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THEORETICAL INVESTIGATION OF UNSTEADY DIFFUSION WITH RECOMBINATION IN A TERNARY MIXTURE OF DIATOMIC MOLECULES, DISSOCIATED ATOMS, AND AN INERT GAS

By Walter A. Reinhardt

Ames Research Center
Moffett Field, Calif.

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THEORETICAL INVESTIGATION OF UNSTEADY DIFFUSION WITH RECOMBINATION IN A TERNARY MIXTURE OF DIATOMIC MOLECULES, DISSOCIATED ATOMS, AND AN INERT GAS

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SUMMARY

An experiment is suggested wherein measurements can be made on parameters leading to the determination of the homogeneous reaction and diffusion rates of oxygen atoms. This is done by studying the decay in the periodic time variation in concentration of atoms. The system to be investigated includes a ternary gas mixture of diatomic molecules, dissociated atoms, and an inert gas. A theoretical investigation is made, starting with equations obtained from rigorous kinetic theory and chemical kinetics, of the unsteady diffusion and recombination processes applicable to the experiment. Boundary conditions are investigated. A qualitative result is given which illustrates the dependence of the decay in the concentration variation on sink strength and frequency.

INTRODUCTION

The present theoretical investigation considers methods for analyzing data from a proposed experiment on the homogeneous recombination of oxygen atoms to determine the diffusion and recombination rates of the atoms at room temperature. In the proposed experiment a periodic concentration of atoms is imposed by dissociation at one end of a test cell. The atoms diffuse into the test cell and recombine, thus providing a continual time-varying supply of freshly recombined molecules. The variation with time is a device for distinguishing between recombined molecules and those not immediately involved in the recombination process. However, to interpret the data from such an experiment, a solution of the unsteady multicomponent diffusion equations is required. The appropriate equations are derived herein and a simplified qualitative solution is given. Although continual reference will be made to the experiment motivating this analysis, the equations derived in this report, except the time-dependent boundary conditions, are general and apply to any ternary diffusion phenomena as well as being unrestricted by the geometry of any experiment.

The problem to be considered is that of unsteady multicomponent diffusion in the presence of chemical reaction inside a tube of circular cross section with the time-dependent condition of the gases specified at the entrance of the tube. The governing diffusion equations for this problem are derived herein starting from a set of fundamental relations given by rigorous kinetic theory. Assumptions appropriate for the experimental conditions are used to simplify these relations. To the lowest order the resulting equation for atom concentration is linear except for a sink term, which represents the atom recombination process. Because of the nonlinearity introduced by the sink term, a numerical procedure utilizing electronic machine computing appears best adapted to the solution of this equation. One can linearize the sink term by use of a rough approximation and, from this linearized form of the equation, obtain a qualitative understanding of the more difficult problem. To illustrate the effects of recombination and diffusion in an unsteady one-dimensional problem, an expression for one component of the ternary mixture (i.e., the atom concentration) is derived and discussed. This expression shows the dependence of the decay of the labile species variation on a linearized sink term and on the frequency of the periodic variation.

PRINCIPAL SYMBOLS

a	dimensionless binary diffusion constant ratio, $\dfrac{D_{23}\ {}_on}{{}_on_2D_{13} + {}_on_3D_{12}}$
c	dimensionless constant, $1 - \dfrac{D_{13}}{D_{12}}$
d	dimensionless constant, $1 - \dfrac{D_{13}}{D_{23}}$
$\vec{d}_j$	species gradient relation arising from rigorous kinetic theory (ref. 5, p. 469)
$f_1(t)$	dissociation time function
$f_i{}^o$	Maxwellian distribution function for species i
g	constant appearing in the defining relation for ν
k_i	dimensionless source strength, $\dfrac{L_2}{{}_onD} K_i$
k_w	wall reaction rate
n	number density, $\sum_{i=1}^{3} n_i$
p	pressure, nkT

$\vec{r}$	coordinate vector
$\vec{v}$	stream velocity
$\bar{v}_i$	mean molecular speed for species i, $2\sqrt{\frac{2kT}{\pi m_i}}$
D	characteristic diffusion constant, $\frac{aD_{12}D_{13}}{D_{23}}$
$\mathbf{D}_{ij}$	multicomponent diffusion coefficient
D_{ij}	binary diffusion coefficient
K_i	source or sink term
L	characteristic length appearing in dimensionless coordinate
N	number of species comprising the multicomponent diffusion system
J_{in}^{+}	a single direction component of "effusive" flux vector for species i
$\vec{V}_i$	peculiar velocity, $\vec{v} - \vec{v}_i$
$\vec{W}_i$	reduced velocity, $\sqrt{\frac{m_i}{2kT}}\,\vec{V}_i$
W	dimensionless angular frequency, $\frac{L^2}{D}\,\omega$
γ	wall reaction fraction
δ_1	Laplacian coefficient appearing in partial differential equation for ν
δ_2	sink strength coefficient appearing in partial differential equation for ν
λ	dimensionless perturbation parameter (see eq. (10))
μ	dimensionless number density, $\frac{n}{{}_on}$
ν	equivalent dimensionless concentration variable, ${}_1^o\mu_2 + g\,{}_1^o\mu_3$
ν_H	homogeneous part of equivalent dimensionless concentration variable which appears in solution for ν
ν_P	particular part of equivalent dimensionless concentration variable which appears in solution for ν

$\vec{\xi}$ dimensionless coordinate variable, $\frac{\vec{r}}{L}$

ρ mass density, $\sum_{j=1}^{3} n_j m_j$

τ dimensionless time variable, $\frac{D}{L^2} t$

ω angular frequency

$\vec{\Lambda}$ dimensionless velocity, $\frac{L}{D} \vec{v}$

Ω square of ratio of diffusion velocity to isothermal sound velocity, $\frac{{}_0\rho D^2}{{}_0nL^2kT}$

$\frac{\partial}{\partial \vec{r}}$ spatial gradient $\left(\text{in Cartesian coordinates } \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}\right)$

Subscripts

i species kind

1 atoms

2 molecules

3 inert species

Subscript appearing before a symbol indicates order in terms of an expansion with respect to λ. Superscript appearing before a symbol indicates order in terms of an expansion with respect to Ω.

ANALYSIS

Before proceeding with the detailed analysis, it may be helpful to consider the physical concept of the problem. Figure 1 shows schematically the pertinent features of the proposed experimental apparatus. (A more detailed description of a similar apparatus may be obtained from ref. 1.) The essential features of the experimental technique are as follows: A mixture of oxygen molecules and some inert gas is allowed to leak into a streamtube; flow through the tube is maintained by a vacuum pumping system. The molecules in the gas stream are then partially dissociated by means of a modulated radio-frequency signal. This process supplies a periodically varying concentration of atoms at the base of a

cylindrical diffusion tube wherein the atoms diffuse and recombine. The variation in concentration of either atoms or molecules, depending on the detector used, is observed. The following analysis will show that it is then possible to determine the "sink strength" associated with the recombination process. The advantage of studying (for example, by means of a detector utilizing oxygen molecule ultraviolet absorption which is described in ref. 2) the variation in concentration is that it is possible to distinguish between the species directly involved in the recombination process and those not immediately involved.

Partial Differential Equations Governing Diffusion

The analysis that follows starts with a set of fundamental equations describing diffusion processes in general. Consideration is then given to a physically consistent linearization of the derivative terms contained in these equations. The nonderivative or sink term is then analyzed in detail and an approximate linearization of this term presented. Finally, boundary conditions appropriate to a particular problem are introduced and discussed.

Development of the derivative terms.- The following equations for diffusion processes, resulting from rigorous kinetic theory, are discussed by Hirschfelder, Curtiss, and Bird in reference 3. With the neglect of body forces, viscous effects, and thermal gradients, the fundamental equations are:

(1) Equation of continuity of individual species

$$\frac{\partial n_i}{\partial t} + \frac{\partial}{\partial \vec{r}} \cdot \left(n_i \vec{v} + n_i \bar{\bar{V}}_i\right) = K_i \tag{1}$$

where

$$\bar{\bar{V}}_i = \frac{n^2}{n_i \rho} \sum_j m_j \mathbf{D}_{ij} \left[\frac{\partial}{\partial \vec{r}}\left(\frac{n_j}{n}\right) + \left(\frac{n_j}{n} - \frac{n_j m_j}{\rho}\right) \frac{\partial \ln p}{\partial \vec{r}}\right] \tag{2}$$

and where K_i is the total increase of particles of species i per unit volume per unit time due to chemical reaction.

(2) Equation of motion or the momentum equation

$$\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \frac{\partial \vec{v}}{\partial \vec{r}} = -\frac{1}{\rho} \frac{\partial p}{\partial \vec{r}} \tag{3}$$

(3) The equation of state

$$p = nkT \tag{4}$$

(4) The defining relations for number and mass densities

$$n = \sum_{i=1}^{N} n_i \tag{5}$$

$$\rho = \sum_{i=1}^{N} n_i m_i \tag{6}$$

(5) The expressions giving the multicomponent diffusion constants in terms of the binary diffusion constants for a ternary mixture with molecules i, j, and k

$$\mathbf{D}_{ii} = 0 \tag{7a}$$

$$\mathbf{D}_{ij} = D_{ij}\left[1 + \frac{n_k\left(\frac{m_k}{m_j} D_{ik} - D_{ij}\right)}{n_i D_{jk} + n_j D_{ik} + n_k D_{ij}}\right] \tag{7b}$$

$$D_{ij} = D_{ji} \tag{7c}$$

(Eq. (7b) follows from ref. 3, eq. (11.2-4), p. 716.)

