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A Turbulent Film Model for Multicomponent Mass Transfer

R. KRISHNA*

Department of Chemical Engineering, University of Manchester Institute of Science and Technology, Manchester, M60 1QD (Great Britain)

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Abstract

This paper analyses steady-state multicomponent mass transfer between an interface and a turbulently flowing fluid phase. The molecular diffusion contribution to the transfer process is modelled by using a matrix of diffusion coefficients **D***, including off-diagonal elements. A turbulent eddy diffusivity* ϵ_m *is used to describe the turbulent mass transfer contribution. For cases (e.g. pipe flow) in which the variation of* ϵ_m *in the boundary layer region can be estimated, an analytic expression is derived for the matrix of multicomponent mass transfer coefficients* $\mathbf{k}^\bullet$*. Appropriate correction factors to take account of the effect of high transfer fluxes on the transfer coefficients are derived in the analysis.*

The analysis shows that increase in the level of turbulence in the system, for example by increasing the Reynolds number, Re, for flow inside a conduit, results in a diminished influence of molecular diffusion coupling on the system transfer behaviour. This is illustrated by means of a numerical example involving mass transfer in the gaseous system acetone–benzene–helium in which, for the chosen conditions, increase in Re for flow along the interface alters the direction of transfer of acetone, a direct consequence of diminished diffusional coupling at increased turbulence levels; i.e. k_{12}/k_{11} *decreases as Re increases.*

Use of the multicomponent generalization of the Chilton–Colburn analogy, recommended in the literature, leads to the conclusion that the ratio k_{12}/k_{11} *is independent of Re; thus the relative importance of diffusional coupling is not affected by the turbulence level, an unlikely circumstance. It is concluded that the Chilton–Colburn analogy cannot be applied for describing mass transfer in strongly coupled multicomponent systems. For such systems a fundamental description of the mass transfer mechanisms, e.g. of the relative contributions of molecular diffusion, turbulent diffusion, interfacial turbulence etc. is essential for the calculation of the individual fluxes.*

INTRODUCTION

The calculation of the interfacial mass transfer fluxes N_i, $i = 1,2, \dots n$, in multicomponent systems ($n \geqslant 3$) is important in many process applications [1], which include distillation, absorption, extraction, condensation and heterogeneous reacting systems. These fluxes N_i can be written in terms of the diffusional and convective contributions

$$N_i = J_i + \omega_i N_t, \qquad i = 1,2, \dots n \tag{1}$$

where J_i is the mass diffusion flux of component i relative to the mass average mixture reference velocity[†]. (Other choices for the mixture reference velocity are possible [1] and the reader will find it easy to carry out a parallel treatment in terms of the molar fluxes and molar average reference velocity.)

There are only $n - 1$ independent mass diffusion fluxes J_i and it is usual to write these in the form

$$J = \rho \mathbf{k}^\bullet(\omega_\mathrm{I} - \omega_\mathrm{b}) \tag{2}$$

where we use $n - 1$ dimensional matrix notation. For many systems of practical interest the matrix of multicomponent mass

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[*] Present address: Weissenbruchstraat, 3A, 2596 GA, The Hague, The Netherlands

[†] This choice is governed by the need later on in the paper to solve the diffusion equations together with the equations of motion; the latter are best expressed using the mass average reference velocity frame.

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transfer coefficients $\mathbf{k}^\bullet$ contains sizeable off-diagonal elements $k^\bullet_{ij}$ $(i \neq j)$ which may strongly influence the transfer of component i, and in some cases dominate its transfer behaviour [2, 3]. The superscript black dot • on the coefficients $k^\bullet_{ij}$ serves as a reminder that these are influenced by the system transfer fluxes [1]. Whichever model one chooses to describe the interface mass transfer process, the coefficients $\mathbf{k}^\bullet$ are expressible in the form:

$$\mathbf{k}^\bullet = \mathbf{k}\Xi \tag{3}$$

where Ξ is a matrix of high flux correction factors, reducing in the limit of vanishingly small transfer fluxes ($N_i \to 0$, $i = 1,2, \dots n$) to the identity matrix $\mathbf{I}$; in this circumstance $\mathbf{k}^\bullet = \mathbf{k}$, the matrix of zero-flux mass transfer coefficients. Knowledge of $\mathbf{k}^\bullet$ and the compositions at either end of the diffusion path enables the calculation of the $n-1$ diffusion fluxes J_i with the help of eqn. (2); the calculation of the n fluxes N_i requires an additional determinancy condition which usually takes the form of a linear constraint on these fluxes [1, 4, 5]. Defining a bootstrap coefficient matrix $\boldsymbol{\beta}$, it is possible to obtain the fluxes from the relation:

$$N = \rho\boldsymbol{\beta}\mathbf{k}^\bullet(\omega_\mathrm{I} - \omega_\mathrm{b}) \tag{4}$$

The elements of the bootstrap matrix $\boldsymbol{\beta}$ are known *a priori* for many cases of practical interest such as equimolar diffusion, Stefan diffusion, *etc.* [4, 5].

The prediction of $\mathbf{k}^\bullet$ from information on the transport characteristics of the constituent binary pairs in the mixture has gained a lot of attention in recent years. One of the most significant advances in this area was made in 1964 when Toor [6] and Stewart and Prober [7] independently put forward a linearized theory of multicomponent mass transfer based on the assumption that the matrix of molecular diffusion coefficients $\mathbf{D}$ is independent of composition. With the help of this assumption direct multicomponent generalizations, in $n-1$ dimensional matrix notation, of well-known binary mass transfer relationships [8] are possible and expressions for $\mathbf{k}$ and Ξ may be written down straightforwardly [1, 6, 7].

