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ADDITION OF PHASE RESISTANCES FOR NON-ISOTHERMAL MULTICOMPONENT MASS TRANSFER

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Introduction

In many chemical engineering operations such as absorption, distillation, condensation and evaporation we have interphase transport of mass between vapour (gas) and liquid phases. In many, if not most, systems of practical interest the number of components in either phase exceeds two, i.e. we have multicomponent systems. Each of the contiguous fluid phases will offer resistance to transfer of mass (and heat) and so may the interface itself, in some cases. It is useful in practice to define, and calculate, overall mass transfer coefficients which depict the overall resistance offered by the two (fluid-fluid) phase system; such overall coefficients will determine the system behaviour. For $\underline{n}$-component systems, the transport behaviour in either phase is adequately described by a matrix of transport coefficients with $(n-1)^2$ elements [1,2,3]. Though procedures for adding mass transfer phase resistances are well established for binary systems [4], the corresponding extension to the general $\underline{n}$-component case is available only for the case of equimolar counter transfer [3], which is relevant to distillation operations. In many practical cases we encounter transfer of $\underline{n-1}$ species through an inert (non-transferring) $\underline{n}$th component. Such a situation arises, for example, when we have condensation of a mixture of vapours in the presence of an inert gas. This paper is concerned with the development of a procedure for adding phase resistances for non-equimolar mass transfer and is a generalization of the analysis of Toor [3]. The interfacial resistance is ignored in the analysis.

Analysis

We consider a vapour (gas) - liquid system with n components, $n \geq 3$, in either phase and maintained at constant pressure. If we assume equilibrium at the interface itself, there are n-1 unknown intensive interfacial state conditions, corresponding to the thermodynamic degrees of freedom. It is convenient to choose the n-1 mole fractions x_{iI} as the independent state variables. The interfacial temperature T_I and the n-1 interfacial vapour compositions y_{iI} will be determined by the vapour-liquid equilibrium relationship. If this equilibrium relationship is linearized over the range of temperatures involved in passing from the bulk (subscript b) to the interfacial (subscript I) conditions, we can write at the interface

$$(y_I) = [M] (x_I) + (b) \tag{1}$$

where $[M]$ is the matrix of equilibrium 'constants', with elements

$$M_{ij} = \partial y_i^*/\partial x_j, \qquad i,j = 1,2,\ldots n-1 \tag{2}$$

The matrix $[M]$ will be non-diagonal, in general, for non-ideal systems. (b) is a column matrix of intercepts, whose elements will be generally non-zero.

If we wish to combine mass transfer driving forces and resistances of each phase, we must require that at least one phase be saturated; this is necessary for 'eliminating' the partial driving force for that phase. Here we assume that the liquid phase is saturated; this allows us to calculate the composition of the vapour which would be in equilibrium with the bulk liquid phase as

$$(y^*) = [M] (x_b) + (b) \tag{3}$$

Now, it is easy to show by a material balance that if N_i is the normal constituent material flux in a given phase at the interface and with respect to it,

$$N_i^y = N_i^x = N_i, \qquad i = 1,2,\ldots n \tag{4}$$

The only assumptions required are that no surface reaction is occurring and there are no constituent adsorptions at the interface. The flux N_i is thus a phase invariant. If we further assume that (i) the average state of each phase can be characterized by the bulk properties, (ii) that the transport rates in the interfacial region in directions tangent to the interface are negligible compared to the normal interfacial transport rates and (iii) that under unsteady state conditions, the rate of accumulation in the interfacial region is negligible compared to the normal interphase transport rate (or at least that the average rate of accumulation is negligible), we can similarly show that

$$N^y_{ib} = N^x_{ib} = N_i, \qquad i = 1,2,\ldots n \qquad (5)$$

In addition to these total transport fluxes, it is also convenient to define normal constituent material diffusion fluxes J_i in the interface or in the bulk phase. Many choices are possible, but the simplest for our purpose is the diffusion flux defined with respect to the total mixture material transport flux, N_t, defined as

$$N_t = \sum_{i=1}^{n} N_i, \qquad (6)$$

i.e.

