JUNE 15, 1941 PHYSICAL REVIEW VOLUME 59

On the Theory of the Thermal Diffusion Coefficient for Isotopes. II

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(Received March 11, 1941)

The temperature dependence of the thermal diffusion constant α of a mixture of isotopes is determined for the 9,5 Lennard-Jones model of intermolecular forces by the use of the Chapman-Enskog theory of transport phenomena in gases. The treatments of the Sutherland model and the special Lennard-Jones model given in the first paper of this series were subject to the drastic restriction that the depth ϵ of the potential energy minimum must be small compared with kT. The present treatment of the 9,5 model is valid to all orders of ϵ/kT; this advantage is gained, however, at the expense of substituting laborious numerical methods for the analytical methods that were used in the previous paper. The results indicate that the thermal diffusion constant first increases slightly as the temperature decreases, and then decreases rapidly, passing through zero and becoming negative at a temperature about 1.5 times the critical temperature. The constant becomes strongly negative as the temperature decreases still further, and then approaches zero as the absolute temperature approaches zero. When the theoretical results are modified to account for the fact that the neon molecule is much harder than is indicated by a repulsive force index of 9, a quantitative agreement is obtained with Nier's experimental data on mixtures of the neon isotopes. Fair agreement is obtained with the data of Atkins, Bastick, and Ibbs on mixtures of the noble gases. An approximate method is presented which permits one to obtain from the results for the inverse power model, the first two terms of the series development of α in powers of ϵ/kT for the general Lennard-Jones model of intermolecular forces.

THE present paper is a continuation of the previous one of the same title,[1] and is devoted primarily to a treatment of the Lennard-Jones 9,5 model which is not restricted by the requirement that the attractive force be weak. Although this model of intermolecular forces is more specialized than any of those treated in I, it has turned out to be of much greater interest because the results are free of the restriction just mentioned.

In order to avoid too extensive reference to I, the general formulae will be given briefly in Section I.

I. INTRODUCTION

The equation of diffusion, with the effect of thermal diffusion included, may be written in the form

$$c_1(\mathbf{v}_1-\mathbf{v})=c_1c_2(\mathbf{v}_1-\mathbf{v}_2)=c_2(\mathbf{v}-\mathbf{v}_2)$$
$$=D_{12}(-\operatorname{grad}c_1+\alpha c_1c_2\operatorname{grad}\log T) \quad (1)$$

for a mixture of two gases. In Eq. (1), c_1 is the fractional particle density of the first gas, and c_2 is the fractional particle density of the second gas; $\mathbf{v}_1$ and $\mathbf{v}_2$ are the convection velocities of the molecules of the first and second gases, respectively, and $\mathbf{v}$ is defined as

$$\mathbf{v}=c_1\mathbf{v}_1+c_2\mathbf{v}_2; \quad (2)$$

D_{12} is the coefficient of diffusion; and α is the thermal diffusion constant.

It is to be noted that since $\mathbf{v}$ is obtained by averaging with respect to the *number* of the molecules of each kind, the total mass flux is not given by $\rho\mathbf{v}$, where ρ is the density, but is rather given by $\rho\mathbf{v}_m$, where $\mathbf{v}_m$ is defined by

$$\mathbf{v}_m=\frac{c_1m_1\mathbf{v}_1+c_2m_2\mathbf{v}_2}{c_1m_1+c_2m_2}, \quad (3)$$

where m_1 and m_2 are the masses of the molecules of the first and second gas. A confusion between $\mathbf{v}$ and $\mathbf{v}_m$ led to the publication of an incorrect formula in a previous paper.[2]

From here on, we restrict our discussion to the case in which the two gases represent different isotopes of what is chemically the same gas. In this case it is a close approximation to replace D_{12} by D, the coefficient of self-diffusion of either gas.

The rigorous Chapman-Enskog theory of transport phenomena in gases yields the value of the

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[1] R. Clark Jones, Phys. Rev. **58**, 111 (1940). This paper will be referred to as I.

[2] W. H. Furry, R. Clark Jones and L. Onsager, Phys. Rev. **55**, 1083 (1939). Equation (10) of this paper is correct only if ρ is regarded as the density the gas would have if all of the molecules were of species 1.

thermal diffusion constant in terms of certain cross section integrals which refer to collisions between molecules of the first and second gas. Let the impact parameter of such a collision be indicated by b, and the relative velocity at infinity by g. Now let us reduce b and g to dimensionless form by means of the transformation:

$$\begin{aligned} g &= (2kT/m)^{\frac{1}{2}}\gamma, \\ b &= s\sigma(\gamma)\beta, \end{aligned} \tag{4}$$

where $m = m_1m_2/(m_1+m_2)$ is the reduced mass, s is an arbitrary constant length, and $\sigma(\gamma)$ is an arbitrary function of γ and therefore of g. Finally, let $\theta(\beta, \gamma)$ be the angle of deflection suffered by either molecule when it is deflected by the field of force of another, as measured in the center-of-gravity coordinate system.

We may now define the quantities

$$\Theta^{(l)}(\gamma) = \int_0^\infty \{1 - P_l(\cos\theta)\}\beta d\beta \tag{5}$$

and in turn the quantities

$$\Omega^{(l,\,k)} = \int_0^\infty \exp(-\gamma^2)\sigma^2(\gamma)\gamma^k\Theta^{(l)}(\gamma)d\gamma. \tag{6}$$

The Ω's are dimensionless collision cross sections suitably averaged over β and γ.

In first approximation, the Chapman-Enskog theory yields the following general formula:

$$R_T = \frac{177}{7}\cdot\frac{(2\Omega^{(1,7)} - 5\Omega^{(1,5)})(15\Omega^{(1,5)} + 2\Omega^{(2,7)})}{\Omega^{(2,7)}(165\Omega^{(1,5)} - 60\Omega^{(1,7)} + 12\Omega^{(1,9)} + 16\Omega^{(2,7)})}, \tag{7}$$

where R_T is the ratio of α to the value predicted by the theory for molecules which behave as hard smooth elastic spheres:

$$R_T = \alpha/\alpha_{\text{hard spheres}}, \tag{8}$$

$$\alpha_{\text{hard spheres}} = \frac{105}{118}\,\frac{m_2 - m_1}{m_2 + m_1}. \tag{9}$$

Equation (7) cannot be given in any more explicit form without specifying the nature of the intermolecular forces.

The material presented thus far is given in much greater detail in the first three pages of I.

It seems worth while to indicate the general formulae for the first approximations to the coefficients of viscosity and of diffusion in terms of the Ω's; we have

$$\eta = \frac{15}{32s^2\Omega^{(2,7)}}\left(\frac{mkT}{\pi}\right)^{\frac{1}{2}} \tag{10}$$

and for the coefficient of self-diffusion:

$$D = \frac{3}{16\rho s^2\Omega^{(1,5)}}\left(\frac{mkT}{\pi}\right). \tag{11}$$

In Eqs. (10) and (11), and only in these two equations, m is the mass of the molecules, rather than the reduced mass. The elimination of s^2 between (10) and (11) leads to the useful formula

$$D = \left\{\frac{2}{5}\,\frac{\Omega^{(2,7)}}{\Omega^{(1,5)}}\right\}\frac{\eta}{\rho}. \tag{12}$$

We may now obtain the result (29,I), which was stated without proof, by substituting (26,I) in (12).

Note added in proof.—As we pointed out in I, Eq. (7) is an approximation in the further sense that the expression on the right is the first term of a power series expansion in the relative mass difference $(m_2 - m_1)/(m_2 + m_1)$. The equation is approximately correct, however, even when the ratio of the masses m_2/m_1 is large compared with unity. In a recent paper[2a] Chapman has discussed numerically the dependence of R_T on the relative mass difference for the special case of the inverse power model.

