KINETIC THEORY OF
BIMOLECULAR CHEMICAL REACTION,
DIFFUSIVE DRAG, AND OTHER
PROCESSES IN A GAS MIXTURE

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SUMMARY

For two gas species with a temperature difference and a bulk velocity difference neither of which is necessarily small in magnitude, the kinetic theory of gases has been used to derive explicit expressions for the collision frequency, diffusive drag force, molecular translational energy transfer rate, and the bimolecular chemical reaction frequency. The derivations, which are based upon hypothesized mutual collision diameters, activation energies, and steric factors, are of interest in connection with theoretical studies of low-pressure gas mixtures with large departures from equilibrium. A binary temperature concept is introduced as an aid in condensing and interpreting the expressions derived from the kinetic theory. The expression derived for the diffusive drag force is used to give a more definite form to the equations of motion of the individual species in a mixture of several interdiffusing gases.

INTRODUCTION

The theory of diffusion and chemical reaction in gas mixtures must be extended substantially if it is to meet effectively the challenging demands of a number of recent problems encountered in aerospace research, for example, the theoretical problem associated with the release of a gas in the upper atmosphere which reacts with the ambient atomic oxygen to produce chemiluminescence. The problems in question are characterized by low gas pressures and by large departures from thermodynamic equilibrium which are not adequately represented by the Chapman-Enskog theory.

The branch of kinetic theory developed largely by Chapman and Enskog (see, for example, refs. 1 and 2) provides a rather detailed treatment of gas mixtures which are locally near equilibrium, but it embraces neither diffusion nor reaction kinetics when diffusion speeds are not small in comparison with typical molecular speeds. Large departures from equilibrium are, of course, admissible in certain special theories, for example, the kinetic theory of shock waves, that of individual or crossed molecular
beams, and Maxwell's theory (ref. 3) of the dynamics of gases the intermolecular forces of which vary inversely as the fifth power of the distance between centers.

An approach to the approximate dynamical analysis of a mixture of interdiffusing gases which are subject to chemical reactions and other phenomena can be based on a mathematical model in which each gas species has a molecular velocity distribution which is locally Maxwellian with respect to a reference frame moving with the species. Some situations of gas mixtures in which such a distribution of molecular velocities is especially appropriate have been discussed by Grad (ref. 4), Morse (ref. 5), and others. Before the accuracy and usefulness of this kind of model in a given nonequilibrium situation is tested theoretically or experimentally, it is of interest to ascertain various implications by performing appropriate kinetic theory derivations. Representative derivations of this type and the statement of the results in forms which should facilitate their application and the understanding of their physical significance comprise the main content of this paper. As an example of the application of these results, the expression derived for the drag or tractive force acting between two gas species is used to formulate equations of motion of the individual species in a mixture of several interdiffusing gases. The dynamical model envisaged encompasses diffusion speeds which are not necessarily small compared with thermal molecular speeds.

When the present paper had been completed, the author learned that some of the kinetic theory results had been given previously by Tanenbaum (ref. 6), who also considered some other intermolecular potentials and compared the results with those of Maxwell (ref. 3).

SYMBOLS

\( b \)
impact parameter (see, for example, ref. 13)

\( \bar{c}_i \)
mean molecular velocity of \( i \)th species (ref. 1); equivalent to \( \bar{u}_i \) of present paper

\( \vec{D}_{ji} \)
drag force, per unit volume, exerted by species \( j \) on species \( i \); magnitude, \( D_{ji} \)

\( \bar{D}_i \)
sum of drag forces on species \( i \)

\( E_a \)
activation energy per reactant pair of molecules

\( E_\sigma \)
kinetic energy of molecular pair relative to their center of mass, along line of centers before collision

2
\( \vec{F}_i \)  body force, per unit mass, on species i

\( \vec{G}_i \)  divergence of stress dyadic of species i

\( \vec{I} \)  impulse on molecule 2 in collision (see eq. (C3))

\( I_1 \)  defined by equation (E6)

\( I_2 \)  defined by equation (E9)

\( K_{12} \)  defined in appendix C

\( M(v) \)  defined by equation (A14)

\( m_i \)  mass of molecule of species i

\( m_{ij} \)  reduced mass, \( \frac{m_im_j}{m_i + m_j} \)

\( N(v) \)  defined by equation (A3)

\( N_{12} \)  frequency of collisions, per unit volume, per unit time, involving one molecule of species 1 and one of species 2

\( N'_{12} \)  frequency of collisions, per unit volume, per unit time, involving one molecule of species 1 and one of species 2 and leading to chemical reaction

\( n_i \)  number density of species i (molecules per unit volume)

\( n \)  summation index

\( P(v) \)  defined by equation (B2)

\( P \)  defined by equations (E1)

\( P_{12} \)  probability or steric factor

\( Q(v) \)  defined by equation (B4)
\[ R_{12} \] defined by equation (B10)

\[ r \] dimensionless relative speed defined by equation (3)

\[ S(v) \] defined by equation (C10)

\[ s, s', s'' \] integration variables

\[ T, T_i \] absolute temperatures; subscript \( i \) refers to species \( i \)

\[ T_{12} \] binary temperature defined by equation (10)

\[ t \] time

\[ \overline{u}_i \] bulk velocity of species \( i \)

\[ \overrightarrow{V} \] defined by equations (A4) or (A5)

\[ V_x, V_y, V_z \] rectangular Cartesian components of \( \overrightarrow{V} \)

\[ v \] magnitude of \( \overrightarrow{V} \)

\[ \overrightarrow{v} \] bulk relative velocity, \( \overline{u}_1 - \overline{u}_2 \)

\[ \overrightarrow{v}_i \] molecular velocity for species \( i \)

\[ v_i \] magnitude of \( \overrightarrow{v}_i \)

\[ \{v_{ix}, v_{iy}, v_{iz}\} \] rectangular Cartesian components of \( \overrightarrow{v}_i \)

\[ W \] activation speed defined by equation (E2)

\[ W(v) \] defined by equation (C13)

\[ w \] magnitude of \( \overrightarrow{w} \)

\[ w_1 \] magnitude of \( \overrightarrow{v}_1 - \overrightarrow{v} \)
\( w_2 \) magnitude of \( \vec{v}_2 + \vec{v} \)

\( \vec{w} \) molecular relative velocity, \( \vec{v}_1 - \vec{v}_2 \)

\( \{ w_x, w_y, w_z \} \) rectangular Cartesian components of \( \vec{w} \)

\( w_{o1}, w_{o2} \) molecular approach speeds defined by equations (D1)

\( z \) dimensionless activation speed, \( \beta_{12}^{1/2} \)

\( \alpha \) dimensionless parameter defined by equation (2); see figure 1

\( \beta_1, \beta_2, \beta_{12} \) defined by equations (4)

\( \theta_{12} \) diffusive drag coefficient (ref. 1, p. 415)

\( \theta \) co-latitude in spherical coordinate system

\( \theta_w \) angle between \( \vec{\sigma} \) and \( \vec{w} \) immediately before collision

\( \kappa \) dimensionless parameter defined by equation (B14)

\( \kappa_{ij} \) defined by equation (B14) with \( r \) replaced by \( r_{ij} \)

\( \vec{\lambda} \) vector defined by equation (C1); magnitude, \( \lambda \)

\( \nu \) number of gas species in mixture

\( \rho_i \) density of \( i \)th species

\( \sigma_{ij} \) collision diameter, \( \frac{\sigma_i + \sigma_j}{2} \)

\( \sigma_i \) diameter of molecule of species \( i \)

\( \tau_{12} \) energy flow from species 1 to species 2, per unit volume, per unit time
\( v_{12} \) dissipative heating rate of species 2 due to diffusive drag of species 1, per unit volume

\( \varphi \) azimuth in spherical coordinate system

\( \varphi_w \) angle defined following equation (C7)

\( \omega \) dimensionless parameter defined by equation (11)

\( \zeta \) dimensionless relative molecular speed, \( \beta_{12}^{1/2} \)

\( \nabla \) gradient operator

\[ \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \]

An overbar denotes a mean value of associated quantity. An arrow denotes a vector. An underline denotes volume element in velocity space, for example, \( \overline{dV} = dV_x \, dV_y \, dV_z \).

**ANALYSIS**

The kinetic theory of gases will be used to derive analytic expressions for those properties or rates which are most essential to a dynamic description of a chemically reacting mixture of gases with different temperatures and different bulk velocities.

In the mathematical analyses performed herein, each gas species is assumed to have a velocity distribution which is locally Maxwellian when viewed from an inertial frame moving with the bulk velocity of the species. The smooth, elastic, hard-sphere molecular model is employed because of its simplicity, its use in yielding reference values to which more refined values can be normalized (see ref. 2, pp. 523ff), and the fact that it roughly approximates the strong, short-range repulsive forces which often predominate in molecular collisions. Since diffusion speeds are not restricted in the present study and temperature differences between species are admissible, this analytical work represents an extension of the existing kinetic theory of gas mixtures of rigid-sphere molecules. (See refs. 1, 2, and 7.) Expressions in closed form are derived for the interspecies (binary) collision frequency (appendix A), diffusive drag (appendix B), molecular translational energy transfer rate (appendix C), definition of a binary temperature (appendix D), and number of bimolecular collisions resulting in chemical reaction (appendix E). In appendix E, the additional assumptions required, which are simple and
well known, are concerned with the nature of molecular collisions leading to chemical reaction, the quantum theory of which is largely undeveloped. (See, for example, ref. 8.)

The expressions derived herein are asymptotically equivalent to well-known expressions of kinetic theory for equal temperatures and relative species velocities which are of small magnitude compared with typical molecular speeds.

