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Virial Coefficients and Models of Molecules in Gases. B*

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TOTAL CONTENTS

IV. THE SECOND VIRIAL COEFFICIENT OF HELIUM

HAVING treated nonquantum gases, we investigate in this part the second virial coefficient of helium for which quantum effects are important.

10. The Depth Parameter, *s*, of an Intermolecular Potential

The notion of depth parameter introduced by Blatt and Jackson[17] for nuclear potentials can also be applied to the potential between helium atoms. Let $U(r)$ be the intermolecular potential, r being the distance between the centers of atoms. We can always choose a dimensionless positive number, s, in such a way that the reduced potential, $s^{-1}U(r)$, give a resonance at the zero energy and no discrete energy level. The number s is called the depth parameter. If one or more discrete levels exist in the two-body system, s is greater than unity; if no discrete level exists, s is less than unity.

The Schroedinger equation

$$\frac{d^2}{dr^2}R-\frac{2m^*}{\hbar^2}\frac{U(r)}{s}R=0 \qquad (10.1)$$

with the reduced potential U/s must be satisfied by a nodeless spherically symmetric wave function $r^{-1}R(r)$. Here m^* is the reduced mass of the two-body system; $\hbar$ is Planck's constant divided by 2π.

For the Lennard-Jones potential

$$U(r)=U_0\left[\frac{6}{n-6}\left(\frac{r_0}{r}\right)^n-\frac{n}{n-6}\left(\frac{r_0}{r}\right)^6\right],\quad n>6, \qquad (10.2)$$

with the potential minimum $-U_0$ at $r=r_0$, (10.1) becomes

$$r_0^2\frac{d^2}{dr^2}R-6c\left[\frac{6}{n-6}\left(\frac{r_0}{r}\right)^n-\frac{n}{n-6}\left(\frac{r_0}{r}\right)^6\right]R=0, \qquad (10.3)$$

where

$$6c=\frac{2m^*}{\hbar^2}\frac{U_0}{s}r_0^2. \qquad (10.4)$$

For $n=10$, the eigenvalue problem can be solved exactly with $c=1$ and

$$R=\exp\left[-\frac{3}{4}\left(\frac{r_0}{r}\right)^4\right]. \qquad (10.5)$$

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* This is a continuation of a previous article with the same title [Revs. Modern Phys. **25**, 831 (1953)], which will be referred to as A. In part A a discussion of pure gases with no quantum effects is given; in Part B gas mixtures and quantum effects are considered.

[17] J. M. Blatt and J. D. Jackson, Phys. Rev. **26**, 21 (1949).

In general, the eigenvalue c of (10.3) is determined by a variational principle, i.e., by the extremum

$$6c=\text{Extr}\frac{\int^{\infty} r_0^2\left(\frac{dR}{dr}\right)^2 d\left(\frac{r}{r_0}\right)}{-\int^{\infty}\left[\frac{6}{n-6}\left(\frac{r_0}{r}\right)^n-\frac{n}{n-6}\left(\frac{r_0}{r}\right)^6\right]R^2 d\left(\frac{r}{r_0}\right)}. \tag{10.6}$$

For n not far from 10, we can obtain a sufficiently accurate value of c making use of the approximation

$$R=\exp[-a(r_0/r)^b],$$

where a and b are positive constants to be adjusted˙ By virtue of this approximation we can integrate analytically the numerator and denominator of (10.6), and obtain

$$c=0.905 \text{ for } n=9, \tag{10.7}$$

$$c=1.174 \text{ for } n=12. \tag{10.8}$$ [18]

For the square-well potential

$$U(r)=\begin{cases}\infty & \text{for } r<\sigma\\ -\epsilon & \text{for } \sigma<r<g\sigma\\ 0 & \text{for } g\sigma<r\end{cases} \tag{10.9}$$

the nodeless solution of (10.1) is

$$R=\begin{cases}0 & \text{for } r<\sigma\\ \sin[\pi(r-\sigma)/2(g-1)\sigma] & \text{for } \sigma<r<g\sigma\\ 1 & \text{for } g\sigma<r,\end{cases} \tag{10.10}$$

the eigenvalue condition being

$$\frac{2m^*}{\hbar^2}\frac{\epsilon\sigma^2}{s}=\frac{\pi^2}{4(g-1)^2}. \tag{10.11}$$

These results will be used in the following sections.

11. Quantum-Mechanical Expression for the Second Virial Coefficient

In this section the classical second virial coefficient'

$$B=2\pi\int_0^{\infty}\left[1-\exp\left(\frac{-U(r)}{kT}\right)\right]r^2dr \tag{11.1}$$

is generalized to a quantum-mechanical expression. Here, as the first step, the wave nature of molecules is considered; the symmetry effect, which is important only at low temperatures, will be taken into account in the following section.

Let us consider the density matrix which is defined by

$$\rho(\mathbf{r},\mathbf{r}')=\sum_\nu \exp(-\beta E_\nu)\psi_\nu(\mathbf{r})\bar{\psi}_\nu(\mathbf{r}'), \tag{11.2}$$

$$\beta\equiv 1/kT.$$

Here $\{\psi_\nu\}$ is a complete orthonormal set of eigenfunctions of the relative motion of the two molecules, so that

$$\int\psi_\nu(\mathbf{r})\bar{\psi}_{\nu'}(\mathbf{r})d\tau=\delta_{\nu\nu'},\quad d\tau\equiv dxdydz, \tag{11.3}$$

for all ν and ν', $\mathbf{r}=(x,y,z)$ being the position vector of one molecule relative to the other; E_ν are energies corresponding to ψ_ν. In the limit of infinite temperature, the density matrix becomes

$$\lim_{\beta\to 0}\rho(\mathbf{r},\mathbf{r}')=\sum_\nu\psi_\nu(\mathbf{r})\bar{\psi}_\nu(\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}'), \tag{11.4}$$

in which $\delta(\mathbf{r}-\mathbf{r}')$ is the Dirac δ function.

The density matrix satisfies the Bloch differential equation

$$\frac{\partial}{\partial\beta}\rho(\mathbf{r},\mathbf{r}')=-\mathrm{H}\rho(\mathbf{r},\mathbf{r}') \tag{11.5}$$

with the Hamiltonian

$$\mathrm{H}=-\frac{\hbar^2}{2m^*}\Delta+U(r),\quad \Delta\equiv\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}, \tag{11.6}$$

operating on the first argument $\mathbf{r}$, for which $\mathrm{H}\psi_\nu=E_\nu\psi_\nu$. In the particular case where $U(r)\equiv 0$, the solution of the Bloch equation with the "initial" condition (11.4) is

$$\rho(\mathbf{r},\mathbf{r}')=\left(\frac{m^*}{2\pi\hbar^2\beta}\right)^{\frac{3}{2}}\exp\left[-\frac{m^*}{2\hbar^2\beta}(\mathbf{r}-\mathbf{r}')^2\right].$$

We can therefore assume the general solution to be of the form

$$\rho(\mathbf{r},\mathbf{r}')=\left(\frac{m^*}{2\pi\hbar^2\beta}\right)^{\frac{3}{2}}\exp\left[-\frac{m^*}{2\hbar^2\beta}(\mathbf{r}-\mathbf{r}')^2+W(\mathbf{r},\mathbf{r}')\right] \tag{11.7}$$

with

$$W(\mathbf{r},\mathbf{r}')\longrightarrow 0 \text{ for } \beta U\longrightarrow 0. \tag{11.8}$$

The diagonal element of the density matrix then becomes

$$\rho(\mathbf{r},\mathbf{r})=(m^*/2\pi\hbar^2\beta)^{\frac{3}{2}}\exp W(\mathbf{r},\mathbf{r}).$$

We therefore obtain

$$(2\pi\hbar^2/m^*kT)^{\frac{3}{2}}\rho(\mathbf{r},\mathbf{r})=\exp W(\mathbf{r},\mathbf{r}). \tag{11.9}$$

Both sides of (11.9) are quantum-mechanical generalizations of the Boltzmann factor, $\exp(-\beta U)$, in (11.1), since they indicate the probability of finding two molecules a distance r apart from each other. They are called Slater sums. The expression on the left-hand side of (11.9) will be used for low-temperature expansion; that on the right-hand side will be used for high-temperature expansion.

The argument in this section was chiefly taken from Husimi's[19] comprehensive paper on the density matrix.

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[18] This value for $n=12$ agrees with the result of J. E. and M. F. Kilpatrick, J. Chem. Phys. **19**, 930 (1951).

[19] K. Husimi, Proc. Phys.-Math. Soc. Japan **22**, 264 (1940).