His results may be summarized as follows. For the sake of specificity we assume that $m_2 \geqslant m_1$. When the concentration of the heavier molecules is small, we find by inspection of Chapman's Table 6 that R_T is essentially independent of the relative mass difference for all values of the force index ν. When the concentration of the heavier molecules is not small, however, we find from Tables 4 and 5 that R_T decreases as the relative mass difference increases from zero to

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[2a] S. Chapman, Proc. Roy. Soc. **A177**, 38–62 (1940).

unity, and that the amount of the decrease is greater the greater the value of c_2 and the greater the value of ν. In the most extreme case, when the mass ratio and ν are both infinite, the value of R_T decreases by the factor 2.3 as the concentration of the heavier molecules rises from zero to unity. The corresponding factor is much closer to unity, however, for the isotopic mixtures which one meets in practice. For example, when $m_2=2m_1$ and ν is infinite, the factor is 1.2; and when $\nu=15$ with the same mass ratio, the factor is 1.1.

In the same paper, Chapman points out that the values of $A_1^{(3)}$ and $A_2^{(3)}$ which he had previously given and which were used in I, 0.812 and 1.825, are incorrect. He states that the correct values are 0.796 and 1.584. As a consequence of this change, the first line of Table I in I should read

0.796	1.584	1.327	1.592	0.807

The next line, which was obtained by interpolation, should be modified, and the first line of Table V should also be changed in an obvious manner. The correction of these errors removes a noticeable discontinuity in the functions $f(\nu)$ and $C(\nu)$.

Ternary and Higher Order Mixtures

Note added in proof.—Further on in this paper it is suggested that measurements of the thermal diffusion constant of xenon are desirable, and this suggestion brings squarely before us the question of mixtures of more than two isotopes. The results presented below have been known to the author for some time on the basis of plausibility arguments, but only recently have they been derived from the rigorous general theory.

The general theory of thermal diffusion in ternary and higher order gas mixtures has been given by Hellund.[2b] In his article Hellund stresses quite properly that thermal diffusion in ternary and higher order mixtures contains essentially new features, and that the results, therefore, cannot be obtained by extrapolation from the theory of binary mixtures. In the special case, however, in which the molecules differ only with respect to their mass, the equations of thermal diffusion in higher order mixtures may be written in terms of the binary thermal diffusion constants.

In order to indicate the nature of the generalization, it is convenient first to rewrite Eq. (1) in the following form:

$$\mathbf{v}_1-\mathbf{v}=D(-\text{grad}\,\log c_1+\alpha_{12}c_2\,\text{grad}\,\log T)\quad\text{(A)}$$

where α_{12} is the value of α defined by Eqs. (7)–(9). We see that the presence of the second gas occurs explicitly only in the combination $\alpha_{12}c_2$. It is plausible to suppose that in a mixture of three isotopes the factor $\alpha_{12}c_2$ would be replaced by $\alpha_{12}c_2+\alpha_{13}c_3$, and similarly for the case of more than three isotopes. This suggestion has been confirmed by the general theory of ternary and higher order mixtures.

The following relations have been derived from Hellund's general theory for a mixture whose component gases are all isotopic with respect to one another. Let the number of components be N, and let the fractional particle density of the ith component be c_i, where

$$\Sigma_k c_k=1.\quad\text{(B)}$$

The remaining relations in this section are valid only to terms of the first order in the relative mass differences $(m_i-m_j)/(m_i+m_j)$. We have

$$\alpha_{ij}=-\alpha_{ji},\quad \alpha_{ii}=0,\quad\text{(C)}$$

$$\alpha_{ij}+\alpha_{jk}=\alpha_{ij}-\alpha_{kj}=\alpha_{ik}.\quad\text{(D)}$$

The equation of diffusion for the ith component is

$$\mathbf{v}_i-\mathbf{v}=D(-\text{grad}\,\log c_i+(\Sigma_k\alpha_{ik}c_k)\,\text{grad}\,\log T)\quad\text{(E)}$$
$$k=1,2,\cdots,N$$

where

$$\mathbf{v}\equiv\Sigma_k c_k\mathbf{v}_k\quad\text{(F)}$$

is the particle convection velocity of the gas as a whole. The equation for $\mathbf{v}_i$ which has just been given involves all of the c's. From Eqs. (B), (C) and (D), however, we find that the expression for $\mathbf{v}_i-\mathbf{v}_j$ contains only c_i and c_j:

$$\mathbf{v}_i-\mathbf{v}_j=D(-\text{grad}\,\log c_i/c_j+\alpha_{ij}\,\text{grad}\,\log T).\quad\text{(G)}$$

This equation is identical in form with the equation for a mixture of only two isotopes.

In application to the Clusius-Dickel thermal separation column, we find by the use of (E) that the equations for the *equilibrium* concentration

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[2b] E. J. Hellund, Phys. Rev. 57, 328 (1940).

distribution are of the form

$$dc_i/dy = c_i \Sigma_k \alpha_{ik} c_k \qquad \text{(H)}$$

where y is proportional to the coordinate along the column. In analogy with Eq. (G), we find from (H)

$$d \log(c_i/c_j)/dy = \alpha_{ij}. \qquad \text{(I)}$$

The Eqs. (H) or (I) form a set of simultaneous, nonlinear differential equations for which the general solution may be found as follows: Integration of (I) yields $N-1$ independent equations of the form

$$\log(c_i/c_j) = \alpha_{ij}(y - y_{ij}). \qquad \text{(J)}$$

The $N-1$ constants y_{ij} may be determined from the $N-1$ independent conditions that the total mass of each component be conserved.

II. THE GENERAL LENNARD-JONES MODEL

General formulation

Lennard-Jones has proposed[3] and used extensively[4] in theoretical treatments a law of intermolecular force of the form

$$F = \kappa/r^{\nu} - \kappa'/r^{\nu'}, \qquad (13)$$

where r is the distance between the centers of the molecules, and where κ, κ', ν and ν' are positive constants. A positive value of F corresponds to a repulsive force.

The modern quantum theory of van der Waals forces suggests that ν' should have the value seven; quantum theory further suggests that the first term of (13) should be replaced by a term involving the radius exponentially. For the ranges of radii which are concerned in molecular collisions at ordinary temperatures, however, an exponential term can be approximated closely by a term involving a large inverse power of the radius.

As in I, we use a polar coordinate system r, ϕ, with its plane in the plane of motion of the two molecules whose collision we wish to study, and with its origin at one of the two molecules. In terms of the reciprocal radius $u = 1/r$, the first integral of the equation of motion in a spherically symmetrical field of force may be written

$$\left(\frac{du}{d\phi}\right)^2 = \frac{1}{b^2} - u^2 - \frac{2}{mg^2b^2}\int_r^{\infty} F dr. \qquad (14)$$

We now substitute (13) in (14), and subject b and g to the transformation (4) with

$$s = (\kappa/2kT)^{1/(\nu-1)}, \quad \sigma(\gamma) = \gamma^{-2/(\nu-1)}. \qquad (15)$$

With the further substitution

$$x = bu, \qquad (16)$$

Eq. (14) becomes

$$\left(\frac{dx}{d\phi}\right)^2 = 1 - x^2 - \frac{2}{\nu-1}\left(\frac{x}{\beta}\right)^{\nu-1} + \frac{2p}{\nu'-1}\left(\frac{x}{\beta}\right)^{\nu'-1} \qquad (17)$$

where we have used the abbreviation

$$p = \frac{\kappa'}{\kappa^{(\nu'-1)/(\nu-1)}(2kT\gamma^2)^{(\nu-\nu')/(\nu-1)}}. \qquad (18)$$

The quantity p is important because it is the means by which the temperature dependence is introduced into the final results.

