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A FILM MODEL ANALYSIS OF NON-EQUIMOLAR DISTILLATION OF MULTICOMPONENT MIXTURES

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Abstract—Differences in the molar heats of vaporizations of component species in a multicomponent mixture lead to non-equimolar mass transfers during distillation separations The interphase mass transfer process is analysed using a film model and a procedure developed for calculating multicomponent transfer coefficients and transfer rates from information on binary transport coefficients and partial molar enthalpies of the constituent species in either fluid phase It is shown with the aid of a numerical example that the commonly made assumption of equimolar transfer during distillation may lead to significant errors in the calculation of constituent species transfers

INTRODUCTION

The two-film resistance model is widely used for calculating the transfer efficiencies for distillation operations[1–3] For a tray column the first step in the calculation of the overall column efficiency is the determination of the point efficiency For binary separations $\mathcal{E}_{oy}$, the point vapour efficiency, is usually related to the overall number of vapour phase transfer units $\mathcal{NTU}_{oy}$ by

$$\mathcal{E}_{oy} = 1 - \exp(-\mathcal{NTU}_{oy}) \tag{1}$$

The overall number of vapour phase transfer units $\mathcal{NTU}_{oy}$ is calculated from the partial numbers of transfer units in the vapour and liquid phases using the additivity of resistances formula

$$\mathcal{NTU}_{ov}^{-1} = \mathcal{NTU}_y^{-1} + \frac{mG_t}{L_t}\mathcal{NTU}_x^{-1} \tag{2}$$

For packed column distillation design the transfer efficiency is reflected in the overall height of a transfer unit $\mathcal{HTU}_{oy}$, calculable from the individual heights of transfer units for the vapour and liquid phases by use of the relation[3]

$$\mathcal{HTU}_{oy} = \mathcal{HTU}_y + \frac{mG_t}{L_t}\mathcal{HTU}_x \tag{3}$$

The additivity of resistances formulae (2) and (3) above are derived from the formula for addition of mass transfer coefficients

$$\mathcal{K}_{oy}^{-1} = \mathcal{K}_y^{-1} + m\mathcal{K}_x^{-1} \tag{4}$$

Strictly speaking eqns (2)–(4) are valid only for binary systems under conditions of low mass transfer rates As discussed by Bird, Stewart and Lightfoot[4] the effect of finite to high transfer rates on binary systems is to alter the composition profiles in the diffusion zone and thus alter the values of the mass transfer coefficients themselves The analysis of the effect of finite mass transfer rates on the transport behaviour of multicomponent systems has been carried out by Stewart[5, 6] and others[7, 8] Traditionally in the mass transfer analysis of distillation processes, the assumption of equimolar transfer

$$N_t = \sum_{i=1}^{n} N_i = 0 \tag{5}$$

is made, validating the relations (2) and (3), at least for binary systems The basis of the assumption (5) is that the molar heats of vaporizations of many chemical species have values close to one another For the mixture ethanol–water, for example, the molar heats of vaporization differ by about 5% In general case an energy balance at the interface between the vapour and liquid phases must be considered in addition to the mass balance relations Significantly different molar latent heats would lead to net condensation or evaporation and the consequent finite transfer rates would alter the mass transfer coefficients and invalidate equations (2)–(4) The simultaneous heat and mass transfer process during distillation of binary mixtures has been considered by many authors[9–16] but a proper treatment for multicomponent mixtures does not seem to have been carried out Multicomponent systems show many transport characteristics not possible for simple two component systems, diffusional interactions in multicomponent systems can give rise to osmotic diffusion, diffusion barrier and reverse diffusion as discussed in detail by Toor[17] It is the purpose of this paper to consider a local film model analysis of non-equimolar mass transfer process during multicomponent distillation Proper account is taken in the analysis of the possibility of diffusional interactions between the transferring species Such diffusional interactions become significant in systems made up of species with widely different molecular sizes and nature, i e non-ideal systems For such systems one may expect the molar latent heats to also be significantly different and therefore it may be anticipated that for systems showing large non-idealities both multicomponent diffusional interactions and effects due to non-equimolar transfer

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may combine to give rise to large effects on transfer rates and efficiencies

