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AUTOMATIC CALCULATION OF THE TRANSPORT COLLISION INTEGRALS
WITH TABLES FOR THE MORSE POTENTIAL

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AUTOMATIC CALCULATION OF THE TRANSPORT COLLISION INTEGRALS
WITH TABLES FOR THE MORSE POTENTIAL

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ABSTRACT

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A computer programme is described for calculating the classical and quantal JWKB Chapman-Enskog collision integrals $\Omega^{(\ell, s)}(T)$ for any reasonable interaction potential. With the programme it was possible in about 10 or 15 minutes on a fast computer to calculate more than 500 collision integrals covering a complete range of values of ℓ , s , and T to an accuracy of better than 1 part in 1,000. This was made possible by the use of efficient numerical techniques such as weighted Gaussian quadratures and by the general optimization of all numerical and logical processes.

The programme was checked against previous tables for the Lennard-Jones and Stockmayer potentials. It was also used to list values of the collision integrals and Kihara's corrections to the coefficients of viscosity, thermal conductivity, diffusion and thermal diffusion for the Morse potential.

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I. INTRODUCTION

In the Chapman-Enskog theory¹ of a dilute gas the transport properties of the gas can be expressed in terms of a set of collision integrals, $\Omega^{(\ell,s)}(T)$. These are functions of the temperature, T , and they depend on the interaction potentials between the atoms or molecules of the gas. They have been tabulated at different temperatures for a number of special interaction potentials involving a small number of parameters²⁻⁴ and these tables have been used extensively in calculations of the transport properties of gases. Evidence has been accumulating which indicates that these interaction potentials may be inadequate for describing the equilibrium and transport properties of gases over a wide range of physical conditions.⁴⁻⁶ More flexible potentials are needed to represent the interactions between real atoms and molecules and an efficient method for calculating the collision integrals for these potentials is therefore needed. Such a method should be able to deal with as many as possible of the shapes of interaction potentials which are likely to be found between atoms and molecules, and for calculations on a large scale it should be designed for automatic rather than for manual computation.

This paper describes the numerical methods used in a computer programme built to calculate the collision integrals for any reasonable interaction. In the last part of the paper tables of collision integrals obtained for the Morse potential are listed.

General Formulas

In the theory of Chapman and Enskog the collision integrals take the form

$$\Omega^{(\ell, s)}(T) = \left(\frac{kT}{2\pi\mu} \right)^{\frac{1}{2}} \int_0^{\infty} \exp(-x^2) x^{2s+3} S^{(\ell)}(kTx) dx, \quad (1)$$

in which μ is the reduced mass of the two interacting systems and k is Boltzmann's constant. The collision cross section $S^{(\ell)}(E)$ is a function of E , the initial kinetic energy of the colliding particles in their center-of-mass coordinates.

In the classical approximation, valid at high energies, the cross section is given by

$$S^{(\ell)}(E) = 2\pi \int_0^{\infty} b(1 - \cos^{\ell} \chi) db, \quad (2)$$

where b is the impact parameter and χ is the classical angle of deflection of the relative velocity vector,

$$\chi = \pi - 2b \int_{r_m}^{\infty} \frac{dr/r^2}{F(r)}, \quad (3)$$

where r_m , the classical turning point, is the outermost zero of $F(r) = \left[1 - \varphi(r)/E - b^2/r^2 \right]^{\frac{1}{2}}$ and $\varphi(r)$ is the interaction potential.

In the quantum theory⁷ the cross sections are given by

$$S^{(\ell)}(E) = 2\pi \int_0^{\pi} |f(\chi)|^2 (1 - \cos^{\ell} \chi) \sin \chi d\chi, \quad (4)$$

in which $f(\chi)$ is the scattering amplitude given by

$$f(\chi) = \frac{1}{2ik} \sum_{n=0}^{\infty} (2n+1) P_n(\cos \chi) \left[\exp(2i\delta_n) - 1 \right], \quad (5)$$

where δ_n is the scattering phase shift, n is the angular momentum quantum number, and $k = (2\mu E)^{\frac{1}{2}}/\hbar$ is the wave number. By substitution of (5) into (4) it can be shown⁸ that $S^{(1)}(E)$ and $S^{(2)}(E)$ reduce to

$$\begin{aligned} S^{(1)}(E) &= \frac{4\pi}{k^2} \sum_n (n+1) \sin^2(\delta_n - \delta_{n+1}), \\ S^{(2)}(E) &= \frac{4\pi}{k^2} \sum_n \frac{(n+1)(n+2)}{2n+3} \sin^2(\delta_n - \delta_{n+2}). \end{aligned} \quad (6)$$

The phase shift, δ_n , can be evaluated accurately only by the solution of a differential equation,^{9,10} which is a lengthy process if numerical methods have to be used. The phase shift is therefore often evaluated by the approximate JWKB formula¹¹

$$\delta_n = k \lim_{R \rightarrow \infty} \left\{ \int_{r'_m}^R \left[1 - \frac{\varphi(r)}{E} - \frac{p^2}{r^2} \right]^{\frac{1}{2}} dr - \int_p^R \left[1 - \frac{p^2}{r^2} \right]^{\frac{1}{2}} dr \right\}, \quad (7)$$

where $p = (n + \frac{1}{2})/\hbar$ and r'_m is the outermost zero of the integrand in the first integral. In the semiclassical limit¹² $b=p$ and it follows that

$$\chi = 2 \frac{d\delta}{dn} \quad \text{and} \quad r'_m = r'_m.$$

Further, if the summations in (6) are replaced by integrals, the resulting semiclassical cross sections can be shown to be

identical with the classical cross sections. (This is used later to check the accuracy of the computer programme).

Numerical Difficulties

The calculation of the collision integrals thus reduces in the classical approximation to the evaluation of a triple integral represented by the equations (1), (2) and (3), and to a problem of similar difficulty in the JWKB case. The numerical integration of any triple integral is laborious even when the integrands are well behaved. In the present case there are two additional problems: (i) the singularities in the integral expressions for the deflection angle and the JWKB phase shift at $r = r_m$, and (ii) the rapid oscillation of the integrand in (2) corresponding to the spiralling of the particles about one another at certain impact parameters when the interaction potential is attractive - a phenomenon known as orbiting.^{2,12}

These difficulties considerably lengthen the calculations; so for rapid computation it was necessary to use efficient numerical techniques. In particular, in place of the more usual finite difference formulae, Aitken's method¹³ was used for interpolation and integrals were evaluated with weighted Gaussian quadratures¹⁴ involving a large number of abscissas. These methods are suitable for use with digital computers but they are less convenient for desk machine calculations.

