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A GENERALIZED FILM MODEL FOR MASS TRANSFER IN NON-IDEAL FLUID MIXTURES

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Abstract—Expressions for calculating steady state mass transfer rates in n-component fluid mixtures across planar, cylindrical and spherical interfaces are presented in a common format using matrix formulations The resulting generalized multicomponent film model for non-ideal fluid mixtures is based on an analytic solution to the Maxwell–Stefan equations

INTRODUCTION

In many interphase mass transfer processes the film model affords a convenient and simple method for estimating the transfer rates In the development of the film model it is assumed that the mass transfer process is governed by steady-state molecular diffusion across a "film", a thin layer adjacent to the interface Expressions for the transfer coefficients and transfer rates are obtained by solution of the equations of continuity in the appropriate coordinate system For two component mixtures, solution of the steady-state diffusion equations have been discussed thoroughly in the literature (e g [1]) For systems with three or more species, multicomponent systems, solutions are available for various special cases [2–10] The object of the current work is to provide a common format for representing the steady-state solutions for diffusion of n-component non-ideal fluid mixtures across planar, cylindrical and spherical interfaces The analysis is similar to that presented in Refs [8–10] and is based on a matrix method of solution to the Maxwell–Stefan equations, suitably generalized for non-ideal fluid mixtures

ANALYSIS

For steady-state diffusion in n-component fluid mixtures, the equations of continuity reduce to [1]

$$\nabla \ \mathbf{N}_i = 0, \qquad i = 1, 2, \quad n \tag{1}$$

where $\mathbf{N}_i$ is the molar flux of species i in the diffusing mixture with respect to a stationary coordinate frame of reference and is given by

$$\mathbf{N}_i = c_i \mathbf{u}_i, \qquad i = 1, 2, \quad n \tag{2}$$

where $\mathbf{u}_i$ is the velocity of the diffusing species i The mixture molar flux $\mathbf{N}_t$ is obtained by summing eqn (2) over the n species in the mixture

$$\mathbf{N}_t = \sum_{i=1}^{n} c_i \mathbf{u}_i = c \sum_{i=1}^{n} x_i \mathbf{u}_i = c\mathbf{u} \tag{3}$$

where $\mathbf{u}$ is the molar average velocity of the diffusing mixture Other choices for the mixture velocity are possible [11–13] but for most applications in chemical engineering the molar average velocity is convenient and will be used here We may define diffusion fluxes relative to the mixture velocity as

$$\mathbf{J}_i = c_i(\mathbf{u}_i - \mathbf{u}), \qquad i = 1, 2, \quad n \tag{4}$$

and therefore the molar fluxes $\mathbf{N}_i$ can be written, in view of eqns (2)–(4), in terms of the diffusive and convective contributions as

$$\mathbf{N}_i = \mathbf{J}_i + c_i \mathbf{u} = \mathbf{J}_i + x_i \mathbf{N}_t, \qquad i = 1, 2, \quad n \tag{5}$$

The n diffusion fluxes $\mathbf{J}_i$ are not all independent for on summing (4) we find in view of eqn (3) that

$$\sum_{i=1}^{n} \mathbf{J}_i = 0 \tag{6}$$

and therefore only $n-1$ of the diffusion fluxes are independent

The diffusional transport process within the fluid mixture is correctly portrayed by the diffusion fluxes $\mathbf{J}_i$ whereas the molar fluxes $\mathbf{N}_i$ are the ones which are important from an engineering point of view and appear in material and energy balance relationships The object of our analysis will therefore be to obtain a convenient expression for calculation of the molar fluxes $\mathbf{N}_i$

For uni-r-directional diffusion, eqns (1) simplify to give for transfer across planar, cylindrical and spherical interfaces

Planar

$$\frac{dN_{ir}}{dr} = 0, \qquad i = 1, 2, \quad n \tag{7}$$

Cylindrical

$$\frac{d(rN_{ir})}{dr} = 0, \qquad i = 1, 2, \quad n \tag{8}$$

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Spherical

$$\frac{\mathrm{d}(r^2 N_{ir})}{\mathrm{d}r} = 0, \qquad i = 1, 2, \quad n \tag{9}$$

Consistent with the film model, we assume that the molecular diffusion process is restricted to a region between the surfaces $r = r_0$ and $r = r_\delta$ The thickness of the film is therefore given by

$$\delta \equiv r_\delta - r_0 \tag{10}$$

Equations (7) imply that the molar fluxes N_i are invariant across the thickness of the planar film

$$N_{ir} = N_{i0} = N_{i\delta}, \qquad i = 1, 2, \quad n \tag{11}$$

For cylindrical films we have from eqns (8)

$$rN_{ir} = r_0 N_{i0} = r_\delta N_{i\delta}, \qquad i = 1, 2, \quad n \tag{12}$$

and for spherical films, eqns (9) give

$$r^2 N_{ir} = r_0{}^2 N_{i0} = r_\delta{}^2 N_{i\delta}, \qquad i = 1, 2, \quad n \tag{13}$$