(6) Conservation of mass in chemical reaction

$$\sum m_i K_i = 0 \tag{8}$$

Equations (1) through (8) form a system of coupled nonlinear partial-differential equations. When supplemented with the chemical equations governing possible chemical reactions, these relations are sufficient to define the three-component diffusion problem under consideration.

The diffusion process is investigated under conditions where the concentrations of the various species are forced to vary in a prescribed periodic manner at one of the boundaries. The reaction of the species of primary interest is assumed to be governed by the chemical equation

$$[A_2] \rightarrow [A_1] + [A_1] \tag{9}$$

where the subscript 2 labels the undissociated species in the three-component system and the subscript 1, the dissociated species. This subscript notation will be kept consistent throughout the report (in addition a subscript 3 will be introduced which will be associated with a chemically inert species). Equation (9)

indicates that a unit concentration of species 2 dissociates into two unit concentrations of species 1. Depending on the gases used, more than one chemical equation may be necessary to describe the chemical reactions possible with such species as 1 and 2. The analysis will include the more significant of those reactions possible with diatomic molecules, their dissociated atoms, and an inert buffer gas.

Expressions for the quantities K_i appearing in equations (1) and (8) are also needed. These are determined by the form of equation (9) and a consideration of chemical kinetics. We shall return to this point later.

One can not make immediate assumptions as to the constancy of pressure, stream velocity, or mass density without quickly running into inconsistencies. For this reason only those minimal assumptions necessary are made within the framework of a plausable model. It will be assumed that the molecules can be dissociated in a periodic manner without external pressure disturbances and that the degree of dissociation will be small. Thus the symbol λ is assigned to designate the ratio

$$\lambda = \frac{n_1(o)_{max}}{n(o)} \tag{10}$$

where $n_1(o)_{max}$ is the maximum concentration of species 1 and $n(o)$ is the total concentration (see eq. (5)), both evaluated on one boundary of the system (e.g., the input end of a cylindrical diffusion tube). It is assumed that $\lambda \ll 1$. All of the dependent variables are then expanded in terms of λ as follows:

$$n_i = ({}_0n_i) + ({}_1n_i)\lambda + \ldots \qquad i = 1,2,3 \tag{11a}$$

$$\vec{v} = ({}_0\vec{v}) + ({}_1\vec{v})\lambda + \ldots \tag{11b}$$

$$\rho = ({}_0\rho) + ({}_1\rho)\lambda + \ldots \tag{11c}$$

$$n = ({}_0n) + ({}_1n)\lambda + \ldots \tag{11d}$$

$$p = ({}_0p) + ({}_1p)\lambda + \ldots \tag{11e}$$

$$K_i = ({}_0K_i) + ({}_1K_i)\lambda + \ldots \qquad i = 1,2 \tag{11f}$$

$$\mathbf{D}_{ij} = ({}_0\mathbf{D}_{ij}) + ({}_1\mathbf{D}_{ij})\lambda + \ldots \qquad i,j = 1,2,3 \qquad i \neq j \tag{11g}$$

Notice that the subscript denoting the power of λ is written on the left of each expansion coefficient to avoid confusion with the subscripts on the right, which refer to the species involved.

At $\lambda = 0$, the gas would be in a uniform state. Therefore, all the zero order terms are constant; that is, gradients exist only for the higher order terms. When $\lambda = 0$ (no dissociation), species 1 will not be present. It follows that

$${}_0n_1 = 0 \tag{12}$$

In the experiment it would be convenient to include a stream velocity with the gas moving axially down a cylindrical tube. It is expected that viscous effects would lead to a parabolic velocity profile at the low Reynolds numbers involved. However, this complication will be ignored for the present and the equations for a constant value of ${}_0\vec{v}$ derived. For values of ${}_0\vec{v}$ different from zero, the results strictly apply only for a flow far from any solid boundaries.

The expanded variables (eqs. (11a) through (11g)) are now substituted into the original basic equations (eqs. (1) through (8)) and coefficients of like powers of λ are equated. Since the zero-order terms of the variables are constant, the zero-order terms occurring in equations (1), (2), and (3) vanish. When the relevant substitutions are made, the basic equations become:

(1) Equations of continuity of individual species

$$\frac{\partial({}_1n_1)}{\partial t} + \frac{\partial}{\partial \vec{r}} \cdot \left\{ ({}_1n_1)\ {}_0\vec{v} + \frac{{}_0n^2}{{}_0\rho} \sum_{j=1}^{3} m_j\ {}_0\mathbf{D}_{1j} \left[\frac{\partial}{\partial \vec{r}} \left(\frac{{}_1n_j}{{}_0n} \right) - \left(\frac{{}_0n_j}{{}_0\rho} \right) m_j \frac{\partial}{\partial \vec{r}} \left(\frac{{}_1n}{{}_0n} \right) \right] \right\} = {}_1K_1 \tag{13}$$

$$\frac{\partial({}_1n_2)}{\partial t} + \frac{\partial}{\partial \vec{r}} \cdot \left[({}_0n_2)\ {}_1\vec{v} + ({}_1n_2)\ {}_0\vec{v} + ({}_0n_2)\ {}_1\vec{\bar{V}}_2 \right] = {}_1K_2 \tag{14}$$

$$\frac{\partial({}_1n_3)}{\partial t} + \frac{\partial}{\partial \vec{r}} \cdot \left[({}_0n_3)\ {}_1\vec{v} + ({}_1n_3)\ {}_0\vec{v} + ({}_0n_3)\ {}_1\vec{\bar{V}}_3 \right] = 0 \tag{15}$$

where

$${}_1\vec{\bar{V}}_{i=2,3} = \frac{{}_0n^2}{({}_0\rho)\ {}_0n_i} \sum_{j=1}^{3} m_j\ {}_0\mathbf{D}_{ij} \left[\frac{\partial}{\partial \vec{r}} \left(\frac{{}_1n_j}{{}_0n} \right) - \left(\frac{{}_0n_j}{{}_0\rho} \right) m_j \frac{\partial}{\partial \vec{r}} \left(\frac{{}_1n}{{}_0n} \right) \right] \tag{16}$$

(2) Momentum equation

$$\frac{\partial({}_1\vec{v})}{\partial t} + ({}_0\vec{v}) \cdot \frac{\partial({}_1\vec{v})}{\partial \vec{r}} = - \frac{kT}{{}_0\rho} \frac{\partial({}_1n)}{\partial \vec{r}} \tag{17}$$

(3) Equation of state

$${}_0p = {}_0nkT \tag{18a}$$

$${}_1p = {}_1nkT \tag{18b}$$

etc.

(4) Defining relations for number and mass densities

$$ {}_0n = {}_0n_2 + {}_0n_3 \tag{19a} $$

$$ {}_1n = \sum_j {}_1n_j \tag{19b} $$

etc.

$$ {}_0\rho = {}_0n_2 m_2 + {}_0n_3 m_3 \tag{20a} $$

$$ {}_1\rho = \sum_j {}_1n_j m_j \tag{20b} $$

etc.

(5) Multicomponent diffusion constants

$$ {}_0\mathbf{D}_{12} = D_{12}\left[1 + \frac{{}_0n_3\left(\frac{m_3}{m_2} D_{13} - D_{12}\right)}{{}_0n_2 D_{13} + {}_0n_3 D_{12}}\right] = \frac{a}{m_2}\,\frac{D_{12}D_{13}}{D_{23}}\,\frac{{}_0\rho}{{}_0n} \tag{21a} $$

$$ {}_0\mathbf{D}_{13} = D_{13}\left[1 + \frac{{}_0n_2\left(\frac{m_2}{m_3} D_{12} - D_{13}\right)}{{}_0n_2 D_{13} + {}_0n_3 D_{12}}\right] = \frac{a}{m_3}\,\frac{D_{12}D_{13}}{D_{23}}\,\frac{{}_0\rho}{{}_0n} \tag{21b} $$

$$ {}_0\mathbf{D}_{21} = D_{21}\left[1 + \frac{{}_0n_3\left(\frac{m_3}{m_1} D_{23} - D_{12}\right)}{{}_0n_2 D_{13} + {}_0n_3 D_{12}}\right] = \frac{a}{{}_0n}\,\frac{D_{21}}{D_{23}}\left({}_0n_2 D_{13} + {}_0n_3\,\frac{m_3}{m_1} D_{23}\right) \tag{21c} $$

$$ {}_0\mathbf{D}_{31} = D_{31}\left[1 + \frac{{}_0n_2\left(\frac{m_2}{m_1} D_{32} - D_{13}\right)}{{}_0n_2 D_{13} + {}_0n_3 D_{12}}\right] = \frac{a}{{}_0n}\,\frac{D_{31}}{D_{23}}\left({}_0n_3 D_{12} + {}_0n_2\,\frac{m_2}{m_1} D_{32}\right) \tag{21d} $$

$$ {}_{o}\mathbf{D}_{23} = D_{23} \tag{21e} $$

$$ {}_{o}\mathbf{D}_{32} = D_{32} \tag{21f} $$

$$ D_{ij} = D_{ji} \qquad i,j = 1,2,3 \qquad i \neq j \tag{21g} $$

where the dimensionless constant a is defined as

$$ a = \frac{D_{23}\ {}_{o}n}{{}_{o}n_2 D_{13} + {}_{o}n_3 D_{12}} \tag{22} $$

(6) Conservation of mass in chemical reaction

$$ {}_{o}K_1 = {}_{o}K_2 = 0 \tag{23a} $$

$$ m_1({}_{1}K_1) + m_2({}_{1}K_2) = 0 \tag{23b} $$

etc.

