			
2.20	-2639	-2824	-3020	-3235	-3487	-3781	-4039	-4258			
2.40	-2697	-2878	-3069	-3277	-3527	-3822	-4078				
2.60	-2748	-2924	-3111	-3314	-3560	-3858	-4117				
2.80	-2790	-2965	-3147	-3346	-3588	-3888	-4152				
3.00	-2828	-2999	-3177	-3371	-3611	-3910					
3.20	-2862	-3029	-3203	-3393	-3631	-3928					
3.40	-2890	-3055	-3224	-3408	-3647						
3.60	-2916	-3075	-3242	-3422	-3653						
3.80	-2936	-3095	-3259	-3433	-3661						
4.00	-2952	-3110	-3271	-3441							
4.20	-2964	-3123	-3282	-3448							
4.40	-2976	-3135	-3292	-3455							
4.60	-2984	-3146	-3300								
4.80	-2992	-3156	-3310								
5.00	-2998	-3165	-3321								
5.20	-3005	-3171									
5.40	-3010	-3183									
5.60	-3013	-3186									
5.80	-3016										
6.00	-3016										
6.20	-3016										

^a Obtained from Ref. 8.^b Obtained from Ref. 9.

pressure work.^{8,9} Details of the calculational procedure used are available elsewhere¹ and will not be repeated here. The results obtained from these calculations, together with values of P and V numerically interpolated from Table II, are presented in Tables III through VIII. The entropies and energies given are

⁸ A. Michels, J. M. Levelt, and G. J. Wolkers, *Physica* **24**, 769 (1958).

⁹ F. Din, in *Thermodynamic Functions of Gases*, F. Din, Ed. (Butterworths Scientific Publications Ltd., London, 1962), Vol. 2.

"absolute" values, referenced to $S=0$ at $T=0^\circ\text{K}$ in the perfect crystal and $U=0$ at $T=0^\circ\text{K}$ in the ideal gas. The estimated accuracy of the tabulated entropies is ± 0.5 J/mole $\cdot^\circ\text{K}$, while the accuracy of the tabulated values of the energy is estimated to be ± 10 J/mole at temperatures above and including 140°K and as ± 70 J/mole at temperatures below 140°K . The greater uncertainty in the low-temperature values for the energy is due to the greater uncertainty in the initial values U_0 at these temperatures.

TABLE VI. Pressure (in kilobars) of argon at round values of molar volume and temperature.

V (cm ³ /mole)	T										
	200°K	190°K	180°K	170°K	160°K	150°K	140°K	130°K	120°K	110°K	100°K
42.0	0.395	0.335	0.273	0.212							
41.0	0.426	0.362	0.298	0.232							
40.0	0.463	0.394	0.327	0.257							
39.0	0.506	0.432	0.360	0.288	0.214						
38.0	0.557	0.478	0.401	0.324	0.245						
37.0	0.618	0.534	0.450	0.367	0.283						
36.0	0.691	0.601	0.510	0.420	0.331	0.240					
35.0	0.780	0.681	0.584	0.486	0.390	0.292					
34.0	0.887	0.780	0.675	0.569	0.464	0.357	0.247				
33.0	1.016	0.901	0.787	0.674	0.559	0.442	0.322	0.201			
32.0	1.173	1.048	0.926	0.805	0.680	0.551	0.419	0.285			
31.0	1.366	1.229	1.093	0.964	0.831	0.690	0.545	0.398	0.250		
30.0	1.603	1.455	1.307	1.162	1.019	0.866	0.708	0.547	0.384	0.218	
29.0	1.900	1.738	1.577	1.418	1.258	1.092	0.920	0.744	0.564	0.382	
28.0	2.270	2.094	1.916	1.741	1.569	1.384	1.195	1.004	0.807	0.601	0.397
27.0	2.743	2.548	2.353	2.157	1.971	1.761	1.557	1.345	1.129	0.904	0.667
26.0	3.346	3.132	2.915	2.702	2.491	2.265	2.034	1.796	1.564		
25.0	4.117	3.883	3.636	3.400	3.167	2.921	2.655				
24.0	5.143	4.863	4.578	4.304							

TABLE VII. Molar entropy (in joules per mole·°K) of argon at round values of molar volume and temperature.