The physical significance of p is more easily grasped when it is expressed in terms of ϵ, the depth of the potential energy minimum expressed as a positive quantity. When $\nu > \nu'$, such a minimum exists for the law of force (13), and is easily shown to have the value

$$\epsilon = \frac{(\nu-\nu')}{(\nu-1)(\nu'-1)} \cdot \frac{\kappa'^{(\nu-1)/(\nu-\nu')}}{\kappa^{(\nu'-1)/(\nu-\nu')}}. \qquad (19)$$

The elimination of the κ's between (18) and (19) leads to the result

$$p = \left[\frac{(\nu-1)(\nu'-1)}{2(\nu-\nu')} \cdot \frac{\epsilon}{kT\gamma^2}\right]^{(\nu-\nu')/(\nu-1)} \qquad (20)$$

The appearance of the temperature at this stage of the derivation is somewhat fictitious, of course; it appears explicitly because of the substitution (4). According to (4), $kT\gamma^2$ is equal to $\frac{1}{2}mg^2$, so that p is a quantity which is proportional to a power of the ratio of ϵ to the kinetic energy of the molecules at infinity.

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[3] J. E. Lennard-Jones, Proc. Roy. Soc. **A106**, 441 (1924).

[4] See, for example, R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge, 1939), Chapters VII and VIII; or R. H. Fowler, *Statistical Mechanics* (Cambridge, 1936), Chapter X.

By exactly the same procedure that was used for the case of the inverse power model in I, we find from (17) for the angle of deflection

$$\theta(\beta,\gamma)=\pi-2\int_0^{x_0}\left\{1-x^2-\frac{2}{\nu-1}\left(\frac{x}{\beta}\right)^{\nu-1}+\frac{2p}{\nu'-1}\left(\frac{x}{\beta}\right)^{\nu'-1}\right\}^{-\frac{1}{2}}dx, \qquad (21)$$

where $x_0(\beta, p)$ is the smallest positive root of the equation obtained by setting the right-hand side of (18) equal to zero.

The integration indicated in (21) cannot be performed in terms of known functions for the general case, so that it is usually necessary to resort to numerical methods from here on.

Specialization to the 9,5 case

The Sutherland model ($\nu=\infty$) and the special Lennard-Jones model ($\nu'=3$) represent special cases of the general Lennard-Jones model, and have been worked out as far as terms of the first order in ϵ/kT. Subject to this limitation, the derivation of the value of α for these models was given in I.

For the 9,5 model, Hassé and Cook[5] have proceeded from Eq. (21) by purely numerical methods, and have obtained the values of $\Theta^{(1)}$ and $\Theta^{(2)}$ for 18 different values of p. The authors exhibited admirable foresight in computing the values of both $\Theta^{(1)}$ and $\Theta^{(2)}$, inasmuch as they were interested in the coefficient of viscosity, which involves only $\Theta^{(2)}$.

The work of Hassé and Cook appeared only a year before London[6] showed by a simple calculation that the interaction energy of two molecules without permanent moments would fall off as the inverse sixth power of the distance; it was later shown quite generally by Lennard-Jones[7] that the leading term in the energy of mutual polarization is always of the form $-\mu r^{-6}$, where μ is positive. We may feel quite certain, therefore, that Hassé and Cook would have performed their computations for the 13,7 model if they had done their work slightly later, inasmuch as the trigonometrical substitution which they used to facilitate the numerical evaluation of (21) is equally effective for any pair of values of ν and ν' which satisfy the relation $\nu=2\nu'-1$. The 13,7 model has since found extensive use in the statistical-mechanical treatment of the properties of fluids and solids.[4]

TABLE I. *Comparison of the notation used by Hassé and Cook, and by Jones, I and II.*

H AND C	J	H AND C	J	H AND C	J
θ	χ	λ	κ		
θ	ϕ	μ	κ'	*For the* (9,5) *model only*:	
$\pi-2\theta$	θ	n	ν	$1/s$	q
V	g	m	ν'	$I_1(k)/2\pi=(2k)^{\frac{1}{2}}Y_1(k)$	$\Theta^{(1)}(\gamma)$
z	γ	a	β	$I_2(k)/2\pi=(2k)^{\frac{1}{2}}Y_2(k)$	$\frac{1}{3}\Theta^{(2)}(\gamma)$
p	b	$\xi=ay$	x	$I(s)$	$\frac{1}{3}\Omega^{(2,7)}$
R	k	at	x_0		
		k	p		

Because a substantial part of the task of computing the Ω's has already been accomplished for the 9,5 model, it seems worth while to determine the temperature dependence of α for this model before proceeding to the working out of the 13,7 model from the beginning. This order of procedure is further justified by the expectation that the results for the 13,7 model will not be greatly different.

For the special case $\nu=9$, $\nu'=5$, Eqs. (15) and (20) reduce to

$$s^2=(\kappa/2kT)^{\frac{1}{4}}, \quad \sigma^2(\gamma)=\gamma^{-\frac{1}{2}} \qquad (22)$$

$$p=\frac{2}{\gamma}\left(\frac{\epsilon}{kT}\right)^{\frac{1}{2}}. \qquad (23)$$

The relation between the notation used by Hassé and Cook and that used here is given in Table I for the convenience of those who wish to refer to the paper of Hassé and Cook.*

The values of $\Theta^{(1)}$ and $\Theta^{(2)}$ determined by Hassé and Cook are given in Table II. The values of θ were determined to an accuracy of one second of arc, and the writers state that the Θ's

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[5] H. R. Hassé and W. R. Cook, Proc. Roy. Soc. **A125**, 196 (1929).

[6] F. London, Zeits. f, physik. Chemie **B11**, 222 (1930).

[7] J. E. Lennard-Jones, Proc. Phys. Soc. London **43**, 461 (1931).

* It may also be helpful to point out the few typographical errors which occur in their paper: 1. The statement on p. 207 that $I(s)$ is the integral with respect to z in (13) should be replaced by the statement that $I(s)$ is $1/2\pi$ times the integral with respect to z in (12); 2. The variable of integration in (12) should be changed from k to z; and 3. The four polynomial approximations on p. 207 which are indicated as expressions for $I_2(k)$ are actually approximations to $I_2(k)/2\pi$.

TABLE II. *The exact values of* $\Theta^{(1)}$ *and* $\Theta^{(2)}$, *and the values given by the approximate formulae.*

p	$\Theta^{(1)}$ Exact	$\Theta^{(1)}$ Eq. (25)	$\Theta^{(1)}$ Eq. (32)	$\Theta^{(1)}/(2p)^{\frac{1}{2}}$ Exact	$\frac{1}{3}\Theta^{(2)}$ Exact	$\frac{1}{3}\Theta^{(2)}$ Eq. (26)	$\frac{1}{3}\Theta^{(2)}$ Eq. (33)	$\frac{1}{3}\Theta^{(2)}/(2p)^{\frac{1}{2}}$ Exact
0.00	0.38080	0.38080			0.16520	0.16520		
0.25	0.35947	0.35947			0.15108	0.15110		
0.50	0.34766	0.34766			0.14435	0.14431		
0.75	0.34972	0.34988			0.14929	0.14931		
1.00	0.37066	0.37066			0.17059	0.17059		
1.25	0.41584	0.41450			0.21165	0.21262		
1.50	0.49001	0.48592			0.27171	0.27988		
1.75	0.59603	0.58944			0.34269	0.37686		
2.00	0.73297	0.72956	0.95377	0.36648	0.40754	0.50802	0.38640	0.20377
2.3835	0.98228		1.06480	0.44990	0.44926		0.42190	0.20577
2.8563	1.23697		1.18818	0.51754	0.44778		0.46189	0.18735
3.4641	1.32953		1.33076	0.50511	0.50824		0.50866	0.19309
4.0	1.44530		1.44530	0.51099	0.54659		0.54658	0.19325
6.0	1.81155		1.81153	0.52295	0.66923		0.66927	0.19319
8.0	2.11888		2.11658	0.52972	0.77264		0.77264	0.19316
10.0	2.38356		2.38357	0.53298	0.86366		0.86368	0.19312
∞	∞		∞	0.55260	∞		∞	0.19257

are accurate to five significant figures. The values of the Ω's are now to be determined by performing the integration with respect to γ which is indicated in Eq. (6). In this integration the dependence on γ is, of course, eliminated, so that the Ω's are functions of the quantity

$$q = p\gamma = 2(\epsilon/kT)^{\frac{1}{2}}. \qquad (24)$$

The temperature dependence of the Ω's will enter through their dependence on q.

