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Second Virial Coefficients of He^3 and He^4†

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The second virial coefficients of He^3 and He^4 have been calculated at closely spaced temperatures over the range 0.3°K to 60°K using the Lennard-Jones 12–6 potential with constants determined by de Boer and Michels. The necessary phase shifts were calculated on a high-speed electronic digital computer. The resulting He^4 second virial coefficients agree very well with the available experimental data. They also join nicely at 60°K with the coefficients calculated from the high-temperature classical equation with quantum corrections. The second cross virial coefficients for He^3, He^4 have also been calculated. The deviation of a gaseous solution of He^3 and He^4 from an ideal solution is comparatively small at temperatures above about 2°K, while at very low temperatures pronounced quantum solution imperfection appears.

I. INTRODUCTION

THE second virial coefficient of He^4 at low temperatures has been calculated by Massey and Buckingham[1] and by Buckingham, Hamilton, and Massey,[2] from several intermolecular potentials, the constants of which are theoretical or semitheoretical in origin. A similar calculation has been made by de Boer and Michels[3] with the Lennard-Jones 12–6 potential. The constants of this equation were determined empirically by fitting the high-temperature statistical equations (with quantum corrections) to experimental (above 50°K) virial coefficient data. Of these several calculations, that of de Boer and Michels best fits the experimental low-temperature virial coefficient data. The same Lennard-Jones potential has also been used by de Boer, van Kranendonk, and Compaan[4] to calculate the second virial coefficients of He^3. There are as yet no experimental data in this case.

The most difficult and lengthy part of such a calculation is the determination of the very large number of phase shifts needed to describe the binary atomic collision. Most of the phase shifts given by de Boer and co-workers[3,4] were determined by numerical integration of the one-dimensional radial Schrödinger equation with the Lennard-Jones potential. Relatively few details are given of the numerical technique used, so that it is difficult for one to judge the probable accuracy of the calculation. However, it is safe to assert that at least a lifetime of work on a desk calculator would be needed to achieve moderately high accuracy in the results. This problem obviously calls for the use of a modern high-speed digital computer.

Although one observes that the second virial coefficients of de Boer and Michels[3] for He^4 are a pretty good representation of the experimental results, we decided to recalculate these coefficients for He^4 and He^3, using constants given by de Boer and Michels[5] for the Lennard-Jones potential, for two reasons: (1) to establish how much of the small deviation of the previous work[3] from the experimental data is due to the potential and how much is due to accumulated numerical error, and (2) to extend the temperature range of the calculated second virial coefficients. In addition, we have calculated the cross He^3, He^4 coefficients using the same Lennard-Jones potential.

II. THEORY

The equation of state of a gas may be expressed in either the pressure or the inverse volume expansion:

$$Pv=RT+BP+CP^2+\cdots, \tag{1}$$

$$Pv=RT(1+B'/v+C'/v^2+\cdots, \tag{2}$$

where $B=B'$ is the second virial coefficient ($C\neq C'$, etc.). In this section the method used to obtain B will be briefly developed inasmuch as the several aspects of this theory have not been consolidated in the earlier literature. In Part (a), an expression for B in terms of the density of energy levels for an ideal gas relative to that for a real gas is derived from the statistical mechanical relationship for B. In Part (b), the potential energy between the two particles is inserted into the radial wave equation from the solution of which one obtains the relative energy density. In Part (c), the results of the quantum-mechanical operations are introduced into the formula for B.

(a) Transformation of the B Equation

The statistical mechanical expression for B is given by[6]

$$B=-NV(Z_2-\tfrac{1}{2}Z_1^2)/Z_1^2, \tag{3}$$

where N is Avogadro's number, Z_1 is the partition function for one molecule, and Z_2 is the partition function for two molecules. This expression is correct

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[1] H. S. W. Massey and R. A. Buckingham, Proc. Roy. Soc. (London) **A168**, 378 (1938); **A169**, 205 (1939).

[2] Buckingham, Hamilton, and Massey, Proc. Roy. Soc. (London) **A179**, 103 (1941).

[3] J. de Boer and A. Michels, Physica **6**, 409 (1939).

[4] de Boer, van Kranendonk, and Compaan, Phys. Rev. **76**, 998 (1949); **76**, 1728 (1949); Physica **16**, 545 (1950).

[5] J. de Boer and A. Michels, Physica **5**, 945 (1938).

[6] J. E. Kilpatrick, J. Chem. Phys. **21**, 274 (1953).

both quantum-mechanically and classically. Z_1 is given by

$$Z_1 = (2s+1)\lambda^{-3}V, \tag{4}$$

where[7]

$$\lambda^2 = h^2/2\pi mkT, \tag{5}$$

and s is the nuclear spin.[8]

In the following discussion we shall use the term "ideal" to refer to a hypothetical gas identical with the real gas except that the potential of interaction is zero for all distances. Properties of such a gas will be denoted by attaching an asterisk to the appropriate symbols. It is convenient to divide B into two parts, B^* and $B-B^*$. Equation (3) then takes the form

$$B = \mp\frac{2^{-5/2}N\lambda^3}{2s+1} - \frac{N\lambda^6(Z_2-Z_2^*)}{(2s+1)^2V}. \tag{6}$$