V (cm ³ /mole)	T										
	200°K	190°K	180°K	170°K	160°K	150°K	140°K	130°K	120°K	110°K	100°K
42.0	84.2	83.4	82.6	81.7							
41.0	83.6	82.8	82.0	81.0							
40.0	82.9	82.1	81.3	80.4							
39.0	82.2	81.4	80.6	79.6	78.7						
38.0	81.5	80.7	79.8	78.9	77.9						
37.0	80.6	79.9	79.1	78.1	77.1						
36.0	79.8	79.0	78.2	77.2	76.2	75.0					
35.0	78.8	78.1	77.2	76.3	75.2	74.0					
34.0	77.8	77.0	76.2	75.3	74.2	73.0	71.9				
33.0	76.7	75.9	75.1	74.2	73.1	71.9	70.7	69.4			
32.0	75.4	74.7	73.9	73.0	71.9	70.6	69.4	68.1			
31.0	74.1	73.4	72.7	71.7	70.5	69.2	68.1	66.7	65.1		
30.0	72.7	72.0	71.3	70.3	69.1	67.8	66.5	65.1	63.5	61.7	
29.0	71.2	70.5	69.7	68.8	67.6	66.1	64.9	63.4	61.8	59.9	
28.0	69.5	68.8	68.1	67.1	65.8	64.4	63.1	61.6	59.8	57.9	55.7
27.0	67.6	67.0	66.2	65.2	64.0	62.4	61.1	59.5	57.8	55.7	53.5
26.0	65.6	64.9	64.1	63.2	61.9	60.3	58.9	57.3	55.5		
25.0	63.4	62.6	61.9	60.9	59.6	57.8	56.3				
24.0	60.8	60.0	59.3	58.4							

TABLE VIII. Molar energy (in joules per mole) of argon at round values of molar volume and temperature.

V (cm ³ /mole)	T										
	200°K	190°K	180°K	170°K	160°K	150°K	140°K	130°K	120°K	110°K	100°K
42.0	-1041	-1198	-1358	-1520							
41.0	-1126	-1280	-1441	-1607							
40.0	-1215	-1368	-1529	-1696							
39.0	-1310	-1461	-1621	-1788	-1943						
38.0	-1409	-1559	-1718	-1886	-2047						
37.0	-1514	-1663	-1819	-1986	-2154						
36.0	-1623	-1774	-1928	-2093	-2265	-2445					
35.0	-1741	-1888	-2044	-2207	-2381	-2567					
34.0	-1864	-2009	-2163	-2327	-2501	-2691	-2854				
33.0	-1992	-2135	-2288	-2453	-2628	-2822	-2991	-3129			
32.0	-2125	-2263	-2416	-2582	-2762	-2961	-3130	-3273			
31.0	-2262	-2396	-2544	-2713	-2900	-3102	-3277	-3423	-3623		
30.0	-2399	-2530	-2677	-2842	-3035	-3248	-3428	-3577	-3781	-3992	
29.0	-2533	-2663	-2810	-2976	-3171	-3393	-3579	-3733	-3940	-4158	
28.0	-2661	-2792	-2937	-3104	-3306	-3534	-3728	-3889	-4103	-4324	-4555
27.0	-2778	-2913	-3058	-3225	-3432	-3669	-3870	-4036	-4258	-4492	-4722
26.0	-2883	-3019	-3165	-3331	-3542	-3795	-4002	-4168	-4399		
25.0	-2959	-3102	-3245	-3408	-3628	-3901	-4127				
24.0	-3003	-3159	-3299	-3452							