It is clear from eqns (11)–(13) that if the molar fluxes N_{i0} are calculated at the surface $r = r_0$, then the fluxes at any other surface can be obtained straightforwardly In order to calculate the fluxes N_{i0} we require to solve the differential eqns (7)–(9) In many applications of chemical engineering importance the compositions (expressed conveniently in terms of mole fractions) are known at either end of the diffusion path, we thus have the boundary conditions

$$r = r_0, x_i = x_{i0}, \qquad i = 1, 2, \quad n \tag{14}$$

$$r = r_\delta, x_i = x_{i\delta}, \qquad i = 1, 2, \quad n \tag{15}$$

To determine the composition profiles across the film, which will allow calculation of the fluxes, we need constitutive equations relating fluxes to the compositions and composition gradients For binary mixtures the constitutive relations are given by the Fick's law

$$J_{1r} = -c\mathscr{D}_{12}\frac{\mathrm{d}x_1}{\mathrm{d}r} \tag{16}$$

where $\mathscr{D}_{12}$ is the binary diffusion coefficient of species 1 in 2 We may write an analogous expression for component 2 as

$$J_{2r} = -c\mathscr{D}_{21}\frac{\mathrm{d}x_2}{\mathrm{d}r} \tag{17}$$

but in view of eqns (6) and the constraint

$$\sum_{i=1}^{n}\frac{\mathrm{d}x_i}{\mathrm{d}r} = 0 \tag{18}$$

it is easy to check that

$$\mathscr{D}_{12} = \mathscr{D}_{21} \tag{19}$$

and therefore there is only one independent diffusion coefficient describing the diffusional transport in a two-component system

For an n-component mixture if we consider a naive extension of (16) as

$$J_{ir} = -c\mathscr{D}_i\frac{\mathrm{d}x_i}{\mathrm{d}r}, \qquad i = 1, 2, \quad n \tag{20}$$

then it can be shown[14] that the constituent diffusivities $\mathscr{D}_i$ must all be identical

$$\mathscr{D}_i = \mathscr{D}_n, \qquad i = 1, 2, \quad n-1 \tag{21}$$

Equations (21) require that each species in the n-component mixture to have equal facility for transfer irrespective of its molecular size and nature Clearly, this simple description of diffusional transport can only be expected to hold for ideal fluid mixtures For the general case of non-ideal fluid mixtures we must allow for the coupling between the various species transfers The proper generalization of eqn (16) is

$$J_{ir} = -c\sum_{k=1}^{n-1} D_{ik}\frac{\mathrm{d}x_k}{\mathrm{d}r}, \qquad i = 1, 2, \quad n-1 \tag{22}$$

where D_{ik}, i, $k = 1, 2, \quad n-1$, are the generalized Fick's law diffusivities The cross coefficients D_{ik} ($i \neq k$) account for the coupling between the various species transfers In view of eqns (6) and (18) only $n-1$ diffusion fluxes and composition gradients are considered in eqn (22) For $n = 2$, eqns (22) simplify to eqn (16)

A more fundamental formulation of the constitutive relations for n-component diffusion is obtained by using the principles of Irreversible Thermodynamics[11] For isothermal-isobaric diffusion under conditions in which mechanical equilibrium may be assumed we get the expression for the rate of entropy production as

$$\sigma = -\frac{1}{T}\sum_{i=1}^{n} J_{ir}\frac{\mathrm{d}\mu_i}{\mathrm{d}r} \tag{23}$$

The molar chemical potential gradients $\mathrm{d}\mu_i/\mathrm{d}r$ arise as the proper driving forces for diffusion in non-ideal mixtures However, the n chemical potential gradients are not all independent because of the Gibbs–Duhem restriction

$$\sum_{i=1}^{n} x_i\frac{\mathrm{d}\mu_i}{\mathrm{d}r} = 0 \tag{24}$$

Incorporating the restraints (6), (18) and (24) in eqn (23) we may write σ in terms of independent fluxes and driving forces as

$$\sigma = \sum_{i=1}^{n-1} J_{ir}Y_i \tag{25}$$

where the modified driving forces are defined as

$$Y_i = -\frac{1}{T}\sum_{k=1}^{n-1} A_{ik}\frac{\mathrm{d}\mu_k}{\mathrm{d}r}, \qquad i = 1, 2, \quad n-1 \tag{26}$$

where

$$A_{ik} = \delta_{ik} + x_k/x_n, \qquad i, k = 1, 2, \quad n-1 \tag{27}$$

If we postulate linear constitutive relations of the form

$$J_{ir} = \sum_{k=1}^{n-1} L_{ik} Y_k, \qquad i = 1, 2, \quad n-1 \tag{28}$$

then the matrix of coefficients $[L]$ is symmetric

$$L_{ik} = L_{ki}, \qquad i, k = 1, 2, \quad n-1 \quad i \neq k \tag{29}$$

according the Onsager Reciprocal Relations

Now, the $n-1$ independent chemical potential gradients may be related to the mole fraction gradients as

$$\frac{d\mu_i}{dr} = \sum_{k=1}^{n-1} \frac{\partial \mu_i}{\partial x_k} \frac{dx_k}{dr} = RT \sum_{k=1}^{n-1} \frac{\partial \ln(\gamma_i x_i)}{\partial x_k} \frac{dx_k}{dr}, \qquad i = 1, 2, \quad n-1 \tag{30}$$

