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International Journal of Heat and Mass Transfer 44 (2001) 753–761

International Journal of
HEAT and MASS
TRANSFER

www.elsevier.com/locate/ijhmt

Characterization of energy transport by mass diffusion including an application to elliptic channel flow

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Received 22 July 1999; received in revised form 29 March 2000

Abstract

Energy transport in diffusing systems is studied with special attention devoted to the transport that occurs as a result of mass diffusion, $\sum c_{pk}\vec{j}_k \cdot \nabla T$. Dimensionless parameters are presented for determining the importance of this transport mechanism; as an example of the application to heat and mass transfer, mixing of a binary gas in a heated, elliptic channel flow is studied. It is shown that the energy transport by mass diffusion can be an important transport mechanism which should be considered in non-isothermal systems, e.g. in CVD processes where it has often been neglected. The literature also refers to the divergence of the energy flux by species interdiffusion, $\nabla \cdot \vec{q}^{(d)} = \nabla \cdot \sum h_k\vec{j}_k$. It is pointed out that this term depends on the enthalpy datum states of the species. Therefore, neglecting this term in the energy equation requires that another term also be neglected so that the resulting energy equation is independent of the enthalpy datum states. Neglecting only the divergence of the energy flux by species interdiffusion would be incorrect because the resulting energy equation would then (incorrectly) depend on the enthalpy datum states. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Heat and mass transfer are essential transport mechanisms with broad applications, e.g. in thermal protection, materials processing, combustion, evaporation, etc. Early comprehensive studies were motivated by the need to protect surfaces from the effects of high temperatures generated in thin boundary layers and stagnation regions during reentry. Hartnett and Eckert [1] and Eckert et al. [2,3] studied the complex transport processes in transpiration cooling in boundary layers for flat plate and stagnation flow configurations. Sparrow et al. [4–6] included energy transport due to the Dufour (diffusion-thermo) effect and mass transfer due to thermal diffusion (the Soret effect) in transpiration cooling in stagnation flow; they also studied the effect of buoyancy in a horizontal cylinder configuration. Lees [7] examined chemical reactions in boundary layers with transpiration cooling, where the effects of thermal diffusion were considered to be small; Kendall et al. [8] studied multicomponent transport in boundary layer flow with ablation and chemical reactions; they included the Dufour energy transport mechanism and the Soret mass transfer effect.

Important heat and mass transfer contributions are also present in materials processing where the transport is often elliptic. Mahajan and Wei [9] studied silicon chemical vapor deposition (CVD) in a channel flow including the effects of buoyancy, variable properties, mass-transfer by thermal diffusion and energy

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PII: S0017-9310(00)00135-6

Nomenclature

D	substantial derivative
$\mathscr{D}$	binary diffusion coefficient (cm^2/s)
H	height of channel (1 cm in present study) (cm)
L_{ch}	characteristic length (cm)
Le	Lewis number $(=\alpha/\mathscr{D}=Sc/Pr)$
Pe_{M}	Peclet number for mass transfer $(=u_{\mathrm{ch}}L_{\mathrm{ch}}/\mathscr{D})$
Pr	Prandtl number $(=\nu/\alpha=c_p\mu/k)$
Sc	Schmidt number $(=\nu/\mathscr{D})$
T	temperature (K)
Y_k	mass fraction of species k
c_p	mixture specific heat at constant pressure $(=\Sigma\, c_{pk}Y_k)$ (erg/g K)
c_{pk}	specific heat at constant pressure of species k (erg/g K)
h	enthalpy of mixture $(=\Sigma\, h_kY_k)$ (erg/g K)
h_k	enthalpy of species k (erg/g K)
$\vec{j}_k$	mass diffusion flux of species k (g/cm^2 s)
k	mixture thermal conductivity (erg/cm s K)
$\vec{q}$	energy flux (erg/cm^2 s)
$\vec{q}^{(d)}$	energy flux due to species interdiffusion $(=\Sigma\, h_k\vec{j}_k)$ (erg/cm^2 s)
q_{ref}	reference conduction heat flux $(=k_{\mathrm{mix}}(T_{\mathrm{upper}}-T_{\mathrm{lower}})/H)$ (erg/cm^2 s)
$\dot{r}_k$	mass production rate of species k due to homogeneous chemical reaction (g/cm^3 s)
$\vec{u}$	mass average velocity vector (cm/s)
u_{ch}	characteristic velocity (cm/s)
u, v	axial and transverse components of velocity, respectively (cm/s)
x, y	axial, transverse coordinates (cm)
Greek symbols	
α	mixture thermal diffusivity (cm^2/s)
μ	mixture dynamic viscosity (g/cm s)
ν	mixture kinematic viscosity $(=\mu/\rho)$ (cm^2/s)
ρ	mixture density (g/cm^3)
Subscripts	
lower	evaluated at lower surface of channel ($y=0$)
mix	evaluated at fully mixed conditions downstream of splitter plate
nd	non-dimensional
l, u	evaluated at lower and upper surfaces of channel, respectively
ref	reference quantity
upper	evaluated at upper surface of channel ($y=H$)

