

Diffusion Effects in Hypersonic Flows with a Ternary Mixture

Bokhyun Yoon* and Maurice L. Rasmussen**

(Received August 21, 1998)

An evaluation of multi-component diffusion effects in hypersonic flows is presented. A comparison is made of the results obtained from the common simplifying assumption of Fick's law with the results obtained from the precise constitutive relations stemming from the kinetic theory of gases. To fix the ideas, the flow of a ternary mixture past a flat plate is considered, for which pressure diffusion is negligible. Whereas the precise analysis is more complicated, the results for the mass-fraction distribution can be significantly different from the corresponding simpler analysis stemming from Fick's Law.

Key Words: Mass Diffusion, Hypersonic Flow, Fick's Law, Boundary-Layer Flow

Nomenclature			
A	: A_2/A_1	R_α	: Specific gas constant for species α
A^*	: Defined in Eq. (21a)	Sc_1, Sc_2	: Representative Schmidt numbers defined in Eqs. (17b, c)
A_1, A_2, A_3	: Defined below Eq. (12b)	t	: Time
A_0	: Avogadro's number	T	: Temperature
B	: B_1/B_2	u, v	: Velocity components in the x and y direction
B^*	: Defined in Eq. (21b)	X_α	: Mole fraction for species α
B_1, B_2, B_3	: Defined below Eq. (12b)	Y_α	: Mass fraction for species α
\vec{d}_α	: Diffusion vector for species α	Y_α^*	: Defined in Eqs. (24a, b, c)
D_m	: Mean diffusion coefficient	$Y_{\alpha e}, Y_{\alpha w}$: Mass fractions of species α for the outer boundary layer edge and wall
$D_{\alpha\beta}$: Multi-component mass-diffusion coefficient between species α and β	W_α	: Molecular weight for species α
$\bar{D}_{\alpha\beta}$: Binary mass-diffusion coefficient between species α and β	α	: $Y_{1e} - Y_{1w}$
D_α^T	: Multi-component thermal-diffusion coefficient for species α	β	: $Y_{2e} - Y_{2w}$
f	: Blasius function	γ	: $\ln f''(0) + 1.103$
h_α	: Specific enthalpy for species α	η	: Self-similarity variable
\vec{j}_α	: Mass-diffusion flux vector for species α	μ	: Viscosity of mixture
k_B	: Boltzmann constant	μ_α	: Specific viscosity for species α
m_α	: Molecular mass for species α	ρ	: Density of mixture
p	: Pressure	ρ_α	: Specific density for species α
\vec{q}	: Energy-diffusion flux vector	σ_α	: Molecular diameter of species α
R	: Gas constant for mixture	$\sigma_{\alpha\beta}$: $(\sigma_\alpha + \sigma_\beta)/2$
		ω	: Defined in Eq. (22b)
		ω_α	: Rate of creation of mass of species α per unit volume
		Ω	: Defined below Eq. (12b)

* Fellow KSME, Associate Professor, Dept. of Mechanical Engineering, Mokpo National University

** Professor, Aerospace and Mechanical Engineering, University of Oklahoma, U. S. A.

1. Introduction

Most hypersonic flows (Yoon, 1996) involve multi-component mixtures, which can be treated as inert sometimes and reacting at other times, depending upon the situation. Various problems of interest stem from calculating the aerodynamic forces and moments on missiles and aircraft, calculating the reacting flow properties of propulsion units, determining the missile signatures associated with mass injection, and other situations. In virtually every CFD calculation scheme, the mass-diffusion fluxes are approximated by Fick's law of diffusion, and thermal diffusion, pressure diffusion and forced diffusion are neglected. This approximation has not been substantiated for hypersonic flows in general, and it has been taken as an article of faith based on low-speed applications. This study seeks to evaluate the use of Fick's law by using the correct multi-component diffusion laws to calculate various flow problems and establish rational baseline comparisons. By this means, it can be demonstrated how different constitutive relations for the mass-diffusion flux vectors influence the results of hypersonic flow calculations for multi-component mixtures.

One avenue of approach would be to take a problem that has already been solved using Fick's law, and to solve the problem again using correct multi-component diffusion. Many practical hypersonic flow problems can involve as many as seven species or more and must be handled by using one CFD code or another. This can involve an elaborate numerical analysis, and such differences that occur may be obscure and difficult to trace fundamental principles.

A second avenue of approach is to sort out some of the implications of multi-component diffusion from a more basic analysis. The general diffusion laws, stemming from kinetic theory, are substantially more complicated than the Fick's law. Many essential features can be illustrated by using simple ternary mixture, and later on simple reaction models. With these restrictions, fundamental hypersonic flow problems can be studied,

such as the boundary layer flow past a flat plate and the flow structure of a normal shock wave. By this means, some progress can be made analytically, and general insight and methodologies can be established. Some properties of hypersonic flow fields can be determined together with implications on wall friction and heat transfer effects. This study will present the background and general considerations for mass diffusion phenomena first, and then concentrate on the compressible boundary layer flow past a flat plate by means of a simple ternary mixture model.

2. Background

The equation of change for the mass of species α can be expressed as

$$\rho \frac{DY_\alpha}{Dt} = \dot{\omega}_\alpha - \text{div } \vec{j}_\alpha, \quad \alpha = 1, 2, \dots, N \quad (1)$$

where $Y_\alpha \equiv \rho_\alpha / \rho$ is the mass fraction of species α , ρ the mass density of the mixture, ρ_α the mass density of species α , $\dot{\omega}_\alpha$ the rate of creation of mass of species α per unit volume of mixture, \vec{j}_α the mass-diffusion flux vector of species α , N the total number of species in the mixture, and D/Dt the material derivative associated with the mass average velocity. Since

$$\sum_{\alpha=1}^N Y_\alpha \equiv 1 \quad (2)$$

mass conservation of the overall mixture requires that

$$\sum_{\alpha=1}^N \dot{\omega}_\alpha \equiv 0 \quad (3)$$

$$\sum_{\alpha=1}^N \vec{j}_\alpha \equiv 0 \quad (4)$$

The reaction rate $\dot{\omega}_\alpha$ and the mass-diffusion flux vector \vec{j}_α need to be specified by some sort of constitutive relations. Typically, the mass-diffusion flux vector also enter into the constitutive relation for the energy-diffusion flux vector (see Eq. (9)).