12. Low-Temperature Expansion of the Second Virial Coefficient

Since the intermolecular potential U is a function of the distance r only, the eigenfunctions ψ_ν in (11.2) can be factorized into

$$\psi_\nu = r^{-1}R_{nl}(r)Y_{lm}(\theta,\varphi),\quad \nu=(n,l,m), \tag{12.1}$$

with radial functions $r^{-1}R_{nl}$ normalized as

$$\int |R_{nl}(r)|^2 dr = 1$$

and spherical harmonics Y_{lm} also normalized to one:

$$\int_0^{2\pi}\int_0^{\pi} |Y_{lm}(\theta,\varphi)|^2 \sin\theta d\theta d\varphi = 1 \tag{12.2}$$

(compare (11.3)). Then, according to (11.2) the diagonal element of the density matrix assumes the form

$$\rho(\mathbf{r},\mathbf{r}) = \frac{1}{4\pi r^2}\sum\nolimits_{nl}(2l+1)\exp\left(-\frac{E_{nl}}{kT}\right)|R_{nl}(r)|^2$$

by virtue of the addition theorem

$$\sum\nolimits_m |Y_{lm}(\theta,\varphi)|^2 = (2l+1)/4\pi.$$

With this expression the second virial coefficient is given by

$$B = -2\pi\left(\frac{2\pi\hbar^2}{m^*kT}\right)^{\frac{3}{2}}\int_0^\infty [\rho(\mathbf{r},\mathbf{r}) - \rho^0(\mathbf{r},\mathbf{r})]r^2 dr, \tag{12.3}$$

where ρ^0 is the matrix written for $U(r)\equiv 0$, namely

$$\rho^0(\mathbf{r},\mathbf{r}) = \frac{1}{4\pi r^2}\sum\nolimits_{nl}(2l+1)\exp\left(-\frac{E_{nl}{}^0}{kT}\right)|R_{nl}{}^0(r)|^2,$$

$E_{nl}{}^0$ and $r^{-1}R_{nl}{}^0(r)$ being, respectively, the energies and the radial functions for $U(r)\equiv 0$. Thus, performing the integration with respect to r, we obtain

$$B = \sum\nolimits_l (2l+1)B_l, \tag{12.4}$$

$$B_l = -\frac{1}{2}\left(\frac{2\pi\hbar^2}{m^*kT}\right)^{\frac{3}{2}}\sum\nolimits_n\left[\exp\left(-\frac{E_{nl}}{kT}\right) - \exp\left(-\frac{E_{nl}{}^0}{kT}\right)\right]. \tag{12.5}$$

In general some of E_{nl} may be negative; and the summation over n can be separated into two parts, one is for negative energy levels which are discrete, the other for positive energy levels which are continuous. The latter can be transformed into the integral

$$\frac{1}{\pi}\int_0^\infty \exp\left(-\frac{E}{kT}\right)\frac{d\eta_l}{dE}dE.$$

Here η_l is the phase shift defined by the a symptotic form,

$$R(r) \sim \sin(\kappa r - \tfrac{1}{2}l\pi + \eta_l) \text{ for } r\to\infty \tag{12.6}$$

of the regular solution of

$$\left[\frac{d^2}{dr^2} + \kappa^2 - \frac{2m^*}{\hbar^2}U(r) - \frac{l(l+1)}{r^2}\right]R(r) = 0, \tag{12.7}$$

where

$$\kappa^2 = 2m^*E/\hbar^2. \tag{12.8}$$

(When $U(r)\equiv 0$, the wave function is $R^0(r)\sim\sin(\kappa r - \frac{1}{2}l\pi)$; hence η_l/π is the difference between the number of stationary states below E of the real two-body system and that of the ideal system for $U(r)\equiv 0$.) Hence it follows that

$$B_l = -\frac{1}{2}\left(\frac{2\pi\hbar^2}{m^*kT}\right)^{\frac{3}{2}}\left[\sum_{\text{discrete}}\exp\left(-\frac{E_{nl}}{kT}\right) + \frac{1}{\pi}\int_0^\infty \exp\left(-\frac{E}{kT}\right)\frac{d\eta_l}{dE}dE\right]. \tag{12.9}$$

Up to this point we have been considering only the quantum effect due to wave nature. For ordinary helium, He^4, we must take account of the fact that wave functions ψ_ν are symmetric with respect to the interchange of atomic coordinates. In this case, only the spherical harmonics with even l should be taken and the left-hand side of (12.2) should be divided by the symmetry number 2. As a result the right-hand side of (12.4) should be replaced by $2\sum(2l+1)B_l$ in which the summation is to be taken over even l. Furthermore, we see from (12.3) that the left-hand side of (12.4) should be replaced by the difference between the real second virial coefficient and that of the ideal Bose-Einstein gas with zero spin. Thus we obtain

$$B = -\frac{1}{16}\left(\frac{2\pi\hbar^2}{m^*kT}\right)^{\frac{3}{2}} + 2\sum_{\text{even } l}(2l+1)B_l. \tag{12.10}$$

The expression (12.10) with (12.9) was first obtained by Uhlenbeck and Beth[20] and by Gropper.[21] (The present author avoids discussing the virial coefficient of He^3, which is more complicated because of the fact that the spin $\frac{1}{2}$ requires the inclusion of both odd and even terms; see, for instance, Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids*.)

In case no discrete energy level exists, B_l can be transformed, by integration by parts, into

$$B_l = \frac{1}{2}\left(\frac{2\pi\hbar^2}{m^*kT}\right)^{\frac{3}{2}}\frac{1}{\pi}\int_{E=0}^{E=\infty}\eta_l d\exp\left(-\frac{E}{kT}\right) \tag{12.11}$$

for $l=0, 1, \cdots$. This expression holds for $s\leqq 1$, not only for $s<1$.

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

[21] L. Gropper, Phys. Rev. **50**, 963 (1936); **51**, 1108 (1937).

In the particular case, where the depth parameter s of the intermolecular potential is unity, we can make use of Schwinger's variation principle[22] to write the asymptotic form

$$\eta_0 = \frac{\pi}{2} - \kappa \int_0^\infty (1-R^2)dr + 0(\kappa) \tag{12.12}$$

at low energies. Here R is the eigenfunction of (12.7) with $l=\kappa=0$ normalized as $R \rightarrow 1$ for $r \rightarrow \infty$. At very low temperatures η_l, and therefore B_l, can be neglected for $l>0$; and η_0 can be approximated by the first two terms of (12.12) so that

$$2B_0 \sim \left(\frac{2\pi\hbar^2}{m^*kT}\right)^{\frac{3}{2}} \left[-\frac{1}{2} + \left(\frac{m^*kT}{2\pi\hbar^2}\right)^{\frac{1}{2}} \int_0^\infty (1-R^2)dr\right].$$

For the Lennard-Jones potential (10.2) with $n=10$ we get

$$\int_0^\infty (1-R^2)dr = (\tfrac{3}{2})^{\frac{1}{4}}\Gamma(\tfrac{3}{4})r_0 = 1.356\, r_0$$

by virtue of (10.5); for the square-well potential (10.9) we have

$$\int_0^\infty (1-R^2)dr = \tfrac{1}{2}(g+1)\sigma$$

by virtue of (10.10).

De Boer and Michels[23] pointed out the fact that the depth parameter s for helium is not far from unity.

13. The Second Virial Coefficient for the Square-Well Potential†

For the square-well potential (10.9) the phase shifts can be expressed analytically by means of the spherical Bessel functions

$$j_l(\kappa) \equiv (\pi/2x)^{\frac{1}{2}} J_{l+\frac{1}{2}}(x).$$

The function R in (12.7) with the asymptotic (12.6) is given by

$$R = \kappa r[\cos\eta_l j_l(\kappa r) + (-1)^l \sin\eta_l j_{-l-1}(\kappa r)]$$

for $r > g\sigma$, while the solution which vanishes at $r=\sigma$ may be written as

$$R = \text{const}\kappa' r[j_{-l-1}(\kappa'\sigma)j_l(\kappa' r) - j_l(\kappa'\sigma)j_{-l-1}(\kappa' r)]$$

for $\sigma < r < g\sigma$, where

$$\kappa'^2 = \kappa^2 + 2m^*\epsilon/\hbar^2$$

or, by use of (10.11),

$$(\kappa'\sigma)^2 = (\kappa\sigma)^2 + \pi^2 s/4(g-1)^2. \tag{13.1}$$

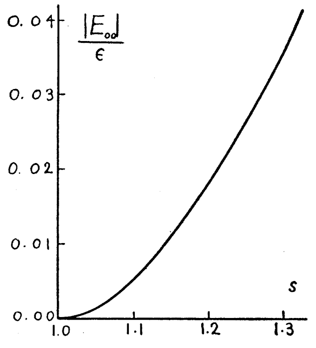

FIG. 12. The depth parameter s *vs* negative energy level divided by the potential depth for the square-well potential.