It is convenient at this point to make equations (13) through (17) dimensionless. For this purpose a characteristic length (L) and a characteristic diffusion constant (D) are introduced. In terms of these two constants and the zero-order expressions for number density and mass density, all the variables can be made dimensionless. The transformation equations for the dimensionless variables in terms of the independent variables are:

$$ \vec{\xi} = \frac{\vec{r}}{L} \tag{24a} $$

$$ \tau = \left(\frac{D}{L^2}\right) t \tag{24b} $$

$$ \omega = \left(\frac{D}{L^2}\right) W \tag{24c} $$

where W is a dimensionless frequency, which is needed later. The dependent variables become

$$ \mu = n/{}_{o}n \tag{25a} $$

$$ \mu_i = n_i/{}_{o}n \qquad i = 1,2,3 \tag{25b} $$

$$ R = \rho/{}_{o}\rho \tag{25c} $$

$$ \vec{\Lambda} = (L/D)\vec{v} \tag{25d} $$

$$ k_i = (L^2/{}_{o}nD)K_i \tag{25e} $$

The subscripts that will be used before and after the symbols representing the dimensionless equivalents of the physical variables will carry precisely the same significance as they did for the physical variables.

A parameter Ω will now be defined that represents the ratio of the squares of the diffusion velocity to isothermal sound velocity; that is,

$$\Omega = \frac{{}_o\rho}{{}_on} \frac{D^2}{L^2kT} \sim \left(\frac{v_d}{v_s}\right)^2 \tag{26}$$

The significance of this parameter is that if Ω is small, then a pressure pulse (or acoustic wave) travels at a rate large compared to any speed associated with the diffusion process. The limit $\Omega = 0$ implies that the speed of sound is infinite relative to any speed associated with diffusion. It is interesting to note that in the opposite limit of free molecule flow, Ω is of order 1. In this limit, the fundamental equations do not apply. In that case the velocity associated with diffusion is of the same order of magnitude as the speed of sound. Generally speaking, under those conditions where the fundamental equations (eqs. (1) through (8)) apply, Ω is small compared to 1.

Transforming the equations of continuity of individual species into dimensionless form, equations (13) through (15) become,

$$\frac{\partial}{\partial\tau}({}_1\mu_1) + {}_o\vec{\Lambda} \cdot \frac{\partial}{\partial\vec{\xi}}({}_1\mu_1) + \frac{{}_on}{{}_o\rho} m_2 \frac{{}_o\mathbf{D}_{12}}{D}\left[\frac{\partial}{\partial\vec{\xi}} \cdot \frac{\partial}{\partial\vec{\xi}}({}_1\mu_2) - \frac{{}_on}{{}_o\rho} m_2({}_o\mu_2) \frac{\partial}{\partial\vec{\xi}} \cdot \frac{\partial}{\partial\vec{\xi}}({}_1\mu)\right]$$

$$+ \left(\frac{{}_on}{{}_o\rho}\right) m_3 \frac{{}_o\mathbf{D}_{13}}{D}\left[\frac{\partial}{\partial\vec{\xi}} \cdot \frac{\partial}{\partial\vec{\xi}}({}_1\mu_3) - \frac{{}_on}{{}_o\rho} m_3({}_o\mu_2) \frac{\partial}{\partial\vec{\xi}} \cdot \frac{\partial}{\partial\vec{\xi}}({}_1\mu)\right] = {}_1k_1 \tag{27}$$

$$\frac{\partial}{\partial\tau}({}_1\mu_2) + {}_o\vec{\Lambda} \cdot \frac{\partial}{\partial\vec{\xi}}({}_1\mu_2) + ({}_o\mu_2) \frac{\partial}{\partial\vec{\xi}} \cdot ({}_1\vec{\Lambda}) + \frac{{}_on}{{}_o\rho} m_1 \frac{{}_o\mathbf{D}_{21}}{D} \frac{\partial}{\partial\vec{\xi}} \cdot \frac{\partial}{\partial\vec{\xi}}({}_1\mu_1)$$

$$+ \left(\frac{{}_on}{{}_o\rho}\right) m_3 \frac{{}_o\mathbf{D}_{23}}{D}\left[\frac{\partial}{\partial\vec{\xi}} \cdot \frac{\partial}{\partial\vec{\xi}}({}_1\mu_3) - \frac{{}_on}{{}_o\rho} m_3({}_o\mu_3) \frac{\partial}{\partial\vec{\xi}} \cdot \frac{\partial}{\partial\vec{\xi}}({}_1\mu)\right] = {}_1k_2 \tag{28}$$

$$\frac{\partial}{\partial\tau}\left({}_1\mu_3\right) + {}_0\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}_1\mu_3\right) + \left({}_0\mu_3\right)\frac{\partial}{\partial\vec{\xi}}\cdot\left({}_1\vec{\Lambda}\right) + \frac{{}_0n}{{}_0\rho}\,m_1\,\frac{{}_0\mathbf{D}_{31}}{D}\,\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}_1\mu\right)$$

$$+ \frac{{}_0n}{{}_0\rho}\,m_2\,\frac{{}_0\mathbf{D}_{32}}{D}\left[\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}_1\mu_2\right) - \frac{{}_0n}{{}_0\rho}\,m_2\left({}_0\mu_2\right)\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}_1\mu\right)\right] = 0 \tag{29}$$

In dimensionless form, the momentum equation (17) becomes

$$\Omega\left[\frac{\partial}{\partial\tau}\left({}_1\vec{\Lambda}\right) + \left({}_0\vec{\Lambda}\right)\cdot\frac{\partial}{\partial\vec{\xi}}\left({}_1\vec{\Lambda}\right)\right] + \frac{\partial}{\partial\vec{\xi}}\left({}_1\mu\right) = 0 \tag{30}$$

Since Ω is small, equation (30) can be greatly simplified by an expansion in terms of Ω as follows:

$$\begin{aligned} {}_1\mu &= \left({}^0_1\mu\right) + \left({}^1_1\mu\right)\Omega + \ldots \\ &\text{etc.} \end{aligned} \tag{31}$$

The upper left superscript is used here to denote the power of Ω involved. When these expressions are substituted into equation (30), and coefficients of each power of Ω are equated to zero, the following relations are obtained:

$$\frac{\partial}{\partial\vec{\xi}}\left({}^0_1\mu\right) = 0 \tag{32a}$$

$$\frac{\partial}{\partial\tau}\left({}^0_1\vec{\Lambda}\right) + \left({}_0\vec{\Lambda}\right)\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^0_1\vec{\Lambda}\right) + \frac{\partial}{\partial\vec{\xi}}\left({}^1_1\mu\right) = 0 \tag{32b}$$

Thus to lowest order in Ω, $\left({}^0_1\mu\right)$ is independent of coordinate. If the first-order expression for the equation of state (eq. (18b)) is transformed into dimensionless form, equation (32a) is equivalent to stating that the pressure is constant to lowest order in Ω. The lowest order approximation indicates that if a pressure pulse is induced in the system, this pulse will carry instantaneously throughout the system. If such pulses are not induced, pressure is independent of both space and time. From equations (19b) and (25b), the following identity results:

$${}^0_1\mu_1(\vec{\xi},\tau) + {}^0_1\mu_2(\vec{\xi},\tau) + {}^0_1\mu_3(\vec{\xi},\tau) = {}^0_1\mu \equiv \text{constant} \tag{33}$$

Since the zero-order pressure term in Ω is constant and since the expansions are about a uniform state, the constant is set equal to zero.

$$\left\{\left[\frac{\partial}{\partial\tau}\left({}^{o}_{1}\mu_2\right) + {}_{o}\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_2\right)\right] - \frac{aD_{12}}{D}\left[\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_2\right)\right]\right\}$$

$$- \frac{{}_{o}\mu_2}{{}_{o}\mu_3}\left\{\left[\frac{\partial}{\partial\tau}\left({}^{o}_{1}\mu_3\right) + {}_{o}\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_3\right)\right] - \frac{aD_{13}}{D}\left[\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_3\right)\right]\right\} = {}^{o}_{1}k_2 \tag{38}$$

The separated portions of equation (38) are similar to each other and, in addition, each is equivalent in form to the left side of equation (35). This suggests that a differential equation in a new variable ν can be found that will be equivalent in form to equation (35). The new variable ν will be a linear combination of the variables $({}^{o}_{1}\mu_2)$ and $({}^{o}_{1}\mu_3)$. Substitution of equation (33) into equation (35) yields

$$\left\{\left[\frac{\partial}{\partial\tau}\left({}^{o}_{1}\mu_2\right) + {}_{o}\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_2\right)\right] - \frac{aD_{12}D_{13}}{DD_{23}}\left[\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_2\right)\right]\right\}$$

$$+ \left\{\left[\frac{\partial}{\partial\tau}\left({}^{o}_{1}\mu_3\right) + {}_{o}\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_3\right)\right] - \frac{aD_{12}D_{13}}{DD_{23}}\left[\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_3\right)\right]\right\} = -{}^{o}_{1}k_1 \tag{39}$$