Assumptions

The detailed kinetic-theory derivations given in appendixes A to E of this paper are based upon the assumptions that:

(1) Binary molecular collisions prevail.

(2) Molecules collide as smooth, elastic, hard spheres.

(3) Each gas species has a Maxwellian velocity distribution when viewed from an inertial frame moving with the species bulk velocity.

(4) Collisions leading to chemical reaction are delimited by a steric factor and an activation energy. (This assumption is needed only in appendix E.)

Temperature and bulk velocity are both permitted to differ, without restriction, from one species to another. No explicit consideration is given to ionization, dielectric polarization, or diamagnetic or paramagnetic susceptibility, even though the results may be of some value in studying problems involving these phenomena.

In connection with assumption (2), it will be seen that only the mutual collision diameters, not the individual radii, appear in the final equations. Moreover, it will be observed that the notion of collision diameter is interpretatively flexible in the case of the chemical considerations of appendix E, because it occurs multiplied by a steric or probability factor.

In the dynamical considerations of diffusion in gas mixtures, no refinement has been made to account for thermal diffusion. It is assumed here that the interaction between the gas species in a mixture is solely that of the diffusive drag forces associated with species bulk velocity differences.

Principal Derived Expressions

In this section, the principal expressions which are derived in the appendixes are presented. For additional discussion and details the reader is referred to the appropriate appendix.

The expression derived in appendix A for the number \( N_{12} \) of collisions between molecules of species 1 and species 2 per unit volume, per unit time, can be written
\[
N_{12} = \left(8\pi\right)^{1/2}n_{1}n_{2}\sigma_{12}^{2}\left(\frac{kT_{1}}{m_{1}} + \frac{kT_{2}}{m_{2}} + \frac{\alpha}{3}v^{2}\right)^{1/2}
\]  

(1)

where \(n_{i}\), \(m_{i}\), and \(T_{i}\) (\(i = 1,2\)) are the number density, molecular mass, and absolute temperature of species \(i\), \(\sigma_{12}\) is the collision diameter, \(k\) is Boltzmann's constant, \(v\) is the magnitude of the species relative bulk velocity, and \(\alpha\) is the nearly constant parameter defined by

\[
\alpha = \frac{3}{2r^{2}}\left\{ \frac{1}{4}\left[e^{-r^{2}} + \left(\frac{1}{r} + 2r\right)\int_{0}^{r} e^{-s^{2}}ds\right]^{2} - 1 \right\}
\]  

(2)

The dimensionless speed parameter \(r\) in equation (2) is defined by

\[
r = \beta_{12}^{1/2}v
\]  

(3)

where, by definition,

\[
\begin{align*}
\frac{1}{\beta_{12}} &= \frac{1}{\beta_{1}} + \frac{1}{\beta_{2}} \\
\frac{1}{\beta_{1}} &= \frac{2kT_{1}}{m_{1}}
\end{align*}
\]  

(4)

Equations (A19), (A21), and (A28) are, in view of the definition of \(\alpha\), alternative forms of equation (1). For \(v = 0\) (or, equivalently, \(r = 0\)) and \(T_{1} = T_{2}\), equation (1) reduces to the well-known collision-frequency equation of the kinetic theory of gases. (See, for example, ref. 1, p. 90, eq. (4).)

The diffusive drag force \(\vec{D}_{12}\), per unit volume, exerted by species 1 on species 2, is derived in appendix B and can be written in the form:

\[
\vec{D}_{12} = \frac{4}{3}(8\pi)^{1/2}n_{1}n_{2}\sigma_{12}^{2}\left(\frac{kT_{1}}{m_{1}} + \frac{kT_{2}}{m_{2}} + \frac{\kappa}{5}v^{2}\right)^{1/2}m_{12}\vec{v}
\]  

(5)

where \(m_{12}\) is the reduced mass \(\frac{m_{1}m_{2}}{m_{1} + m_{2}}\), \(\vec{v}\) is the bulk velocity (magnitude \(v\)) of species 1 relative to species 2, and \(\kappa\) is the nearly constant parameter defined by
With this definition of $\kappa$, equations (B9) and (B16) are equivalent forms of equation (5).

For small $v$ (or, more precisely, for $r << 1$) and $T_1 = T_2$, equation (5) yields an expression for the resistance opposing diffusion which is asymptotically equivalent to $\theta_{12} n_1 n_2 (c_1 - c_2)$ of reference 1, page 415. The same limiting result was obtained by Stefan (ref. 9) and, except for the factor $4/3$, by Maxwell (ref. 7), who first analyzed the resistance opposing diffusion. For large $v$ (that is, for $r >> 1$), the magnitude of the diffusive drag force given by equation (5) is proportional to $v^2$. By comparison, Maxwell's analysis (ref. 3) of a gas mixture in which the intermolecular forces are repulsive and vary inversely as the fifth power of the distance between centers yielded a diffusive drag proportional to $v$, even for large $v$; it should be recognized that the analysis in reference 3 holds for all relative velocities because of the mathematical simplification wrought by the selection of the inverse fifth power model.

The time rate of change of the molecular translational energy, per unit volume, of the second gas species (viewed from an inertial frame moving with species 2) is derived in appendix C and can be expressed as

$$K_{12} = \frac{4m_{12}}{m_1 + m_2} k(T_1 - T_2) N_{12} + \frac{m_1}{m_1 + m_2} v D_{12}$$

(7)

where $N_{12}$ is the collision frequency given by equation (1) and $D_{12}$ is the magnitude of the diffusive drag force given by equation (5). (Eq. (7) is equivalent to eq. (C17).) If the first and second terms on the right-hand side of equation (7) are denoted by $\tau_{12}$ and $u_{12}$, respectively, it is seen that $\tau_{12}$ is the flow of energy from species 1 to species 2 due to the temperature difference and $u_{12}$ is the dissipative heating rate of species 2 associated with the diffusive drag. It is also noted that

$$\tau_{12} = -\tau_{21}$$

(8)

and since $D_{12} = D_{21}$,

$$u_{12} + u_{21} = v D_{12}$$

(9)

Equation (9) states that the total dissipation rate due to diffusive drag is $v D_{12}$.
In equation (94) of reference 3 (which should be corrected for typographical omissions by inserting the factor 1/2 before the expression in braces on the left side and the factor \( \beta_1 \), different in meaning from \( \beta \) of the present paper, before the expression in brackets on the right side), the expression on the right-hand side is analogous to the present one for \( K_{12} \), except for the number of molecular degrees of freedom involved and the independence of velocity distribution made possible by Maxwell's assumption of an inverse fifth-power intermolecular repulsive force. If Maxwellian velocity distributions are assumed for the two gases, the terms of Maxwell's expression which correspond to the terms \( \tau_{12} \) and \( u_{12} \) are, respectively, proportional to \( T_1 - T_2 \) (with no dependence on temperatures in the coefficients) and proportional to \( v^2 \). Thus, the present assumption of elastic, hard-sphere molecules leads to a more complicated functional dependence on \( T_1, T_2, \) and \( v \); see equation (7) in the light of equations (1) and (5).

In the collision theory of chemical reactions (see, for example, ref. 10), the most significant single variable seems to be the total kinetic energy along the intermolecular line of centers immediately before collision. Its hypothesized threshold value is then called the activation energy. With the added notion of a probability or steric factor, the probability of chemical reaction resulting from molecular collision can be expressed in mathematical terms. This theoretical approach to the kinetic theory of gas reactions, which is of course not without shortcomings, is followed in appendixes D and E.

For the purposes of this paper, it is convenient to introduce a binary temperature \( T_{12} \), which is a measure of the collisional energy available to produce bimolecular gas reactions, according to the definition

\[
\frac{kT_{12}}{m_{12}} = \frac{kT_1}{m_1} + \frac{kT_2}{m_2} + \frac{\omega}{3} v^2
\]

where \( \omega \) is a nearly constant parameter defined by

\[
\omega = \frac{3}{4} \frac{1}{r^2} \left[ \frac{1}{2} + r^2 - \frac{1}{r} \int_0^r e^{-s^2} ds \right] + \frac{1}{r} \int_0^r e^{-s^2} ds
\]

The analytical basis for the definition of the binary temperature \( T_{12} \) is provided in appendix D and equations (D13) and (D14) given therein are equivalent to equation (10). It should be noted that the right-hand side of equation (10) is similar to forms occurring
in equations (1) and (5). Therefore, two other binary temperatures $T_{12}^{(1)}$ and $T_{12}^{(2)}$ can be defined by the equations

\[
\frac{kT_{12}^{(1)}}{m_{12}} = \frac{kT_1}{m_1} + \frac{kT_2}{m_2} + \frac{\alpha}{3} v^2
\]

and

\[
\frac{kT_{12}^{(2)}}{m_{12}} = \frac{kT_1}{m_1} + \frac{kT_2}{m_2} + \frac{\kappa}{5} v^2
\]

and used to write equations (1) and (5) in simpler forms more akin to existing kinetic theory; although these equations are not needed herein, they relate to a considerable extent the principal derived expressions. The parameters $\alpha$, $\kappa$, and $\omega$, which are plotted in figures 1, 2, and 3, respectively, all approach unity asymptotically as $v$ (or $r$) approaches zero.

Figure 1. Coefficient $\alpha$ required for equation (A21) to be exact formula for collision frequency and, correspondingly, for eq. (A27) to equal each side of eq. (A20).
The expression derived in appendix E for the number \( N_{12}' \) of bimolecular collisions per unit time, involving one molecule of each gas species and leading to chemical reaction, can be written

\[
N_{12}' = P_{12}^{n_1}n_2\sigma_{12}^2\left(\frac{\pi}{\beta_{12}}\right)^{1/2}\frac{1}{2r}\left\{\frac{z+r}{e(z-r)^2} - \frac{z-r}{e(z+r)^2} + \left[1 - 2(z^2 - r^2)\right] \int_{z-r}^{z+r} e^{-s^2}ds\right\} (14)
\]
where $P_{12}$ is the probability or steric factor and

$$ z = \left( \frac{2\beta_{12}E_a}{m_{12}} \right)^{1/2} $$

in which $E_a$ denotes the activation energy; $z$, like $r$, is dimensionless. Equation (14) is equivalent to equation (E14).