The requirement that R and dR/dr be continuous leads to

$$(-1)^l \tan\eta_l = \frac{Aj_{l-1}(g\kappa\sigma) - j_l(g\kappa\sigma)}{Aj_{-l}(g\kappa\sigma) + j_{-l-1}(g\kappa\sigma)}, \tag{13.2}$$

$$A \equiv \frac{\kappa}{\kappa'} \frac{j_{-l-1}(\kappa'\sigma)j_l(g\kappa'\sigma) - j_l(\kappa'\sigma)j_{-l-1}(g\kappa'\sigma)}{j_{-l-1}(\kappa'\sigma)j_{l-1}(g\kappa'\sigma) + j_l(\kappa'\sigma)j_{-l}(g\kappa'\sigma)} \tag{13.3}$$

for $l=0, 1, 2, \cdots$. Here relations

$$\frac{d}{dx}[x^{l+1}j_l(x)] = x^{l+1}j_{l-1}(x),$$

$$\frac{d}{dx}[x^{l+1}j_{-l-1}(x)] = -x^{l+1}j_{-l}(x)$$

have been used.

For the square-well potential discrete energy levels, E_{nl}, can be calculated easily. For s slightly greater than unity we need consider only one discrete level, E_{00}, which is for $l=0$. Since the function R in (12.7) with $l=0$ and $\kappa^2 = -2m^*|E_{00}|/\hbar^2$ is then given by

$$\text{const}\exp[-(2m^*|E_{00}|)^{\frac{1}{2}}r/\hbar] \quad \text{for } r > g\sigma,$$

$$\text{const}\sin[\{2m^*(\epsilon - |E_{00}|)\}^{\frac{1}{2}}(r-\sigma)/\hbar] \quad \text{for } \sigma < r < g\sigma,$$

the requirement that R and dR/dr be continuous leads to

$$\cot\left[\left(s\frac{\epsilon - |E_{00}|}{\epsilon}\right)^{\frac{1}{2}}\frac{\pi}{2}\right] = -\left(\frac{|E_{00}|}{\epsilon - |E_{00}|}\right)^{\frac{1}{2}}$$

where (10.11) has been used. This relation can be transformed into

$$s = \frac{\epsilon}{\epsilon - |E_{00}|}\left[1 + \frac{2}{\pi}\tan^{-1}\left(\frac{|E_{00}|}{\epsilon - |E_{00}|}\right)^{\frac{1}{2}}\right]^2, \tag{13.4}$$

which is shown in Fig. 12. (Figures 1 to 11 are in Part A.)

The second virial coefficient (12.10) for the square-well potential then assume, for each g and s,

$$B \equiv \left(\frac{2\pi\hbar}{m^*kT}\right)^{\frac{3}{2}} f(\tau) \quad \text{where} \quad \tau \equiv \frac{\pi^2 skT}{4(g-1)^2\epsilon}, \tag{13.5}$$

the function f being given in Table XIII.

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[22] See H. A. Bethe, Phys. Rev. **77**, 441 (1950).

[23] J. de Boer and A. Michels, Physica **5**, 945 (1938); **6**, 409 (1939). See also Kilpatrick, Keller, Hammel, and Metropolis, Phys. Rev. **94**, 1103 (1954).

† This section was prepared with the assistance of S. Kaneko.

TABLE XIII. The function $f(\tau)$ in Eq. (13.5).

τ	$f(\tau)$ for $g=1.5$ $s=1.0$	$f(\tau)$ for $g=1.5$ $s=1.1$	$f(\tau)$ for $g=2.0$ $s=1.0$	$f(\tau)$ for $g=2.0$ $s=4/3$
0	−0.5625	−∞	−0.5625	−∞
0.5	−0.380	−0.667	−0.384	−1.017
0.75	⋯	−0.648	⋯	⋯
1	−0.422	−0.670	−0.453	−1.017
2	−0.522	−0.791	−0.535	−1.132
4	−0.551	−0.872	−0.456	−1.149
6	−0.423	−0.783	−0.202	−0.983
8	−0.174	−0.568	0.153	−0.701
10	0.152	−0.253	0.600	−0.333
12	0.559	0.133	1.111	0.106
14	1.059	0.584	1.65	0.612
16	1.59	1.110	2.26	1.161
18	2.16	1.68	2.93	1.74
20	2.78	2.31	3.69	2.41

In Fig. 13 calculated curves of $(m^*kT/2\pi\hbar^2)^{\frac{3}{2}}B$ for ordinary helium, He^4, are compared with experimental results, which are given in Table XIV. The comparison shows that the depth parameter s is within the range

$$1.0<s<1.1 \text{ for } \mathrm{He}^4-\mathrm{He}^4 \tag{13.6}$$

(probably $s\approx 1.03$), which corresponds to the range

$$0.85<s<0.95 \text{ for } \mathrm{He}^4-\mathrm{He}^3,$$
$$0.75<s<0.83 \text{ for } \mathrm{He}^3-\mathrm{He}^3.$$

Although the relation (13.6) has been derived by means of the square-well potential, it is not very sensitive to the used potential. We, therefore, draw the conclusion: *the two-body system of* He^4—He^4 *probably has a discrete energy level while both the* He^4—He^4 *and* He^3—He^3 *systems definitely have no discrete level.*

Figure 13 shows, furthermore, that the adequate value of the model parameter g for helium is 1.5, which is conspicuously smaller than the value found in Sec. 2, i.e. $g=2.0$. A discussion on this discrepancy will be given in Sec. 18.

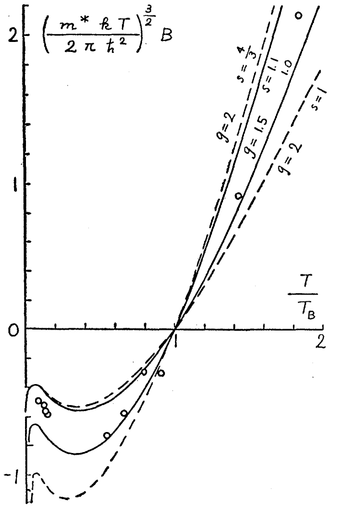

FIG. 13. Reduced second virial coefficient of helium *vs* T/T_B, T_B being the Boyle temperature 26.0°K. The curves are for the square-well potential with the depth parameter s.

14. High-Temperature Expansion of the Second Virial Coefficient

Above the Boyle temperature, where high-temperature expansions will be used, the symmetry effect is negligible. We therefore consider only the quantum effect due to wave nature in the following. The second virial coefficient is then given by

$$B=2\pi\int_0^\infty [1-\exp W(\mathbf{r},\mathbf{r})]r^2dr. \tag{14.1}$$

Here $W(\mathbf{r},\mathbf{r})$ is the diagonal element of $W(\mathbf{r},\mathbf{r}')$ which is to be determined from (11.5), (11.7), and (11.8). Let us in this section denote $W(\mathbf{r},\mathbf{r}')$ simply by W.

TABLE XIV. Second and third virial coefficients of He^4.

T°K	BA^3	$C\times10^{-2}A^6$	Reference
2.15	−293		a
2.32	−262		
2.86	−205		
3.35	−172		
3.96	−139		
14.16	−25.7		b
17.30	−15.0		
20.58	−6.0		
23.35	−5.1		
37.4	7.6		
48.2	12.0		
20.35	−4.6	11.3	c
65.15	15.6	7.0	
90.15	17.6	5.0	
123	18.9	5.2	
173	19.8	5.3	
223	19.8	5.0	
273	19.5	⋯	
273	19.7	2.1	d
323	19.2	2.0	
373	18.8	2.5	
423	18.4	3.0	

[a] W. E. Keller, Phys. Rev. 97, 1 (1955).
[b] Data are due to Nijihoff, Keesom, and Iliin; the values are taken from Keesom, *Helium* (Elsevier, Amsterdam, London and New York, 1942), p. 34.
[c] The values are taken from J. Otto, Handbuch d. Experimentalphysik, Bd. 8, Teil 2 (Akademische Verl. Leipzig, 1929), p. 144.
[d] A. Michels and H. Wouters, Physica 8, 923 (1941).

