Short Communication

Binary and multicomponent mass transfer at high transfer rates

R. KRISHNA*

Department of Chemical Engineering, University of Manchester Institute of Science and Technology, Manchester (Gt. Britain)

An examination is made as to whether an explicit method can be obtained for calculation of the transfer fluxes of individual species N_i during steady-state diffusion of an ideal gas mixture across a planar film.

It is shown that the transfer fluxes can be calculated explicitly, without an iterative procedure, for the following three cases:
  (i) all cases of binary mass transfer,
  (ii) multicomponent mass transfer with equal constituent binary pair diffusivities, and
  (iii) multicomponent mass transfer with small driving forces.

It is demonstrated that for the general case of multicomponent mass transfer with high transfer fluxes an iterative procedure is inevitable. An improved iterative procedure for the calculation of N_i is suggested and arguments, including a numerical example, are presented to support it.

Introduction

In the closing paragraph of their recent article, Pratt and Tuohey [1] state: "The Krishna–Standart model represents the best available method of computing multicomponent mass transfer in the absence of a method giving the total flux (*i.e.* including bulk flow) directly." The purpose of the present communication is to examine whether it is possible to obtain the total fluxes N_i explicitly, *i.e.* without employing an iterative procedure.

*Present address: Koninklijke/Shell-Laboratorium, Badhuisweg 3, 1031 CM Amsterdam, The Netherlands.

During the course of our analysis, which complements our work in earlier publications [2 - 6], we note further parallels, and contrasts, between binary ($n = 2$) and multicomponent ($n \geqslant 3$) mass transport phenomena at high transfer rates. Though the treatment in the present article is restricted to steady-state diffusion in ideal gas mixtures across a planar film, extension to other geometries and to non-ideal mixtures can be carried out in a straightforward manner using the generalized approach developed earlier [3].

Analysis

Let us consider steady-state diffusion in an n-component mixture across a film of thickness δ. Let the compositions at either end of the diffusion path be denoted as y_{i0} (at $r = 0$) and $y_{i\delta}$ (at $r = \delta$), where r represents the coordinate along the direction of diffusion. We have basically two types of diffusion problems in chemical engineering. In the first type, encountered in, for example distillation, absorption, and evaporation, the compositions y_{i0} and $y_{i\delta}$ can be identified with the bulk and interface compositions respectively in either of the fluid phases; the bulk compositions are specified by column material balances and the interface compositions are either known or can be 'eliminated' by use of overall transfer coefficients. In this class of problems the total fluxes N_i are further constrained by a linear relationship of the form

$$\sum_{i=1}^{n} \lambda_i N_i = 0,$$

$$(1)$$

$$N_n = -\sum_{k=1}^{n-1} \frac{\lambda_k}{\lambda_n} N_k$$

Equation (1) covers, for example, *equimolar diffusion* ($N_t = 0$; $\lambda_1 = \lambda_2 = \ldots = \lambda_n$), *Stefan diffusion* ($N_n = 0$; $\lambda_n \neq 0$; $\lambda_1 = \lambda_2 = \ldots = \lambda_{n-1} = 0$) and *Graham diffusion* inside porous catalysts ($\lambda_i \equiv \sqrt{M_i}$). For distillation of a mixture in which the components have unequal molar heats of vaporization, an energy balance at

the vapour–liquid interface leads to the constraint

$$\sum_{i=1}^{n} (\bar{H}_i^y - \bar{H}_i^x)N_i = 0$$

and therefore λ_i in the general linear constraint equation (1) can be identified with the molar heat of vaporization of component i in the mixture (see ref. 5 for a detailed analysis of non-equimolar distillation). In problems of this first type there will be $n - 1$ independent fluxes N_i to be determined (N_n being determined by eqn. (1)), given the compositions at either end of the diffusion path.