If the parameter $z$ is not greater than approximately unity, table I shows that equation (14) can be written in the simpler, approximate form

$$ N'_{12} \approx P_{12}N_{12}e^{-E_a/kT_{12}} \quad (15) $$

This form (or the equivalent, eq. (E19)) becomes an exact representation of equation (14) when the parameter $\omega$ in $T_{12}$ (of eq. (10)) is replaced by the parameter $\omega'$ presented graphically in figure 4.

### TABLE I.- RATIO OF APPROXIMATE VALUE OF $N'_{12}$ (EQ. (E19)) TO EXACT VALUE (EQ. (14)) FOR VARIOUS COMBINATIONS OF DIMENSIONLESS PARAMETERS $r$ AND $z$

<table>
<thead>
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<th>$z$</th>
<th>0.1</th>
<th>0.2</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>50</th>
<th>100</th>
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<td>1.0000</td>
<td>0.99992</td>
<td>0.99950</td>
<td>0.99908</td>
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<td>1.0211</td>
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<td>*</td>
<td>*</td>
<td>*</td>
<td>23.895</td>
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</tr>
</tbody>
</table>

*Denotes extremely large number.
APPLICATION TO DIFFUSION IN GAS MIXTURES

The dynamics of a mixture of interdiffusing gas species with emphasis on the drag forces due to substantial relative bulk velocities is considered briefly. The effect of chemical reactions on the species bulk acceleration, which may not be negligible in the case of fast reactions (for example, many reactions involving free radicals), is not considered here.

The equation of motion of the \( i \)th species \((i = 1, \ldots, \nu)\) in a gas mixture can be written (see refs. 11 and 12)

\[
\rho_i \left( \frac{\partial}{\partial t} + \mathbf{u}_i \cdot \nabla \right) \mathbf{u}_i = \rho_i \mathbf{F}_i + \nabla \mathbf{G}_i + \mathbf{D}_i \tag{16}
\]

where \( \rho_i \) and \( \mathbf{u}_i \) are the density and bulk velocity, respectively, of the \( i \)th species, \( t \) denotes the time, \( \nabla \) is the gradient operator, \( \mathbf{F}_i \) is the body force per unit mass acting on species \( i \), \( \nabla \mathbf{G}_i \) is the divergence of the stress dyadic (in a simple case, \( \nabla \mathbf{G}_i \) is the negative of the gradient of the partial pressure \( p_i \)), and \( \mathbf{D}_i \) is the total force per unit volume exerted by the other gas species on species \( i \). If the frame of reference in which equations (16) are employed is not an inertial frame, each body force \( \mathbf{F}_i \) will include one or more inertial forces, for example, centrifugal force, Coriolis force (dependent upon \( \mathbf{u}_i \)), etc.

For the purposes of this analysis, the density of the gas mixture is assumed to be sufficiently low for binary molecular collisions to prevail; each \( \mathbf{D}_i \) is then a vector sum.
of binary drag forces,\(^1\) that is,

\[
\overline{D}_i = \sum_{j=1}^{\nu} \overline{D}_{ji}
\]

(17)

where \(\overline{D}_{ji}\) is the drag or tractive force, per unit volume, which species \(j\) exerts on species \(i\); for \(j = i\), \(\overline{D}_{jj} = \overline{0}\), by definition.

The calculation of \(\overline{D}_{ji}\) in a specific case is generally difficult. One notable exception is the binary gas mixture considered by Maxwell (ref. 3) in which each molecule repels every other molecule with a force along the line of centers of mass and inversely proportional to the fifth power of the distance between these centers, the proportionality constant being determined by the particular type of molecular pair involved; in this case a remarkable analytical simplification appears and \(\overline{D}_{ij}\) is proportional to the product of the densities and to the relative bulk velocity of the two species no matter what molecular velocity distributions exist in the two gas species. Linear drag forces are discussed generally in reference 11.

Another notable exception is a gas mixture whose molecules behave in collisions as hard elastic spheres (which is the model employed in the present paper), provided that the distribution of molecular velocities in each species can be adequately approximated by a Maxwell-Boltzmann distribution with appropriate temperature. The temperatures of the different species need not be equal for the calculation to be completed as in appendix B. For a mixture with more than two species, equation (B16) together with the assumed prevalence of binary collisions yields the nonlinear drag force

\[
\overline{D}_{ji} = \frac{8}{3}(2\pi)^{1/2}m_{ij}n_in_j\sigma_{ij}^2 \left[ \frac{1}{2\beta_{ij}} + \frac{\kappa_{ij}}{5\left(\overline{u}_j - \overline{u}_1\right)^2} \right]^{1/2} \left(\overline{u}_j - \overline{u}_1\right)
\]

(18)

Here, \(n_i\) and \(\overline{u}_i\) are the number density and bulk velocity, respectively, of the \(i\)th gas species, \(\sigma_{ij}\) is the collision diameter of the molecular pair \((i,j)\), \(\kappa_{ij}\) is given by equation (B14) with \(r\) replaced by \(\beta_{ij}^{1/2}\left|\overline{u}_j - \overline{u}_1\right|\), and, by definition,

\(^1\)In a real gas mixture at sufficiently high pressures, the separability into binary drag forces may not be possible. Moreover, the binary forces of interaction of real gas species may not be pure drags, but may have components normal to the relative bulk velocity vectors.
where $m_i$ and $T_i$ are the molecular mass and molecular translational temperature, respectively, of species $i$.

Equations (17) and (18) provide an explicit expression for the drag or tractive force $D_i$ in equation (16). The selection of values of the collision diameters $\sigma_{ij}$ can be based upon theoretical interpretations of gas or molecular data.

If considerable fractions of the molecules of one or more gas species are in excited electronic energy states, the corresponding collision diameters may require substantial correction from those applicable to molecules in the electronic ground states.

Equations (16), (17), and (18) yield species equations of motion which reduce to equations (1) of reference 1 (p. 415) for near-equilibrium flows for which the species stress dyadic is the product of the species partial pressure and the unit dyadic.

### CONCLUDING REMARKS

Some of the basic dynamic characteristics of a model of a reacting gas mixture which is not necessarily near equilibrium have been examined. The comparison of the results with the corresponding ones of more elementary kinetic theory has been facilitated by the introduction of the binary temperature concept.

Simple models or approximations which are analytically tractable are needed in preliminary investigations where a high degree of accuracy is not essential. Ultimately, theoretical structures of greater accuracy and detail, requiring electronic computers for their implementation, must be developed.

The results presented in this study provide one starting point for further development of the kinetic theory and continuum dynamics of gas mixtures which are far from equilibrium. This development can evidently proceed along several lines, such as

\[
\begin{align*}
\beta_{ij} & = \frac{\beta_i \beta_j}{\beta_i + \beta_j} \\
\beta_i & = \frac{m_i}{2kT_i} \\
m_{ij} & = \frac{m_i m_j}{m_i + m_j}
\end{align*}
\]
the incorporation of more elaborate models of molecular collisions, the inclusion of radiation effects, and the admission of more general molecular distribution functions.

Langley Research Center, 
National Aeronautics and Space Administration, 
Langley Station, Hampton, Va., August 19, 1966, 
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APPENDIX A

COLLISION FREQUENCY FOR TWO GASES
WITH DIFFERENT TEMPERATURES AND
DIFFERENT BULK VELOCITIES

Consider a mixture of two gas species with hard-sphere molecules of diameters $a_i$ ($i = 1, 2$) and number densities $n_i$. Their mutual collision diameter is, then, $\sigma_{12} = \frac{a_1 + a_2}{2}$. Let each gas have a Maxwellian velocity distribution with respect to an inertial frame and let the velocity of the first frame with respect to the second be $\vec{v}$. Let the gas temperatures and molecular masses be denoted by $T_i$ and $m_i$, respectively. The frequency of collisions $N_{12}$, that is, the number of collisions between molecules of species 1 and species 2 per unit volume per unit time, is derived in this appendix.

With the aid of the kinetic theory of gases (see, for example, ref. 13, chs. 2 to 5, especially pp. 21 and 22), the collision frequency can be written, the molecular velocities $\vec{v}_i$ being referred to the second frame,

$$N_{12} = n_1 n_2 \left( \frac{\sigma_{12}}{\pi} \right)^2 (\beta_1 \beta_2)^{3/2} \int \int e^{-\beta_1 v_1^2 - \beta_2 v_2^2} dv_1 dv_2$$  \hspace{1cm} (A1)

or, the molecular velocities $\vec{v}_i$ being referred to the first frame,

$$N_{12} = n_1 n_2 \left( \frac{\sigma_{12}}{\pi} \right)^2 (\beta_1 \beta_2)^{3/2} \int \int e^{-\beta_1 v_1^2 - \beta_2 v_2^2} dv_1 dv_2$$  \hspace{1cm} (A2)

where

$$\int = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty}$$

$$\beta_i = \frac{m_i}{2kT_i} \hspace{1cm} (i = 1, 2)$$
APPENDIX A

\[ w = \left| \vec{w} \right| = \left| \vec{v}_1 - \vec{v}_2 \right| = \left[ (v_{1x} - v_{2x})^2 + (v_{1y} - v_{2y})^2 + (v_{1z} - v_{2z})^2 \right]^{1/2} \]

\[ w_1 = \left| \vec{v}_1 - \vec{v} \right| \]

\[ w_2 = \left| \vec{v}_2 + \vec{v} \right| \]

\[ v_i = \left| \vec{v}_i \right| \quad (i = 1, 2) \]

\[ dv_i = dv_{ix} \, dv_{iy} \, dv_{iz} \quad (i = 1, 2) \]

For given values of the parameters \( n_{11}, \sigma_{12}, \) and \( \beta_i \) \( (i = 1, 2) \), the collision frequency \( N_{12} \) is a function of the relative speed \( v = \left| \vec{v} \right| \) of the two gas species. Let

\[ N(v) = \int \frac{w}{w_1 \, w_2} \, e^{-\beta_1 w_1^2 - \beta_2 w_2^2} \, dv_1 \, dv_2 \]  

(A3)

which is the sextuple integral appearing on the right-hand side of equation (A1).

