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Extended Graetz problem accompanied by Dufour and Soret effects

R.M.L. Coelho, A. Silva Telles *

Curso de Pós-Graduação em Tecnologia de Processos Químicos e Bioquímicos (TPQB), Departamento de Engenharia Química, Escola de Química, Bloco E, Centro de Tecnologia, Universidade Federal do Rio de Janeiro, Cep 21949-900, Rio de Janeiro, RJ, Brazil

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Abstract

Simultaneous heat and mass transfer between parallel plates are analyzed taking into account the Soret and Dufour effects. Both heat and mass transport are examined considering conduction in the axial and transverse directions plus longitudinal advection. The equations differ from the classical heat and mass transfer ones in considering the effect of the temperature gradient upon the mass flux, and conversely the effect of the concentration gradient upon heat flux, in accordance with the dictates of thermodynamics of irreversible processes. The special problems solved evaluate the effect of an imposed temperature difference between the confining walls upon the solute concentration distribution of a multisolute which diffuses against the concentration gradient forced by the prevailing temperature gradient. Details and numerical results are presented only for binary solutions.

The asymptotic concentration difference, for a specified temperature difference, depends on the Soret and Dufour coefficients. The approach to the asymptotes is determined by the complete solution of the governing equations. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Graetz problem; Dufour and Soret effects; Heat and mass transfer; Irreversible phenomena

1. Introduction

Simultaneous heat, mass, and momentum transport are governed by constitutive equations determining the diffusive fluxes as functions of the gradients of temperature, concentration, and velocity. As separate laws these are due to Fourier, Fick, and Newton. If the fluid obeys these three laws, then aside from the temperature and composition dependence of physical properties, the energy and mass balance equations are independent and the solution of heat and mass transfer problems can be obtained independently of each other.

Interference between heat and mass transport, at the level of constitutive equations, has been observed, and the linear theory of non-equilibrium thermodynamics has been formulated as a constitutive theory capable of fully expressing the dependence of all fluxes as a function of all thermodynamic forces. In special, in a multicomponent fluid the temperature and concentration gradients interfere in the constitutive equations for the heat and mass flux of all components. Thermal diffusion, i.e. the flow of matter caused by a temperature gradient, is called the Soret [1] effect, and its reciprocal, i.e. the flow of heat caused by concentration gradients, is named after Dufour [2]. The two effects occur simultaneously, non-equilibrium of either temperature or concentrations causes both heat and mass transport. Thermal diffusion is of importance in achieving difficult purifications, such as isomeric substances of various types, including isotopic elements. It is of additional importance in models for the prediction of the composition profile of oil fields.

The linear theory of irreversible thermodynamics was consistently set by Meixner [3] in 1941, and later revised by Prigogine [4], both resting on a local equilibrium assumption. The text by De Groot [5] presents the theory in its full generality. The dissipation of energy takes the form of a sum of products of conjugate forces and

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* Corresponding author. Tel.: +55-2562-7653; fax: +55-2562-7567.

E-mail address: affonso@eq.ufrj.br (A. Silva Telles).

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Nomenclature

A, B, C, D	constants defined in Eq. (29)
c_a	solute concentration
C_p	specific heat
d_k, e_k	constants of integration
D_{ab}	diffusion coefficients
g_k	functions defined in Eq. (1)
H	semi-distance between plates
$\mathbf{j}_a$	mass flux of solute
k	thermal conductivity
K_a	mass transfer coefficient
N_s	number of solutes
p	function in Eq. (1)
Pe	Peclet number
P_k	polynomials defined in Appendix A
$\mathbf{q}$	heat flux
r_a, s_a	constants of integration
S	stepping constant in wall temperature description
T	temperature
u	dimensionless velocity profile
v (v_m)	velocity profile (maximum value)
x	dimensionless axial coordinate
y	transversal coordinate
z	axial coordinate.

Greek letters

Γ	matrix of phenomenological dimensionless coefficients
Θ	dimensionless temperature
α	thermal diffusivity
β_a	dimensionless mass transfer coefficient
χ_a	dimensionless solute concentrations
γ_{ab}, γ_{qb}, $\gamma_{a\theta}$	dimensionless phenomenological coefficients
η	dimensionless transversal coordinate
κ_{ab}	entries in the inverse phenomenological coefficients matrix
λ_{aq}, λ_{ab}	phenomenological coefficients defined in Eqs. (6) and (7)
ρ	fluid density.

Subscripts

$i, j, k, m, n, \ldots$	refer to terms in the series expansion
$a, b, \ldots$	refer to properties of the solutes
∞	refer to asymptotic solution of the differential equations.

fluxes associated to the problem under consideration. The fluxes are expressed as linear functions of all forces, as constitutive equations, subjected to the reciprocal relations of Onsager and to the exclusion theorem of Curie. These generalize Fourier and Fick laws, and lead to coupled field equations for the temperature and species concentrations. A review of the linear theory of irreversible phenomena, especially applicable to the coupled heat and mass transfer, was recently presented by Demirel and Sandler [6].

The Graetz [7] problem was originally posed for the description of heat transfer to a pure fluid in instances where the axial conduction can be neglected. The differential equations and, in part, the boundary conditions apply; equally well to the description of mass transfer problems. Mikhailov and Ozisik [8] have applied a generalized transform method to the solution of a large set of heat and mass transfer problems. In most of the cases analyzed heat and mass transfer are uncoupled, except for the presentation of the work of Luikov and Mikhailov [9] for the description of drying processes where the migration of moisture is caused by the temperature gradient. The constitutive equations employed describe only the Soret effect but disregard the Dufour.

Graetz problem has been extended to cover conditions of low Peclet number, cases in which the axial conduction in the fluid cannot be neglected. Silva Telles et al. [10] have recently presented an analytical solution to this problem, in which the flow domain and temperature field extend through the whole real axis. The method is applicable to the three main types of boundary conditions, which are allowed to vary along the axial coordinate in quite a general fashion.