BASIC INTERPHASE MASS TRANSFER RELATIONS

Consider a local point in a distillation equipment (tray or packed column) in which vapour (denoted by "y") and liquid (denoted by "x") phases are brought into contact We assume that each fluid phase contains $\underline{n}$ components which transfer across the interface The interfacial properties are denoted by a subscript I As mass (and heat) transfer takes across the interface composition (and temperature) profiles develop from one bulk fluid phase to the other We use a film model to describe the mass (and heat) transfer process and assume that the bulk fluid phases are well mixed and the composition profiles in either phase are restricted a thin fluid layer ("film") adjacent to the interface The transport process of heat and mass are assumed to take place under steady–state conditions

If N_i represents the molar flux of species $\underline{i}$ in the mixture, it is easy to show that if there is no adsorption of components at the interface we must have

$$N_i^x = N_i^y = N_i, \quad i = 1, 2, \quad n \tag{6}$$

which expresses the fact that species molar fluxes are continuous across the interface The molar fluxes N_i are called phase invariants The mixture flux N_t defined by

$$N_t = \sum_{i=1}^{n} N_i = N_t^x = N_t^y \tag{7}$$

is also a phase invariant

The molar fluxes N_i incorporate both the purely diffusive and the convective fluxes of mass across the interface It is convenient, and useful, to define diffusive fluxes of the species $\underline{i}$ by

$$J_i^x \equiv N_i - x_i N_t, \quad i = 1, 2, \quad n \tag{8}$$

with an analogous definition for the vapour phase

$$J_i^y \equiv N_i - y_i N_t, \quad i = 1, 2, \quad n \tag{9}$$

The mole fractions x_i and y_i are not all independent for we must have

$$\sum_{i=1}^{n} x_i = 1, \quad \sum_{i=1}^{n} y_i = 1 \tag{10}$$

From eqns (7)–(10) we see that the $\underline{n}$ diffusion fluxes in either phase, J_i^x and J_i^y, are not all independent for they must each sum to zero

$$\sum_{i=1}^{n} J_i^x = 0, \quad \sum_{i=1}^{n} J_i^y = 0 \tag{11}$$

Only $\underline{n-1}$ of the diffusion fluxes can be independent From the defining eqns (8) and (9) we see that J_i^x and J_i^y are not phase invariants and because of the variation of the compositions x_i and y_i along the direction of the diffusion path, they vary in either fluid phase from the bulk phase to the interface In spite of the fact that the diffusion fluxes are not invariant along the diffusion path, they are useful measures of the transfer processes in either phase As discussed in detail by Bird, Stewart and Lightfoot[4] for the binary diffusion case, the diffusion fluxes present a correct portrayal of the intrinsic diffusion process, free from bulk flow effects By analogy with the two-component case, the correct definition of multicomponet mass transfer coefficients is also in terms of the diffusion fluxes[4–6] Thus we may write for the liquid phase

$$J_i^x = \sum_{j=1}^{n-1} k^{\bullet}_{xij}(x_{jb} - x_{jI}), \quad i = 1, 2, \quad n-1 \tag{12}$$

where we define a $\underline{n-1} \times \underline{n-1}$ dimensional square matrix of multicomponent mass transfer coefficients, $[k_x^{\bullet}]$ Only $\underline{n-1}$ driving forces

$$\Delta x_i \equiv x_{ib} - x_{iI}, \quad i = 1, 2, \quad n-1 \tag{13}$$

are considered because only $\underline{n}$th driving force is given by

$$\Delta x_n = -\sum_{j=1}^{n-1} \Delta x_j \tag{14}$$

For the same reason only $\underline{n-1}$ diffusion fluxes J_i^x have been used in eqn (12) to define the mass transfer coefficient matrix $[k_x^{\bullet}]$

For the transfer process in the vapour phase we write

$$J_i^y = \sum_{j=1}^{n-1} k^{\bullet}_{yij} \Delta y_j, \quad i = 1, 2, \quad n-1 \tag{15}$$

where the $\underline{n-1}$ independent vapour phase driving forces are taken as

$$\Delta y_i \equiv y_{iI} - y_{ib}, \quad i = 1, 2, \quad n-1 \tag{16}$$

Equations (15) define the matrix of multicomponent mass transfer coefficients in the vapour phase, $[k_y^{\bullet}]$