In order to evaluate the integral defined by equation (A3), it is convenient to change from the variables \( (\vec{v}_1, \vec{v}_2) \) to variables \( (\vec{V}, \vec{w}) \) in accordance with the linear transformation

\[ \begin{align*}
\vec{v}_1 - \vec{v} &= \vec{V} + \frac{\beta_2}{\beta_1 + \beta_2} (\vec{w} - \vec{v}) \\
\vec{v}_2 &= \vec{V} - \frac{\beta_1}{\beta_1 + \beta_2} (\vec{w} - \vec{v})
\end{align*} \]  

(A4)

This linear transformation has a constant Jacobian, the absolute value of which is unity, and has the inverse given by

\[ \begin{align*}
\vec{V} &= \frac{\beta_1}{\beta_1 + \beta_2} (\vec{v}_1 - \vec{v}) + \frac{\beta_2}{\beta_1 + \beta_2} \vec{v}_2 \\
\vec{w} &= \vec{v}_1 - \vec{v}_2
\end{align*} \]  

(A5)
The fact that the second of equations (A5) is consistent with the earlier usage of the symbol $\tilde{w}$ in relation to $\bar{v}_1$ and $\bar{v}_2$ is essential to the intended application of the transformation. The transformation (A4) maps one six-dimensional space $(\bar{V}, \bar{w})$ onto the other $(\bar{v}_1, \bar{v}_2)$ in a one-to-one manner.

Equations (A4) yield

$$\beta_1 (\bar{v}_1 - \bar{v})^2 + \beta_2 v_2^2 = (\beta_1 + \beta_2) V^2 + \beta_{12} (\bar{w} - \bar{v})^2$$

where $\beta_{12} = \frac{\beta_1 \beta_2}{\beta_1 + \beta_2}$.

Before applying these results to the evaluation of the integral (A3), it is interesting to note that equations (A3), (A4), (A5), and (A6) can be written in the symmetric forms

$$N(v) = \int \beta_1 v_1^2 - \beta_2 v_2^2 - \beta_{12} [\bar{w} - \bar{v}]^2 \, dv_1' \, dv_2'$$

$$\bar{v}_1' = \bar{V} + \frac{\beta_2}{\beta_1 + \beta_2} \bar{w}$$

$$\bar{v}_2' = \bar{V} - \frac{\beta_1}{\beta_1 + \beta_2} \bar{w}$$

$$\bar{V} = \frac{\beta_1}{\beta_1 + \beta_2} \bar{v}_1' + \frac{\beta_2}{\beta_1 + \beta_2} \bar{v}_2'$$

$$\bar{w} = \bar{v}_1' - \bar{v}_2'$$

$$\beta_1 v_1'^2 + \beta_2 v_2'^2 = (\beta_1 + \beta_2) V^2 + \beta_{12} w^2$$

where

$$\bar{v}_1' = \bar{v}_1 - \frac{\beta_1}{\beta_1 + \beta_2} \bar{v}$$

$$\bar{v}_2' = \bar{v}_2 - \frac{\beta_1}{\beta_1 + \beta_2} \bar{v}$$
APPENDIX A

The molecular velocities $\vec{v}_1'$ and $\vec{v}_2'$ are now referred to the natural inertial frame, which moves with velocity $\frac{\beta_1 \vec{v}}{\beta_1 + \beta_2}$ relative to the second inertial frame described earlier. In the natural inertial frame, equation (A10) reduces, in the special case for which $T_1 = T_2 = T$, upon multiplication of both sides by $kT$, to the usual kinetic energy transformation to a center-of-mass system; similarly, the velocity $\vec{v}$, by the first of equations (A9), reduces to the velocity of the center of mass of the two molecules in the natural frame. Moreover, in this case of equal temperatures, the velocity of the natural frame can be interpreted as the velocity of the center of mass of two molecules, one of which has mass $m_1$ and is at rest in the first inertial frame, and the other of mass $m_2$ and at rest in the second inertial frame; this fact follows from the preceding discussion since $\vec{v}_1 = \vec{v}$ and $\vec{v}_2 = \vec{0}$ imply $\vec{V} = \vec{0}$.

Equation (A6), with $(\vec{v}_1 - \vec{v})^2 = w_1^2$, and the related linear transformation (A4) can be used to rewrite equation (A3) in the form

$$N(v) = \int \text{we}^{-(\beta_1 + \beta_2) V^2 - \beta_12 (\vec{w} - \vec{v})^2} dV dw $$

(A12)

where

$$dV = dV_x dV_y dV_z$$

$$dw = dw_x dw_y dw_z$$

Performing the integrations with respect to $V_x$, $V_y$, and $V_z$ yields

$$N(v) = \left(\frac{\pi}{\beta_1 + \beta_2}\right)^{3/2} \int \text{we}^{-\beta_12 (\vec{w} - \vec{v})^2} dw$$

$$= \left(\frac{\pi}{\beta_1 + \beta_2}\right)^{3/2} e^{-\beta_12 v^2} M(v)$$

(A13)

where, by definition,

$$M(v) = \int \text{we}^{-\beta_12 (\vec{w}^2 - 2\vec{v} \cdot \vec{w})} dw$$

(A14)
APPENDIX A

Changing to spherical coordinates \((w, \theta, \varphi)\), with the half-line whose co-latitude is \(\theta = 0\) having the direction of \(\vec{v}\) gives

\[
M(v) = \int_0^{2\pi} \int_0^\pi \int_0^\infty w 2\beta_{12}wv \cos \theta e^{-\beta_{12}w^2} w^2 \sin \theta \, dw \, d\theta \, d\varphi
\]

\[
= \frac{2\pi}{\beta_{12}v} \int_0^\infty w^2 e^{-\beta_{12}w^2} \sinh(2\beta_{12}w^2) \, dw
\]

\[
= \frac{2\pi}{\beta_{12}^2 r} \int_0^\infty \zeta^2 e^{-\zeta^2} \sinh(2r\zeta) \, d\zeta
\]

(A15)

where \(\zeta = \beta_{12}^{1/2}w\) and \(r = \beta_{12}^{1/2}v\), by definition. Hence,

\[
M(v) = \frac{\pi}{\beta_{12}^2 r} e^r \int_0^\infty \zeta^2 \left[e^{-\zeta^2} - e^{-(\zeta+r)^2}\right] \, d\zeta
\]

\[
= \frac{\pi}{\beta_{12}^2 r} e^r \left[\int_{-r}^r (s + r)^2 e^{-s^2} \, ds - \int_{r}^\infty (s - r)^2 e^{-s^2} \, ds\right]
\]

(A16)

wherein the substitutions \(\zeta - r = s'\) and \(\zeta + r = s''\) were made and the primes were subsequently dropped. Equation (A16) can be written as

\[
M(v) = \frac{\pi}{\beta_{12}^2 r} e^r \left[\int_{-r}^r (s^2 + 2rs + r^2) e^{-s^2} \, ds + \int_r^\infty 4rse^{-s^2} \, ds\right]
\]

(A17)

The first of the four quadratures requires one integration by parts in order to reduce equation (A17) to the form

\[
M(v) = \frac{\pi}{\beta_{12}^2 r} e^r \left[re^{-r^2} + (1 + 2r^2) \int_0^r e^{-s^2} \, ds\right]
\]

(A18)

which can be evaluated numerically with the aid of tables of the error function.

Equations (A1), (A3), (A13), and (A18) yield, therefore,
APPENDIX A

\[ N_{12} = n_1 n_2 \sigma_{12} \left( \frac{\pi}{\beta_{12}} \right)^{1/2} \left[ e^{-r^2} + \left( \frac{1}{r} + 2r \right) \int_0^r e^{-s^2} ds \right] \]  \hspace{1cm} (A19)

Equation (A19) gives, then, the number \( N_{12} \) of collisions per unit volume per unit time between molecules of two gases with Maxwellian velocity distributions and a relative bulk speed \( v = \beta_{12}^{-1/2} r \). The formula is exact for hard-sphere molecules with collision diameter \( \sigma_{12} \). Equation (A19), in the limit in which the temperature of one gas approaches zero, reduces to the expression for the collision frequency for a molecular beam of zero temperature impinging on a gas at equilibrium. (See ref. 14, p. 108.)

In equation (A19), the function (of \( r \)) in brackets is an entire analytic function (with removable singularity) whose power-series representation is given by the right-hand side of the equation

\[ e^{-r^2} + \left( \frac{1}{r} + 2r \right) \int_0^r e^{-s^2} ds = 2 \sum_{n=0}^{\infty} (-1)^{n+1} \frac{r^{2n}}{n! (4n^2 - 1)} \]  \hspace{1cm} (A20)

For real numbers \( r \neq 0 \), the first two terms of the series are positive and subsequent terms alternate in sign.