transport by the Dufour effect. Kleijn [10,11] studied CVD in stagnation flow and channel flow reactor geometries including the Soret and Dufour effects. Weaver and Viskanta [12] examined heat and mass transport in a binary gas system in an enclosure including the Soret and Dufour effects and species interdiffusion. Evans and Greif [13] studied the multicomponent mass transfer in a tubular CVD reactor with surface chemical reactions. Kuijlaars et al. [14] studied the CVD of tungsten in a stagnation flow reactor including multicomponent diffusion and the Soret and Dufour effects. In the analysis of elliptic CVD problems, the energy transport by mass diffusion, $\sum c_{pk}\vec{j}_k\cdot\nabla T$ (Eq. (2b)) has often been omitted. The present study considers the energy transport by mass diffusion in an elliptic system and derives dimensionless parameters to establish its importance. We note that the energy transport by mass diffusion is not the Dufour (diffusion-thermo) effect; this effect, along with the mass diffusion due to the temperature gradient (Soret effect), are not included here but both have been studied by Sparrow et al. [4], Mahajan and Wei [9], and Kleijn [11].

2. Analysis

Heat and mass transport in non-isothermal conditions requires that the energy equation be solved. One form of the energy equation (neglecting viscous dissipation, pressure and body force work, Dufour effect, and internal heat generation terms) for multicomponent ideal solutions [15] is,

$$\rho\,\frac{\mathrm{D}h}{\mathrm{D}t}+\nabla\cdot\sum h_k\vec{j}_k=\nabla\cdot(k\nabla T). \tag{1}$$

Approximations to this form of the energy equation must be made very carefully, and a detailed examination is presented in Appendix A. A form of the energy equation that is often more convenient (which is obtained by making the same assumptions that were invoked to derive Eq. (1)) is:

$$\rho c_p\,\frac{\mathrm{D}T}{\mathrm{D}t}+\sum\vec{j}_k\cdot\nabla h_k=\nabla\cdot(k\nabla T)-\sum h_k\dot{r}_k \tag{2a}$$

or when the enthalpy h_k of species k depends on temperature only ($\nabla h_k=c_{pk}\nabla T$, [16]):

$$\rho c_p \frac{\partial T}{\partial t} + \left(\rho c_p \vec{u} + \sum c_{pk}\vec{j}_k\right)\nabla T$$
$$= \nabla \cdot (k\nabla T) - \sum h_k \dot{r}_k. \tag{2b}$$

The term $pc_p\vec{u} \cdot \nabla T$ is the well-known energy transport by convection. The term $(\sum c_{pk}\vec{j}_k) \cdot \nabla T$ is the energy transport by mass diffusion (we note that this differs from the term $\nabla \cdot \vec{q}^{(d)}$, where $\vec{q}^{(d)} = \sum h_k\vec{j}_k$, which is denoted as species interdiffusion in Bird et al. [15], and is discussed in Appendix A; Bird et al. use $\vec{q}$ to denote the sum of the energy fluxes due to conduction, interdiffusion, and the Dufour effect). We now study the importance of the contribution of the energy transport by mass diffusion in gas mixtures and begin with a scaling analysis of the energy equation.

2.1. Scaling analysis

We consider a steady flow of a non-isothermal binary ideal gas system; we neglect chemical reactions and consider ordinary concentration gradient diffusion only. Note that in general $\vec{j}_k$ can include thermal diffusion as well as ordinary concentration gradient diffusion but in this study thermal diffusion is neglected. We utilize Eq. (2b) with Fick's law, $\vec{j}_k = -\rho\mathscr{D}\nabla Y_k$, to obtain,

$$\rho\left[c_p\vec{u} - \mathscr{D}(c_{p1} - c_{p2})\nabla Y_1\right] \cdot \nabla T = \nabla \cdot (k\nabla T). \tag{3}$$

Mills [17] has presented the boundary layer form of the energy equation including the viscous dissipation and pressure work terms in a form analogous to Eq. (3). For constant thermal conductivity, k, Eq. (3) can be written as:

$$\left[c_p\vec{u} - \mathscr{D}(c_{p1} - c_{p2})\nabla Y_1 - \frac{k\nabla}{\rho}\right] \cdot \nabla T = 0. \tag{4}$$

The relative importance of energy transport by mass diffusion can be determined by examining the ratios of the mass diffusion transport term to the convection and conduction transport terms, respectively, in Eq. (4), i.e.:

$$\frac{\mathscr{D}(c_{p1} - c_{p2})\nabla Y_1}{c_p\vec{u}} \tag{5}$$

and

$$\frac{\rho\mathscr{D}(c_{p1} - c_{p2})\nabla Y_1}{k\nabla}. \tag{6}$$

More general ratios may be obtained utilizing Eqs. (2a) and (2b) or Eq. (3). Non-dimensional parameters can be obtained from the ratios given by Eqs. (5) and (6). Eq. (5) leads to:

$$\frac{(c_{p1} - c_{p2})}{c_p}\frac{\mathscr{D}}{u_{\mathrm{ch}}L_{\mathrm{ch}}} = \frac{(c_{p1} - c_{p2})}{c_p}\frac{1}{Pe_{\mathrm{M}}} \tag{7}$$

where Pe_{M} is the Peclet number for mass transfer, $u_{\mathrm{ch}}L_{\mathrm{ch}}/\mathscr{D}$. Eq. (6) leads to:

$$\frac{(Pr_1 - Pr_2)}{Sc} = \left(\frac{1}{Le_1} - \frac{1}{Le_2}\right). \tag{8}$$

3. Example problem

A binary gas mixture flowing in a heated channel is studied to illustrate the transport phenomena. The two species (H_2 and N_2) entering the channel are separated by a splitter plate (Fig. 1); the lower and upper channel surfaces (at $y = 0$ and 1 cm, respectively) are isothermal and are at different temperatures. At the downstream end of the splitter plate, mixing of the species and heat transfer between the channel surfaces and the gas mixture takes place. The effects of buoyancy are not included in this study (the gravitational term in the momentum equation is neglected); however, the effects of variable fluid properties are included.