$$J^y_i \equiv N_i - y_i N_t, \qquad i = 1,2,\ldots n \qquad (7)$$

with an analogous expression for the liquid phase. Only <u>n-1</u> of the diffusion fluxes J^y_i are independent for we have

$$\sum_{i=1}^{n} J^y_i = 0 \qquad (8)$$

These diffusion fluxes J^y_i are not phase invariants and vary from the bulk to the interface. In separation operations it is the bulk vapour (or liquid) compositions which appear in material balances and therefore it is the bulk diffusion fluxes, J^y_{ib}, defined by

$$J^y_{ib} \equiv N_i - y_{ib} N_t, \qquad i = 1,2,\ldots n-1 \qquad (9)$$

which are useful. The <u>n-1</u> independent bulk diffusion fluxes (9) are related to the <u>n-1</u> independent partial vapour phase driving forces by

$$(J^y_b) = [k^\bullet_{yb}]\,(y_b - y_I) \qquad (10)$$

where we define a matrix $[k^{\bullet}_{yb}]$,$\underline{n-1}\times\underline{n-1}$, of partial vapour phase mass transfer coefficients. The superscript black dot • serves as a reminder that these transfer coefficients are themselves dependent on the interfacial mass transfer rates [1,2,4].

Alternatively, we may define a matrix of overall vapour phase mass transfer coefficients by

$$(J^y_b) = [K^{\bullet}_{oyb}]\ (y_b - y^*) \tag{11}$$

where (y*), the composition of the vapour in equilibrium with the bulk liquid phase, is obtained from equation (3).

The knowledge of the $(n-1)^2$ elements of the matrix of transfer coefficients, either partial or overall, is sufficient to calculate the $\underline{n-1}$ diffusion fluxes J^y_{ib}; the $\underline{n}$th diffusion flux J^y_{nb} is obtained from equation (8). In order to calculate the $\underline{n}$ interfacial transfer rates N_i we require an additional determinancy condition. Two special determinancy conditions are usually quoted in the literature:

(i) equimolar counter transfer: Here we have

$$N_t = 0 \tag{12}$$

and is usually referred to as the distillation case.

(ii) no transfer of a reference component (inert carrier):

$$N_n = 0 \tag{13}$$

called the absorption case, which arises due to the insolubility of the reference component in the other phase.

The determination of the $\underline{n}$ total fluxes $\underline{N_i}$ from the $\underline{n-1}$ independent diffusion fluxes J^y_{ib}, hereinafter termed the bootstrap solution, is simple for the distillation case for we have

$$N_i = J^y_{ib}, \qquad i = 1,2,\ldots n-1 \tag{14}$$

with the $\underline{n}$th total flux determined from

$$N_n = N_t - \sum_{i=1}^{n-1} N_i = - \sum_{i=1}^{n-1} N_i \tag{15}$$

The bootstrap solution (14) may be rewritten in <u>n-1</u> dimensional matrix notation as

$$(N) = [B_b^y] (J_b^y) \tag{16}$$

where the elements of $[B_b^y]$, which may be termed the bootstrap solution matrix, are given by

$$B_{bij}^y = \delta_{ij}, \qquad i,j = 1,2\ldots n-1 \tag{17}$$

For the absorption case, we note that in view of equation (13) we have

$$N_n = J_{nb}^y + y_{nb} N_t = 0 \tag{18}$$

and therefore

$$N_t = - J_{nb}^y / y_{nb} = (J_{1b}^y + J_{2b}^y + \ldots\ldots + J_{n-1,b}^y)/y_{nb} \tag{19}$$

which gives in view of equations (9)

$$\begin{aligned} N_i &= (1 + y_{ib}/y_{nb}) J_{ib}^y + \sum_{\substack{j=1 \\ j\neq i}}^{n-1} y_{jb} J_{jb}^y / y_{nb}, \\ &= \sum_{\substack{j=1 \\ j\neq i}}^{n-1} (\delta_{ij} + y_{ib}/y_{nb}) J_{jb}^y, \qquad i = 1,2,\ldots n-1 \end{aligned} \tag{20}$$

The bootstrap solution matrix for the absorption case, therefore, has its elements given by

$$B_{bij}^y = \delta_{ij} + y_{ib}/y_{nb}, \qquad i,j = 1,2,\ldots n-1 \tag{21}$$