A similar method is now applied to this more general problem in which the heat flux and the diffusive mass flux of each solute depend simultaneously on the temperature and concentration gradients. The multicomponent fluid is admitted at $x = -\infty$ with a fully developed parabolic velocity profile to the region between parallel plates, whose walls are held at specified temperatures, variable along the axial coordinate. At the entrance the fluid temperature and concentrations are uniform. Contact with the heated walls introduces a temperature gradient, which in turn produces mass fluxes and concentration gradients. The concentration gradients alter the heat flux, and this change has effect upon the Nusselt number. Permeable and impervious walls lead to different boundary conditions, which are analyzed in view of their potential use as a separation process. The flow configuration is depicted in Fig. 1.

The solution is based on a convenient basis for the Hilbert space of square integrable functions of a real variable. The construction of the solution involves a change of the dependent variables aiming at their re-

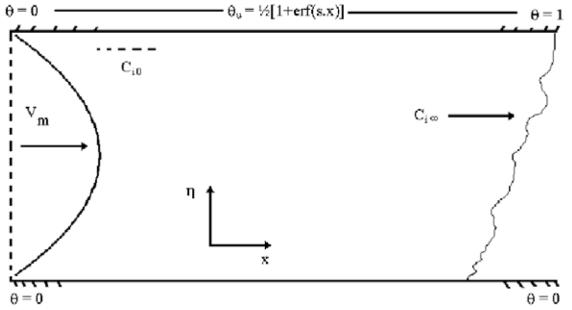

Fig. 1. Geometry and main variables.

duction to square integrable function, accomplished by subtraction of asymptotic solutions. For these new variables, solutions are proposed as expansion in a series with respect to a basis chosen in view of two important properties. Firstly, each of the basis functions is obtained by successive differentiation of a specified function, Eq. (1), and secondly each of which is orthogonal to all but one previously determined polynomial, Eq. (2), obtained following a general procedure explained in Appendix A:

$$g_0 = \exp\{-p(x)\}, \quad g_{k+1} = \frac{\mathrm{d}g_k}{\mathrm{d}x}, \; k = 0..\infty, \tag{1}$$

$$\int_{-\infty}^{\infty} g_i(Z)P_j(x)\,\mathrm{d}x = \delta_{ij}, \quad \text{the Kronecker delta}, \tag{2}$$

where $p(x)$ is a polynomial of the second degree, and this implies that P_j are polynomials of increasing degrees starting with $j = 0$, $P_0 = \text{constant}$. This allows the establishment of an infinite set of ordinary differential equations for the coefficients of the solutions expansion. Each equation depends exclusively upon the two previous ones, a fact that allows their solution in sequence, with no recourse to approximations of any kind.

2. Analytical formulation

Consider the fully developed flow of a Newtonian fluid between parallel plates with a parabolic velocity profile given by Eq. (3). The fluid composition comprises a solvent and a set of N_s solutes. It is admitted with uniform concentrations c_a^0 $\{a = 1..N_s\}$ and uniform temperature T_0. At inlet, consequently, the fluid and confining walls are in thermodynamic equilibrium at the temperature T_0. The walls are held at specified, variable temperatures along the axial coordinate z, $T_U = T_U(z)$ and $T_L = T_L(z)$.

$$\frac{v}{v_m} \equiv u = (1-\eta^2), \quad \eta = \frac{y}{H}, \tag{3}$$

where H is the semi-gap between plates.

Mass and energy balances are assumed of the following forms:

$$\rho v \partial_z c_a = -\mathrm{div}(\mathbf{j}_a), \quad a = 1..N_s, \tag{4}$$

$$\rho C_p v \partial_z T = -\mathrm{div}(\mathbf{q}). \tag{5}$$

The mass and heat fluxes are determined by constitutive equations, and these should transform the balance laws into field equations for the concentrations of the chemical species, and for the temperature. Fick and Fourier laws are generalized by the dictates of thermodynamics of irreversible processes as linear expressions for the fluxes as functions of the gradients of temperature and chemical potential of all solutes. The reciprocal relations due to Onsager apply to these expressions. As consequence of the local equilibrium hypothesis the chemical potentials are determined as functions of temperature and concentration only, and by means of these expressions the constitutive equations can be transformed into linear functions of the gradients of concentration and temperature. The solution possesses N_s independent components, and N_s independent concentration gradients; it is therefore permissible to write

$$\mathbf{j}_a = -\lambda_{aT}\,\mathrm{grad}\,T - \sum_{b=1}^{N_s} D_{ab}\,\mathrm{grad}\,c_b, \tag{6}$$

$$\mathbf{q} = -k\,\mathrm{grad}\,T - \sum_{b=1}^{N_s} \lambda_{qb}\,\mathrm{grad}\,c_b, \tag{7}$$

where λ_{aT} are thermal diffusion coefficients determining the mass flux of each component generated by the temperature gradient (Soret effect), D_{aa} is the coefficient of self-diffusion, D_{ab}, for $b \neq a$ give the coupling effects between different chemical components. Eq. (7) expresses heat conduction determined firstly by the thermal conductivity k with the interference of the concentration gradients giving rise to the Dufour effect, with coefficients λ_{qa}.

Gurtin and Vargas [11] have extended the theory to incorporate non-linear expressions. As consequence of frame indifference, and material isotropy the resulting constitutive equations do not differ significantly from the above, except for the possible dependence on the symmetric part of the velocity gradient, and the possible dependence of all coefficients on the combined invariants [12,13] of the gradients present in the representation given by Eqs. (6) and (7). In general, therefore, the coefficients of Eqs. (6) and (7) are determined by functions of the temperature, composition, and of the combined scalar products of $N_s + 1$ gradients of concentration and temperature. In the present work all coefficients are considered constants, i.e. independent of temperature, concentrations and independent of all gradients.