We may write eqn (30) in the form

$$x_i \frac{d\mu_i}{dr} = RT \sum_{k=1}^{n-1} \Gamma_{ik} \frac{dx_k}{dr}, \qquad i = 1, 2, \quad n-1 \tag{31}$$

where we have defined thermodynamic factors Γ_{ik} by

$$\Gamma_{ik} = \delta_{ik} + \frac{x_i}{x_k} \frac{\partial \ln \gamma_i}{\partial \ln x_k}, \qquad i, k = 1, 2, \quad n-1 \tag{32}$$

Combination of eqns (26), (28) and (31) gives in matrix notation

$$(J_r) = -R[L][A] \ulcorner \frac{1}{x} \lrcorner [\Gamma] \frac{d(x)}{dr} \tag{33}$$

which when compared with the eqn (22) shows the relation between the generalized Fick's law diffusivities D_{ik} and the Onsager coefficients L_{ik}

$$c[D] = R[L][A] \ulcorner \frac{1}{x} \lrcorner [\Gamma] \tag{34}$$

The Onsager Reciprocal Relations (29) reduce the number of independent diffusion coefficients D_{ik} describing n-component diffusion from $(n-1)^2$ to $n(n-1)/2$

As an alternative to the Onsager formulation of the constitutive relations, we may relate the chemical potential gradients to the diffusion fluxes by the generalized Maxwell–Stefan equations [12, 15, 16]

$$\frac{1}{RT} x_i \frac{d\mu_i}{dr} = \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{x_i N_{kr} - x_k N_{ir}}{c\text{Đ}_{ik}} = \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{x_i J_{kr} - x_k J_{ir}}{c\text{Đ}_{ik}}, \qquad i = 1, 2, \quad n-1 \tag{35}$$

where Đ_{ik} are the generalized Maxwell–Stefan diffusion coefficients

If we define a matrix $[B]$ with elements given by

$$B_{ii} = \frac{x_i}{\text{Đ}_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{x_k}{\text{Đ}_{ik}}, \qquad i = 1, 2, \quad n-1 \tag{36}$$

$$B_{ij} = -x_i(1/\text{Đ}_{ij} - 1/\text{Đ}_{in}), \qquad i, k = 1, 2, \quad n-1 \quad i \neq k \tag{37}$$

we may write eqns (35) in view of eqn (31) as

$$c[\Gamma] \frac{d(x)}{dr} = -[B](J_r) \tag{38}$$

Comparison of eqns (22) and (38) shows that

$$[D] = [B]^{-1}[\Gamma] \tag{39}$$

and therefore the generalized Maxwell–Stefan equations are consistent with the generalized Fick's law formulation and (22) and also the Onsager formulation (28) From eqns (34) and (39) we get

$$[L] = \frac{c}{R} [B]^{-1} \ulcorner \frac{1}{x} \lrcorner^{-1} [A]^{-1} \tag{40}$$

It may be checked with the aid of eqn (40) that the Onsager Reciprocal Relations (29) lead to the relationship

$$\text{Đ}_{ik} = \text{Đ}_{ki}, \qquad i, k = 1, 2, \quad n \quad i \neq k \tag{41}$$

The generalized Maxwell-Stefan equations are particularly convenient because of the inbuilt symmetry relation (41) and therefore only $n(n-1)/2$ diffusion coefficients are used in (35) The coefficients Đ_{ik} can be related to the molecular transport processes occurring within the fluid mixture and therefore the relation (39) may be used for predicting the elements of the matrix of Fick's law diffusivities $[D]$, as discussed in detail by Cussler[17] Another advantage of the generalized Maxwell–Stefan formulation is that the composition gradients can be related directly to the molar fluxes N_{ir} (see eqn 35) and therefore afford a convenient method for determination of the fluxes when combined with the continuity relations (7)–(9)

In order to present the expressions for the molar fluxes N_i in a common format we define a dimensionless distance along the direction of diffusion, η, by

Planar

$$\eta = \frac{r - r_0}{r_\delta - r_0} = \frac{r - r_0}{\delta} \tag{42}$$

Cylindrical

$$\eta = \ln(r/r_0) \tag{43}$$

Spherical

$$\eta = 1 - r_0/r \tag{44}$$

With definitions (42)–(44) we may write eqns (35) in terms of the molar fluxes N_{i0} at surface $r = r_0$ ($\eta = 0$) as

$$\sum_{k=1}^{n-1} \Gamma_{ik} \frac{dx_k}{d\eta} = \sum_{\substack{k=1\\k\neq i}}^{n} \frac{x_i N_{k0} - x_k N_{i0}}{c\text{Đ}_{ik}/l} \tag{45}$$

where l is a characteristic distance, for planar interfaces this characteristic distance is the film thickness δ, for cylindrical and spherical interfaces the characteristic distance is the radius r_0.