Before proceeding to the numerical evaluation of the Ω's, we shall derive expressions for the Ω's which are valid for the two limiting cases of q small, and q large, compared with unity.

For values of p lying between zero and unity, the following polynomials are very close approximations to the data given in Table II:

$$\Theta^{(1)} = 0.38080 - 0.09834p + 0.04004p^2 + 0.04816p^3, \qquad (25)$$

$$\tfrac{1}{3}\Theta^{(2)} = 0.16520 - 0.06507p + 0.02268p^2 + 0.04778p^3. \qquad (26)$$

It happens that (25) fits the data in Table II to within two percent for values of p between unity and two, but such is not the case for (26).

For small values of q, we may obtain the Ω's by substituting (25) and (26) in (6). This procedure may at first seem questionable, since the integral involves large values of q as well as the small values for which (25) and (26) are good approximations. The error would be expected to be greatest for small values of γ, which correspond to large values of q. It is easily confirmed, however, that the factor γ^k in the integrand of (6) vanishes so strongly at the origin that the error is inappreciable for sufficiently small values of q, when k takes values as large as 5, 7 or 9. We find

$$\Omega^{(1,5)} = 0.30623 - 0.05571q + 0.01840q^2 + 0.02183q^3, \qquad (27)$$

$$\Omega^{(1,7)} = 0.84213 - 0.12535q + 0.03220q^2 + 0.02728q^3, \qquad (28)$$

$$\Omega^{(1,9)} = 3.15801 - 0.40738q + 0.08855q^2 + 0.06139q^3, \qquad (29)$$

$$\tfrac{1}{3}\Omega^{(2,7)} = 0.36534 - 0.08294q + 0.01824q^2 + 0.02707q^3. \qquad (30)$$

If now the expressions (27–30) are regarded, not as polynomial approximations, but as power series expansions of the Ω's about the point $q=0$, they may be substituted in (7), and the result expanded in ascending powers of q. One finds at length

$$\begin{aligned} R_T &= 0.43241\{1 + 0.4026q - 0.1392q^2 - 0.1616q^3 + \cdots\} \\ &= 0.43241\{1 + 0.8052(\epsilon/kT)^{\frac{1}{2}} - 0.5568\epsilon/kT - 1.2930(\epsilon/kT)^{\frac{3}{2}} + \cdots\}. \end{aligned} \qquad (31)$$

This expression is compared with the precise result in Fig. 1.

Similarly, for values of p greater than four, the following expressions are very close approximations

$$\Theta^{(1)} = 0.78149_5 p^{\frac{1}{2}} - 0.03621 - 0.16295 p^{-\frac{1}{2}}, \quad (32)$$

$$\tfrac{1}{3}\Theta^{(2)} = 0.27234 p^{\frac{1}{2}} + 0.00344 - 0.00309 p^{-\frac{1}{2}}. \quad (33)$$

For sufficiently large values of q, the values of the Θ's for which (32) and (33) are not good approximations will not contribute appreciably to the integrals (6). Substituting (32–33) in (6) yields

$$\Omega^{(1,5)} = 0.51944 q^{\frac{1}{2}} - 0.02912 - 0.16295 q^{-\frac{1}{2}}, \quad (34)$$

$$\Omega^{(1,7)} = 1.29859 q^{\frac{1}{2}} - 0.08008 - 0.48885 q^{-\frac{1}{2}}, \quad (35)$$

$$\Omega^{(1,9)} = 4.5451 q^{\frac{1}{2}} - 0.3003 - 1.9554 q^{-\frac{1}{2}}, \quad (36)$$

$$\tfrac{1}{3}\Omega^{(2,7)} = 0.45254 q^{\frac{1}{2}} + 0.00761 - 0.00927 q^{-\frac{1}{2}}. \quad (37)$$

If now we substitute these expressions in (7), and expand the result in descending powers of $p^{\frac{1}{2}}$, we find that the constant term is identically zero, and we are left with

$$\begin{aligned} R_T &= -0.03390 q^{-\frac{1}{2}} - 0.37935 q^{-1} + \cdots \\ &= -0.02397 (kT/\epsilon)^{\frac{1}{4}} \\ &\qquad - 0.18968 (kT/\epsilon)^{\frac{1}{2}} + \cdots. \end{aligned} \quad (38)$$

This expression is also compared with the precise result in Fig. 1.

Numerical results

The values of the Ω's have been obtained by purely numerical methods from the data given in Table II. The values of $\Omega^{(2,7)}$ for $0.25 \leqslant q \leqslant 20$ were determined by Hassé and Cook;[5] the remainder of the entries in Table III were determined by the writer.

The method of integration used by Hassé and Cook was to split the range of the variable p into four parts, and to find accurate polynomial approximations to $\Theta^{(2)}$ for each of these ranges. The integration was then accomplished by use of tables on the incomplete gamma-function.

The writer used a different method, which was essentially ordinary numerical integration. Instead of integrating $\Theta^{(1)}$ itself, however, the integration was actually performed using as the integrand the difference between (25) or (32) and the exact value of $\Theta^{(1)}$ as given in Table II. The numbers obtained were then applied as corrections to the approximate values of the Ω's obtained from (27–29) or from (34–36). This method has the advantage that the quantity obtained by numerical integration was nearly always a small fraction of the final value of the Ω in question.

For values of q equal to or less than four, the correction to (27–29) was determined, whereas for values of q equal to or greater than five, the correction to (34–36) was determined by numerical integration. The interval used in the integration (6) with respect to γ was 0.25; in only one case, that of $q = 5$, it was necessary to subdivide the interval of integration over part of the range. It was usually sufficient to carry the numerical integration out to $\gamma = 5.0$. All of the calculations were carried to six significant figures although the accuracy of the results did not always warrant such precision.

The one drastic limitation on the accuracy of the results obtained lies in the fact that because of the great labor of the calculations, Hassé and Cook computed only three values of $\Theta^{(1)}$ and $\Theta^{(2)}$ in the range $2 < p < 4$. Although these values were computed to an accuracy of five significant figures, the function behaves so irregularly in this interval that the interpolated values may be in error by as much as one percent. The irregularity is more apparent in the values of $\Theta/(2p)^{\frac{1}{2}}$, which are also given in Table II. Accordingly, the values of the Ω's for which the main contribution comes from Θ's in this range have a probable error of something less than one percent. The

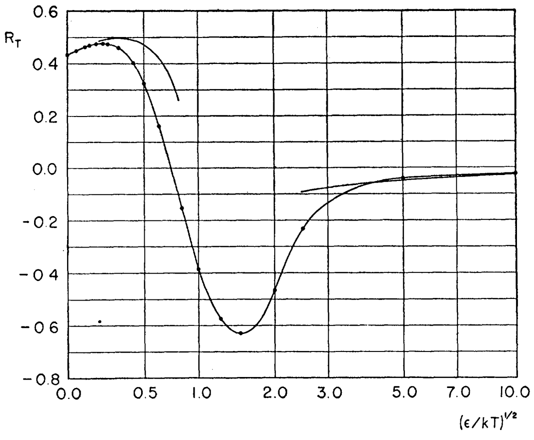

FIG. 1. Showing the dependence of R_T on ϵ/kT for the Lennard-Jones 9,5 model. For approximate purposes, the abscissa may be considered as the square root of T_c/T, where T_c is the critical temperature. The two shorter curves represent the results yielded by the approximate formulae (31) and (38).