It was also not practical to build a computer programme

to deal with any shape of interaction potential. Some limitations had to be set on the form of the potential. It was possible, however, to choose these limitations such that they included all the known interactions between atoms and molecules. The programme could deal with any interaction potential having the following characteristics:

- (i) the potential and all its derivatives should be smooth for all values of r ;
- (ii) the potential should have at most one minimum and at most one long range maximum;
- (iii) the potential should fall off at infinity at least as fast as r^{-2} . Almost all the potentials used in earlier calculations satisfy these conditions, the exception being potentials involving a discontinuity. The computer programme could therefore be checked using existing tabulations, and these could in turn be checked by the programme. Such a comparison of results is discussed at the end of the paper. In the following chapter the numerical methods are discussed in more detail.

II. NUMERICAL METHODS

One of the principal difficulties encountered in the evaluation of the classical collision integrals is the pole in the integral expression in (1) for the classical deflection

angle at $r=r_m$. A similar problem arises in the evaluation of the JWKB phase shift. The singularity can be removed either by a change of variable^{3,15,16} or by the use of a suitably weighted Gaussian quadrature (this will be discussed later).

If the variable of integration in the integral expression for $S^{(\ell)}(E)$ in (2) is left unchanged, it is necessary to calculate r_m with great accuracy for each value of b required. Because of the difficulty of finding a method for determining r_m accurately, a method independent of the form of the potential, the variable of integration in (2) is conveniently changed from b to r_m .^{3,15,17} Although this simplifies the classical calculations it cannot be used for the evaluation of the JWKB cross sections in which r_m must be found for each integral value of the angular momentum quantum number arising in the summation in (6). For this reason and because a fast numerical method was found for determining r_m accurately, a change of variable was not used in the present programme and the integral in (2) was evaluated directly.

The calculation of the integral in (2) and of χ , δ , and r_m is complicated at energies which exhibit the phenomenon of orbiting. For this reason it was essential to be able to predict the orbiting collisions. Thus one of the earliest features of the present method is the determination of a set of parameters which define at which energies and at which impact parameters orbiting occurs.

The Orbiting Parameters

Orbiting occurs at an energy E and an impact parameter b_0 if there is an internuclear separation r_0 at which

$$\varphi'_{\text{eff}}(r_0) = \varphi_{\text{eff}}(r_0) - E = 0, \quad (9)$$

where $\varphi_{\text{eff}}(r)$ is the effective potential defined by

$$\varphi_{\text{eff}}(r) = \varphi(r) + \hbar^2(n+\frac{1}{2})^2 / 2\mu r^2. \quad (10)$$

$\hbar^2(n+\frac{1}{2})^2/2\mu$ is replaced by b^2E in the classical case. Provided that the potential is attractive for some values of r there is an energy range which exhibits orbiting. The upper limit of the range is the critical energy, E_C , at which

$$\varphi'_{\text{eff}}(r_0) = \varphi''_{\text{eff}}(r_0) = 0, \quad (11)$$

and

$$\varphi_{\text{eff}}(r_0) = E_C. \quad (12)$$

The lower limit, E_{LC} , is non-zero if the potential has a long range maximum and E_{LC} is given by

$$E_{LC} = \varphi(r)_{\text{max}}. \quad (13)$$

If the potential is always repulsive then $E_C = 0$, and if the potential is always attractive then $E_{LC} = 0$ and $E_C = \infty$.

The computer programme calculated these two parameters by examining the sign of $\varphi'(r)$ over the whole range of internuclear

distances r . E_{LC} was found from (1) after first finding the position of the maximum by interpolating $\phi'(r)$ to zero. E_C was found by noting that in a plot of the orbiting impact parameter b_o against r_o , a maximum value, $b_o = b_C$, is obtained at a certain internuclear distance, $r_o = r_C$. It is readily shown that this maximum corresponds to the critical energy and that E_C is given by

$$E_C = \phi_{\text{eff}}(r_C)$$

with b set equal to b_C .

The calculations are simplified since in practice it is possible to estimate two energies E_{max} and E_{min} above and below which there is no effective contribution to the $\Omega^{(\ell, s)}(T)$ integrals for the range of temperatures of interest. Thus the cross sections $S^{(\ell)}(E)$ need only be evaluated between E_{max} and E_{min} . The practical estimation of E_{max} and E_{min} will be discussed later. If the critical energies E_C and E_{LC} lie outside the range $(E_{\text{min}}, E_{\text{max}})$ their exact numerical values are immaterial provided only that they lie on the correct side of the energy range. For example, if no orbiting occurs between E_{min} and E_{max} then it is sufficient to set $E_C = E_{LC} = 0$ whether or not orbiting occurs at other energies. In the first subprogramme, therefore, the parameters E_C and E_{LC} were found by scanning the potential only at internuclear distances corresponding to the energy range $(E_{\text{min}}, E_{\text{max}})$. At the same

time if orbiting occurred between E_{\min} and E_{\max} then a table of corresponding triads (r_o, b_o, E) was determined. This table was used in the calculation of the turning point described in the following section.

The Approximate Turning Point

Except in the case of some special potentials r_m is determined most rapidly by inverse interpolation. To ensure that this interpolation converges it is necessary to know close upper and lower bounds to the turning point. At orbiting energies these can be estimated with the help of the orbiting parameters.

At Orbiting Energies. If $E_{LC} < E < E_C$ then the parameters r_o and b_o corresponding to E can be obtained by interpolation in the table of orbiting parameters calculated in the earlier sub-programme. By examining the three curves in Fig. 1, one for $b < b_o$, one for $b = b_o$ and one for $b > b_o$, it is clear that r_o is an upper bound to r_m when $b < b_o$ and that it is a lower bound when $b > b_o$. This eliminates the possibility of finding a zero of $f(r) = \varphi_{\text{eff}}(r) - E$ other than the zero corresponding to the turning point when $f(r)$ has more than one zero. Lower and upper bounds respectively can be obtained by scanning $f(r)$ for $r < r_o$ and for $r > r_o$ respectively. These limits on r_m can then be brought closer together by halving the interval four or five times and examining the sign of $f(r)$.

This procedure was used in the programme only for the lowest impact parameter below b_0 arising in the quadrature replacing the integral in (2). It was also used for the lowest value of $b > b_0$. In other cases the process could be speeded up by noting that if b_i and b_{i+1} are two impact parameters and $r_{m,i}$ and $r_{m,i+1}$ their respective turning points and if $b_{i+1} > b_i$ then $r_{m,i+1} > r_{m,i}$. So in the programme the impact parameters in the quadrature were chosen in order of magnitude beginning with the smallest, i.e., $b_1 < b_2 < b_3$, etc. Then $r_{m,1}$ was first found using r_0 ; close bounds to $r_{m,2}$ were found by scanning just above $r_{m,1}$ and the same process was followed for $r_{m,3}$; $r_{m,4}$; etc.