3.1. Results

In the section of the channel that includes the splitter plate, H_2 enters the upper portion of the channel ($y > 0.5$ cm) at a temperature of 310 K which equals both the temperature of the upper channel surface and the temperature of the upper surface of the 5 cm long splitter plate; N_2 enters the lower portion of the channel ($y < 0.5$ cm) at a temperature of 300 K which equals both the temperature of the lower channel surface and the temperature of the lower surface of the splitter plate. There is essentially no heat transfer between the channel surfaces and the gas streams throughout the inlet region containing the splitter plate ($0 < x < 5$ cm). Both gas streams have uniform velocity at the inlet (100 cm/s); both gas streams attain fully developed parabolic velocity profiles with the same average velocity of 100 cm/s (maximum velocity of 150 cm/s) in the inlet region (the pressure is 100 Torr; the Reynolds numbers based on the channel half-height of 0.5 cm are approximately 41 for N_2 in the lower region and 6 for H_2 in the upper region; the Schmidt numbers are approximately 0.2 in an H_2–N_2 mixture containing a small amount of H_2 and 1.4 in a H_2–N_2 mixture containing a small amount of N_2; the Peclet number, Pe_{M}, based on the channel height of 1 cm is approximately 16). The numerical solution including the methodology and convergence criteria that were used to solve the coupled equations were dis-

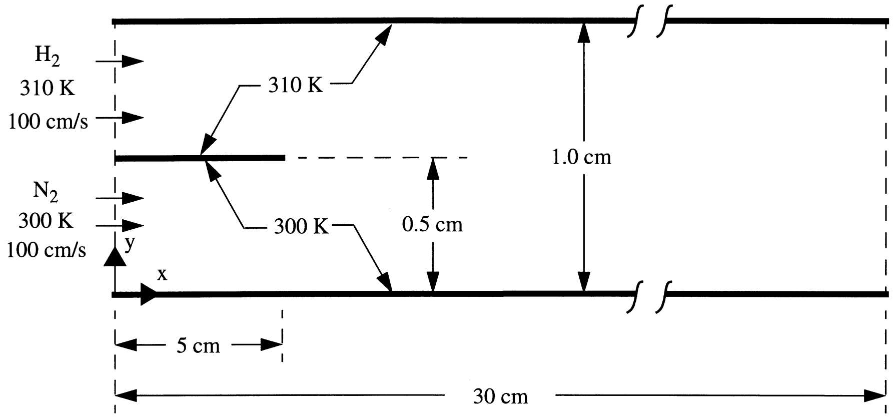

Fig. 1. Geometry and boundary conditions (not to scale).

cussed by Evans and Greif [13]. Calculations were carried out with underrelaxation factors of 0.3 for obtaining velocities and 0.2 for temperatures and species. The grid system consisted of 20 axial by 30 lateral control volumes in the splitter region (before mixing, $0 < x < 5$ cm), 30 axial by 30 lateral in the first 5 cm downstream of the splitter plate, and 50 axial by 30 lateral control volumes in the subsequent 20 cm. Iterations were continued until variations in the dependent variables were less than 1–2%, where these variations were calculated over an interval of several thousand iterations. Changes in the number of grids by 20% resulted in changes in the heat flux on the lower surface by less than 4% in the region near the splitter plate (where there is a step change in the surface temperature) and less than 1% further downstream.

Downstream of the splitter plate ($x > 5$ cm), the gases mix and heat is transferred from the upper surface through the gas mixture to the lower surface. At the upper surface, for x somewhat larger than 5 cm, there is a larger conduction heat flux than at the lower surface (Fig. 2, where the magnitudes of the heat fluxes are shown). This is due to the predominance of H_2 near the upper surface, while at the lower surface the predominant species is N_2 ($k_{H_2}/k_{N_2} = 7.2$ at 305 K). The conduction fluxes approach the same value as the flow develops downstream and the mixture becomes uniform ($X_{H_2} = 0.492, X_{N_2} = 0.508$) for $x > 20$ cm. The non-dimensional heat flux shown in Fig. 2 is defined as:

$$q_{\mathrm{nd}_{\mathrm{l,u}}} = \frac{\left(k\frac{\partial T}{\partial y}\right)\Big|_{\mathrm{l,u}}}{q_{\mathrm{ref}}} \tag{9}$$

where $q_{\mathrm{ref}} = k_{\mathrm{mix}}(T_{\mathrm{upper}} - T_{\mathrm{lower}})/H$.