Thus the film model for multicomponent mass transfer gives:

$$\mathbf{k} = \mathbf{D}/\delta, \tag{5}$$

$$\Xi = \boldsymbol{\Phi}[\exp \boldsymbol{\Phi} - \mathbf{I}]^{-1} \tag{6}$$

where $\boldsymbol{\Phi}$ is the dimensionless mass transfer rate factor, defined as

$$\boldsymbol{\Phi} = \frac{N_\mathrm{t}}{\rho}\mathbf{k}^{-1} \tag{7}$$

A suitably averaged diffusion coefficient matrix $\mathbf{D}$ must be used. It may be remarked that for ideal gas mixtures the assumption of constant $\mathbf{D}$ is unnecessary and an exact solution is possible [9].

The Higbie penetration model gives the following expression for the mass transfer coefficients $\mathbf{k}$ and the correction factor Ξ

$$\mathbf{k} = 2\left[\frac{\mathbf{D}}{\pi t_\mathrm{c}}\right]^{1/2} \tag{8}$$

$$\Xi = \left[\mathbf{I} + \operatorname{erf}\frac{\boldsymbol{\Phi}}{\sqrt{\pi}}\right]^{-1}[\exp(-\boldsymbol{\Phi}^2/\pi)] \tag{9}$$

The dimensionless mass transfer rate factor $\boldsymbol{\Phi}$ is again given by eqn. (7). (See reference [1] for further details on the penetration model).

In a limited number of practical cases *a priori* estimates of the film thickness δ and the contact time for mass transfer t_c are available and the film and penetration models above can be used for calculating $\mathbf{k}^\bullet$. However, in a majority of examples of chemical engineering interest such *a priori* estimates are not possible and binary mass transfer data are usually correlated by use of dimensionless groups, such as:

$$\mathrm{Sh} = kd/\mathcal{D}; \quad \mathrm{St} = k/\bar{u}; \quad j_\mathrm{m} = \mathrm{St}\,\mathrm{Sc}^{2/3} \tag{10}$$

The Gilliland–Sherwood correlation for gas phase binary mass transfer in a wetted-wall column is, for example,

$$\mathrm{Sh} = 0.023\,\mathrm{Re}^{0.83}\,\mathrm{Sc}^{0.44} \tag{11}$$

For mass transfer from a pipe wall to a turbulently flowing fluid phase, the Chilton–Colburn analogy takes the form:

$$j_\mathrm{m} = f/2 \quad \text{or} \quad \mathrm{St} = f\,\mathrm{Sc}^{-2/3}/2 \tag{12}$$

Provided the Fanning friction factor f is based on shear friction and not total drag, eqn. (12) has been found to hold remarkably well for many types of flow systems and geometries [10, 11].

In the literature on multicomponent mass transfer it has been suggested that correlations of the type given by eqns. (11) and (12) can be generalized by replacing the binary diffusivity $\mathcal{D}$ with $\mathbf{D}$ and the binary mass transfer coefficient k with $\mathbf{k}$ (see *e.g.* refs. 1, 2, 3, 6, 7]). Thus for mass transfer between a pipe wall and a multicomponent fluid mixture in turbulent flow we have

$$\mathrm{St} = \mathbf{k}/\bar{u} = f\,\mathrm{Sc}^{-2/3}/2 \tag{13}$$

There is experimental evidence to support this matrix generalization procedure [1 - 3, 12 - 15], albeit limited in number and restricted to ideal contacting devices *e.g.* wetted-wall columns, well mixed trays *etc.*

Let us examine eqn. (13) in some more detail. The ratio of the off-diagonal element in $\mathbf{k}$ to the main one:

$$k_{ij}/k_{ii} \qquad (i \neq j)$$

is independent of f and hence independent of the Reynolds number. Now, we might expect that increasing the Re for fluid flow inside a conduit will have the effect of increasing the turbulent eddy transport relative to the molecular diffusion contribution. Since turbulent eddy transport is not species specific, we might expect a corresponding decrease in the influence of molecular diffusional coupling. This expectation is not fulfilled by the predictive model given by eqn. (13). Clearly, the resolution of this problem lies in the proper modelling of the molecular diffusion and turbulent eddy contributions to the interphase mass transfer process; this is the objective of the present communication. We shall restrict ourselves to fully developed turbulent flow inside a smooth conduit and assume steady-state conditions.

TURBULENT FILM MODEL

Consider mass transfer between the interface (subscript I) and the bulk fluid phase at any position z in the direction of flow. Let y represent the position coordinate along the direction of mass transfer, assumed unidimensional. No chemical reactions are considered in the ensuing analysis.