The sign of the first (ideal gas) term is negative for a Bose-Einstein gas and positive for a Fermi-Dirac gas. In general

$$Z_2 = \sum{}' e^{-E/kT} = Z_{2(\mathrm{trans})}\cdot Z_{2(\mathrm{rel})} = 2^{\frac{3}{2}}\lambda^{-3}V\cdot Z_{2(\mathrm{rel})}, \tag{7}$$

where the prime on the summation indicates it is to be taken over all quantum states, $Z_{2(\mathrm{trans})}$ is the partition function of the translatory motion of the center of gravity of the two-molecule system, and $Z_{2(\mathrm{rel})}$ is the partition function of the two-molecule system summed over only the quantum states due to the relative motion. We can then write Eq. (6) as

$$B = \mp\frac{2^{-5/2}N\lambda^3}{2s+1} - \frac{2^{\frac{3}{2}}N\lambda^3(Z_{2(\mathrm{rel})}-Z_{2(\mathrm{rel})}^*)}{(2s+1)^2}. \tag{8}$$

The only term in Eq. (8) that offers any difficulty is $Z_{2(\mathrm{rel})}-Z_{2(\mathrm{rel})}^*$. Its value depends principally upon the difference in density of the energy levels of relative motion between the two cases.

(b) The Quantum-Mechanical Relations

The energy levels of relative motion are the eigenvalues of the radial wave equation

$$-\frac{\hbar^2}{2\mu}(r\psi)'' + \frac{l(l+1)\hbar^2}{2\mu r^2}r\psi + V(r)r\psi = Er\psi, \tag{9}$$

where μ is the reduced mass and $V(r)$ is the actual intermolecular potential for the real pair of molecules and is identically zero for the ideal pair. It is convenient to reduce Eq. (9) to a dimensionless form by the substitutions

$$R = r/\rho, \tag{10}$$

$$U(R) = (2\mu/\hbar^2)\rho^2V(r), \tag{11}$$

$$q^2 = (2\mu/\hbar^2)\rho^2E, \tag{12}$$

$$R\psi(R) = r\psi(r). \tag{13}$$

Here we introduce the symbol ρ, rather than the usual σ, to emphasize the fact that in the above expressions ρ is an arbitrary parameter, whereas the σ in the Lennard-Jones potential (see further on) has special significance; for this potential it is convenient to let $\rho=\sigma$.

We then obtain

$$-(R\psi)'' + [-q^2 + l(l+1)R^{-2} + U(R)]R\psi = 0. \tag{14}$$

The energy levels fall into two classes: (1) a finite number (possibly zero) of negative levels for the real pair of molecules (there are never any negative levels for the ideal pair) whose contribution to Z_2 can be directly summed, and (2) an infinite number of very closely spaced positive levels for both the real and the ideal pair. The relative density of these two near-continua can best be treated by the method of phase shifts, introduced for this problem by Gropper[9] and by Beth and Uhlenbeck.[10]

For values of R large enough that $l(l+1)R^{-2}+U(R)$ is negligible,

$$R\psi = \sin(qR - \tfrac{1}{2}\pi l + \eta_l). \tag{15}$$

The phase shift η_l of course is zero for the case $U(R)=0$. With very little loss in generality[11] we can set a boundary condition of $R\psi=0$ at $R=L$, a fairly large number. The possible values of q for the two cases [real $U(R)$ and ideal $U\equiv 0$] are given by

$$qL - \tfrac{1}{2}\pi l + \eta_l = n\pi, \tag{16}$$

$$qL - \tfrac{1}{2}\pi l = n\pi, \tag{17}$$

where n is a positive integral quantum number and is equal to the number of zeros of the wave function (excluding the one at the origin). The difference in density of the energy levels between the real and the ideal cases is obtained by taking the variation of these two equations and rearranging:

$$(\delta n/\delta q) - (\delta n/\delta q)^* = (1/\pi)(\delta\eta_l/\delta q). \tag{18}$$

This difference in density then is measured by the rate of change of the phase shift η_l with the energy parameter q.

(c) Final Expression for B

We may divide $Z_{2(\mathrm{rel})}$ into two sums, one extending over the discrete negative states (if any) and the other extending over the positive states. Since the positive levels are so very close together no appreciable error is introduced into $Z_{2(\mathrm{rel})}$ by replacing the sum over all

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[7] Values of the fundamental physical constants used in this paper were obtained from F. D. Rossini *et al.*, J. Am. Chem. Soc. **74**, 2699 (1952). The values employed for the isotopic masses were obtained from C. W. Li *et al.*, Phys. Rev. **83**, 512 (1951).

[8] We assume a monatomic gas since this theory is of interest principally for helium.

[9] L. Gropper, Phys. Rev. **51**, 1108 (1937).

[10] E. Beth and G. E. Uhlenbeck, Physica **4**, 915 (1937).

[11] The error is only in the very minor shape-of-container effect upon the equation of state.

quantum states by an integration with respect to n. We then convert to an integration with respect to q and obtain

$$Z_{2(\mathrm{rel})}=\sum{}' \exp(-E_{n,l}{}^{-}/kT)+\sum{}' \exp(-E_{n,l}{}^{+}/kT)$$
$$=\sum_{l}\Omega(s,l)\left[\sum_{n}\exp(-E_{n,l}{}^{-}/kT)+\int_{q=0}^{\infty}\exp(-q^2/q_0{}^2)\frac{dn}{dq}dq\right], \quad (19)$$

where $\Omega(s,l)$ gives the appropriate quantum weighting factors, the summation in n is over all negative energy levels of the system, and $E_{n,l}{}^{+}$ has been replaced by its equivalent according to Eq. (12), so that

$$q_0{}^2=2\mu\rho^2kT/\hbar^2=2\pi\rho^2\lambda^{-2}. \quad (20)$$

The corresponding expression for $Z_{2(\mathrm{rel})}{}^*$ may then be combined with Eq. (19) using Eq. (18) to obtain $Z_{2(\mathrm{rel})}-Z_{2(\mathrm{rel})}{}^*$ in terms of the phase shifts η_l.

