LETTERS TO THE EDITORS

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Density and Expansivity of Solid Argon

A FULL knowledge of the thermodynamic properties of some simple solid, such as a solidified inert gas, is necessary for the satisfactory development of a rigorous lattice dynamics. When a simple interatomic potential containing two constants is applied to a given substance (see, for example, Barron and Domb[1], Henkel[2]), it is necessary to know at least the density and energy of sublimation at absolute zero so as to determine the constants. In order to verify the theory in detail, it is then necessary to measure three independent quantities such as C_p, α and κ_s, where α is the volume expansivity and κ_s is the adiabatic compressibility.

For various reasons, argon is the most suitable substance for such a study; but until recently only one of the three coefficients, C_p, has been known accurately for the solid[3]. Last year, Stewart[4] determined the isothermal compressibility (κ_T) at 65° and 77° K. and Barker and Dobbs[5], in this laboratory, determined κ_s over the same temperature-range by an ultrasonic method. We have now measured the density between 20° and 80° K., and have thus obtained values of α.

Up to 60° K. we have used the X-ray method of measuring the lattice parameter by taking Debye–Scherrer 'powder' photographs. Details of the experimental arrangement as applied to metallic specimens at low temperatures are given elsewhere[6]; in the present work, a polycrystalline specimen of argon was deposited from the vapour on an aluminium wire subjected to precise temperature control. Recrystallization became evident at about 60° K., so that the method became increasingly inaccurate; and above this temperature we have determined the bulk density of polycrystalline specimens by finding the volume of gas at N.T.P. required to fill with solid argon a glass bulb of about 3 c.c. maintained at a given temperature. All the solid specimens used were transparent and free from visible flaws. The argon was stated by the British Oxygen Co., Ltd., to be of at least 99·999 per cent purity.

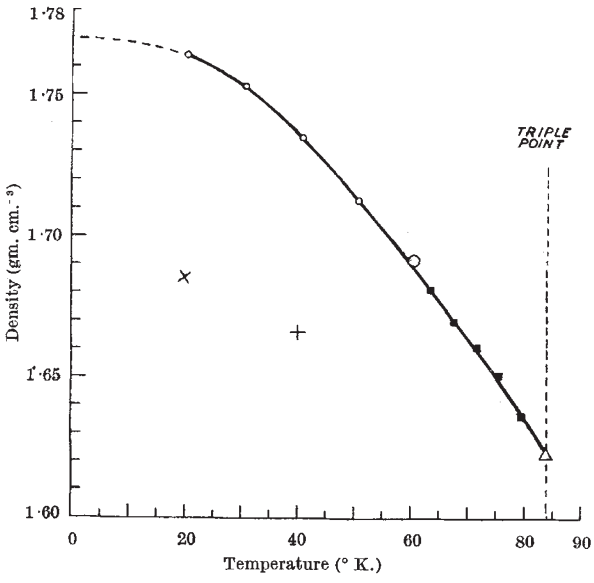

Fig. 1. Density of solid argon. Present results: ○, X-ray method. ■, bulk density method. Earlier results: △, Clusius and Weigand; ×, de Smedt and Keesom; +, Simon and von Simson

The results are shown in Fig. 1; it will be seen that the two methods give good agreement where they overlap, within our estimated accuracy of about 0·001 gm. cm.$^{-3}$. Our results differ appreciably from those of the X-ray measurements at single temperatures of de Smedt and Keesom[7] and Simon and von Simson[8], but agree with the value of the density at the melting point deduced by Clusius and Weigand[9] from observations of the melting curve and of the density of the liquid.

In the following table we summarize our results for the density (ρ), and give estimates at four temperatures of the expansivity and of the Gruneisen parameter $\gamma = \alpha V/\kappa_s C_p$.

T (° K.)	20	40	60	80
ρ (gm. cm.$^{-3}$)	1·764	1·737	1·691	1·636
$\alpha \times 10^4$ (deg.$^{-1}$ C.)	4	12	15	18
γ	2·0	2·7	2·8	2·4

The values of α, much larger than suggested by the previous independent measurements at three temperatures, account for the large difference between the results of Stewart for κ_T and those of Barker and Dobbs for κ_s, since the ratio $\kappa_T/\kappa_s = 1 + \alpha^2 TV/\kappa_s C_p$ rises to a maximum of 1·45 at the melting point. The large ratio (equal to C_p/C_v) also accounts for the unusually high value of C_p (8·5 cal. mole^{-1} deg.$^{-1}$ C.) found by Clusius[3] at the melting point, since C_v is now reduced to 5·9 cal.mole^{-1} deg.$^{-1}$ C., the classical value. The value of the Grüneisen parameter appears to go through a maximum, with an average value of about 2·5. More accurate experiments at the lower temperatures are required before the detailed form of this variation can be known.

It is important to note that our results lead to an estimate of the density at absolute zero of 1·77 gm. cm.$^{-3}$, corresponding to a lattice parameter of 5·31 A., as compared with the previously accepted value of 5·40 A.

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