The substitution of the constitutive equations into the mass and energy balances, Eqs. (4) and (5), yields the desired field equations for the concentration of all solutes, and for the temperature. The system is made dimensionless with the use of the following variables:

$$\Theta = \frac{T - T_0}{\Delta T}, \quad \chi_a = \frac{c_a}{c_a^0}, \quad \eta = \frac{y}{H}, \quad x = \frac{z}{HPe},$$
$$Pe = \frac{Hv_{\mathrm{m}}}{\alpha}, \quad \alpha = \frac{k}{\rho C_{\mathrm{p}}}, \tag{8}$$

where ΔT is a reference temperature difference.

The system of equations (6) and (7) accounting to Soret and Dufour effects becomes:

$$\sum \gamma_{ab}\Delta^2\chi_b + \gamma_{a\theta}\Delta^2\Theta = (1-\eta^2)\partial_x\chi_a = u\partial_x\chi_a, \tag{9}$$

$$\sum \gamma_{qb}\Delta^2\chi_b + \Delta^2\Theta = (1-\eta^2)\partial_x\Theta = u\partial_x\Theta, \tag{10}$$

where

$$\gamma_{qb} = \frac{\lambda_{qb}}{k}\frac{c_b^0}{\Delta T}, \quad \gamma_{ab} = \frac{D_{ab}C_{\mathrm{p}}c_b^0}{kc_a^0}, \quad \gamma_{a\theta} = \frac{\lambda_{a\mathrm{T}}\Delta TC_{\mathrm{p}}}{kc_a^0} \tag{11}$$

and

$$\Delta^2 = \partial_\eta^2 + \frac{1}{Pe^2}\partial_x^2,$$

is the dimensionless Laplacian operator in Cartesian coordinates.

The system of $N_{\mathrm{s}} + 1$ partial differential equations is written in matrix form

$$\begin{pmatrix} \gamma_{11} & \gamma_{12} & \cdots & \gamma_{1N_{\mathrm{s}}} & \gamma_{1\theta} \\ \gamma_{21} & \gamma_{22} & \cdots & \gamma_{2N_{\mathrm{s}}} & \gamma_{2\theta} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \gamma_{q1} & \gamma_{q2} & \cdots & \gamma_{qN_{\mathrm{s}}} & 1 \end{pmatrix} \begin{pmatrix} \Delta^2\chi_1 \\ \Delta^2\chi_2 \\ \vdots \\ \Delta^2\Theta \end{pmatrix} = \begin{pmatrix} u\partial_x\chi_1 \\ u\partial_x\chi_2 \\ \vdots \\ u\partial_x\Theta \end{pmatrix}, \tag{12}$$

comprising a matrix of dimensionless phenomenological coefficients, Γ, operating on a vector with components consisting of the Laplacian operator acting on the $N_{\mathrm{s}} + 1$ field variables, and yielding the vector of advective transport. The assumption that Γ is non-singular, i.e. $\det \Gamma \neq 0$, is equivalent to the frequently employed assumption that the system of constitutive equations (6) and (7) can be solved for the gradients. Including this assumption, the system of equations (12) is equivalent to

$$\begin{pmatrix} \partial_\eta^2\chi_1 \\ \partial_\eta^2\chi_2 \\ \vdots \\ \partial_\eta^2\Theta \end{pmatrix} = \begin{pmatrix} \kappa_{11} & \kappa_{12} & \cdots & \kappa_{1N_{\mathrm{s}}} & \kappa_{1\theta} \\ \kappa_{21} & \kappa_{22} & \cdots & \kappa_{1N_{\mathrm{s}}} & \kappa_{1\theta} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \kappa_{q1} & \kappa_{q2} & \cdots & \kappa_{qN_{\mathrm{s}}} & \kappa_{q\theta} \end{pmatrix} \begin{pmatrix} u\partial_x\chi_1 \\ u\partial_x\chi_2 \\ \vdots \\ u\partial_x\Theta \end{pmatrix} - \frac{1}{Pe^2}\begin{pmatrix} \partial_x^2\chi_1 \\ \partial_x^2\chi_2 \\ \vdots \\ \partial_x^2\Theta \end{pmatrix}, \tag{13}$$

where the matrix entries are the components of inverse of the matrix Γ. The coupling phenomena persist in Eqs. (13) originating in the advective terms on the right-hand side of Eqs. (12). Inversion of the matrix of phenomenological coefficients permits the isolation of the derivatives of the field variables with respect to η, leaving to the right the derivatives with respect to x.

2.1. Boundary conditions

The boundary conditions for Θ result from the specification of the wall temperature on both plates:

$$\Theta(x,-1) = \Theta_{\mathrm{w}}^{\mathrm{L}}(x), \quad \Theta(x,1) = \Theta_{\mathrm{w}}^{\mathrm{U}}(x), \tag{14}$$

$$\lim_{x\to-\infty} \Theta_{\mathrm{w}}^{\mathrm{L}}(x) = \Theta_{\mathrm{w}}^{\mathrm{U}}(x) = 0,$$

and

$$\lim_{x\to\infty} \Theta_{\mathrm{w}}^{\mathrm{L}}(x) = \Theta_{\mathrm{w}}^{\mathrm{L}\infty}, \qquad \lim_{x\to\infty} \Theta_{\mathrm{w}}^{\mathrm{U}}(x) = \Theta_{\mathrm{w}}^{\mathrm{U}\infty}. \tag{15}$$

According to the above conditions, both plates are held at specified, variable temperatures. The left limits for both plates are equal to the temperature of the incoming fluid, while the right limit for each wall attains possibly unequal asymptotic values $T_{\mathrm{w}}^{\mathrm{U}\infty}$ and $T_{\mathrm{w}}^{\mathrm{L}\infty}$. The reference temperature difference appearing in Eq. (8) may be set equal to $T_{\mathrm{w}}^{\mathrm{U}\infty} - T_0$, in which case $\Theta_{\mathrm{w}}^{\mathrm{U}\infty} = 1$. In most instances the lower plate is held at the entrance temperature T_0, i.e. $\Theta_{\mathrm{w}}^{\mathrm{L}} = 0$ for all values of x.

