

STEADY-STATE MASS TRANSPORT IN MULTICOMPONENT LIQUID MIXTURES

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Introduction

In many practical engineering operations such as absorption, distillation, extraction and ion-exchange processes, it is essential to calculate the rates of transport in the liquid phase. Often the number of components in the liquid phase exceeds two, i.e. we have multicomponent systems. The description of the transport behaviour in the liquid state is complicated by two factors: (i) the thermodynamic non-ideality of the liquid mixture and (ii) diffusional interactions between species transfers.

It is our object here to formulate the rate relations for liquid phase transport in a convenient form and to obtain solutions to steady-state  $n$ -component diffusion problems. The analysis presented here is essentially an extension of the ideal gas phase treatment of Krishna and Standart [1]. The treatment is restricted to unidirectional transport under isothermal - isobaric conditions and thermal diffusion effects are considered negligible.

Constitutive Relations

The generalized Fick's law formulation

$$J_i^x = -c \sum_{j=1}^{n-1} D_{xij} \frac{dx_j}{dz}, \quad i = 1, 2, \dots, n-1 \quad (1)$$

has been used in recent years to describe isobaric-isothermal  $n$ -component mass transport. In equation (1),  $J_i^x$  is the diffusion flux of species  $i$  with respect to the molar average reference velocity frame (other reference velocity frames are possible [2,3]):

$$J_i^x = c_i(u_i - u), \quad i = 1, 2, \dots, n \quad (2)$$

but only  $n-1$  of the diffusion fluxes in (2) are independent for we have

$$\sum_{i=1}^n J_i^x = 0 \quad (3)$$

The total molar fluxes  $N_i$  (relative to a stationary coordinate reference frame):

$$N_i = c_i u_i = J_i^x + c_i u = J_i^x + x_i \sum_{i=1}^n N_i, \quad i = 1, 2, \dots, n \quad (4)$$

are the ones which appear in process calculations. These total fluxes are the ones which need to be calculated for design or rating purposes.

The coefficients  $D_{xij}$  ( $i, j = 1, 2, \dots, n-1$ ) are the multicomponent diffusion coefficients and may be considered 'practical' in the sense that mole fraction gradients, which are directly measurable, appear as driving forces in (1). The elements  $D_{xij}$  reflect both the thermodynamic and kinetic interactions in the liquid state and in recent years there has been growing interest in their measurement (a complete bibliography on multicomponent diffusion coefficient measurements is available in Cussler [4]). This interest has been sparked off with the appreciation of the importance of diffusional interaction phenomena in liquid phase transport behaviour. The magnitude of the diffusional interaction may be characterized, somewhat loosely, by the size of the cross coefficients,  $D_{xij}$  ( $i \neq j$ ) relative to the main ones  $D_{xii}$ . For the system polystyrene (1) - cyclohexane (2) - toluene (3),  $|D_{x12}/D_{x11}|$  exceeds unity for a certain range of concentrations [5] and therefore the diffusion fluxes will be coupled to a large extent.

From a practical engineering viewpoint, it is important to predict the values of the elements of the matrix  $[D_x]$ . However, since the elements of  $[D_x]$  portray both the thermodynamic and kinetic interactions in the liquid state, they cannot be related simply to the molecular collision processes within the phase and are therefore not amenable to simple interpretation and prediction.

An alternative, and more fundamental, formulation of the constitutive relations is the generalized Maxwell-Stefan equations [6,7]:

$$\frac{1}{R T} \frac{d\mu_i}{dz} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j (u_j - u_i)}{D_{ij}}, \quad i = 1, 2, \dots, n \quad (5)$$

Only  $n-1$  of the chemical potential gradients are independent for we have the Gibbs-Duhem relationship

$$\sum_{i=1}^n x_i \frac{d\mu_i}{dz} = 0 \quad (6)$$

The generalized Maxwell-Stefan equations (5) are consistent with the theory of irreversible thermodynamics and the Maxwell-Stefan diffusion coefficients  $\mathfrak{D}_{ij}$  exhibit the symmetry property

$$\mathfrak{D}_{ij} = \mathfrak{D}_{ji}, \quad \begin{matrix} i, j = 1, 2, \dots, n \\ i \neq j \end{matrix} \quad (7)$$

consistent with the Onsager relations. The  $\mathfrak{D}_{ij}$  essentially reflect the  $i$ - $j$  pair collision phenomena and may be closely related to the molecular processes within the liquid phase; they can be estimated from information on the constituent binary pairs [4].