To facilitate the following manipulations let the coefficients of the second, third, and fourth bracketed expressions in equation (39) be P_1, Q_1, and S_1, respectively, and the coefficients of the identical bracketed terms in equations (38) be P_2, Q_2, and S_2; that is, let

$$P_1 = S_1 = \frac{aD_{12}D_{13}}{D_{23}D} \tag{40a}$$

$$Q_1 = 1 \tag{40b}$$

$$P_2 = \frac{aD_{12}}{D} \tag{40c}$$

$$Q_2 = -\frac{{}_{o}\mu_2}{{}_{o}\mu_3} \tag{40d}$$

$$S_2 = \frac{{}_{o}\mu_2}{{}_{o}\mu_3}\,\frac{aD_{13}}{D} \tag{40e}$$

The continuity equation for species 1 (eq. (27)), when the terms of order Ω or greater are neglected, becomes

$$\frac{\partial}{\partial\tau}\left({}^{0}_{1}\mu_1\right) + {}_{0}\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_1\right) + \frac{{}_{0}n}{{}_{0}\rho}\left[m_2\,\frac{{}_{0}\mathbf{D}_{12}}{D}\,\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_2\right) + m_3\,\frac{{}_{0}\mathbf{D}_{13}}{D}\,\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_3\right)\right] = {}^{0}_{1}k_1 \tag{34}$$

Substituting the multicomponent diffusion constants (eqs. (21a) and (21b)) and simplifying, we obtain

$$\frac{\partial}{\partial\tau}\left({}^{0}_{1}\mu_1\right) + {}_{0}\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_1\right) - \frac{aD_{12}D_{13}}{DD_{23}}\,\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_1\right) = {}^{0}_{1}k_1 \tag{35}$$

It is interesting to observe that equation (35) is independent of the first-order concentrations of other species as a consequence of the assumption that λ and Ω are small. Then this equation can be solved for ${}^{0}_{1}\mu_1$. The continuity equations for species 2 and 3, equations (28) and (29), respectively, become

$$\frac{\partial}{\partial\tau}\left({}^{0}_{1}\mu_2\right) + {}_{0}\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_2\right) + \left({}_{0}\mu_2\right)\frac{\partial}{\partial\vec{\xi}}\cdot\left({}^{0}_{1}\vec{\Lambda}\right)$$

$$+ \frac{{}_{0}n}{{}_{0}\rho}\,m_1\,\frac{{}_{0}\mathbf{D}_{21}}{D}\,\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_1\right) + \frac{{}_{0}n}{{}_{0}\rho}\,m_3\,\frac{{}_{0}\mathbf{D}_{23}}{D}\,\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_3\right) = {}^{0}_{1}k_2 \tag{36}$$

$$\frac{\partial}{\partial\tau}\left({}^{0}_{1}\mu_3\right) + {}_{0}\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_3\right) + \left({}_{0}\mu_3\right)\frac{\partial}{\partial\vec{\xi}}\cdot\left({}^{0}_{1}\vec{\Lambda}\right)$$

$$+ \frac{{}_{0}n}{{}_{0}\rho}\,m_1\,\frac{{}_{0}\mathbf{D}_{31}}{D}\,\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_1\right) + \frac{{}_{0}n}{{}_{0}\rho}\,m_2\,\frac{{}_{0}\mathbf{D}_{32}}{D}\,\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{0}_{1}\mu_2\right) = 0 \tag{37}$$

There are four equations (eqs. (33), (35), (36), and (37)) for the dimensionless dependent variables representing concentration, ${}_{1}\mu_1$, ${}_{1}\mu_2$, ${}_{1}\mu_3$, and stream velocity ${}^{0}_{1}\vec{\Lambda}$. It is convenient to combine equations (36) and (37) to eliminate ${}^{0}_{1}\vec{\Lambda}$ and thereby reduce the number of equations and number of dependent variables to three. To this end equation (37) is multiplied by the ratio ${}_{0}\mu_2/{}_{0}\mu_3$ and the resulting expression subtracted from equation (36). Using equations (21c) through (21g), we express the multicomponent diffusion coefficients in terms of the binary diffusion coefficients, and substituting equation (33) for $\left({}^{0}_{1}\mu_3\right)$ we obtain an equation in $\left({}^{0}_{1}\mu_2\right)$ and $\left({}^{0}_{1}\mu_3\right)$ alone. The resulting equation can be expressed as a sum of two terms, one dependent on $\left({}^{0}_{1}\mu_2\right)$ and the other on $\left({}^{0}_{1}\mu_3\right)$, to obtain

An equivalent form for the differential equation in ν can be achieved by multiplying equation (38) by an arbitrary constant F and then adding the resulting expression to equation (39) to obtain

$$\left[\frac{\partial}{\partial\tau}\left({}^{o}_{1}\mu_2\right) + {}_{o}\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_2\right)\right] + \left(\frac{P_2 + FP_1}{F + 1}\right)\left[\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_2\right)\right]$$

$$+\left(\frac{Q_2 + FQ_1}{F + 1}\right)\left[\frac{\partial}{\partial\tau}\left({}^{o}_{1}\mu_3\right) + {}_{o}\vec{\Lambda}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_3\right)\right] + \left(\frac{S_2 + FS_1}{F + 1}\right)\left[\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_3\right)\right] = \frac{F\left({}^{o}_{1}k_2\right) - \left({}^{o}_{1}k_1\right)}{F + 1} \tag{41}$$

It then follows that if F is required to satisfy the relation

$$\frac{Q_2 + FQ_1}{F + 1} = \frac{S_2 + FS_1}{P_2 + FP_1} \tag{41a}$$

the new variable will be defined by

$$\nu = \left({}^{o}_{1}\mu_2\right) + \left(\frac{Q_2 + FQ_1}{F + 1}\right)\left({}^{o}_{1}\mu_3\right) \tag{42}$$

and ν will satisfy the differential equation

$$\frac{\partial\nu}{\partial\tau} + {}_{o}\vec{\Lambda}\cdot\frac{\partial\nu}{\partial\vec{\xi}} - \left(\frac{P_2 + FP_1}{F + 1}\right)\frac{\partial}{\partial\vec{\xi}}\cdot\frac{\partial}{\partial\vec{\xi}}\,\nu = \frac{\left({}^{o}_{1}k_2\right) - F\left({}^{o}_{1}k_1\right)}{F + 1} \tag{43}$$

which on the left side is of the same form as the left side of equation (35); F is determined in terms of the coefficient expressions by solving equation (41a) and is given by

$$F = \frac{S_2 - P_2S_2}{P_2 + P_1(Q_2 - 1) - S_2} \tag{44}$$

The relevant coefficients in equations (42) and (43) and F can be evaluated using equations (40a) through (40e) to obtain

$$F = \frac{{}_{o}\mu_2 c}{d - {}_{o}\mu_2 c} \tag{45}$$

$$\frac{Q_2 + FQ_1}{F + 1} = \frac{{}_{o}\mu_2}{{}_{o}\mu_3}\left(\frac{c - d}{d}\right) \equiv g \tag{46}$$

$$\frac{P_2 + FP_1}{F + 1} = \frac{aD_{12}}{D} (1 - {}_o\mu_2 c) \equiv \delta_1 \tag{47}$$

Here new constants defined by

$$c = 1 - \frac{D_{13}}{D_{12}} \tag{48a}$$

$$d = 1 - \frac{D_{13}}{D_{23}} \tag{48b}$$

are introduced. Using the conservation of mass relation, equation (23b), ${}^{o}_{1}k_1$ can be expressed in terms of ${}^{o}_{1}k_2$. The problem then reduces to solving the two partial differential equations

$$\frac{\partial}{\partial\tau} ({}^{o}_{1}\mu_1) + {}_o\vec{\Lambda} \cdot \frac{\partial}{\partial\vec{\xi}} ({}^{o}_{1}\mu_1) - \frac{aD_{12}D_{13}}{DD_{23}} \frac{\partial}{\partial\vec{\xi}} \cdot \frac{\partial}{\partial\vec{\xi}} ({}^{o}_{1}\mu_1) = {}^{o}_{1}k_1 \tag{49a}$$

$$\frac{\partial}{\partial\tau} \nu + {}_o\vec{\Lambda} \cdot \frac{\partial}{\partial\vec{\xi}} \nu - \frac{aD_{12}}{D} (1 - {}_o\mu_2 c) \frac{\partial}{\partial\vec{\xi}} \cdot \frac{\partial}{\partial\vec{\xi}} \nu = -{}^{o}_{1}k_1 \left[\frac{m_1}{m_2} + \frac{{}_o\mu_2 c}{d} \left(1 - \frac{m_1}{m_2}\right)\right] \tag{49b}$$

where

$$\nu = ({}^{o}_{1}\mu_2) + g({}^{o}_{1}\mu_3) \tag{49c}$$

along with appropriate expressions for the source terms and the boundary conditions.