The Fick's law in terms of the mass flux is classical and simple approximation for \vec{j}_α :

$$\vec{j}_\alpha = -\rho D_m \nabla Y_\alpha, \quad \alpha = 1, 2, \dots, N \quad (5)$$

Here D_m is a mean diffusion coefficient, being the same for all species in order to satisfy Eqs. (2) and (4). For binary mixtures, Fick's law is theoretically correct when the effects of pressure gradients and temperature gradients are neglected. Thus D_m is a mean pseudo binary-diffusion coefficient. For multi-component mixtures, Fick's law does not have an equivalent firm foundation as for binary mixtures, and D_m depends on the local composition as well as the temperature and pressure. Various empirical and semi-empirical relations have been used for D_m (Rasmussen, 1994 ; Kee, 1993)

Fick's law is very commonly used not only because of its simplicity, but also because it presumably yields reasonably good results. However, Dorrance (1962) states that Fick's law does not offer a general justification. In a recent two volumes of Hypersonics, (Bertin, 1989), all the CFD (Computational Fluid Dynamics) papers that were cited there made use of Fick's law. The scant justification for using the Fick's law was given by Heimerl and Coffee (1982), but they were concerned only with low-speed laminar flames. Kee et al. (1993) encountered applications in which approximate averaging schemes for the diffusion coefficient were inadequate, and they noted further that the ones they propose violate the conservation condition in Eq. (4). The significance of mass diffusion near stagnation points has been measured (Guy, 1975). It seems that a general evaluation of Fick's law, especially applied for hypersonic flows, is not available.

3. General Considerations

The general representation of the mass-diffusion flux vectors stems from the kinetic theory of gases. These theories have been expounded in great detail by Chapman and Cowling (1952) and Hirschfelder et al. (1954). A recent textbook on multi-component mass transfer by Taylor and Krishna (1993) contains comprehensive materials, but it does not deal with hypersonic flows. Refer to Rasmussen (1994) for discussions pertaining to hypersonic flow.

From the kinetic theory of gases, the multi-

component mass-diffusion vectors are expressed in terms of the diffusion vector \vec{d}_a :

$$\vec{d}_a \equiv \nabla X_a + (X_a - Y_a) \nabla \ln p, \quad \alpha = 1, 2, \dots, N \quad (6)$$

where X_a is the mole fraction of species a and p is the mixture pressure. Effects of concentration gradients and of pressure gradients always appear in this combination. The multi-component mass-diffusion vectors are now given by

$$\vec{j}_\alpha = \rho \frac{Y_\alpha}{X_\alpha} \sum_{\beta=1}^N \frac{Y_\beta}{X_\beta} D_{\alpha\beta} \vec{d}_\beta - D_\alpha^T \nabla \ln T, \quad \alpha = 1, 2, \dots, N \quad (7)$$

Here, $D_{\alpha\beta}$ is the *multi-component mass-diffusion* coefficient and D_α^T is the multi-component thermal-diffusion coefficient. The diffusion coefficients $D_{\alpha\beta}$ and D_α^T are not equal to the binary diffusion coefficient denoted by $\bar{D}_{\alpha\beta}$. The multi-component diffusion coefficients are instead complicated functions of the binary diffusion coefficients together with component concentrations. Thermal-diffusion coefficients are generally small, and being identically zero for Maxwellian molecules. Notice that the mass-diffusion vectors are linear combinations of the component concentration gradients and thus not necessarily collinear with the concentration gradient of their own corresponding species, as for Fick's law. The diffusion constitutive equation (7) is not at all obvious, and yet it can be regarded as one of the prominent achievements of the kinetic theory of gases.

The multi-component diffusion coefficient $D_{\alpha\beta}$ is difficult to evaluate when there are a large number of components (say, four or more). This difficulty can be overcome when Eq. (7) is inverted so that the diffusion vector \vec{d}_a is expressed in terms of the mass-diffusion vector \vec{j}_a :

$$\vec{d}_a = \frac{1}{\rho} \sum_{\beta=1}^N \frac{X_\alpha X_\beta}{D_{\alpha\beta}} \left(\frac{\vec{j}_\beta}{Y_\beta} - \frac{\vec{j}_\alpha}{Y_\alpha} \right) - \frac{\nabla \ln T}{\rho} \sum_{\beta=1}^N \frac{X_\alpha X_\beta}{D_{\alpha\beta}} \left(\frac{D_\alpha^T}{Y_\alpha} - \frac{D_\beta^T}{Y_\beta} \right), \quad \alpha = 1, 2, \dots, N \quad (8)$$

This equation, sometimes, called as the generalized Stefan-Maxwell equation, is expressed in terms of the binary-diffusion coefficient $\bar{D}_{\alpha\beta}$ rather than the multi-component coefficient

$D_{\alpha\beta}$. The binary-diffusion coefficient $\bar{D}_{\alpha\beta}$ can be evaluated for each pair of mixture components by means of kinetic-theory formulas.

The mass-diffusion vector also appears in the energy equation by means of the constitutive relation for the energy-diffusion flux vector \vec{q} :

$$\vec{q} = -k\nabla T - \sum_{\alpha=1}^N h_{\alpha} \vec{j}_{\alpha} + \frac{T}{\rho} \sum_{\alpha=1}^N \sum_{\beta=1}^N R_{\alpha} X_{\beta} \frac{D_{\alpha}^T}{\bar{D}_{\alpha\beta}} \left(\frac{\vec{j}_{\alpha}}{Y_{\alpha}} - \frac{\vec{j}_{\beta}}{Y_{\beta}} \right) \quad (9)$$

Here k is the thermal conductivity for the mixture, h_{α} the specific enthalpy for species α , and R_{α} the specific gas constant for species α . When there is no mass diffusion, Eq. (9) reduces to what is normally called the heat-flux vector and Fourier's law. Whatever constitutive relation for the mass-diffusion vector may be used, it can significantly affect the energetics of a diffusion problem.