The degeneracy $\Omega(s,l)$ of a particular energy level depends on the statistics of the two atoms, their nuclear spin, and the value of the angular-momentum quantum number. For a pair of identical Fermi-Dirac atoms, each with nuclear spin s, the weight is $(s+1)(2s+1)(2l+1)$ for l odd and $s(2s+1)(2l+1)$ for l even [the factor $(2l+1)$ arises from the spatial degeneracy]; these two weights are interchanged for a pair of Bose-Einstein atoms.

We may now write for a pair of Fermi atoms, for example,

$$Z_{2(\mathrm{rel})}-Z_{2(\mathrm{rel})}{}^*$$
$$=(s+1)(2s+1)\sum_{l\ \mathrm{odd}}(2l+1)\left\{\sum_{n}\exp(-E_{n,l}{}^{-}/kT)+\frac{1}{\pi}\int_{q=0}^{\infty}\exp(-q^2/q_0{}^2)\frac{d\eta_l}{dq}dq\right\}$$
$$+s(2s+1)\sum_{l\ \mathrm{even}}(2l+1)\left\{\sum_{n}\exp(-E_{n,l}{}^{-}/kT)+\frac{1}{\pi}\int_{q=0}^{\infty}\exp(-q^2/q_0{}^2)\frac{d\eta_l}{dq}dq\right\}. \quad (21)$$

Integration of Eq. (21) by parts, insertion of the resulting expression into Eq. (18) and re-arrangement with the aid of Eq. (20), yields the final expression for B,

$$B=\frac{N\pi^{\frac{3}{2}}\rho^3}{2(2s+1)q_0{}^3}-\frac{8N\pi^{\frac{3}{2}}\rho^3}{q_0{}^3}$$
$$\times\sum_{n}\left\{\frac{s+1}{2s+1}\sum_{l\ \mathrm{odd}}(2l+1)[\exp(-E_{n,l}{}^{-}/kT)-1]+\frac{s}{2s+1}\sum_{l\ \mathrm{even}}(2l+1)[\exp(-E_{n,l}{}^{-}/kT)-1]\right\}$$
$$\mp\frac{16N\pi^{\frac{1}{2}}\rho^3}{q_0{}^5}\int_0^{\infty}(\textstyle\sum)\exp(-q^2/q_0{}^2)q\,dq, \quad (22)$$

were

$$(\textstyle\sum)=\frac{s+1}{2s+1}\sum_{l\ \mathrm{odd}}(2l+1)\eta_l+\frac{s}{2s+1}\sum_{l\ \mathrm{even}}(2l+1)\eta_l. \quad (23)$$

Again, Eqs. (22) and (23) apply to a pair of identical Fermi atoms. The nuclear spin weighting factors $s+1$ and s are to be interchanged for a pair of Bose atoms. The Boltzman factors arise directly from Z_2, but the associated minus unity comes from the integration by parts of the phase shift integral. Phase shifts in general are arbitrary to the extent of any integral multiple of π. They are made definite by the convention that (1) $\eta_l=0$ for all q and l when $U(R)\equiv 0$, and (2) η_l be continuous for all q and l as $U(R)$ varies. This convention necessitates that $\eta_l=\pi n_l$ for $q=0$, when n_l is the number of discrete negative energy states associated with the angular quantum number l.

If the same analysis[6] that led to Eq. (3) is applied to a gaseous solution such as a mixture of He^3 and He^4, the following equation is obtained for the second virial coefficient:

$$B=N_3{}^2B_{33}+2N_3N_4B_{34}+N_4{}^2B_{44}. \quad (24)$$

The mole fractions of the two components are N_3 and N_4. B_{33} and B_{44} are the second virial coefficients of pure He^3 and pure He^4. B_{34}, the second cross virial coefficient of the mixture, is defined by

$$2B_{34}=-NV(Z_{2(3,4)}-Z_{1(3)}Z_{1(4)})/Z_{1(3)}Z_{1(4)}, \quad (25)$$

where $Z_{2(3,4)}$ is summed over all of the states of a system composed of an He^3 and an He^4 atom. The initial ideal gas term of Eq. (22) is exactly zero since the two atoms are distinguishable. The sum $(\sum)=\frac{1}{2}\sum(2l+1)\eta_l$ is taken over all values of l and the nuclear spin weighting factors cancel identically.

III. NUMERICAL SOLUTION OF EQUATIONS

With the exception of some preliminary, exploratory calculations that were performed on an IBM CPC computer, all of the numerical calculations of this work were carried out on the MANIAC, the Los Alamos electronic digital computer. This is a single address, binary, fixed decimal machine with electrostatic storage. The access time of a word in storage is about 10 μsec, and the multiplication time of two forty place binary numbers (approximately twelve decimal places) is about 1000 μsec.

The radial wave equation in the reduced form of Eq. (14) was integrated by a method given by Milne.[12] This method is quite advantageous in that it requires relatively few operations, only two starting values, and has the same error term as the more commonly used three-point closed double integration formula. We used the integration pattern $R=0.625(1/128)1.5(1/64)4\times(1/32)8$, since it was necessary to use a finer inte-

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[12] W. E. Milne, Amer. Math. Mon. 49, 96 (1942).

gration interval when R was small. This choice was made after considerable experimentation in order to determine the effect of integration interval pattern upon the phase shifts. The numerical procedure was so arranged that the integration interval was doubled automatically at the preselected values of R.