For $b > b_0$ provided that the potential was attractive the speed with which r_m was determined was improved by noting that $r_m < b$. Then since

$$r_{m,i} < r_{m,i+1} < b_{i+1},$$

close upper and lower bounds were known without calculation.

At Non-Orbiting Energies. The same methods were used at non-orbiting energies except that there was no initial starting point corresponding to the parameter r_0 except when $E < E_{LC}$. Then $r_m > r_{LC}$ for all impact parameters. r_{LC} is the position of the long range potential maximum. Otherwise the computer scanned $f(r)$ on either side of b_1 using logarithmic intervals till approximate upper and lower bounds were found to the turning

point corresponding to b_1 . These were then improved by halving the interval four or five times. For all subsequent impact parameters the turning points were found in the same way as in the orbiting case.

The Exact Turning Point

When an upper and a lower bound to r_m had been obtained, that is two values of r such that

$$\varphi_{\text{eff}}(r_1) - E < 0 < \varphi_{\text{eff}}(r_2) - E,$$

an accurate value of r_m was found rapidly by the successive use of Aitken's interpolation formula¹³. Let $x = \varphi_{\text{eff}}(r) - E$ and consider r as a function of x such that $r_1 = r(x_1)$, $r_2 = r(x_2)$, and $r_m = r(0)$. Aitken's two-point formula was used to find a first approximation to $r(0)$, $r = r_3$, by interpolating between x_1 and x_2 . x_3 was calculated and the three points (x_1, r_1) , (x_2, r_2) and (x_3, r_3) were used in Aitken's three-point formula to obtain a better approximation, r_4 . This process was repeated using higher order interpolating formulae till two successive approximations to r_m were sufficiently close together. In general r_5 was accurate to 6 or 7 figures provided that r_1 and r_2 were not too distant from r_m .

The Classical Deflection Angle

The integral in the expression for the classical deflection angle in (3) can be evaluated using the Gauss-Mehler quadrature formula¹⁸, which eliminates the pole at r_m by effectively dividing the integrand in (3) by $(1-r_m^2/r^2)^{\frac{1}{2}}$. The classical deflection angle then becomes

$$\chi = \pi - \frac{\pi b}{N r_m} \sum_{j=1}^{\frac{1}{2}N} a_{(N/2)-j+1} / F(r_m/a_j), \quad (14)$$

in which N is an even integer and $a_j = \cos(2j-1)\pi/2N$. This method was adopted in preference to earlier methods of evaluating χ because of its accuracy and simplicity.¹⁸ The coefficients a_j were calculated at the beginning of the programme. In practice less than 10 points ($N=20$) were needed to ensure several figure accuracy both for non-orbiting energies and for orbiting energies when $b > b_0$.

When the impact parameter is less than but close to b_0 , a large sharp maximum appears to the integrand of (3) resulting in a loss of accuracy. In an attempt to take fuller account of this maximum the variable in the integral in (3) was changed^{3,15,16} to $\theta = \sin^{-1}(r_m/r)$ to eliminate the singularity at r_m . Each of the intervals $(0, \pi/4)$ and $(\pi/4, \pi/2)$ was then evaluated by Gaussian quadratures using as many as 64 points in each interval. Although a great deal clumsier this only gave significantly different results from a 60 point Gauss-Mehler quadrature at the

very lowest energies when the maximum in the integrand occurred at very large values of r .

The JWKB Phase Shift

Like the classical deflection angle the JWKB phase shift in (7) was evaluated by Gauss-Mehler quadratures.¹⁸ Two formulae were used. The first is

$$\delta = \frac{k\pi}{2N} \sum_{j=1}^{N-1} \omega_j \left\{ \alpha r_j^2 F(r_j) + \frac{R_j^2}{b} \left[F(R_j) - \omega_j \right] \right\} + \frac{\alpha k\pi}{4N} b^2 F(b) \quad (15)$$

in which

$$\alpha = \frac{b-r_m}{br_m}, \quad r_j = \frac{r_m b}{(b-r_m) \cos\left(\frac{j\pi}{2N}\right) + r_m},$$

$$R_j = b/\cos\left(\frac{j\pi}{2N}\right), \text{ and } \omega_j = \sin\left(\frac{j\pi}{2N}\right).$$

Because the abscissas, r_j and R_j , and weights, ω_j , are functions of $j\pi/N$, it was possible to evaluate successive approximations to δ with $N = 2, 4, 8$, etc. with only a small amount of extra computing. For example, $\delta(N=8)$ was calculated from $\delta(N=4)$ and the four terms in the series corresponding to $j = 1, 3, 5$ and 7 . This process was repeated with successively higher values of N till δ was found with sufficient accuracy. It needed about 64 points to reach about 3 figure accuracy in most cases.

Two other Gauss-Mehler quadrature formulae have been derived

by Smith¹⁷ for an effective potential which is repulsive for $r > r_m$. These are considerably more efficient than (15). It was found that the more complicated of these formulae was the simpler to use:

$$\delta = \frac{k\pi}{2Nr_m} \sum_{j=1}^{\frac{1}{2}N} \frac{r_j^2 (q_j - \frac{1}{2}) \left[2b^2/r_j^3 - \varphi'(r_j)/E \right] a_{(N/2)-j+1}}{F(r_j)} \quad (16)$$

in which

$$r_j = r_m / \cos \left(\frac{2j-1}{2N} \right) \pi, \quad q_j = b / \left[\frac{b^2}{r_j^2} + \frac{\varphi(r_j)}{E} \right].$$

(The other formula, Eq.(3.5) in the paper by Smith, was not adopted because it involved inverse interpolation). The accuracy of (16) is illustrated in Table I, which lists values of the phase shifts for different impact parameters when $\varphi(r)/E = 4(r^{-12} - r^{-6})$ and $2\mu=4$. Only two points are needed in the integration to obtain phase shifts accurate to several decimal places. This method made it possible to calculate as many as a hundred phase shifts per second on an IBM 7090 computer.

The Cross Sections

The quantal cross sections in (6) were evaluated by summing over the angular momentum quantum numbers without difficulty. The classical cross sections were calculated by

the evaluation of the integral in (2). The integral had to be evaluated by different methods at orbiting and non-orbiting energies.

At Orbiting Energies. The principal difficulty in evaluating (2) at orbiting energies is the infinite oscillation of the integrand at b_0 . This difficulty has usually been overcome in the past by breaking the integral into three regions, one about b_0 and two more on either side of b_0 . The integral about b_0 was either evaluated analytically^{3,19} or approximated by its mean value¹⁵. These methods lengthen the calculations; so a more straightforward method was tried.