4. Simple Ternary Mixture

Some basic results can be sorted out by starting with a simple ternary and simple reaction models. A simple model that bears some relation to reality is that of dissociating oxygen in the presence of a neutral species, say nitrogen. The ternary mixture is thus composed of O_2 , O , and N_2 , which we refer to as species 1, 2, and 3, respectively, for computational purposes. Their physical properties are given in **Appendix**. It could be further supposed that the oxygen non-equilibrium dissociation is governed by the model for the ideal disassociating gas (Rasmussen, 1994). For the ternary mixture, the multi-component diffusion coefficient $D_{\alpha\beta}$ can be determined explicitly in terms of separate binary diffusion coefficients and the mixture composition (Rasmussen, 1994).

$$D_{\alpha\beta} = \bar{D}_{\alpha\beta} \left[1 + \frac{Y_{\gamma} \{ R_{\beta} \bar{D}_{\alpha\gamma} - R_{\gamma} \bar{D}_{\alpha\beta} \}}{R_{\alpha} Y_{\alpha} \bar{D}_{\beta\gamma} + R_{\beta} Y_{\beta} \bar{D}_{\alpha\gamma} + R_{\gamma} Y_{\gamma} \bar{D}_{\alpha\beta}} \right] \quad (10)$$

where α , β , and γ are non-repeated permutations of 1, 2, and 3. The mass-diffusion flux vectors thus appear as

$$\vec{j}_1 = \rho \frac{Y_1}{X_1} \left[\frac{Y_2}{X_2} D_{12} \vec{d}_2 + \frac{Y_3}{X_3} D_{13} \vec{d}_3 \right] \quad (11a)$$

$$\vec{j}_2 = \rho \frac{Y_2}{X_2} \left[\frac{Y_1}{X_1} D_{21} \vec{d}_1 + \frac{Y_3}{X_3} D_{23} \vec{d}_3 \right] \quad (11b)$$

$$\vec{j}_3 = \rho \frac{Y_3}{X_3} \left[\frac{Y_1}{X_1} D_{31} \vec{d}_1 + \frac{Y_2}{X_2} D_{32} \vec{d}_2 \right] \quad (11c)$$

with thermal diffusion omitted. (Note that $D_{11} = D_{22} = D_{33} = 0$). Treating Y_1 , Y_2 and p as independent variables, we can get for \vec{j}_1 and \vec{j}_2

$$\vec{j}_1 = -\rho [A_1 \nabla Y_1 + A_2 \nabla Y_2 + A_3 \nabla \ln p] \quad (12a)$$

$$\vec{j}_1 = -\rho [B_1 \nabla Y_1 + B_2 \nabla Y_2 + B_3 \nabla \ln p] \quad (12b)$$

where

$$\begin{aligned} A_1 &\equiv D_{13} + a_1 Y_2, \\ a_1 &\equiv \frac{1}{R_1} \{ (R_1 - R_3) D_{12} - (R_1 - R_2) D_{13} \}, \\ A_2 &\equiv \left[\frac{\bar{D}_{23}}{\Omega} (R_2 \bar{D}_{13} - R_3 \bar{D}_{12} - a_1) \right] Y_1, \\ A_3 &\equiv \frac{R^2 (X_1 - Y_1)}{R_1 R_3} D_{13} \\ &\quad + \frac{R^2 (X_2 - Y_2)}{R_1 R_2 R_3} (R_2 D_{13} - R_3 D_{12}), \\ B_1 &\equiv \left[\frac{\bar{D}_{13}}{\Omega} (R_1 \bar{D}_{23} - R_3 \bar{D}_{21} - b_2) \right] Y_2, \\ B_2 &\equiv D_{23} + b_2 Y_1, \\ b_2 &\equiv \frac{1}{R_2} \{ (R_2 - R_3) D_{21} - (R_2 - R_1) D_{23} \}, \\ B_3 &\equiv \frac{R^2 (X_2 - Y_2)}{R_2 R_3} D_{23} \\ &\quad + \frac{R^2 (X_1 - Y_1)}{R_1 R_2 R_3} (R_1 D_{23} - R_3 D_{21}), \\ \Omega &\equiv Y_1 R_1 \bar{D}_{23} + Y_2 R_2 \bar{D}_{13} + Y_3 R_3 \bar{D}_{12}. \end{aligned}$$

This model is simple enough to apply to classical hypersonic flow problems, such as the boundary layer flow on a flat plate, a normal shock wave, the stagnation-point flow near a blunt nose, and so on. We consider here the case of the compressible boundary layer flow only.

5. Boundary Layer Flow on a Flat Plate

5.1 Basic formulation

We shall make some simplifying assumptions here for the compressible boundary layer flow on a flat plate. The pressure diffusion is negligible since the pressure is constant across the boundary layer. Moreover, we shall ignore thermal diffusion for the simplicity. For a ternary mixture, we

suppose that the mass fractions Y_1 and Y_2 are independent, and that Y_3 can be obtained from $Y_3 = 1 - Y_1 - Y_2$. Likewise, the mass-diffusion fluxes \vec{j}_1 and \vec{j}_2 are treated as independent and $\vec{j}_3 = -\vec{j}_1 - \vec{j}_2$. Then there are two coupled independent equations of change for Y_1 and Y_2 :

$$\rho u = \frac{\partial Y_1}{\partial x} + \rho v \frac{\partial Y_1}{\partial y} = \dot{\omega}_1 + \frac{\partial}{\partial y} \left(\rho A_1 \frac{\partial Y_1}{\partial y} + \rho A_2 \frac{\partial Y_2}{\partial y} \right) \quad (13a)$$

$$\rho u \frac{\partial Y_2}{\partial x} + \rho v \frac{\partial Y_2}{\partial y} = \dot{\omega}_2 + \frac{\partial}{\partial y} \left(\rho B_1 \frac{\partial Y_1}{\partial y} + \rho B_2 \frac{\partial Y_2}{\partial y} \right) \quad (13b)$$