The potential term was so coded that with relatively little work any new potential function, even one given in the form of a numerical table, could be easily substituted. The Lennard-Jones potential used has the form

$$V(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]. \qquad (26)$$

The two parameters were determined from the statement of de Boer *et al.*[4] that for helium $\epsilon/k=10.22$°K and $N\sigma^3=10.06$ cc.

The reduced Lennard-Jones 12–6 potential may be written as

$$U(R)=p^2(R^{-12}-R^{-6}), \qquad (27)$$

where $\rho=\sigma$ and $p^2=8\mu\epsilon\sigma^2/\hbar^2$. In the region of small R,

$$R\psi=\exp(-pR^{-5}/5). \qquad (28)$$

For the Milne integration formula the first-order error per cycle is $\delta^6(R\psi)/240$. To obtain accurate phase shifts, it is necessary in solving the wave equation to preserve accuracy in $R\psi$ or in $(R\psi)'/R\psi$. Whereas a prohibitively small integration interval would be necessary in the region of small R to obtain $R\psi$ exactly, only a moderately coarse interval ($\Delta R=1/128$) is sufficient to preserve accuracy in $(R\psi)'/R\psi$. Furthermore, the phase shift in the wave function (determined at large R) is pretty nearly independent of the particular starting values of $R\psi$ used in the neighborhood of $R=0.6$. For example, the phase shifts for He^3 for $q=1$ and $l=0$, 1, 2, 3, etc., were determined using the following arbitrarily chosen starting values: R_0 and $R_1=0.625$ and $0.625+1/128$; $(R\psi)_0$ and $(R\psi)_1=$ (1) 2^{-12} and 2^{-4}; (2) 2^{-4} and 2^{-4}; (3) 2^{-4} and 2^{-12}. The phase shifts for each value of l were the same to at least six significant (decimal) figures in all three trials.

It would be necessary to integrate out to a prohibitively large value of R in order that $R\psi$ be given accurately by Eq. (15). For much smaller values of R [namely, when $U(R)$ is negligible] an expression in half-integral Bessel functions may be used,

$$R\psi=AR^{\frac{1}{2}}J_{l+\frac{1}{2}}(qR)+BR^{\frac{1}{2}}J_{-l-\frac{1}{2}}(qR), \qquad (29)$$

$$\eta_l=\tan^{-1}[(-)^lB/A]. \qquad (30)$$

To obtain B/A, two equations of the form of Eq. (29) were solved simultaneously, using values of $R\psi$ corresponding to two values of R separated by two integration intervals. In the course of our exploratory work we observed a smooth systematic trend in the apparent value of η_l (determined in the region of some particular value of R) as R increased. This error in η_l, due to stopping at a finite value of R, was shown to be

$$\eta_l(\text{true})-\eta_l(\text{apparent})=p^2/10qR^5+\cdots. \qquad (31)$$

This error expression is the first term of an asymptotic series. The integration proceeded until the error term was less than 0.0001 radian, at which point η_l (apparent) was obtained. This value of η_l was corrected by means of Eq. (31). The proper quadrant for η_l was determined automatically by a series of discriminations upon the trend in the apparent value of η_l from Eq. (30).

The Bessel functions of Eq. (29) are simple algebraic functions in qR, $\sin qR$ and $\cos qR$. Since according to Eq. (31) the same stopping point in R for a particular value of q can be used for all l, it was possible to have the computer first generate the necessary trigonometric functions and then higher-order Bessel functions by recursion as they were needed.

The over-all pattern of operation was as follows. Starting with some particular value of q, the first integration would be carried out with $l=0$; the phase shift would be calculated; the necessary Bessel functions for the next higher value of l would be generated, l advanced by unity (by two in the case of He^4) and the next integration begun. At the end of each integration the following information was printed out: q, l, $(2l+1)\eta_l$ and the running sum of $(2l+1)\eta_l$ (over even and odd l separately). Whenever $(2l+1)\eta_l$ reached a predetermined small value, q was advanced by $\Delta q=1/16$, l set to zero, the paper spaced and a new series begun at once. The running time required per phase shift was about 7 seconds.

The phase shift η_l was probably determined (for a given value of q) to the same number of decimal places accuracy for all l. It is the sum with respect to l of $(2l+1)\eta_l$ that is needed. For each value of q a value of l was soon reached at which it was better to use phase shifts calculated from the Born approximation in preference to those determined by numerical integration. The Born approximation[13] becomes good whenever l is several times q in magnitude. The definite integral can be evaluated in a simple form by means of equations given by Watson[14] to yield

$$\eta_l=3\pi p^2q^4/(2l+5)(2l+3)(2l+1)(2l-1)(2l-3), \qquad (32)$$

where p^2 is interpreted as the coefficient of R^{-6} in $U(R)$. The repulsive term contributes essentially nothing. For each value of q the summation over l of $(2l+1)\eta_l$ was extended until $(2l+1)\eta_l<0.00001$ radian.

A curious relation was observed between the phase shifts computed by numerical integration and those obtained from the Born approximation. For sufficiently large values of l these two series always agreed very well in the mean. However, although η_l(Born) is a smooth function of l, η_l(num. int.) continued to oscillate about η_l(Born) with a wavelength of perhaps ten units in l. This effect is perfectly real and was not affected by drastic changes in the integration pattern or in the

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[13] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949).