The integral was separated into two parts only, the first from 0 to b_0 and the second from b_0 to infinity. The first integral was evaluated using only the positive abscissas, x_i , and the corresponding weights, ω_i , of a Gaussian quadrature^{20,21}

$$\int_0^{b_0} b(1 - \cos^{\ell} \chi) db = \sum_{i=1}^N \omega_i b_i (1 - \cos^{\ell} \chi_i), \quad (17)$$

where $b_i = b_0 x_i$ and χ_i is evaluated for $b=b_i$. If x_N is the Gaussian abscissa closest to unity the abscissas are concentrated near b_0 where the integrand was largest and where it was changing most rapidly. It was found that the rapid oscillations were so close to b_0 that even when 32 positive Gaussian points were being used the integrand was oscillating only two or three times between 0 and b_N . Because of the closeness of b_N to b_0

and because of the small magnitude of the last few weights, ω_N and ω_{N-1} , it was hoped that the rapid oscillations between b_N and b_0 could be neglected. It was found that this simplification is surprisingly accurate: a comparison of the integrations of $S^{(1)}(E)$ with 24 and 32 Gaussian points is illustrated in Table II.

The same principle applies to the integration from b_0 to infinity. In this the Gauss-Laguerre method described by Dalgarno and Smith²⁰ was adopted. The integral was replaced by the quadrature

$$\int_{b_0}^{\infty} b (1 - \cos^{\ell} \chi) db = \alpha \sum_{j=1}^N (W_j \exp y_j) b_j (1 - \cos^{\ell} \chi_j), \quad (18)$$

in which χ_j was evaluated for the impact parameter $b_j = b_0 + \alpha y_j$, and y_j and W_j were the Gauss-Laguerre abscissas and weights²² with y_N the largest abscissa. The rapid oscillation at b_0 occurs between b_0 and the first abscissa, b_1 ; it was therefore neglected. The scaling factor, α , was found not to affect the quadrature significantly provided that the integrand was just falling below the maximum premissable error near $b = b_0 + \alpha y_N$. The factor, α , was computed initially using this condition.

At Non-Orbiting Energies. At energies well above the critical energy ($E > 2E_C$ say) and for $E < E_{LC}$ the integrand in (2) has only one or two oscillations and the quadrature formula (18) can be used with b_0 set equal to zero. This normally gave cross sections accurate to 3 and more figures with 32 Gauss-Laguerre

points in the integration.

At energies above but close to E_C (say $E_C < E < 2E_C$) χ has a large negative value near the rainbow angle¹² at an impact parameter b_r and this causes considerable oscillations in the integrand of (2). So for these energies the integral was evaluated by the same technique used for the orbiting energies but with b_o replaced by approximations to b_r found by extrapolating the orbiting impact parameters to energies above E_C .

The Collision Integrals

The collision integrals in (1) were also evaluated by the Gauss-Laguerre quadrature formula,

$$\Omega^{(\ell, S)}(T) = \left(\frac{kT}{2\pi\mu} \right)^{\frac{1}{2}} \sum_{j=0}^N w_j y_j^{S+1} S^{(\ell)}(kT y_j). \quad (19)$$

This requires that $S^{(\ell)}(E)$ be known for a different set of energies at each temperature T . Since the collision integrals are normally calculated for a number of temperatures it is not practical to calculate the cross sections in each case from first principles. So instead a set of energies was chosen and the appropriate cross sections were found by accurate interpolation.

The energies were chosen as follows. From the maximum and minimum temperatures of interest, T_{\max} and T_{\min} , the energy range over which the cross sections were needed was found from

the equations

$$E_{\max} = kT_{\max} y_N , \quad (20)$$

$$E_{\min} = kT_{\min} y_1 ,$$

where y_1 and y_N were already defined for equation (19). Because $\log S^{(\ell)}$ is such a slowly varying function of $\log E$ for $E < E_C$ and for $E > 2E_C$, in these regions energies were chosen at equal logarithmic intervals and subsequent interpolations were used with tables of $\log S^{(\ell)}$ against $\log E$ rather than with tables of $S^{(\ell)}$ against E . Between E_C and $2E_C$ the cross sections usually show some oscillation and it was found simpler to choose the energies at equal intervals and to interpolate with tables of $S^{(\ell)}$ against E .

Because of the simplicity with which it can be used and programmed, Aitken's method¹³ was used for interpolations with two tabulated energies (when possible) on either side of each energy arising in (19). It was found that even when E_{\max} was several orders of magnitude larger than E_{\min} accurate interpolation was possible with only fifteen energies in each of the regions $\log (E_{\min})$ to $\log (E_C)$ and $\log (2E_C)$ to $\log (E_{\max})$ and with only ten energies between E_C and $2E_C$. The cross sections had therefore to be calculated at only about 40 energies.

Accuracy

The number of points taken in each integration has already been stated; they were designed to give an accuracy of one part in 1,000 in the cross sections. The accuracy was appreciably greater than this at high energies but near E_C the cross sections may be in error by at most 3 parts in 1,000. Since the collision integrals are integrated over these cross sections they should be more accurate than this at all temperatures.

The speed of the programme depends principally on the number of times it is necessary to calculate $F(r)$. For orbiting energies this is about 2,000 times per cross section and about 500 times at non-orbiting energies. It was found that on an IBM 7090 computer the cross sections $S^{(\ell)}(E)$ for $\ell = 1, 2, 3$ and 4 could be calculated for the 40 energies necessary in about three minutes. A further 10 seconds was sufficient to evaluate $\Omega^{(\ell, S)}(T)$ for $\ell = 1, 2, 3, 4$ and $s = 1, 2, 3, 4$ at each temperature.

For an accuracy of about 1% about ten times fewer points are needed to evaluate $S^{(\ell)}(E)$ and only 5 energies are necessary in each of the three energy ranges. So even the smallest computer could be used to produce the collision integrals to this accuracy.

III. RESULTS

The programme was checked by comparison with existing tables of collision integrals for a few potentials. Three of these are the Lennard-Jones (12-6) potential,^{2,3b}

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \quad (21)$$

the Stockmayer (12-6-3) potential,^{3b}

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \delta \left(\frac{\sigma}{r}\right)^3 \right] \quad (22)$$

and the Morse potential,¹⁷

$$\varphi(r) = \epsilon \left\{ \exp \left[-2 \left(\frac{C}{\sigma} \right) (r-r_e) \right] - 2 \exp \left[- \left(\frac{C}{\sigma} \right) (r-r_e) \right] \right\}, \quad (23)$$

in which $r_e/\sigma = 1 + \ln(2)/C$, and C is a parameter determined by the width of the well. A comparison of the results for these three potentials is discussed below.