The boundary conditions for concentrations reflect the asymptotic approach to the fluid composition at admittance, and the permeability condition at both walls, which requires the normal component of the mass fluxes to be proportional to the difference between the solute concentration at the wall and the concentration of the same solute prevailing in the ambient space outside the walls:

$$\lim_{x\to-\infty} \chi_a(x,\eta) = 1, \tag{16}$$

$$\mathbf{j}_a(z,-1)\cdot\mathbf{n} = K_a^-[c_a(x,-1) - c_a^-], \qquad \mathbf{j}_a(z,1)\cdot\mathbf{n} = K_a^+[c_a(x,1) - c_a^+], \tag{17}$$

where K_a are mass transfer coefficients (permeabilities) for each wall, and c_a^+, c_a^- are the concentrations of each chemical species prevailing in the ambient space outside the two walls. The case in which both mass transfer coefficients are equal to zero is given special attention. Selective membranes may be used letting through some of the chemical species, but rejecting some others. In purification system for one of the solution components, the membrane could be chosen permeable only to that component. In a concentration system both walls can be impermeable to the desired solute.

Notice that the flux condition of Eqs. (17) presents significant differences to the classical flux condition when there is no interference between the various effects. Substitution of the constitutive equation (6) into Eqs. (17) yields the same type of interference between the various forces in action. In terms of the dimensionless variables conditions (17) are rephrased as

$$\begin{aligned}\gamma_{a\theta}\partial_\eta\Theta\big|_{\eta=1} + \sum\gamma_{ab}\partial_\eta\chi_b\Big|_{\eta=1} &= \beta_a^+[\chi_a(x,1) - \chi_a^+],\\ \gamma_{a\theta}\partial_\eta\Theta\big|_{\eta=-1} + \sum\gamma_{ab}\partial_\eta\chi_b\Big|_{\eta=-1} &= \beta_a^-[\chi_a(x,-1) - \chi_a^-],\end{aligned} \tag{18}$$

where $\beta_a = K_a/(kc_a^0)$ is the dimensionless mass transfer coefficient for each wall.

2.2. Asymptotic solution

The solution method employed depends on the existence of asymptotes valid as $x \to \infty$. They are obtained, in the present cases, by setting to zero the derivatives with respect to x in Eqs. (13):

$$\begin{aligned}&\partial_\eta^2\chi_a^\infty = 0 \;\Rightarrow\; \chi_a^\infty = r_a^\infty\eta + s_a^\infty,\\ &\partial_\eta^2\Theta^\infty = 0 \;\Rightarrow\; \Theta^\infty = d^\infty\eta + \mathrm{e}^\infty.\end{aligned} \tag{19}$$

The asymptotic solutions of the above equations have coefficients of integration, which are allowed to be functions of the axial variable, x. The asymptotic solution for temperature is given by a linear expression in η with coefficients determined by the wall temperature distributions

$$\Theta^\infty = \tfrac{1}{2}(\Theta^\mathrm{U} - \Theta^\mathrm{L})\eta + \tfrac{1}{2}(\Theta^\mathrm{U} + \Theta^\mathrm{L}). \tag{20}$$

For the special case in which the lower wall temperature is kept constant at T_0 then

$$\Theta^\infty = \Theta^\mathrm{U}\frac{\eta+1}{2}. \tag{21}$$

Linear expressions hold, equally, for the asymptotic concentration profiles whose coefficients must satisfy Eqs. (18)

$$\begin{aligned}\tfrac{1}{2}\gamma_{a\theta}\Theta^\mathrm{U} + \sum\gamma_{ab}r_b^\infty &= \beta_a^+[r_a^\infty + s_a^\infty - \chi_a^+],\\ \tfrac{1}{2}\gamma_{a\theta}\Theta^\mathrm{U} + \sum\gamma_{ab}r_b^\infty &= \beta_a^-[-r_a^\infty + s_a^\infty - \chi_a^-].\end{aligned} \tag{22}$$

This system contains $2N_\mathrm{s}$ equations for the same number of unknowns and can, in principle, be solved. For the case when the lower wall is impervious ($\beta_b^- = 0$), and held isothermal, Eq. $(22)_2$ can be solved to determine the r_a. Once this is accomplished their values are substituted into Eq. $(22)_1$ to yield s_a. Full details of the solution are given only for the case in which both walls are impermeable

$$\sum\gamma_{ab}r_b^\infty = -\gamma_{a\theta}\frac{\Theta^\mathrm{U}}{2}, \tag{23}$$

$$s_a^\infty = 0. \tag{24}$$

If both walls are impervious, the two equations (22) become identical and independent of s_a, which may be set equal to zero.

2.3. Complete solution

The method proposed by Silva Telles et al. [10] is used to obtain the complete solution. The modification presented in Appendix A results in a significant improvement of the convergence rate. The solutions for the temperature and concentration fields are proposed as

$$\Theta = \frac{\Theta^\mathrm{U}(x)}{2}(\eta+1) + \sum_0^\infty\vartheta_k(\eta)g_k(x), \tag{25}$$

$$\chi_a = r_a^\infty(x)\eta + s_a^\infty(x) + \sum_0^\infty\varphi_k^a(\eta)g_k(x), \tag{26}$$

where the g_k are defined in Eq. (1).