It will also be shown in this appendix that equation (A19) can, with both justification and advantage, be written in the form

\[ N_{12} = n_1 n_2 \sigma_{12} \left( \frac{\pi}{\beta_{12}} \right)^{1/2} 2 \left( 1 + \frac{2}{3} \alpha r^2 \right)^{1/2} \]

\[ = 2(2\pi)^{1/2} n_1 n_2 \sigma_{12} \left( \frac{1}{2\beta_{12}} + \frac{\alpha}{3} v^2 \right)^{1/2} \]  \hspace{1cm} (A21)

where \( \alpha \) is defined by equating the right-hand side of equation (A19) and the first right-hand side of equation (A21); therefore,

\[ \alpha = \frac{3}{2r^2} \left\{ \frac{1}{4} \left[ e^{-r^2} + \left( \frac{1}{r} + 2r \right) \frac{\sqrt{\pi}}{2 \sqrt{\pi}} \text{erf} \left( \frac{r}{\sqrt{\pi}} \right) \right]^2 - 1 \right\} \]  \hspace{1cm} (A22)

where, by the usual definition,

\[ \text{erf} \left( \frac{r}{\sqrt{\pi}} \right) = \frac{2}{\sqrt{\pi}} \int_0^r e^{-s^2} ds \]
APPENDIX A

For \( 0 \leq r \leq r_{\text{max}} \leq 1 \), the first two terms of the power series (eq. (A20)) yield the approximation \( 2 \left( 1 + \frac{r^2}{3} \right) \) with an error which is positive and less than \( r_{\text{max}}^4/15 \). The power series (eq. (A20)), rewritten as a series of nonpositive powers of \( 1/r \), is the Laurent expansion about the ideal point at infinity; thus, the function has an essential singularity there and no expansion in nonnegative powers of \( 1/r \) is possible. However, if consideration is restricted to real values of \( r > 1 \), it is easy to show with the aid of tables that the left-hand side of equation (A20) is approximated by \( \pi^{1/2} \left[ r + (2r)^{-1} \right] \), and somewhat less accurately by \( \pi^{1/2} r \). The preceding results suggest combining the features of the function on the left-hand side of equation (A20) at small and large \( r \) in approximations such as

\[
2 \left( 1 + \frac{2}{3} r^2 \right)^{1/2}
\]  
(A23)

\[
2 \left( 1 + \frac{\pi}{4} r^2 \right)^{1/2}
\]  
(A24)

\[
2 \left( 1 + \frac{4}{3} r^2 + \frac{\pi^2}{16} r^4 \right)^{1/4}
\]  
(A25)

and so forth. These approximations, in ratio to the given function (A20), are plotted in figure 5.

The approximation (A23) yields, with equation (A19), the approximate collision frequency

\[
N_{12} \approx n_1 n_2 \sigma_{12} \left( \frac{\pi}{\beta_{12}} \right)^{1/2} 2 \left( 1 + \frac{2}{3} r^2 \right)^{1/2}
\]

or, upon rearranging and substituting for \( \beta_{12} \) and \( r^2 \),

\[
N_{12} \approx 4 \left( \frac{\pi}{3} \right)^{1/2} n_1 n_2 \sigma_{12} \left( \frac{3 kT_1}{2 m_1} + \frac{3 kT_2}{2 m_2} + \frac{1}{2} v^2 \right)^{1/2}
\]  
(A26)

which has an obvious physical interpretation in terms of the thermal translational energies and the kinetic energy, per unit mass, of either gas relative to the other.
The graphical representations of the approximations (A23) and (A24) in figure 5 suggest expressing the function on the left-hand side of equation (A20) in the simple and exact form

\[ 2 \left(1 + \frac{2}{3} \alpha r^2\right)^{1/2} \]

which corresponds to the collision frequency (exact)

\[ N_{12} = 4 \left(\frac{\pi}{3}\right)^{1/2} n_1 n_2 \sigma_{12} \left(\frac{3 kT_1}{2 m_1} + \frac{3 kT_2}{2 m_2} + \frac{\alpha v^2}{2}\right)^{1/2} \]

where \( \alpha \) is nearly constant. Equation (A28) is equivalent to equation (A21) and \( \alpha \), which is given explicitly by equation (A22), is plotted as a function of \( r \) in figure 1. The dimensionless parameter \( \alpha \), as a function of \( r \), is asymptotically equivalent to the constant 1 for \( r << 1 \), and to the constant \( 3\pi/8 \) for \( r >> 1 \).
APPENDIX A

Another way of deriving the form of equation (A21), which is less intuitive and synthetic but more satisfactory from an analytical standpoint, consists of squaring both sides of equation (A19), expanding the resulting right-hand side to the second power in \( r \) by Taylor's theorem with a remainder, and demonstrating (with a plot such as fig. 1) the limited variability of the (second derivative) coefficient of the final or remainder \( (r^2/2!) \) term. Since the expanded function \( N_{12}^2 \) is known, the final coefficient can be evaluated for each value of \( r \). The linear term in \( r \) is absent from the aforementioned quadratic expression \( (N_{12}^2) \) and the latter therefore leads to an expression for \( N_{12} \) of the form of equation (A21). This alternative derivation provides a firm theoretical basis for adopting the expression for the collision frequency in the form of equation (A21).
APPENDIX B

DRAG OR TRACTIVE FORCES FOR TWO GASES
WITH DIFFERENT TEMPERATURES AND
DIFFERENT BULK VELOCITIES

The drag or tractive force per unit volume exerted by the first gas on the second is derived in this appendix. The kinetic theory of gases (see, for example, ref. 13, chs. 2 to 5, especially eqs. (2.27), (2.33), and expression (5.4)) yields, for the forementioned drag force,

\[
\bar{D}_{12} = \frac{v}{v} \left( \beta_1 \beta_2 \right)^{3/2} \int n_1 n_2 w e^{-\beta_1 w_1^2 - \beta_2 w_2^2} \frac{v}{v} \cdot \frac{w}{w} \int_0^{\sigma_1 12} m_{12} \left[ 2 \left( 1 - \frac{b^2}{\sigma_1 12} \right) \right] 2\pi b db dv_1 dv_2
\]

\[
= \frac{v^2}{v^2} m_{12} \left( \frac{\sigma_1 12}{\pi} \right)^{2} n_1 n_2 \left( \beta_1 \beta_2 \right)^{3/2} P(v)
\]

where \( b \) and \( m_{12} \) denote the impact parameter and reduced mass, respectively, and

where, by definition,

\[
P(v) = \int \frac{v}{v} \cdot \frac{w}{w} w e^{-\beta_1 w_1^2 - \beta_2 w_2^2} dv_1 dv_2
\]  

(B2)

With the change from the variables \( v_1, v_2 \) to the variables \( \bar{v}, \bar{w} \) defined by equation (A4), equation (B2) becomes

\[
P(v) = \int \bar{v} \cdot \bar{w} we^{-\beta_1 \bar{v}^2 - \beta_2 \bar{w}^2} d\bar{v} d\bar{w} = \left( \frac{\pi}{\beta_1 + \beta_2} \right)^{3/2} e^{-\beta_1 \bar{v}^2} Q(v)
\]

(B3)

where, by definition,

\[
Q(v) = \int \bar{v} \cdot \bar{w} we^{-\beta_1 \bar{v}^2 - \beta_2 \bar{w}^2} d\bar{w}
\]

(B4)

Changing to spherical coordinates \( w, \theta, \phi \) with the half-line whose co-latitude is \( \theta = 0 \) having the direction of \( \bar{v} \) gives
APPENDIX B

\[ Q(v) = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \frac{w^2 \cos \theta e^{2\beta_12\beta_12\beta_12 w \cos \theta e^{-\beta_12 w^2}} \sin \theta \, dw \, d\theta \, d\varphi \]

\[ = 2\pi \int_0^{\infty} \left[ \frac{w^3 \cosh(2\beta_12 w)}{\beta_12} - \frac{w^2 \sinh(2\beta_12 w)}{2\beta_12} \right] e^{-\beta_12 w^2} \, dw \]

\[ = \frac{2\pi}{\beta_12^3} \int_0^{\infty} \left[ \zeta^3 \cosh(2r\zeta) - \frac{\zeta^2 \sinh(2r\zeta)}{2r} \right] e^{-\zeta^2} \, d\zeta \quad \text{(B5)} \]

where, by definition, \( \zeta = \beta_12 \frac{1}{2} w \) and \( r = \beta_12 \frac{1}{2} v \). It follows from equation (A15) that equation (B5) can be written as

\[ Q(v) = -\frac{M(v)}{2\beta_12} + \frac{2\pi}{\beta_12^3} \int_0^{\infty} \zeta^3 e^{-\zeta^2} \cosh(2r\zeta) \, d\zeta \]

\[ = \left( r^2 - \frac{1}{2} \right) \frac{M(v)}{\beta_12} + \frac{2\pi}{\beta_12^3} \int_0^{\infty} \zeta e^{-\zeta^2} \cosh(2r\zeta) \, d\zeta \]

\[ = \left( r^2 - \frac{1}{2} \right) \frac{M(v)}{\beta_12} + \frac{2\pi}{\beta_12^3} \left[ \frac{1}{2} + r \int_0^{\infty} e^{-\zeta^2} \sinh(2r\zeta) \, d\zeta \right] \quad \text{(B6)} \]

where, in two instances, the factor \( \zeta \exp(-\zeta^2) \) was singled out for integration by parts. The remaining integral in equation (B6) can be transformed as follows:

\[ \int_0^{\infty} e^{-\zeta^2} \sinh(2r\zeta) \, d\zeta = \frac{1}{2} e^{r^2} \int_0^{\infty} \left[ e^{-(\zeta - r)^2} - e^{-(\zeta + r)^2} \right] \, d\zeta \]

\[ = \frac{1}{2} e^{r^2} \left( \int_{-r}^{\infty} e^{-s^2} \, ds - \int_r^{\infty} e^{-s^2} \, ds \right) \]

\[ = e^{r^2} \int_0^r e^{-s^2} \, ds \quad \text{(B7)} \]