[14] G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1952), p. 396.

value of R at which η_l was determined. It probably contributes very little error to $\sum(2l+1)\eta_l$.

To obtain $\sum(2l+1)\eta_l$, for a given value of q, the procedure was to join

$$\sum_{l=0}^{l=l_0}(2l+1)\eta_l(\text{num. int.}) \quad \text{to} \quad \sum_{l=l_0+\Delta}^{l=\infty}(2l+1)\eta_l(\text{Born})$$

at a value of $l=l_0$ when η_l(num. int.) was very nearly equal to η_l(Born). For example, for He^4, $q=10$,

$$l_0=34; \qquad \eta_{l_0}(\text{num. int.})=0.09215;$$

$$\eta_{l_0}(\text{Born})=0.09206; \qquad \sum_{l=0}^{l=\infty}(2l+1)\eta_l=-63.6064.$$

The values of l_0 chosen were roughly proportional to q.

Phase shifts and the sums $\sum(2l+1)\eta_l$ were calculated directly at intervals of $\Delta q=1/16$ from $q=1/16$ to $q=10$. From $q=10$ to $q=15$, numerical integrations were performed at intervals of $\Delta q=0.5$ and the values of $\sum(2l+1)\eta_l$ at intervals of 1/16 determined by interpolation.

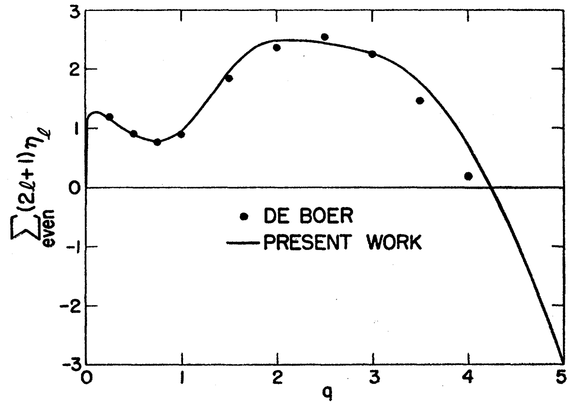

FIG. 1. $\Sigma(2l+1)\eta_l$ *versus* q for He^4.

A total of about 15 000 individual phase shifts were calculated by numerical integration in the course of this work, with an even larger total calculated from the Born approximation. Fortunately this tremendous mass of numbers did not have to be handled in detail by hand; the computer tabulated the final sums $\sum(2l+1)\eta_l$ in a form convenient for examination and checking. Periodically, detailed spot checks were run on individual phase shifts.

It is difficult to make an estimate of the accuracy of our final values of $(\sum)$ [as defined in Eq. (23)]. In the region around $q=1$ they are probably good to better than 0.0005 radian. The accuracy decreases as q increases until at $q=10$, the error may be as large as 0.05 radian.

The radial wave equation for a pair of He^3 atoms certainly has no discrete negative energy levels. The He^4 system, with the Lennard-Jones potential we used, almost has a negative level but clearly just fails to have one. Our value of p^2 in this case is 22.049. The critical value for the appearance of a negative level is 22.37 according to calculations of Kilpatrick and Kilpatrick.[15]

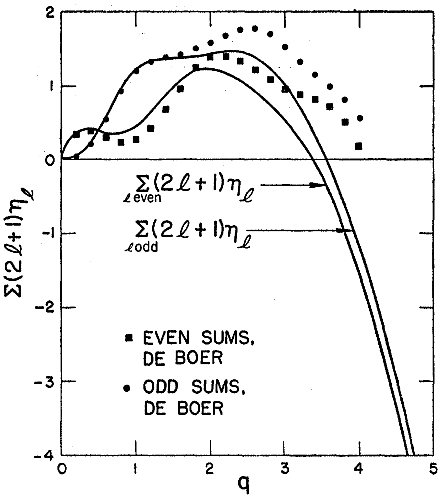

FIG. 2. $\Sigma(2l+1)\eta_l$ *versus* q for He^3.

The phase shift integral of Eq. (22) was evaluated numerically by both Simpson's and Weddle's rules. At all temperatures between 0.1° and 60°K results were very nearly the same.

IV. RESULTS

The results of our phase shift calculations are presented graphically. In Fig. 1, $\sum_e[\sum(2l+1)\eta_l$ summed over even $l]$ for He^4 is plotted against q. The sums calculated by de Boer and Michels[3] are shown as solid circles. The agreement is fairly good. In Fig. 2, $\sum_e$ and $\sum_o$ for He^3 are plotted against q. De Boer's[4] sums are shown in squares and circles. The agreement in certain ranges, particularly for large q is not so good.

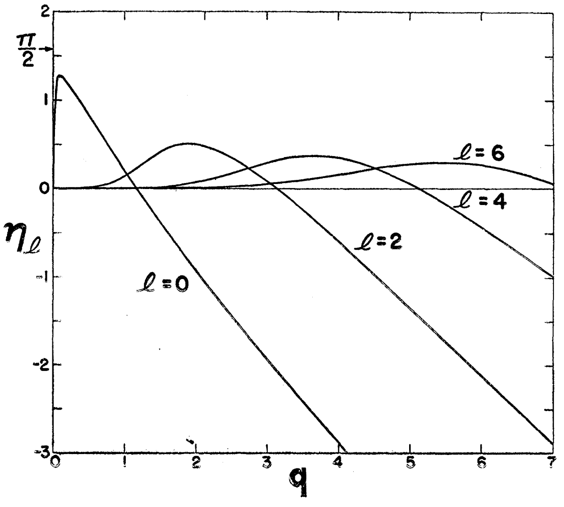

FIG. 3. He^4 phase shifts.