Substituting the proposed solutions into Eqs. (13) yields

$$\begin{pmatrix}\sum\partial_\eta^2\varphi_k^1g_k\\ \sum\partial_\eta^2\varphi_k^2g_k\\ \vdots\\ \sum\partial_\eta^2\vartheta_kg_k\end{pmatrix} = u\begin{pmatrix}\kappa_{11} & \kappa_{12} & \cdots & \kappa_{1N_\mathrm{s}} & \kappa_{1\theta}\\ \kappa_{21} & \kappa_{22} & \cdots & \kappa_{1N_\mathrm{s}} & \kappa_{1\theta}\\ \vdots & \vdots & \ddots & \vdots & \vdots\\ \kappa_{q1} & \kappa_{q2} & \cdots & \kappa_{qN_\mathrm{s}} & \kappa_{q\theta}\end{pmatrix} \times\begin{pmatrix}\sum\varphi_{k-1}^1g_k + \partial_x(r_1\eta + s_1)\\ \sum\varphi_{k-1}^2g_k + \partial_x(r_2\eta + s_2)\\ \vdots\\ \sum\vartheta_{k-1}g_k + \frac{\eta+1}{2}\partial_x(\theta^\mathrm{U})\end{pmatrix} - \frac{1}{Pe^2}\begin{pmatrix}\sum\varphi_{k-2}^1g_k + \partial_x^2(r_1\eta + s_1)\\ \sum\varphi_{k-2}^2g_k + \partial_x^2(r_2\eta + s_2)\\ \vdots\\ \sum\vartheta_{k-2}g_k + \frac{\eta+1}{2}\partial_x^2(\theta^\mathrm{U})\end{pmatrix}, \tag{27}$$

where $\varphi^a_{-1} = \varphi^a_{-2} = \vartheta_{-1} = \vartheta_{-2} = 0$.

Multiplying each equation, successively, by each of the polynomials with the bi-orthogonality property generates an infinite set of ordinary differential equations for the coefficient functions φ_j^a and ϑ_j:

$$
\begin{pmatrix} \partial^2_\eta \varphi^1_j \\ \partial^2_\eta \varphi^2_j \\ \vdots \\ \partial^2_\eta \vartheta_j \end{pmatrix} = (1-\eta^2) \begin{pmatrix} \kappa_{11} & \kappa_{12} & \cdots & \kappa_{1N_\mathrm{s}} & \kappa_{1\theta} \\ \kappa_{21} & \kappa_{22} & \cdots & \kappa_{1N_\mathrm{s}} & \kappa_{1\theta} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \kappa_{q1} & \kappa_{q2} & \cdots & \kappa_{qN_\mathrm{s}} & \kappa_{q\theta} \end{pmatrix}
\times \begin{pmatrix} \varphi^1_{j-1} + A^1_j\eta + B^1_j \\ \varphi^2_{j-1} + A^2_j\eta + B^2_j \\ \vdots \\ \vartheta_{j-1} + \frac{\eta+1}{2}A^\theta_j \end{pmatrix}
- \frac{1}{Pe^2} \begin{pmatrix} \varphi^1_{j-2} + C^1_j\eta + D^1_j \\ \varphi^2_{j-2} + C^2_j\eta + D^2_j \\ \vdots \\ \vartheta_{j-2} + \frac{\eta+1}{2}C^\theta_j \end{pmatrix}
= \begin{pmatrix} f^1_j(\eta) \\ f^2_j(\eta) \\ \vdots \\ f^\theta_j(\eta) \end{pmatrix}, \tag{28}
$$

where the coefficients A, B, C, and D are determined by the application of the functional

$$
\mathfrak{P}_j(\cdot) = \frac{1}{h_j}\int_{-\infty}^{\infty} (\cdot) H_j(Z)\,\mathrm{d}Z
$$

to the terms in Eqs. (27) dependent on the boundary conditions. They are calculated by expressions (29):

$$
\begin{aligned}
&A^a_j = \mathfrak{P}_j(\partial_x r^\infty_a), \quad A^\theta_j = \mathfrak{P}_j(\partial_x \theta^\mathrm{U}),\\
&B^a_j = \mathfrak{P}_j(\partial_x s^\infty_a),\\
&C^a_j = \mathfrak{P}_j(\partial^2_x r^\infty_a), \quad C^\theta_j = \mathfrak{P}_j(\partial^2_x \theta^\mathrm{U}),\\
&D^a_j = \mathfrak{P}_j(\partial^2_x s^\infty_a).
\end{aligned} \tag{29}
$$

The vector of $N_\mathrm{s}+1$ f's stands for the right-hand side of Eqs. (28). They are known functions, exclusively of η.

The set can be solved to give the coefficient functions of η, starting with $j = 0$. For this case the right-hand side reduces to linear functions of that variable, multiplied by the velocity profile. Its coefficients are determined by the physical properties that compose Γ, and by the boundary conditions, which determine the coefficients in Eq. (29). They can be integrated twice leading to a polynomial of the fifth degree. For $j = 1$ the set depends on the same variables, to which are added the coefficient functions for $j = 0$. The right-hand side is completely determined, and is a polynomial of seventh degree. Double integration yields terms of the ninth degree. In sequence, for $j \geqslant 2$, the solution depends on the two previous solutions and on the same physical parameters. Integration results in polynomials of degree $4j + 5$.

Integration of each of Eqs. (28) introduces two arbitrary constants, which must be evaluated in order to satisfy the boundary conditions:

$$
\begin{aligned}
\varphi^a_j &= \int\!\!\int f^a_j\,\mathrm{d}\eta + r^a_j\eta + s^a_j = F^a_j + r^a_j\eta + s^a_j,\\
\vartheta_j &= \int\!\!\int f^\theta_j\,\mathrm{d}\eta + d_j\eta + e_j = F^\theta_j + d_j\eta + e_j,
\end{aligned} \tag{30}
$$

and that yields

$$
\begin{aligned}
d_j &= \tfrac{1}{2}\Big[F^\theta_j(1) - F^\theta_j(-1)\Big],\\
e_j &= \tfrac{1}{2}\Big[F^\theta_j(1) + F^\theta_j(-1)\Big],
\end{aligned} \tag{31}
$$

$$
\begin{aligned}
&\sum \gamma_{ab} r^\infty_b = -\gamma_{a\theta}\frac{\Theta^\mathrm{U}}{2},\\
&s^a_j = 0.
\end{aligned} \tag{32}
$$

Calculation of these constants concludes the solution.