TABLE IX. Thermodynamic functions of argon at the melting curve.*

T_m	P_m	V_{fl}	V_{sol}	ΔV_m	ΔS_m	S_{fl}	S_{sol}	U_{fl}	U_{sol}
100	0.687	26.94	24.22	2.72	12.1	53.4	41.3	-4733	-5750
110	1.146	26.39	23.96	2.44	11.5	54.3	42.8	-4590	-5580
120	1.630	25.89	23.66	2.23	11.0	55.2	44.1	-4415	-5380
130	2.136	25.42	23.38	2.04	10.5	55.9	45.3	-4243	-5180
140	2.662	25.01	23.07	1.93	10.4	56.3	45.9	-4126	-5070
150	3.210	24.62	22.80	1.82	10.2	56.9	46.7	-3929	-4870
160	3.781	24.26	22.54	1.72	10.0	57.8	47.8	-3660	-4610
170	4.374	23.94	22.31	1.63	9.9	58.3	48.4	-3454	-4420
180	4.987	23.66	22.10	1.56	9.6	58.3	48.7	-3319	-4270
190	5.614	23.38	21.90	1.49	9.4	58.2	48.8	-3187	-4130
200	6.250	23.13	21.71	1.42	9.1	58.3	49.2	-3016	-3950

* Temperature is in degrees Kelvin, pressure is in kilobars, volumes are in cubic centimeters per mole, entropies are in joules per mole·°K, and energies are in joules per mole.

Values for the entropy and energy of the fluid and solid phases at melting have been obtained by extrapolation of the above results, together with the data of Table I, and by use of Clapeyron's equation. These values are listed in Table IX. These tabulated values for S and U for both phases are estimated to be accurate to about 1%.

The isothermal bulk modulus $B_T = -V(\partial P/\partial V)_T$ and the thermal expansivity $\alpha = V^{-1}(\partial V/\partial T)_P$ were obtained for the fluid phase as by-products of the calculational procedure discussed above. The behavior of these quantities is indicated in Fig. 6. An attempt was also made to evaluate the specific heats C_P and C_V from the relationships $C_P = T(\partial S/\partial T)_P$ and $C_V = T(\partial S/\partial T)_V$. Unfortunately, the uncertainty in the tabulated values of the entropy is sufficiently large, compared to the changes in entropy over the temperature range investigated, that only rough estimates of C_P and C_V could be obtained. The values found for C_P ranged between 25 and 50 J/mole \cdot° K while those for C_V lay between 11 and 24 J/mole \cdot° K in the P - V - T range covered in this experiment.

DISCUSSION

Solid-Fluid Phase Transition

Perhaps the best-known theoretical model for melting is the Lindemann model, in which it is assumed that a solid melts whenever the *rms* amplitude of the thermal vibrations of a nucleus, $(\langle u^2 \rangle)^{1/2}$, reaches a certain critical fraction of the nearest-neighbor distance a . This leads to the Lindemann equation relating melting temperature T to solid molar volume V :

$$T/(M\theta^2 V^{2/3}) = C, \quad (4)$$

where θ is some temperature characteristic of the solid, M is the molecular weight, and C is a constant. When the Einstein model is used to calculate θ , and values for T and V are taken from Table I, the calculated values for the "constant" C range from 1.17×10^{-4} to 1.31×10^{-4} (g/mole) $^{-1}$ ($^\circ$ K) $^{-1}$ (cm 3 /mole) $^{-2/3}$ as the temperature changes from 94 $^\circ$ to 201 $^\circ$ K. This indicates that at 94 $^\circ$ K the solid melts when $(\langle u^2 \rangle/a^2)^{1/2} = 0.098$ while at 201 $^\circ$ K the solid does not melt until $(\langle u^2 \rangle/a^2)^{1/2} = 0.104$. Thus $(\langle u^2 \rangle/a^2)^{1/2}$ changes by 6% with a 100 $^\circ$ K change in melting temperature, while the "constant" C changes by 12% over this same range. Similar results have been obtained by Goldman,¹⁰ who used a more realistic model to calculate θ .