TABLE III. *Values of the Ω's.*

$1/q$	$\Omega^{(1,5)}$	$\Omega^{(1,7)}$	$\Omega^{(1,9)}$	$\frac{1}{3}\Omega^{(2,7)}$
∞	0.30623	0.84213	3.1580	0.36534
20.0	0.30349	0.83595	3.1379	0.36124
10.0	0.30086	0.82994	3.1182	0.35726
8.0	0.29960	0.82702	3.1097	0.35531
6.0	0.29756	0.82230	3.0928	0.35215
5.0	0.29600	0.81857	3.0806	0.34970
4.0	0.29379	0.81323	3.0626	0.34617
3.0	0.29051	0.80494	3.0343	0.34072
2.4	0.28779	0.79746	3.0081	0.33590
2.0	0.28570	0.79092	2.9841	0.33181
1.6	0.28390	0.78303	2.9530	0.32722
1.2	0.28484	0.77581	2.9156	0.32445
1.0	0.28982	0.77621	2.9006	0.32735
0.8	0.30485	0.78895	2.9072	0.34138
0.6	0.35051	0.84733	3.0101	0.39214
0.5	0.40624	0.93189	3.1899	0.45523
0.4	0.51020	1.12014	3.6433	0.57470
0.3333	0.63116	1.37246	4.3201	0.70133
0.25	0.86044	1.95803	6.1680	0.90432
0.2	1.03951	2.48879	8.1644	1.02595
0.1	1.56006	3.87286	13.4659	1.44991
0.05	2.25604	5.61808	19.5888	2.02936
0.025	3.22935	8.05563	28.1362	2.86826
0.0125	4.59797	11.48021	40.1337	4.05421
0.005	7.30491	18.25020	63.8389	6.40684

TABLE IV. *Table of R_T as a function of ϵ/kT.*

$1/q$	ϵ/kT	R_T	$1/q$	ϵ/kT	R_T
∞	0.0	0.43241	0.8	0.3906	0.1617
10.0	0.0025	0.44898	0.6	0.6944	−0.153
5.0	0.01	0.46304	0.5	1.0	−0.384
4.0	0.0156	0.4687	0.4	1.5625	−0.573
3.0	0.0277	0.4753	0.3333	2.25	−0.629
2.4	0.0434	0.4771	0.25	4.0	−0.465
2.0	0.0625	0.4753	0.2	6.25	−0.232
1.6	0.0977	0.4605	0.1	25.0	−0.040
1.2	0.1736	0.4036	0.05	100.0	−0.023
1.0	0.25	0.3243	0.0	∞	0.000

TABLE V. *Quantities for the special Lennard-Jones model.*

ν	$G(\nu)$	$H(\nu)$
3	1.000	0.000
5	0.833	0.833
7	0.392	0.557
9	0.156	0.293
11	0.030	0.120
15	−0.0928	−0.0833
∞	−0.2662	−0.4822

relative accuracy of the Ω's is much higher, of course.

The Ω's given in Table III were then substituted in Eq. (7). The values of R_T so obtained are given in Table IV as well as in Fig. 1.

We shall defer the discussion of these results to Section IV.

III. THE SPECIAL LENNARD-JONES MODEL ($\nu'=3$)

This model has already been treated in I.* The result, however, can be presented more simply and in a more useful form than was done in I. Furthermore, the present formulation is better adapted for the generalization which will be attempted in Section IV.

Equation (45,I) may be written in the form

$$\Theta^{(l)}=A_l^{(\nu)}+B_l^{(\nu)}\left(\frac{\nu-1}{\nu-3}\cdot\frac{\epsilon}{kT\gamma^2}\right)^{(\nu-3)/(\nu-1)}, \tag{39}$$

where $A_l^{(\nu)}$ and $B_l^{(\nu)}$ are the quantities tabulated in Tables I and V of I. The expression (39) is valid only to the terms of the first order in $(\epsilon/kT)^{(\nu-3)/(\nu-1)}$. From (6) and (39) we find the formula corresponding to (47,I):

$$\Omega^{(l,k)}=\tfrac{1}{2}A_l^{(\nu)}\Gamma\left(\frac{k+1}{2}-\frac{2}{\nu-1}\right)+\tfrac{1}{2}B_l^{(\nu)}\Gamma\left(\frac{k-1}{2}\right)\cdot\left(\frac{\nu-1}{\nu-3}\cdot\frac{\epsilon}{kT}\right)^{(\nu-3)/(\nu-1)}. \tag{40}$$

The substitution of this expression in (7) now leads to

$$R_T=C(\nu)\frac{\left[\dfrac{\nu-5}{\nu-1}+G\left(\dfrac{\epsilon}{kT}\right)^{(\nu-3)/(\nu-1)}\right]\left[1-G\dfrac{15+4B_2/B_1}{15+6f}\left(\dfrac{\epsilon}{kT}\right)^{(\nu-3)/(\nu-1)}\right]}{\left[1-G\dfrac{2B_2}{3fB_1}\left(\dfrac{\epsilon}{kT}\right)^{(\nu-3)/(\nu-1)}\right]\left[1-G\dfrac{117+32B_2/B_1}{177+48(f-1/(\nu-1)+1/(\nu-1)^2)}\left(\dfrac{\epsilon}{kT}\right)^{(\nu-3)/(\nu-1)}\right]}, \tag{41}$$

$$\cong C(\nu)\left[\frac{\nu-5}{\nu-1}+H(\nu)\left(\frac{\epsilon}{kT}\right)^{(\nu-3)/(\nu-1)}\right]. \tag{42}$$

---

[*] The writer is aware of two errors in I, both of which involve the special Lennard-Jones model: 1. The κ immediately preceding the $D(\nu)$ in Eq. (IV) should be κ', and 2. The value of $D(15)$ in Table V should be 0.012 instead of 0.088.

The function $G(\nu)$ is defined by

$$G(\nu)=-\left(\frac{\nu-3}{\nu-1}\right)^{-(\nu-3)/(\nu-1)}\cdot\frac{B_1^{(\nu)}}{A_1^{(\nu)}\Gamma(3-2/(\nu-1))}.$$

The second expression for R_T is equivalent to the first as far as terms of the first order in $(\epsilon/kT)^{(\nu-3)/(\nu-1)}$. The functions $C(\nu)$ and $f(\nu)$ are tabulated in Table I of I; $G(\nu)$ and $H(\nu)$ are tabulated in Table V of this paper.

IV. Discussion of Results

The results indicated in Fig. 1 were derived explicitly for the Lennard-Jones 9,5 model. In the absence of evidence to the contrary, however, it seems reasonable to assume that the qualitative features of the result will be much the same for other molecular models which are similar to the 9,5 model. In particular, we shall suppose for the present that the behavior indicated in Fig. 1 is typical of Lennard-Jones models in which the attractive force index is about half of the repulsive force index, and we know that such molecular models have had considerable success in explaining the properties of fluids and solids.

The negative portion

By far the most striking aspects of the results given in Fig. 1 and Table IV are the rapid decrease of R_T as $(\epsilon/kT)^{\frac{1}{2}}$ increases beyond one-half, and the large negative values of R_T as the temperature decreases still further. This behavior of R_T was quite unexpected, and it has not yet received any definite confirmation from experiment. The negative portion, if it exists, should not be at all difficult to observe, as we shall now indicate.