In the second class of problems encountered in chemical engineering, the ratios of fluxes

$$z_i \equiv N_i/N_t \qquad i = 1, 2, ..., n \qquad (2)$$

are specified. An example is when we have diffusion with heterogeneous chemical reaction: the reaction stoichiometry determines the ratios of the fluxes. Thus for the catalytic dehydrogenation of ethanol to acetaldehyde,

$$C_2H_5OH \ (1) \to CH_3CHO \ (2) + H_2 \ (3)$$
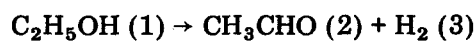
the flux ratios are $z_1 = -1$, $z_2 = 1$, $z_3 = 1$. In this case there is only one independent flux to be determined. Typically in problems of this type the bulk-phase compositions, $y_{i\delta}$ say, are known or are accessible from material balances. The compositions at the catalyst surface, y_{i0}, are unknown. The reaction rate expression at the catalyst surface connecting the transfer fluxes N_i to the compositions y_{i0} makes the diffusion problem determinate. In the dehydrogenation problem cited above, we may, for example, have a first-order reaction rate expression for the rate of production of ethanol:

$$N_1 = -k_r y_{10}$$

Again here, in the second class of problems, we have $n - 1$ unknowns to be determined. These unknowns can be chosen to be either y_{i0} ($i = 1, 2, ..., n - 1$) or N_1, y_{20}, y_{30}, ..., $y_{n-1,0}$.

Another example where the flux ratios z_i are specified by the physics of the problem is during condensation of mixed vapours (no inerts) when $N_i/N_j = x_i/x_j$, the ratio of mole fractions of the condensed liquid phase. (See ref. 7 for a discussion on this topic.)

In either class of problems discussed above, there is a total of $n - 1$ unknowns to be determined and we need $n - 1$ relations to make the problem determinate. The determinancy is provided by the constitutive relations and for ideal-gas mixtures these are best written as [2]

$$\frac{dy_i}{d\eta} = \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{y_iN_j - y_jN_i}{\ell_{ij}} \qquad i = 1, 2, ..., n - 1 \ (3)$$

where $\ell_{ij} \equiv c_t \mathcal{D}_{ij}/\delta$ are the binary pair mass transfer coefficients in the multicomponent mixture.

The solution to the diffusion problem can be represented in $n - 1$ dimensional matrix notation as [3]

$$(N) = [\beta_0][B_0]^{-1}[\Xi_0](y_0 - y_\delta) \equiv$$
$$[W_0^\bullet](y_0 - y_\delta) \qquad (4)$$

where we have evaluated the gradient $dy_i/d\eta$ at $r = 0$. Analogously it is easy to derive the following in terms of the gradients at $r = \delta$:

$$(N) = [\beta_\delta][B_\delta]^{-1}[\Xi_\delta](y_0 - y_\delta) \equiv$$
$$[W_\delta^\bullet](y_0 - y_\delta) \qquad (5)$$

Equation (4) or (5) can be used to calculate the fluxes N_i but these are not explicitly determined because the correction factors for finite mass transfer rates,

$$[\Xi_0] \equiv [\Phi][\exp[\Phi] - \ulcorner I_\lrcorner]^{-1}$$

and

$$[\Xi_\delta] \equiv [\Phi] \exp[\Phi][\exp[\Phi] - \ulcorner I_\lrcorner]^{-1} \equiv$$
$$[\Xi_0] \exp[\Phi] \equiv \exp[\Phi][\Xi_0]$$

are functions of the mass transfer fluxes N_i. To reiterate our objective: we wish to examine whether it is possible to claculate the fluxes N_i explicitly. We first analyse the binary case before proceeding to the general treatment of multicomponent mixtures.