We first seek a relation between the  $D_{xij}$  and the  $\mathfrak{D}_{ij}$  and then a solution to the equations (5) for steady-state transport.

Multiplying both sides of equations (5) by  $x_i$  yields

$$\frac{1}{R T} x_i \frac{d\mu_i}{dz} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_i x_j (u_j - u_i)}{\mathfrak{D}_{ij}} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_i^N x_j^N - x_j^N x_i^N}{c \mathfrak{D}_{ij}} \quad (8)$$

or in view of equations (4) we have

$$\frac{1}{R T} x_i \frac{d\mu_i}{dz} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_i x_j^X - x_j x_i^X}{c \mathfrak{D}_{ij}}, \quad i = 1, 2, \dots, n-1 \quad (9)$$

The chemical potential gradients may be expressed in terms of composition gradients:

$$\begin{aligned} \frac{1}{R T} x_i \frac{d\mu_i}{dz} &= \sum_{j=1}^{n-1} \frac{x_i}{RT} \frac{\partial \mu_i}{\partial x_j} \frac{dx_j}{dz} = \sum_{j=1}^{n-1} x_i \frac{\partial \ln \gamma_i x_i}{\partial x_j} \frac{dx_j}{dz} = \\ &= \sum_{j=1}^{n-1} \frac{x_i}{x_j} \frac{\partial \ln \gamma_i x_i}{\partial \ln x_j} \frac{dx_j}{dz} = \sum_{j=1}^{n-1} \left( \delta_{ij} + \frac{x_i}{x_j} \frac{\partial \ln \gamma_i}{\partial \ln x_j} \right) \frac{dx_j}{dz} = \\ &= \sum_{j=1}^{n-1} \Gamma_{ij} \frac{dx_j}{dz}, \quad i = 1, 2, \dots, n-1 \end{aligned} \quad (10)$$

where we define thermodynamic factors

$$\Gamma_{ij} \equiv \delta_{ij} + \frac{x_i}{x_j} \frac{\partial \ln \gamma_i}{\partial \ln x_j}, \quad i, j = 1, 2, \dots, n-1 \quad (11)$$

If we further define a matrix [A] with its elements given by

$$A_{ii} = \frac{x_i}{\mathfrak{D}_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^n \frac{x_k}{\mathfrak{D}_{ik}}, \quad i = 1, 2, \dots, n-1 \quad (12)$$

$$A_{ij} = -x_i (1/\mathfrak{D}_{ij} - 1/\mathfrak{D}_{in}), \quad \begin{matrix} i, j = 1, 2, \dots, n-1 \\ i \neq j \end{matrix} \quad (13)$$

we may rewrite equations (9) in view of equations (10) - (13) as

$$c [\Gamma] \frac{d(x)}{dz} = - [A] (J^X) \quad (14)$$

where all the matrices are of dimension  $n-1$ . Comparison of equation (14) with the matrix form of equations (1)

$$(J^X) = -c [D_x] \frac{d(x)}{dz} \quad (15)$$

shows that

$$[D_x] = [A]^{-1} [\Gamma] \quad (16)$$

For binary systems, equation (16) reduces to the scalar form

$$D_{x12} = D_{12} \left[ 1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1} \right] \quad (17)$$

The Maxwell-Stefan binary diffusivity  $D_{12}$  can be predicted over the entire composition range given the infinite dilution values [8,9]. It is important to note that both  $D_{x12}$  and  $D_{12}$  vary with composition but the latter transport parameter shows a more predictable composition dependence. In the limiting case of ideal gas mixtures, the activity coefficients reduce to unity and

$$D_{y12} = D_{12}, \quad (18)$$

the binary vapour phase diffusivity is almost composition independent. By analogy with the two-component case, we may expect for the multicomponent system that the  $D_{ij}$  coefficients would show a weaker and predictable composition dependence as compared to the Fick's law diffusivities,  $D_{xij}$ .