3. Binary mixtures

The simple case where the fluid comprises a solvent and a single solute flowing between impervious walls is presently examined. The writing of the field equations depends upon the matrix Γ, and its inverse:

$$
\Gamma = \begin{pmatrix} \gamma_1 & \gamma_\theta \\ \gamma_q & 1 \end{pmatrix}
$$

and

$$
\Gamma^{-1} = \frac{1}{\gamma_1 - \gamma_\theta\gamma_q}\begin{pmatrix} 1 & -\gamma_\theta \\ -\gamma_q & \gamma_1 \end{pmatrix}, \tag{33}
$$

$$
\begin{aligned}
\partial^2_\eta \chi^1 &= \frac{1-\eta^2}{\gamma_1 - \gamma_q\gamma_\theta}[\partial_x\chi^1 - \gamma_\theta\partial_x\Theta] - \frac{1}{Pe^2}\partial^2_x\chi^1,\\
\partial^2_\eta \Theta &= \frac{1-\eta^2}{\gamma_1 - \gamma_q\gamma_\theta}[-\gamma_q\partial_x\chi^1 + \gamma_1\partial_x\Theta] - \frac{1}{Pe^2}\partial^2_x\Theta.
\end{aligned} \tag{34}
$$

In the above equations and in what follows the doubling of indices of the phenomenological coefficients was omitted ($\gamma_1 = \gamma_{11}$; $\gamma_q = \gamma_{q1}$; $\gamma_\theta = \gamma_{1\theta}$).

The asymptotic solutions are given for the temperature by Eq. (21) [$\Theta^\infty = \Theta^\mathrm{U}\frac{1}{2}(\eta + 1)$] and for the concentration equations (23) and (24) reduce to

$$
r^\infty_1 = -\frac{\gamma_\theta}{\gamma_1}\frac{\Theta^\mathrm{U}}{2}, \quad \mathbf{s}^\infty_1 = 1. \tag{35}
$$

The complete solution is therefore

$$
\chi_1 = 1 - \frac{\gamma_\theta}{2\gamma_1}\theta^\mathrm{U}\eta + \sum[F^1_k + r^1_k\eta]g_k, \tag{36}
$$

$$
\Theta = \Theta^\mathrm{U}(x)\frac{(1+\eta)}{2} + \sum[F^\theta_k + d_k\eta + e_k]g_k, \tag{37}
$$

where the functions F^1 and F^θ satisfy the infinite set of equations derived from (34),

$$\partial_\eta^2 F_k^1 = \frac{1-\eta^2}{\gamma_1 - \gamma_q\gamma_\theta}\left[F_{k-1}^1 + A_k^1\eta + B_k^1 - \gamma_\theta\left(F_{k-1}^\theta + A_k^\theta\frac{1+\eta}{2}\right)\right], \tag{38}$$

$$\partial_\eta^2 F_k^\theta = \frac{1-\eta^2}{\gamma_1 - \gamma_q\gamma_\theta}\left[-\gamma_q\left(F_{k-1}^1 + A_k^1\eta + B_k^1\right) + \gamma_1\left(F_{k-1}^\theta + A_k^\theta\frac{1+\eta}{2}\right)\right]. \tag{39}$$

The general aspect of the solutions obtained via a Maple program, for sample values of the dimensionless phenomenological constants, is presented in Figs. 2–8. The temperature profile follows the wall temperature with a steep rise around the origin. It approaches the linear dependence with η as $x \to \infty$, in accordance with the asymptotic solution (21). The general aspect of the evolution of the temperature profile is shown in Fig. 2. As the limiting and wall temperatures are set independently of all physical–chemical parameters, the temperature profiles are quite insensitive to changes in the γ, s. In fact it is completely analogous to the temperature profile in purely heat transfer problem.

A similar plot obtained with the same parameter values gives the evolution of the concentration profile in Fig. 3. This starts with a flat profile at $-\infty$, and the solute migrates to the cold plate reaching the linear profile predicted by Eq. (36). This behavior is a direct consequence of the Soret effect, which produces a mass flux from lower to higher solute concentration driven by the temperature gradient. This effect is explored in greater detail.

The concentration profile along the x-axis for various values of position η is shown in Fig. 4 with its dependence upon the Soret coefficient γ_θ. This coefficient is responsible for the terminal concentration distribution. In fact, the concentration span of the single solvent asymptotically approaches the limiting value

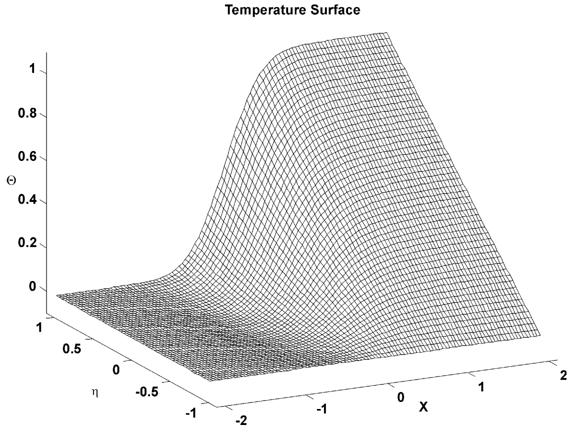

Fig. 2. Temperature surface for $Pe = 5$, $\gamma_1 = 1$, $\gamma_\theta = 0.3$, $\gamma_q = 0$, and $S = 2$.

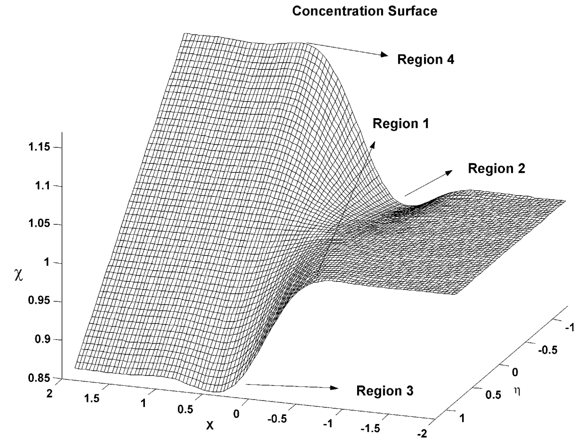

Fig. 3. Concentration surface for $Pe = 5$, $\gamma_1 = 1$, $\gamma_\theta = 0.3$, $\gamma_q = 0$, and $S = 2$.