The equations of continuity of component i reduce for steady-state conditions to:

$$\frac{\mathrm{d}N_{iy}}{\mathrm{d}y} = 0, \qquad i = 1,2, \ldots n \tag{14}$$

and therefore the mass flux N_i is y-invariant:

$$N_i = N_{iy} = N_{i\mathrm{I}} = N_{i\mathrm{b}}, \qquad i = 1,2, \ldots n \tag{15}$$

The mixture total flux $N_\mathrm{t} = N_1 + N_2 + N_3 + \ldots N_n$ is also y-invariant. Let us define the mass diffusion flux with respect to the mass averaged reference velocity of the mixture J_i as:

$$J_i \equiv N_i - \omega_i N_\mathrm{t}, \qquad i = 1,2, \ldots n \tag{16}$$

Since the mass fractions ω_i vary along y, so do the mass diffusion fluxes J_i. For turbulent flow conditions we use time-smoothed fluxes and compositions. The constitutive relation for J_i, taking account of the molecular diffusion and turbulent eddy contributions, is given by (see ref. [16, 17] for a justification of this):

$$J = -\rho[\mathbf{D} + \boldsymbol{\epsilon}_\mathrm{m}]\,\frac{\mathrm{d}\boldsymbol{\omega}}{\mathrm{d}y} \tag{17}$$

where $\boldsymbol{\varepsilon}_\mathrm{m}$ is the matrix of turbulent eddy diffusivities. Since eddy mass transport is not species specific we must have the matrix $\boldsymbol{\epsilon}_\mathrm{m}$ reduce to the form of a scalar times the identity matrix, *i.e.*

$$\boldsymbol{\epsilon}_\mathrm{m} = \epsilon_\mathrm{m}\mathbf{I} \tag{18}$$

Let us define in the usual manner, the friction velocity:

$$u^* = (\tau_\mathrm{I}/\rho)^{1/2} = (f/2)^{1/2}\bar{u}, \tag{19}$$

the dimensionless distance parameter y^+:

$$y^+ = yu^*/\nu, \tag{20}$$

and the dimensionless velocity u^+:

$$u^+ = u/u^* = (2/f)^{1/2}u/\bar{u}. \tag{21}$$

With these definitions, equation (17) may be re-written as

$$J = -\rho u^*\left[\mathrm{Sc}^{-1} + \mathrm{Sc}_\mathrm{t}^{-1}\frac{\epsilon}{\nu}\,\mathbf{I}\right]\frac{\mathrm{d}\boldsymbol{\omega}}{\mathrm{d}y^+} \tag{22}$$

where we have additionally defined Sc_t, the turbulent Schmidt number:

$$\mathrm{Sc}_\mathrm{t} = \epsilon/\epsilon_\mathrm{m} \tag{23}$$

where ϵ is the turbulent eddy kinematic viscosity.

Combining equations (14 - 16) and (22) we obtain

$$N = -\rho u^* \left[\mathrm{Sc}^{-1} + \mathrm{Sc}_t^{-1} \frac{\epsilon}{\nu} \mathbf{I} \right] \times$$

$$\times \frac{\mathrm{d}\omega}{\mathrm{d}y^+} + \omega N_t = \textit{constant} \qquad (24)$$

In developing the integration of eqn. (24) we shall find it convenient to define a matrix $\boldsymbol{\Psi}$, which is position dependent:

$$\boldsymbol{\Psi} = \int_0^{y^+} \frac{N_t}{\rho u^*} \left[\mathrm{Sc}^{-1} + \mathrm{Sc}_t^{-1} \frac{\epsilon}{\nu} \mathbf{I} \right]^{-1} \mathrm{d}y^+ \qquad (25)$$

Let us denote by $\boldsymbol{\Phi}$, the matrix evaluated by taking the upper integration limit as y_b^+, the position at which the bulk composition ω_{ib} is reached. With the above definitions it is easy to solve the matrix differential eqn. (24), with the boundary conditions:

$$y^+ = 0, \quad \omega_i = \omega_{iI}; \quad y^+ = y_b^+, \quad \omega_i = \omega_{ib}, \qquad (26)$$

to obtain the composition profile as (see Appendix I for derivation):

$$(\omega - \omega_I) = [\exp \boldsymbol{\Psi} - \mathbf{I}][\exp \boldsymbol{\Phi} - \mathbf{I}]^{-1} \times$$

$$\times (\omega_b - \omega_I) \qquad (27)$$

Evaluation of the composition gradient at $y^+ = 0$ enables the calculation of the interfacial mass diffusion fluxes J_{iI} with the help of eqn. (22). We may thus derive:

$$J_I = N_t [\exp \boldsymbol{\Phi} - \mathbf{I}]^{-1} (\omega_I - \omega_b) \qquad (29)$$

Comparing eqn. (2) with eqn. (29) we obtain an expression for the matrix of high flux mass transfer coefficients $\mathbf{k}^\bullet$

$$\mathbf{k}^\bullet = \frac{N_t}{\rho} [\exp \boldsymbol{\Phi} - \mathbf{I}]^{-1} \qquad (30)$$

Inversion of eqn. (30) gives

$$\mathbf{k}^{\bullet -1} = [\exp \boldsymbol{\Phi} - \mathbf{I}] \rho / N_t \qquad (31)$$

Taking the limit of eqn. (31) for vanishing total flux ($N_t \rightarrow 0$), we obtain

$$N_t \overset{\mathrm{Lt}}{\longrightarrow} 0 \; \mathbf{k}^{\bullet -1} \equiv \mathbf{k}^{-1} = \frac{\rho}{N_t} \boldsymbol{\Phi} \qquad (32)$$

and therefore we may write eqn. (30) as

$$\mathbf{k}^\bullet = \mathbf{k} \boldsymbol{\Phi} [\exp \boldsymbol{\Phi} - \mathbf{I}]^{-1} \qquad (33)$$

whence we obtain, on comparing with eqn. (3), the matrix of high flux correction factors $\boldsymbol{\Xi}$ as:

$$\boldsymbol{\Xi} = \boldsymbol{\Phi} [\exp \boldsymbol{\Phi} - \mathbf{I}]^{-1} \qquad (34)$$