Binary mass transfer
In this case all the matrices in eqns. (4) and (5) reduce to scalar quantities and we have

$$\Phi = N_t/\ell, \qquad B_0 = 1/\ell$$

$$N_2 = -\frac{\lambda_1}{\lambda_2}N_1 \quad \text{or} \quad N_2 = \frac{z_2}{z_1}N_1$$

Equations (4) and (5) can be combined to give

$$N_1 = \beta_0 \mathscr{k} \frac{\Phi}{\exp\Phi - 1}(y_{10} - y_{1\delta})$$

$$= \beta_\delta \mathscr{k} \frac{\Phi\exp\Phi}{\exp\Phi - 1}(y_{10} - y_{1\delta}) \tag{6}$$

whence we obtain, on equating the right-hand sides of eqn. (6),

$$\Phi = \ln(\beta_0/\beta_\delta) \tag{7}$$

Equation (7) gives the mass transfer rate factor Φ directly in terms of the bootstrap coefficients β_0 and β_δ; knowledge of Φ can be used to evaluate N_1 explicitly from either one of the equalities (6).

Various special cases may be recognised. For equimolar diffusion we have

$$N_t = 0, \beta_0 = \beta_\delta = 1, \Phi = 0$$

$$\Xi_0 = \Xi_\delta = 1, N_1 = \mathscr{k}(y_{10} - y_{1\delta}) = -N_2$$

For diffusion of component 1 through stagnant 2 (Stefan diffusion) we have

$$N_2 = 0$$

$$\beta_0 = 1/y_{20} = 1/(1 - y_{10})$$

$$\beta_\delta = 1/y_{2\delta} = 1/(1 - y_{1\delta})$$

$$\Phi = \ln(y_{2\delta}/y_{20}) = \ln((1 - y_{1\delta})/(1 - y_{10}))$$

$$N_1 = \mathscr{k}\Phi$$

When the flux ratios z_1 and z_2 are fixed by the physics (or chemistry) of the problem we have

$$\beta_0 = 1/(1 - y_{10}/z_1);$$

$$\beta_\delta = 1/(1 - y_{1\delta}/z_1)$$

$$\Phi = \ln(\beta_0/\beta_\delta), \quad N_1 = z_1\mathscr{k}\Phi, \quad N_2 = z_2\mathscr{k}\Phi$$

Multicomponent mass transfer. Equal binary diffusivities

We now consider the case in which the n components in the mixture are all similar in size and nature, giving $\mathscr{k}_{ij} = \mathscr{k}$ for all binary pairs in the mixture. With this simplification the matrix of mass transfer rate factors $[\Phi]$ reduces to a scalar times the identity matrix: $\Phi \ulcorner I \lrcorner$ with $\Phi = N_t/\mathscr{k}$. The correction factor matrices also reduce to the form of scalar times identity matrix:

$$[\Xi_0] = \Phi/(\exp\Phi - 1)\ulcorner I \lrcorner$$

$$[\Xi_\delta] = \Phi\exp\Phi/(\exp\Phi - 1)\ulcorner I \lrcorner$$

Equations (4) and (5) can be reduced to

$$(N) = [\beta_0]\mathscr{k}\frac{\Phi}{\exp\Phi - 1}(y_0 - y_\delta)$$

$$= [\beta_\delta]\mathscr{k}\frac{\Phi\exp\Phi}{\exp\Phi - 1}(y_0 - y_\delta) \tag{8}$$

where we note that the bootstrap matrices $[\beta_0]$ and $[\beta_\delta]$ are non-diagonal in general. The mass transfer rate factor Φ can be obtained by equating the right-hand sides of equations (8), yielding the $n - 1$ dimensional matrix relation

$$e^\Phi(y_0 - y_\delta) = [\beta_\delta]^{-1}[\beta_0](y_0 - y_\delta) \tag{9}$$