Equations (B6) and (B7), together with the expression for \( M(v) \) in equation (A18), yield
APPENDIX B

\[ Q(v) = \frac{\pi}{\beta_{12}^3} \delta^2 r^2 \left[ \left( 1 + \frac{1}{2r^2} \right) e^{-r^2} + \left( 2r + \frac{2}{r} - \frac{1}{2r^3} \right) \int_0^r e^{-s^2} ds \right] \]

\[ = \frac{\pi}{\beta_{12}^3} \delta^2 r^2 \left[ \sum_{n=0}^{\infty} \frac{(-1)^n+1}{n! \left( 4n^2 - 1 \right) (2n + 3)} r^{2n} \right] \] (B8)

Equations (B1), (B3), and the first of equations (B8) provide the following equation for the drag or tractive force:

\[ \bar{D}_{12} = \frac{\delta}{\rho_{12}} \frac{n_1 n_2 \sigma_{12}}{\beta_{12}} \left( \frac{\pi}{\beta_{12}} \right)^{1/2} \left[ \left( 1 + \frac{1}{2r^2} \right) e^{-r^2} + \left( 2r + \frac{2}{r} - \frac{1}{2r^3} \right) \int_0^r e^{-s^2} ds \right] \] (B9)

Thus, equation (B9) gives the drag or tractive force, per unit volume, exerted by the first gas on the second under the assumptions that each gas has a Maxwellian velocity distribution and that the molecules behave as hard spheres with the mutual collision diameter \( \sigma_{12} \); the symbol \( \bar{v} \) denotes the bulk velocity of the first gas with respect to the second.

The right-hand side of equation (B9) consists of a momentum vector \( \bar{v}m_{12} \) multiplied by the quantity \( \bar{D}_{12} \) defined by

\[ R_{12} = \frac{n_1 n_2 \sigma_{12}}{\beta_{12}} \left( \frac{\pi}{\beta_{12}} \right)^{1/2} \left[ \left( 1 + \frac{1}{2r^2} \right) e^{-r^2} + \left( 2r + \frac{2}{r} - \frac{1}{2r^3} \right) \int_0^r e^{-s^2} ds \right] \] (B10)

which is plotted, as a ratio to the collision frequency \( N_{12} \) given by equation (A19), in figure 6. Figure 6 shows that for \( r >> 1 \), the quantity \( R_{12} \) is practically identical to
the collision frequency $N_{12}$, but that, for $r \ll 1$, $R_{12}$ is approximately $4/3$ of $N_{12}$.

These results can be verified analytically by observing that the expression in brackets in equation (B10) is asymptotically equivalent to

$$\frac{8}{3} \left(1 + \frac{1}{5} r^2\right) \quad (r \to 0) \quad (B11)$$

and to

$$\pi^{1/2} r \quad (r \to \infty) \quad (B12)$$

As in appendix A, one is led to define a parameter $\kappa$ by

$$\frac{8}{3} \left(1 + \frac{2}{5} \kappa r^2\right)^{1/2} = \left(1 + \frac{1}{2} \frac{r}{r^2}\right) e^{-r^2} + \left(2r + \frac{2}{r} - \frac{1}{2r^3}\right) \int_0^r e^{-s^2} ds \quad (B13)$$

or

$$\kappa = \frac{5}{2} \frac{9}{64} \left(\frac{1}{r^2}\right) e^{-r^2} + \left(2r + \frac{2}{r} - \frac{1}{2r^3}\right) \int_0^r e^{-s^2} ds \left[2 - 1\right] \quad (B14)$$

which is shown graphically in figure 2. For $r \ll 1$, $\kappa = 1$, and for $r >> 1$, $\kappa = \frac{45\pi}{128}$.

Equation (B10) and the definition (B13) yield

$$R_{12} = n_1 n_2 \sigma_{12} \left(\frac{\pi}{\beta_{12}}\right)^{1/2} \frac{8}{3} \left(1 + \frac{2}{5} \kappa r^2\right)^{1/2}$$

$$= \frac{8}{3} (2\pi)^{1/2} n_1 n_2 \sigma_{12} \left(\frac{1}{2\beta_{12}} + \frac{\kappa}{5} \nu^2\right)^{1/2} \quad (B15)$$

The corresponding expression for the drag or tractive force is

$$\overline{D}_{12} = \overline{v} m_{12} R_{12}$$

$$= \frac{8}{3} (2\pi)^{1/2} m_{12} n_1 n_2 \sigma_{12} \left(\frac{1}{2\beta_{12}} + \frac{\kappa}{5} \nu^2\right)^{1/2} \overline{v} \quad (B16)$$

which is proportional to $\nu$ for $r \ll 1$ and to $\nu^2$ for $r >> 1$.

---

This approximation (applicable for $r \ll 1$) was first derived by Stefan (ref. 9).
APPENDIX C

RATES OF CHANGE OF MOLECULAR TRANSLATIONAL ENERGIES RESULTING FROM ELASTIC COLLISIONS BETWEEN MOLECULES OF TWO GASES WITH DIFFERENT TEMPERATURES AND DIFFERENT BULK VELOCITIES

The time rate of change of the molecular translational energy per unit volume of the second gas, viewed from the second inertial frame, is derived in this appendix.

Let \( \vec{\sigma} \) be a unit vector drawn from the center of molecule 1 of the first gas toward the center of molecule 2 of the second gas at the instant of collision. Let \( \theta_w \ (0 \leq \theta_w \leq \pi/2) \) be the angle which \( \vec{\sigma} \) makes with the relative velocity vector \( \vec{w} = \vec{v}_1 - \vec{v}_2 \) immediately before collision. Then,

\[
\vec{\sigma} = \frac{\vec{w}}{w} \cos \theta_w + \vec{\lambda}
\]  

where

\[
\vec{\lambda} \cdot \vec{w} = 0
\]

\[
\lambda = |\vec{\lambda}| = \sin \theta_w = \frac{b}{\sigma_{12}}
\]

In the collision, molecule 2 receives the impulse

\[
\vec{I} = 2m_{12} \vec{w} \cdot \vec{\sigma} \vec{\sigma} = 2m_{12}w \cos \theta_w \vec{\sigma} = 2m_{12} \cos \theta_w \left( \vec{w} \cos \theta_w + w\vec{\lambda} \right)
\]

The velocity \( \vec{v}_2'' \) of molecule 2 after collision is given by

\[
m_2 \vec{v}_2'' = m_2 \vec{v}_2 + \vec{I}
\]

whence

\[
v_{2''}^2 - v_2^2 = \frac{2}{m_2} \vec{v}_2 \cdot \vec{I} + \left( \frac{I}{m_2} \right)^2
\]
APPENDIX C

With the use of equations (C2), (C3), and (C5), the change in kinetic energy of molecule 2, resulting from the collision with molecule 1, can be written as

\[
\frac{1}{2} m_2 (v_2')^2 - v_2^2 = 2 m_1 \left( \frac{v_2 \cdot \bar{w} + \frac{m_2}{m_1} w^2}{w^2} \right) \left( 1 - \frac{b^2}{\sigma_{12}^2} \right) + 2 m_1 \bar{w} v_2 \cdot \bar{\lambda} \left( 1 - \frac{b^2}{\sigma_{12}^2} \right)^{1/2}
\]

(C6)

Since \( \bar{\lambda} \cdot \bar{w} = 0 \), by equation (C2), the decomposition of \( \bar{v}_2 \) into vectors perpendicular to \( \bar{w} \) (\( \bar{v}_{2\perp} \)) and parallel to \( \bar{w} \) yields

\[
\bar{v}_2 \cdot \bar{\lambda} = \bar{v}_{2\perp} \frac{b}{\sigma_{12}} \cos \varphi_w
\]

(C7)

where \( \varphi_w \) is the angle \( \bar{v}_{2\perp} \bar{\lambda} \), that is, the angle between two half-planes emanating from the line of \( \bar{w} \) which are parallel to the vectors \( \bar{v}_2 \) and \( \bar{\sigma} \).

The variables of integration are the six velocity components \( v_{1x} \ldots v_{2z} \) (relative to the second inertial frame), the impact parameter \( b \) (or the corresponding angle \( \theta_w \)), and the angle \( \varphi_w \). The last of these enters the right-hand side of equation (C6) only in the last term and therein, according to equation (C7), simply as \( \cos \varphi_w \); the integration of this term from \( \varphi_w = 0 \) to \( 2\pi \) yields zero. Consequently, the time rate of change of the molecular translational energy per unit volume of the second gas, viewed from the second inertial frame, is simply

\[
K_{12} = \left( \frac{\beta_1 \beta_2}{\pi} \right)^{3/2} \int n_1 n_2 \frac{\beta_1}{w_1^2 - \beta_2 v_2^2} \frac{m_1}{m_2} \left( \frac{v_2 \cdot \bar{w} + \frac{m_2}{m_1} w^2}{w^2} \right) \sigma_{12} \int_0^{\pi/2} \left( 1 - \frac{b^2}{\sigma_{12}^2} \right) 2\pi b \, db \, dv_1 \, dv_2
\]

(C8)

or

\[
K_{12} = m_1 \frac{\left( \frac{\sigma_{12}}{w} \right)^2}{\pi} n_1 n_2 \left( \frac{\beta_1 \beta_2}{\pi} \right)^{3/2} S(v)
\]