The solutions of equations (49) are achieved in a straightforward manner. If the "sink" or "source" term has the following functional dependence

$${}^{o}_{1}k_1 = {}^{o}_{1}k_1({}^{o}_{1}\mu_1) \tag{50}$$

which would be implied in any chemical equation, then the problem requires solving one partial differential equation (linear or nonlinear depending on the functional dependence included in equation (50)) for ${}^{o}_{1}\mu_1$. Let the solution be expressed as

$${}^{o}_{1}\mu_1 = {}^{o}_{1}\mu_1(\vec{\xi},\tau;\ c_1,c_2) \tag{51}$$

where c_1 and c_2 are parameters and are the constant coefficients of the Laplacian and sink term, that is,

$$c_1 = \frac{aD_{12}D_{13}}{DD_{23}} \tag{51a}$$

$$c_2 = 1 \tag{51b}$$

On substitution of this solution into equation (50) the final problem will then be equivalent to solving a linear inhomogeneous differential equation (eq. (49b)) with the appropriate boundary conditions. This solution will be a sum of two separate parts, that is,

$$\nu(\vec{\xi},\tau) = \nu_P(\vec{\xi},\tau) + \nu_H(\vec{\xi},\tau) \tag{52}$$

where the particular solution $\nu_P(\vec{\xi},\tau)$ and the homogeneous solution $\nu_H(\vec{\xi},\tau)$ are solutions of

$$\frac{\partial \nu_P}{\partial \tau} + {}_o\vec{\Lambda} \cdot \frac{\partial}{\partial \vec{\xi}} \nu_P - \frac{aD_{12}}{D}(1 - {}_o\mu_2 c) \frac{\partial}{\partial \vec{\xi}} \cdot \frac{\partial}{\partial \vec{\xi}} \nu_P = -{}_1^o k_1({}_1^o\mu_1)\left[\frac{m_1}{m_2} + {}_o\mu_2 \frac{c}{d}\left(1 - \frac{m_1}{m_2}\right)\right] \tag{53a}$$

and

$$\frac{\partial \nu_H}{\partial \tau} + {}_o\vec{\Lambda} \cdot \frac{\partial}{\partial \vec{\xi}} \nu_H - \frac{aD_{12}}{D}(1 - {}_o\mu_2 c) \frac{\partial}{\partial \vec{\xi}} \cdot \frac{\partial}{\partial \vec{\xi}} \nu_H = 0 \tag{53b}$$

respectively, with proper boundary conditions. It turns out that a particular solution is given by $\nu_P = -{}_1^o\mu_1(\vec{\xi},\tau;\ \delta_1,\delta_2)$ where δ_1 and δ_2 are different from c_1 and c_2. The equations to be solved are as follows:

$$\frac{\partial}{\partial \tau}({}_1^o\mu_1) + {}_o\vec{\Lambda} \cdot \frac{\partial}{\partial \vec{\xi}}({}_1^o\mu_1) - \frac{\partial}{\partial \vec{\xi}} \cdot \frac{\partial}{\partial \vec{\xi}}({}_1^o\mu_1) = {}_1^o k_1({}_1^o\mu_1) \tag{54a}$$

$$\frac{\partial}{\partial \tau}(\nu_P) + {}_o\vec{\Lambda} \cdot \frac{\partial}{\partial \vec{\xi}}(\nu_P) - \delta_1 \frac{\partial}{\partial \vec{\xi}} \cdot \frac{\partial}{\partial \vec{\xi}}(\nu_P) = {}_1^o k_1(\nu_P)\delta_2 \tag{54b}$$

$$\frac{\partial}{\partial \tau}(\nu_H) + {}_o\vec{\Lambda} \cdot \frac{\partial}{\partial \vec{\xi}}(\nu_H) - \delta_1 \frac{\partial}{\partial \vec{\xi}} \cdot \frac{\partial}{\partial \vec{\xi}}(\nu_H) = 0 \tag{54c}$$

where

$$D = \frac{aD_{12}D_{13}}{D_{23}} \tag{54d}$$

$$\delta_1 = \frac{aD_{12}}{D}\left(1 - {}_0\mu_2 c\right) = \frac{1 - {}_0\mu_2 c}{1 - d} \tag{54e}$$

$$\delta_2 = \frac{m_1}{m_2} + {}_0\mu_2 \frac{c}{d}\left(1 - \frac{m_1}{m_2}\right) \tag{54f}$$

The arbitrary characteristic diffusion constant D is chosen according to equation (54d) in order to simplify equation (54a).

Development of the sink term.- The preceding analysis has been directed toward reducing equations (1) through (8) into the more manageable equations (54) for solving the multicomponent diffusion problem, where the concentrations of the individual components are fluctuating in some prescribed periodic manner at one boundary. The effects of the chemical reactions have not yet been included in the problem beyond carrying a lumped term K_i which represents the rate of change in concentration of species i due to the chemical processes possible with the reactants species 1 and 2. The nature of this "sink" or "source" term and its expanded version ${}_i^0k_i$ will now be discussed.

The first chemical reaction to be considered is recombination, which is described by the chemical equation

$$[A_1] + [A_1] + [M] \rightarrow [A_2^*] + [M] + \text{excess energy as heat} \tag{55}$$

The symbol M is used to denote a third body, which may be any one of the gas particles in the system, and which is catalytic in its effect on the reaction. The asterisk denotes that the diatomic molecule may be in an excited state (electronic or vibrational) and the brackets denote "concentration of" as in equation (9). The excited molecule subsequently decays to its ground state either by radiating or through collision as illustrated by the following equations.

$$[A_2^*] \rightarrow [A_2] + \text{radiated energy} \tag{56a}$$

$$[A_2^*] + [M] \rightarrow [A_2] + [M] + \text{heat energy} \tag{56b}$$

Generally speaking, because of radiation or binary collisions, the lifetime of an excited molecule is small compared to any time associated with diffusion. Therefore it is reasonable to expect that after recombining, the excited molecule will decay to its ground state before diffusing any appreciable distance in the system. Equation (55) can then be replaced without appreciable error by an equivalent equation

$$[A_1] + [A_1] + [M] \rightarrow [A_2] + [M] + \text{heat of recombination} \tag{57}$$

The applicability of this simplification is opportune since it eliminates the necessity for solving a four component diffusion problem. There may be apparent exceptions to the foregoing assumption in that the lifetimes of vibrational excited states at room temperature can be quite long. However, it is probable that such excitation is removed in a few collisions with the wall. Then the assumption of a negligible population of excited molecules is valid. Although the population of excited states may be small enough to have negligible effect on the solution of the diffusion problem, the excited molecules may exist long enough to permit ultraviolet absorption studies.

Recombination is not the only chemical reaction possible with reactant species 1 and 2. In an experiment with oxygen, for example, recombination competes with ozone production. The chemical equation for this reaction is

$$[O] + [O_2] + [M] \rightarrow [O_3] + [M] \tag{58}$$

Ozone formation is, in turn, followed by the reaction

$$[O_3] + [O] \rightarrow 2[O_2] \tag{59}$$

A complete "source" or "sink" term will consist of a linear sum of terms each representing the rate of loss or gain, indicative of a possible chemical reaction, of a respective species. The problem then becomes quite complicated because of the number of unknown parameters that enter. By adjusting the amount of molecular oxygen available, that is, ${}_on_2$, it is possible to control the predominance of either chemical reaction. It will be assumed that the parameters are such that recombination (eq. (57)) is the dominant reaction. The sink term associated with this reaction (ref. 4, p. 8) is given by

$$-K_{r_M} n_1 n_1 n_M \tag{60}$$

for the rate of loss of species 1 due to a triple collision with reactants n_1 and a third body M. The constant K_{r_M} is called the reaction or recombination rate constant and has the dimension $(\text{cc/particle})^2\ \text{sec}^{-1}$. The subscript M indicates that the constant may depend on the kind of third body involved.

Let K_{r_1}, K_{r_2}, and K_{r_3} be the rate constants associated with reactions resulting from a triple collision wherein the third body is species 1, 2, and 3, respectively. Then the total rate constant for a change in species 1 resulting from collisions is

$$K_1 = -(K_{r_1} n_1^3 + K_{r_2} n_1^2 n_2 + K_{r_3} n_1^2 n_3) \tag{61}$$

By expansion in terms of λ using the pertinent relations in equations (11), the following relations are obtained

$$_0K_1 = 0 \tag{62a}$$

$$_1K_1 = -[(K_{r_2}\lambda)\ {}_1n_1^2\ {}_0n_2 + (K_{r_3}\lambda)\ {}_1n_1^2\ {}_0n_3] \tag{62b}$$

In equation (62b), the quantities $(K_{r_2}\lambda)$ and $(K_{r_3}\lambda)$ are taken to be of order zero with respect to the expansion for small λ. This is done in order to make the sink term of the same order as the diffusion terms. In the experiment the parameters will be chosen in just this way; that is, the pressure and the geometry of the diffusion tube will be adjusted so that the homogeneous recombination and the diffusion terms are of comparable magnitude.

When equation (62b) is substituted into equation (25e) and the number density expressions are made dimensionless (using eq. (25a)), the resulting expression becomes

$$_1k_1 = -\left[\left(\frac{L^2}{D}\ {}_0n^2\lambda K_{r_2}\right)\ {}_1\mu_1^2\ {}_0\mu_2 + \left(\frac{L^2}{D}\ {}_0n^2\lambda K_{r_3}\right)\ {}_1\mu_1^2\ {}_0\mu_3\right] \tag{63}$$

Letting k_{r_2} and k_{r_3} be the dimensionless constants associated with the reaction constants K_{r_2} and K_{r_3}, where

$$k_{r_2} = \left(\frac{L^2}{D}\ {}_0n^2\lambda\right) K_{r_2} \tag{64a}$$

$$k_{r_3} = \left(\frac{L^2}{D}\ {}_0n^2\lambda\right) K_{r_3} \tag{64b}$$

and

$$_1k_1 = -(k_{r_2}\ {}_0\mu_2 + k_{r_3}\ {}_0\mu_3)\ {}_1\mu_1^2 \tag{65}$$

the zero-order term with respect to our parameter Ω using equation (31b) becomes

$$\overset{o}{_1}k_1 = -(k_{r_2}\ \overset{o}{_o}\mu_2 + k_{r_3}\ \overset{o}{_o}\mu_3)(\overset{o}{_1}\mu_1)^2 \tag{66}$$

If $k_{r_2} = k_{r_3}$, equation (66) then becomes

$$\overset{o}{_1}k_1 = -k_{r_2}(\overset{o}{_1}\mu_1)^2 \tag{66a}$$

For the experiment discussed in the introduction, solutions based on a sink term defined by equations (61) through (66a) are needed. This requires solution of a nonlinear equation. A numerical procedure for solving this equation by machine computation is being developed. If only a qualitative understanding is desired, the equations can be linearized since closed-form solutions can be found for the linearized problem. Equation (66a) can be linearized by replacing $(\overset{o}{_1}\mu_1)^2$ with $\overline{\overset{o}{_1}\mu_1}(\overset{o}{_1}\mu_1)$, where $(\overline{\overset{o}{_1}\mu_1})$ is a constant average value. This method is used, rather than a conventional linearization about a constant value of $\overset{o}{_1}\mu_1$, in order to obtain a zero value of $\overset{o}{_1}k_1$ at $\overset{o}{_1}\mu_1 = 0$, in qualitative agreement with the nonlinear expression. Then equation (66a) is replaced by

$$\overset{o}{_1}k_1 = -k_r\ \overset{o}{_1}\mu_1 \tag{67a}$$

where

$$k_r = -k_{r_2}\ \overline{\overset{o}{_1}\mu_1} = -\frac{1}{2}\,k_{r_2} \tag{67b}$$

Here $\overline{\overset{o}{_1}\mu_1}$ is taken equal to 1/2 because in the results to be given $\overset{o}{_1}\mu_1$ varies between 0 and 1.