For equimolar diffusion we have, of course, $\Phi = 0$ and $N_i = \mathscr{k}(y_{i0} - y_{i\delta})$. For Stefan diffusion, $N_n = 0$, we have $\beta_{ij} = \delta_{ij} + y_i/y_n$, and it can easily be seen that eqn. (9) leads to $\Phi = \ln(y_{n\delta}/y_{n0})$. The fluxes N_i for this case can be evaluated explicitly from either one of the right-hand members of eqn. (8). When the flux ratios z_i are fixed, it can be seen that eqn. (9) leads to

$$\Phi = \ln((1 - y_{i\delta}/z_i)/(1 - y_{i0}/z_i))$$

for each of the n components; the fluxes N_i are then given by

$$N_i = z_i\mathscr{k}\Phi.$$

Multicomponent mass transfer. Small driving forces

Let us now consider the case in which the driving forces for mass transfer are small, i.e. $\Delta y_i \to 0$ and so $y_{i0} \cong y_{i\delta}$. This would lead to the following: $N_i \to 0$, $[B_0] \cong [B_\delta]$, $[\Phi] \to [0]$, $[\beta_0] \cong [\beta_\delta]$, and $[\Xi_0] \cong [\Xi_\delta] \to \ulcorner I \lrcorner$, the identity matrix. Therefore

$$[W_0^\bullet] \equiv [\beta_0][B_0]^{-1}[\Xi_0] \cong [W_\delta^\bullet]$$

$$\equiv [\beta_\delta][B_\delta]^{-1}[\Xi_\delta] \tag{10}$$

If we assume equality of overall mass transfer coefficients $[W_0^\bullet]$ and $[W_\delta^\bullet]$, then it is easy to see that the dimensionless mass transfer rate factor $[\Phi]$ is given by (see eqns. (4) and (5))

$$[\Phi] = \ln[[B_\delta][\beta_\delta]^{-1}[\beta_0][B_0]^{-1}] \tag{11}$$

which can be evaluated by means of Sylvester's theorem. If we further have the restriction of equimolar diffusion then eqn. (11) reduces to

$$[\Phi] = \ln[[B_\delta][B_0]^{-1}] \qquad (12)$$

The satisfaction of eqn. (11) for the rate factor matrix $[\Phi]$, could serve as a definition for the condition of small fluxes, a previously imprecisely defined situation. From the knowledge of $[\Phi]$, the fluxes N_i could be explicitly determined from either eqn. (4) or (5).

Multicomponent mass transfer. Large driving forces

For conditions of large driving forces ($y_{i0} - y_{i\delta}$), the transfer fluxes will be large and the matrix of dimensionless rate factors $[\Phi]$ will show large deviations from the null matrix $[0]$. In this case the two overall transfer coefficient matrices $[W_0^\bullet]$ and $[W_\delta^\bullet]$ will be significantly different from each other. The inequality of these two coefficient matrices is in direct, striking, contrast to a corresponding binary system for which we *must* have $W_0^\bullet = W_\delta^\bullet$. This last equality was in fact used earlier to derive an explicit relation for the mass transfer rate factor (see eqn. (7)). It may be noted here that, even though $(N) = [W_0^\bullet](\Delta y) = [W_\delta^\bullet](\Delta y)$, there is *no* requirement in matrix algebra that $[W_0^\bullet] = [W_\delta^\bullet]$. In other words, there is no unique set of overall transfer coefficients $W_{ij}^\bullet$. It follows that if measurements are made in a ternary system, of N_1, N_2 and N_3, and of Δy_1 and Δy_2, it is not possible to have a unique determination of the four elements of the system transfer coefficients, $W_{ij}^\bullet$ ($i, j = 1, 2$). The interpretation of ternary and, in general, multicomponent mass transfer data must therefore proceed via a model relating the multicomponent transfer behaviour to that of the constituent binary pairs. This latter approach was used by Krishna *et al.* [8] to validate the film model for multicomponent mass transfer [2 - 6] by analysing experimental data obtained for both Stefan diffusion and equimolar distillation in wetted-wall columns.