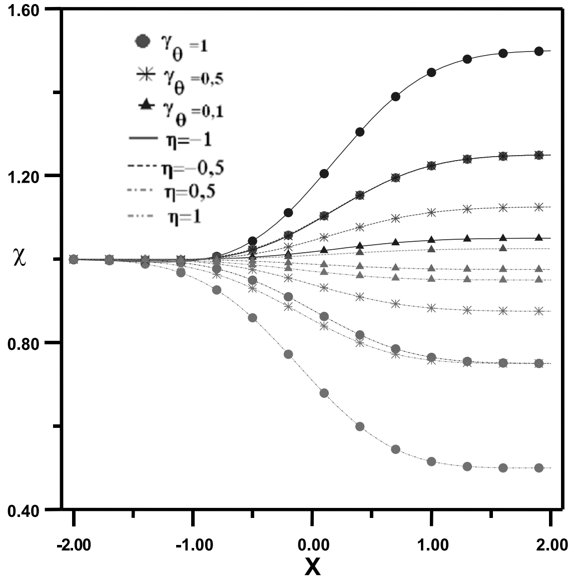

Fig. 4. Concentration profiles: sensitivity with respect to γ_θ.

$$\Delta\chi_1 = \chi_1|_{\eta=1} - \chi_1|_{\eta=-1} = \frac{\gamma_\theta}{\gamma_1}. \tag{40}$$

For the stepping parameter for the wall temperature $S = 1$, the solution reaches the asymptotic value at $x \approx 1.5$, or $z/H \approx 1.5Pe$. Larger values of S result in a faster approach to the asymptotes. For $S = 2$, the asymptote is reached at $x \approx 0.9$, or $z/H \approx 0.9Pe$. Convergence to a previously specified term of the order of 10^{-4} is slower requiring 34 terms as opposed to 6 in the

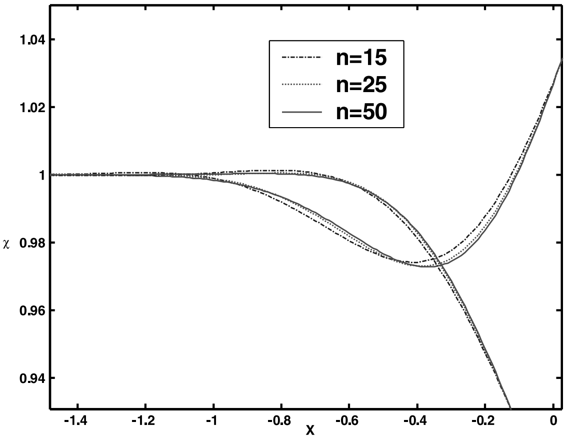

Fig. 5. Concentration profiles at upper and lower walls.

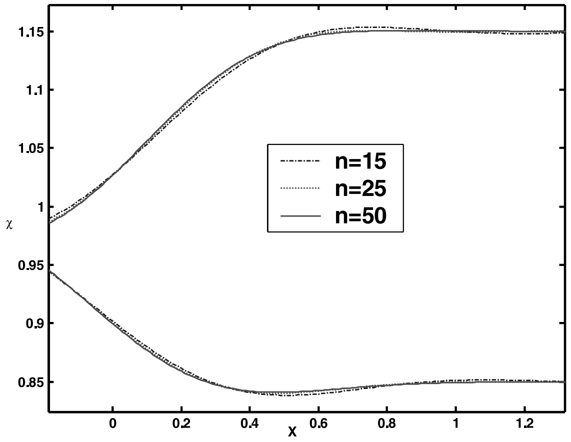

Fig. 6. Concentration profiles at upper and lower walls.

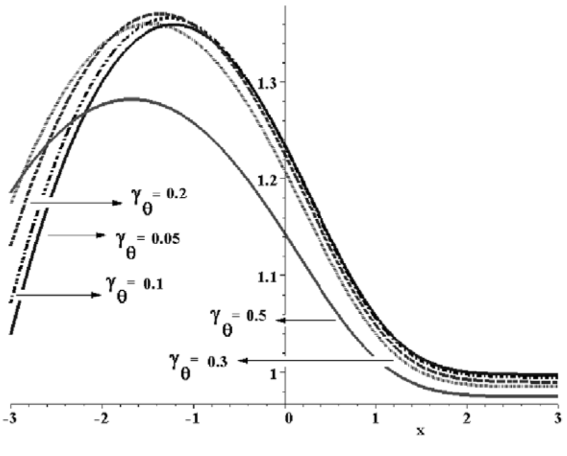

Fig. 7. Local Nusselt number for sample values of γ_θ.

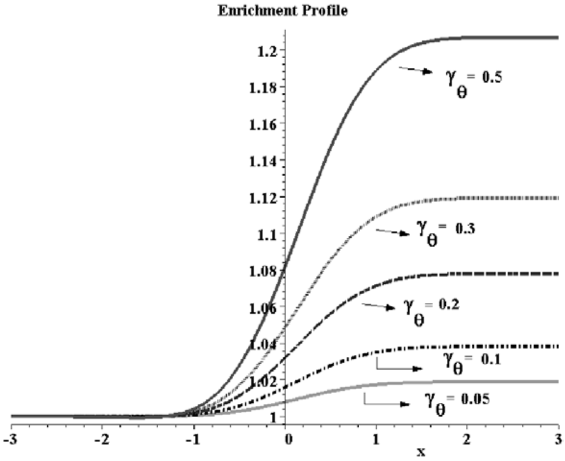

Fig. 8. Enrichment profile for sample values of γ_θ.