In order to calculate the interfacial mass transfer rates we need to be able to estimate the elements of the matrices $[k_x^{\bullet}]$ and $[k_y^{\bullet}]$ We consider first the estimation of the mass transfer coefficients in the liquid phase For diffusion in an $\underline{n}$-component liquid mixture the correct and fundamental formulation of the constitutive relations is afforded by the Generalized Maxwell–Stefan equations[18, 19]

$$\frac{1}{RT}\frac{\mathrm{d}\mu_i}{\mathrm{d}z} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j(u_j - u_i)}{\text{Đ}_{ij}}, \quad i = 1, 2, \quad n \tag{17}$$

where μ_i represents the molar chemical potential of species $\underline{i}$, u_i is the velocity of the diffusing species $\underline{i}$ ($\equiv N_i/c_i$), z is the distance coordinate along the diffusion path, Đ_{ij} represent the Generalized Maxwell–Stefan diffusivities which have the inherent symmetry property equivalent to the Onsager Reciprocal relations[20]

$$\text{Đ}_{ij} = \text{Đ}_{ji}, \quad \begin{matrix} i, j = 1, 2, \quad n \\ i \neq j \end{matrix} \tag{18}$$

Only $\underline{n-1}$ of the chemical potential gradients are independent if we assume mechanical equilibrium in the diffusing mixture for we have the Gibbs–Duhem relationship [20]

$$\sum_{i=1}^{n} x_i \frac{d\mu_i}{dz} = 0 \tag{19}$$

Multiplying both sides of eqns (17) by x_i we obtain

$$\frac{1}{RT} x_i \frac{d\mu_i}{dz} = \sum_{\substack{j=1\\j\neq i}}^{n} \frac{x_i x_j (u_j - u_i)}{Đ_{ij}} = \sum_{\substack{j=1\\j\neq i}}^{n} \frac{x_i N_j - x_j N_i}{c\,Đ_{ij}}, \quad i = 1, 2, \quad n-1 \tag{20}$$

where we have used the defining relations

$$N_i = c_i u_i, \quad c = \sum_{i=1}^{n} c_i, \quad c_i = x_i c, \quad u = \sum_{i=1}^{n} x_i u_i \tag{21}$$

In view of eqns (8), we may also write eqns (20) in the form

$$\frac{1}{RT} x_i \frac{d\mu_i}{dz} = \sum_{\substack{j=1\\j\neq i}}^{n} \frac{x_i J_j^x - x_j J_i^x}{c\,Đ_{ij}}, \quad i = 1, 2, \quad n-1 \tag{22}$$

If we adopt a film model for transfer in the liquid phase we have for steady state transfer through the film adjoining the interface

$$\frac{dN_i}{dz} = 0, \quad i = 1, 2, \quad n \tag{23}$$

which expresses the invariance of N_i along the diffusion path The boundary conditions may be expressed as

$$\begin{array}{lll} z = 0, \text{ bulk liquid phase}, & x_i = x_{ib}, & \multirow{2}{*}{} \\ z = \delta, \text{ interface}, & x_i = x_{iI}, & \end{array} \quad i = 1, 2, \quad n \tag{24}$$

where the diffusion process is assumed to be restricted to a "film" of thickness δ

Krishna [7] has developed an analytic solution to eqns (22)–(24) The bulk diffusion fluxes, J_{ib}^x, defined by

$$J_{ib}^x \equiv N_i - x_{ib} N_t, \quad i = 1, 2, \quad n \tag{25}$$

have been obtained in the form

$$(J_b^x) = [k_{xb}][\theta]\{\exp[\theta] - [I]\}^{-1}(\Delta x) \tag{26}$$

where $[k_{xb}]$ has been defined as the matrix, $\underline{n-1} \times \underline{n-1}$ dimensional, of zero flux multicomponent mass transfer coefficients Comparison of eqns (12) and (26) gives the film model estimation of the matrix of finite flux mass transfer coefficients $[k_{xb}^\bullet]$ as

$$[k_{xb}^\bullet] = [k_{xb}][\Xi] \tag{27}$$

where we further define a matrix of finite flux correction factors

$$[\Xi] \equiv [\theta]\{\exp[\theta] - [I]\}^{-1} \tag{28}$$

It is important to appreciate that since the diffusion fluxes J_i^x vary from the bulk (J_{ib}^x) to the interface (J_{iI}^x), so do the matrix of mass transfer coefficients $[k_x^\bullet]$ defined by eqns (12) Since in practice the bulk liquid compositions are the ones which are measurable and appear in material balances, it is the matrix $[k_{xb}^\bullet]$ defined in terms of the bulk diffusion fluxes J_{ib}^x which are important and useful