The boundary conditions required for the solution of eqns (45) are obtained from (14), (15), (42)–(44) as

$$r = r_0,\ \eta = 0,\ x_i = x_{i0}, \qquad i = 1, 2, \ldots, n \tag{46}$$

$$r = r_\delta,\ \eta = \eta_\delta,\ x_i = x_{i\delta}, \qquad i = 1, 2, \ldots, n \tag{47}$$

(*plane* $\eta_\delta = 1$, *cylinder* $\eta_\delta = \ln(r_\delta/r_0)$, *sphere* $\eta_\delta = 1 - r_0/r_\delta$)

The first step in the calculation of the fluxes N_{i0} is the determination of the composition profiles across the film, to obtain these profiles it becomes convenient to represent eqns (45) in matrix notation as

$$[\Gamma]\frac{d(x)}{d\eta} = [\Phi](x) + (\zeta) \tag{48}$$

where the elements of $[\Phi]$ are given by

$$\Phi_{ii} = \frac{N_{i0}}{c\text{Đ}_{in}/l} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{N_{k0}}{c\text{Đ}_{ik}/l}, \qquad i = 1, 2, \ldots, n-1 \tag{49}$$

$$\Phi_{ij} = -N_{i0}\left(\frac{1}{c\text{Đ}_{ij}/l} - \frac{1}{c\text{Đ}_{in}/l}\right), \qquad i, j = 1, 2, \ldots, n-1,\quad i \neq j \tag{50}$$

and the elements of th column matrix (ζ) are given as

$$\zeta_i = -\frac{N_{i0}}{c\text{Đ}_{in}/l}, \qquad i = 1, 2, \ldots, n-1 \tag{51}$$

Both Đ_{ik} and Γ_{ik} are functions of the compositions x_i in the fluid mixture and therefore, strictly speaking, eqn (48) represents a set of $n-1$ coupled non-linear differential equations. If complete information on the activity coefficients in solution are available together with data on the Đ_{ik}, the eqn (48) may be solved using numerical techniques. However, a simple analytical solution is possible if we make some simplifying assumptions. Experimental data on diffusion in both binary and ternary mixtures[17–19] show that the generalized Maxwell–Stefan diffusion coefficients show a predictable composition dependence and this dependence is less strong than that exhibited by the generalized Fick's law diffusivities D_{ik}. For the purposes of our analysis we assume that the coefficients $c\text{Đ}_{ik}$ are independent of composition. For small composition changes the activity coefficient variation with composition may also be assumed constant, i.e. we assume that Γ_{ik} is independent of composition. In practice, we must use suitably averaged values of $c\text{Đ}_{ik}$ and Γ_{ik}. For thermodynamically ideal fluid mixtures the matrix $[\Gamma]$ degenerates to the identity matrix and therefore the assumption of constant Γ_{ik} would seem to be a good one for not-too-nonideal mixtures. Similarly, for mixtures of ideal gases, the Maxwell–Stefan diffusivities Đ_{ik} become identical to the diffusivities of the corresponding binary pairs, $\mathscr{D}_{ik}$, which are essentially composition independent.

With the simplifying assumptions as discussed above, the eqns (48) reduce to a set of $n-1$ coupled linear differential equations, the solution to these equations may be obtained straightforwardly as[8–10, 20]

$$(x - x_0) = \{\exp[\theta]\eta - \lceil I \rfloor\}\{\exp[\theta]\eta_\delta - \lceil I \rfloor\}^{-1}(x_\delta - x_0) \tag{52}$$

where we further define a matrix $[\theta]$ by

$$[\theta] \equiv [\Gamma]^{-1}[\Phi] \tag{53}$$

The composition gradient at the surface $r = r_0$ ($\eta = 0$) can be obtained by differentiating eqn (52), we get

$$\left.\frac{d(x)}{d\eta}\right|_{\eta=0} = -[\theta]\{\exp[\theta]\eta_\delta - \lceil I \rfloor\}^{-1}(x_0 - x_\delta) \tag{54}$$

Evaluating equation (38) at the surface $r = r_0$ ($\eta = 0$) we obtain the column matrix of $n-1$ diffusion fluxes (J_0) as

$$(J_0) = -\frac{c}{l}[B_0]^{-1}[\Gamma]\left.\frac{d(x)}{d\eta}\right|_{\eta=0} \tag{55}$$

where the elements of $[B_0]$ are evaluated from eqns (36) and (37) using the compositions x_{i0}.

Combining equations (54) and (55) we obtain and expression for calculating the $n-1$ diffusion fluxes J_{i0} as

$$(J_0) = \frac{c}{l}[B_0]^{-1}[\Gamma][\theta]\{\exp[\theta]\eta_\delta - \lceil I \rfloor\}^{-1}(x_0 - x_\delta) \tag{56}$$

It is clear from equations (5) that the knowledge of the $n-1$ independent diffusion fluxes J_{i0} are insufficient by themselves to allow calculation of the n molar fluxes N_{i0}, we need an additional piece of information.