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[15] J. E. Kilpatrick and M. F. Kilpatrick, J. Chem. Phys. **19**, 930 (1951).

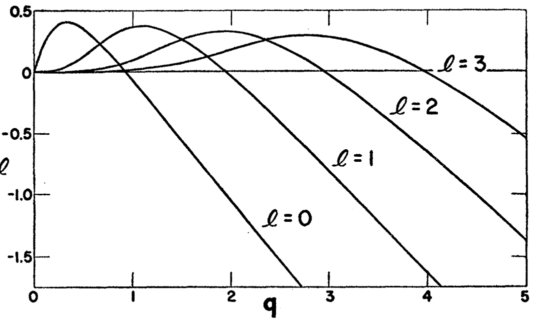

FIG. 4. He^3 phase shifts.

In Fig. 3, η_l (for $l=0$, 2, 4 and 6) for He^4 is plotted against q. Figure 4 shows η_l *vs* q for He^3. Figure 5 shows the relation of our calculated second virial coefficients for He^4 to the available experimental data and to de Boer and Michels'[3] calculated points. In the case of He^3, there is no experimental data. The agreement between our calculations and those of de Boer *et al.*[3,4] is fairly good. This was surprising, since for He^3 there is considerable disagreement in the phase shifts. The small disagreement between de Boer and Michels' He^4 calculations and the experimental data appears to be almost wholly accumulated numerical error. Here our curve gives a somewhat better representation of the experimental data.

In Table I we give our final virial coefficients at closely spaced temperature intervals. They probably represent the second virial coefficient (for the exact potential used) correct to the number of figures given. Between 40°K and 60°K it was necessary to add a small correction to our virial coefficients, due to the fact that we directly determined phase shifts only up to $q=15$. This correction was evaluated by fitting a quadratic expression in q to the values of $(\sum)$ from $q=10$ to 15 and then integrating the phase integral analytically from $q=15$ to infinity. This correction had a maximum value of 0.19 cc/mole for He^4 at 60° and of 0.03 cc/mole for He^3 at the same temperature.

The Boyle points of He^3 and He^4, interpolated from our B_{33} and B_{44} tables, are 19.64°K and 23.18°K, respectively. By means of de Boer's[16] quantum theory of corresponding states we extrapolate a value of T(Boyle) for He^3 of 19.9°K. The agreement is satisfactory considering the uncertainty in the extrapolation curve.

The theory of corresponding states does not include the effect of nuclear spin or of statistics. We thought it would be of interest to calculate the second virial coefficients of a hypothetical He with zero spin and Bose-Einstein statistics but with a mass exactly that of He^3 for comparison with the normal He^3. The appropriate values of $\sum_{l\text{ even}}(2l+1)\eta$ were already on hand. There was practically no difference between the two except at very low temperatures. The difference amounted to 0.003 cc/mole at 8°, 0.4 cc at 4°, 2.0 cc at 3°, 22 cc at 2°, and 107 cc at 1°. It can easily be shown that in order for these two He^3 molecules to have the same second virial coefficients, it is necessary for $\sum_{\text{odd}}-\sum_{\text{even}}=\pi/8$. For $q\geq 5$, this is true within 0.02 radian from our data for He^3. Therefore essentially

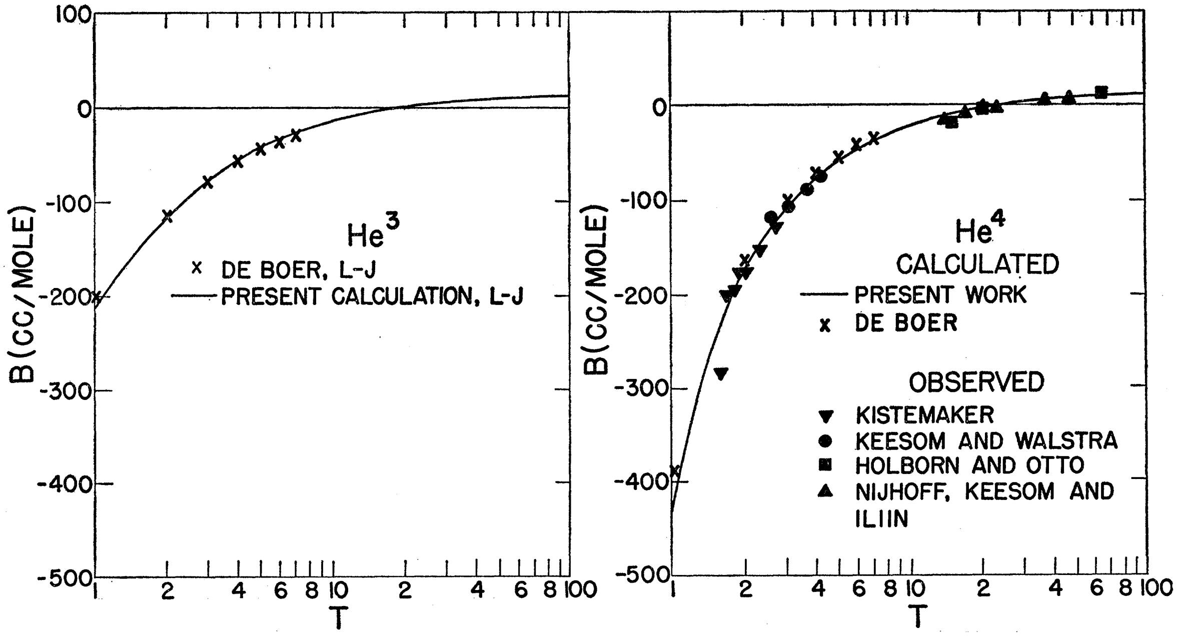

FIG. 5. Low-temperature second virial coefficients for He^3 and He^4.