The matrix $[\theta]$ is defined as

$$[\theta] \equiv [\Gamma]^{-1}[\Phi] \tag{29}$$

where $[\Gamma]$ is the matrix of thermodynamic factors with elements

$$\Gamma_{ij} = \delta_{ij} + \frac{x_i}{x_j}\frac{\partial \ln \gamma_i}{\partial \ln x_j}, \quad i, j = 1, 2, \quad n-1 \tag{30}$$

and $[\Phi]$ is a matrix of dimensionless mass transfer rate factors whose elements are given by

$$\Phi_{ii} = \frac{N_i}{\mathcal{K}_{in}} + \sum_{\substack{j=1\\j\neq i}}^{n} \frac{N_j}{\mathcal{K}_{ij}}, \quad i = 1, 2, \quad n-1 \tag{31}$$

and

$$\Phi_{ij} = -N_i(1/\mathcal{K}_{ij} - 1/\mathcal{K}_{in}), \quad i, j = 1, 2, \quad n-1 \quad i \neq j \tag{32}$$

The k_{ij} in eqns (31) and (32) represent the zero flux mass transfer coefficients for the constituent binary pairs in the $\underline{n}$-component mixture, they correspond to the coefficients defined by Bird, Stewart and Lightfoot [4] and are given by

$$\mathcal{K}_{ij} = c\,Đ_{ij}/\delta, \quad i, j = 1, 2, \quad n \tag{33}$$

The elements of the matrix of zero flux multicomponent mass transfer coefficients $[k_{xb}]$ is obtained as

$$[k_{xb}] = [B_{xb}]^{-1}[\Gamma] \tag{34}$$

where the elements B_{xbij} are given by

$$B_{xbii} = \frac{x_{ib}}{\mathcal{K}_{in}} + \sum_{\substack{j=1\\j\neq i}}^{n} \frac{x_{jb}}{\mathcal{K}_{ij}}, \quad i = 1, 2, \quad n-1 \tag{35a}$$

and

$$B_{xbij} = -x_{ib}(1/\mathcal{K}_{ij} - 1/\mathcal{K}_{in}), \quad i, j = 1, 2, \quad n-1 \quad i \neq j \tag{35b}$$

The assumption made in deriving the analytic solution (26) to the eqn (22) are (i) the coefficients $\mathcal{K}_{ij}$ are constant over the length of the diffusion path and (ii) the elements of the thermodynamic matrix Γ_{ij} can be considered independent of composition In practice suitably averaged values must be used

For ideal fluid mixtures the above relations simplify considerably because

$$\Gamma_{ii} = 1, \quad i = 1, 2, \quad n-1 \tag{36}$$

and

$$\Gamma_{ij} = 0, \quad i, j = 1, 2, \quad n-1 \atop i \neq j \tag{37}$$

for this case

For transfer in the vapour phase, if considered ideal, we obtain a further simplification in that the Maxwell–Stefan diffusion coefficients can be identified with the Fickian diffusion coefficients of the constituent binary pairs

$$\text{Đ}_{ij} = \mathcal{D}_{y,ij}, \quad i, j = 1, 2, \quad n \atop i \neq j \tag{38}$$

which are essentially composition independent Therefore the solution considered above is exact for ideal gas mixtures and corresponds to the analysis of Krishna and Standart[8]

Thus for ideal gas mixtures the expression for the bulk diffusion fluxes (26) reduces to

$$(J_b{}^y) = [k_{yb}][\Phi]\{\exp[\Phi] - \lceil I \rfloor\}^{-1}(y_b - y_I) \tag{39}$$

where the driving forces $(y_{ib} - y_{iI})$ are directed from the bulk gas phase $(z = 0)$ to the interface $(z = \delta)$ If the driving forces are written as in eqns (16) it can be easily shown using the analysis of Krishna and Standart[8] that the diffusion fluxes will now be given by

$$(J_b{}^y) = [k_{yb}][\Phi]\exp[\Phi]\{\exp[\Phi] - \lceil I \rfloor\}^{-1}(y_I - y_b) \tag{40}$$

