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EFFECT OF THERMODYNAMIC NON-IDEALITIES ON FLUID-FLUID INTERPHASE MASS TRANSFER

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ABSTRACT

The two film resistance model for n-component mass transfer across fluid-fluid interfaces is developed. Arguments are presented in favour of the use of the Generalized Maxwell-Stefan (GMS) diffusion coefficients to describe the transport process. The GMS diffusion coefficients are amenable to molecular interpretation and prediction and multicomponent mass transfer coefficients defined in terms of them are shown to possess simple addivity property. The effect of thermodynamic non-idealities on intra- and inter-phase mass transport processes are brought out in the analysis.

Introduction

Diffusion in a two component system is described by the Fick's law:

$$J_1 = - c\, \mathcal{D}_{12} \frac{dx_1}{dz} \tag{1}$$

where $\mathcal{D}_{12}$ is the binary diffusivity. For equimolar diffusion across a film of thickness δ equation (1) can be integrated to yield the molar flux N_1, referred to a stationary coordinate reference frame, as:

$$N_1 = \frac{c\, \mathcal{D}_{12}}{\delta} (x_{1b} - x_{1I}) = k_{12}(x_{1b} - x_{1I}) \tag{2}$$

where we define k_{12} as the binary mass transfer coefficient.

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For mass transfer across two non-ideal fluid phases, e.g. two liquid phases as in extraction and membrane processes, we have equation (2) applicable to either side of the interface. We denote the two phases by superscripts ' and " respectively. The system transport behaviour is governed by the overall resistance offered by the two phases and this overall resistance will be the sum of the individual phase resistances. In order to obtain an expression for the overall mass transfer coefficient it is essential to assume that equilibrium prevails at the interface. This equilibrium relationship reduces to:

$$\gamma'_1 \, x'_1 = \gamma''_1 \, x''_1 \tag{3}$$

We may write the equilibrium relationship at the interface as:

$$x'_{1I} = (\gamma''_1 / \gamma'_1) x''_{2I} \tag{4}$$

Further, if we define the composition in phase ' which is in equilibrium with the bulk liquid phase ", we have

$$x'_{1e} = (\gamma''_1 / \gamma'_1) \, x''_{2b}$$

then it is easy to derive that the overall mass transfer coefficient $\mathcal{K}'_{o12}$ referred to the phase ' , defined by:

$$N_1 = \mathcal{K}'_{o12} \, (x'_{1b} - x'_{1e}) \tag{5}$$

will be related to the individual phase resistances by:

$$\mathcal{K}'^{-1}_{o12} = k'^{-1}_{12} + (\gamma''_1 / \gamma'_1) \, k''^{-1}_{12} \tag{6}$$

The thermodynamics of equilibria affects the distribution of mass transfer resistances between the phases. But this is not the only effect of thermodynamics on the system transport behaviour; it has been appreciated in recent years that thermodynamic non-idealities also influence the diffusivity $\mathcal{D}_{12}$ in a particular phase [1,2,3]. Thus the diffusivity $\mathcal{D}_{12}$ can be split up into kinetic and thermodynamic factors:

$$\mathcal{D}_{12} = \text{Đ}_{12} \, \Gamma \tag{7}$$

where Đ_{12} is the Generalized Maxwell-Stefan diffusion coefficient. The factor Γ in equation (7) is given by:

$$\Gamma = 1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1} \tag{8}$$

It can be seen that the equations (7) and (8) also bring out the effect of solution thermodynamics, embodied in the factor Γ, on the diffusion behaviour. The separation of kinetic and thermodynamic contributions to the diffusion promises to yield a general prediction of diffusion coefficients in the liquid phase [3].

Our object in this communication is to examine the effect of solution thermodynamics on the inter-phase mass transport in n-component systems. As has been noted repeatedly in recent years, systems of three or more species exhibit transport characteristics sometimes completely different from a corresponding binary system. Our analysis may therefore help in the modeling of multicomponent mass transfer processes.

Analysis

The correct generalization of equation (1) to n-component systems is

$$J_i = -c \sum_{k=1}^{n-1} D_{ik} \frac{dx_k}{dz} \quad , \; i = 1,2,..n-1 \tag{9}$$

D_{ik} are multicomponent Fick's law diffusivities; the cross coefficients D_{ik} $(i \neq k)$ give the effect of the composition gradient of component k on the diffusion flux of component i, this effect is called the coupling effect.