#### Solution to Steady-State Diffusion Problems: Film Model

For steady-state conditions, the equations of continuity for the diffusing species reduce to

$$\frac{dN_i}{dz} = 0, \quad i = 1, 2, \dots, n \quad (19)$$

which show that the total molar fluxes  $N_i$  are constant along the diffusion path; for interphase transport in fluid-fluid systems, these total fluxes are also phase invariants. In contrast, the diffusion fluxes are not phase invariant and indeed due to the variation of compositions along the diffusion path, they vary from one end of the diffusion path to the other (cf. equation (4)).

In many separation and processing operations the compositions at either end of the diffusion path are known. We thus have the boundary conditions:

$$\begin{aligned} \text{at } z = 0, \text{ bulk liquid, } & (x) = (x_b) \\ \text{at } z = \delta, \text{ interface, } & (x) = (x_I) \end{aligned} \quad (20)$$

where  $\delta$  is the length of the diffusion path (or 'film' thickness).

In order to obtain a solution for the fluxes  $N_i$  using equations (8) it becomes convenient to define the following quantities:

a dimensionless distance within the film

$$\eta = z/\delta \quad (21)$$

'mass transfer coefficients' of the pair  $i$ - $j$  in the multicomponent mixture

$$k_{ij} = c \mathfrak{D}_{ij}/\delta, \quad \begin{matrix} i, j = 1, 2, \dots, n \\ i \neq j \end{matrix} \quad (22)$$

and a matrix of dimensionless 'rate' factors,  $[\Phi]$ , with elements given by

$$\Phi_{ii} = \frac{N_i}{k_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^n \frac{N_k}{k_{ik}}, \quad i = 1, 2, \dots, n-1 \quad (23)$$

$$\Phi_{ij} = -N_i(1/k_{ij} - 1/k_{in}), \quad \begin{matrix} i, j = 1, 2, \dots, n-1 \\ i \neq j \end{matrix} \quad (24)$$

and a column matrix,  $(\zeta)$ , with elements given by

$$\zeta_i = -N_i/k_{in}, \quad i = 1, 2, \dots, n-1 \quad (25)$$

With definitions (21) - (25), equations (8) can be written in view of equations (10) - (13) in  $n-1$  dimensional matrix notation as

$$[\Gamma] \frac{d(x)}{d\eta} = [\Phi](x) + (\zeta) \quad (26)$$

Equation (26) represents a first order ordinary matrix differential equation. The matrices  $[\Gamma]$  and  $[\Phi]$  have elements which are strictly dependent on composition dependent and therefore a general solution, taking such composition variations into account, to equation (26) is not possible. If we make the assumptions that: (i) the  $\mathfrak{D}_{ij}$  (and hence the  $k_{ij}$ ) are composition independent or alternatively use values suitably averaged over the composition range of interest and (ii) the activity coefficient variation with composition is constant over the composition range of interest then the elements of the matrices  $[\Gamma]$  and  $[\Phi]$  will be independent of composition. The equation (26) may therefore be solved for the boundary conditions:

$$\begin{aligned} \text{at } \eta = 0, \text{ bulk liquid, } (x) &= (x_b) \\ \text{at } \eta = 1, \text{ interface, } (x) &= (x_I) \end{aligned} \quad (27)$$

to give the composition profiles within the 'film' as  $[1, 10]$

$$(x - x_b) = \{\exp[\Theta]\eta - \Gamma_I\} \{\exp[\Theta] - \Gamma_I\}^{-1} (x_I - x_b) \quad (28)$$

where we define the matrix  $[\Theta]$  as

$$[\Theta] \equiv [\Gamma]^{-1}[\Phi] \quad (29)$$

The composition gradient in the bulk liquid,  $\eta = 0$ , may be evaluated from equation (28) and the result is

$$\left. \frac{d(x)}{d\eta} \right|_{\eta=0} = - [\Theta] \{ \exp[\Theta] - \mathbf{r}_{L_1} \}^{-1} (x_b - x_I) \quad (30)$$