(C9)

where, by definition,

\[
S(v) = \int \left( \frac{v_2 \cdot \bar{w} + \frac{m_2}{m_1} w^2}{w^2} \right) \frac{\beta_1}{w_1^2 - \beta_2 v_2^2} \frac{dv_1}{dv_2}
\]

(C10)
APPENDIX C

With the change from the variables $\mathbf{v}_1, \mathbf{v}_2$ to the variables $\mathbf{v}, \mathbf{w}$ defined by equations (A4), equation (C10) becomes

$$S(v) = \int \left[ \mathbf{V} \cdot \mathbf{w} + \left( \frac{m_{12}}{m_2} - \frac{\beta_{12}}{\beta_2} \right) w^2 + \frac{\beta_{12}}{\beta_2} \mathbf{V} \cdot \mathbf{w} \right] e^{-\left( \beta_1 + \beta_2 \right) V^2 - \beta_{12} (\mathbf{w} - \mathbf{V})^2} \, dv \, dw$$  \hspace{1cm} (C11)

Since the term of the integrand of equation (C11), of which $\mathbf{V} \cdot \mathbf{w}$ is a factor, can be resolved into three odd functions of the three components of $\mathbf{v}$, its contribution to $S(v)$ is nihil. Hence, upon recalling the first of equations (B3) and carrying out, for the other part of $S(v)$, the integrations with respect to the components of $\mathbf{V}$, equation (C11) can be written

$$S(v) = \left( \frac{\pi}{\beta_1 + \beta_2} \right)^{3/2} e^{-\beta_{12} v^2} \left( \frac{m_{12}}{m_2} - \frac{\beta_{12}}{\beta_2} \right) W(v) + \frac{\beta_{12}}{\beta_2} P(v)$$ \hspace{1cm} (C12)

where, by definition

$$W(v) = \int w^3 e^{-\beta_{12} (w^2 - 2V \cdot \mathbf{w})} \, dw$$  \hspace{1cm} (C13)

Changing from the rectangular Cartesian coordinates $w_x, w_y, w_z$ to spherical coordinates $w, \theta, \phi$, where the half-line whose co-latitude is $\theta = 0$ has the direction of $\mathbf{v}$, and integrating over the intervals $0 \leq \phi \leq 2\pi$ and $0 \leq \theta \leq \pi$ yield

$$W(v) = \frac{2\pi}{\beta_{12} 3} \int_0^\infty \zeta^4 e^{-\zeta^2} \sinh(2r\zeta) \, d\zeta$$ \hspace{1cm} (C14)

where, by definition, $\zeta = \beta_{12}^{1/2} w$ and $r = \beta_{12}^{1/2} v$. By singling out the factor $\zeta \exp(-\zeta^2)$ and integrating once by parts, a comparison of the results with the third of equations (A15) and the first of equations (B6) shows that

$$W(v) = \frac{2}{\beta_{12}} M(v) + Q(v)$$  \hspace{1cm} (C15)

The second of equations (A13) and of equations (B3) together with equations (C12) and (C15) give
APPENDIX C

\[ S(v) = \frac{2}{\beta_{12}} \left( \frac{m_{12}}{m_2} - \frac{\beta_{12}}{\beta_2} \right) N(v) + \frac{m_{12}}{m_2} P(v) \]  

(C16)

Furthermore, equations (A1), (A3), (the second of) (B1), and (C16) yield

\[ K_{12} = \frac{2m_{12}}{\beta_{12}} \left( \frac{m_{12}}{m_2} - \frac{\beta_{12}}{\beta_2} \right) N_{12} + \frac{m_{12}}{m_2} vD_{12} \]  

(C17)
APPENDIX D

DEFINITION OF A BINARY TEMPERATURE FOR CHEMICAL-KINETIC CONSIDERATIONS

For considerations of the kinetics of chemical reactions, it is of interest to define a binary temperature \( T_{12} \) which is a measure of the amount of translational energy available for chemical reaction in bimolecular collisions. For bimolecular reactions within a species, that is, when the reacting molecules are chemically identical, the temperature of the species serves a similar purpose and no newly defined special temperature is required.

For definiteness, let all velocities be measured, unless otherwise indicated, with respect to the second inertial frame. If, immediately before collision, molecule 1 has velocity \( \vec{w} = \vec{v}_1 - \vec{v}_2 \) relative to molecule 2, the relative molecular speed along the line of centers is \( \vec{w} \cdot \vec{\sigma} = w \cos \theta_w \). (See appendix C.) This speed is the sum of the speeds \( w_{\sigma 1} \) and \( w_{\sigma 2} \) with which the two molecules approach their mutual center of mass; thus,

\[
\begin{align*}
  w_{\sigma 1} + w_{\sigma 2} &= w \cos \theta_w \\
  m_1 w_{\sigma 1} &= m_2 w_{\sigma 2}
\end{align*}
\]  

(D1)

The corresponding total kinetic energy is

\[
E_\sigma = \frac{1}{2} m_1 w_{\sigma 1}^2 + \frac{1}{2} m_2 w_{\sigma 2}^2 = \frac{1}{2} m_{12} w^2 \cos^2 \theta_w = \frac{1}{2} m_{12} w^2 \left( 1 - \frac{b^2}{\sigma_{12}^2} \right)
\]  

(D2)

and its mean value per collision is

\[
\overline{E}_\sigma = \frac{1}{N_{12}} \left( \frac{\beta_1 \beta_2}{\pi^3} \right)^{3/2} \int n_1 n_2 \omega e^{-\beta_1 w_1^2 - \beta_2 v_2^2} \frac{1}{2} m_{12} w^2 \int_{0}^{\sigma_{12}} \left( 1 - \frac{b^2}{\sigma_{12}^2} \right)^2 \pi b \, db \, dv_1 \, dv_2
\]  

(D3)

The inner integral (with respect to \( b \)) is equal to \( \frac{1}{2} \pi \sigma_{12}^{-2} \). With the aid of equations (A1) and (A3), equation (D3) can therefore be written

\[
\overline{E}_\sigma = \frac{1}{N(v)} \frac{m_{12}}{4} \int w^3 e^{-\beta_1 w_1^2 - \beta_2 v_2^2} \, dv_1 \, dv_2
\]  

(D4)
APPENDIX D

Transforming to the variables $\vec{V}, \vec{w}$ by equations (A4) and carrying out the integrations with respect to the three components of $\vec{V}$ yield

$$\bar{E}_\sigma = \frac{m_{12}}{4} \left( \frac{\pi}{\beta_1 + \beta_2} \right)^{3/2} e^{-\beta_1 12 v^2} \frac{W(v)}{N(v)}$$  

(D5)

where $W(v)$ is given by equation (C13). Equations (A13) and (C15) can be used to write equation (D5) in the respective forms

$$\bar{E}_\sigma = \frac{m_{12}}{4} \frac{W(v)}{M(v)}$$

$$= \frac{m_{12}}{4} \left[ \frac{2}{\beta_1 12} + \frac{Q(v)}{M(v)} \right]$$  

(D6)

Equation (D6), together with equations (A18), (B6), and (B7), yields

$$\bar{E}_\sigma = \frac{1}{4} \frac{m_{12}}{\beta_1 12} \left[ \frac{5}{2} + r^2 - \frac{1}{r} \int_0^r e^{-s^2} ds \right] - \frac{1}{e^{-r^2} + (1 + 2r^2) \frac{1}{r} \int_0^r e^{-s^2} ds}$$

(D7)

whence, for $r << 1$,

$$\bar{E}_\sigma = \frac{1}{2} \frac{m_{12}}{\beta_1 12} \left[ 1 + \frac{2}{3} r^2 - \frac{4}{45} r^4 + \ldots \right]$$  

(D8)

and, for $r >> 1$, the asymptotic formula

$$\bar{E}_\sigma \approx \frac{1}{2} \frac{m_{12}}{\beta_1 12} \left( \frac{r^2}{2} + \frac{5}{4} \right) \approx \frac{1}{4} \frac{m_{12} v^2}{2}$$

(D9)

is applicable. The content of equations (D7), (D8), and (D9) is conveniently expressed by

$$\bar{E}_\sigma = \frac{1}{2} \frac{m_{12}}{\beta_1 12} \left( 1 + \frac{2}{3} \omega r^2 \right)$$

(D10)
APPENDIX D

where

\[
\omega = \frac{3}{4} \frac{1}{r^2} \left[ \frac{1}{2} + r^2 - \frac{1}{r} \int_0^r e^{-s^2} ds \right]
\]

\[\text{(D11)}\]

The parameter \( \omega \), which is given by equation (D11) and is plotted as a function of the dimensionless speed parameter \( r \) in figure 3, has the asymptotic values 1 and 3/4, respectively, as \( r \to 0 \) and \( r \to \infty \).

It follows from equation (D8) that, for \( v = 0 \) and \( T_1 = T_2 = T \),

\[ \bar{E}_v = kT \]

\[\text{(D12)}\]

This result and either equation (D7) or preferably its equivalent, equation (D10), provide a basis for defining a binary temperature \( T_{12} \) which is a measure of the amount of translational energy available for chemical reaction in bimolecular collisions, that is,

\[
kT_{12} = \frac{1}{2} \frac{m_{12}}{\beta_{12}} \left( 1 + \frac{2}{3} \omega \beta_{12} v^2 \right)
\]

\[\text{(D13)}\]

or, to afford a better comparison with equation (A28),

\[
\frac{3}{2} \frac{kT_{12}}{m_{12}} = \frac{3}{2} \frac{kT_1}{m_1} + \frac{3}{2} \frac{kT_2}{m_2} + \frac{\omega v^2}{2}
\]

\[\text{(D14)}\]

When the comparison is made with equation (A28), it should be recalled that \( \omega \) and \( \alpha \) are roughly equal to unity. Hence, \( T_{12} \) is approximately equal to another binary temperature \( T_{12}^{(1)} \) defined by equation (7) on the basis of the form of equation (A28); the two binary temperatures are, in fact, asymptotically equivalent, as \( r \to 0 \). Similarly, they are asymptotically equivalent (as \( r \to 0 \)) to the expression for \( T_{12} \) given by equation (D14) with \( \omega \) taken as unity.

