Theoretical Calculations on Solid Argon

It is well known that a knowledge of the second virial coefficient of a gas does not suffice to specify the intermolecular potential of the constituent molecules. In fact, even if a simple formula of Mie–Lennard-Jones type is used as an approximation to the potential, the parameters are not uniquely determined by the second virial coefficient. On the other hand (as mentioned in the preceding communication) certain elementary properties of the solid state are sufficient to determine these parameters uniquely, and further observations on the solid and gaseous states can then be used as a test of the region of validity of this type of approximation to the potential. The recent development of experimental technique enabling data on the solid state to be determined with accuracy over a wide range of pressures and temperatures has provided valuable material for theoretical analysis.

When the isotherms for solid argon at high pressures determined by Stewart[1] at the Massachusetts Institute of Technology became available, one of us (I. J. Z.[2]) undertook detailed calculations to determine how the results compared with the theoretical predictions, and, if necessary, to modify the estimates of intermolecular potentials for the inert gases concerned. Although quite good agreement was obtained, the form of potential used was not completely satisfactory because of the uncertainty in the value of the density at absolute zero. The present accurate experimental results obtained at Queen Mary College for argon enable this uncertainty to be removed, and further detailed comparisons to be made between theory and experiment for this substance.

We have used the following approximation to the intermolecular potential energy :

$$\varepsilon(r) = \lambda/r^{12} - \mu/r^6$$
$$\lambda = 1\cdot63 \times 10^{-7}\ \text{A.}^{12}\ \text{erg.} \tag{1}$$
$$\mu = 1\cdot05 \times 10^{-10}\ \text{A.}^{6}\ \text{erg.}$$

To calculate the thermal expansion and Gruneisen's γ ($= \alpha V/\varkappa_T C_v$ or $\alpha V/\varkappa_S C_p$), we have used the approximation of Henkel[3]. This approximation is of Einstein type but takes account also of anharmonic effects ; it should be reliable at temperatures not too low compared with the Debye θ value. The results are as follows :

T (° K.)	20	40	60	80
ρ (gm. cm.$^{-3}$)	1·764	1·732	1·690	1·634
$\alpha \times 10^{4}$ (deg.$^{-1}$ C.)	4·6	10·5	14·6	20·0
γ	2·03	2·62	2·86	2·50

These are to be compared with the experimental values of the preceding communication.

It will be seen that the theoretical calculations are in good agreement with the experimental results. Calculations at higher pressures based on the above estimate of the intermolecular potential are also in good agreement with experimental isotherms given by Stewart[1]. A further check on the estimate of the potential is provided by the Debye θ value for solid argon at low temperatures. This can be calculated approximately and simply[4] for a potential of the form (1) and yields the value of 80° K., in good agreement with the experimental value derived by R. W. Hill[5] from measurements of the specific heat of solid argon at low temperatures. The values of λ and μ given in (1) are very close to those determined recently by Whalley and Schneider[6] from data for gaseous argon.

We may thus conclude that theoretical calculations of solid-state data based on the intermolecular potential (1) give results in reasonable agreement with experiment. Further experimental data, particularly at high pressures, would be desirable to provide a more searching test of the theory.

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Nuclear Spin of Americium-241

During the recording of the spark spectrum of americium[1] in the third order of the Baird three-metre grating spectrograph, a number of spectral lines appeared as four resolved components of a probable six-member flag pattern. While describing the performance of a 30-ft. Paschen–Runge spectrograph, Tomkins and Tomkins[2] have published a photograph of the Am I line at 6405 A. showing it resolved into six components. The six component flag patterns, which lead to a nuclear spin of 5/2 for $_{95}$Am^{241}, have been confirmed by interferometric studies.

In the present investigation americium was excited in a hollow cathode cooled with liquid nitrogen. High dispersion was achieved by crossing a Hilger Universal Prism spectrograph with Fabry–Perot étalon plates coated with $\lambda/4$ layers of cryolite and zinc sulphide. A series of different spacers were used for eliminating errors due to overlapping orders. Fig. 1 shows the six components of the Am I lines at 4662·80 and 4681·67, the separations between the components being 0·230 ± 0·0015 cm.$^{-1}$, 0·212 ± 0·001 cm.$^{-1}$, 0·184 ± 0·0015 cm.$^{-1}$, 0·147 ± 0·002 cm.$^{-1}$, 0·104 ± 0·003 cm.$^{-1}$, and 0·274 ± 0·001 cm.$^{-1}$, 0·226 ± 0·002 cm.$^{-1}$, 0·180 ± 0·001 cm.$^{-1}$, 0·138 ± 0·002 cm.$^{-1}$, 0·101 ± 0·002 cm.$^{-1}$, respectively.

Since these and other hyperfine separations show a marked divergence from the interval rule, a relatively large quadrupole-moment is expected for americium.

On the assumption that the $5f_{5/2}$ shell is filled preferentially to the $5f_{7/2}$, the value of a nuclear spin of 5/2 for $_{95}$Am^{241} is in accordance with Klinkenberg's[3] nuclear shell structure tables which are based on
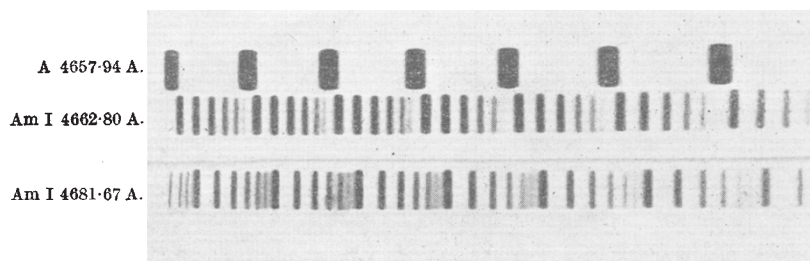

A 4657·94 A.

Am I 4662·80 A.

Am I 4681·67 A.

Fig. 1. Hyperfine structure of Am I lines at 4662·80 and 4681·67 A.