Immediately downstream of the splitter plate ($5 \leq x \leq 6$ cm), the temperature of the gas in the lower region of the channel remains closer to the lower surface temperature as compared to the gas temperature near the upper surface, which deviates more from the upper surface temperature (cf. the solid curve in Fig. 3 which shows the temperature profile across the channel at $x = 5.5$ cm; also cf. the isotherms in Fig. 4). This effect is due to the predominance of lower conductivity N_2 gas in the lower region of the channel compared with the higher conductivity H_2 gas in the upper region of the channel. The upper surface conduction heat flux reaches a maximum (Fig. 2) at $x \approx 6$ cm (approximately 1 cm downstream of the end of the splitter plate). As the gases continue to mix (Fig. 5) the thermal conductivity decreases at the upper surface as the smaller conductivity N_2 diffuses into this region; near the lower surface the thermal conductivity increases

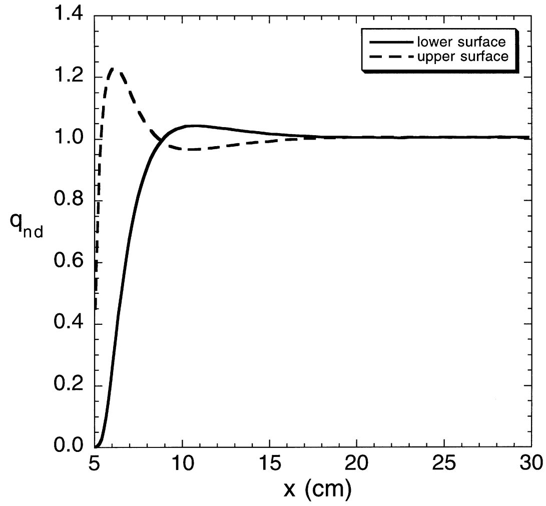

Fig. 2. Non-dimensional conduction heat fluxes $(k(\frac{\partial T}{\partial y})|_{\mathrm{l,u}}/q_{\mathrm{ref}})$ at lower (solid line) and upper (dashed line) surfaces of the channel downstream of the splitter plate.

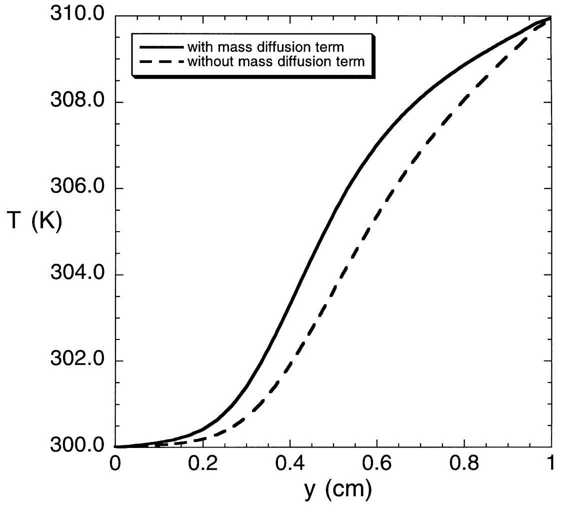

Fig. 3. Transverse (y) temperature profiles just downstream (at $x = 5.5$ cm) of the splitter plate with (solid line) and without (dashed line) the energy transport by mass diffusion term ($\sum c_{pk}\vec{j}_k \cdot \nabla T$).

downstream as the larger conductivity H_2 diffuses into this region.

On both sides of the splitter plate the velocities (not shown) are 0 at the surfaces ($y = 0.5+$, $0.5-$ cm). Immediately downstream of and near the splitter plate the velocities increase; the lower kinematic viscosity of N_2 (1/7th of H_2) results in larger velocities below the centerline ($y = 0.5$ cm). In general, the effects of composition, geometry, and heat transfer affect the velocity distribution; in particular, the changes in the density and viscosity due to mixing are most important in determining the change in the velocity distribution for this problem because changes due to the temperature difference are small due to the small temperature difference of 10 K.

As noted above, far downstream the composition becomes uniform (not shown). The isotherms are almost uniformly separated in the y direction (Fig. 4) and the velocity distribution attains an almost fully developed parabolic profile (not shown).

The relative importance of the energy transport by mass diffusion, $\sum c_{pk}\vec{j}_k \cdot \nabla T$, to conduction is now considered by first utilizing Eqs. (4), (6) and (8), i.e.:

$$\begin{aligned}\frac{\rho\mathscr{D}(c_{p1}-c_{p2})\nabla Y_1}{k\nabla} &\sim \frac{\rho\mathscr{D}(c_{p\mathrm{H}_2}-c_{p\mathrm{N}_2})}{(k/H)}\,\frac{(Y_{\mathrm{H}_2,\mathrm{top}}-Y_{\mathrm{H}_2,\mathrm{bot}})_{x=0}}{H}\\ &\sim\left(\frac{1}{Le_{\mathrm{H}_2}}-\frac{1}{Le_{\mathrm{N}_2}}\right)\left(Y_{\mathrm{H}_2,\mathrm{top}}-Y_{\mathrm{H}_2,\mathrm{bot}}\right)_{x=0}\\ &\sim(6.5-0.5)\times 1 = 6.0.\end{aligned} \tag{10}$$

The relative importance of the energy transport by mass diffusion to the contribution by convection is (Eqs. (4), (5) and (7)) obtained from:

$$\begin{aligned}\frac{\mathscr{D}(c_{p1}-c_{p2})\nabla Y_1}{c_p\vec{u}} &\sim \left(\frac{\mathscr{D}}{vH}\right)\left(\frac{c_{p\mathrm{H}_2}-c_{p\mathrm{N}_2}}{c_p}\right)\big(Y_{\mathrm{H}_2,\mathrm{top}}\\ &\quad - Y_{\mathrm{H}_2,\mathrm{bot}}\big)_{x=0}\sim 0.5\times 7\times 1\\ &= 3.5.\end{aligned} \tag{11}$$