Inserting (11.7) into the Bloch equation (11.5) we have

$$U+\frac{\partial}{\partial\beta}W+\frac{\mathbf{r}-\mathbf{r}'}{\beta}\cdot\nabla W=q(\nabla W)^2+q\Delta W, \tag{14.2}$$

where ∇ means gradient with respect to $\mathbf{r}$, $\Delta\equiv\nabla\cdot\nabla$, and

$$q\equiv\hbar^2/2m^*. \tag{14.3}$$

Let us expand W into a power series in q:

$$W=W_0+qW_1+q^2W_2+\cdots. \tag{14.4}$$

We then obtain from (14.2), as regards the coefficients of $q^0, q^1, q^2, q^3, \cdots$,

$$U+\frac{\partial}{\partial\beta}W_0+\frac{\mathbf{r}-\mathbf{r}'}{\beta}\cdot\nabla W_0=0,$$

$$\frac{\partial}{\partial\beta}W_1+\frac{\mathbf{r}-\mathbf{r}'}{\beta}\cdot\nabla W_1=(\nabla W_0)^2+\Delta W_0,$$

$$\frac{\partial}{\partial\beta}W_2+\frac{\mathbf{r}-\mathbf{r}'}{\beta}\cdot\nabla W_2=2\nabla W_0\cdot\nabla W_1+\Delta W_1,$$

$$\frac{\partial}{\partial\beta}W_3+\frac{\mathbf{r}-\mathbf{r}'}{\beta}\cdot\nabla W_3=(\nabla W_1)^2+2\nabla W_0\cdot\nabla W_2+\Delta W_2,$$

$$\cdots. \tag{14.5}$$

Taking the condition (11.8) into account we have from the first equation of (14.5)

$$W_0(\mathbf{r},\mathbf{r})=-\beta U. \tag{14.6}$$

Multiplying the first equation of (14.5) by ∇ and Δ we have

$$\nabla U+\frac{\partial}{\partial\beta}\nabla W_0+\frac{1}{\beta}\nabla W_0+\frac{\mathbf{r}-\mathbf{r}'}{\beta}\cdot\nabla\nabla W_0=0,$$

$$\Delta U+\frac{\partial}{\partial\beta}\Delta W_0+\frac{2}{\beta}\Delta W_0+\frac{\mathbf{r}-\mathbf{r}'}{\beta}\cdot\nabla\Delta W_0=0,$$

from which, taking the limit $\mathbf{r}'\to\mathbf{r}$, we have

$$(\nabla W_0)_{\mathbf{r}'\to\mathbf{r}}=-\tfrac{1}{2}\beta\nabla U,\quad(\Delta W_0)_{\mathbf{r}'\to\mathbf{r}}=-\tfrac{1}{3}\beta\Delta U.$$

Inserting these into the second equation of (14.5) we obtain

$$W_1(\mathbf{r},\mathbf{r})=-\frac{\beta^2}{6}\Delta U+\frac{\beta^3}{12}(\nabla U)^2. \tag{14.7}$$

Similarly,[‡]

$$W_2(\mathbf{r},\mathbf{r})=-\frac{\beta^5}{60}\nabla\nabla U:\nabla U\nabla U+\frac{\beta^4}{30}\nabla U\cdot\nabla\Delta U$$
$$+\frac{\beta^4}{90}\nabla\nabla U:\nabla\nabla U-\frac{\beta^3}{60}\Delta\Delta U,$$

$$W_3(\mathbf{r},\mathbf{r})=\frac{17\beta^7}{5040}\nabla U\cdot\nabla\nabla U\cdot\nabla\nabla U\cdot\nabla U$$
$$+\frac{\beta^7}{840}\nabla\nabla\nabla U\vdots\nabla U\nabla U\nabla U$$
$$-\frac{17\beta^6}{2520}\nabla\Delta U\cdot\nabla\nabla U\cdot\nabla U$$
$$-\frac{\beta^6}{280}\nabla\nabla\Delta U:\nabla U\nabla U$$
$$-\frac{\beta^6}{210}\nabla\nabla\nabla U\vdots\nabla\nabla U\nabla U$$
$$-\frac{4\beta^6}{2835}(\nabla\nabla U\cdot\nabla\nabla U):\nabla\nabla U$$
$$+\frac{17\beta^5}{5040}\nabla\Delta U\cdot\nabla\Delta U$$
$$+\frac{\beta^5}{280}\nabla\Delta\Delta U\cdot\nabla U$$
$$+\frac{\beta^5}{210}\nabla\nabla\Delta U:\nabla\nabla U$$
$$+\frac{\beta^5}{840}\nabla\nabla\nabla U\vdots\nabla\nabla\nabla U$$
$$-\frac{\beta^4}{840}\Delta\Delta\Delta U.$$

These altogether give

$$W(\mathbf{r},\mathbf{r})=\textstyle\sum_i q^iW_i(\mathbf{r},\mathbf{r}). \tag{14.8}$$

Transforming $\exp W(\mathbf{r},\mathbf{r})$ into

$$\exp(-\beta U)\{1+qW_1(\mathbf{r},\mathbf{r})+q^2[W_2(\mathbf{r},\mathbf{r})+\tfrac{1}{2}W_1(\mathbf{r},\mathbf{r})^2]$$
$$+q^3[W_3(\mathbf{r},\mathbf{r})+W_1(\mathbf{r},\mathbf{r})W_2(\mathbf{r},\mathbf{r})+W_1(\mathbf{r},\mathbf{r})^3/6]+\cdots\}$$

and inserting this expression into (14.1) we finally obtain the second virial coefficient in the form

$$B=B^{(0)}+qB^{(1)}+q^2B^{(2)}+\cdots, \tag{14.9}$$

where

$$B^{(0)}=2\pi\int_0^\infty(1-e^{-\beta U})r^2dr,$$

$$B^{(1)}=\frac{\pi}{6}\beta^3\int_0^\infty e^{-\beta U}U'^2r^2dr,$$

$$B^{(2)}=-\frac{\pi}{6}\beta^4\int_0^\infty e^{-\beta U}\left(\frac{1}{10}U''^2+\frac{1}{5}\frac{U'^2}{r^2}+\frac{\beta}{9}\frac{U'^3}{r}-\frac{\beta^2}{72}U'^4\right)r^2dr,$$

$$B^{(3)}=\pi\beta^5\int_0^\infty e^{-\beta U}\left(\frac{U'''^2}{840}+\frac{U''^2}{140r^2}+\frac{\beta U''^3}{756}\right.$$
$$+\frac{\beta U'U''^2}{180r}+\frac{\beta U'^3}{945r^3}-\frac{\beta^2U'^2U''^2}{720}-\frac{\beta^2U'^4}{6480r^2}$$
$$\left.-\frac{\beta^3U'^5}{2160r}+\frac{\beta^4U'^6}{25920}\right)r^2dr,$$

q being defined by (14.3), β being $1/kT$.

[‡] As regards the : and ⋮ notation, see, for instance, Chapman and Cowling, reference 7.

The quantum correction in the form of expansion (14.9) was first given by Wigner[24] and then by Uhlenbeck and Gropper.[25] Kirkwood[26] supplemented their method by furnishing a more convenient means of obtaining the expansion, which was used by Uhlenbeck and Beth[27] and by Gropper[21] in their recalculations of the quantum correction up to the term proportional to q^2. The term proportional to q^3 was recently calculated by Midzuno, Shizume, and the present author.[28] The most elegant method here used is essentially due to Husimi.[19]