The theoretical results can be more easily understood when they are expressed in terms of the critical temperature of the gas in question. Since the critical temperature is the temperature at which the attractive forces are just able to overpower the disrupting effects of thermal agitation, it is clear that the critical temperature is given approximately by the relation $kT_c=\epsilon$. Using the Lennard-Jones 13,7 model, and a simplified model of a liquid, Lennard-Jones and Devonshire[8] have found by detailed calculation the more precise result

$$T_c=(z/9)\cdot(\epsilon/k), \tag{43}$$

where z is the number of nearest neighbors of any given molecule in the liquid. Fowler and Guggenheim[9] suggest in this connection that a suitable value of z is 11. With $z=11$, Eq. (43) reduces to

$$T_c=1.22\epsilon/k. \tag{44}$$

If now we use the relation (44) to interpret the results in Fig. 1, we find that R_T is positive for temperatures greater than $1.54T_c$, and negative for temperatures less than $1.54T_c$. We also find that the minimum of R_T occurs at the temperature $0.36T_c$.

Now it is not at all difficult to work with gases at temperatures less than $1.54T_c$. In Table VI we have given the boiling points at atmospheric pressure and the critical temperatures of the noble gases and a few others chosen at random. From this table we may draw the very rough but rather general conclusion that at atmospheric pressure one may work with gases at temperatures greater than about $0.6T_c$.

For xenon, the range of temperature from the boiling point to $1.54T_c$ is the range from −109°C to 173°C. An experimental determination of the thermal diffusion constant of xenon in this temperature range would thus provide a useful and highly desirable check on this theory.

Application to isotope separation

It is clear that the attempt to separate isotopes with a thermal separation column having $1.54T_c$ as its mean temperature would meet with disappointing results, since the integral[10] yielding the value of H would be nearly zero as a consequence of the reversal of the sign of α. As we have just seen, however, there is usually a comfortable range of temperature between the temperature of condensation and $1.54T_c$. If, therefore, it is

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[8] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A163**, 53 (1937); Proc. Roy. Soc. **A165**, 1 (1938).

[9] See Fowler and Guggenheim, reference 4, p. 345.

[10] W. H. Furry, R. Clark Jones, and L. Onsager, Phys. Rev. **55**, 1083 (1939); R. Clark Jones and W. H. Furry, Rev. Mod. Phys., to be published.

TABLE VI. *Values of the critical temperature and the boiling point at atmospheric pressure for the noble gases and for a few others chosen at random.*

GAS	B.P. AT ATMOS. PRESS.	T_c	B.P./T_c
He	4.3	5.3	0.81
Ne	27	44	0.61
A	88	151	0.58
Kr	121	211	0.58
Xe	164	290	0.57
Cl_2	239	417	0.57
CCl_4	349	556	0.63
O_2	90	154	0.58
CH_4	108	191	0.57

inconvenient or impossible to operate the column over the range of temperature in which α is positive, it should usually be possible to operate the column so that it utilizes the negative portion of the curve shown in Fig. 1.

The hardness function

It will be noted that the initial slope of the curve in Fig. 1 is positive. This corresponds to the fact that the coefficient of $(\epsilon/kT)^{\frac{1}{2}}$ in (31) is positive. We shall find it convenient to use the term "initial slope" in a more general sense in connection with the general Lennard-Jones model; more generally, we shall mean by the "initial slope" the initial slope of the plot of R_T against $(\epsilon/kT)^{(\nu-\nu')/(\nu-1)}$. We then find that the initial slope for the special Lennard-Jones model is also positive when ν is less than about 15; according to Table V, the function $H(\nu)$ is positive for values of ν less than about 15.

In I, this positive "initial slope" was felt to be a defect of the special Lennard-Jones model, since the experiments seemed to indicate a negative slope. This difficulty has been resolved by the results in Fig. 1, which indicate that the initial slope is only a small part of the whole story.

The writer also stated in I that he did not know whether the positive initial slope was due to the choice of $\nu'=3$, or whether the "difficulty is more deeply seated." The writer now believes that he knows the reason for the positive initial slope, and that it can be explained on the basis of the inverse power model. Since Frankel[11] has shown that the essential properties of the inverse power model can be derived from elementary considerations, the argument to be given below furnishes another crumb of information about the thermal diffusion constant that can be obtained from elementary considerations.

The argument itself is somewhat arbitrary and approximate, and derives its real justification from the fact that its result is in good agreement with the results already obtained for the special Lennard-Jones model and for the 9,5 model. The argument follows.

Let r_0 be the distance of separation which corresponds to the minimum of the potential energy. Then, for values of r greater than r_0, the force is an attractive one, whereas for smaller values of r the force is repulsive. We propose that these two ranges of r make opposing contributions to the initial slope.

In the case of the Sutherland model r cannot be less than r_0, so that we are concerned only with the effect of the first of these two ranges. We saw in I that, for the Sutherland model, the initial slope is negative for all values of ν'. It therefore appears that the contribution of the first range to the initial slope is negative.

In order to discuss the contribution of the second range let us first recall some of the results for the inverse power model. This model is the special case of the Lennard-Jones model in which κ' is zero. For the inverse power model, we found in I that R_T is given by

$$R_T=C(\nu)(\nu-5)/(\nu-1), \qquad (45)$$

where $C(\nu)$ is a slowly varying function of ν which increases from 0.8 to 0.9 as ν rises from 5 to 15. R_T thus increases as ν increases, or as the "hardness" of the molecule increases. The derivative $d\log F/d\log r$ is constant for the inverse power model, and is equal to $-\nu$. Let us therefore introduce a "hardness function"

$$\mu(r)=-d\log F/d\log r. \qquad (46)$$

For the general Lennard-Jones model, we find the hardness function to be

$$\begin{aligned}\mu(r)&=(\nu-Q\nu')/(1-Q)\\&=\nu+Q(\nu-\nu')+O(Q^2),\end{aligned} \qquad (47)$$

where Q is the ratio of the attractive to the repulsive term in (13):

$$Q(r)=\kappa'/(\kappa r^{\nu-\nu'}). \qquad (48)$$

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[11] S. P. Frankel, Phys. Rev. 57, 661L (1940).

Now for all values of r in the second range, Q is positive and less than unity. This means that for all values of r in the second range, $\mu(r)$ is greater than ν; *the effect of the second term in (13) is to increase the hardness of the repulsive force.* We should thus expect that the presence of a weak attractive force would increase the value of R_T.

In order to put this argument in a more quantitative form, it is necessary to perform some sort of an averaging process on $\mu(r)$ in order to eliminate the dependence on r. We shall perform this averaging by the arbitrary device of evaluating Q at the distance of separation which corresponds to an energy of interaction equal to $\frac{1}{2}kT$. We shall also approximate by treating Q as a number small compared with unity.

As a first approximation, we find

$$Q \cong \frac{\kappa'}{\kappa}\left(\frac{2\kappa}{(\nu-1)kT}\right)^{(\nu-\nu')/(\nu-1)} = \left(\frac{\nu'-1}{\nu-\nu'}\cdot\frac{2\epsilon}{kT}\right)^{(\nu-\nu')/(\nu-1)} \tag{49}$$

If now we substitute (49) in (47), and then substitute the average value of μ so obtained for ν in (45), we find after a little manipulation

$$R_T = C(\nu)\left(\frac{\nu-5}{\nu-1} + \left\{4\frac{\nu-\nu'}{(\nu-1)^2}\left(\frac{2(\nu'-1)}{\nu-\nu'}\right)^{(\nu-\nu')/(\nu-1)}\right\}\left(\frac{\epsilon}{kT}\right)^{(\nu-\nu')/(\nu-1)}\right). \tag{50}$$

This is the result toward which we have been working. The quantity in the curly bracket (multiplied by $C(\nu)$) is the value of the initial slope predicted by the argument just presented.