previous case. The concentration profile is particularly sensitive to the stepping parameter, and presents an interesting phenomenon. Fig. 3 shows the concentration profile of a plot as a function of x and η, for $S = 2$. For this value the solution presents in the four regions close to the walls, and in the neighborhood of the stepping in temperature, the concentration profile presents unusual maxima and minima, which seem analogous to those observed in Fourier transform methods. In many cases these phenomena are persistent and insensitive to the number of terms used in the expansion. This is shown in Figs. 5 and 6, where the behavior of the solution is accompanied increasing the number of terms up to 50. The dip below 1 just before the increase toward the asymptote appears frequently and markedly. The concentration process is so fast requiring transport in the x direction to have significant contribution. Analogous maxima, or minima occur in regions shown in Fig. 3, although not as persistently. A final comment on this point is on the observation that the maxima and minima occur at the boundaries, even though it has not established the existence of a maximum principle for the set of equations (34), or more generally Eqs. (13).

The Nusselt number shows a marked dependence on the dimensionless phenomenological coefficients, especially on γ_θ. Fig. 7 demonstrates this sensitivity showing a plot of the Nusselt number based on the heat flux at the upper wall versus position along the plate for diverse values of γ_θ. In the absence of cross-effects the Nusselt curve reproduces the purely heat transfer solution.

A measure of the separation potential of the Soret–Dufour effects is shown in Fig. 8, as the ratio of the amounts of solute flowing through a plane at position x in the lower to upper midsection. The enrichment thus obtained is defined by

$$\text{Enrichment} = \frac{\int_{-1}^{0} u(\eta)\chi(x,\eta)\,\mathrm{d}\eta}{\int_{0}^{1} u(\eta)\chi(x,\eta)\,\mathrm{d}\eta}. \tag{41}$$

This is shown in Fig. 8 for sample values of γ_θ and $\gamma_1 = 1$. It is observed that the final enrichment is determined by γ_θ/γ_1, and the approach to the asymptotic values follows closely the stepping in wall temperature. Enrichment can be as high as 20%, for $\gamma_\theta/\gamma_1 = (\lambda_\mathrm{T}\Delta T/k)/Dc_1^0 = 0.5$. Concentration systems based on the division of the outlet into two equal streams will double the inlet concentration in four steps of a stagewise purification system. The temperature difference between the two walls and the initial concentration are the operational variables available to obtain a high enough value for the enrichment, as the remaining variables in γ_θ/γ_1 are physical properties.

4. Concluding remarks

The solution of coupled heat and mass transfer in convective processes between parallel plates utilizing bi-orthogonality properties of special polynomials yields accurate results. The interference at the level of constitutive equations, as dictated by thermodynamics of irreversible processes, does not present insurmountable difficulties, opening space for the examination of more complex problems, including possible new effects due to the use of non-linear constitutive equations which can show, e.g., interference of the velocity gradient upon the heat and mass flux.

More complex geometries, such as the annular space between cylindrical pipes and its association with permeable walls, can present interesting aspects related to membrane technology.

The method can be applied to turbulent flows, in which case hybrid (analytical/numerical) methods must be applied.

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Appendix A

The function g_0 is defined in Eq. (1), and the sequence g_n is obtained by its derivatives. This procedure yields a sequence of functions with a common exponential factor multiplying a polynomial $Q_n(x)$ in x of increasing degrees. If $p(x)$ is of the second degree $Q_n(x)$ is a polynomial of degree n. A general procedure for the determination of a set of polynomials, $P_m(x)$, orthogonal to all but one of the g_k follows. Let

$$P_m(x) = \sum_{q=0}^{m} a_q^m x^q \tag{A.1}$$

be such that

$$\int_{-\infty}^{\infty} P_m(x) g_n(x)\,\mathrm{d}x = \delta_{nm}. \tag{A.2}$$

This condition is necessary and sufficient for the unique determination of the coefficients a_q^m. To demonstrate this it is noticed firstly that the integrals $G_{qm} \equiv \int_{-\infty}^{\infty} g_q(x) x^m\,\mathrm{d}x$ exist for all non-negative values of m. Then multiplying (A.1) by each of the g_k and integrating, there follows:

$$\sum G_{kq} a_q^n = \delta_{kn}. \tag{A.3}$$

Solutions of the above set, for the coefficients a_q^n, give the desired result, i.e. the coefficients of the polynomials P_n.

A special case, utilized in the present work, starts with the following value for

$$g_0 = \exp\{-x^2 + x\}. \tag{A.4}$$

The sequence of derivatives of this function yields a sequence of Q_k polynomials:

$$\begin{aligned} \mathrm{Q}_0 &= 1, \\ \mathrm{Q}_1 &= -2x + 1, \\ \mathrm{Q}_2 &= 4x^2 - 4x - 1, \\ \mathrm{Q}_3 &= -8x^3 + 12x^2 + 6x - 5, \\ \mathrm{Q}_4 &= 16x^4 - 32x^3 - 24x^2 + 40x + 1. \end{aligned} \tag{A.5}$$

The solution of the set of linear equations yields the polynomials with the bi-orthogonality property. The first five are:

$$\begin{aligned} \alpha P_0 &= 1, \quad \alpha = \sqrt{\pi}\mathrm{e}^{1/4}, \\ \alpha P_1 &= \frac{1}{2} - \frac{x}{1}, \\ \alpha P_2 &= \frac{x^2}{2} - \frac{x}{2} + \frac{1}{8}, \\ \alpha P_3 &= -\frac{x^3}{6} + \frac{x^2}{4} + \frac{x}{8} + \frac{5}{48}, \\ \alpha P_4 &= \frac{x^4}{24} - \frac{x^3}{12} - \frac{x^2}{16} + \frac{5x}{48} + \frac{1}{384}. \end{aligned} \tag{A.6}$$

A Maple program calculates the matrix G of an arbitrary size, solves the system (A.3), and composes the polynomials P_k.

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