Lennard-Jones and Stockmayer Potentials

Because the Lennard-Jones potential is the same as the Stockmayer potential with $\delta = 0$ the two potentials are considered together. The collision integrals for the (12-6) potential have been calculated by a number of people² including Itean, Glueck, and Svehla²³; Monchick and Mason^{3b}; and recently

Barker, Fock, and Smith⁴. These separate calculations are in good agreement for most values of the reduced temperature, $T^* = kT/\epsilon$. They therefore served as an excellent check on the accuracy of our programme.

It was found that our computed collision integrals agreed best with the calculations of Monchick and Mason; agreement was better than 1 part in 1,000 except for $T^* > 30$ when the difference was not more than 3 parts in 1,000. At these high temperatures the computer collision integrals agreed to four and five figures with those of Itean et al., suggesting that Mason and Monchick are slightly in error above $T^* = 30$. Otherwise our results showed that Monchick and Mason's tables are the most accurate available and suggested that the programme was accurate at all temperatures.

Similar small discrepancies for $T^* > 30$ were noted between the computer collision integrals and those calculated by Monchick and Mason for the Stockmayer potential when δ was positive. Otherwise the computer was able to reproduce Monchick and Mason's tables on the Stockmayer potential to better than 1 part in 1,000, confirming again both the accuracy of these tables and the computer programme.

Morse Potential

After the programme was fully tested on the Stockmayer and Lennard-Jones potentials it was used to evaluate the collision integrals for the Morse potential for different values

of the parameter C . Good agreement was obtained in most cases with the results of Lovell and Hirschfelder¹⁷. In the case of $C = 8$ and $C = 10$, however, disagreement was as much as 10% at the lowest reduced temperatures ($T^* = 0.2$). This disagreement was traced to discrepancies in the low-energy cross sections.

In case this might be due to some error in the programme, some JWKB cross sections were calculated by summing over the phase shifts. When μ was small the JWKB cross sections oscillated about the classical cross sections. As μ increased the amplitudes of the oscillations grew smaller until they effectively disappeared when $\mu = 10^6$. At this value of μ the present classical and JWKB cross sections agreed to three figures at those energies where disagreement was obtained with Lovell and Hirschfelder. This suggested that the present collision integrals were correct.

Since our results are partly in disagreement with those of Lovell and Hirschfelder and since their results are as yet unpublished, we have computed some quantities useful in the calculations of transport properties for systems interacting with a Morse potential. As is well known, the Morse potential function does not become infinite at zero separation:

$$\phi(0) = 4E \left[\exp(C) \right] \left[\exp(C) - 1 \right].$$

Whereas the computer program could deal with a potential that did not have a hard core, it was felt that it was physically unrealistic to calculate cross sections at energies in excess of $\phi(0)$.

In Table III, $\phi(0)$ is shown for a number of values of C . For values of $C > 4.0$, the energies of interest in the present calculations all fell below $\phi(0)$ and for $C < 4.0$, an upper energy bound was set such that

$$E_{\max} = \phi(0).$$

This upper energy bound in turn sets an upper bound on the temperature range for which collision integrals could be calculated. This upper temperature bound is also noted in Table III.

The results of our calculations are presented for different values of C in Table IV. The quantities listed are $\Omega^{(1,1)*}_{(T^*)}$, $\Omega^{(2,2)*}_{(T^*)}$, f_{η} , f_{λ} , $f_{\mathcal{D}}$, A^* , B^* , C^* , E^* , F^* , and $\left[\alpha_o^k \right]_2$. The reduced collision integrals $\Omega^{(1,1)*}_{(T^*)}$ and $\Omega^{(2,2)*}_{(T^*)}$ are defined as

$$\Omega^{(\ell,S)*}_{(T^*)} = \frac{2(2\pi\mu/k)^{\frac{1}{2}} \Omega^{(\ell,S)}(T)}{(S+1)! \left[1 - \frac{1}{2} \frac{1+(-1)^{\ell}}{1+\ell} \right] \pi \sigma^2} \quad (24)$$

The quantities f_{η} , f_{λ} and $f_{\mathcal{D}}$ are factors used to obtain Kihara's second approximation²⁴ to the coefficients of viscosity, thermal conductivity and diffusion, respectively:

$$\begin{aligned} f_{\eta} &= 1 + \frac{3}{196} (8E^* - 7)^2, \\ f_{\lambda} &= 1 + \frac{1}{42} (8E^* - 7)^2, \\ f_{\mathcal{D}} &= 1 + (6C^* - 5) / (16A^* + 40). \end{aligned} \quad (25)$$

The quantity $[\alpha_o^k]_2$ is Kihara's second approximation to the isotopic thermal diffusion factor given by

$$[\alpha_o^k]_2 = \frac{15(6C^* - 5)(2A^* + 5)}{2A^*(16A^* - 12B^* + 55)} (1 + \delta^k). \quad (26)$$

where δ^k is a correction factor given by Mason²⁵. The quantities A^* , B^* , C^* , E^* , and F^* are defined as

$$\begin{aligned} A^* &= \Omega^{(2,2)*} / \Omega^{(1,1)*}, \\ B^* &= [5\Omega^{(1,2)*} - 4\Omega^{(1,3)*}] / \Omega^{(1,1)*}, \\ C^* &= \Omega^{(1,2)*} / \Omega^{(1,1)*}, \\ D^* &= \Omega^{(2,3)*} / \Omega^{(2,2)*}, \\ F &= \Omega^{(3,3)*} / \Omega^{(1,1)*}. \end{aligned} \quad (27)$$

The table lists values of the above quantities only for $C = 1, 2, 4, 6, 8$, and 20 . This set of values of C was found to be sufficient for interpolation between $C = 1$ and $C = 20$ to an accuracy of a small fraction of 1% if graphs of the quantities in the tables were drawn against $\log C$. (In some cases a log-log graph gives more accurate results).

In the same way it was found that it was possible to interpolate for any reduced temperature with a table containing many fewer temperatures than are usually given in tables of collision integrals. The list of temperatures in Table III was

sufficient for interpolation to a few parts in 1,000 if the quantities were drawn against $\log T^*$. In the case of the collision integrals themselves greatest accuracy was obtained from a plot of $\log \Omega^{(\ell, S)^*}$ against $\log T^*$.