For further discussion it is convenient to represent the equation (9) in n-1 dimensional matrix notation:

$$(J) = -c\,[D]\,\frac{d(x)}{dz} \tag{10}$$

For equimolar diffusion in n-component system under steady state conditions, combination of equations (10) with the continuity relations for the n species yields the differential equation:

$$\frac{d}{dz}\left\{ c\,[D]\,\frac{d(x)}{dz} \right\} = (0) \tag{11}$$

If c [D] is assumed independent of z, the equation (11) may be integrated over a thickness δ to give the fluxes N_i as [4,5]:

$$(N) = \frac{c\,[D]}{\delta}\,(x_b - x_I) = [k]\,(x_b - x_I) \tag{12}$$

In equation (12) $(x_b - x_I)$ represents an n-1 dimensional column matrix of driving forces and we define a matrix of mass transfer coefficients [k] by analogy to equation (2) as:

$$[k] = c\,[D]\,/\,\delta \tag{13}$$

In order to predict the matrix of multicomponent mass transfer coefficients [k] within a fluid phase we need to predict the matrix of Fick's law diffusivities. For non-ideal liquid mixtures we may expect a strong thermodynamic influence in line with binary systems for which equations (7),(8) form a starting point for prediction methods. In order to separate the Fickian matrix into kinetic and thermodynamic factors we must turn towards a more fundamental constitutive relation than that given by the 'practical' Fickian approach, equation (9). Irreversible Thermodynamics [6] provides a framework within which fundamental diffusion models may be built. The irreversible thermodynamic approach shows that the proper driving forces for multicomponent diffusion are the chemical potential gradients. This is not surprising because thermodynamic equalibrium is described by equality of chemical potentials and departures from equilibrium must be described by gradients in the chemical potential. There are many ways of relating the chemical potential gradients to the diffusion fluxes. One of the most convenient ways is to use the Generalized Maxwell-Stefan formulation [7,8], which is essentially equivalent to the frictional formulation of Lamm [9,10]:

$$\frac{x_i}{R\,T}\frac{d\mu_i}{dz} = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_i J_j - x_j J_i}{c\,Đ_{ij}}, \quad i = 1,2,..n-1 \tag{13}$$

where the GMS diffusion coefficients $Đ_{ik}$ exhibit the Onsager symmetry relation:

$$Đ_{ik} = Đ_{ki}, \quad \substack{i,k = 1,2,..n\\ i\neq k} \tag{14}$$

By defining thermodynamic factors Γ_{ij}:

$$\Gamma_{ij} = \delta_{ij} + \frac{x_i}{x_j}\frac{\partial \ln \gamma_i}{\partial \ln x_j}, \quad i,j = 1,2,..n-1 \tag{15}$$

the chemical potential gradients may be expressed as [11]:

$$\frac{d\mu_i}{dz} = x_i\,R\,T \sum_{j=1}^{n-1} \Gamma_{ij}\frac{dx_j}{dz}, \quad i = 1,2,..n-1 \tag{16}$$

By further defining a matrix [A] with elements given by

$$A_{ii} = \frac{x_i}{Ð_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{x_k}{Ð_{ik}} , \quad i = 1,2,..n-1 \tag{17}$$

$$A_{ij} = - x_i \left(\frac{1}{Ð_{ij}} - \frac{1}{Ð_{in}} \right) , \quad i,j = 1,2,..n-1, \ i \neq j \tag{18}$$

the equations (13) may be written in n-1 dimensional matrix notation as [11]:

$$c \, [\Gamma] \frac{d(x)}{dz} = - [A] \, (J) \tag{19}$$

Comparison of equations (10) and (19) gives the matrix of Fick's law diffusivities as

$$[D] = [A]^{-1} [\Gamma] \tag{20}$$

which is the correct generalization of the binary relationship (7). Equation (20) is the starting point for the estimation of multicomponent diffusion coefficients D_{ik} [12]. The GMS coefficients $Ð_{ik}$ can be estimated from binary transport parameters and solution thermodynamic models may be used to predict the multicomponent activity coefficients, and hence the elements Γ_{ij}, from binary thermodynamic parameters such as the Wilson or NRTL parameters.