15. The Second Virial Coefficient for the Lennard-Jones Potential

Integration of each term in the expansion (14.9) can be performed for the Lennard-Jones potential

$$U(r)=\lambda r^{-n}-\mu r^{-6}$$

$$=U_0\left[\frac{6}{n-6}\left(\frac{r_0}{r}\right)^n-\frac{n}{n-6}\left(\frac{r_0}{r}\right)^6\right],\quad n>6,\qquad(15.1)$$

the result being a power series in

$$y\equiv\frac{\mu}{kT}\left(\frac{kT}{\lambda}\right)^{6/n},$$

i.e.,[29]

$$B^{(0)}=-\frac{2\pi}{n}\left(\frac{\lambda}{kT}\right)^{3/n}\sum_{t=0}^{\infty}\Gamma\left(\frac{6t-3}{n}\right)\frac{y^t}{t!},$$

$$B^{(1)}=\frac{2\pi}{n}\,\frac{1}{kT}\left(\frac{\lambda}{kT}\right)^{1/n}\sum_{t=0}^{\infty}\Gamma\left(\frac{6t-1}{n}\right)\frac{y^t}{t!}J_t^{(1)}(6,n),$$

$$B^{(2)}=-\frac{2\pi}{n}\left(\frac{1}{kT}\right)^2\left(\frac{\lambda}{kT}\right)^{-1/n}\sum_{t=0}^{\infty}\Gamma\left(\frac{6t+1}{n}\right)\frac{y^t}{t!}J_t^{(2)}(6,n),$$

$$B^{(3)}=\frac{2\pi}{n}\left(\frac{1}{kT}\right)^3\left(\frac{\lambda}{kT}\right)^{-3/n}\sum_{t=0}^{\infty}\Gamma\left(\frac{6t+3}{n}\right)\frac{y^t}{t!}J_t^{(3)}(6,n),$$

where

$$12J_t^{(1)}(6,n)=(n-6)6t-(n-1),$$

$$\begin{aligned}4320J_t^{(2)}(6,n)=\;&21(n-6)^2 6^2 t^2\\&+(6n^2+30n-42)(n-6)6t\\&+6n^3-27n^2+30n+63,\end{aligned}$$

$$\begin{aligned}362880J_t^{(3)}(6,n)=\;&93(n-6)^3 6^3 t^3\\&+(82n^2+657n-741)(n-6)^2 6^2 t^2\\&+(24n^4+348n^3+93n^2-810n+2241)(n-6)6t\\&+72n^5-126n^4-531n^3+1755n^2-405n-3645.\end{aligned}$$

Let us express the second virial coefficient in the final form

$$B=\tfrac{2}{3}\pi r_0^3\left[F^{(0)}(z)+\frac{F^{(1)}(z)}{cs}+\frac{F^{(2)}(z)}{(cs)^2}+\cdots\right],$$

$$z\equiv\frac{U_0}{kT},\qquad(15.2)$$

where (see (10.4))

$$\frac{1}{cs}=6\frac{\hbar^2}{2m^*}\,\frac{1}{U_0r_0^2}=\frac{6q}{U_0r_0^2},\qquad(15.3)$$

$$F^{(i)}(z)=\sum_{t=0}^{\infty}\beta_t^{(i)}z^{[3+(n-2)i+(n-6)t]/n},\quad i=0,1,2,\cdots.\qquad(15.4)$$

The coefficients β are given in Table XV for $n=9$ and 12. (The functions $F^{(i)}$ for $n=9$ are included in Table XVII.)

Making use of these tables and depending on the observed values given in Table XIV, we can determine

Table XV. Coefficients in the expansion (15.4) for L.-J. (6,n)-potential.

		For $n=9$		
t	$\beta_t^{(0)}$	$\beta_t^{(1)}$	$\beta_t^{(2)}$	$\beta_t^{(3)}$
0	1.7061	0.3880	−0.0426	0.0287
1	−2.1263	0.1513	−0.0990	0.0956
2	−0.7500	0.2282	−0.1740	0.2055
3	−0.4259	0.2475	−0.2400	0.3376
4	−0.2654	0.2350	−0.2822	0.4633
5	−0.1685	0.2039	−0.2949	0.5561
6	−0.1065	0.1652	−0.2813	0.6008
7	−0.0664	0.1265	−0.2490	0.5958
8	−0.0406	0.0924	−0.2071	0.5498
9	−0.0244	0.0648	−0.1632	0.4771
10	−0.0144	0.0438	−0.1228	0.3923
11	−0.00831	0.0286	−0.0886	0.3076
12	−0.00471	0.0182	−0.0616	0.2312
13	−0.00263	0.0112	−0.0414	0.1672
14	−0.00144	0.0067	−0.0270	0.1168
15	−0.00077	0.0040	−0.0171	0.0790
16	−0.00041	0.0023	−0.0106	0.0519
17	−0.00021	0.0013	−0.0064	0.0331
18	−0.00011	0.0007	−0.0037	0.0206
19	−0.00006	0.0004	−0.0022	0.0126
20	−0.00003	0.0002	−0.0012	0.0075
		For $n=12$		
t	$\beta_t^{(0)}$	$\beta_t^{(1)}$	$\beta_t^{(2)}$	$\beta_t^{(3)}$
0	1.2254	0.4838	−0.1276	0.1692
1	−1.8128	0.3694	−0.3768	0.6512
2	−0.6127	0.4471	−0.6189	1.3133
3	−0.3021	0.3981	−0.7254	1.8454
4	−0.1532	0.2979	−0.6815	2.0343
5	−0.0755	0.1965	−0.5447	1.8740
6	−0.0357	0.1173	−0.3838	1.4994
7	−0.0162	0.0645	−0.2440	1.0694
8	−0.00702	0.0330	−0.1422	0.6923
9	−0.00292	0.0159	−0.0769	0.4124
10	−0.00117	0.0072	−0.0390	0.2284
11	−0.00045	0.0031	−0.0186	0.1186
12	−0.00017	0.0013	−0.0084	0.0581
13	−0.00006	0.0005	−0.0036	0.0270

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[24] E. Wigner, Phys. Rev. **40**, 749 (1932).

[25] G. E. Uhlenbeck and L. Gropper, Phys. Rev. **41**, 79 (1932).

[26] J. G. Kirkwood, Phys. Rev. **44**, 31 (1933).

[27] G. E. Uhlenbeck and E. Beth, Physica **3**, 729 (1936).

[28] Kihara, Midzuno, and Shizume, J. Phys. Soc. Japan **10**, 249 (1955).

[29] Lennard-Jones, see reference 3; de Boer and Michels, see reference 23; Kihara, Midzuno, and Shizume, see reference 28.

the model parameters for He^4:

$$r_0=3.11\text{ A},\quad U_0/k=\ 7.82^\circ\text{K},\quad s=1.15\text{ for }n=9;$$
$$r_0=2.88\text{ A},\quad U_0/k=10.80^\circ\text{K},\quad s=1.05\text{ for }n=12$$

of which the latter agrees with (13.6).[30] (The choice of $n=12$, however, is not compatible with the statement in Sec. 3: "The bowl of the Lennard-Jones potential with $n=12$ is too narrow for molecules of the rare gases." This discrepancy will be discussed in Sec. 18.)

V. THE THIRD VIRIAL COEFFICIENT OF HELIUM

In this part the third virial coefficient of helium at higher temperatures is treated under the assumption of additivity of the intermolecular potential. This assumption is shortly discussed in the last section of this part.

16. High-Temperature Expansion of the Third Virial Coefficient§

The expansion (14.8) of $W(\mathbf{r},\mathbf{r})$ for a two-molecule system can be generalized to $W(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N;\ \mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ for an N-molecule (single component) system, where $\mathbf{r}_i$ is the position of the ith molecule. Namely,

$$W(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{r}_1,\cdots,\mathbf{r}_N)=W_0(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{r}_1,\cdots,\mathbf{r}_N)+qW_1(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{r}_1,\cdots,\mathbf{r}_N)+\cdots,\tag{16.1}$$

where q is $\hbar^2$ divided by the mass of a molecule. (Compare (14.3) where m^* is the reduced mass.) The first term on the right-hand side is, like (14.6),

$$W_0(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{r}_1,\cdots,\mathbf{r}_N)=-\beta\Phi(\mathbf{r}_1,\cdots,\mathbf{r}_N),\qquad \beta\equiv 1/kT,\tag{16.2}$$

Φ being the potential energy of the system. For the second term we have, like (14.7),

$$W_1(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{r}_1,\cdots\ \mathbf{r}_N)=-\frac{\beta^2}{12}\sum_{i=1}^{N}\frac{\partial}{\partial\mathbf{r}_i}\cdot\frac{\partial}{\partial\mathbf{r}_i}\Phi+\frac{\beta^3}{24}\sum_{i=1}^{N}\left(\frac{\partial}{\partial\mathbf{r}_i}\Phi\right)^2.\tag{16.3}$$

The classical third virial coefficient can be expressed in the form

$$4B^2+\frac{1}{3V}\int\int\int\{-2+\exp[-\beta\Phi(\mathbf{r}_1,\mathbf{r}_2)]+\exp[-\beta\Phi(\mathbf{r}_1,\mathbf{r}_3)]+\exp[-\beta\Phi(\mathbf{r}_2,\mathbf{r}_3)]-\exp[-\beta\Phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)]\}d\tau_1d\tau_2d\tau_3,$$

V being the volume of the system. Replacing in this expression the Boltzmann factors, $\exp[-\beta\Phi(\mathbf{r}_1,\mathbf{r}_2)],\cdots$, $\exp[-\beta\Phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)]$, by the corresponding Slater sums, $\exp[W(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1,\mathbf{r}_2)],\cdots$, $\exp[W(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)]$, we obtain the quantum-mechanical expression.[31]