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Fig. 1 An illustration of the use of the orbiting
parameters r_o and b_o in the calculation of the
turning point: if $b_1 > b_o$ then $r_1 > r_o$; if $b_2 < b_o$
then $r_2 < r_o$.

$$\varphi_{\text{eff}}(r) = \varphi(r) + b^2 E / r^2$$

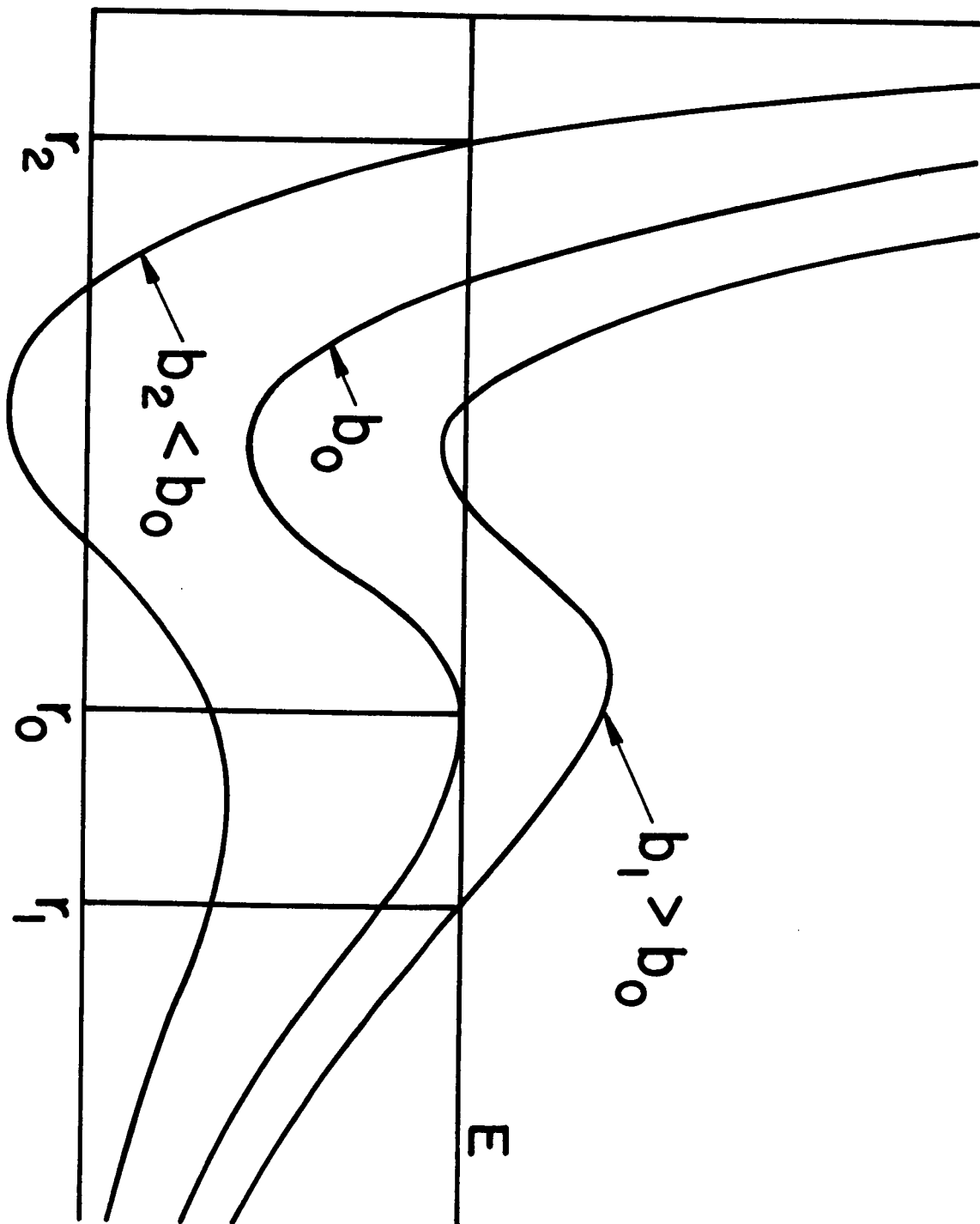


TABLE I

Comparison of calculations of δ by the Gauss-Mehler formula in (16) for the Lennard-Jones (12-6) potential with $\delta = 1$ and $E = \epsilon$

$\frac{1}{2} N^a$	Impact Parameter		
	2	3	4
2	0.082165	0.009779	0.002305
4	0.081824	0.009776	0.002304
12	0.081823	0.009776	0.002304

^a $\frac{1}{2} N$ is the number of integration points.

TABLE II

A comparison of the cross sections $S^{(\ell)}(E)$ evaluated for the Lennard-Jones (12-6) potential with $\delta = 1$ and $\epsilon = 1$, by Gaussian integration with different numbers of integration points, N .

N	E				
	0.0063	0.0710	0.2382	0.7985	1.278
32	42.34	18.89	12.58	8.166	6.337
24	42.35	18.86	12.57	8.157	6.335

TABLE III

Upper bounds on the temperature range at which collision integrals have been calculated because $\phi(0)$ is finite for the Morse potential.

C	$\phi(0)$	T^*_{\max}
1.0	18.7	0.46
2.0	188.8	4.6
3.0	1,533.4	37.4
4.0	11,705.4	285.5

TABLE IV

The collision integrals and related quantities for calculating
the transport properties for a Morse potential

T*	$\Omega(1,1)^*$	$\Omega(2,2)^*$	f_η	f_λ	$f_{\lambda'}$	A*	B*	C*	E*	F*	$\begin{bmatrix} k \\ \alpha_o \end{bmatrix}_2$
0.004	81.543	68.632	1.0044	1.0069	1.0085	0.8417	1.1212	0.9458	0.9421	0.9558	0.75771
0.010	68.217	54.950	1.0036	1.0056	1.0056	0.8055	1.1592	0.9240	0.9358	0.9169	0.64177
0.020	57.238	45.519	1.0028	1.0043	1.0037	0.7953	1.1819	0.9074	0.9280	0.8954	0.53113
0.040	46.596	36.871	1.0021	1.0033	1.0027	0.7913	1.1900	0.8962	0.9213	0.8850	0.45181
0.100	32.674	28.463	1.0028	1.0043	1.0001	0.8711	1.4321	0.8197	0.9284	0.7885	-0.07101
0.200	19.597	20.628	1.0027	1.0042	1.0130	1.0526	1.5130	0.6898	0.8227	0.7446	-0.81993
0.400	9.169	10.731	1.0264	1.0411	1.0374	1.1704	1.4219	0.5864	0.7109	0.7366	-1.24045

TABLE IV (Cont.)

