

that determined by conduction is of the order of 0.4 cm, and thus may certainly be neglected.

The calculations given above for C<sup>13</sup> are based on the value  $\alpha=0.0106$  which is given by Eq. (3). This equation is, however, only a rough guess, albeit the best one possible. It may be found by experiment that the actual values of  $H$  and  $A$  for any given gas are distinctly different from those calculated from values of  $\alpha$  given by (3), perhaps by as much as a factor 2. In practice, therefore, it will be necessary to do some preliminary work to find the actual value of  $\alpha$ . It is suggested that this be done by running the apparatus at a fairly high pressure. For instance, in the example just discussed, the use of a pressure of two atmospheres instead of one will multiply  $H$  by 4, and divide  $A$  by approximately 4, so that the separation factor will be small, but so will also be the equilibrium time. If one now measures  $c_1^1$  as a function of the time, one will obtain the values of both  $H$  and  $A$ . Either one will yield the value of  $\alpha$ , by (30), or by (31),

(32) and (33). We may now extrapolate  $A$  to the desired value by changing the pressure, since we know that  $H, A$  and  $K_d/K$  vary, respectively, as the second, inverse second, and inverse fourth power of the pressure.

Preliminary adjustments such as those just described will of course be necessary only in the first work on each gas. Once the correct value of  $\alpha$  is known from experiment, our equations should make it possible to design apparatus which will perform in acceptable agreement with specifications.

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### Calculation of the Second Virial Coefficient of Helium Gas for the Lowest Measured Temperature

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IN RECENT articles<sup>1</sup> an explicit and calculable expression has been derived for the second virial coefficient of a monatomic gas. This is the  $B$  in the equation of state,

$$pV/RT = (1 + B(T)/V + C(T)/V^2 + \dots)$$

and, assuming the Einstein-Bose statistics, is given by the formula,

$$B_{E.B.} = -\frac{N\pi^3\lambda^3}{2} - 16N\pi^3\lambda^3 \sum_{n, \text{ even } l} (l + \frac{1}{2}) \times \exp[\lambda^2 k_0^2(n, l)/a_0^2] - 16\pi^3 N\lambda^3 \sum_{\text{even } l} (l + \frac{1}{2}) \int_0^\infty dk_0 \times \exp[-\lambda^2 k_0^2/a_0^2](d\eta_l/dk_0). \quad (1)$$

Here,  $\lambda^2 = \hbar^2/mkT$ ,  $\eta_l$  is the phase found from the wave equation for the relative motion of two radially interacting molecules,

$$\frac{d^2v}{d\rho^2} + \left( k_0^2 - \frac{m}{\hbar^2} a_0^2 V - \frac{l(l+1)}{\rho^2} \right) v = 0.$$

$k_0^2(\eta, l)$  are the discrete states for two such molecules,  $a_0$  is the Bohr radius, and  $V$  is the interaction potential between the two molecules.

Extensive calculations have recently been made with formula (1) by Massey and Buckingham<sup>2</sup> on the inert gases, in particular, helium. These calculations are based on the use of the Slater-Kirkwood potential for the calculation of

<sup>1</sup>E. Beth and G. E. Uhlenbeck, *Physica* **4**, 915 (1937); L. Gropper, *Phys. Rev.* **51**, 1108 (1937).

<sup>2</sup>H. S. W. Massey, and R. A. Buckingham, *Proc. Roy. Soc.* **168**, 378 (1938).

TABLE I. Comparison of analytical values of  $\eta_0$  with those found by numerical integration.

$k_0$	ANALYTICAL $k_0$	NUMERICAL $\eta_0$
$\frac{2}{3}$	-1.76	-1.8212
0.1	+1.66	+1.6480
0.02	+2.78	+2.7816
0	$\pi$	-

the phases for helium. In this paper we use the Slater-Margenau potential, which presumably takes into account all the more important Van der Waals' forces.

To compare (1) with the experimental values at low temperatures it is advisable to consider the case of helium because: 1. extensive low temperature measurements have been made with helium; 2. helium remains a monatomic gas down to the lowest temperatures ( $T \cong 4^\circ\text{K}$ ); 3. the statistical wave-length of the helium molecule,  $\lambda = (\hbar^2/mKT)^{1/2}$ , is relatively large because the mass is so small, and the larger the wave-length the more pronounced should be the quantum effect; 4. the potential between two helium molecules has been theoretically calculated, so that, in principle at least, one should be able to deduce the experimental results solely from theory.

A comparison of (1) was made for the case of the lowest temperature for which  $B$  has been determined; namely,  $T = 3.708^\circ\text{K}$ . At this temperature the experimental value of  $B$  for a cubic centimeter of helium is,  $-4.17 \times 10^{-3}$  cc<sup>3</sup> so that for a mole  $B = -93.6$  cc.

The phases  $\eta_l$  were calculated by using the Slater-Margenau potential<sup>4</sup> in the region where  $V$  is presumed to be valid, and joining

$$V = \left\{ 7.7e^{-2.43\rho} - \left( \frac{0.68}{\rho^6} + \frac{5.37}{\rho^8} + \frac{28.4}{\rho^{10}} \right) \right\} \times 10^{-10} \text{erg}$$

with an expression  $a/\rho^2 - b$  for small values of  $\rho$  down to  $\rho = 0$ . The reason for this choice of joining-on function is that it leads to Bessel functions for the solution of the wave equation, and these are tabulated. This joining on process could not appreciably alter the results, for the energies considered in the integral of (1) were

very small, and over this region of small energies  $V$  and  $a/\rho^2 - b$  practically coincided.