Equations (13) and (20) may be combined to give the method for predicting multicomponent mass transfer coefficients:

$$[k] = \frac{c \, [A]^{-1} [\Gamma]}{\delta} \tag{21}$$

We shall see below that multicomponent mass transfer coefficients defined by

$$[B] = c \, [A]^{-1} / \delta \tag{22}$$

have some fundamental and convenient property. Following the discussion on the GMS coefficients $Ð_{ik}$, it can be appreciated from equations (17), (18) and (22) that the mass transfer coefficients B_{ik} are free from thermodynamic influences and may be estimated from kinetic parameters alone.

Let us now consider mass transfer from phase ' to the phase ". The molar fluxes can be written for phase ' by the matrix equation:

$$(N) = [k'] \, (x'_b - x'_I) = [B'] \, [\Gamma'] (x'_b - x'_I) \tag{23}$$

For phase " we have similarly:

$$(N) = [k''] \, (x''_I - x''_b) = [B''] \, [\Gamma''] (x''_I - x''_b) \tag{24}$$

As in the binary case we assume that thermodynamic equilibrium at the interface. The equilibrium relation between two non-ideal liquid phases may be expressed as:

$$\gamma'_i \, x'_{iI} = \gamma''_i \, x''_{iI} \,, \quad i = 1,2,..n-1 \tag{25}$$

The activity coefficients in the two phases, γ'_i and γ''_i, are strictly functions of all the intensive state variables in the two phases respectively:

$$\gamma'_i = \gamma'_i \, (x'_{1I}, x'_{2I}, \ldots . x'_{n-1,I}, T), \quad i = 1,2,..n-1 \tag{26}$$

$$\gamma''_i = \gamma''_i \, (x''_{1I}, x''_{2I}, \ldots . x''_{n-1,I}, T), \quad i = 1,2,..n-1 \tag{27}$$

We may linearize the equilibrium relations (25) over the composition range of interest in the form:

$$(x'_I) = [\Gamma']^{-1} \ulcorner m_{eq} \lrcorner \, [\Gamma''] \, (x''_I) \tag{28}$$

where the diagonal matrix of equilibrium constants m_{eqi} is obtained by the ratio:

$$m_{eqi} = \gamma''_i / \gamma'_i \,, \quad i = 1,2,..n-1 \tag{29}$$

The activity coefficients on the right hand side of equations (29) are calculated at some appropriately averaged compositions x'_i and x''_i.

In order to calculated an overall mass transfer coefficient matrix it is necessary to define an equilibrium composition x'_{ie} which is in equilibrium with the bulk compositions in phase ", x''_{ib}; thus we have:

$$(x'_e) = [\Gamma']^{-1} \ulcorner m_{eq} \lrcorner \, [\Gamma''] \, (x''_b) \tag{30}$$

Thus if we define an overall mass transfer coefficient matrix by:

$$(N) = [K'_o] \, (x'_b - x'_e) = [B'_o] \, [\Gamma'] \, (x'_b - x'_e) \tag{31}$$

then we obtain the addivity relation for the coefficient $[K'_o]$ [13]:

$$[K'_o]^{-1} = [k']^{-1} + [\Gamma']^{-1} \lceil m_{eq} \rfloor [\Gamma''] [k'']^{-1} \tag{32}$$

The equation (32), which represents represents the matrix analogue of equation (6), follows from equations (23) - (31); these equations may also be used to derive the addivity formula for the B_{ik} coefficients:

$$[B'_o]^{-1} = [B']^{-1} + \lceil m_{eq} \rfloor [B'']^{-1} \tag{33}$$

It follows from equation (32) that the k_{ik} coefficients for either phase contain both kinetic and thermodynamic factors and the overall coefficient matrix $[K'_o]$ will be non-diagonal if the matrix of thermodynamic factors in either fluid phase are non-diagonal. Thus the overall coefficient will be more sensitive to the system thermodynamics. On the other hand the coefficients B_{ik} in either phase, defined in terms of the GMS diffusion coefficients (cf. equations (17),(18) and (22)), are less sensitive to thermodynamic factors. It follows from equation (33) that if both the coefficient matrices $[B']$ and $[B'']$ are diagonal, signifying negligible kinetic coupling between the diffusing species, then the overall matrix $[B'_o]$ will also be diagonal. The separation of the kinetic and thermodynamic factors as in equation (20), leading to the definition of the kinetic mass transfer coefficient matrices B_{ik}, leads to a simpler description of interphase mass transfer.