Our object in this section is to calculate the first quantum correction $qC^{(1)}$ to the third virial coefficient

$$C=C^{(0)}+qC^{(1)}+\cdots\tag{16.4}$$

which is similar to the expansion (14.9) of B. By use of (14.9) we have

$$C^{(1)}=8B^{(0)}B^{(1)}+C_1,\tag{16.5}$$

$$\begin{aligned}C_1=\frac{1}{3V}\cdot\frac{\beta^3}{24}\int\int\int\Big\{&-\exp[-\beta\Phi(\mathbf{r}_1,\mathbf{r}_2)]\sum_i\left[\frac{\partial}{\partial\mathbf{r}_i}\Phi(\mathbf{r}_1,\mathbf{r}_2)\right]^2\\&-\exp[-\beta\Phi(\mathbf{r}_1,\mathbf{r}_3)]\sum_i\left[\frac{\partial}{\partial\mathbf{r}_i}\Phi(\mathbf{r}_1,\mathbf{r}_3)\right]^2\\&-\exp[-\beta\Phi(\mathbf{r}_2,\mathbf{r}_3)]\sum_i\left[\frac{\partial}{\partial\mathbf{r}_i}\Phi(\mathbf{r}_2,\mathbf{r}_3)\right]^2\\&+\exp[-\beta\Phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)]\sum_i\left[\frac{\partial}{\partial\mathbf{r}_i}\Phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\right]^2\Big\}d\tau_1d\tau_2d\tau_3.\end{aligned}\tag{16.6}$$

Here we have used integration by parts such as

$$\frac{1}{V}\int\int\int\exp(-\beta\Phi)\sum\frac{\partial}{\partial\mathbf{r}_i}\cdot\frac{\partial}{\partial\mathbf{r}_i}\Phi d\tau_1d\tau_2d\tau_3=\frac{1}{V}\int\int\int\exp(-\beta\Phi)\sum\left(\frac{\partial}{\partial\mathbf{r}_i}\Phi\right)^2d\tau_1d\tau_2d\tau_3.$$

We are assuming from the outset that the potential energy of the system is equal to the sum of the potential energies of pairs. Hence, in terms of $r_{ij}\equiv|\mathbf{r}_i-\mathbf{r}_j|$, the potential energy of a three atom cluster is

$$\Phi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=U(r_{12})+U(r_{13})+U(r_{23}).\tag{16.7}$$

Taking into account such relations as

$$\frac{1}{2V}\int\int\int\exp[-\beta U(r_{12})]\sum_i\left(\frac{\partial U(r_{12})}{\partial\mathbf{r}_i}\right)^2d\tau_1d\tau_2d\tau_3=\frac{1}{V}\int\int\int\exp[-\beta U(r_{12})][U'(r_{12})]^2d\tau_1d\tau_2d\tau_3$$

and using the transformation

$$V^{-1}d\tau_1d\tau_2d\tau_3=8\pi^2r_{12}r_{13}r_{23}dr_{12}dr_{13}dr_{23}$$

of integration variables, we finally obtain

$$C_1=\frac{2\pi^2}{9}\beta^3\int\int\int(A_{12}+A_{13}+A_{23})r_{12}r_{13}r_{23}dr_{12}dr_{13}dr_{23},\tag{16.8}$$

---

[30] De Boer and Michels' result, reference 23, is $r_0=2.87$A, $U_0/k=10.22^\circ$K for $n=12$ which corresponds to $s=0.99$.

§ Sections 15 and 16 were prepared with the assistance of Y. Midzuno and T. Shizume.

[31] Uhlenbeck and Beth, see reference 27; see also B. Kahn and G. E. Uhlenbeck, Physica **5**, 399 (1938).

where,

$$A_{12}\equiv\{[U'(r_{12})]^2+U'(r_{13})U'(r_{23})(r_{13}^3+r_{23}^2-r_{12}^2)/2r_{13}r_{23}\}$$
$$\times\exp[-\beta U(r_{12})-\beta U(r_{13})-\beta U(r_{23})]$$
$$-[U'(r_{12})]^2\exp[-\beta U(r_{12})]$$

with similar expressions for A_{13} and A_{23}. The integral is to be taken over all values of r_{12},r_{13},r_{23}, which form three sides of a triangle.

17. The Third Virial Coefficient for the Lennard-Jones Potential

Here again let us adopt the Lennard-Jones potential (15.1) for which the classical $C^{(0)}$ was treated in Sec. 3.[32] Using

$$R\equiv r_{12},\quad \xi\equiv r_{13}/R,\quad \eta\equiv r_{23}/R$$

as integration variables, we can transform (16.8) into

$$C_1=\frac{2\pi^2}{3}\beta^3\int_0^1\int_{1-\xi}^1\left[\int_0^\infty(A_{12}+A_{13}+A_{23})R^5dR\right]\xi\eta d\eta d\xi.$$

The integration with respect to R can be performed by the usual series-expansion technique. The result is as follows:

$$C_1=\frac{2\pi^2}{3n}\frac{1}{kT}\left(\frac{\lambda}{kT}\right)^{4/n}\sum_{t=0}^{\infty}y^tI_t(6,n),\qquad(17.1)$$

in which y is the same as in Sec. 15, and

$$I_t(6,n)=\frac{1}{t!}\Gamma\left(\frac{6t-4}{n}\right)\int_0^1\int_{1-\xi}^1F_t\xi\eta d\eta d\xi,$$

$$F_t=(6t+n-4)(6t-4)[\langle n,n\rangle\langle n\rangle^{(4-6t)/n-2}\langle 6\rangle^t-\langle 6\rangle]$$
$$-12t(6t-4)[\langle n,6\rangle\langle n\rangle^{(4-6t)/n-1}\langle 6\rangle^{t-1}-\langle 6\rangle]$$
$$+36t(t-1)[\langle 6,6\rangle\langle n\rangle^{(4-6t)/n}\langle 6\rangle^{t-2}-\langle 6\rangle],$$

TABLE XVI. Coefficients in the expansion (17.1) for L.-J. (6,9)-potential.

t	$I_t(6,9)$
0	−118.7
1	+56.0
2	12.61
3	10.00
4	7.32
5	4.60
6	2.59
7	1.338
8	0.651
9	0.300
10	0.133
11	0.057
12	0.024

TABLE XVII. Functions in the expansions (15.2) and (17.2) for L.-J. (6,9)-potential.

$-\log_{10}z$	$F^{(0)}(z)$	$F^{(1)}(z)$	$F^{(2)}(z)$	$F^{(3)}(z)$	$G^{(0)}(z)$	$G^{(1)}(z)$
0.1	−1.583	1.194	−1.007	1.684	0.369	1.0
0.2	−1.071	0.741	−0.444	0.564	0.409	0.37
0.3	−0.6995	0.4793	−0.2056	0.2024	0.357	0.187
0.4	−0.4255	0.3200	−0.0992	0.0757	0.303	0.127
0.5	−0.2218	0.2195	−0.0495	0.0295	0.264	0.100
0.6	−0.0700	0.1538	−0.0255	0.0119	0.237	0.078
0.7	0.0430	0.1095	−0.0136	0.0050	0.219	0.062
0.8	0.1265	0.0791	−0.0073	0.0021	0.206	0.050
0.9	0.1874	0.0578	−0.0040	0.0009	0.194	0.039
1.0	0.2309	0.0426	−0.0022	0.0004	0.183	0.030
1.1	0.2610	0.0316	−0.0013		0.172	0.020
1.2	0.2806	0.0236	−0.0007		0.160	0.015
1.3	0.2922	0.0177	−0.0004		0.149	0.012
1.4	0.2974	0.0134			0.137	0.010
1.5	0.2979	0.0101			0.125	0.008
1.6	0.2946	0.0077			0.114	0.006
1.7	0.2885	0.0058			0.103	0.004
1.8	0.2805	0.0044			0.093	
1.9	0.2709	0.0034			0.083	
2.0	0.2603	0.0026			0.074	

where the bracket notation has been used in the sense

$$\langle a\rangle\equiv 1+\xi^{-a}+\eta^{-a},$$

$$\langle a\rangle\equiv 1+\xi^{-a}+\eta^{-a},$$

$$\langle a,b\rangle\equiv\langle a+b+2\rangle$$
$$+(\xi^{-a-2}+\xi^{-b-2})(1+\xi^2-\eta^2)/4$$
$$+(\eta^{-a-2}+\eta^{-b-2})(1+\eta^2-\xi^2)/4$$
$$+(\xi^{-a-2}\eta^{-b-2}+\eta^{-a-2}\xi^{-b-2})(\xi^2+\eta^2-1)/4.$$

The values of $I_t(6,9)$ obtained by numerical integrations are given in Table XVI.