Now, equation (15) may be used to calculate the bulk diffusion fluxes as

$$(J_b^x) = - [k_{xb}] \left. \frac{d(x)}{d\eta} \right|_{\eta=0} \quad (31)$$

where we define a matrix of 'zero flux' multicomponent mass transfer coefficients in the bulk liquid phase by

$$[k_{xb}] \equiv c [D_{xb}] / \delta \quad (32)$$

in which the elements  $D_{xbij}$  of the matrix of diffusion coefficients are evaluated using relation (16) with all compositions taken to be the bulk values.

Combination of equations (30) and (31) gives us the result for calculating the bulk diffusion fluxes as

$$(J_b^x) = [k_{xb}] [\Theta] \{ \exp[\Theta] - \mathbf{r}_{L_1} \}^{-1} (x_b - x_I) \quad (33)$$

Equation (33) determines the  $n-1$  independent bulk diffusion fluxes in terms of a matrix of 'zero flux' mass transfer coefficients, which may be estimated from binary transport parameters, the composition driving forces  $(x_b - x_I)$  and a matrix of correction factors defined by

$$[\Xi] \equiv [\Theta] \{ \exp[\Theta] - \mathbf{r}_{L_1} \}^{-1} \quad (34)$$

The matrix expansion in (34) can be carried out using Sylvester's theorem described, for example, in Amundson [10]. The calculation of the elements of  $[\Theta]$  requires prior knowledge of the total molar fluxes  $N_i$ . The determination of  $n$  total molar fluxes from  $n-1$  independent diffusion fluxes  $J_{ib}^x$  using

$$N_i = J_{ib}^x + x_{ib} N_t, \quad i = 1, 2, \dots, n \quad (35)$$

requires an additional determinancy condition. If conditions of equimolar counter transfer are specified, then we have

$$N_t = \sum_{i=1}^n N_i = 0 \quad (36)$$

which gives

$$N_i = J_{ib}^x, \quad i = 1, 2, \dots, n \quad (37)$$

Alternatively, we may have transfer of n-1 species through a stagnant nth component, i.e.

$$N_n = J_{nb}^x + x_{nb} N_t = 0 \quad (38)$$

for which case we may calculate the total molar fluxes from

$$N_i = \sum_{j=1}^{n-1} (\delta_{ij} + x_{ib}/x_{nb}) J_{jb}^x, \quad i = 1, 2, \dots, n-1 \quad (39)$$

Equations (33) and (35), together with an additional determinancy condition such as (36) or (38), represent the final solution to the steady-state diffusion problem considered. The form of the solution is not explicit and therefore a trial-and-error procedure is involved. Convergence is assured if the following scheme is adopted [1]:

- (i) calculate the elements of  $[k_{xb}]$  using equations (32) and (16),
- (ii) assume the correction factor matrix  $[\epsilon]$  to be the identity matrix  $[I]$ ,
- (iii) calculate the bulk diffusion fluxes using (33),
- (iv) the total molar fluxes may now be calculated with the aid of an additional determinancy condition, such as (36) or (38), from relations (37) or (39),
- (v) with this estimate of the total molar fluxes, the elements of the matrix  $[\theta]$  may be calculated from equations (29), (22)-(24) and (11). The correction factor matrix  $[\epsilon]$  can now be calculated using (34). Explicit expressions for  $[\epsilon]$  for the ternary case are given in [1].,
- (vi) a matrix of 'finite flux' mass transfer coefficients may now be calculated as

$$[k_{xb}^\bullet] = [k_{xb}] [\epsilon] \quad (40)$$

and the diffusion fluxes from (cf. equations (33), (34) and (40))

$$(J_b^x) = [k_{xb}^\bullet] (x_b - x_I) \quad (41)$$

- (vii) steps (iv)-(vi) are repeated till convergence is obtained for each individual  $N_i$ .