The mass transport process in the liquid phase may be analysed in an analogous manner. The bulk diffusion fluxes in the liquid phase are given in terms of the partial liquid phase composition driving forces by

$$(J_b^x) = [k_{xb}^\bullet] (x_I - x_b) \tag{22}$$

where $[k_{xb}^\bullet]$ is the matrix of partial liquid phase mass transfer coefficients. The phase invariant total fluxes N_i may be calculated from the liquid phase diffusion fluxes J_{ib}^x by the bootstrap solution in the liquid phase

$$(N) = [B_b^x]\,(J_b^x) \tag{23}$$

Now, from equations (11) and (16), the overall vapour phase driving forces may be obtained as

$$(y_b - y^*) = [K^\bullet_{oyb}]^{-1}[B_b^y]^{-1}\,(N) \tag{24}$$

Equations (10) and (16) similarly yield

$$(y_b - y_I) = [k^\bullet_{yb}]^{-1}[B_b^y]^{-1}\,(N) \tag{25}$$

The partial driving forces in the liquid phase are obtained explicitly, in view of equations (22) and (23) as

$$(x_I - x_b) = [k^\bullet_{xb}]^{-1}[B_b^x]^{-1}\,(N) \tag{26}$$

Premultiplying both sides of equation (26) by $[M]$, the equilibrium constant matrix, and using equations (1) and (3) we obtain

$$(y_I - y^*) = [M]\,[k^\bullet_{xb}]^{-1}[B_b^x]^{-1}\,(N) \tag{27}$$

Combination of equations (24), (25) and (27) gives the general formula for adding mass transfer resistances in multicomponent systems, under conditions of finite transfer rates, as

$$[K^\bullet_{oyb}]^{-1}[B_b^y]^{-1} = [k^\bullet_{yb}]^{-1}[B_b^y]^{-1} + [M]\,[k^\bullet_{xb}]^{-1}[B_b^x]^{-1} \tag{28}$$

which is the result we sought; it allows calculation of the overall matrix of transfer coefficients from a knowledge of the partial mass transfer coefficient matrices, equilibrium relationship and the determinancy condition. Equation (28) is the proper generalization of the result for the special case of equimolar counter transfer (12), obtained earlier by Toor [3]. Toor's result is recovered quite simply from the equation (28) with the bootstrap solution matrices taken to be identity matrices (cf. equation (17)):

$$[K^\bullet_{oyb}]^{-1} = [k^\bullet_{yb}]^{-1} + [M]\,[k^\bullet_{xb}]^{-1} \tag{29}$$

Examination of equation (28) shows that, unlike the case of binary systems, it is not possible, in general, to state whether one or other phase controls the transport behaviour of a multicomponent system. For non-ideal mixtures the elements of the matrix $[M]$ could change dramatically change magnitude and possibly sign in the same column with varying intensive properties. The mass transfer 'control' could then shift from one phase to the other. It is also clear from equation (28) that the requirement that the overall matrix $[K^{\bullet}_{oyb}]$ be diagonal is very stringent; it requires that all the constituent matrices: $[k^{\bullet}_{yb}]$, $[k^{\bullet}_{xb}]$, $[M]$, $[B^{y}_{b}]$ and $[B^{x}_{b}]$ be severally diagonal. The general conclusion to be drawn here is that multicomponent interphase mass transfer must always be described by non-diagonal matrices of transfer coefficients, i.e. coupled rate relations.

Nomenclature

(b)	column matrix of intercepts
$[B]$	bootstrap solution matrix
J_i	molar diffusion flux of species *i*
$[k^{\bullet}]$	partial matrix of multicomponent mass transfer coefficients
$[K^{\bullet}_{o}]$	overall matrix of multicomponent mass transfer coefficients
$[M]$	matrix of equilibrium constants
n	number of species in mixture
N_i	total molar flux of species *i*
N_t	mixture total flux
T	temperature
x_i	mole fraction of species *i* in liquid phase
y_i	mole fraction of species *i* in vapour phase
δ_{ij}	Kronecker delta

Matrix Notation

$(\ )$	column matrix of dimension $\underline{n-1}$
$[\ ]$	square matrix of dimension $\underline{n-1}\times\underline{n-1}$
$[\ ]^{-1}$	inverted matrix, $\underline{n-1}\times\underline{n-1}$

Subscripts

b	bulk phase property
I	interfacial property
i	species *i*
n	species *n*

Subscripts (cont'd)

x	liquid phase property
y	vapour phase property

Superscripts

x	liquid phase property
y	vapour phase property
$*$	equilibrium value
●	coefficient corresponding to finite transfer rates

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