This additional relationship usually takes the form of a linear dependence between the fluxes N_{i0}

$$\sum_{i=1}^{n} \lambda_i N_{i0} = 0 \tag{57}$$

From eqns (2)–(6) and (57) we obtain

$$N_{i0} = -\frac{\sum_{k=1}^{n-1}(\lambda_k - \lambda_n)J_{k0}}{\sum_{k=1}^{n}\lambda_k x_{k0}} \tag{58}$$

and

$$N_{i0} = \sum_{k=1}^{n-1} \beta_{ik} J_{k0}, \qquad i = 1, 2, \ldots, n-1 \tag{59}$$

where the elements of the matrix $[\beta]$ are given by

$$\beta_{ik} = \delta_{ik} - x_{i0}\Lambda_k, \qquad i, k = 1, 2, \quad n-1 \tag{60}$$

with

$$\Lambda_k = \frac{\lambda_k - \lambda_n}{\sum_{i=1}^{n} \lambda_i x_{i0}}, \qquad k = 1, 2, \quad n-1 \tag{61}$$

For conditions of equimolar counter diffusion

$$N_{t0} = 0 \tag{62}$$

we have

$$\lambda_i = \lambda_n, \Lambda_i = 0, \beta_{ik} = \delta_{ik}, \qquad \begin{matrix} i = 1, 2, & n-1 \\ k = 1, 2, & n-1 \end{matrix} \tag{63}$$

For diffusion of $n-1$ species through a stagnant nth species

$$N_{n0} = 0 \tag{64}$$

we get

$$\lambda_i = 0, \qquad \Lambda_i = -1/x_{n0}, \qquad \beta_{ik} = \delta_{ik} + x_{i0}/x_{n0}, \qquad \begin{matrix} i = 1, 2, & n-1 \\ k = 1, 2, & n-1 \end{matrix} \tag{65}$$

For simultaneous heat and mass transfer processes in vapour–liquid systems in the absence of inert gases, the parameters λ_i are obtained from a material balance at the interface giving[21]

$$\lambda_i = \bar{H}_i^y - \bar{H}_i^x, \qquad i = 1, 2, \quad n \tag{66}$$

where $\bar{H}_i^y$ and $\bar{H}_i^x$ are the partial molar enthalpies of species i in the vapour and liquid phases

Combining eqns (56) and (59) we get the final expression for the calculation of the molar fluxes N_{i0} as

$$(N_0) = \frac{c}{l}[\beta][B_0]^{-1}[\Gamma][\theta]\{\exp[\theta]\eta_\delta - {}^{\ulcorner}I_{\lrcorner}\}^{-1}(x_0 - x_\delta) \tag{67}$$

The expression (67) is not truly explicit in the fluxes N_{i0} and requires a trial and error solution as described in [8, 9] For the purposes of discussions it is convenient to define five further matrices

(i) A matrix of correction factors showing the effect of finite mass transfer rates on the transfer coefficients and transfer rates

$$[\Xi] \equiv [\theta]\{\exp[\theta]\eta_\delta - {}^{\ulcorner}I_{\lrcorner}\}^{-1} \tag{68}$$

(ii) A matrix of zero flux diffusive mass transfer coefficients

$$[k] \equiv \frac{c}{l}[B_0]^{-1}[\Gamma] \tag{69}$$

(iii) A matrix of finite flux diffusive mass transfer coefficients

$$[k^\bullet] \equiv [k][\Xi] \tag{70}$$

The superscript black dot ● is used to remind us that the coefficients $k^\bullet_{ik}$ are themselves dependent on the transfer rates N_{i0}

(iv) Matrix of zero flux total transfer coefficients

$$[\mathcal{W}] \equiv [\beta][k] \tag{71}$$

(v) A matrix of finite flux total transfer coefficients

$$[\mathcal{W}^\bullet] \equiv [\mathcal{W}][\Xi] \equiv [\beta][k][\Xi] \equiv [\beta][k^\bullet] \tag{72}$$

The definitions of the finite flux mass transfer coefficients is the generalization of this concept for binary mass transfer discussed clearly by Bird, Stewart and Lightfoot[1], who also show that it is the diffusive set of mass transfer coefficients, k_{ik}, which correctly portray the diffusional transport process taking place within the fluid phase The total transfer coefficients $\mathcal{W}_{ik}$ reflect not only the diffusive nature of transport but also contain the effect of the bulk flow of the mixture

It is easy to check from eqns (49), (50), (53) and (68) that for vanishingly low rates of mass transfer, i e $N_{i0} \to 0$, the matrix of correction factors $[\Xi]$ reduces to the identity matrix and the set of finite flux mass transfer coefficients become equal to the set of zero flux mass transfer coefficients

DISCUSSION OF SPECIAL CASES

The foregoing analysis applies to the general case of diffusion in n-component non-ideal fluid mixtures For special cases we recover many of the classic results available in the literature We discuss some of these special cases below

For diffusion in binary mixtures, all matrices above degenerate to scalars and eqn (67)–(72) give

$$N_{10} = \mathcal{W}^\bullet_{11}(x_{10} - x_{1\delta}) \tag{73}$$

where

$$\mathcal{W}^\bullet_{11} = \beta_{11}k^\bullet_{11}, \; k^\bullet_{11} = k_{11}\Xi_{11}, \; \Xi_{11} = \frac{\theta_{11}}{\exp(\theta_{11}\eta_\delta) - 1} \tag{74}$$

The zero flux binary mass transfer coefficient k_{11} is given by

$$k_{11} = \frac{c}{l}\mathcal{D}_{12} \tag{75}$$

where $\mathcal{D}_{12}$ is the binary diffusivity in the fluid mixture related to the Maxwell–Stefan diffusivity Đ_{12} by

$$\mathcal{D}_{12} = \text{Đ}_{12}\Gamma_{11} = \text{Đ}_{12}\left(1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1}\right) \tag{76}$$

The Maxwell–Stefan diffusivity Đ_{12} can be predicted over the entire composition range if the infinite dilute values are known[18, 19], eqn (76) thus provides a method for predicting $\mathcal{D}_{12}$.