identical to the film theory result of eqn. (6). Since the matrix of correction factors depends on the total flux N_t, a trial and error procedure is necessary for the calculation of the individual fluxes N_i [1 - 5]; we concentrate now on the evaluation of the zero flux mass transfer coefficient matrix $\mathbf{k}$. We shall find it convenient to proceed further with the evaluation of the inverse matrix of Stanton numbers, $\mathbf{St}^{-1}$, which is given by the expression (*cf.* eqns. (10), (25) and (32)):

$$\mathbf{St}^{-1} = \left(\frac{2}{f} \right)^{1/2} \int_0^{y_b^+} \left[\mathrm{Sc}^{-1} + \mathrm{Sc}_t^{-1} \frac{\epsilon}{\nu} \mathbf{I} \right]^{-1} \mathrm{d}y^+ \qquad (35)$$

A major difficulty in the calculation of $\mathbf{St}$ using eqn. (35) is that the position y_b^+ at which the bulk phase composition ω_{ib} is reached is not known precisely. We proceed further by adopting the approach used in the solution of the binary problem; the approach is well described in standard sources [10, 11, 18, 19] and we shall only state the assumptions made and present the final solution to the multicomponent problem.

We divide the region 0 - y_b^+ into two subregions as follows:

0 - y_I^+: in which both molecular and turbulent contributions to mass transfer are important, and

y_I^+ - y_b^+: in which the turbulent eddy transport predominates over the molecular diffusion one.

Further we assume, as is commonly done in heat and mass transfer analyses, that the turbulent Schmidt is unity, *i.e.* $\mathrm{Sc}_t = 1$. With these assumptions and further taking the shear stress profile as:

$$\frac{\tau}{\tau_I} = \left(1 + \frac{\epsilon}{\nu} \right) \frac{\mathrm{d}u^+}{\mathrm{d}y^+} \cong 1, \qquad (36)$$

we may derive the final working relationship for $\mathbf{St}^{-1}$:

$$\mathbf{St}^{-1} = (2/f)\mathbf{I} + (2/f)^{1/2} \int_0^{y_I^+} \left\{ \left[\mathrm{Sc}^{-1} + \frac{\epsilon}{\nu} \mathbf{I} \right]^{-1} - \right.$$

$$\left. - \left[\mathbf{I} + \frac{\epsilon}{\nu} \mathbf{I} \right]^{-1} \right\} \mathrm{d}y^+ \qquad (37)$$

When y_I^+ and the eddy kinematic viscosity profile are specified, the right hand side of eqn. (37) can be evaluated and the matrix of zero flux mass transfer coefficients obtained from $\mathbf{k} = \mathbf{St}\bar{u}$. There are many such models in the literature and these are discussed in the excellent reviews of Sherwood [10, 11] and Sideman and Pinczewski [19]. We discuss here only one such model, the classic one due to von Kármán, in order to illustrate the use of the developed multicomponent turbulent film model. According to the von Kármán model the position $y_1^+ = 30$ and the eddy kinematic viscosity profile is given by the following:

$$\frac{\epsilon}{\nu} = 0, \qquad 0 < y^+ < 5 \tag{38}$$

$$\frac{\epsilon}{\nu} = \frac{y^+}{5} - 1, \qquad 5 < y^+ < 30 \tag{39}$$

Equation (37) yields:

$$\mathbf{St}^{-1} = \frac{2}{f}\mathbf{I} + 5\left(\frac{2}{f}\right)^{1/2}\left[\mathbf{Sc} - \mathbf{I} + \ln\left(\mathbf{I} + \frac{5}{6}[\mathbf{Sc} - \mathbf{I}]\right)\right] \tag{40}$$

We note in passing that there appear to be typographical errors in the binary version of eqn. (40) given in the reviews of Sherwood [10, 11]; the correct binary form is available elsewhere [*e.g.* 20]. Another observation concerns the Reynolds analogy for multicomponent systems; when $\mathbf{Sc} = \mathbf{I}$ it is easy to check from eqn. (37) that $\mathbf{St} = (f/2)\mathbf{I}$. The requirement $\mathbf{Sc} = \mathbf{I}$ for a multicomponent system is a much more special case than for the corresponding binary system for it requires that all the constituent binary pair diffusivities in the multicomponent system be equal to one another, a very stringent condition indeed.

Equations (10), (32), (33) and (37) represent the final working relations of the turbulent film model developed in this paper and the consequences of the analysis are best illustrated by means of a numerical example in ternary mass transfer.

ILLUSTRATIVE EXAMPLE

Consider gas phase mass transfer in a wetted wall column; the system consisting of a downward flowing liquid film of the liquid mixture acetone(1) and benzene(2), in contact with co-current flow of a vapour mixture of acetone(1)–benzene(2) in the presence of a non-transferring inert gas helium(3). Experiments with the objective of demonstrating the diffusional interactional effects in the gas phase were carried out by Modine [21]; these experiments have been re-interpreted in terms of matrix formulations of multicomponent mass transfer by Krishna [2, 22]. We will compare the predictions of N_i by the developed turbulent film model, assuming a von Kármán universal velocity profile in the gas phase, with those of the Chilton–Colburn multicomponent model, given by eqn. (13) for the following set of conditions:

compositions at the gas–liquid interface:
$\omega_{1\mathrm{I}} = 0.1347$; $\omega_{2\mathrm{I}} = 0.6478$.
composition of the bulk flowing gas phase:
$\omega_{1\mathrm{b}} = 0.3102$; $\omega_{2\mathrm{b}} = 0.3188$.