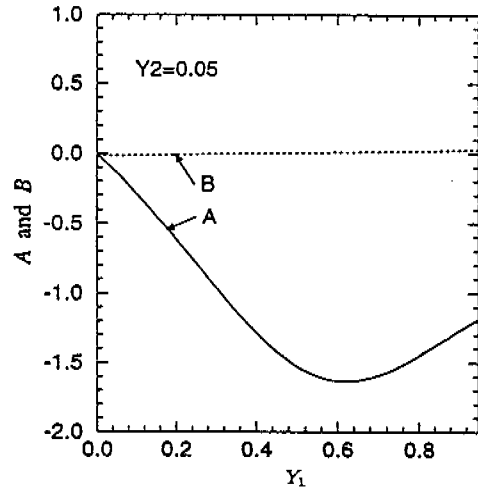
When $A_2=0$ and $B_1=0$, Eqs. (13a, b) essentially reduce to those obtained from Fick's law. It is our purpose here to illustrate the differences between the results stemming from Eqs. (13a, b) and the corresponding results associated with Fick's law (that is, essentially setting $A_2=B_1=0$ in Eqs. (13a, b)). For a sophisticated boundary layer treatment involving four species and the use of Fick's law, refer to Inger (1964). For the binary diffusion coefficient in a ternary mixture, we make use of the hard-sphere billiard-ball model (Rasmussen, 1994).

$$\bar{D}_{\alpha\beta} = \frac{3}{16\sigma_{\alpha\beta}^2} \left\{ \frac{2k_B^3(m_\alpha + m_\beta)}{\pi m_\alpha m_\beta} \right\}^{1/2} \frac{RT^{3/2}/p}{R_\alpha Y_\alpha + R_\beta Y_\beta} \quad (14)$$

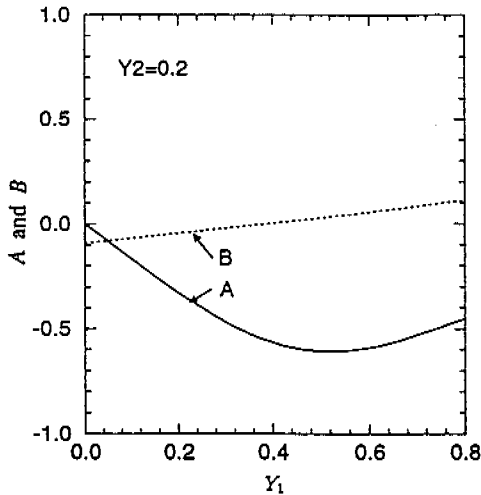
where

- m_α, m_β = molecular masses,
- $\sigma_\alpha, \sigma_\beta$ = molecular diameters,
- $\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2$,
- k_B = Boltzmann constant,
- $R_\alpha = k_B/m_\alpha$ = specific gas constant,
- $R = Y_1 R_1 + Y_2 R_2 + Y_3 R_3$,
- $p = \rho RT$.

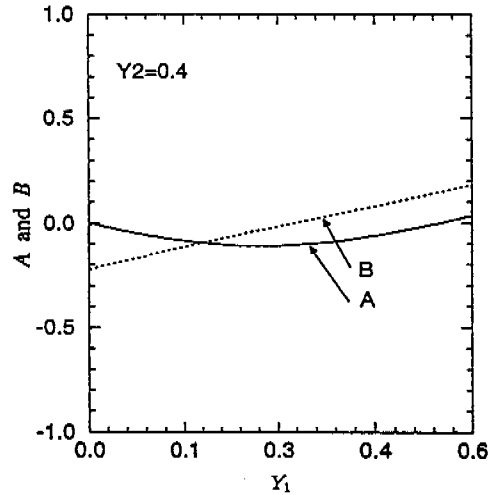
With these assumptions, we can examine variations of ratios $A \equiv A_2/A_1$ and $B \equiv B_1/B_2$ with respect to the mass fraction Y_α . Note that A and B are independent on temperature and pressure,



(a) For $Y_2=0.05$



(b) For $Y_2=0.20$



(c) For $Y_2=0.40$

Fig. 1 Variations of A and B with respect to Y_1 in Eqs. (16a, b)

since both of them cancel out. This can be easily seen from the definitions of A and B with Eq. (14). Figure 1 shows the variation of $A \equiv A_2/A_1$ and $B \equiv B_1/B_2$ with respect to Y_1 for various Y_2 's. It can be found from Fig. 1 that for particular values of mass fraction, A and B can differ significantly from zero.

In order to get boundary-layer equations, we introduce a well-known similarity coordinate transformation :

$$\xi(x) = \int_0^x \rho_w \mu_w u_e dx \quad (15a)$$

$$\eta(x, y) \equiv \frac{u_e}{\sqrt{2\xi}} \int_0^y \rho dy \quad (15b)$$

and the Blasius function f such as :

$$\frac{u}{u_e} \equiv \frac{\partial f}{\partial \eta} \quad (15c)$$

where the subscripts e and w refer to the external-stream and the wall boundary.

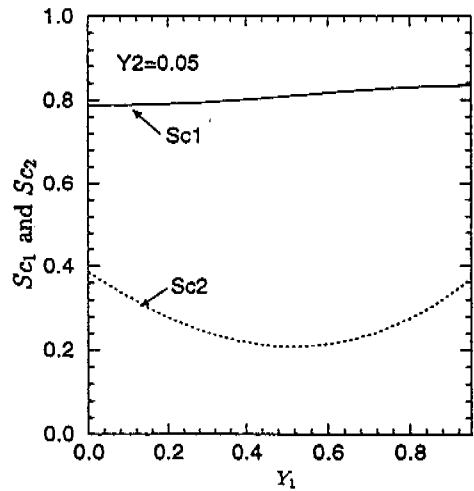
Then Eqs. (13a, b) become :

$$\frac{\partial}{\partial \eta} \left\{ \frac{C}{Sc_1} \left(\frac{\partial Y_1}{\partial \eta} + A \frac{\partial Y_2}{\partial \eta} \right) \right\} + f \frac{\partial Y_1}{\partial \eta} = 2\xi \left(\frac{\partial f}{\partial \eta} \frac{\partial Y_1}{\partial \xi} - \frac{\partial f}{\partial \xi} \frac{\partial Y_1}{\partial \eta} \right) - \frac{2\xi \dot{\omega}_1}{\rho u_e^2 \rho_w \mu_w} \quad (16a)$$