For conditions of equimolar counter diffusion in a binary mixture, eqns (73) simplifies to give (see eqns 62 and 63)

$$N_{10} = k_{11}(x_{10} - x_{1\delta}) \tag{77}$$

where k_{11} is given by eqn (75).

For binary mixtures of ideal gases $\Gamma_{11} = 1$ and eqn (76) gives

$$\mathcal{D}_{y12} = Đ_{12}, \tag{78}$$

i.e. the binary gas phase diffusivity, $\mathcal{D}_{y12}$, is identical to the Maxwell–Stefan diffusivity and is essentially composition independent.

For binary mass transfer to spherical bodies, it is easy to check with the aid of eqn (75) that the Sherwood number defined as

$$Sh \equiv \frac{k_{11} \times (\text{diameter of spherical body})}{c\mathcal{D}_{12}} \tag{79}$$

equals 2, a classical result.

For diffusion of species 1 through stagnant 2, eqn (73) simplifies to (see eqns 64 and 65)

$$N_{10} = \frac{c\mathcal{D}_{12}}{l\eta_\delta} \ln\left(\frac{1 - x_{1\delta}}{1 - x_{10}}\right) \tag{80}$$

which represents another well-known result.

For diffusion in n-component ideal gas mixtures eqn (67) reduces to

$$(N_0) = \frac{c}{l}[\beta][B_0]^{-1}[\Phi]\{\exp[\Phi]\eta_\delta - [I]\}^{-1}(y_0 - y_\delta) \tag{81}$$

which for planar interfaces ($\eta_\delta = 1, l = \delta$) is equivalent to the expression derived by Krishna and Standart[9] and for spherical "films" ($\eta_\delta = 1 - r_0/r_\delta, l = r_0$), we recover the result obtained by Krishna[10].

For ternary gas diffusion in ideal gas mixtures, analytic solutions to the Maxwell–Stefan equations in parametric form are also available in the literature, thus Gilliland[4] presents a solution for diffusion of two gases through a stagnant third ($N_{30} = 0$) and Toor[22] has presented a solution for equimolar counter diffusion in three component gas mixtures. These analytic solutions are however unstable and may give rise to multiple roots. To illustrate the problem of determining the uniqueness of solutions to ternary gas diffusion we consider a problem first set by Sherwood[23], rewritten here in SI units.

Ammonia is diffusing from an air-ammonia mixture into water under a total pressure of 20265 N/m^2. Assume that the diffusion takes place through a stagnant gas layer 0.001 m thick at an average temperature of 328.15 K. At one point in the contacting apparatus the gas contains 3% ammonia by volume and the concentration of ammonia in the water is so low that the partial pressure of ammonia over the solution may be neglected at the point under consideration. The bulk gas is dry. Allowing for water vaporization, calculate the rate of diffusion of ammonia. Label ammonia ≡ 1, water ≡ 2, air ≡ 3.

Data: the vapour pressure of water at 328.15 K is 7359 N/m^2. The diffusivities of the binary gas pairs at the system pressure and temperature are

$$\mathcal{D}_{y12} = 0.0001470\ \text{m}^2/\text{s}, \mathcal{D}_{y13} = 0.0001075\ \text{m}^2/\text{s},$$
$$\mathcal{D}_{y23} = 0.0001245\ \text{m}^2/\text{s}$$

From the given data the boundary conditions for steady state diffusion across the interface, assumed to be planar, can be written

$$\begin{aligned} r = r_0, \eta_0 = 0, &\quad \text{bulk gas}, \quad y_{10} = 0.03, y_{20} = 0.00 \\ r = r_\delta, \eta_\delta = 1, &\quad \text{interface}, \quad y_{1\delta} = 0.00, y_{2\delta} = 0.36315 \end{aligned} \tag{82}$$

The diffusion problem requires $N_{30} = N_{3\delta} = 0$ and therefore we may apply the parametric solution obtained by Gilliland to calculate the fluxes N_1 and N_2. Gilliland's equations are

$$\frac{N_1}{\mathcal{K}_{13}} + \frac{N_2}{\mathcal{K}_{23}} = \ln(y_{3\delta}/y_{30}) \tag{83}$$

$$\frac{N_1 + N_2}{\mathcal{K}_{12}} = \ln\left[\frac{\dfrac{y_{1\delta}}{z_1} - \dfrac{\alpha_{12}}{\alpha_{21}}\dfrac{y_{2\delta}}{z_2} - \dfrac{\alpha_{21} - \alpha_{12}}{\alpha_{21}}}{\dfrac{y_{10}}{z_1} - \dfrac{\alpha_{12}}{\alpha_{21}}\dfrac{y_{20}}{z_2} - \dfrac{\alpha_{21} - \alpha_{12}}{\alpha_{21}}}\right] \tag{84}$$

where the following parameters have been defined

$$\mathcal{K}_{ij} = c\mathcal{D}_{yij}/\delta, \qquad ij = 12, 13, 23 \tag{85}$$

$$z_i = N_i/(N_1 + N_2), \qquad i = 1, 2 \tag{86}$$

$$\alpha_{ij} = 1/\mathcal{K}_{ij} - 1/\mathcal{K}_{i3}, \qquad ij = 12, 21 \tag{87}$$

The solution to eqns (83), (84) requires a trial and error approach, depending on the starting guess values for N_1, N_2 three sets of solutions are obtained.