In Table VII we compare the value of the curly bracket in (50) with the value of the corresponding coefficient as given by the results for the special Lennard-Jones model and for the 9,5 model. The agreement is satisfying; the approximate treatment yields substantially correct results as long as the second range is not too small in extent; that is to say, as long as ν is not too great a multiple of ν'.

The precise value of the initial slope obtained by this approximate treatment depends, of course, on the particular method of averaging which is used to eliminate the dependence of μ on r. Any method of averaging which is physically reasonable will yield about the same result, however, so that the writer feels that Eq. (50) affords a reliable approximate evaluation of the "initial slope" for the general Lennard-Jones model, subject to the restriction that ν may not be too great a multiple of ν'.

It is interesting to contemplate that if the van der Waals forces were non-existent for any molecule, and if the only energy of interaction were an overlap energy of the asymptotic form

$$E = \alpha e^{-\beta r}, \tag{51}$$

then the hardness function would be given by

$$\mu(r) = \beta r. \tag{52}$$

According to (52), R_T would *rise* monotonically as the temperature decreased, and would approach unity as the absolute temperature approached zero.

The approximate formulae (31) and (38)

These formulae are indicated by the dotted lines in Fig. 1. Equation (31) affords the correct initial slope, but it is clear that the second- and third-order terms are far from correct. The error

TABLE VII. *Comparison of the results yielded by the use of the hardness function with the results of detailed calculation.*

ν	ν'	EXACT COEFFICIENT	CURLY BRACKET IN EQ. (50)
3	3	0.000	0.0000
3.25	3		0.2688
3.50	3		0.4850
4	3		0.7055
5	3	0.833	0.7071
7	3	0.557	0.4444
9	3	0.293	0.2767
11	3	0.120	0.1838
15	3	−0.0833	0.09551
9	5	0.4026	0.35355

TABLE VIII. *The temperature dependence of n according to the 9,5 model.*

ϵ/kT	n	ϵ/kT	n	ϵ/kT	n	ϵ/kT	n
0.0	0.75	0.20	0.77	0.50	0.98	1.50	1.30
0.01	0.73	0.25	0.80	0.60	1.04	2.0	1.28
0.02	0.73	0.30	0.84	0.70	1.10	2.5	1.24
0.05	0.72	0.35	0.87	0.80	1.15	3.0	1.19
0.1	0.73	0.40	0.91	1.00	1.22	∞	1.00
0.15	0.75	0.45	0.94	1.25	1.27		

TABLE IX. *Values of α determined experimentally by Nier.*

MIXTURE	TEMP. RANGE	α	$\bar{R}_T$
$C^{12}H_4-C^{13}H_4$	296°–728°K	$0.0080\pm\sim5\%$	0.30
	296°–573°K	$0.0074\pm\sim5\%$	0.27
$Ne^{20}-Ne^{22}$	283°–617°K	$0.0302\pm2\%$	0.71
	90°–294°K	$0.0188\pm2\%$	0.44
	90°–195°K	$0.0165\pm8\%$	0.39

is due to the impropriety of considering the polynomial approximations as series expansions. The approximate relation (38) is quite accurate for values of q greater than about 20.

Viscosity

By substituting (22) and the numerical values of $\Omega^{(2,7)}$ given in Table III in Eq. (10), one obtains the temperature dependence of the coefficient of viscosity according to the Lennard-Jones 9,5 model. Hassé and Cook have compared with experiment the theoretical predictions so obtained.

During the time since the work of Hassé and Cook was published, Trautz and his associates[12] have measured the temperature dependence of the viscosity of a large number of gases. We do not intend to make here any detailed examination of these more recent data. We should like to point out, however, that with nearly all of their data, Trautz and his associates have given also the experimentally determined values of

$$n=d\log\eta/d\log T \tag{53}$$

as a function of the temperature. The quantity n is important because of its simple interpretation in terms of the inverse power model, as we pointed out in detail in I.

The writer has determined n as a function of ϵ/kT for the 9,5 model. The results are given in Table VIII. The predictions of Table VIII are in qualitative agreement with the experimental data; the data show a general tendency for n to increase as the temperature decreases. Values of n as large as 1.30, however, have not been observed; the value $n=1.14$ for SO_2 in the range 287°–370°K is the largest found by Trautz *et al.*

In conclusion, we may say that the 9,5 model is in qualitative agreement with the tendency of nearly all molecules to become, with respect to viscosity, more "soft" as the temperature decreases.

There is remarkable agreement between the values of R_T given in Table IV, and those obtained from Table VIII by the approximate relation (32,I):

$$R_T=1.7(1-n), \tag{54}$$

which was derived on the basis of the inverse power model. To two significant figures, the two methods agree in predicting a maximum of 0.48 at $\epsilon/kT=0.05$, and they both indicate that R_T changes sign at $\epsilon/kT=0.53$. Equation (54), however, predicts a minimum of -0.51 at $\epsilon/kT=1.5$, whereas Table IV indicates a minimum of -0.63 at $\epsilon/kT=2.2$. In the opinion of the writer, the close correspondence between the values of R_T obtained by the two methods should be considered as fortuitous, since the use of (54) in the present connection has no theoretical justification.

If such a close correspondence should turn out to hold for other Lennard-Jones models, however, the existence of an empirical relation of the form (54) should have considerable practical utility, since it would be possible to obtain an estimate of the value of R_T at any given temperature by a naïve application of the inverse power model to viscosity data for the gas in question.

The fact that values of n as large as 1.3 are not found experimentally, however, may be taken to suggest that negative values of R_T as large as those indicated by Table IV will also not be found experimentally.

V. COMPARISON WITH EXPERIMENT

The only direct experimental determinations of α for isotopic mixtures which have been published up to the present are those of Nier.[13]

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[12] For references, see Table II of reference 1.

[13] A. O. Nier, Phys. Rev. **56**, 1009 (1939); Phys. Rev. **57**, 338 (1940).

His results are given in Table IX, which is reprinted from I.

The values of $\bar{R}_T$ given in Table IX are "average" values over the temperature interval in question; that is to say, they are the values of R_T which would give the observed separations if R_T were independent of the temperature. The relation between $\bar{R}_T$ and R_T for the "two-bulb" method used by Nier is

$$\bar{R}_T = \int_{T_1}^{T_2} R_T \, d \log T \Big/ \log T_2/T_1. \qquad (55)$$

For the Sutherland model, with the approximate expression for R_T given by Eq. (43,I), Brown[14] has shown by the use of (55) that for any values of T_1 and T_2, $\bar{R}_T$ is equal to the value of R_T at the temperature

$$T_r = \frac{T_1 T_2}{T_2 - T_1} \log \frac{T_2}{T_1}. \qquad (56)$$

When R_T cannot be expressed analytically, however, it is possible to use a simple graphical method: R_T is plotted against $\log T$; the value of $\bar{R}_T$ is then the average value of the ordinate between the abscissae corresponding to T_1 and T_2.

Neon

In attempting to compare Nier's data for neon with our theoretical results for the 9,5 model, we are immediately faced by the difficulty that the largest experimental value of R_T is much greater than any of those found in Table IV. This difficulty simply corresponds to the fact that neon is much harder than $\nu = 9$. The experimental value $\bar{R}_T = 0.71$ is in good agreement with the high temperature viscosity data of Trautz and Sorg, which according to Table II of I, predict the value $\bar{R}_T = 0.69$ at the temperature $T = 1030°$ on the basis of the inverse power model; at such a high temperature, the inverse power model should be adequate for neon because of the small magnitude of the attractive forces.