Equation (67a) can also be interpreted as a result corresponding to the reactions represented by equations (58) and (59), as follows. If it is assumed that any ozone molecules formed are quickly converted to oxygen molecules by the reaction described by equation (59), then the total sink term associated with equations (58) and (59) is linear in [O]. That is, it is assumed that in a very short time (compared to diffusion time) after an ozone molecule is formed by the chemical reaction (eq. (58)), the molecule will undergo a binary collision and that the efficiency of reaction is so high that the collision will cause a chemical change. This reaction is thus presumed to depend only on the species number density n_1. With these assumptions our general system can still be treated as a three-component system, but the sink term can be treated, with respect to species 1, as linearly proportional to the concentration of species 1. In terms of these assumptions the sink term with respect to species 1 corresponding to ozone formation (eq. (59)) is

$$-K_r' n_1 \tag{68}$$

The term corresponding to recombination (eq. (58)) is

$$-K_r n_1 n_2 \, {}_o n \tag{69}$$

Here differences that might arise because of the kind of third body involved in the triple collision required for equation (58) are not considered. When equations (68) and (69) are summed, the expression obtained represents the loss of species 1 in the assumed chain of reactions; that is, the sink term becomes

$$K_1 = -(K_r' n_1 + K_r n_1 n_2 \, {}_o n) \tag{70}$$

When a procedure similar to that leading to equation (70) is used, equation (63) then becomes

$$\overset{o}{_1 k_1} = -\left[\left(\frac{L^2}{D} K_r'\right) \overset{o}{_1 \mu_1} + \left(\frac{L^2}{D} K_r \, {}_o n^2\right) \overset{o}{_1 \mu_1} \, {}_o \mu_2\right] \tag{71}$$

Letting

$$k_r = \left[\frac{L^2}{D} K_r' + \left(\frac{L^2}{D} K_r \, {}_o n^2\right) {}_o \mu_2\right] \tag{72}$$

Equation (71) can be represented by the expression

$$\overset{o}{_1 k_1} = -k_r \overset{o}{_1 \mu_1} \tag{73}$$

In summarizing we observe that a quantitative representation of the sink term is given by equation (66) or (66a), but the partial differential equations (eqs. (54a), (54b), and (54c)) resulting from this substitution require electronic machine computation because of their nonlinearity. However, qualitative results may be obtained from the closed-form solutions resulting from the linear approximation to the sink term, equation (67a) or (73).

Boundary Conditions (Including Wall Reaction Effects)

The equations have been kept general up to this point since their derivation is not affected by any specific choice of coordinate system. In the discussion of the boundary conditions a specific configuration will be used, as described in the introduction. The experimental technique motivating this analysis utilizes

a flowing gas made up of known amounts of an inert gas and molecular oxygen. The oxygen is partially dissociated in such a way that there is a periodic variation in the concentrations of both the atoms and the molecules. In this respect the concentration of the various species at the base of a cylindrical diffusion tube, where the recombination process is being studied and which is tangent to the flowing gas, is expressed in terms of the total gas density by

$$n(o) = n_1(o) + n_2(o) + n_3(o) \tag{74}$$

The zero in parenthesis signifies that these concentrations are evaluated at the inlet end of the diffusion tube.

When equation (74) is expanded about a uniform state in terms of the parameter λ, as was done to obtain equations (11a) through (11g) and when coefficients of like powers of λ are equated, the following equations are obtained

$$_0n(o) = {}_0n_2(o) + {}_0n_3(o) \tag{75a}$$

$$_1n(o) = {}_1n_1(o) + {}_1n_2(o) + {}_1n_3(o) \tag{75b}$$

The zero-order terms are constant. Also, as was described earlier, there are no external variations in pressure. The following identities result:

$$_0n(o) = {}_0n \tag{76a}$$

$$_0n_2(o) = {}_0n_2 \tag{76b}$$

$$_0n_3(o) = {}_0n_3 \tag{76c}$$

$$_1n_1(o) + {}_1n_2(o) + {}_1n_3(o) = 0 \tag{76d}$$

To determine the boundary conditions on the inlet surface of the diffusion tube, expressions must be found for $_1n_1(o)$, $_1n_2(o)$, and $_1n_3(o)$. Before these expressions can be determined, it is necessary to introduce a dimensionless function that represents the time variation applied to the dissociation process. Let $f_1(t)$ be a periodic function representing the dissociation time function for species 1, such that

$$n_1(o) = n_1(o)_{max}f_1(t) \tag{77}$$

represents the concentration of species 1 on a two-dimensional surface representing the inlet boundary of the diffusion tube. The dimensions of the system are such that $n_1(o)_{max}$ can be considered constant with respect to the radial variable on the base of the diffusion tube. If the dissociation is periodic, the dissociation time function can be expressed as

$$f_1(t) = 1 - \cos \omega t \tag{78}$$

where ω is the frequency of the time variation.

When equation (77) is expanded in terms of the parameters λ and Ω and the density is made dimensionless, it then follows that

$$\overset{o}{_1\mu_1}(o) = f_1(t) \tag{79}$$

Equation (79) is the inlet boundary condition applied to equation (49a).

The variable ${}_1n_2(o)$ is related to ${}_1n_1(o)$ through the dissociation process. This is expressed by the equation

$$m_1 \, {}_1n_1(o) + m_2 \, {}_1n_2(o) = 0 \tag{80}$$

This relation neglects diffusion processes in the outer flow tube. Making equation (80) dimensionless and then substituting equation (79) into the resulting relation we have

$$\overset{o}{_1\mu_2}(o) = -\frac{1}{2} f_1(t) \tag{81a}$$

When the relations for $\overset{o}{_1\mu_1}(o)$ and $\overset{o}{_1\mu_2}(o)$ and equation (76d) are used, the equivalent condition for species 3 is obtained. It then follows that

$$\overset{o}{_1\mu_3}(o) = -\frac{1}{2} f_1(t) \tag{81b}$$

Sufficient information is now available to determine the boundary conditions on the inlet end of the diffusion tube for use in solving equation (49b). The condition for equation (49b) is determined by substituting equations (81a) and (81b) into equation (49c). The result is

$$\nu(o) = -\frac{1}{2} f_1(t)(1 + g) \tag{82}$$

It is now necessary to determine the effect of the other surfaces that constitute the boundaries of the side-arm diffusion tube. Here the normal gradient in the number density of all species is related to a fraction γ, which represents the fraction of atoms that recombine upon collision with a surface. For this problem only the case where the stream velocity is zero will be considered. The fraction γ is defined in the following manner. If J_{1n}^{+} represents the effusive flux of particles of species 1 into a surface, and J_{1n}^{-} represents the effusive flux in the opposite direction, the net flux of atoms in the region of the surface is given by

$$(J_{1n}^{+} - J_{1n}^{-} = \gamma J_{1n}^{+})_{\text{at wall}} \tag{83}$$

The effusive flux J_{1n}^{+}, which represents the number of particles that cross the plane ds per unit time per unit area in the positive direction with respect to ds, is determined from (see ref. 3, p. 456)

$$J_{1n}^{+} = \frac{d\vec{s}}{ds} \cdot \int_S f_1 \vec{V}_1 \, d\vec{V}_1 \tag{84}$$

The region of integration S includes only those values of $\vec{V}_{1n}$ which have a positive component with respect to the normal to the plane ds. The distribution function is given by (ref. 3, ch. 7)

$$f_1 = f_1^{o} \left[1 + n \sum_j \vec{W}_j \cdot \vec{d}_j C_1^{j}(W_1^{2}) \right] \tag{85}$$

where f_1^{o} is the Maxwellian distribution given by

$$f_1^{o} = n_1 \left(\frac{m_1}{2\pi kT} \right)^{3/2} e^{-m_1 V_1^{2}/2kT} \tag{85a}$$

and C_1^{j} is a scalar parameter which is determined in reference 3, chapter 7. The quantity $\vec{d}_j$ is given by

$$\vec{d}_j = \frac{\partial}{\partial \vec{r}} \left(\frac{n_j}{n} \right) + \left(\frac{n_j}{n} - \frac{n_j m_j}{\rho} \right) \frac{\partial \ln p}{\partial \vec{r}} \tag{86}$$

and the reduced velocity $\vec{W}_i$ is defined by

$$\vec{W}_i = \sqrt{\frac{m_i}{2kT}} \, \vec{V}_i \tag{87}$$

When equation (85) is substituted into equation (84), in suffix notation ($\alpha = 1, 2, 3$) with the usual convention that repeated dummy subscripts denote summation, it follows that

$$J_{1Z}^{+} = \int_S f_1^{o} V_{1Z} \, d\vec{V}_1 + n \sum_j d_{j\alpha} I_{1j\alpha}^{d} \tag{88}$$

where the integrals are defined by

$$I_{1j\alpha}^{d} = \sqrt{\frac{2kT}{m_1}} \int_S W_{1\alpha} W_{1Z} f_1^{o} C_1^{j}(W_1^{2}) \, d\vec{V}_1 \tag{89}$$