Set I $N_1 = -2.47 \times 10^{-2}$ kmol/(s)(m^2),
$N_2 = 2.47 \times 10^{-2}$ kmol/(s)(m^2)
Set II $N_1 = 4.46 \times 10^{-4}$ kmol/(s)(m^2),
$N_2 = -9.08 \times 10^{-4}$ kmol/(s)(m^2)
Set III, $N_1 = 2.11 \times 10^{-5}$ kmol/(s)(m^2),
$N_2 = -4.14 \times 10^{-4}$ kmol/(s)(m^2)

By a process of physical reasoning, Sherwood[23] concludes that the correct root is that given by Set III. Physical reasoning is not always possible, especially if the solution to the equations form part of a computerized step-wise design procedure for say an absorption column, we require a stable solution which will always converge to the correct solution. The matrix solution (81) is stable in its convergence, especially if the iterations are started assuming the matrix of correction factors [Ξ] is the identity matrix. Thus, solution of (81) gives the Set III fluxes

APPLICATION TO INTERPHASE MASS TRANSPORT PROCESSES

The analysis thus far has been concerned with the derivation of an analytical expression (67) for the calculation of the transfer fluxes N_{i0} within a single fluid phase For fluid–fluid interphase mass transport processes, the above analysis will hold for either phase if the compositions (x_0) and (x_δ) are identified with those prevailing in the well-mixed core of bulk fluid and the interface respectively In view of the increased interest in the application of the theory of irreversible thermodynamics to interphase transport processes [24–37], it is interesting to examine the validity of the assumption that symmetry relations analogous to eqn (29) hold for fundamentally defined *inter*phase transfer coefficients, as assumed in Refs [24, 31, 33–35]

In view of equation of eqn (31), we may express the composition difference driving force $(x_0 - x_\delta)$ as

$$(x_0 - x_\delta) = \frac{1}{RT}[\Gamma]_{av}^{-1} \ulcorner x_{av} \lrcorner (\mu_0 - \mu_\delta) \tag{88}$$

where $\ulcorner x_{av} \lrcorner$ represents a diagonal matrix of averaged compositions and $[\Gamma]_{av}$ represents the matrix of thermodynamic factors with averaged elements

Thus if we define a matrix of fundamental transport coefficients by

$$(J_0) = [k_\mu^\bullet](\mu_0 - \mu_\delta) \tag{89}$$

then it is seen from eqns (56), (88) and (89) that

$$[k_\mu^\bullet] \equiv \frac{c}{RTl}[B_0]^{-1}[\Gamma][\Xi][\Gamma]_{av}^{-1} \ulcorner x_{av} \lrcorner \tag{90}$$

It can be checked with the aid of eqns (29), (40) and (90) that the fundamental interphase transfer coefficient matrix $[k_\mu^\bullet]$ will only be symmetric for vanishingly small driving forces and therefore vanishingly small fluxes N_{i0}

If we define total mass transfer coefficients $[K_\mu^\bullet]$ using

$$(N_0) = [K_\mu^\bullet](\mu_0 - \mu_\delta) \tag{91}$$

then

$$[K_\mu^\bullet] = [\beta][k_\mu^\bullet] \tag{92}$$

will only be symmetric for equimolar counter diffusion under conditions of vanishingly small fluxes In the analysis of the experimental data for interphase mass transfer in the system water–acetone–glycerol, Standart *et al* [35] assumed that the matrix $[K_\mu^\bullet]$ is symmetric Their experimental data, showing very large diffusional interactions, needs to be re-examined in the light of the analysis presented in this paper

In most interphase mass transport processes of chemical engineering interest, the transfer takes place by both molecular and turbulent transport mechanism The mass transfer coefficient for two-component systems is found to be proportional to the diffusion coefficient to a power ranging from 0 5 to 0 7 In such cases the analysis presented in this paper may be used to calculate the matrix of mass transfer coefficients in the multicomponent systems from information on the mass transfer coefficients of the constituent binary pairs in the mixture For gas phase mass transfer, for example, we first calculate the mass transfer coefficients $\mathscr{K}_{ij}$ from an appropriate mass transfer correlation, say of the j-factor type These binary mass transfer coefficients can be used to generate the matrix of zero flux multicomponent mass transfer coefficients $[k]$ For a ternary system the elements of $[k]$ are given by (see eqns 69, 78 and 85)

$$k_{11} = \mathscr{K}_{13}(y_{10}\mathscr{K}_{23} + (1 - y_{10})\mathscr{K}_{12})/S \tag{93}$$

$$k_{12} = y_{10}\mathscr{K}_{23}(\mathscr{K}_{13} - \mathscr{K}_{12})/S \tag{94}$$

$$k_{21} = y_{20}\mathscr{K}_{13}(\mathscr{K}_{23} - \mathscr{K}_{12})/S \tag{95}$$

$$k_{22} = \mathscr{K}_{23}(y_{20}\mathscr{K}_{13} + (1 - y_{20})\mathscr{K}_{12})/S \tag{96}$$

where

$$S = y_{10}\mathscr{K}_{23} + y_{20}\mathscr{K}_{13} + y_{30}\mathscr{K}_{12} \tag{97}$$