The evaluation of these parameters indicates the importance of energy transport by mass diffusion and the need to consider this transport mechanism in systems or phenomena involving non-isothermal mixtures. In evaluating Eq. (11), based on numerical results, $v/u \sim$

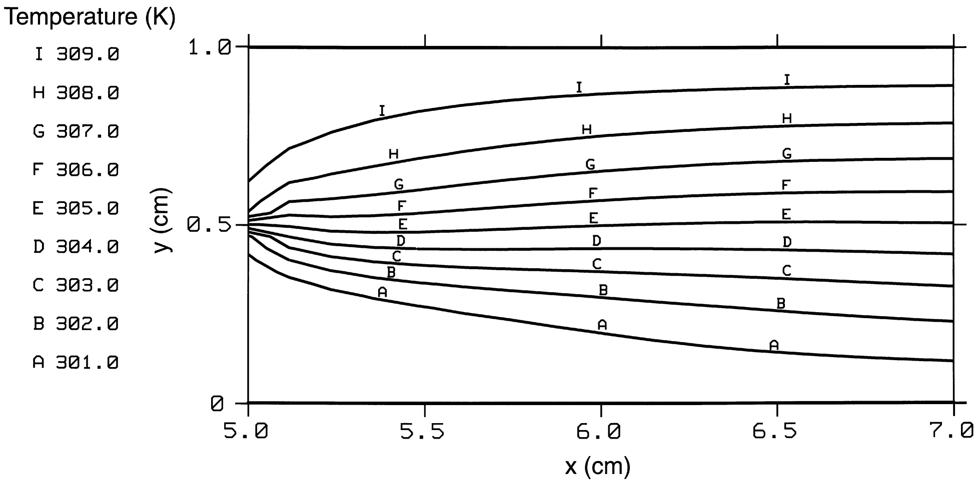

Fig. 4. Temperature field (isotherms) in a region immediately downstream of the splitter plate ($5.0 \leq x \leq 7.0$ cm).

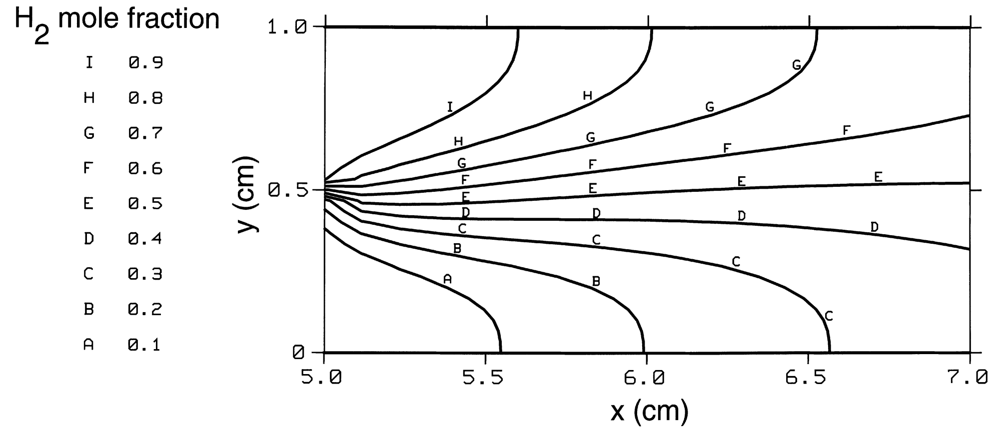

Fig. 5. Concentration field of H_2 (contour lines of constant H_2 mole fraction) in a region immediately downstream of the splitter plate ($5.0 \leq x \leq 7.0$ cm).

$v_{ch}/u_{ch} \sim 0.1$ and the mixture specific heat, $c_p = Y_{H_2}c_{pH_2} + Y_{N_2}c_{pN_2}$, was taken to be the average value for mixed conditions and, as mentioned previously, $Pe_M = u_{ch}L_{ch}/\mathscr{D} \approx 16$.

The effects of neglecting the energy transport by mass diffusion, $\sum c_{pk}\vec{j}_k \cdot \nabla T$, on the gas temperature profiles and the heat transfer at the upper and lower surfaces are shown in Figs. 3 and 6. In Fig. 6, at the upper surface, the dimensionless surface heat flux, q_{nd}, is larger when the energy transport by mass diffusion is neglected (compare large-dashed and dash-dotted lines); but at the lower surface the surface heat flux is smaller when this transport is neglected (compare solid and short-dashed lines). Note that far downstream ($x > 20$ cm) the composition becomes uniform, all four curves of Fig. 6 merge, and the energy transport by mass diffusion becomes 0. At $x = 5.5$ cm, neglecting the energy transport by mass diffusion results in lower gas temperature (Fig. 3). Since the energy transport by mass diffusion goes to 0 far downstream, the temperature profiles, with and without this energy transport mechanism, coincide downstream (not shown).