Before discussing the contribution to (1) from the  $l=0$  term we shall investigate how many terms of the sum on  $l$  must be taken along at the lowest temperatures ( $T \cong 4^\circ\text{K}$ ). For sufficiently low temperatures the integrand in (1) will be appreciable only for very small  $k_0$  say,  $\lambda k_0/a_0 \leq 1$ , because of the presence of the exponential. But for small  $k_0$  and sufficiently large  $l$  the distance of closest approach will be well beyond the point where the potential is appreciably different from zero. Hence the phase shifts will be zero for such values of  $l$ . The question is what is meant by sufficiently large  $l$ ? It was found that already for  $l=4$ , the distance of closest approach for an energy such that  $\lambda k_0/a_0 = 1$  was  $\rho = 14.8$ , far beyond the point where  $V$  is appreciably different from zero. For values of  $k_0$  such that  $\lambda k_0/a_0 < 1$  the distance of closest approach will be still farther out. And for values of  $k_0$  such that  $\lambda k_0/a_0 > 1$  the integrand in (1) rapidly diminishes because of the exponential. Hence the phases for  $l=4, 6$ , etc. at the low temperature  $T = 3.708^\circ\text{K}$  may be neglected.

On the other hand, the phases for  $l=2$  are not negligible. This can be understood if one plots  $(a_0^2 m V / \hbar^2 + l(l+1)/\rho^2)$  for  $l=2$ . One finds a very low broad maximum, 0.05. For all  $k_0^2 \geq 0.05$  the molecule will pass over the hump into the potential field, and one should expect considerable positive phase shift when one realizes that the depth of  $a_0^2 m V / \hbar^2$  is very large compared to this energy; namely, it is 0.36 as compared to  $k_0^2 = 0.05$ . Further, since values of  $k_0^2$  considerably larger than 0.05 may be allowed before the exponential in (1) is negligible, one might then expect, qualitatively, that the contribution for  $l=2$  is considerable. As a matter of fact it amounts to  $-91.3$  at  $T = 3.708^\circ\text{K}$ . This result was obtained by first integrating (1) by parts. One gets for  $l=2$

$$-40\pi^3 \lambda^3 N [\eta_2 \exp(-\lambda^2 k_0^2/a_0^2)]_0^\infty - 40\pi^3 \lambda^3 N \frac{2\lambda^2}{a_0^2} \int_0^\infty \exp(-\lambda^2 k_0^2/a_0^2) k_0 \eta_2 dk_0.$$

Now  $\eta_2(0) = 0$  since there is no penetration as  $k_0 \rightarrow 0$ . Hence the integrated part of (1) vanishes. The remainder of (1) was evaluated by trape-

<sup>3</sup> Van Itterbeek, Leiden Comm., Supp. 70C (1932).

<sup>4</sup> H. Margenau, Phys. Rev. 38, 742 (1931).

zoidal integration with the help of the following calculated phases

$\eta_2$	0	0.163	0.560	0.849	0.583	0.300
$\kappa_0$	0	0.2	0.3	0.4	0.5	$\frac{2}{3}$

Since the integration was carried out with such a few phases, a partial test of the error made through trapezoidal integration was carried out by employing parabolic integration. There was only about one percent difference in the results.

We return to the contribution for  $l=0$  and a discussion of the discrete states. It was found that the Slater-Margenau potential was just deep enough to accommodate one discrete level ( $n=0, l=0$ )  $k_0^2=0.0051$ . This discrete contribution came to  $-148$  cc.

For the continuous contribution with  $l=0$ , the phases were calculated analytically, as well as numerically, by passing a Morse potential very accurately through the Slater-Margenau potential. This analytic expression for the phases is rather complicated and is the form of an infinite series, which, however, is rapidly convergent for small  $k_0$ . In any case the numerical and analytic values were almost identical. The important range of values of  $k_0$  was between zero and about two-thirds. Above that the factor  $\exp(-\lambda^2 k_0^2/a_0^2)$  cuts out the contribution to the integral. In Table I some analytic values of  $\eta_0$  are compared with those found by numerical integration. This

table includes the extremes of the range. Enough values of  $\eta_0$  were found to make the integration of (1) after first integrating by parts and noting that  $\eta_0(0)=\pi$ . This gave a contribution of  $+125$ . This together with the contributions from the  $l=2$  term, the discrete term, and the pure Bose term, the net result for the second virial coefficient at  $T=3.708^\circ\text{K}$  was found to be  $B=-123$ . Comparing this with the experimental result  $-93.6$ , one sees that there is about a thirty percent discrepancy. Since we estimate the numerical work to be within an error of 10 percent it is clear that the potential must be altered.

It is necessary to decrease either the depth or the range or both. This would have the double effect of raising towards zero the discrete energy and decreasing the positive phases. Both effects would contribute to making the virial coefficient less negative. While one cannot make quantitative statements about the potential one can, however, now set certain limitations on it. It must lie somewhere between the Slater-Kirkwood potential which gives a smaller well, and the Slater-Margenau potential. It cannot be smaller than the former, for the former does not take into account all the Van der Waals' forces. And it cannot be larger than the latter, since the latter already gives too large a negative virial coefficient.