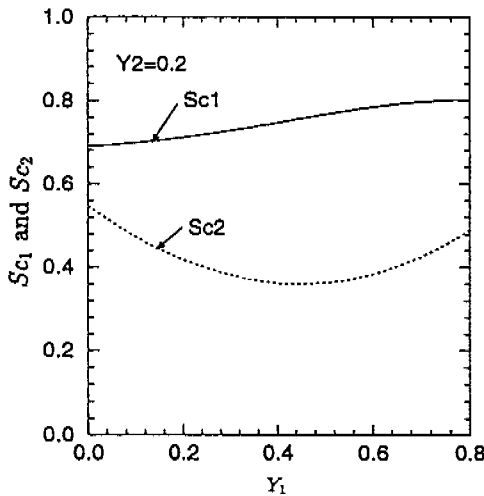
$$\frac{\partial}{\partial \eta} \left\{ \frac{C}{Sc_2} \left(\frac{\partial Y_2}{\partial \eta} + B \frac{\partial Y_1}{\partial \eta} \right) \right\} + f \frac{\partial Y_2}{\partial \eta} = 2\xi \left(\frac{\partial f}{\partial \eta} \frac{\partial Y_2}{\partial \xi} - \frac{\partial f}{\partial \xi} \frac{\partial Y_2}{\partial \eta} \right) - \frac{2\xi \dot{\omega}_2}{\rho u_e^2 \rho_w \mu_w} \quad (16b)$$

where $C \equiv \frac{\rho \mu}{\rho_e \mu_e}$, $Sc_1 \equiv \frac{\mu}{\rho A_1}$, $Sc_2 \equiv \frac{\mu}{\rho B_2}$. (17a, b, c)

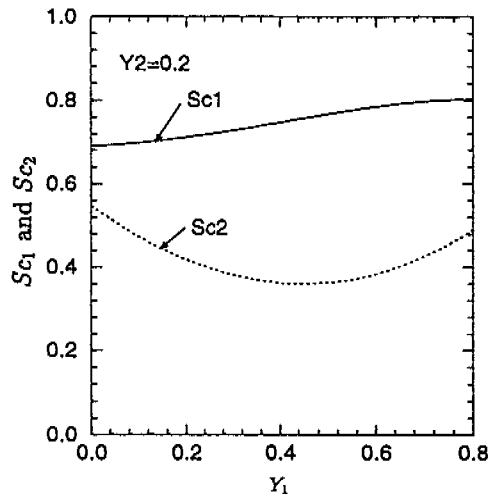
Here Sc_1 and Sc_2 are the representative Schmidt numbers, and C is the Chapman-Rubens parameter. The Schmidt numbers Sc_1 and Sc_2 (corresponding to O_2 and O in mixture with N_2) are plotted as functions of Y_1 for various Y_2 's in Fig. 2. The Schmidt numbers can vary substantially with composition and can have substantially different values. The viscosity μ in the definition of Schmidt numbers was calculated on the basis of Wilke's formula (see Appendix). The Blasius function $f(\eta)$ in Eqs (16a, b) is the solution to the well known Blasius equation f'''



(a) For $Y_2=0.05$



(b) For $Y_2=0.20$



(c) For $Y_2=0.40$

Fig. 2 Variations of Sc_1 and Sc_2 with respect to Y_1 in Eqs. (16a, b)

+ $ff''=0$.

We can proceed further by utilizing the boundary layer similarity ($\partial/\partial\xi=0$) in a conventional way (Rasmussen, 1994 ; Dorrance, 1962 ; Inger, 1964), setting $C=1$, treating A and B as constants, and using constant representative Schmidt numbers. For the flow with no chemical reactions ($\dot{\omega}_a=0$), the partial differential equations of Eqs. (16a, b) reduce to the following ordinary differential equations :

$$\frac{d^2 Y_1}{d\eta^2} + A \frac{d^2 Y_2}{d\eta^2} + Sc_1 f \frac{dY_1}{d\eta} = 0 \quad (18a)$$

$$\frac{d^2 Y_2}{d\eta^2} + A \frac{d^2 Y_1}{d\eta^2} + Sc_2 f \frac{dY_2}{d\eta} = 0 \quad (18b)$$

To obtain approximate solutions analytically by means of the perturbation method, the Eqs. (18a, b) can be rewritten as :

$$\frac{d^2 Y_1}{d\eta^2} + f \frac{dY_1}{d\eta} = \left(1 - \frac{1}{Sc_1}\right) \frac{d^2 Y_1}{d\eta^2} - \frac{A}{Sc_1} \frac{d^2 Y_2}{d\eta^2} \quad (19a)$$

$$\frac{d^2 Y_2}{d\eta^2} + f \frac{dY_2}{d\eta} = \left(1 - \frac{1}{Sc_2}\right) \frac{d^2 Y_2}{d\eta^2} - \frac{B}{Sc_2} \frac{d^2 Y_1}{d\eta^2} \quad (19b)$$

Again, when $A=B=0$, these reduce to the well-known results obtained for Fick's law, with Sc_1 and Sc_2 taken as equal. The subsequent analysis is based on the solutions of Eqs. (19a, b) for various values of A , B , Sc_1 , and Sc_2 together with specified boundary conditions. It will facilitate the discussion to obtain an approximate solution. This can be done by taking A and B as small, and Sc_1 and Sc_2 as only slightly different from unity. When this is done, the right-hand sides of Eqs. (19a, b) are small, and thus we can use the perturbation method for approximate solutions. The base equations for Eqs. (19a, b) reduce to the Blasius equation. When the base solutions are substituted into the right-hand sides, the following first-approximations can be obtained :

$$\frac{Y_1 - Y_{1w}}{Y_{1e} - Y_{1w}} = f' - A^* \left[f' \ln f'' + \frac{f^2}{2} + 1.103 f' \right] \quad (20a)$$

$$\frac{Y_2 - Y_{2w}}{Y_{2e} - Y_{2w}} = f' - B^* \left[f' \ln f'' + \frac{f^2}{2} + 1.103 f' \right] \quad (20b)$$

where

$$A^* \equiv \frac{A(Y_{2e} - Y_{2w})}{Sc_1(Y_{1e} - Y_{1w})} - \left(1 - \frac{1}{Sc_1}\right) \quad (21a)$$

$$B^* \equiv \frac{B(Y_{1e} - Y_{1w})}{Sc_2(Y_{2e} - Y_{2w})} - \left(1 - \frac{1}{Sc_2}\right) \quad (21b)$$

When $A=B=0$, the results reduce to those for Fick's law (with $Sc_1=Sc_2$).

