Second Virial Coefficient of He⁴ in the Temperature Range from 2 to 20 °K

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We present preliminary values for the second virial coefficient of He⁴ in the temperature range from 2 to 20 °K. They were derived from recent sound velocity measurements in the gas made by Plumb and Cataland using an ultrasonic interferometer.

Key Words: He⁴, low temperature, second virial.

In this communication we present values for the second virial coefficient of He⁴ in the temperature range from 2 to 20 °K. They were derived from recent sound velocity measurements in the gas made by Plumb and Cataland using an ultrasonic interferometer [1].[1] Our values for the virials must be considered as preliminary since the method for determining them from sound velocity data places such stringent demands on the numerical accuracy of the latter that it will be necessary to accumulate a much larger body of data than is now available to achieve more exact virials.

However, the problem of discrepancies existing between various provisional temperature scales below 20 °K is currently of strong interest [2] and contributes a note of urgency to the problem of obtaining new measured values of the second virial coefficient in this temperature range. Currently, the only values available are obtained either by extrapolating upward from the PVT data of Keller [3] in the 2 to 4 °K region, by relying on a very few points obtained by Keesom and Walstra [4] more than twenty years ago, or by using theoretical calculations based on assumed intermolecular potential functions. We thus believe that our values, although they must be regarded as tentative, are probably the best now available and may therefore prove useful as guides toward resolving the international temperature scale difficulties. Further measurements of sound velocity isotherms which should enable more accurate and reliable values to be determined are now in progress in this laboratory.

Isotherms of the speed of sound as a function of pressure were obtained [1] at pressures low enough that the isotherms could be represented by a linear relationship, $W^2 = C(1 + \alpha p)$, where W is the sound

velocity, $C = \frac{5}{3} RT/M$, and $C\alpha$ is the slope of the isotherm. The coefficient α is related to the second virial coefficient B by [5] the equation

$$\alpha(T) = (RT)^{-1}\left[2B + \frac{4}{3}TB' + \frac{4}{15}T^2B''\right]$$

where the primes denote differentiation with respect to T, the temperature. To obtain the second virial from the α's it is thus necessary to assume a functional form for $B(T)$ with coefficients to be determined, differentiate it twice, and determine the constants by least squares fitting of the data for $\alpha(T)$. This approximation of B by an arbitrarily chosen expression introduces a strong uncertainty in the results in addition to the uncertainties involved in determining the α's from the isotherms.

Many experimentalists have used the form $B = a + b/T$, and recent experience of two of the authors (MEB and SYL) [6] in fitting results of an accurate phase-shift calculation of B for He⁴, using a Lennard-Jones potential with deBoer parameters, indicates that this is a reasonable form in the temperature range of this data. However, curvature as a function of $1/T$ does become increasingly apparent for the L-J virials at about 20 °K, as well as at the low T end.

Using, then, $B = a + b/T$ we find the results shown in table 1. An idea of the accuracy may be obtained by both observing the changes in the results when fitting to different temperature ranges separately and by noting the effect of adding additional terms in the functional form for B. Of these two types of changes the first is the least serious in its effects on the results. Comparing the virials obtained when fitting the middle temperature range to those obtained fitting the high and low ranges separately we find them to differ by

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Second virial coefficient of He⁴ from 2 to 20 °K*

Range fitted	Derived formula for B	σ_α	B calculated from derived formula (cm³/mol)				
			2 °K	4 °K	10 °K	16 °K	20 °K
2–10 °K	$(21.28 \pm 0.46) - (449.2 \pm 3.2)/T$	1.30	-203.3	-91.0	-23.64	....	....
	$(19.6 \pm 1.1) - (422 \pm 17)/T - \dfrac{(69 \pm 42)}{T^2}$	1.19	$-209.$	-90.0	-23.3	....	....
	$(24.4 \pm 2.3) - (459.9 \pm 8.3)/T - (0.18 \pm 0.13)T$	1.23	-205.9	-91.3	-23.4	....	
11–20 °K	$(17.00 \pm 0.20) - (379.1 \pm 5.0)/T$	0.25	....	....	-20.91	-6.69	-1.96
	$(14.30 \pm 0.71) - (246 \pm 34)/T - \dfrac{(1223 \pm 314)}{T^2}$	.15	....	....	-22.5	-5.8	-1.1
	$(22.6 \pm 1.3) - (446 \pm 25)/T - (0.111 \pm 0.026)T$	.15	....	....	-23.1	-7.1	-1.9
4–16 °K	$(19.43 \pm 0.24) - (430.3 \pm 3.1)/T$	.73	-195.8	-88.2	-23.60	-7.46	-2.08
	$(17.60 \pm 0.39) - (378 \pm 11)/T - \dfrac{(235 \pm 47)}{T^2}$	.42	$-230.$	-91.6	-22.6	-6.9	-1.9
	$(23.40 \pm 0.73) - (455.1 \pm 4.8)/T - (0.131 \pm 0.024)T$	.39	-204.5	-90.9	-23.42	-7.14	-1.98

amounts varying from about 7 cm³/mol at 2 °K down to about 0.1 at 20 °K.

Introduction of another term in the expression for B, can, depending on the particular form, lead to drastically differing results, even though the standard deviations (σ_α) for the fitting of α are similar. This is illustrated in table 1. Thus it would appear that the fitting of more complicated expressions for B than the simple 2-constant function used here cannot be justified unless either more extensive data are available or a strong theoretical justification of a particular functional form for $B(T)$ can be made.

References

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