Other relevant physical and thermodynamic data are as follows:

total pressure = 1.3 bar;

temperature = 35.0 °C.

binary pair diffusivities: $\mathcal{D}_{12} = 2.93$ mm^2 s^{-1}; $\mathcal{D}_{13} = 31.8$ mm^2 s^{-1}; $\mathcal{D}_{23} = 29$ mm^2 s^{-1} (these values corresponding to 35 °C).

mixture gas density: $\rho = 0.641$ kg m^{-3};

gas mixture viscosity: $\mu = 15.4$ μPa s.

friction factor: $f/2 = 0.926(0.0007 + 0.0625/\mathrm{Re}^{0.32})$, correlation obtained from binary mass transfer data by Modine [21].

diameter of conduit: $d = 0.025019$ m (= 0.985 inch).

Now, since helium is non-transferring, *i.e.* $N_3 = 0$, the elements of the bootstrap matrix $\boldsymbol{\beta}$ will be given by (see Krishna [2]):

$$\beta_{ij} = \delta_{ij} + \omega_i/\omega_3, \qquad i,j = 1,2 \tag{41}$$

Since the interfacial fluxes $J_{i\mathrm{I}}$ will be calculated by use of eqns. (2) and (33), the elements of the bootstrap matrix will have to be calculated using the interfacial mass fractions in eqn. (41).

Next we need to calculate the elements of the matrix $\mathbf{D}$ in a mass averaged reference velocity frame from the binary pair diffusivities $\mathcal{D}_{ij}$. The estimation procedure for $\mathbf{D}$ in the *molar* average reference velocity frame is widely available in the literature [*e.g.* [1]]; we detail in Appendix II a step-by-step procedure for calculating $\mathbf{D}$ in the mass average reference velocity frame. For the set of conditions chosen above for the system acetone(1)–benzene(2)–helium(3), the elements D_{ij} have the values (calculated at the

TABLE 1

Comparison of model predictions for gas phase mass transfer in the system acetone(1)–benzene(2)–helium(3)

Reynolds Number	Acetone flux, N_1, mg m^{-2} s^{-1}		Benzene flux, N_2, g m^{-2} s^{-1}		k_{12}/k_{11}	
	von Kármán	Chilton–Colburn	von Kármán	Chilton–Colburn	von Kármán	Chilton–Colburn
9000	169	388	11.8	11.8	0.162	0.189
10000	164	419	12.7	12.7	0.160	0.189
15000	130	566	17.2	17.2	0.152	0.189
20000	85	701	21.3	21.3	0.147	0.189
25000	34	829	25.2	25.1	0.143	0.189
30000	−22	951	28.9	28.8	0.140	0.189
40000	−141	1183	36.0	35.8	0.136	0.189
50000	−268	1402	42.8	42.5	0.132	0.189

arithmetic average compositions) (Units: mm^2 s^{-1})

D_{11} = 21.2; D_{12} = 5.97; D_{21} = 10.2; D_{22} = 23.5

Table 1 presents the results of the calculations of N_1, N_2 and the ratio k_{12}/k_{11} using the von Kármán turbulent film model and the Chilton–Colburn model, for a range of values of the Reynolds number.

Let us first discuss the ratio k_{12}/k_{11}; this ratio is predicted to be constant by the generalized Chilton–Colburn approach, eqn. (13). This because the model assumes that **k** is proportional to **D**$^{2/3}$. The ratio k_{12}/k_{11} = 0.189, as predicted by the model, is thus smaller than the ratio D_{12}/D_{11}; this is because of the influence of the turbulent mass transport. Thus while the Chilton–Colburn model recognises that coupling effects are reduced due to eddy mass transport, the reduction is assumed to be independent of the Reynolds number. Since the eddy diffusivity increases with the Reynolds number we should really expect coupling effects to decrease gradually with increasing Re. Thus the extension, eqn. (13), of the classic Chilton–Colburn analogy is physically unrealistic.

The turbulent film model using the von Kármán universal velocity profile, eqn. (40), properly recognises that the turbulent eddy mass transport contribution should increase relative to the molecular contribution as Re is increased. This is reflected in the values of the ratio k_{12}/k_{11} decreasing from a value 0.162 at Re = 9000 to a value 0.132 at Re = 50 000.

Let us now consider the flux predictions by the two models. Since the driving force for component 2, $\Delta\omega_2$, is larger than that of component 1, $\Delta\omega_1$, and opposite in sign, the flux N_1 is strongly linked with the driving force of component 2. At Re = 9000 both the von Kármán and the Chilton–Colburn models predict that N_1 is *positive* even though $\Delta\omega_1 \equiv (\omega_{1I} - \omega_{1b})$ is *negative*. In other words both models predict reverse mass transfer for component 1. The conditions chosen in the calculation at Re = 9000 correspond almost exactly with the conditions prevailing near the top of the wetted-wall in one particular run (Run 7) of the experiments carried out by Modine [2]. Reverse mass transfer was experimentally confirmed, lending credence to coupled multicomponent mass transfer formulations; the experimental results cannot be explained even qualitatively if the cross coefficients in **k** are assumed to be zero, as is implied by effective diffusivity approaches. Both the von Kármán and Chilton–Colburn model predictions are not too far apart when Re = 9000, the predictions of N_2 being identical to each other. Therefore it is not surprising that we had, in an earlier analysis of the Modine experiments, concluded that eqn. (13) can be safely used in design calculations for design purposes [1, 2]. The picture changes dramatically when the Re is increased. Due to the fact that in the Chilton–Colburn model k_{12}/k_{11} remains constant, the flux N_1 monotonically *increases* with increasing Re. The turbulent von Kármán film model predictions are quite the reverse. Due to reduced coupling effects, the acetone flux is influenced to a lesser extent by the benzene flux as Re is increased. At Re = 30 000 the coupling effect is reduced to such an extent that acetone(1) flux is directed from the bulk to the interface, a direction to be naturally expected from its driving force