5.2 Boundary conditions

The boundary conditions that will be considered in the subsequent analysis specify that nitrogen N_2 and oxygen O_2 are neutral species, and the mass-diffusion flux \vec{j}_3 is thus zero at the wall. It follows that $\vec{j}_1 + \vec{j}_2 = 0$ at the wall. It is supposed that the wall is arbitrarily catalytic for the purposes of numerical example, and \vec{j}_1 and \vec{j}_2 are not separately zero accordingly. Thus, the only chemical reactions that occur are at the wall between species 1 and 2 (the dissociation-association between O_2 and O , respectively). At the wall, therefore, it follows from Eqs. (12a, b) that

$$Y_2'(0) = -\omega Y_1'(0) \quad (22a)$$

where

$$\omega \equiv \frac{A_1 + B_1}{A_2 + B_2} = \frac{Sc_2 + BSc_1}{Sc_1 + ASc_2} \quad (22b)$$

The condition of Eq. (22a) must be enforced in the integration of the coupled equations (19a, b).

The two second-order coupled equations (19a, b) require three boundary conditions. In this case they are to be specified in terms of Y_{1e} , Y_{1w} , and Y_{2w} . Only three of these can be specified independently, and the fourth must be determined. We shall arbitrarily select Y_{1e} , Y_{1w} , and Y_{2w} . And then Y_{2e} is to be determined. An approximation that elucidates above considerations can be obtained by means of the approximate solutions, Eqs. (20a, b). Evaluating the derivatives of Y_1 and Y_2 at the wall with Eq. (22a) leads to the relation between $\alpha \equiv Y_{1e} - Y_{1w}$ and $\beta \equiv Y_{2e} - Y_{2w}$:

$$\beta = -\frac{\alpha \omega \left[1 + \gamma \left(1 - \frac{1}{Sc_1} \right) - \frac{\gamma B}{\omega Sc_2} \right]}{1 + \gamma \left(1 - \frac{1}{Sc_2} \right) - \frac{\gamma \omega A}{Sc_1}} \quad (23)$$

where $\gamma \equiv \ln f'(0) + 1.103 = 0.347$. Thus, when Y_{1e} , Y_{1w} , and Y_{2w} are specified, Y_{2e} can be

determined. Note that Eq. (23) is strictly valid when A and B are small, and Sc_1 and Sc_2 are near unity.

The results are cast in terms of the functions

$$\begin{aligned} Y_1^* &\equiv \frac{Y_1 - Y_{1w}}{Y_{1e} - Y_{1w}} \\ Y_2^* &\equiv \frac{Y_2 - Y_{2w}}{Y_{2e} - Y_{2w}} \\ Y_3^* &\equiv \frac{Y_3 - Y_{3w}}{Y_{3e} - Y_{3w}} \end{aligned} \quad (24a, b, c)$$

all of which vary between zero at the wall and unity at the free stream. It can be shown that Y_3^* is related to Y_1^* and Y_2^* by

$$Y_3^* = \frac{\alpha Y_1^* + \beta Y_2^*}{\alpha + \beta} \quad (25)$$

Eqs. (20a, b) can be used to obtain an explicit approximation for Y_3^* .

5.3 Fick's law

The results for Fick's law, stemming from Eq. (5), can be obtained by setting $A=B=0$ and $Sc_1 = Sc_2 = Sc_m$ in Eqs. (19a, b). Since the resulting diffusion equations are the same, solutions are the same, that is, $Y_1^*(\eta) = Y_2^*(\eta)$. Also, Eqs. (22a, b) yield $\omega=1$ and $Y_2'(0) = -Y_1'(0)$. It follows from Eq. (23) that $\beta = -\alpha$, and thus Eq. (25) for the neutral species Y_3^* is indeterminate. The result is that the mass fraction for the neutral species is a constant, that is, $Y_3 = Y_{3e} = Y_{3w}$. These results are in direct contrast to previous results for the correct ternary-mixture. Since the Fick's-law problem is not obtained from the correct multi-component analysis by a step-by-step rational procedure, there is no definitive means for determining a single average diffusion coefficient D_m and Schmidt number $Sc_m \equiv \mu/\rho D_m$. A common approximation is to use Wilke's formula, as explained in **Appendix**. Presumably, Wilke's formula is sensible when one of the species is quite different from the others such that a pseudo-binary mixture is assumed, with one component being the distinct species and the other component being an average of the remaining species. In our example, this would amount to species O for one component and an average of O_2 and N_2 for the other pseudo component. In this case, we

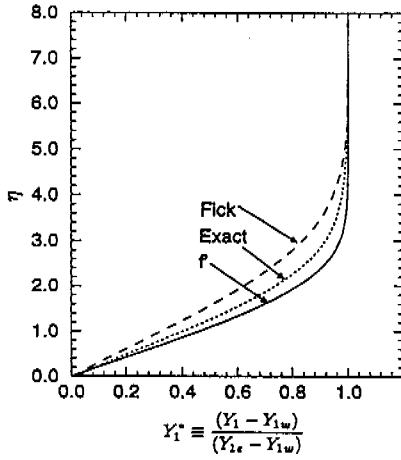
would refer to D_m as D_{2m} in Wilke's formula. A constant average value of Sc_m will be used for further calculations.