The first integral on the right side of equation (88) when integrated becomes

$$\frac{1}{4} n_1 \bar{v}_1 \tag{90}$$

where

$$\bar{v}_1 = 2\sqrt{\frac{2kT}{\pi m_1}} \tag{90a}$$

is defined as the mean molecular speed. From symmetry properties alone and the fact that the integrations are over the entire space of V_{1x} and V_{1y} the only nonvanishing integral in equation (89) is I_{1jZ}^{d}. The integrand of this integral is even in the reduced velocity W_1 and is therefore equivalent to

$$\frac{1}{6} \int W_1^{2} f_1^{o} C_1^{j} \, d\vec{V}_1 \tag{91}$$

Noting that this integral is the same as that occurring in the definition for the multicomponent diffusion coefficients (ref. 3, p. 479), we obtain the identity

$$I_{1jZ}^{d} = \frac{1}{2} \frac{n m_j}{\rho} \mathbf{D}_{1j} \tag{92}$$

When equations (90) and (92) are substituted into equation (88), the effusive flux becomes

$$J_{1Z}^{+} = \frac{1}{4} n_1 \bar{v}_1 + \frac{n^2}{2\rho} \sum_j m_j \, d_{jZ} \mathbf{D}_{1j} \tag{93}$$

By using a similar method of analysis we obtain for the number density flux in the opposite relative direction

$$J_{1Z}^{-} = \frac{1}{4} n_1 \bar{v}_1 - \frac{n^2}{2\rho} \sum_j m_j \, d_{jZ} \mathbf{D}_{1j} \tag{94}$$

Equations (93) and (94) are now substituted into equation (83) and after making the resulting expression dimensionless and expanding it in terms of λ and Ω, it follows that

$$\left[\frac{{}_0n}{{}_0\rho} \sum_j m_j \frac{{}_0\mathbf{D}_{1j}}{D} \frac{\partial}{\partial \vec{\xi}} \left({}_1^0\mu_j \right) \cdot \frac{d\vec{s}}{ds} = \frac{{}_1n_1}{4} \left(\frac{\bar{v}_1 L}{D} \right) \left(\frac{\gamma}{1 - \frac{\gamma}{2}} \right) \right]_{\substack{\text{evaluated} \\ \text{at wall}}} \tag{95}$$

Upon substitution of the multicomponent diffusion constant relations, equations (21a) and (21b), equation (95) reduces to

$$\left[\frac{\partial}{\partial \vec{\xi}} \left({}_1^0\mu_1 \right) \cdot \frac{d\vec{s}}{ds} = -{}_1^0\mu_1 k_{w_1} \right]_{\text{at wall}} \tag{96}$$

where

$$k_{w_1} = \frac{D D_{23}}{a D_{12} D_{13}} \left(\frac{\bar{v}_1 L}{4D} \right) \frac{\gamma}{1 - \frac{\gamma}{2}} \tag{96a}$$

Equations (96) and (79) are sufficient to define the boundary conditions for equation (49a). It only remains now to determine a relation similar to equation (96) as a boundary condition for the quantity ν appearing in equation (49b). Since species 3 is chemically inert, it does not react upon collision with the wall. The surface equation equivalent to equation (83) for species 3 is

$$\left(J_{3n}^{+} - J_{3n}^{-} \right)_{\text{at wall}} = 0 \tag{97}$$

The number fluxes J_{3n}^{+} and J_{3n}^{-} are determined by the same scheme used to derive equations (93) and (94) to obtain

$$\left(\frac{n^2}{\rho} \sum_j m_j \; d_{jn} \mathbf{D}_{3j} \right)_{\text{at wall}} = 0 \tag{98}$$

When operations similar to those utilized in going from equation (95) to (96) are used, it follows that

$$\left\{\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_2\right) \cdot \frac{d\vec{s}}{ds} = {}^{o}_{1}\mu_1 \frac{1}{(1 - {}_{o}\mu_2 c)}\left[{}_{o}\mu_3 \frac{m_1}{m_2}(1 - d) + {}_{o}\mu_2(1 - c)\right] k_{w_1}\right\}_{\text{at wall}} \tag{99}$$

after equations (96) and (99) are substituted into an expression found by taking the gradient of equation (76), the corresponding equation for species 3 is obtained. The result is

$$\left\{\frac{\partial}{\partial\vec{\xi}}\left({}^{o}_{1}\mu_3\right) \cdot \frac{d\vec{s}}{ds} = -{}^{o}_{1}\mu_1 \frac{\left[{}_{o}\mu_3 \frac{m_1}{m_2}(1 - d) - {}_{o}\mu_3\right] k_{w_1}}{(1 - {}_{o}\mu_2 c)}\right\}_{\text{at wall}} \tag{100}$$

The equation for ν becomes

$$\left(\frac{\partial\nu}{\partial\vec{\xi}} \cdot \frac{d\vec{s}}{ds} = {}^{o}_{1}\mu_1 k_{w_2}\right)_{\text{at wall}} \tag{101}$$

where

$$k_{w_2} = \left(\frac{1 - d}{1 - {}_{o}\mu_2 c}\right)\left[\frac{m_1}{m_2} + {}_{o}\mu_2 \frac{c}{d}\left(1 - \frac{m_1}{m_2}\right)\right] k_{w_1} \tag{101a}$$

When the boundary equations (96) and (101) are applied to a three-dimensional cylindrical diffusion tube, there will be a separate equation for each surface (cylinder and end wall). In the event that the various surfaces are constructed of different materials, the fraction ν will be different and will depend on the material used. (See ref. 5.)

DISCUSSION

The proposed experiment which prompted the analysis contained in this report will utilize the decay of the time variation in species concentration in determining the diffusion and homogeneous recombination coefficients of oxygen atoms. The preceding analysis establishes the mathematical formulation for this problem. A complete solution to the equations that constitute a formulation of the problem, that is, the determination of the concentrations of all species for all coordinates in space and time, will not be covered in this report. Instead, a solution will be given that illustrates the dependence of the concentration variation decay on chemical recombination and diffusion. This solution will apply to a one-dimensional system where diffusion and recombination occur with zero stream velocity in a region between two infinite planes and where the species concentration is being varied on one plane. At the other plane the

condition of equation (96) is imposed. In this example the linear sink term is used and heterogeneous recombination is neglected. The time variation is that given by equation (78).

The solution is found by following a scheme similar to that given by Sommerfeld (ref. 6) in his solution to the diurnal temperature problem. It follows that a solution which includes parameters that are determined so that the differential equation and the boundary conditions, equations (78) and (96), are satisfied, is given by

$$\overset{o}{i}\mu_1(\xi,\tau) = u_o(\xi) + \text{Real}\,[\exp(iW\tau)u_1(\xi)] \tag{102}$$

where

$$u_l(o) = 1 \qquad l = 0,1 \tag{102a}$$

When equation (102) is substituted into equation (54a), where the sink term is given by equation (67a) or (73), the resulting expression is a linear ordinary differential equation in u_l. The solution of this equation is

$$u_l = A_{P_+} \exp(P_+\xi) + A_{P_-} \exp(P_-\xi) \tag{103}$$

where (P_+) and (P_-) are roots of the characteristic equation

$$P^2 - (1 + iWl) = 0 \qquad l = 0,1 \tag{104}$$

and where A_{P_+} and A_{P_-} are determined by the boundary conditions, equations (96) and (102a). When the wall reaction is neglected, the solution becomes

$$\overset{o}{i}\mu_1(\xi,\tau) = \frac{\cosh\left[\sqrt{k_r}\,(\xi - 1)\right]}{\cosh\sqrt{k_r}} + \text{Real}\left\{e^{iW\tau}\,\frac{\cosh\left[P_1(\xi - 1)\right]}{\cosh P_1}\right\} \tag{105}$$

where

$$P_1 = \sqrt{\frac{k_r}{2}}\left[\sqrt{\sqrt{1 + \left(\frac{W}{k_r}\right)^2} + 1} + i\sqrt{\sqrt{1 + \left(\frac{W}{k_r}\right)^2} - 1}\right] \tag{105a}$$

This solution consists of one time-independent term superimposed on a term that includes time dependence. The average concentration is given by the time-independent term, that is, the first term on the right side of equation (105).

The concentration time variation is given by the second term. To illustrate the dependence of the decay on diffusion and recombination, a depth parameter ξ_1 will be introduced that represents a distance at which the variation in concentration is reduced to e^{-1} of its initial value. The depth parameter is defined by

$$\left| \frac{\cosh \left[P_1(\xi_1 - 1)\right]}{\cosh P_1} \right| = e^{-1} \tag{106}$$

where the expression on the left of equation (106) is the magnitude of the time variation that results from the second term on the right side of equation (105).