A number of additional melting models have been proposed over the years, but none has as yet proven entirely satisfactory.¹ The Monte Carlo calculations of Ross and Alder¹¹ give better agreement with the present melting data than do any other theoretical

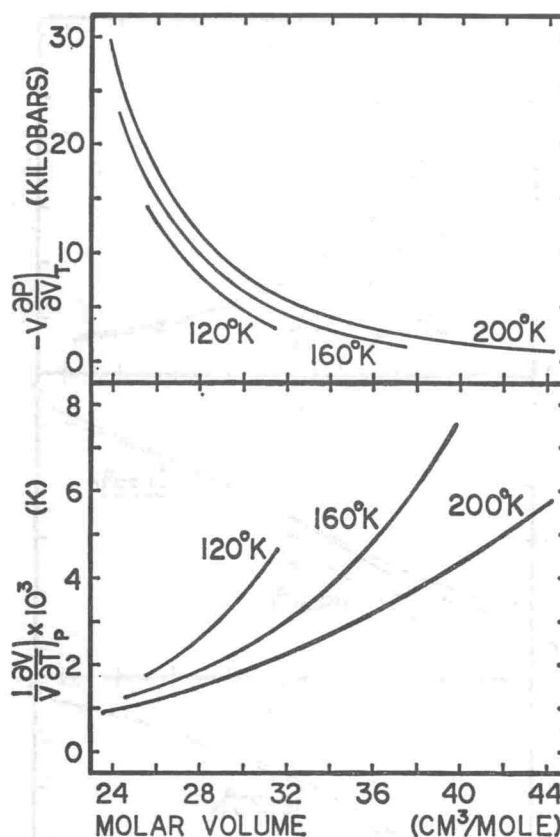


FIG. 6. Isothermal bulk modulus and thermal expansivity for argon in the fluid phase.

calculations. However, these still yield a solid molar volume which is more than 1% too great.

The authors have recently proposed a model for melting which is based on the behavior of a system of hard spheres.⁴ This model, which leaves no free parameters to be fitted to the melting data, is able to predict the solid and fluid molar volumes at the transition to better than 5% over the temperature range covered in this experiment. An added advantage of this model is that it clearly indicates the dependence of various qualitative features of the transition upon details of the intermolecular pair potential.

Fluid

Only three types of theories at present seem capable of satisfactorily representing the equilibrium behavior of argon in the dense fluid phase. These are the Monte Carlo¹² and molecular dynamics¹³ computer calculations, and the recently developed perturbation approach.¹⁴ A number of other theories have been pro-

¹² I. R. McDonald and K. Singer, *Discussions Faraday Soc.* **43**, 40 (1967); *J. Chem. Phys.* **47**, 4766 (1967).

¹³ L. Verlet, *Phys. Rev.* **159**, 98 (1967).

¹⁴ J. A. Barker and D. Henderson, *J. Chem. Phys.* **47**, 4714 (1967).

¹⁰ V. V. Goldman (to be published).

¹¹ M. Ross and B. J. Alder, *Phys. Rev. Letters* **16**, 1077 (1966).