($\Delta\omega_1 = -0.1755$). As Re is increased beyond 30000, the absolute value of N_1 increases and the component 1 behaves 'normally'. Unfortunately, no experiments were performed with varying Re to check the dramatic differences in the model predictions. Physical intuition would suggest that the predictions of the von Kármán turbulent film model are more realistic.

In many ways the sensitivity of multicomponent mass transfer calculations to the choice of the model, as noted above, is similar to our earlier published observation that under certain conditions the film and penetration models could predict different directions of mass transfer [26]. In one way this is unfortunate because for really interesting multicomponent systems where molecular diffusional coupling effects are large, the precise calculation of the mass transfer fluxes is very sensitive to the choice of the model. Looking at the bright side of the problem, we could use multicomponent mass transfer coupling effects as an experimental tool to discriminate between the many mass transfer models available in the literature; the study presented in this communication highlights the limitations of the Chilton–Colburn analogy as applied to multicomponent systems. Of course, to a design engineer faced with the task of, *e.g.*, designing vapour condensers this is somewhat worrying because of the doubtful applicability of the matrix generalization procedure of all types of binary correlations. On the basis of the evidence of this paper we consider it necessary to retract our statement that the multicomponent mass transfer problem is essentially 'solved', if the corresponding binary problem is [1].

For weakly coupled multicomponent systems, all multicomponent mass transfer models will predict similar results, even models based on the effective diffusivity [15]. In a way this also reflected in Table 1 where both models are seen to predict identical values of the benzene flux N_2; benzene is only weakly coupled to the acetone driving force.

CONCLUDING REMARKS

In this paper we have developed a turbulent film model for multicomponent mass transfer. The major result of this communication is eqn. (37) which enables calculation of the zero-flux mass transfer coefficients. The correction factor for high mass transfer rates is given by eqn. (34), identical in form to the film model for multicomponent mass transfer [1, 2]. The turbulent film model correctly describes the relative influences of the molecular and turbulent eddy contributions to mass transfer. Equation (37) can only be applied for the calculation of $\mathbf{k}$ if information on y_1^+ and $\epsilon(y^+)$ is available; this kind of information is available in the literature for only a limited number of cases *e.g.* flows inside tubes and over flat plates. One important practical problem which can be solved with the help of the turbulent film model is condensation of mixed vapours inside vertical tubes. Thus the design procedure published in the literature [24, 25] can be applied with the new recommendation that eqn. (37) be used instead of the earlier suggested eqn. (13) for estimation of $\mathbf{k}$ for gas phase transport.

One worrying conclusion reached in this paper is that for strongly coupled systems, the calculation of the transfer fluxes is very sensitive to the chosen model. For strongly coupled systems, empirical binary correlations of the type given by eqns. (12) and (13) cannot be safely generalized. A deeper understanding of the various mechanisms of mass transfer (molecular diffusion, turbulent eddy transport, interfacial turbulence *etc.*), with appropriate quantification of the various constituent mechanisms, is required. The turbulent film model developed in this paper is a step towards this end.

NOMENCLATURE

$\mathbf{A}(y^+)$	matrix defined by eqn. (I.2)
c	total molar concentration of mixture, kmol m^{-3}
d	diameter of conduit, m
$\mathcal{D}$	molecular diffusion coefficient for binary mixture, m^2 s^{-1}
D_{ij}^{CH}	Curtiss–Hirschfelder diffusion coefficients (eqn. (II.1)), m^2 s^{-1}
$\mathbf{D}$	matrix of molecular diffusion coefficients in the mass average reference velocity frame, m^2 s^{-1}
D_{ij}''	coefficients given by eqn. (II.6), m^2 s^{-1}

f	Fanning friction factor
$\mathbf{I}$	Identity matrix with elements δ_{ik}
j_m	j-factor for mass transfer, defined by eqn. (10)
J_i	mass diffusion flux of component i relative to the mass average reference velocity, kg m^{-2} s^{-1}
J_I	column matrix of mass diffusion fluxes evaluated at the interface, kg m^{-2} s^{-1}
k	binary zero-flux mass transfer coefficient, m s^{-1}
$\mathbf{k}$	matrix of multicomponent zero-flux mass transfer coefficients, m s^{-1}
$\mathbf{k}^\bullet$	matrix of finite flux multicomponent mass transfer coefficients, m s^{-1}
M_i	molecular weight of component i, kg $kmol^{-1}$
n	number of components in mixture
N_i	mass flux of component i in a stationary coordinate reference frame, kg m^{-2} s^{-1}
N	column matrix of mass fluxes, kg m^{-2} s^{-1}
N_t	mass transfer flux of total mixture relative to a stationary coordinate reference frame, kg m^{-2} s^{-1}
$\mathbf{R}$	n dimensional matrix with elements given by eqns. (II.3) and (II.4), m^{-2} s
Sc	Schmidt number for binary system, $Sc = \nu/\mathcal{D}$
$\mathbf{Sc}$	matrix of multicomponent Schmidt numbers, $\mathbf{Sc} = \nu\mathbf{D}^{-1}$
Sc_t	turbulent Schmidt number, defined by eqn. (23)
Sh	Sherwood number for binary mass transfer, defined by eqn. (10)
$\mathbf{Sh}$	matrix of multicomponent Sherwood numbers $\mathbf{Sh} = \mathbf{k}\mathbf{D}^{-1}d$
St	Stanton number for binary system
$\mathbf{St}$	matrix of multicomponent Stanton numbers
t_c	contact time between phases, s
u	fluid velocity along conduit, function of y, m s^{-1}
$\bar{u}$	average flow velocity in conduit, m s^{-1}
u^*	friction velocity defined by eqn. (19)
u^+	reduced velocity defined by eqn. (21)
x_i	mole fraction of component i
y	position coordinate measured from the interface, m
y^+	dimensionless distance coordinate defined by eqn. (20)
y_I^+	position beyond which turbulent transport mechanisms predominate
y_b^+	position at which bulk fluid composition is reached
z_i	$i = 1,2\ldots$; dummy variables used in eqn. (I.5)