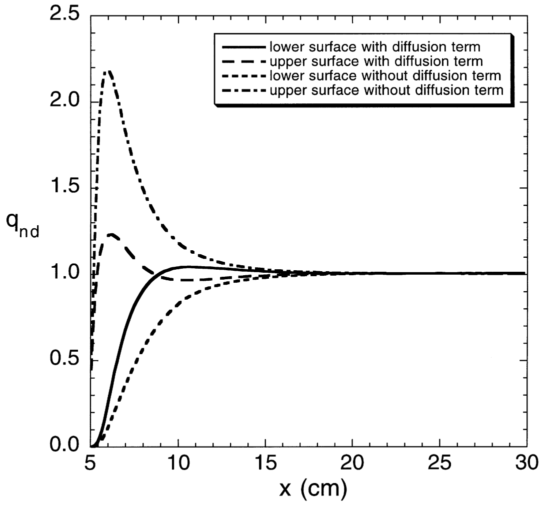

Fig. 6. Non-dimensional conduction heat fluxes $(k(\frac{\partial T}{\partial y})|_{l,u}/q_{ref})$ at lower (solid and short-dashed lines) and upper (large-dashed and dash-dotted lines) surfaces of the channel downstream of the splitter plate with (solid and large-dashed lines) and without (short-dashed and dash-dotted lines) the energy transport by mass diffusion term ($\sum c_{pk}\vec{j}_k \cdot \nabla T$).

4. Conclusions

The energy transport in diffusing systems is studied with special attention devoted to the energy transport by mass diffusion, $\sum c_{pk}\vec{j}_k \cdot \nabla T$. Dimensionless parameters are derived and evaluated in the context of diffusion in non-isothermal channel flow to ascertain the importance of the energy transport by mass diffusion.

The literature refers to the divergence of the energy transport by species interdiffusion, $\nabla \cdot \vec{q}^{(d)} = \nabla \cdot \sum h_k\vec{j}_k$, which depends on the enthalpy datum states of the species. Simply omitting the divergence of the energy transport by species interdiffusion then results in an energy equation that depends on the enthalpy datum states and is therefore incorrect. Omitting the divergence of the energy transport by species interdiffusion and also omitting the term $\sum h_k\nabla \cdot \vec{j}_k$ does result in an energy equation which is independent of enthalpy datum states; however, the accuracy of the resulting equation must be examined for the phenomena/system being studied.

A non-isothermal binary ideal gas flow in a channel is studied to illustrate the transport phenomena and the effect of the energy transport by mass diffusion term, $\sum c_{pk}\vec{j}_k \cdot \nabla T$, on the temperature profiles and the heat transfer. It is shown that the energy transport by mass diffusion is an important transport mechanism, which should considered to be in non-isothermal systems.

Acknowledgements

This work was supported by the United States Department of Energy under contract DE-AC04-94AL85000. We are also indebted to Rich Larson for his detailed comments and recommendations.

Appendix A

Eq. (1) is repeated here:

$$\rho \frac{\mathrm{D}h}{\mathrm{D}t} + \nabla \cdot \sum h_k\vec{j}_k = \nabla \cdot (k\nabla T). \tag{A1}$$

We examine this form of the energy equation and in particular the term $\nabla \cdot \sum h_k\vec{j}_k = \nabla \cdot \vec{q}^{(d)}$. Bird et al. [15] (p. 566) have denoted $\vec{q}^{(d)}$ as the energy flux caused by interdiffusion for a fluid containing n species. Expanding the first term on the left-hand side of Eq. (A1), where $h = \Sigma\, h_k Y_k$ and $c_p = \Sigma\, c_{pk} Y_k$, yields:

$$\rho \sum Y_k \frac{\mathrm{D}h_k}{\mathrm{D}t} + \rho \sum h_k \frac{\mathrm{D}Y_k}{\mathrm{D}t} + \nabla \cdot \sum h_k\vec{j}_k = \nabla \cdot (k\nabla T) \tag{A2}$$

or

$$\rho c_p \frac{\mathrm{D}T}{\mathrm{D}t} + \rho \sum h_k \frac{\mathrm{D}Y_k}{\mathrm{D}t} + \nabla \cdot \sum h_k\vec{j}_k = \nabla \cdot (k\nabla T). \tag{A3}$$

Lavine [18] has pointed out that Eqs. (A1), (A2) and (A3) contain terms (e.g. $\nabla \cdot \sum h_k\vec{j}_k$ and $\rho\mathrm{D}h/\mathrm{D}t$ in Eq. (A1)) whose values change if different constants are added to the enthalpies of the individual species. For example, if the temperature datum at which the enthalpies of the species are assigned to be 0 is changed, then in general these terms (e.g. $\nabla \cdot \sum h_k\vec{j}_k$ and $\rho\mathrm{D}h/\mathrm{D}t$) would have different values. However, for completeness, we note that there is a special case, i.e. when the same constant, c, is added to the enthalpy of each species; for this case these terms would have the same values. In detail:

$$\begin{aligned}\rho \frac{\mathrm{D}h}{\mathrm{D}t} &= \rho \sum Y_k \frac{\mathrm{D}h_k}{\mathrm{D}t} + \rho \sum h_k \frac{\mathrm{D}Y_k}{\mathrm{D}t}\\ &= \rho \sum Y_k \frac{\mathrm{D}(h_k + c)}{\mathrm{D}t} + \rho \sum (h_k + c)\frac{\mathrm{D}Y_k}{\mathrm{D}t}\\ &= \rho \frac{\mathrm{D}h}{\mathrm{D}t}.\end{aligned} \tag{A4}$$

Note that $\Sigma\, Y_k = 1$ so that $(\mathrm{D}/\mathrm{D}t)\Sigma\, Y_k = 0$. For the other term in Eq. (A3) that is cited above,

$$\begin{aligned}\nabla \cdot \sum h_k\vec{j}_k &= \sum h_k \nabla \cdot \vec{j}_k + \sum \vec{j}_k \cdot \nabla h_k\\ &= \sum (h_k + c)\nabla \cdot \vec{j}_k + \sum \vec{j}_k \cdot \nabla(h_k + c)\\ &= \nabla \cdot \sum h_k\vec{j}_k.\end{aligned} \tag{A5}$$

Note that $\sum \nabla \cdot \vec{j}_k = \nabla \cdot \sum \vec{j}_k = 0$.