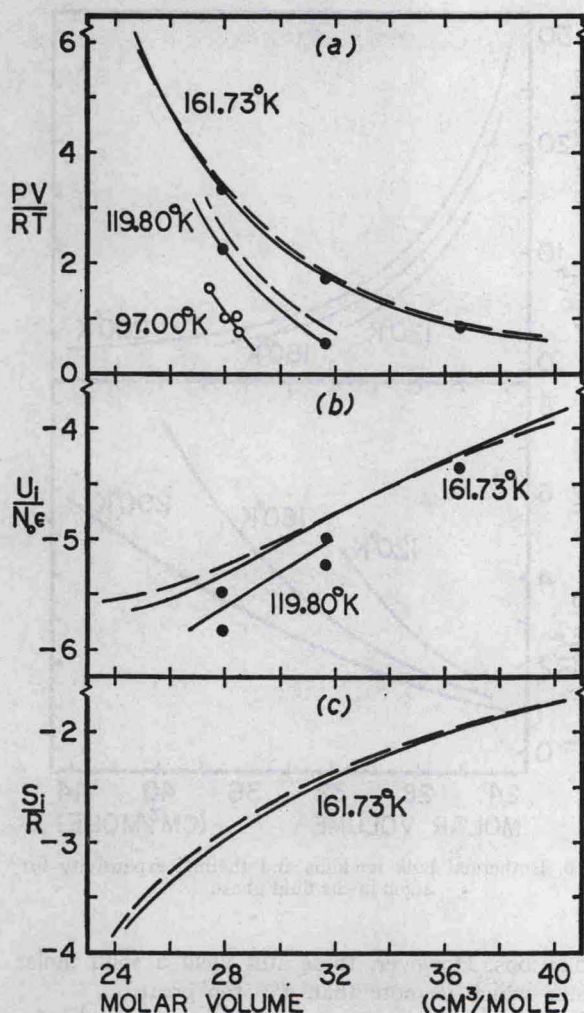


FIG. 7. Thermodynamic variables for argon: comparison with theory. The solid lines are experimental results interpolated from Tables VI through VIII. The open and solid circles result, respectively, from the Monte Carlo calculations of Ref. 12 and the molecular dynamics calculations of Ref. 13. The broken lines are the results of the perturbation calculations of Ref. 14. [The entropy and energy are given in dimensionless units defined by $S_i/R = [S - S(\text{ideal gas})]/R$ and $U_i/N_0\epsilon = (U - 3RT/2)/N_0\epsilon$ where R is the molar gas constant, ϵ is the depth of the intermolecular potential well, and N_0 is Avogadro's number.]

posed to represent the fluid phase, but these theories do not lead to good agreement with the experimental data at moderate and high densities. Since these other theories have been adequately reviewed elsewhere^{1,15,16} they will not be discussed here.

The Monte Carlo method consists of the generation of a chain of successive states of a system (represented by a particular intermolecular potential) in such a

manner that a given state will occur with a frequency proportional to its probability of occurrence in an ensemble, if the chain is sufficiently long. The thermodynamic properties of the system are then obtained by averaging appropriate quantities over such chains. The molecular dynamics method, on the other hand, involves the simultaneous solution of the equations of motion of a system of particles interacting with each other according to a given potential. Both of these methods are limited to calculations for a relatively small number of particles (1000 or less) because of speed and memory limitations of present-day computers. However the errors introduced by considering only a small number of particles are considerably lessened by the use of periodic boundary conditions, so that tests of the dependence of the calculated thermodynamic properties on the number of particles show that this dependence is relatively small for both kinds of calculations for systems of more than 100 particles. Both methods should lead to "exact" results for the particular potential used, subject to small statistical errors and small errors due to the boundary conditions. However, even on the present high-speed computers, such calculations require about an hour to obtain an accuracy of a few percent for one point on the equation of state of a system represented by a particular potential, so they cannot be considered to be entirely satisfactory as liquid theories. Nevertheless, at the present time, comparison of such calculations for different potentials with actual experimental data probably provides the best means of obtaining information about the intermolecular potential governing the behavior of dense fluids.

Up to now only a few machine calculations have been carried out in the volume and temperature range covered by the present experiment. In Fig. 7 the Monte Carlo results of McDonald and Singer¹² and the molecular dynamics results of Verlet¹³ are compared with isotherms obtained by interpolation from the present experimental data. These machine calculations were both carried out using the Lennard-Jones potential:

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad (5)$$

where ϵ gives the depth of the attractive well and σ is the distance at which the potential is equal to zero. The values $\epsilon/k = 119.8^\circ\text{K}$ and $\sigma = 3.405 \text{ \AA}$ obtained by Michels *et al.*¹⁷ from second virial coefficient data were used in both sets of calculations.