In the foregoing analysis we have assumed that equimolar diffusion prevails. For the general case in which the molar fluxes N_i are related to the diffusion fluxes J_i by the linear relations:

$$N_i = \sum_{k=1}^{n-1} \beta_{ik} J_k, \quad i = 1,2,..n-1 \tag{34}$$

it can be shown by the analysis given in reference [13] that the addivity formula for the coefficients B_{ik} now takes the form:

$$[B'_o]^{-1} [\beta']^{-1} = [B']^{-1} [\beta']^{-1} + \lceil m_{eq} \rfloor [B'']^{-1} [\beta'']^{-1} \tag{35}$$

Concluding Remarks

The virtues of the GMS diffusion coefficients in describing intraphase diffusion is now well established in the literature. In this paper we have defined multicomponent mass transfer coefficients B_{ik} in terms of these GMS coefficients. The multicomponent coefficients B_{ik} have been shown to possess a simple additivity property. Further, description of the interphase mass transfer in terms of the B_{ik} coefficients correctly brings out the effect of the thermodynamic non-idealities in either fluid phase.

The analysis presented will be useful in modeling distillation, extraction, membrane and other processes involving multicomponent mixtures.

Nomenclature

$[A]$	matrix of inverted diffusion coefficients containing the GMS diffusivities; elements A_{ik} given by (17), (18)
$[B]$	matrix of multicomponent mass transfer coefficients defined in terms of the GMS diffusivities; $[B]$ is given by equation (22)
$[B_o]$	overall matrix of multicomponent mass transfer coefficients defined by equation (31)
c	molar density of fluid mixture
$\mathcal{D}_{12}$	Fick's law diffusivity for binary mixture
$Đ_{ik}$	GMS diffusivity for pair i-k in multicomponent mixture
D_{ik}	generalized Fick's law diffusivities for multicomponent mixture
$[D]$	matrix of Fick's law diffusivities
J_i	molar diffusion flux of species with respect to molar average reference velocity for mixture
k_{12}	binary mass transfer coefficient
K_{o12}	overall mass transfer coefficient in binary system
$[k]$	matrix of multicomponent mass transfer coefficient defined in terms of the Fickian diffusion coefficients; the matrix $[k]$ is defined by equation (13)
$[K_o]$	overall matrix of multicomponent mass transfer coefficients defined in terms of Fickian diffusivities
m_{eqi}	linearized equilibrium constants defined by equations (29)
$\lceil m_{eq} \rfloor$	diagonal matrix with elements m_{eqi}
$\underline{n}$	number of species in multicomponent mixture

N_i	molar flux of species i relative to a stationary coordinate reference frame. For interphase mass transfer, this flux is invariant across the interface
R	gas constant
T	absolute temperature
x_i'	mole fraction of component i in phase '
x_i''	mole fraction of componene i in phase "
x_{ib}	bulk compositions
x_{iI}	interface compositions
x_{ie}'	compositions in equilibrium with bulk x_{ib}''
z	distance along the diffusion path

Greek Letters

$[\beta]$	matrix relating fluxes N_i to the diffusion fluxes; defined by equation (34)
γ_i	activity coefficient of species i in a phase
Γ_{ik}	thermodynamic factors defined by equation (15)
δ	film thickness
δ_{ik}	Kronecker delta
μ_i	molar chemical potential of species in solution

Operational Symbols

$\frac{d}{dz}$	gradient operator

Matrix Notation

( )	n-1 dimensional column matrix
[ ]	n-1×n-1 dimensional square matrix
$[\ ]^{-1}$	n-1×n-1 dimensional inverted matrix
$\ulcorner\ \lrcorner$	diagonal matrix with n-1 non-zero elements

Subscripts

b	bulk phase property
e	equilibrium property
eq	equilibrium property
i,j,k	indices
I	interfacial property

o	overall property
12	property of binary mixture

Superscripts

'	property of phase '
"	property of phase "

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