Similarly, in the energy Eqs. (2a) and (2b) the same constant can be added to the enthalpy of each species without affecting the values of the terms in those equations (note that $\sum \dot{r}_k = 0$). Furthermore, if there are no chemical reactions, the energy Eqs. (2a) and (2b) only contain the derivatives of the species enthalpies, and then enthalpy datum states would not affect those equations; i.e. one could then even add different arbitrary constants to the enthalpies of each species k and (in the absence of chemical reactions) not affect Eq. (2a) or Eq. (2b). A comment on enthalpy datum states may be helpful. Considered separately, the enthalpies of elements or chemical species are arbitrary. However, in a mixture or solution in which chemical reactions can occur, the enthalpies of the individual species are not arbitrary but must be related through heats of formation to the enthalpies of their constituent elements or species.

A.1. Neglecting terms in the energy equation

As noted above in Eq. (A1) both the term $\nabla \cdot \sum h_k\vec{j}_k$ and the term $\rho\mathrm{D}h/\mathrm{D}t$ depend, in general, on the enthalpy datum states of the species but in the absence of chemical reactions the sum of these terms is independent of the datum states [18]. In detail:

$$\begin{aligned}&\rho \sum Y_k \frac{\mathrm{D}(h_k + c_k)}{\mathrm{D}t} + \rho \sum (h_k + c_k)\frac{\mathrm{D}Y_k}{\mathrm{D}t}\\ &\quad= \rho \sum Y_k \frac{\mathrm{D}h_k}{\mathrm{D}t} + \rho \sum h_k \frac{\mathrm{D}Y_k}{\mathrm{D}t}\\ &\qquad + \rho \sum c_k \frac{\mathrm{D}Y_k}{\mathrm{D}t}\\ &\quad= \rho \frac{\mathrm{D}h}{\mathrm{D}t} + \rho \sum c_k \frac{\mathrm{D}Y_k}{\mathrm{D}t}\end{aligned} \tag{A6}$$

and

$$\nabla\cdot\sum(h_k+c_k)\vec{j}_k=\nabla\cdot\sum h_k\vec{j}_k+\sum c_k\nabla\cdot\vec{j}_k \tag{A7}$$

which added together yield:

$$\begin{aligned}&\rho\sum Y_k\frac{\mathrm{D}(h_k+c_k)}{\mathrm{D}t}+\rho\sum(h_k+c_k)\frac{DY_k}{Dt}\\&+\nabla\cdot\sum(h_k+c_k)\vec{j}_k\\&\quad=\rho\frac{\mathrm{D}h}{\mathrm{D}t}+\nabla\cdot\sum h_k\vec{j}_k+\sum c_k\left(\rho\frac{\mathrm{D}Y_k}{\mathrm{D}t}\right.\\&\quad\left.+\nabla\cdot\vec{j}_k\right).\end{aligned} \tag{A8}$$

From the species continuity equation:

$$\rho\frac{\mathrm{D}Y_k}{\mathrm{D}t}=-\nabla\cdot\vec{j}_k+\dot{r}_k, \tag{A9}$$

we see the third term on the right-hand side of Eq. (A8) is 0 in the absence of chemical reactions. Thus, if there are no chemical reactions then the enthalpies of the species are arbitrary, the datum-state is arbitrary, and the *sum* of the first two terms on the right-hand side of Eq. (A8) is independent of the datum states. As noted above, if there are chemical reactions the enthalpies are not arbitrary but must be related through the heats of formation.

Thus, neglecting the divergence of the energy flux caused by species interdiffusion $\nabla\cdot\vec{q}^{(d)}$ $(=\nabla\cdot\sum h_k\vec{j}_k)$ *requires that the term* $\rho\,\Sigma\,h_k\mathrm{D}Y_k/\mathrm{D}t$ *also be neglected* so that the resulting energy equation be independent of the enthalpy datum states. In summary, if only the term $\nabla\cdot\sum h_k\vec{j}_k$ is neglected, but the term $\rho\,\Sigma\,h_k\mathrm{D}Y_k/\mathrm{D}t$ is included, then this resulting form of the energy equation is incorrect because it depends on the enthalpy datum states and the results would also incorrectly depend on the enthalpy datum states.