Figure 7(a) shows a comparison of the calculated and experimental values for the "compressibility factor" PV/RT . Here V is the molar volume and R is the molar gas constant. The molecular dynamics results show good agreement with the experimental

¹⁵ J. M. H. Levelt and E. G. D. Cohen, in *Studies in Statistical Mechanics*, J. De Boer and G. E. Uhlenbeck, Eds. (North-Holland Publ. Co., Amsterdam, 1964), pp. 107-239.

¹⁶ S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience Publishers, Inc., New York, 1965).

¹⁷ A. Michels, Hub. Wijker, and Hk. Wijker, *Physica* **15**, 627 (1949).

values over the entire range. Some of the calculated points lie as much as 5% below the experimental values, but since this is about the statistical uncertainty of the calculated points not much weight can be attached to this apparent disagreement. The Monte Carlo results show considerably more scatter, indicating that not all the chains generated were sufficiently long to obtain good equilibrium averages. Here also, the agreement with the experimental values is well within the statistical uncertainty of the calculations.

In Fig. 7(b) the calculated and experimental values for the "reduced molar internal energy" $U_i/N_0\epsilon$ are compared.

$$U_i/N_0\epsilon = (U - 3RT/2)/N_0\epsilon. \quad (6)$$

Here N_0 is Avogadro's number and U is the total energy per mole. The disagreement between the calculated and experimental energies is definitely greater than the expected statistical errors in the calculated values. The molecular dynamics calculations all yield values for the internal energy which are systematically more than 3% too low, while the maximum statistical error in the calculated values is expected to be less than 2%. This result can be explained by the assumption that the Lennard-Jones potential with the values used for the parameters is not quite appropriate for argon. The fact that the calculated energy is too low does not necessarily mean that the attractive part of the intermolecular potential used in these calculations is too deep. It may also be that this potential well is too wide, that is, that the attractive part of the potential does not approach zero rapidly enough with increasing distance. This latter interpretation is supported by the work of Mikolaj and Pings,¹⁸ who have managed to invert x-ray scattering data in argon at low densities to obtain a representation of the actual intermolecular potential for argon.

Recently another theoretical method for treatment of the fluid state has emerged. In this approach the behavior of a real fluid is represented as a perturba-

tion expansion about the behavior of a similar system of hard spheres, the perturbation being generated by the differences between the actual intermolecular potential and the hard sphere potential. The behavior of the hard sphere system can be calculated from analytical theories to a reasonable degree of accuracy even at high densities, due to the particular simplicity of the hard sphere interaction.

Calculations by Barker and Henderson¹⁴ with such a theory, using the Lennard-Jones potential with the same parameters as used in the computer calculations discussed above, show that the low-order perturbation terms are sufficient to give fairly good agreement with experiment. The results of their calculations are included in Fig. 7 for comparison. It can be seen that these calculations yield somewhat poorer agreement with the experimental data than is obtained from the molecular dynamics calculations, although the agreement is much better than has been obtained with any other *analytical* approach for which calculations have been carried out.

CONCLUSION

An experimental method has been developed and utilized to provide accurate P - V - T data for the dense fluid phase and for the solid-fluid phase transition in argon over a wide temperature and pressure range. A standard thermodynamic analysis has been applied to derive the entropy and energy from the experimental P - V - T data. The best calculations for the equilibrium thermodynamic behavior of the fluid phase were found to be in relatively good agreement with the experimental and derived thermodynamic data. However, indications were found that the Lennard-Jones potential used in the calculations does not quite represent the correct potential for argon. The Lindemann equation for melting was tested using the experimentally determined molar volumes of the solid at melting, and it was found that the Lindemann "constant" varied by about 12% over the range covered by the data. Extension of the method to higher pressures and temperatures and to gases other than argon is planned.

¹⁸ P. G. Mikolaj and C. J. Pings, Phys. Rev. Letters **16**, 4 (1966).