Greek symbols

$\boldsymbol{\beta}$	bootstrap solution matrix relating total fluxes to diffusion fluxes defined by $N = \boldsymbol{\beta}_I J_I = \boldsymbol{\beta}_b J_b$
δ_{ik}	Kronecker delta
ϵ	turbulent eddy (kinematic) viscosity, m^2 s^{-1}
ϵ_m	turbulent eddy mass diffusivity, m^2 s^{-1}
$\boldsymbol{\zeta}$	column matrix of integration constants, see eqn. (I.3)
μ	fluid phase dynamic viscosity, Pa s
ν	$= \mu/\rho$, fluid kinematic (molecular) viscosity, m^2 s^{-1}
$\boldsymbol{\Xi}$	matrix of correction factors to account for high transfer rates
ρ	fluid mixture mass density, kg m^{-3}
τ	shear stress, N m^{-2}
$\boldsymbol{\Phi}$	matrix of mass transfer rate factors defined by eqn. (25) taking $y^+ = y_b^+$
$\boldsymbol{\Psi}$	matrix defined by eqn. (25)
$\boldsymbol{\Omega}_0^{y^+}(A)$	matrizant defined by eqn. (I.5)
ω_i	time-smoothed mass fraction of component i
ω_{ib}	bulk phase time smoothed mass fractions
ω_{iI}	interfacial time smoothed mass fractions
$\Delta\omega_i$	$= \omega_{iI} - \omega_{ib}$, mass fraction driving force

Subscripts

b	pertaining to bulk phase
I	pertaining to interface
n	pertaining to component n

Superscripts

+	non-dimensionalized property
●	parameter corresponding to high mass transfer rate conditions
–	overbar denoting arithmetic averaged composition
y^+	upper limit of intergral

Matrix notation

Bold face (**A**) $n - 1 \times n - 1$ dimensional square matrix

Bold face italic ($\boldsymbol{A}$) column matrix of dimension $n - 1$

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APPENDIX I

Solution of the matrix differential eqn. (24)

For simplicity let us rewrite the matrix differential eqn. (24) in the form

$$\frac{\mathrm{d}\boldsymbol{\omega}}{\mathrm{d}y^+} = \mathbf{A}(y)^+(\omega + \zeta) \tag{I.1}$$

where

$$\mathbf{A}(y)^+ = \frac{N_\mathrm{t}}{\rho u^*}\left[\mathbf{Sc}^{-1} + \mathrm{Sc}_\mathrm{t}^{-1}\frac{\epsilon}{\nu}\mathbf{I}\right]^{-1} \tag{I.2}$$

is dependent on the position y^+. $\boldsymbol{\zeta}$ is a column matrix of constants. It is not necessary to determine these constants ζ_i. We may rewrite eqn. (I.1) in the form

$$\frac{\mathrm{d}(\omega + \zeta)}{\mathrm{d}y^+} = \mathbf{A}(y)^+(\omega + \zeta) \tag{I.3}$$

The solution to the matrix differential eqn. (I.3) can be found in the text by Amundson [27]; here we follow closely the treatment by Taylor [28]. The solution to (I.3) can be written as

$$(\omega + \zeta) = \mathbf{\Omega}_0^{y^+}(\boldsymbol{A})(\omega_\mathrm{I} + \zeta) \tag{I.4}$$

where $\mathbf{\Omega}_0^{y^+}(\boldsymbol{A})$ is the matrizant defined by

$$\begin{aligned}\mathbf{\Omega}_0^{y^+}(\boldsymbol{A}) = \mathbf{I} &+ \int_0^{y^+} \mathbf{A}(z_1)\,\mathrm{d}z_1 + \\ &+ \int_0^{y^+} \mathbf{A}(z_1) \int_0^{z_1} \mathbf{A}(z_2)\,\mathrm{d}z_2\,\mathrm{d}z_1 + \\ &+ \int_0^{y^+} \mathbf{A}(z_1) \int_0^{z_1} \mathbf{A}(z_2) \times \\ &\times \int_0^{z_2} \mathbf{A}z_3\,\mathrm{d}z_3\,\mathrm{d}z_2\,\mathrm{d}z_1 + \ldots\end{aligned} \tag{I.5}$$

where the z_i's are dummy variables.