C = 2.0

T*	$\Omega(1,1)^*$	$\Omega(2,2)^*$	f_η	f_λ	f_D	A*	B*	C*	E*	F*	$\left[\begin{smallmatrix} k \\ \alpha_0 \end{smallmatrix}\right]^2$
0.004	21.3303	21.6425	1.0052	1.0081	1.0091	1.0146	1.0932	0.9523	0.9480	1.0147	0.66181
0.010	18.5383	17.7060	1.0044	1.0069	1.0080	0.9551	1.1151	0.9443	0.9423	0.9870	0.65762
0.020	16.3252	14.9869	1.0038	1.0060	1.0065	0.9180	1.1430	0.9324	0.9375	0.9606	0.61377
0.040	13.9429	12.5350	1.0033	1.0052	1.0045	0.8990	1.1736	0.9153	0.9335	0.9325	0.52172
0.100	10.6486	9.7379	1.0033	1.0051	1.0015	0.9145	1.2757	0.8811	0.9327	0.8855	0.31387
0.200	7.6296	7.8154	1.0003	1.0004	1.0012	1.0243	1.4478	0.7904	0.8912	0.8205	-0.21199
0.400	4.4535	5.0400	1.0062	1.0097	1.0123	1.1317	1.4268	0.6923	0.7953	0.7965	-0.72791
1.000	1.8140	2.1403	1.0121	1.0189	1.0148	1.1799	1.2793	0.6776	0.7637	0.8205	-0.71898
2.000	0.9790	1.1794	1.0041	1.0064	1.0067	1.2047	1.2398	0.7285	0.8104	0.8761	-0.47031
4.000	0.5830	0.7362	1.0010	1.0015	1.0025	1.2627	1.2800	0.7687	0.8431	0.9365	-0.28537

TABLE IV (Cont.)

T*	$\Omega(1,1)^*$	$\Omega(2,2)^*$	f_η	C = 4.0		A*	B*	C*	E*	F*	$\begin{bmatrix} \alpha_k \\ \alpha_o \end{bmatrix}^2$
				f_λ	f_ρ						
0.004	7.0039	7.9153	1.0066	1.0103	1.0084	1.1301	1.0956	0.9497	0.9570	1.0395	0.58526
0.010	6.0782	6.7197	1.0061	1.0094	1.0081	1.1055	1.0991	0.9473	0.9537	1.0308	0.58483
0.020	5.4385	5.8879	1.0056	1.0088	1.0079	1.0826	1.1040	0.9455	0.9508	1.0223	0.58736
0.040	4.8363	5.1122	1.0051	1.0079	1.0073	1.0570	1.1168	0.9411	0.9472	1.0097	0.57870
0.100	4.0509	4.1757	1.0045	1.0069	1.0058	1.0308	1.1497	0.9284	0.9424	0.9866	0.52736
0.200	3.3969	3.5466	1.0038	1.0060	1.0024	1.0441	1.2611	0.8948	0.9377	0.9405	0.35275
0.400	2.5430	2.8232	1.0002	1.0003	1.0000	1.1102	1.3457	0.8262	0.8888	0.8955	-0.03472
1.000	1.4859	1.6903	1.0006	1.0009	1.0005	1.1376	1.2354	0.8046	0.8504	0.8956	-0.13851
2.000	1.0321	1.1708	1.0002	1.0003	1.0002	1.1344	1.1633	0.8491	0.8891	0.9348	0.07560
4.000	0.7889	0.9084	1.0023	1.0036	1.0018	1.1514	1.1498	0.8867	0.9239	0.9761	0.25762
10.000	0.5940	0.7071	1.0034	1.0054	1.0028	1.1904	1.1713	0.9010	0.9343	1.0080	0.32408
20.000	0.4808	0.5856	1.0028	1.0044	1.0022	1.2180	1.1944	0.8941	0.9286	1.0164	0.28576
40.000	0.3806	0.4740	1.0018	1.0028	1.0013	1.2453	1.2204	0.8802	0.9182	1.0193	0.21628
100.000	0.2645	0.3394	1.0005	1.0008	1.0002	1.2831	1.2637	0.8534	0.8984	1.0168	0.09061
100.000	0.1896	0.2491	1.0000	1.0000	1.0000	1.3136	1.3052	0.8252	0.8775	1.0094	-0.03499

TABLE IV (Cont.)
C = 6.0

T*	$\Omega(1,1)^*$	$\Omega(2,2)^*$	f_η	f_λ	f_D	A*	B*	C*	E*	F*	$\begin{bmatrix} k \\ \alpha_O \end{bmatrix}^2$
0.004	4.2323	4.8452	1.0077	1.0120	1.0087	1.1448	1.0905	0.9521	0.9637	1.0390	0.59141
0.010	3.7030	4.2226	1.0073	1.0113	1.0085	1.1403	1.0933	0.9506	0.9613	1.0381	0.58574
0.020	3.3374	3.7824	1.0069	1.0108	1.0083	1.1333	1.0951	0.9494	0.9592	1.0362	0.58285
0.040	3.0005	3.3665	1.0065	1.0102	1.0082	1.1220	1.0979	0.9481	0.9567	1.0323	0.58149
0.100	2.5911	2.8514	1.0059	1.0092	1.0077	1.1005	1.1096	0.9443	0.9525	1.0206	0.57387
0.200	2.2879	2.4906	1.0055	1.0086	1.0063	1.0886	1.1500	0.9335	0.9502	1.0004	0.53012
0.400	1.9261	2.1349	1.0031	1.0049	1.0025	1.1084	1.2434	0.8963	0.9317	0.9617	0.33517
1.000	1.3598	1.5224	1.0003	1.0005	1.0006	1.1195	1.2001	0.8649	0.8934	0.9374	0.15785
2.000	1.0522	1.1611	1.0017	1.0027	1.0021	1.1035	1.1303	0.8917	0.9171	0.9549	0.29148
4.000	0.8685	0.9629	1.0048	1.0075	1.0049	1.1087	1.1068	0.9221	0.9452	0.9843	0.44829
10.000	0.7193	0.8122	1.0067	1.0105	1.0066	1.1292	1.1104	0.9368	0.9579	1.0083	0.52164
20.000	0.6310	0.7228	1.0066	1.0103	1.0065	1.1456	1.1196	0.9363	0.9572	1.0168	0.51374
40.000	0.5504	0.6389	1.0060	1.0094	1.0060	1.1609	1.1304	0.9318	0.9535	1.0211	0.48541
100.000	0.4512	0.5326	1.0051	1.0079	1.0049	1.1804	1.1464	0.9232	0.9469	1.0240	0.43591
200.000	0.38157	0.4561	1.0043	1.0067	1.0041	1.1954	1.1601	0.9153	0.9411	1.0251	0.39258

TABLE IV (Cont.)