Since $[W_0^\bullet] \neq [W_\delta^\bullet]$, it is not possible to evaluate the matrix $[\Phi]$ explicitly as was possible for the three cases examined earlier, so that a trial-and-error solution is inevitable. In previous papers [2 - 8], it has been suggested that a head-to-tail iterative procedure could be employed using either eqn. (4) or (5) with the starting guess $[\Xi_0] = \ulcorner I_\lrcorner$ or $[\Xi_\delta] = \ulcorner I_\lrcorner$, respectively. This suggestion has been used in a variety of problems [2 - 8] with success and

convergence has been fast. Taylor and Webb [9] have recently presented a numerical problem involving vapour-phase diffusion-controlled condensation of butane (1) and octane (2) in the presence of hydrogen (3) to show that, then the eigenvalues of the matrix $[\Phi]$ differ greatly in magnitude from one another, *either* eqn. (4) *or* eqn. (5) may exhibit oscillations during the head-to-tail iteration procedure. In the example cited by Taylor and Webb [9], convergence using eqn. (5) with the starting assumption $[\Xi_\delta] = \ulcorner I_\lrcorner$ is extremely slow and requires about one hundred iterations. On the basis of this evidence we are now of the opinion that the starting *guess* given by eqn. (11) (by eqn. (12) for the case of equimolar diffusion) for the matrix $[\Phi]$ is to be preferred to the one starting with $[\Phi] = [0]$. We discuss below the arguments leading up to this reasoning.

Consider the case of *Stefan diffusion* in a ternary mixture (the case considered also by Taylor and Webb [9]). For $N_3 = 0$, we have $\beta_{ij} = \delta_{ij} + y_i/y_3$ ($i, j = 1, 2$), and it can be shown that one of the eigenvalues of the right-hand member of eqn. (11) is

$$\hat{\Phi}_1 = \ln(y_{3\delta}/y_{30}) \qquad (13)$$

determined purely by the boundary conditions imposed on the system. This eigenvalue also corresponds to the eigenvalue of the final converged value of the matrix $[\Phi]$ (see ref. 2 and Gilliland's first solution, *i.e.* Toor's eqn. (11) [10]):

$$\hat{\Phi}_1 \equiv N_1/\mathcal{k}_{13} + N_2/\mathcal{k}_{23} = \ln(y_{3\delta}/y_{30}) \qquad (14)$$

Put another way, one of the eigenvalues of the matrix $[\Phi]$ determined by eqn. (11), derived for vanishingly small fluxes, is also the correct eigenvalue of the final converged solution $[\Phi]$. The second eigenvalue of the finally converged value of $[\Phi]$, *i.e.* [2]

$$\hat{\Phi}_2 \equiv (N_1 + N_2)/\mathcal{k}_{12} \qquad (15)$$

is a function of the ratios of the transfer fluxes z_1 and z_2, as can be seen from Gilliland's second solution given by Toor's eqn. (12) [10]. Consequently, eqn. (11), obtained for vanishingly small transfer fluxes N_i, cannot estimate this eigenvalue $\hat{\Phi}_2$ correctly.

Since eqn. (11) predicts one of the eigenvalues, $\hat{\Phi}_1$, from eqn. (14), correctly we may expect iterations to proceed faster with this starting assumption as compared to the earlier

recommended [2 - 6] iterative procedure of starting with the assumption $[\Phi] = [0]$. This was indeed found to be the case in a wide variety of examples tested. The numerical example given by Taylor and Webb [9] is used below to illustrate the dramatic improvement in the speed of convergence obtained by using the procedure recommended in this paper.

Taylor and Webb [9] considered condensation of butane (1) and octane (2) in the presence of hydrogen (3) with the boundary conditions: $y_{10} = 0.05$, $y_{20} = 0.05$, $y_{1\delta} = 0.2$, and $y_{2\delta} = 0.6$. The binary pair mass transfer coefficients ℓ_{ij} have the values (units: mol m^{-2} s^{-1}) $\ell_{12} = 0.304$, $\ell_{13} = 4.27$ and $\ell_{23} = 2.91$. One of the eigenvalues of the matrix determined by the right-hand side of eqn. (11) is -1.504, which value corresponds to $\hat{\Phi}_1 = \ln(y_{3\delta}/y_{30})$. Iterations starting with the estimate of $[\Phi]$ from eqn. (11) and using eqn. (5) for the calculation of the fluxes proceeded as follows (units of N_i: mol m^{-2} s^{-1}):