6. Numerical Results

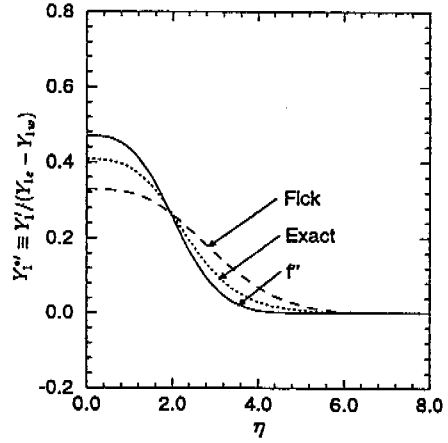
The coupled diffusion equations (19a, b) were integrated numerically by means of a Runge-Kutta scheme with constant values of A , B , Sc_1 , and Sc_2 which were estimated average values across the boundary layer. We will consider the two cases as in **Table 1**. The result was $Y_{2e} = 0.034$ for Case 1, $Y_{2e} = 0.1$ for Case 2, and $Y_{2e} = 0.02$ for Fick's law, for both Case 1 and Case 2. Figures 3a, b and c show Y_1^* , Y_2^* , Y_3^* plotted as a function of η for Case 1. The results $Y_1^* = Y_2^*$ for Fick's law with $Sc_m = 0.37$ are also shown in Figures 3a and b together with the curves $Y_1^* = Y_2^* = f'(\eta)$ which hold for $Sc_m = 1$. The curve for the exact result lies between the Fick's-law curves for Y_1^* , but the exact curve for Y_2^* lies above the two Fick's-law curves. The exact curve for the neutral species Y_3^* shows an overshoot behavior in Fig. 1c. The Fick's-law result is that $Y_3 = Y_{3e} = Y_{3w} = \text{const}$. The curve for the Blasius velocity profile $f'(\eta)$ is shown in Figs 3, 4 for a reference. Corresponding results for the gradients $Y_1^{*'} , Y_2^{*'} , Y_3^{*'}$ are shown in Figs 4a, b and c for Case 1 in **Table 1**. The exact result for $Y_1^{*'}$ lies between the Fick's-law curve and the curve for f'' , whereas the exact curve for $Y_2^{*'}$ lies outside the two Fick's-law curves for $Sc_m = 0.37$ and $Sc_m = 1$. The exact curve for the neutral component $Y_3^{*'}$, shown in Fig. 5c, has an overshoot behavior. The curve for Fick's law is actually indeterminate since $Y_{3e} = Y_{3w}$, but it is shown as the curve $Y_3^{*'}/(Y_{3e} - Y_{3w}) = 0$ since $Y_3^{*'}$ is 0. Differences in the results for Case 1 and Case 2 are shown in Figs. 5a, b and c. The curves for Y_1^* are nearly the same as Fig. 5a, whereas the curves for Y_2^* are

Table 1 Numerical data for two cases (Case 1 and Case 2)

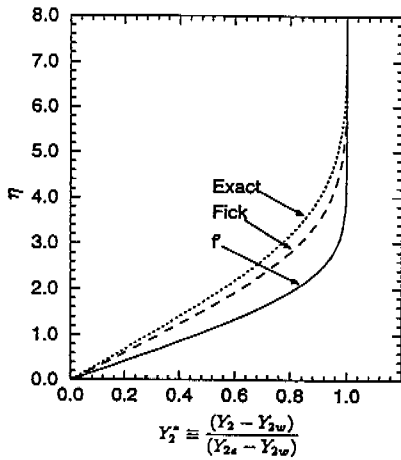
Case	A	B	Sc ₁	Sc ₂	Y _{1e}	Y _{1w}	Y _{2w}
Case 1	-0.63	-0.054	0.81	0.27	0.20	0.18	0.04
Case 2	-0.39	-0.034	0.76	0.36	0.20	0.05	0.17



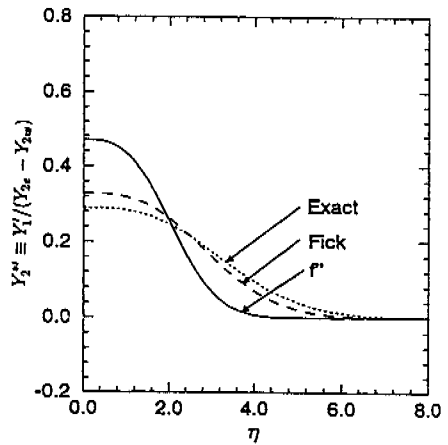
(a) Y_1^* : Oxygen molecule (O_2)



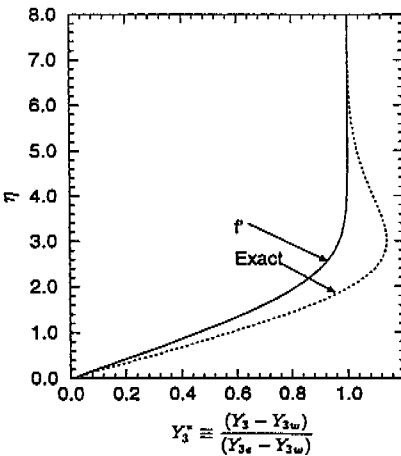
(a) $Y_1^{* \prime}$: Oxygen molecule (O_2)



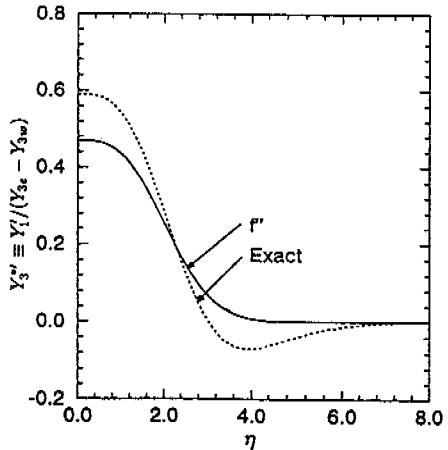
(b) Y_2^* : Oxygen atom (O)



(b) $Y_2^{* \prime}$: Oxygen atom (O)



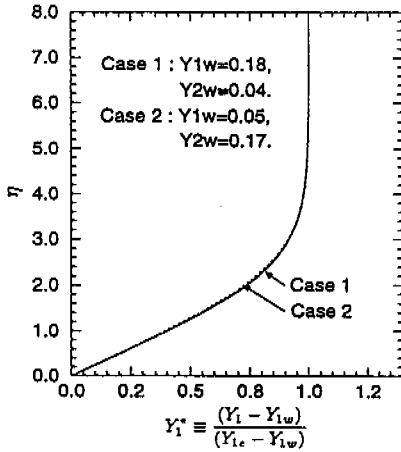
(c) Y_3^* : Nitrogen molecule (N_2)