Figure 2 illustrates the dependence of the depth parameter ξ_1 on frequency and sink strength. It is to be observed that for high frequencies the decay in concentration occurs close to the inlet plane and is little affected by the sink strength k_r. This follows if it is noted that when the dimensionless frequency $W/2\pi$ is of order 20 or greater, the $1/e$ decay characterized by ξ_1 occurs within 1/10 of the diffusion tube length and depends very little on the value of the sink term parameter k_r. As the frequency is reduced, there is a greater dependence of the depth parameter on the sink strength, and the decay occurs farther from the inlet. Also, in the limit of large sink strength the decay occurs near the inlet plane and is little affected by the frequency. For instance, we note that when k_r is of order 100, a change in dimensionless frequency from 0 to 30 produces a change in the decay depth from 0.10 to 0.08. From the preceding discussion we observe that to obtain maximum resolution in the determination of k_r, it is desirable that the frequency of variation be low but not zero since the limiting case of zero frequency (or alternatively, the steady state problem) is not of interest here. The reason for this is that the variation in species concentration is itself a technique for making measurements on the reaction rates. The appropriate frequency will, in part, depend on the electric filter circuitry efficiency in separating the time varying signal from the background. The detection of the concentration variation may also be improved, particularly for large k_r, by superimposing the variation in concentration on a steady gas stream of known velocity. Such a scheme serves to transport the atoms from their source to the region of observation in a shorter time. This is necessary in the event that the recombination time is small and the recombination occurs before the atoms are in the region where the observations are being made (this case is characterized by large k_r). The utility of the proposed experiment arises out of the sensitivity available in photometric detection techniques associated with spectral absorption experiments for measuring relative changes in concentration. It is therefore expected that the decay in the concentration variation may be measured with great accuracy.

CONCLUDING REMARKS

A set of nonlinear and coupled fundamental equations describing diffusion processes in general, obtained from rigorous kinetic theory, has been used to derive a set of simplified expressions applicable to an unsteady problem in

which the species concentrations are made to vary in a prescribed periodic manner. With the set of simplified expressions the concentrations of each species in a ternary gas mixture can be determined as functions of time and spatial coordinate. It was necessary to complement the derivations by introducing chemical kinetics in discussing one term in the fundamental equations (the term representing the recombination processes), and by introducing wall reaction effects to establish the boundary conditions necessary for the final set of simplified expressions. The term representing the recombination processes introduced a nonlinearity in the simplified equations. However, a simplifying assumption could be made which allowed for closed-form solutions to facilitate gaining a qualitative understanding of the unsteady problem. A solution based on this approximation was given. It required the same methods that were applied in determining the diurnal or annual temperature variation of the earth. In fact, there is an obvious analogy between the experimental problem mentioned above and the earth's temperature problem. In the earth's temperature problem the variation in temperature due to the daily solar fluctuation is confined to a thin surface layer. The experiment utilizes measurements on the "width" of the analogous concentration layer in determining the recombination rates. The qualitative picture gained from the solution illustrates that care must be taken in choosing the parameters of the problem. For example, the technique is applicable only if the variation frequency is sufficiently low that the effect of chemical reaction can be observed; also, the experimental method may require that the concentration be superimposed on a gas stream should the reaction rates be too large and the decay confined too close to the inlet boundary.

The next logical development, measuring the recombination and diffusion rates, requires the determination of the solution of the equations with the nonlinear recombination term. This solution will, of necessity, involve recourse to numerical methods. Such a program is under way, and preliminary exploratory work indicates that there will be no difficulty in achieving a solution to this more difficult problem.

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National Aeronautics and Space Administration
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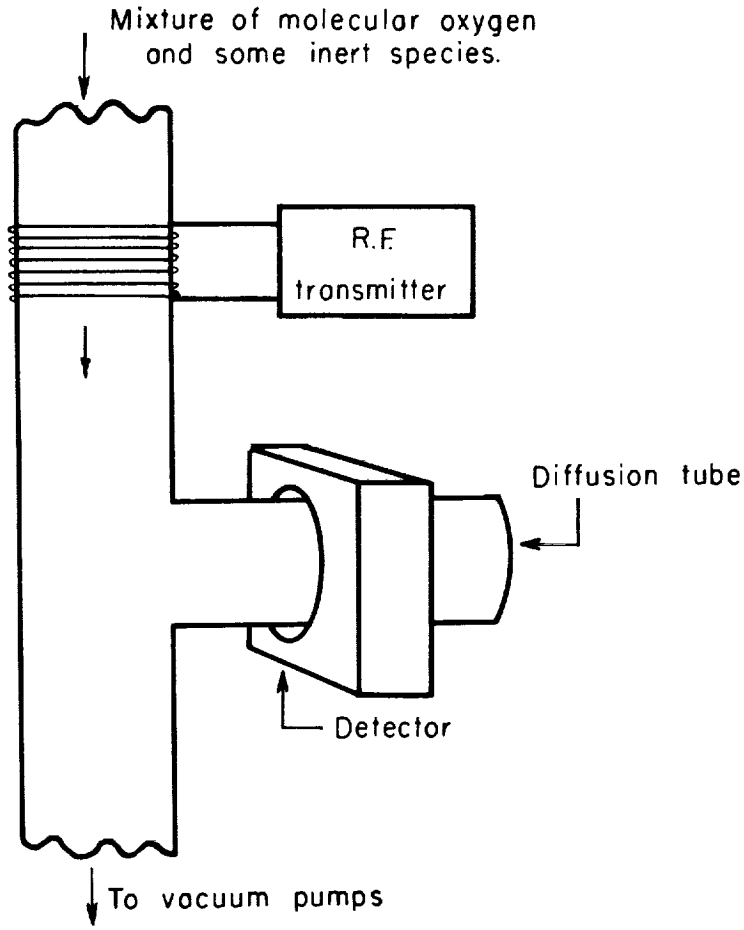

Figure 1.- Sketch illustrating the pertinent features of a proposed experimental apparatus.

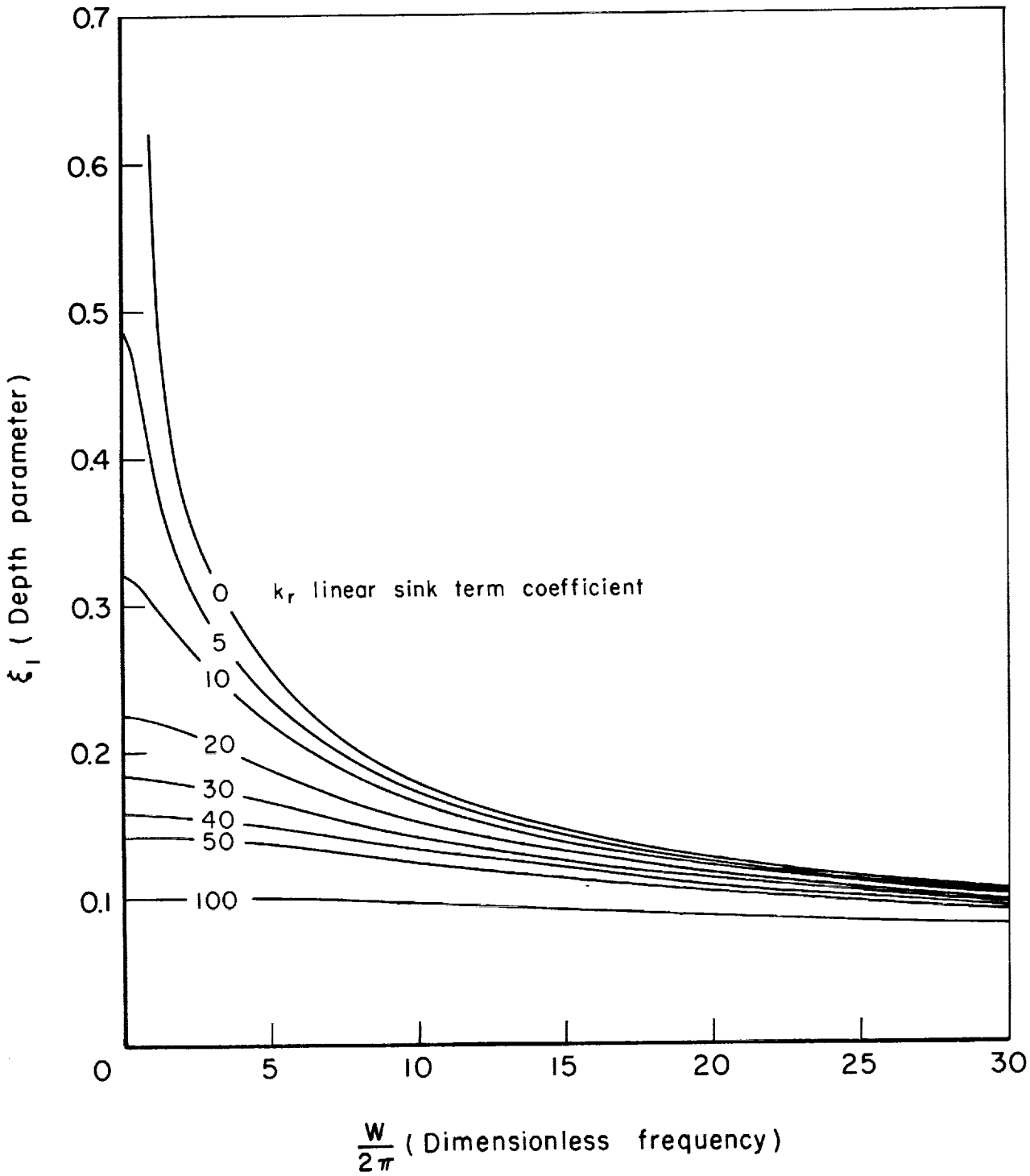

Figure 2.- Curves relating the depth parameter, a parameter which characterizes a 1/e decay in concentration variation, to the dimensionless frequency for various values of the linear sink term coefficient k_r.

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