In summary, the preceding analysis suggests that the binary temperature \( T_{12} \) defined by equation (D13) may be a significant and useful parameter in theoretical considerations of reacting gas mixtures which are not in dynamical equilibrium.
APPENDIX E

NUMBER OF BIMOLECULAR COLLISIONS RESULTING IN CHEMICAL REACTION

Assume that a fraction \( P \) of the bimolecular collisions, involving one molecule of each gas, for which the line-of-centers velocity component \( \vec{w} \cdot \vec{\sigma} \) (immediately before collision; see appendix C) lies in a small interval of positive real values, leads to chemical reaction. For simplicity, it is assumed that \( P \) is a step function, that is,

\[
P = \begin{cases} 
0 & \left( \vec{w} \cdot \vec{\sigma} < W \right) \\
P_{12} = \text{Constant} & \left( \vec{w} \cdot \vec{\sigma} > W \right)
\end{cases}
\] (E1)

where \( W \) is the activation speed; the latter is related to the activation energy \( E_a \) (see eq. (D2)) by

\[
E_a = \frac{1}{2} m_{12} W^2
\] (E2)

The quantity \( P_{12} \) is the probability factor or steric factor for the reaction.

In this appendix, the number of bimolecular collisions, involving one molecule of each gas and leading to chemical reaction, is calculated. This number will be denoted by \( N_{12}' \). The sevenfold integration involves the impact parameter \( b \) and the molecular velocity components, that is, \((b,\vec{V}_1,\vec{V}_2)\) or, by appendix A, \((b,\vec{V},\vec{w})\) or \((b,\vec{V},w,\theta,\phi)\). The last set will be employed here to express \( N_{12}' \).

It follows from equation (E1) that the integration with respect to \( w \) need extend only from \( w = W \) to \( w = \infty \); for, when \( w < W \), it is certain that \( \vec{w} \cdot \vec{\sigma} = w \cos \theta_w < W \) and, therefore, \( P = 0 \). For given \( w > W \), the condition \( P = P_{12} \) is, by equation (E1), equivalent to \( \vec{w} \cdot \vec{\sigma} > W \) or \( w \geq \vec{w} \cdot \vec{\sigma} > W \) or \( 1 \geq \cos \theta_w > W/w \). Since, by equation (C2),

\[
b = \sigma_{12} \sin \theta_w = \sigma_{12} \left( 1 - \cos^2 \theta_w \right)^{1/2}
\] (E3)

it follows that \( P = P_{12} \) if and only if

\[
0 \leq b < \sigma_{12} \left( 1 - \frac{W^2}{w^2} \right)^{1/2}
\] (E4)

Let the quantity to the right of the inequality be denoted by \( b_1(w) \).
APPENDIX E

Consequently, the techniques of appendix A and reference 13 can be used to write

\[ N_{12}' = P_{12} n_{1} n_{2} \left( \frac{\beta_{1} \beta_{2}}{\pi^3} \right)^{3/2} \int I_{1} \, dV \tag{E5} \]

where

\[ I_{1} = \int_{0}^{2\pi} \int_{0}^{\pi} \int_{W} \left( -p_{1} + p_{2} \right) V^{2} - p_{12} (\vec{w} - \vec{v})^{2} \int_{0}^{b_{1}(w)} 2\pi b \, dw \, 2\sin\theta \, d\theta \, d\phi \tag{E6} \]

and

\[ (\vec{w} - \vec{v})^{2} = w^{2} - 2vw \cos\theta + v^{2} \tag{E7} \]

Integrating with respect to \( b, \varphi, \) and the three components of \( \vec{V} \) yields

\[ N_{12}' = 2\pi^{1/2} P_{12} n_{1} n_{2} \beta_{12}^{3/2} \sigma_{12}^{2} e^{\beta_{12} v^{2}} I_{2} \tag{E8} \]

where

\[ I_{2} = \int_{0}^{\pi} \int_{W} w^{2} - w^{2} e^{-\beta_{12} (w^{2} - 2vw \cos\theta)} \sin\theta \, dw \, d\theta \tag{E9} \]

Now

\[ I_{2} = \int_{W}^{\infty} \frac{w^{2} - w^{2}}{\beta_{12} v} e^{-\beta_{12} w^{2}} \sinh(2\beta_{12} v w) \, dw = \frac{1}{\beta_{12} \pi} \int_{z}^{\infty} \left( z^{2} - z^{2} \right) e^{-z^{2}} \sinh(2\pi z) \, dz \tag{E10} \]

where, by definition, \( r = \beta_{12}^{1/2} v, \ z = \beta_{12}^{1/2} w, \) and \( \xi = \beta_{12}^{1/2} w. \) Singling out the factor \( \exp(-\xi^{2}) \) for successive integrations by parts yields

\[ \int \xi^{2} e^{-\xi^{2}} \sinh(2\pi \xi) \, d\xi = \frac{1}{2} e^{-\xi^{2}} \left[ \xi \sinh(2\pi \xi) + r \cosh(2\pi \xi) \right] \]

\[ + \left( r^{2} + \frac{1}{2} \right) \int e^{-\xi^{2}} \sinh(2\pi \xi) \, d\xi + \text{Constant} \tag{E11} \]
APPENDIX E

With this result, equation (E10) becomes

\[
I_2 = \frac{1}{\beta_{12}^2 r} \left\{ \frac{1}{2} e^{-z^2} \left[ z \sinh(2rz) + r \cosh(2rz) \right] + \left( r^2 + \frac{1}{2} - z^2 \right) \int_z^{\infty} e^{-\zeta^2} \sinh(2r\zeta) d\zeta \right\}
\]

(E12)

The changes of variables employed in equations (B7) can be used to reduce the integral in equation (E12); thus

\[
I_2 = \frac{1}{2\beta_{12}^2 r} \left\{ e^{-z^2} \left[ z \sinh(2rz) + r \cosh(2rz) \right] + e^{r^2} \left[ r^2 + \frac{1}{2} - z^2 \right] \int_{z-r}^{z+r} e^{-s^2} ds \right\}
\]

(E13)

Equations (E8) and (E13) finally yield the following expression for the number of bimolecular collisions, involving one molecule of each gas and leading to chemical reaction,

\[
N_{12}' = P_{12} n_1 n_2 \sigma_{12}^2 \left( \frac{\pi}{\beta_{12}} \right)^{1/2} \left\{ \frac{1}{2} \left[ 1 + \frac{z}{r} + \left( 1 - \frac{z}{r} \right) e^{-4rz} \right] e^{-(z-r)^2} \right. \\
\left. + \left[ 1 - 2 \left( z^2 - r^2 \right) \right] \frac{1}{2} \int_{z-r}^{z+r} e^{-s^2} ds \right\}
\]

(E14)

which can be evaluated, for various combinations of \( z \) and \( r \), with the aid of error-function tables and an asymptotic expansion of the complementary error function.

For \( r = 0 \), equation (E14) reduces to

\[
N_{12}' = P_{12} \cdot 2n_1 n_2 \sigma_{12}^2 \left( \frac{\pi}{\beta_{12}} \right)^{1/2} e^{-z^2}
\]

(E15)

which is the product of the steric factor, the collision frequency (see eq. (A21)), and the factor \( e^{-z^2} \). The last factor can, by equation (D10) with \( r = 0 \) and equation (E2), be written

\[
e^{-z^2} = e^{-\beta_{12} W^2} = e^{-E_a / E_0}
\]

(E16)
APPENDIX E

This equation reduces, for \( T_1 = T_2 = T \), by equation (D12), to

\[
e^{-z^2} = e^{-\frac{E_a}{kT}}
\]

which is the well-known Arrhenius factor of reaction-kinetics theory. On the other hand, if \( r \neq 0 \) and \( z = 0 \), equation (E14) reduces to \( N_{12}' = P_{12}N_{12} \) (cf. eq. (A21)).

The observations of the preceding paragraph suggest the following approximate form for the more general but unwieldy equation (E14):

\[
N_{12}' = P_{12}N_{12}e^{-\frac{E_a}{kT_{12}}}
\]

(E18)

where \( N_{12} \) is the collision frequency given by equation (A21) and \( T_{12} \) is the binary temperature given by equation (D13). In terms of the dimensionless parameters \( r \) and \( z \), the approximation (E18) appears as

\[
N_{12}' = P_{12}^2n_1n_2\sigma_{12}^2\left(\frac{\pi}{\beta_{12}}\right)^{1/2}\left(1 + \frac{2}{3}ar^2\right)^{1/2}e^{-z^2}\left(1 + \frac{2}{3}\omega r^2\right)
\]

(E19)

The ratio of this approximate value of \( N_{12}' \) to its exact value (eq. (E14)) is given in table I for several combinations of \( r \) and \( z \).

Since the approximation (E19) approaches zero too slowly as \( z \) approaches \( \infty \), the right-hand sides of equations (E14) and (E19) have been equated and solved for \( \omega \). This value of \( \omega \), denoted by \( \omega' \), which makes equation (E19) exact, is plotted as a function of \( r \) for various values of \( z \) in figure 4.

A comparison of figures 3 and 4, in conjunction with the form of equation (E19), shows that, for \( z \leq 1 \), equation (E19) with \( \omega = 1 \) provides a better approximation for \( N_{12}' \) than does equation (E19) with \( \omega \) given by equation (11) (plotted in fig. 3).
REFERENCES


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