For mass transfer in non-ideal fluid mixtures the elements calculated above in eqns (93)–(96) will have to be corrected for thermodynamic non-idealities by use of eqn (69)

CONCLUSIONS

Using matrix analysis an analytic solution to the generalized Maxwell–Stefan equations for steady-state n-component diffusion in non-ideal fluid mixtures has been obtained for the composition profiles and the transfer rates In the development of the solution it has been assumed that the generalized Maxwell–Stefan diffusion coefficients $Đ_{ij}$ and the elements Γ_{ij} are independent of composition These assumptions are generally true for mixtures of ideal gases, for non-ideal liquid mixtures these assumptions may be taken as good approximations The results have been shown to yield many classical relationships in particular cases The matrix formulation has been shown to be a convenient one and free from convergence difficulties associated with some particular solutions given in the literature for ternary gas diffusion

NOTATION

A_{ik}	elements defined by eqn (27)
B_{ik}	inverted matrix of diffusion coefficients with elements defined by eqns (36) and (37)
c	total molar concentration of the diffusing mixture
c_i	molar concentration of species i in diffusing mixture
D_{ik}	generalized Fick's law diffusivities
$Đ_{ik}$	Maxwell–Stefan diffusivity of pair $i - k$ in multicomponent mixture
$\mathscr{D}_{ij}$	diffusivity of binary pair $i - j$
$\mathscr{D}_{yij}$	diffusivity of binary pair $i - j$ in ideal gas mixture
$\mathscr{D}_i$	pseudo-binary diffusivity of species i in multicomponent mixture

$\bar{H}_i$	partial molar enthalpy of species i in multicomponent mixture
$\lceil I \rfloor$	identity matrix with elements δ_{ik}
J_i	molar diffusion flux of species with respect to the molar average reference velocity frame
$\mathcal{K}_{ij}$	binary mass transfer coefficient for pair $i-j$
$[k]$	matrix of diffusive mass transfer coefficients
$[k_\mu^\bullet]$	matrix of fundamentally defined interphase mass transfer coefficients
$[K_\mu^\bullet]$	matrix of fundamentally defined total interphase mass transfer coefficients
l	characteristic length, $l = \delta$ for planar transport, $l = r_0$ for transfer in cylindrical and spherical films
L_{ik}	fundamental or Onsager coefficients
n	number of components in multicomponent mixture
N_i	molar flux of species i in stationary coordinate reference frame
N_t	mixture molar flux in stationary coordinate reference frame
r	distance coordinate
r_0	coordinate at inner surface of film
r_δ	coordinate at outer surface of film
R	gas constant
S	summation parameter defined in eqn (97)
Sh	Sherwood Number
T	absolute temperature
$\mathbf{u}_i$	diffusion velocity of species i
$\mathbf{u}$	molar average velocity of diffusing mixture
$[\mathcal{W}]$	matrix of total mass transfer coefficients
x_i	mole fraction of species i in multicomponent fluid mixture
$\lceil x_{av} \rfloor$	diagonal matrix of averaged compositions
y_i	mole fraction of species i in ideal gas mixture
Y_i	modified driving forces, given by eqns (26)
z_i	ratio of ith molar flux to mixture molar flux, eqn (86)

Greek symbols

α_{ij}	parameters defined by eqn (87)
β_{ik}	elements defined by eqn (60)
γ_i	activity coefficient of species i in solution
$[\Gamma]$	matrix of thermodynamic factors defined by eqn (32)
δ	thickness of diffusion path or "film", $\delta = r_\delta - r_0$
δ_{ik}	Kronecker delta
(ζ)	column matrix with elements given by eqn (51)
η	dimensionless distance coordinate given by eqns (42)–(44)
η_0	distance coordinate corresponding to $r = r_0$
η_δ	distance coordinate corresponding to $r = r_\delta$, $\eta_\delta = 1$ for planar films, $\eta_\delta = \ln(r_\delta/r_0)$ for cylindrical films, $\eta_\delta = 1 - r_0/r_\delta$ for spherical films
$[\theta]$	matrix defined by eqn (53)
λ_i	parameters defined in eqn (57)
Λ_i	parameters defined in eqn (61)
μ_i	molar chemical potential of species i in mixture
$[\Xi]$	matrix of correction factors defined by eqn (68)
σ	rate of entropy production
$[\Phi]$	matrix of dimensionless rate factors defined by eqns (49) and (50)

Matrix

$(\ )$	column matrix with $n-1$ elements
$[\ ]$	$n-1 \times n-1$ square matrix
$[\ ]^{-1}$	inverted matrix of dimension $n-1 \times n-1$
$\lceil\ \rfloor$	diagonal matrix with $n-1$ non-zero elements

Subscripts

av	parameters suitably averaged over the composition range encountered
n	pertaining to nth species
0	at surface $r = r_0$
y	gas phase
δ	parameter at surface $r = r_\delta$
μ	fundamentally defined parameter

Superscripts

$\bullet$	coefficients corresponding to finite mass transfer rates
x	pertaining to the liquid phase
y	pertaining to the vapour phase

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