Iteration number	N_1	N_2
1	-1.342	-3.462
2	-1.201	-3.558
3	-1.198	-3.560
4	-1.198	-3.561
5	-1.198	-3.561

One of the eigenvalues of $[\Phi]$ throughout the iterations above corresponds to -1.504 and convergence is obtained in four iterations. It is interesting to note that with the starting guess $[\Phi] = [0]$, the solution obtained by Taylor and Webb: $N_1 = -1.198$, $N_2 = -3.563$, does not appear to have fully converged even after 104 iterations.

Finally, it is interesting to note that the converged $[W_\delta^\bullet]$ for the example given above has the elements (units: mol m^{-2} s^{-1}) $W_{\delta 11}^\bullet = 1.711$, $W_{\delta 12}^\bullet = 1.711$, $W_{\delta 21}^\bullet = 5.086$ and $W_{\delta 22}^\bullet = 5.086$, leading to the conclusion that the example coined by Taylor and Webb is probably a very special one.

For conditions of *equimolar diffusion*, one of the eigenvalues of the final solution $[\Phi]$ must be zero, as shown by Krishna and Standart [2]. It can again be checked that the starting guess given by eqn. (12) has one vanishing eigenvalue:

$$\hat{\Phi}_1 \equiv 0 \qquad (16)$$

The other eigenvalue [2],

$$\hat{\Phi}_2 \equiv N_1(1/\ell_{12} - 1/\ell_{23}) + N_2(1/\ell_{12} - 1/\ell_{13}) \qquad (17)$$

is a function of the transfer fluxes N_i, as can be seen from eqn. (10) of Toor [10]. This latter eigenvalue does not correspond with the second, non-vanishing, eigenvalue of the right-hand side of eqn. (12), obtained for small fluxes. A variety of examples in equimolar diffusion was tested by the author with the starting assumption given by eqn. (12) and convergence was obtained within about five iterations.

When conditions correspond to neither Stefan diffusion nor equimolar diffusion, general analytic expressions for the eigenvalues (such as the Toor and Gilliland solutions [10]) have not been published and it is not possible, at this stage, to comment on the eigenvalues of eqn. (11) for this case. However, it is interesting to note that in one numerical example tested involving non-equimolar distillation (this example can be found in ref. 5), the combination of eqn. (11) with either eqn. (4) or (5) leads to the correct final values of the fluxes N_i ($i = 1, 2, 3$), obtained earlier by an exact iterative method [5]. The reason that the starting guess given by eqn. (11) is so successful in this case is because the example on non-equimolar distillation considered in ref. 5 corresponds to a small driving force (thus low mass transfer fluxes) case.

Concluding remarks

For steady-state diffusion in ideal gas mixtures we have examined the possibility of obtaining the total fluxes N_i explicitly. Explicit solutions have been shown to be obtainable in the following three cases:

(1) for binary mass transfer (all cases),

(2) multicomponent mass transfer with all binary pair diffusivities equal to one another,

(3) multicomponent mass transfer with vanishingly small fluxes.

For the general case of multicomponent mass transfer, no explicit solution is possible. In view of some recently reported complications [9] possible with the starting assumption $[\Phi] = [0]$ in the head-to-tail iterative procedure suggested earlier [2 - 8], we have now proposed in this communication that

iterations be started with the matrix $[\Phi]$ estimated from eqn. (11) (which reduces to eqn. (12) for equimolar diffusion). Arguments in support of this suggestion have been presented in the text. The choice between eqns. (4) and (5) may be made following the recommendations given by Taylor and Webb [9].

The ideal gas treatment given in this paper can be extended straightforwardly to the case of non-ideal fluid mixtures following the treatment given earlier [3].

Finally, it must be mentioned that the treatment above is restricted to the case in which the eigenvalues of the matrix $[\Phi]$ are all real. For diffusion with heterogeneous chemical reaction, the possibility of complex eigenvalues exist (see ref. 11) and deserves further study.

