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·°K while those for C_V lay between 11 and 24 J/mole·°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:

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

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} $(\text{g/mole})^{-1}(°\text{K})^{-1}(\text{cm}^3/\text{mole})^{-2/3}$ as the temperature changes from 94° to 201°K. This indicates that at 94°K the solid melts when $(\langle u^2\rangle/a^2)^{1/2}=0.098$ while at 201°K the solid does not melt until $(\langle u^2\langle/a^2)^{1/2}=0.104$. Thus $(\langle u^2\rangle/a^2)^{1/2}$ changes by 6% with a 100°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 Alder[11] give better agreement with the present melting data than do any other theoretical calculations. However, these still yield a solid molar volume which is more than 1% too great.

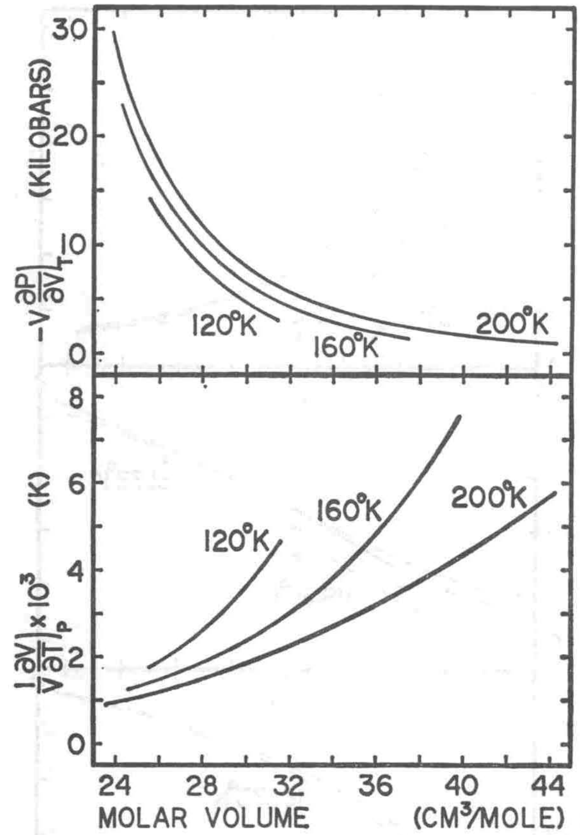

FIG. 6. Isothermal bulk modulus and thermal expansivity for argon in the fluid phase.

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 Carlo[12] and molecular dynamics[13] computer calculations, and the recently developed perturbation approach.[14] A number of other theories have been pro-

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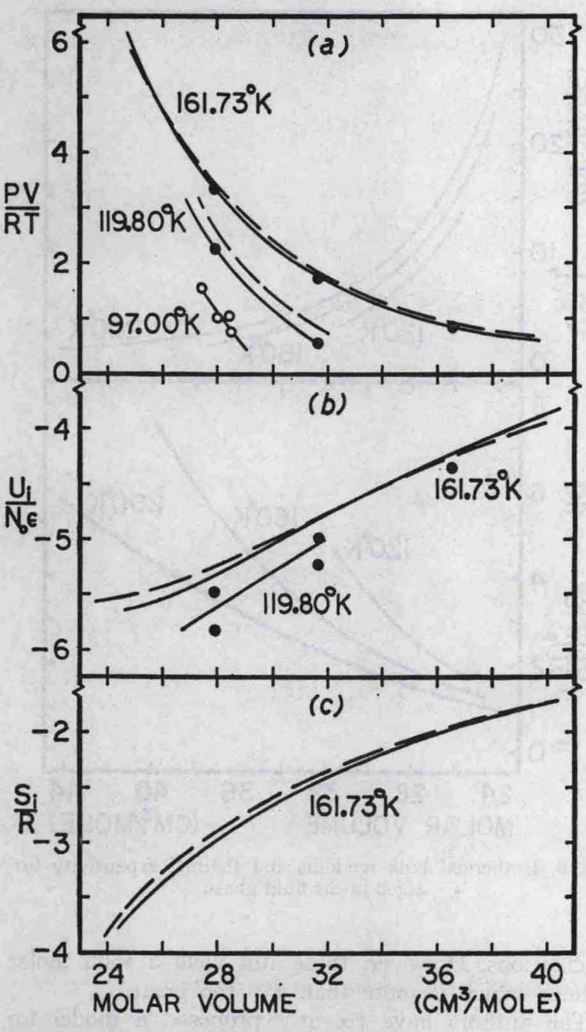

FIG. 7. Thermodynamic variables for argon: comparison with theory. The solid lines are experimental results interpolated from Tables VI through VIII. The open and solid circles result, respectively, from the Monte Carlo calculations of Ref. 12 and the molecular dynamics calculations of Ref. 13. The broken 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 Singer[12] and the molecular dynamics results of Verlet[13] are compared with isotherms obtained by interpolation from the present experimental data. These machine calculations were both carried out using the Lennard-Jones potential:

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

where ϵ gives the depth of the attractive well and σ is the distance at which the potential is equal to zero. The values $\epsilon/k=119.8°\text{K}$ and $\sigma=3.405$ Å 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

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