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[16] J. de Boer, Physica 14, 139 (1948): J. de Boer and B. S. Blaisse, Physica 14, 149 (1948): J. de Boer and R. J. Lunbeck, Physica 14, 520 (1948).

TABLE I. Second virial coefficients of He^4 and He^3 and the solution imperfection as a function of temperature.

T°K	B_{44} cc/mole	B_{33} cc/mole	Δ cc/mole
0.3	−2715.4	−375.1	352.6
0.4	−1712.8	−348.6	175.0
0.5	−1203.2	−320.0	95.3
0.6	−906.6	−293.5	54.8
0.7	−717.6	−269.9	32.4
0.8	−589.0	−249.1	19.4
0.9	−497.2	−230.7	11.5
1.0	−428.9	−214.4	6.6
1.1	−376.5	−200.0	3.5
1.2	−335.2	−187.08	1.5
1.3	−302.0	−175.53	0.2
1.4	−274.6	−165.13	−0.6
1.5	−251.7	−155.73	−1.1
1.6	−232.34	−147.21	−1.41
1.7	−215.69	−139.45	−1.61
1.8	−201.25	−132.36	−1.71
1.9	−188.58	−125.86	−1.76
2.0	−177.39	−119.89	−1.76
2.1	−167.41	−114.38	−1.74
2.2	−158.47	−109.29	−1.71
2.3	−150.39	−104.57	−1.67
2.4	−143.06	−100.18	−1.62
2.5	−136.38	−96.10	−1.56
2.6	−130.26	−92.28	−1.51
2.7	−124.62	−88.72	−1.46
2.8	−119.42	−85.38	−1.41
2.9	−114.60	−82.24	−1.36
3.0	−110.13	−79.29	−1.31
3.1	−105.96	−76.51	−1.26
3.2	−102.06	−73.88	−1.22
3.3	−98.40	−71.40	−1.19
3.4	−94.98	−69.05	−1.15
3.5	−91.75	−66.83	−1.12
3.6	−88.71	−64.72	−1.08
3.7	−85.84	−62.71	−1.05
3.8	−83.12	−60.80	−1.02
3.9	−80.55	−58.98	−0.99
4.0	−78.11	−57.25	−0.97
4.1	−75.79	−55.59	−0.95
4.2	−73.58	−54.01	−0.92
4.3	−71.48	−52.49	−0.90
4.4	−69.47	−51.04	−0.88
4.6	−65.72	−48.32	−0.84
4.8	−62.29	−45.81	−0.81
5.0	−59.14	−43.49	−0.77
5.2	−56.22	−41.34	−0.74
5.4	−53.53	−39.34	−0.71
5.6	−51.03	−37.48	−0.69
5.8	−48.70	−35.74	−0.66
6.0	−46.53	−34.11	−0.64
6.2	−44.50	−32.57	−0.62
6.4	−42.59	−31.13	−0.60
6.6	−40.80	−29.78	−0.58
6.8	−39.12	−28.50	−0.56
7.0	−37.53	−27.29	−0.55
7.2	−36.03	−26.14	−0.53
7.4	−34.61	−25.05	−0.52
7.6	−33.27	−24.02	−0.50
7.8	−31.99	−23.04	−0.49
8.0	−30.78	−22.11	−0.48
8.5	−28.00	−19.95	−0.45
9.0	−25.53	−18.04	−0.42
9.5	−23.32	−16.31	−0.40
10.0	−21.34	−14.75	−0.38
10.5	−19.54	−13.34	−0.36
11.0	−17.90	−12.05	−0.34
11.5	−16.41	−10.87	−0.33
12.0	−15.04	−9.78	−0.31
12.5	−13.79	−8.78	−0.30
13.0	−12.63	−7.86	−0.28
13.5	−11.55	−7.00	−0.27
14.0	−10.56	−6.21	−0.26
14.5	−9.63	−5.46	−0.25
15.0	−8.77	−4.77	−0.24
15.5	−7.96	−4.12	−0.24
16.0	−7.20	−3.51	−0.23
17.0	−5.82	−2.40	−0.21
18.0	−4.60	−1.41	−0.20
19.0	−3.51	−0.52	−0.19
20.0	−2.53	0.28	−0.18
21.0	−1.65	1.00	−0.17
22.0	−0.85	1.65	−0.16
23.0	−0.12	2.25	−0.15
24.0	0.54	2.79	−0.14
25.0	1.15	3.29	−0.14
26.0	1.71	3.76	−0.13
27.0	2.23	4.18	−0.12
28.0	2.71	4.58	−0.12
29.0	3.15	4.94	−0.11
30.0	3.57	5.28	−0.11
35.0	5.25	6.67	−0.09
40.0	6.49	7.70	−0.08
45.0	7.43	8.47	−0.07
50.0	8.16	9.07	−0.06
55.0	8.74	9.55	−0.05
60.0	9.20	9.93	−0.05

all of the difference between B_{33} and B_{44} above 4°K is a mass rather than a statistical effect.