For completeness, we note that the right-hand side of Eq. (A1) that only contains the conduction term is sometimes written in another form:

$$\begin{aligned}&\rho\frac{\mathrm{D}h}{\mathrm{D}t}+\nabla\cdot\sum h_k\vec{j}_k\\&\quad=\nabla\cdot\left(\frac{k}{c_p}\nabla h\right)-\nabla\cdot\left(\frac{k}{c_p}\sum h_k\nabla Y_k\right)\end{aligned} \tag{A10}$$

since $\nabla h=\nabla\,\Sigma\,h_kY_k$. Note that when $\vec{j}_k=-\rho\mathrm{D}\nabla Y_k$ and $Sc=\nu/\mathrm{D}=Pr=\mu c_p/k$ (Lewis number equal to 1), Eq. (A10) becomes:

$$\rho\frac{\mathrm{D}h}{\mathrm{D}t}=\nabla\cdot\left(\frac{k}{c_p}\nabla h\right). \tag{A11}$$

The divergence of the energy flux by species interdiffusion on the left-hand side of Eq. (A10) has cancelled the second term on the right-hand side of the equation.

Eqs. (1), (2a), (2b), (A2), (A3) and (A10) are all equivalent; e.g. substituting the species continuity Eq. (A9) into Eq. (A3) yields:

$$\begin{aligned}&\rho c_p\frac{\mathrm{D}T}{\mathrm{D}t}+\nabla\cdot\sum h_k\vec{j}_k-\sum h_k\nabla\cdot\vec{j}_k\\&\quad=\nabla\cdot(k\nabla T)-\sum h_k\dot{r}_k\end{aligned} \tag{A12}$$

which reduces to Eq. (2a). From the form of the energy equation given in Eq. (A12), we can see that when the divergence of the species interdiffusion flux$(\nabla\cdot\vec{q}^{(d)}=\nabla\cdot\sum h_k\vec{j}_k)$ is neglected, the term $\sum h_k\nabla\cdot\vec{j}_k$ is still present which can depend on the reference state. Thus, omitting one of these terms but keeping the other is incorrect as discussed above.

References

[1] J.P. Hartnett, E.R.G. Eckert, Mass-transfer cooling in a laminar boundary layer with constant fluid properties, Trans. ASME 79 (1957) 247–254.

[2] E.R.G. Eckert, A.A. Hayday, W.J. Minkowycz, Heat transfer, temperature recovery and skin friction on a flat plate with hydrogen release into a laminar boundary layer, Int. J. Heat Mass Transfer 4 (1961) 17–29.

[3] E.R.G. Eckert, W.J. Minkowycz, E.M. Sparrow, W.E. Ibele, Heat transfer and friction in two-dimensional stagnation flow of air with helium injection, Int. J. Heat Mass Transfer 6 (1963) 245–249.

[4] E.M. Sparrow, W.J. Minkowycz, E.R.G. Eckert, Diffusion-thermo effects in stagnation-point flow of air with injection of gases of various molecular weights into the boundary layer, AIAA J. 2 (1964) 652–659.

[5] E.M. Sparrow, W.J. Minkowycz, E.R.G. Eckert, W.E. Ibele, The effect of diffusion thermo and thermal diffusion for helium injection into plane and axisymmetric stagnation flow of air, J. Heat Transfer Trans. ASME Series C 86 (1964) 311–319.

[6] E.M. Sparrow, W.J. Minkowycz, E.R.G. Eckert, Transpiration-induced buoyancy and thermal diffusion–diffusion thermo in a helium–air free convection boundary layer, J. Heat Transfer Trans. ASME Series C 86 (1964) 508–514.

[7] L. Lees, Convective heat transfer with mass addition and chemical reactions, in: Third AGARD Colloquium on Combustion and Propulsion, Pergamon Press, New York, 1959.

[8] R.M. Kendall, R.A. Rindal, E.P. Bartlett, A multicomponent boundary layer chemically coupled to an ablating surface, AIAA J. 5 (1967) 1063–1071.

[9] R.L. Mahajan, C. Wei, Buoyancy, Soret, Dufour, and variable property effects in silicon epitaxy, J. Heat Transfer, Trans. ASME 113 (1991) 688–695.

[10] C.R. Kleijn, On the modelling of transport phenomena in CVD reactors and its use in reactor design and process optimization, Thin Solid Films 206 (1991) 47–53.

[11] C.R. Kleijn, Transport phenomena in chemical vapor deposition reactors, Ph.D. thesis, Delft University of Technology, 1991.

[12] J.A. Weaver, R. Viskanta, Natural convection due to horizontal temperature and concentration gradients 2. Species interdiffusion, Soret and Dufour effects, Int. J. Heat Mass Transfer 34 (1991) 3121–3133.

[13] G. Evans, R. Greif, A two-dimensional model of the chemical vapor deposition of silicon nitride in a low-pressure hot-wall reactor including multicomponent diffusion, Int. J. Heat Mass Transfer 37 (1994) 1535–1543.

[14] K.J. Kuijlaars, C.R. Kleijn, H.E.A. van den Akker, Simulation of selective tungsten chemical vapour deposition, Mater. Sci. Semiconductor Processing 1 (1998) 43–54.

[15] R.B. Bird, W.E. Stewart, E.N. Lightfoot, in: Transport Phenomena, Wiley, New York, 1960, p. 562.

[16] P.A. Libby, F.A. Williams (Eds.), Turbulent Reacting Flows, Topics in Applied Physics, 44, Springer, New York, 1980, p. 10.

[17] A.F. Mills, Mass Transfer Supplement to Heat Transfer, 2nd ed., Prentice Hall, New Jersey, 1999.

[18] A.G. Lavine, personal communication, 1996.