T^*	$\Omega(1,1)^*$	$\Omega(2,2)^*$	f_η	f_λ	f_ρ	A^*	B^*	C^*	E^*	F^*	$\left[\alpha_o^k\right]_2$
0.004	3.1590	3.5914	1.0085	1.0132	1.0095	1.1368	1.0828	0.9571	0.9682	1.0383	0.62159
0.010	2.7997	3.1867	1.0082	1.0128	1.0092	1.1382	1.0855	0.9552	0.9666	1.0376	0.61072
0.020	2.5475	2.8992	1.0080	1.0124	1.0090	1.1381	1.0868	0.9541	0.9652	1.0369	0.60487
0.040	2.3136	2.6269	1.0077	1.0120	1.0089	1.1354	1.0876	0.9534	0.9637	1.0359	0.60205
0.100	2.0331	2.2896	1.0073	1.0113	1.0088	1.1262	1.0897	0.9525	0.9612	1.0328	0.60217
0.200	1.8382	2.0481	1.0068	1.0106	1.0084	1.1142	1.1023	0.9497	0.9584	1.0247	0.59591
0.400	1.6330	1.8131	1.0056	1.0088	1.0061	1.1103	1.1650	0.9322	0.9509	0.9982	0.51729
1.000	1.2870	1.4217	1.0020	1.0031	1.0028	1.1047	1.1721	0.9008	0.9202	0.9624	0.34502
2.000	1.0572	1.1513	1.0032	1.0050	1.0043	1.0890	1.1121	0.9158	0.9322	0.9677	0.42156
4.000	0.9097	0.9874	1.0064	1.0099	1.0070	1.0854	1.0849	0.9389	0.9555	0.9871	0.54641
10.000	0.7872	0.8638	1.0085	1.0133	1.0089	1.0973	1.0818	0.9526	0.9683	1.0062	0.61859
20.000	0.7149	0.7928	1.0087	1.0135	1.0091	1.1090	1.0866	0.9541	0.9691	1.0142	0.62230
40.000	0.6488	0.7262	1.0084	1.0130	1.0088	1.1193	1.0925	0.9522	0.9673	1.0182	0.60740
100.000	0.5659	0.6404	1.0077	1.0120	1.0082	1.1316	1.1009	0.9481	0.9639	1.0213	0.57972
200.000	0.5060	0.5771	1.0073	1.0113	1.0076	1.1406	1.1076	0.9443	0.9611	1.0227	0.55649

TABLE IV (Cont.)

C = 20.0

T*	$\Omega(1,1)^*$	$\Omega(2,2)^*$	f_η	f_λ	f_D	A*	B*	C*	E*	F*	$\left[\frac{k}{a_0}\right]^2$
0.004	1.6882	1.8187	1.0111	1.0173	1.0126	1.0772	1.0492	0.9748	0.9817	1.0183	0.75056
0.010	1.5739	1.6986	1.0110	1.0171	1.0125	1.0793	1.0504	0.9742	0.9811	1.0188	0.74558
0.020	1.4908	1.6105	1.0109	1.0169	1.0124	1.0803	1.0512	0.9737	0.9804	1.0187	0.74223
0.040	1.4109	1.5246	1.0108	1.0168	1.0123	1.0805	1.0512	0.9734	0.9801	1.0185	0.74026
0.100	1.3117	1.4171	1.0108	1.0168	1.0124	1.0803	1.0498	0.9737	0.9800	1.0190	0.74153
0.200	1.2428	1.3410	1.0108	1.0168	1.0125	1.0790	1.0476	0.9745	0.9801	1.0192	0.74608
0.400	1.1800	1.2692	1.0108	1.0168	1.0128	1.0756	1.0450	0.9757	0.9801	1.0184	0.75456
1.000	1.1030	1.1741	1.0099	1.0154	1.0124	1.0644	1.0601	0.9734	0.9755	1.0069	0.75177
2.000	1.0364	1.0821	1.0079	1.0123	1.0114	1.0440	1.0679	0.9674	0.9649	0.9829	0.72933
4.000	0.9673	0.9783	1.0090	1.0140	1.0116	1.0114	1.0481	0.9679	0.9709	0.9631	0.75149
10.000	0.9061	0.9359	1.0142	1.0221	1.0144	1.0329	1.0232	0.9838	0.9955	1.0054	0.83381
20.000	0.8783	0.9174	1.0130	1.0202	1.0145	1.0446	1.0320	0.9845	0.9901	1.0096	0.82865
40.000	0.8488	0.8892	1.0126	1.0195	1.0143	1.0476	1.0343	0.9834	0.9883	1.0098	0.81999
100.000	0.8095	0.8502	1.0124	1.0193	1.0141	1.0503	1.0354	0.9823	0.9874	1.0105	0.81150
200.000	0.7798	0.8205	1.0123	1.0191	1.0139	1.0522	1.0362	0.9817	0.9870	1.0112	0.80655

REFERENCES

- 1 S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases, 2nd. Ed. (Cambridge University Press, New York, 1952).
- 2 J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley and Sons, Inc., New York, 1954).
- 3 (a) E. A. Mason, J. Chem. Phys. 22, 169(1954); (b) L. Monchick and E. A. Mason, J. Chem. Phys. 35, 1676(1961).
- 4 J. A. Barker, W. Fock, and F. Smith, Phys. Fluids 7, 897(1964).
- 5 R. A. Buckingham, in Physical Chemistry in Aerodynamics and Space Flight (Pergamon Press, New York, 1961), pp.205-216.
- 6 R. J. Munn, J. Chem. Phys. 40, 1439(1964).
- 7 H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc., (London) A141, 434(1933); A144, 188(1934).
- 8 This compact result is attributed to H. A. Kramers in ref. 2, Chap.10.
- 9 N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions, 2nd. Ed. (Clarendon Press, Oxford, 1949).
- 10 R. A. Buckingham and J. W. Fox, Proc. Roy. Soc. (London) A267, 102(1962).
- 11 K. W. Ford, D. L. Hill, M. Wakano, and J. A. Wheeler, Ann. Phys. (New York) 7, 239(1959).
- 12 K. W. Ford and J. A. Wheeler, Ann. Phys. (New York) 7, 259, 287 (1959).

- 13 C. Lanczos, Applied Analysis (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1956).
- 14 Z. Kopal, Numerical Analysis (Chapman and Hall, Ltd., London, (1955).
- 15 T. Kihara, and M. Kotani, Proc. Phys.- Math. Soc. Japan 25, 602(1943).
- 16 J. de Boer and J. van Kranendonk, Physica 14, 442(1948).
- 17 J. O. Hirschfelder and S. E. Lovell, unpublished report from University of Wisconsin, WIS-AF-19(1961).
- 18 F. J. Smith, Physica 30, 497(1964).
- 19 J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, J. Chem. Phys. 16, 968(1948).
- 20 A. Dalgarno and F. J. Smith, Proc. Roy. Soc. (London) A267, 477(1962).
- 21 P. Davis and P. Rabinowitz, J. Research Natl. Bur. Standards 56, 35(1956); 60, 613(1958).
- 22 P. Rabinowitz and G. Weiss, Math. Comp. 13, 285(1959).
- 23 E. C. Itean, A. R. Glueck and R. A. Svehla, NASA Technical Note D-481(1961).
- 24 T. Kihara, Rev. Mod. Phys. 25, 831(1953).
- 25 E. A. Mason, J. Chem. Phys. 27, 75(1957).