It is of interest to compare our virial coefficients with those calculated from classical theory corrected by de Boer and Michels[5,17] for quantum effects. The most convenient temperature for this comparison is 61.32°K (corresponding to a reduced temperature of $T^*=kT/\epsilon=6$). From de Boer's equations we calculate

$$B_{44}=6.804-0.147+2.756-0.457=8.96, \quad (33)$$

$$B_{33}=6.804+0.139+3.662-0.805=9.80, \quad (34)$$

$$B_{34}=6.804+0.000+3.137-0.592=9.35. \quad (35)$$

The first term is from the high-temperature, classical equation; the second is the (ideal-gas) nuclear spin—statistical term; and the third and fourth, the first two quantum deviation terms. The next quantum correction term is positive, so these results are low by a few tenths cc. Our data (Table I), extrapolated to 61.32°K, yield

$$B_{44}=9.34, \quad (36)$$

$$B_{33}=10.04, \quad (37)$$

$$B_{34}=9.64. \quad (38)$$

The agreement is within the probable magnitude of the missing terms of Eqs. (33), (34), and (35).

For an ideal solution of He^3 and He^4, $B_{34}=\frac{1}{2}(B_{33}+B_{44})$ and Eq. (24) becomes $B=N_3B_{33}+N_4B_{44}$. Equation (24) can therefore be written in an alternate form

$$B=N_3B_{33}+N_4B_{44}+2N_3N_4\Delta, \quad (39)$$

$$\Delta=B_{34}-\tfrac{1}{2}(B_{33}+B_{44}). \quad (40)$$

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[17] J. de Boer and R. B. Bird, University of Wisconsin Report CF 1509-A, 1952 (unpublished), Chap. 6.

TABLE II. The effect on B_{44} of varying σ and ϵ.

T°K	B_{44} cc/mole		
	$p^2=22.049$	$p^2=22.300$	
	σ_1, ϵ_1	σ_1, ϵ_2	σ_2, ϵ_1
0.5	−1203.2	−1245.2	−1244.6
1.0	−428.93	−441.54	−442.27
1.5	−251.72	−258.57	−259.40
2.0	−177.39	−182.03	−182.73
3.0	−110.13	−112.91	−113.36
4.0	−78.11	−80.07	−80.36
5.0	−59.14	−60.67	−60.85
6.0	−46.53	−47.76	−47.87
8.0	−30.78	−31.66	−31.67
10.0	−21.34	−22.05	−22.00
15.00	−8.77	−9.21	−9.08

The quantity Δ (tabulated in Table I) is a good measure of the deviation of the solution from ideality. Δ approaches plus infinity at very low temperature, passes through zero at about 1.33°K, and stays small and negative at all higher temperatures.

Our data, extrapolated to 61.32°K [Eqs. (36), (37), and (38)] give a value for Δ of -0.05 cc/mole. Equations (33), (34), and (35) yield $\Delta=-0.03$. This latter value of Δ is more accurate than the individual values of the virial coefficients from which it is derived since the effects of the missing higher terms tend to cancel.

We also considered it of interest and importance to determine what effect changes in the potential constants ϵ and σ would have on the low-temperature values of B_{44}. To accomplish this, we first obtained phase shifts for He^4 using a value of $p^2=22.300$ instead of 22.049 and then carried out the quadratures for two cases, both corresponding to the new p^2: (1) $\sigma_1=2.571\times10^{-8}$ cm, $\epsilon_2=1.428\times10^{-15}$ erg; (2) $\sigma_2=2.557\times10^{-8}$ cm, $\epsilon_1=1.411\times10^{-15}$ erg. (The subscript 1 refers to the parameters as used in the original potential.) A brief summary of the results is given in Table II, where some original values of B_{44} are repeated for easy comparison.

Several points are worthy of mention. First, it is seen that for the two cases corresponding to $p^2=22.300$ the B_{44}'s are nearly the same; but curves representing the two sets of points cross at about 0.7°K and at 8.5°K. Next we observe that a $\delta\sigma$ (ϵ constant) of 0.6 percent or a $\delta\epsilon$ (σ constant) of 1.2 percent may change B_{44} by about 3 percent and that the effect on B_{44} is nearly temperature independent (up to 15°K). Simultaneously changing σ and ϵ within the above limits and subject to $p^2=22.300$ would introduce no larger variations in B_{44}. Thus the values of B_{44} computed with this p^2 would adequately fit the existing experimental data but not quite so well as those computed with the original p^2.

A similar analysis, employing only the classical Lennard-Jones treatment, shows that the above variations in σ and ϵ may produce variations in the high-temperature values of B_{44} as great as 5 percent; but this too is within experimental error. We may therefore safely conclude that de Boer and co-workers have chosen parameters for the Lennard-Jones potential which best fit experimental values of the second virial coefficient for He^4 for the temperature range up to 400°K.

Mason and Rice[18] have recently obtained constants for a Slater-type potential which give a fit for the experimental second virial coefficients of He^4 from 40 to 1500°K as good as or better than the Lennard-Jones (12–6) potential. In addition, the three-constant potential gives a clearly superior representation of the observed viscosity and thermal conductivity of He^4 above 100°K. It is therefore of considerable interest to investigate the low-temperature virial coefficients and transport properties calculated from this new potential. Such an undertaking will be the subject of a forthcoming paper from this Laboratory.

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[18] E. A. Mason and W. E. Rice, J. Chem. Phys. 22, 522 (1954).