By use of C_1 the third virial coefficient, C, is given by (16.4) with (16.5) up to the term proportional to the first power of q. For $n=9$, Table XVII gives the functions $G^{(0)}$ and $G^{(1)}$ in the expansion

$$C=\frac{5}{18}\pi^2r_0^6\left[G^{(0)}(z)+\frac{1}{cs}G^{(1)}(z)+\cdots\right],\qquad(17.2)$$

$$z=U_0/kT,\quad 1/cs=6q/U_0r_0^2,$$

together with $F^{(i)}$ in the expansion (15.2) of the second virial coefficient.

Figure 14 shows a comparison with experimental results for He^4. Here curves indicate calculated values based on the model parameters determined from the second virial coefficient. Although the experimental results do not seem to be very accurate, the comparison shows that the bowl of the Lennard-Jones potential with $n=12$ is not sufficiently wide (compare Sec. 3).

It is to be noted that the potential energy of the three-body system has been assumed to equal the sum of the potential energies of pairs. This assumption of potential additivity is now capable of discussion.

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[32] Numerical values of γ_t (9) and γ_t (12) in Table III were recalculated with great accuracy by Epstein, Hibbert, Powers, and Roe, J. Chem. Phys. 22, 464 (1954), and by Rowlinson, Sumner, and Sutton, Trans. Faraday Soc. 50, 1 (1954), respectively.

18. Nonadditivity of the Intermolecular Potential

The intermolecular potential of helium determined from the second virial coefficient has the bowl-width corresponding to

$$g=1.5 \text{ for the square-well potential,} \tag{18.1a}$$

$$n=12 \text{ for the Lennard-Jones potential.} \tag{18.1b}$$

These values of parameters indicating relative bowl-width may belong also to other rare-gas molecules, Ne, A, Kr, and Xe. (This similarity of the intermolecular potential does not strictly hold of course: probably, the larger the molecule, the smaller the relative bowl-width. But such nonsimilarity does not influence the following conclusion.)

In Secs. 2, 3, and 17 the third virial coefficient was represented, under the assumption of additivity of the intermolecular potential, by models having a wider bowl with

$$g\approx 2.0 \text{ for the square-well potential,} \tag{18.2a}$$

$$n\approx 9 \text{ for the Lennard-Jones potential.} \tag{18.2b}$$

Furthermore, we saw in Sec. 6 that a potential with much wider bowl has to be adopted if we want to explain the stability of *cubic* crystal structure for Ne, A, Kr, and Xe under the assumption of the potential additivity.

These circumstances show that the intermolecular potential may not be considered to be strictly additive.[33] The potential with parameters (18.2) should be accepted as "the mean (or effective) additive intermolecular potential" in a three-body system. Therefore, *the bowl of the mean additive intermolecular potential in a many-body system is wider than that of the potential in the two-body system*, as shown in Fig. 15.

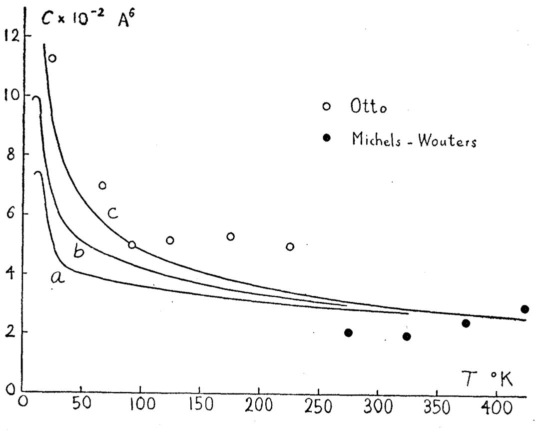

FIG. 14. Third virial coefficient of helium with curves for the Lennard-Jones potential determined from the second virial coefficient. Curve *a* is for (6,12)-potential, classical; curve *b* is for (6,9)-potential, classical; curve *c* is for (6,9)-potential with the first quantum correction.

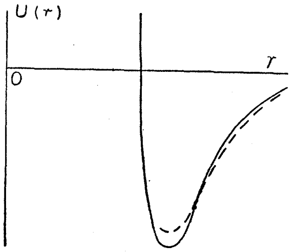

FIG. 15. The full line indicates qualitatively the intermolecular potential in two-body systems; the dotted line shows the mean additive intermolecular potential in three-body systems.

VI. VIRIAL COEFFICIENTS BETWEEN UNLIKE MOLECULES

Up to this point we have been investigating pure gases; the object of this part is to give a brief treatment of typical gaseous mixtures. The equation of state for binary mixtures of species A and B is of the form

$$\begin{aligned} pv=kT[1&+(B_{AA}\xi_A{}^2+2B_{AB}\xi_A\xi_B+B_{BB}\xi_B{}^2)v^{-1} \\ &+(C_{AAA}\xi_A{}^3+3C_{AAB}\xi_A{}^2\xi_B+3C_{ABB}\xi_A\xi_B{}^2 \\ &+C_{BBB}\xi_B{}^3)v^{-2}+\cdots]. \end{aligned}$$

Here ξ_A and $\xi_B=1-\xi_A$ are mole fractions of the species A and B, respectively. B_{AA} and C_{AAA} are second and third virial coefficients for the molecule A; B_{BB} and C_{BBB} for the molecule B. B_{AB}, C_{AAB}, and C_{ABB} are virial coefficients between unlike molecules, in which we are now interested.

19. The Second Virial Coefficient between Helium Isotopes

For mixtures of He^4 and He^3, which will be denoted by A and B, respectively, the intermolecular potentials of A to A, B to B, and A to B are all the same. Hence the second virial coefficients B_{AA}, B_{BB}, and B_{AB} are different only as regards the reduced masses and the statistics. Let us confine our treatment above the Boyle temperature where the statistical effect is negligible.[34] The high-temperature expansion then becomes (compare (14.9))

$$\begin{aligned} B_{AA}&=B^{(0)}+q_{AA}B^{(1)}+q_{AA}{}^2B^{(2)}+\cdots, \\ B_{BB}&=B^{(0)}+q_{BB}B^{(1)}+q_{BB}{}^2B^{(2)}+\cdots, \\ B_{AB}&=B^{(0)}+q_{AB}B^{(1)}+q_{AB}{}^2B^{(2)}+\cdots. \end{aligned}$$

Here q_{AA}, q_{BB}, and q_{AB} are $\frac{1}{2}\hbar^2$ divided by the reduced mass for pairs $A-A$, $B-B$, and $A-B$, respectively, so that $2q_{AB}=q_{AA}+q_{BB}$.

Figure 16 shows these three coefficients calculated by use of the Lennard-Jones potential with parameters determined in Sec. 15.

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[33] In fact, strictly additive is only the van der Waals-London attraction as derived from the perturbation theory to the second order. If the perturbation calculation is pursued to the third order, interactions between triplets of atoms appear; see B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943).

[34] As regards the second virial coefficient of helium mixtures at low temperatures, see Cohen, Offerhaus, and de Boer, Physica **20**, 501 (1954); Kilpatrick, Keller, Hammel, and Metropolis, Phys. Rev. **94**, 1103 (1954); Kilpatrick, Keller, and Hammel, Phys. Rev. **97**, 9 (1955).

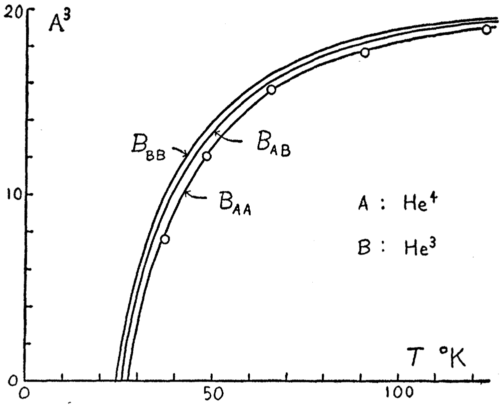

FIG. 16. Second virial coefficient between helium isotopes calculated for the Lennard-Jones potential. The circles are observed values for the pure He^4 gas.

20. The Core-Model of Interaction between Unlike Molecules

The core-model introduced in Sec. 9 can also be applied to the mixed virial coefficient B_{AB}. The model is as follows: We assume an appropriate convex body called core inside each molecule and define the intermolecular distance ρ as the shortest distance between two cores. The intermolecular potential U_{AB} for the pair $A-B$ is assumed to be a function of ρ only, i.e., $U_{AB}=U_{AB}(\rho)$ for which $U_{AB}(0)=\infty$.