### Special Cases

For equimolar counter transfer in two-component systems, the above analysis yields the classical result

$$N_1 = k_{xb}^\bullet (x_{1b} - x_{1I}) \quad (42)$$

where

$$k_{xb}^{\bullet} = c D_{x12} / \delta \quad (43)$$

For transfer of species 1 through stagnant 2, we get

$$N_1 = k_{xb}^{\bullet} (x_{1b} - x_{1I}) / (1 - x_{1b}) \quad (44)$$

where now

$$k_{xb}^{\bullet} = \frac{c}{\delta} D_{x12} \frac{\theta_{11}}{\exp \theta_{11} - 1} \quad (45)$$

It is more common in practice to combine equations (44) and (45) to give

$$N_1 = \frac{c D_{x12}}{\delta} \ln \left( \frac{1 - x_{1I}}{1 - x_{1b}} \right) \quad (46)$$

For transfer in systems with three or more species, simplifications such as equations (42) and (46) are not obtained and the general calculation procedure suggested in this work should be used.

### Nomenclature

#### Latin letters

[A]	matrix whose elements are defined by equations (12) and (13)
c	total molar density of the mixture
$D_{xij}$	generalized Fick's law diffusivities
$\mathfrak{D}_{ij}$	generalized Maxwell-Stefan diffusivities
$\mathfrak{D}_{12}$	Maxwell-Stefan diffusivity for binary pair 1-2
$D_{x12}$	Fick's law diffusivity for binary pair 1-2 in liquid mixture
$D_{y12}$	Fick's law diffusivity for binary pair 1-2 in vapour mixture
$\mathbf{I}_i$	identity matrix with elements $\delta_{ij}$
$J_i$	molar diffusion flux of species $\underline{i}$ in mixture
$k_{xbij}$	elements of matrix of 'zero flux' multicomponent mass transfer coefficients
$k_{xbij}^{\bullet}$	elements of matrix of 'finite flux' multicomponent mass transfer coefficients
$k_{ij}$	mass transfer coefficient for pair i-j in multicomponent mixture, defined by equation (22)
n	number of species in multicomponent mixture
$N_i$	total molar flux of species $\underline{i}$



Latin letters (cont'd)

$N_t$	mixture total molar flux
$R$	gas constant
$T$	temperature
$u_i$	diffusion velocity of species $i$
$u$	molar average velocity of mixture, $u = \sum_{i=1}^n x_i u_i$
$x_i$	mole fraction of species $i$ in liquid mixture
$z$	position coordinate along diffusion path

Greek letters

$\gamma_i$	activity coefficient of species $i$ in solution
$[\Gamma]$	matrix of thermodynamic factors with elements given by (11)
$\delta$	film thickness
$(\zeta)$	column matrix with elements given by equations (25)
$\eta$	dimensionless position coordinate, defined by equation (21)
$[\Theta]$	matrix defined by equation (29)
$[\Xi]$	matrix of correction factors defined by equation (34)
$[\Phi]$	matrix of dimensionless rate factors with elements given by equations (23) and (24)

Matrix notation

$( )$	column matrix with $n-1$ elements
$[ ]$	square matrix, $n-1 \times n-1$
$[ ]^{-1}$	inverted matrix, $n-1 \times n-1$
$\begin{bmatrix} & \\ & \\ & \\ & \end{bmatrix}$	diagonal matrix with $n-1$ elements

Subscripts

$b$	bulk liquid phase property
$i, j, k$	indices
$I$	interfacial property
$n$	$n$ th component property
$t$	pertaining to total mixture
$x$	liquid phase parameter
$y$	vapour phase parameter
$12$	binary pair 1-2
$ij$	pair $i-j$ in multicomponent mixture

Superscripts

- x liquid phase property
- y vapour phase property
- coefficient corresponding to finite transfer rates

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