Nomenclature

$[B]$ matrix of inverted mass transfer coefficients, $mol^{-2}\ m^2\ s$, with elements given by

$$B_{ii} = \frac{y_i}{\ell_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{y_k}{\ell_{ij}}, i = 1, 2, ..., n-1$$

$$B_{ij} = -y_i(1/\ell_{ij} - 1/\ell_{in}),$$
$$i, j = 1, 2, ..., n-1$$
$$i \neq j$$

c_t mixture molar concentration, $mol\ m^{-3}$

$\mathcal{D}_{ij}$ diffusivity of binary pair i–j, $m^2\ s^{-1}$

$\bar{H}_i$ partial molar enthalpy of component i in mixture, $J\ mol^{-1}$

$\ulcorner I \lrcorner$ identity matrix with elements δ_{ij}, dimensionless

ℓ mass transfer coefficient in binary system, $mol\ m^{-2}\ s^{-1}$

ℓ_{ij} mass transfer coefficient of binary pair i–j in multicomponent mixture, $mol\ m^{-2}\ s^{-1}$

k_r heterogeneous reaction rate constant, $mol\ m^{-2}\ s^{-1}$

M_i molar mass of component i, $g\ mol^{-1}$

n number of components in mixture

N_i molar flux of component i in a stationary coordinate reference frame, $mol\ m^{-2}\ s^{-1}$

N_t $= \sum_{i=1}^{n} N_i$, mixture molar flux, $mol\ m^{-2}\ s^{-1}$

r distance coordinate along diffusion path, m

$[W]$ mass transfer coefficient matrix defined in terms of total fluxes N_i, $mol\ m^{-2}\ s^{-1}$

x_i mole fraction of component i in liquid phase

y_i mole fraction of component i in gas phase

Δy_i $= y_{i0} - y_{i\delta}$, mole fraction difference

z_i ratio of flux of i to total molar flux of mixture

Greek symbols

$[\beta]$ bootstrap coefficient matrix. For the linear constraint given by eqn. (1), the elements β_{ij} are given by

$$\beta_{ij} = \delta_{ij} - y_i \left(\frac{\lambda_j - \lambda_n}{\sum_{k=1}^{n} y_k \lambda_k} \right)$$

$$i, j = 1, 2, ..., n-1$$

When the flux ratios are fixed (eqn. (2)), the elements β_{ij} are given by

$$\beta_{ij} = \delta_{ij}/(1 - y_i/z_i)$$

δ length of diffusion path, m

δ_{ij} Kronecker delta

η $= r/\delta$, dimensionless distance along diffusion path

λ_i coefficients in linear constraint, eqn. (1)

$[\Xi]$ matrix of correction factors, dimensionless

$[\Phi]$ matrix of dimensionless rate factors with elements given by

$$\Phi_{ii} = \frac{N_i}{\ell_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{N_k}{\ell_{ik}} \qquad i = 1, 2, ..., n-1$$

$$\Phi_{ij} = -N_i(1/\ell_{ij} - 1/\ell_{in}) \quad i, j = 1, 2, ..., n-1$$

$\hat{\Phi}_i$ ith eigenvalue of the matrix $[\Phi]$

Matrix notation

( )   column matrix with $n-1$ elements

[ ] $n-1$ dimensional square matrix

$[\ ]^{-1}$ $n-1$ dimensional inverted square matrix

$\ulcorner \lrcorner$ diagonal matrix with vanishing off-diagonal elements

Subscripts

i, j, k referring to components i, j and k or summation indices

n referring to component n
t   referring to total mixture
0   referring to position $r = 0$; parameter evaluated at composition y_{i0}
δ referring to position $r = \delta$; parameter evaluated at composition $y_{i\delta}$

Superscripts

x   referring to liquid phase
y   referring to vapour phase
●   coefficient corrected for finite rates of transfer

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