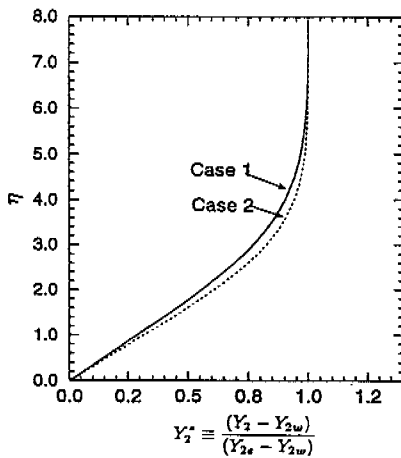
(c) $Y_3^{* \prime}$: Nitrogen molecule (N_2)

Fig. 3 Mass-fraction profiles across the boundary layer

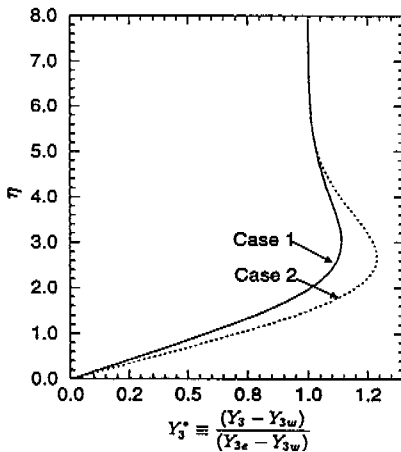
Fig. 4 Mass-fraction gradients across the boundary layer.



(a) For Y_1^* : Oxygen molecule (O_2)



(b) For Y_2^* : Oxygen atom (O)



(c) For Y_3^* : Nitrogen molecule (N_2)

Fig. 5 Comparison of Case 1 and Case 2 for mass fraction.

somewhat different. Curves for the neutral species Y_3^* in Fig. 5c show an overshoot behavior, but are distinctly different. The Fick's-law results are the same as before since the profile functions Y_1^* and Y_2^* depend only on the Schmidt number Sc_m .

7. Concluding Remarks

The mass-diffusion problem for a ternary mixture within a compressible boundary layer on a flat plate has been formulated using the exact constitutive relations stemming from the kinetic theory of gases. Average constant diffusion coefficients were assumed so that the salient features of the ternary-mixture problem could more easily be perceived and calculated, and comparisons were made with the results obtained for the commonly-used assumption of Fick's-law of diffusion. The difference in results for the mass-fraction profiles illustrates the inadequacy of the Fick's law analysis, in spite of its simplicity. These results suggest that chemical reactions and the heat transfer may be in significant error when analyzed within framework of Fick's law of diffusion.

References

Bertin, J. J., Glowinski, R., and Periaux, J., 1989, *Hypersonics, Vols. I and II*, Birkhauser, Boston.

Chapman, S. and Cowling, T. G., 1952, *The Mathematical Theory of Non-Uniform Gases, 2nd Edition*, Cambridge.

Dorrance, W. H., 1962, *Viscous Hypersonic Flow*, McGraw-Hill.

Guy, T. B., 1975, "Correlation of the Probe-induced Molecular Separation Effect in Supersonic Gas Mixtures," *J. Physics D : Applied Physics*, Vol. 8, pp. 2208~2223.

Heimerl, J. M. and Coffee, T. P., 1982, "Results of a Study of Several Transport Algorithms for Premixed, Laminar Steady-State Flames," in *Numerical Methods in Laminar Flame Propagation*, ed. by N. Peters and J. Warnate, Friedr. Vieweg & Sohn, Braunschweig/Weisbaden, pp. 823~836.

Hirschfelder, J. O., Curtiss, C. T., and Bird, R.

B., 1954, *Molecular Theory of Gases and Liquids*, Wiley.

Inger, G. R., 1964, "Highly Nonequilibrium Boundary-layer Flows of a Multicomponent Dissociated Gas Mixture," *Int. J. Heat Mass Transfer*, Vol. 7, pp. 1151~1174.

Kee, R. J., Dixon-Lewis, G., Warnatz, J., Coltrin, M. E., and Miller, J. A., 1993, "A Fortran Computer Code Package for the Evaluation of Gas-phase Multicomponent Transport Properties," Sandian Report SAND 06-8246, UC-401, 1986, Reprinted May.

Rasmussen, M. L., 1994, *Hypersonic Flow*, Chapter 12, Wiley-Interscience.

Taylor, R. and Krishna, R., 1993, *Multicomponent Mass Transfer*, Wiley.

Yoon, B. H. and Rasmussen, M. L., 1996, "Aerodynamic Forces of Elliptic-Cone Derived Waveriders at Hypersonic Velocities," *KSME J.*, Vol. 10, No. 3. pp. 341~350.

Appendix

Physical Properties :

Properties for $O_2(\alpha=1)$, $O(\alpha=2)$, $N_2(\alpha=3)$ are molecular masses,

$$m_\alpha = \frac{W_\alpha}{A_o}, \quad \alpha=1, 2, 3,$$

where

W_α = molecular weight [g(gram mole)⁻¹],

A_o = Avogadro's number,

$$\sigma_1 = 3.62 \times 10^{-8} \text{cm},$$

$$\sigma_2 = 1.46 \times 10^{-8} \text{cm},$$

$$\sigma_3 = 3.76 \times 10^{-8} \text{cm}.$$

Viscosity for Mixture :

The approximation for viscosity according to Wilke (Rasmussen, 1994) is,

$$\mu = \frac{\sum_{\alpha=1}^N \frac{X_\alpha}{\mu_\alpha}}{\sum_{\beta=1}^N X_\beta \Phi_{\alpha\beta}},$$

where $\mu_\alpha = \frac{5}{16} \frac{\sqrt{k_B m_\alpha T}}{\sigma_\alpha^2 \pi}$ and $\Phi_{\alpha\beta} = \frac{1}{\sqrt{8}} \left(1 + \frac{W_\alpha}{W_\beta} \right)^{-1/2} \left[1 + \left(\frac{\mu_\alpha}{\mu_\beta} \right)^{1/2} \left(\frac{W_\beta}{W_\alpha} \right)^{1/4} \right]$.

Mean Binary Diffusion Coefficient :

The average diffusion coefficient for a ternary mixture for use in Fick's law, according to Wilke (Rasmussen, 1994), is

$$D_m = D_{2m} = \frac{1 - X_2}{\frac{X_1}{D_{21}} + \frac{X_3}{D_{23}}}$$