In order to take account of the greater hardness of neon, we take the bold step of increasing the scale of the results given in Table IV so that the maximum value of R_T is 0.74 instead of 0.48. We then find by the graphical method just described that with $\epsilon/k = 42.5°$, the theoretical values of $\bar{R}_T$ corresponding to the three temperature ranges for neon are 0.71, 0.45, and 0.36. These values agree with the experimental values within the experimental error, and the value $\epsilon/k = 42.5°$ is in fair agreement with (44), since we find in Table VI that the critical temperature is 44°.

Now we should not like to lay too much stress on the excellence of the agreement between theory and experiment. After all, anyone can fit three experimental points, two of them close together, with a curve involving two adjustable constants. The important fact is that the large decrease in R_T, which occurs at temperatures well above the critical temperature, can be explained by the use of a value of ϵ/k which is in substantial agreement with the value indicated by other methods of approach.

It should be remembered in this connection that we found in I that the Sutherland model in the approximate form (43,I) could be made to fit the neon data, but that the required value of ϵ/k was about 350°, a value nearly ten times the critical temperature!

Methane

The methane molecule is far from being spherically symmetrical, so that Chapman-Enskog theory does not strictly apply.

If we use the value of ϵ/k indicated by Eq. (44) and the critical temperature:

$$\epsilon/k = 191°/1.22 = 156°,$$

then we find by the graphical method that the theoretical values of $\bar{R}_T$ which correspond to the temperature ranges in Table IX are 0.212 and 0.168. If these numbers are multiplied by $0.71/0.48 = 1.48$, they become 0.31 and 0.25. The fact that the necessary multiplicative factor is slightly smaller than in the case of neon suggests

TABLE X. *Values of $\bar{R}_T$ for mixtures of the noble gases over the temperature range 0°–100°C.*

	Ne	A	Kr	Xe
He	0.80	0.65	0.63	0.59
Ne		0.54	0.51	0.43
A			0.19	0.17
Kr				0.08

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[14] Harrison Brown, Phys. Rev. **58**, 661L (1940).

TABLE XI. *Comparison of the theoretical and experimental values of R_T for certain mixtures of the noble gases.*

MIXTURE	$\bar{T}_c$	ϵ/k	$\bar{R}_T$(THEORY)	$\bar{R}_T$(EXP.)
He-Ne	25	20	0.74	0.80
Ne-A	98	80	0.51	0.54
A-Kr	181	148	0.15	0.19
Kr-Xe	250	205	−0.12	0.08

that the methane molecule is slightly softer than the neon molecule.

We may also use the alternative procedure, and find the value of ϵ/k which permits the best check between experiment and the predictions of the 9,5 model without the use of a correction factor. It is found that the value $\epsilon/k=120°$ leads to a better check than was found in the last paragraph. It is difficult, however, to justify the smaller value of ϵ/k.

Other evidence, both pro and con

Atkins, Bastick and Ibbs[15] have measured the thermal diffusion constant of all of the ten different binary mixtures of the five noble gases. The measurements were all made in the same series of experiments in the same apparatus. The lower and upper temperatures in every case were 0° and 100°C. The results obtained by these authors are given in Table X.

The general formula (7), upon which all of the results derived in the present paper depend, was derived upon the explicit assumption that the molecules of the two gases differed from one another only in that their masses were different. The theory does not strictly apply, therefore, to mixtures of dissimilar molecules, even when they are as much alike as the molecules of the noble gases. There can be little doubt, however, that the mass difference accounts for all but a small part of the observed separations. We shall therefore attempt to compare the experimental results of Atkins, Bastick and Ibbs with the predictions of the Lennard-Jones 9,5 model.

It is, of course, necessary to determine a suitable value of ϵ, which is now the depth of the potential energy minimum for the interaction of the two dissimilar molecules. It is well known[16] that the magnitude of the van der Waals attractive force is proportional to the product of the polarizabilities of the two atoms. If then we should assume that the fields of force of all the noble gases differed only by a multiplicative constant, it is clear that the value of ϵ for the interaction between two dissimilar molecules would be the mean proportional of the values of ϵ for each of the two molecules interacting with molecules of its own kind. Actually the assumption at the beginning of the last sentence is not strictly justified, and we shall omit all detailed considerations by evaluating ϵ from the arithmetic mean of the critical temperatures of the two gases which make up the mixture. Of the four mixtures which we shall discuss, only the first (He − Ne) provides an appreciable ambiguity in the proper choice of ϵ, and in this case any reasonable value of ϵ will lie on the broad maximum of Fig. 1, so that there is no ambiguity in the predicted value of R_T even for this mixture.

We shall discuss only the mixtures of adjacent members of the family of noble gases. We have given in Table XI the value of the mean critical temperature of each of these mixtures, and the value of ϵ/k determined from (44). We then determined from Table IV the value of R_T at the temperature $T=323°$, and have multiplied this value by 0.74/0.48, the factor that was found necessary in the case of the neon isotopes; the result is given as the theoretical value of $\bar{R}_T$.

The comparison between theory and experiment is, for the first three mixtures, better than we might have expected. The discrepancy in the case of the krypton-xenon mixture may be ascribed to a lack of applicability of the 9,5 model, or it may be written off as experimental error. The authors reported considerable difficulty in making the measurement in this case. Since the observed change in concentration was only 0.098 percent, and since the concentrations were estimated from the thermal conductivity of the mixture, it is conceivable that the discrepancy can be attributed to experimental error. The authors do not estimate the probable errors of any of their results.

A serious objection to the present theoretical results is offered by the work of Groth and

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[15] B. E. Atkins, R. E. Bastick and T. L. Ibbs, Proc. Roy. Soc. **A172**, 142 (1939).

[16] See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill, 1940), p. 84.

Harteck,[17] who obtained a partial separation of the mercury isotopes by means of a thermal separation column of the hot-wire type, operating between the temperatures 350°C and 1800°C. Since the free mercury atom is in a spherically symmetrical singlet S state, and since the critical temperature of mercury vapor is about 1650°C, the present theory would indicate that the value of α would be negative, and that therefore the lighter fraction would be concentrated at the bottom of the column. Actually, however, the light fraction was collected at the top of the column. The writer has no explanation for the discrepancy.

Conclusion

The small amount of experimental data which is so far available lends considerable support to the accuracy of the predictions of the 9,5 model for positive values of R_T. There is, however, no experimental evidence for the large negative values predicted, and the work of Groth and Harteck, as well as the failure of the viscosity predictions to be borne out for larger value of ϵ/kT, suggests that the large negative values of R_T may not be found experimentally.

Our theoretical understanding of the temperature dependence of α has increased significantly since the publication of the first paper of this series. It will be remembered that we closed in I on a rather pessimistic note, with the unstated but implied suggestion that the general Lennard-Jones model would turn out to be inadequate for the explanation of Nier's data. This pessimism, the writer now realizes, was founded upon an incomplete realization of the sad inadequacy of the "initial slope" determinations.

Ideally, work on this problem in the near future should proceed along two lines. There is a need for more experimental data on the thermal diffusion constant of isotopic mixtures, particularly at temperatures in the neighborhood of the critical temperature. In order that the Chapman-Enskog theory be capable of application, the measurements should preferably be made on the noble gases and on those metallic vapors whose atoms have a spherically symmetrical ground state. Secondly, we must work out the detailed predictions of other Lennard-Jones models, preferably of the ν,7 type. The necessary numerical calculations are discouragingly onerous, and it is to be hoped that the scientific methods of machine computation, which are just beginning to be developed at this late stage of scientific progress, will be of assistance in the execution of the computations.

Acknowledgment

The writer would like to thank Professor W. H. Furry for helpful comments on the manuscript, and he is indebted to his wife, Lois Kathryn Jones, for assistance in the numerical computations involved in the investigation of the 9,5 model.

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[17] W. Groth and P. Harteck, Naturwiss. **27**, 584L (1939).