$\boldsymbol{\omega}_\mathrm{I}$ is the column matrix of mass fractions at the wall, $y^+ = 0$. Substituting $\boldsymbol{\omega} = \boldsymbol{\omega}_\mathrm{I}$ when $y^+ = 0$ in eqn. (I.4) and subtracting the result from eqn. (I.4) we obtain, after noting that $\mathbf{\Omega}_0^0(\boldsymbol{A}) = \mathbf{I}$, the identity matrix:

$$(\omega - \omega_\mathrm{I}) = [\mathbf{\Omega}_0^{y^+}(\boldsymbol{A}) - \mathbf{I}](\omega_\mathrm{I} + \zeta) \tag{I.6}$$

At the distance $y^+ = y_\mathrm{b}^+$, $\omega = \omega_\mathrm{b}$ and from eqn. (I.6):

$$(\omega_{\mathrm{b}} - \omega_{\mathrm{I}}) = [\Omega_0^{y_{\mathrm{b}}^+}(A) - \mathbf{I}](\omega_{\mathrm{I}} + \zeta) \tag{I.7}$$

Combining eqn.s (I.6) and (I.7) we obtain the composition profile as

$$(\omega - \omega_{\mathrm{I}}) = [\Omega_0^{y^+}(A) - \mathbf{I}][\Omega_0^{y_{\mathrm{b}}^+}(A) - \mathbf{I}]^{-1} (\omega_{\mathrm{b}} - \omega_{\mathrm{I}}) \tag{I.8}$$

Let us now consider the evaluation of the matrizant $\Omega_0^{y^+}(A)$. The matrix $\mathbf{A}(y^+)$ is given by eqn. (I.2) and it is easy to see that the *inverse* matrix $[\mathbf{A}(y^+)]^{-1}$ exhibits a very simple dependence on the position coordinate y^+ (recall that Sc is assumed to be position independent in our model): only the diagonal elements of $[\mathbf{A}(y^+)]^{-1}$ are position dependent. Further, the position dependence is the same for all the principal diagonal elements because ϵ/ν is not species dependent. Thus the transformation matrix which diagonalizes Sc^{-1} also diagonalizes $[\mathrm{Sc}^{-1} + \mathrm{Sc}_{\mathrm{t}}^{-1}\epsilon/\nu\mathbf{I}]$, $[\mathbf{A}(y^+)]^{-1}$ and $[\mathbf{A}(y^+)]$. The transformation matrix then is independent of y^+ and the four matrices listed above all commute with each other and with $\int \mathbf{A}(y^+)\,\mathrm{d}y^+$. Thus the integrations required in eqn. (I.5) can be carried out by parts to give

$$\Omega_0^{y^+}(A) = \exp \Psi = \exp\left[\int_0^{y^+} [\mathbf{A}(y^+)]\, \mathrm{d}y^+\right] \tag{I.9}$$

where Ψ is given by eqn. (25). By combining eqns. (I.8) and (I.9), after noting that Φ is obtained by taking $y^+ = y_{\mathrm{b}}^+$ as the upper limit of integration in eqn. (25), we obtain the composition profile given by eqn. (27).

An alternative derivation of eqn. (27), without the use of matrizants, can be found in the paper by Standart and Krishna [29].

APPENDIX II

Calculation of the matrix D *in the mass averaged reference velocity frame*

The first step is to calculate the Curtiss–Hirschfelder diffusion coefficients [23], defined for purely molecular transport by:

$$J_i = \frac{c^2}{\rho} \sum_{j=1}^{n} M_i M_j D_{ij}^{\mathrm{CH}} \underset{\sim}{\nabla} x_j \tag{II.1}$$

where x_i is the mole fraction of species i. The Curtiss–Hirschfelder diffusion coefficients are given in terms of the binary pair diffusivities by

$$D_{ij}^{\mathrm{CH}} = \frac{\sum\limits_{k=1}^{n} x_k M_k}{M_j} \left(\frac{R^{ji} - R^{ii}}{\det \mathbf{R}}\right) \tag{II.2}$$

R_{ij} $(i,j = 1,2,\ldots n)$ are given by:

$$R_{ii} = 0 \qquad i = 1,2,\ldots n \tag{II.3}$$

$$R_{ij} = \frac{x_i}{\mathcal{D}_{ij}} + \frac{M_j}{M_i} \sum_{k \neq i}^{n} \frac{x_k}{\mathcal{D}_{ik}} \qquad \begin{array}{l} i,j = 1,2,\ldots n \\ (i \neq j) \end{array} \tag{II.4}$$

R^{ji} and R^{ii} are the minors of the ji and ii elements of the $\mathbf{R}$ matrix.

Since in the turbulent film model developed here the matrix $\mathbf{D}$ is assumed constant, we need to evaluate the elements D_{ij}^{CH} using the arithmetic average mole fractions $\bar{x}_i$. Once D_{ij}^{CH} are calculated using eqn. (II.2) we need to calculate D_{ij}'' whose elements are given by:

$$D_{ij}'' = M_i D_{ij}^{\mathrm{CH}} \sum_{k=1}^{n} \frac{\bar{\omega}_k}{M_k} - \frac{M_i}{M_j} \sum_{k=1}^{n} D_{ik}^{\mathrm{CH}} \bar{\omega}_k, \qquad i,j = 1,2,\ldots n \tag{II.5}$$

Finally the elements of the $n-1 \times n-1$ dimensional matrix $\mathbf{D}$ can be calculated from

$$D_{ij} = D_{in}'' - D_{ij}'' \qquad i,j = 1,2,\ldots n-1 \tag{II.6}$$