By means of the core-model of molecules, the mixed second virial coefficient is given by

$$B_{AB}=\int_{\rho=0}^{\rho=\infty}\left[1-\exp\frac{-U_{AB}(\rho)}{kT}\right]db_{AB}(\rho)+b_{AB}(0),$$

where

$$b_{AB}(\rho)=\frac{V_A+V_B}{2}+\frac{M_BS_A+M_AS_B}{8\pi},$$

$$M_A=2\pi\rho+M_{0A},$$

$$S_A=\pi\rho^2+M_{0A}\rho+S_{0A},$$

$$V_A=\frac{\pi}{6}\rho^3+\frac{1}{4}M_{0A}\rho^2+\frac{1}{2}S_{0A}\rho+V_{0A},$$

and similar relations as regards the species B. Here V_{0A}, S_{0A}, and M_{0A} are, respectively, the volume, the surface area, and the mean curvature integrated over the whole surface of the convex core of the molecule A. The function $b_{AB}(\rho)$ may also be expressed in the form [compare (9.2)]

$$b_{AB}(\rho)=\frac{2\pi}{3}\rho^3+\frac{M_{0A}+M_{0B}}{2}\rho^2+\left(\frac{S_{0A}+S_{0B}}{2}+\frac{M_{0A}M_{0B}}{4\pi}\right)\rho+\frac{V_{0A}+V_{0B}}{2}+\frac{M_{0B}S_{0A}+M_{0A}S_{0B}}{8\pi}.$$

In particular, when the potential $U_{AB}(\rho)$ is the Lennard-Jones function,

$$U_{AB}(\rho)=U_{0AB}\left[\left(\frac{\rho_{0AB}}{\rho}\right)^{12}-2\left(\frac{\rho_{0AB}}{\rho}\right)^{6}\right],$$

the second virial coefficient B_{AB} is expressed by a power series with respect to

$$(z_{AB})^{\frac{1}{2}}\equiv(U_{0AB}/kT)^{\frac{1}{2}},$$

that is

$$B_{AB}=\frac{2\pi}{3}\rho_{0AB}{}^3F_3(z_{AB})+\frac{M_{0A}+M_{0B}}{2}\rho_{0AB}{}^2F_2(z_{AB})+\left(\frac{S_{0A}+S_{0B}}{2}+\frac{M_{0A}M_{0B}}{4\pi}\right)\rho_{0AB}F_1(z_{AB})+\frac{V_{0A}+V_{0B}}{2}+\frac{M_{0B}S_{0A}+M_{0A}S_{0B}}{8\pi},$$

where $(s=1,2,3)$

$$F_s(z)=-\frac{s}{12}\sum_{t=0}^{\infty}\frac{1}{t!}\Gamma\left(\frac{6t-s}{12}\right)2^tz^{(6t+s)/12},$$

the table of which is given in Sec. 9.

As regards model constants, the relations

$$2\rho_{0AB}=\rho_{0AA}+\rho_{0BB},$$

$$U_{0AB}{}^2=U_{0AA}U_{0BB}$$

have been verified to hold approximately.[35] An example is shown in Fig. 17, in which curves were calculated by

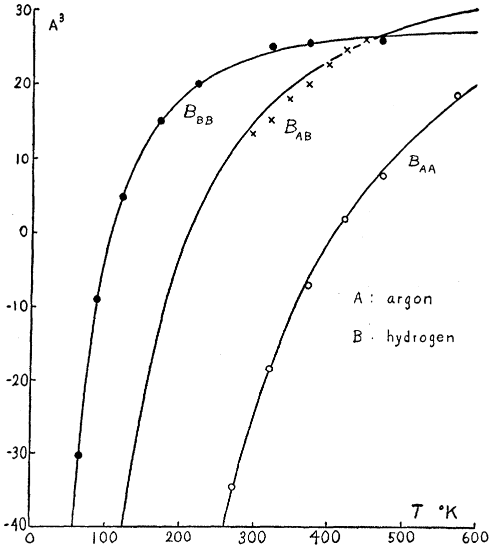

FIG. 17. Second virial coefficient between argon and hydrogen with curves for the core-model.

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[35] T. Kihara and S. Koba, J. Phys. Soc. Japan 9, 688 (1954); see also J. A. Beattie and W. H. Stockmayer, J. Chem. Phys. 10, 473 (1942).

use of these relations and by use of model constants determined in Sec. 9 from the virial coefficients of pure gases.

21. The Third Virial Coefficient for Binary Mixtures

The third virial coefficient for unlike molecules can easily be evaluated only in the case of the square-well potential[36]

$$U_{ij}(r)=\begin{cases}\infty & \text{for } r<\sigma_{ij}\\ -\epsilon_{ij} & \text{for } \sigma_{ij}<r<\rho_{ij}\\ 0 & \text{for } \rho_{ij}<r,\end{cases}$$

where, in the case of a binary mixture, $i=A$ or B, $j=A$ or B, and $k=A$ or B.

The result is a polynomial on the third order in

$$x_{ij}=\exp(\epsilon_{ij}/kT)-1$$

that is

$$\begin{aligned}3C_{ijk}=I^{(0)}&-[x_{ij}I^{(1.1)}+x_{ik}I^{(1.2)}+x_{jk}I^{(1.3)}]\\&+[x_{ij}x_{ik}I^{(2.1)}+x_{ij}x_{jk}I^{(2.2)}+x_{ik}x_{jk}I^{(2.3)}]\\&-x_{ij}x_{ik}x_{jk}I^{(3)}.\end{aligned}$$

Here the coefficients I are given by

$$\begin{aligned}I^{(0)}&=W(\sigma_{ij},\sigma_{ik},\sigma_{jk}),\\I^{(1.1)}&=W(\rho_{ij},\sigma_{ik},\sigma_{jk})-I^{(0)},\\I^{(1.2)}&=W(\sigma_{ij},\rho_{ik},\sigma_{jk})-I^{(0)},\\I^{(1.3)}&=W(\sigma_{ij},\sigma_{ik},\rho_{jk})-I^{(0)},\\I^{(2.1)}&=W(\rho_{ij},\rho_{ik},\sigma_{jk})-I^{(0)}-I^{(1.1)}-I^{(1.2)},\\I^{(2.2)}&=W(\rho_{ij},\sigma_{ik},\rho_{jk})-I^{(0)}-I^{(1.1)}-I^{(1.3)},\\I^{(2.3)}&=W(\sigma_{ij},\rho_{ik},\rho_{jk})-I^{(0)}-I^{(1.2)}-I^{(1.3)},\\I^{(3)}&=W(\rho_{ij},\rho_{ik},\rho_{jk})-I^{(0)}-\textstyle\sum_t I^{(1.t)}-\sum_t I^{(2.t)},\end{aligned}$$

by means of the same function $W(a,b,c)$ defined in Sec. 2.

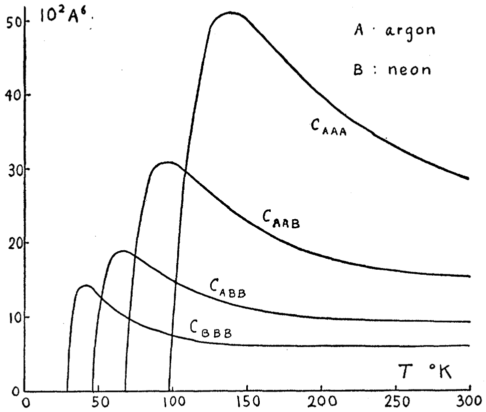

FIG. 18. Third virial coefficient for argon-neon mixtures calculated for the square-well potential.

As regards model parameters, it may be reasonable to assume $\rho_{AA}=2\sigma_{AA}$, $\rho_{AB}=2\sigma_{AB}$, $\rho_{BB}=2\sigma_{BB}$,

$$2\sigma_{AB}=\sigma_{AA}+\sigma_{BB},\quad \epsilon_{AB}{}^2=\epsilon_{AA}\epsilon_{BB}$$

(compare Sec. 2 and Sec. 20). Figure 18 shows C_{AAA}, C_{AAB}, C_{ABB}, and C_{BBB} calculated on these assumptions in case A and B are argon and neon, respectively. The model constants here used are

$$\sigma_{AA}=3.11\text{ A},\quad \epsilon_{AA}/k=54.7\text{°K},$$
$$\sigma_{BB}=2.51\text{ A},\quad \epsilon_{BB}/k=16.4\text{°K},$$

which were determined from the second virial coefficients.

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[36] T. Kihara, see reference 2.