The elements of $[\Phi]$ may be calculated from (31) and (32) and the elements of the correction factor matrix $[\Xi]$ obtained by use of Sylvester's theorem[8]

It is important to appreciate that for calculation of the finite flux coefficient $[k^\bullet]$ from equation (27) we require a prior knowledge of the fluxes N_i as these appear in the elements of $[\Phi]$ and therefore affect the elements of the matrix of correction factors, $[\Xi]$ Clearly a trial and error procedure is involved as discussed in [7, 8] Further, there remains one more problem only $\underline{n-1}$ diffusion fluxes are obtained from relations (26) (or 39 and 40) We require one more relation between the fluxes N_i in order to make the system determinate and allow the calculation of the $\underline{n}$ fluxes N_i In the literature on distillation (e g [1–3]) the assumption is usually made in the analysis of the interphase transport process that conditions of equimolar transfer (5) hold For equimolar transfer the problem simplifies considerably for we have (see eqns 8 and 9)

$$N_i = J_i, \quad i = 1, 2, \quad n \tag{41}$$

It is our purpose here to analyse the case where the simplification (5) does not hold It has been shown by Krishna and Standart[21] that the additional relationship required to make the system determinate is afforded by an energy balance at the interface

INTERPHASE ENERGY TRANSFER RELATIONS

For steady state transfer of energy across the vapour-liquid interface, it can be shown that we must have continuity of energy fluxes, i e

$$E^x = E^y = E \tag{42}$$

The energy flux E plays a role in energy transfer analogous to the role of N_i in mass transfer This energy flux includes not only the purely conductive heat fluxes, q, but also the convective enthalpy transfers due to the diffusing species Thus we have [21]

$$E^x = q^x + \sum_{i=1}^{n} \bar{H}_i^x N_i = E^y = q^y + \sum_{i=1}^{n} \bar{H}_i^y N_i \tag{43}$$

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

Defining the following parameters

(i) $\Delta q = q^x - q^y$ (44)

(ii) $\lambda_i = \bar{H}_i^y - \bar{H}_i^x, \quad i = 1, 2, \quad n$ (45)

(iii) $\bar{\lambda}_x = \sum_{i=1}^{n} x_{ib}\lambda_i$ (46)

(iv) $\bar{\lambda}_y = \sum_{i=1}^{n} y_{ib}\lambda_i$ (47)

(v) $\Lambda_{ix} = (\lambda_i - \lambda_n)/\bar{\lambda}_x \quad i = 1, 2, \quad n-1$ (48)

(vi) $\Lambda_{iy} = (\lambda_i - \lambda_n)/\bar{\lambda}_y, \quad i = 1, 2, \quad n-1$ (49)

(vii) $\beta_{ij}^x = \delta_{ij} - x_{ib}\Lambda_{ix}, \quad i, j = 1, 2, \quad n-1$ (50)

(viii) $\beta_{ij}^y = \delta_{ij} - y_{ib}\Lambda_{iy}, \quad i, j = 1, 2, \quad n-1$ (51)

it can be seen from eqns (6)–(9), (43) that the interfacial fluxes N_i can be related to the diffusion fluxes in either phase by the matrix relations[21]

$$(N) = [\beta^x](J_b{}^x) + (x_b)\frac{\Delta q}{\bar{\lambda}_x} \tag{52}$$

$$= [\beta^y](J_b{}^y) + (y_b)\frac{\Delta q}{\bar{\lambda}_y} \tag{53}$$

It is clear from eqns (44)–(53) that for the simplification of equimolar transfer (5), (41) we must have

$$\Delta q = 0 \tag{54}$$

and

$$\lambda_i = \lambda_n, \quad i = 1, 2, \quad n-1 \tag{55}$$

The condition (54) will be satisfied when the temperatures of the bulk fluid phases and the interfacial temperature are all equal This condition is unlikely to hold in general and therefore there will be some contribution of the heat fluxes to the interfacial mass fluxes as can be seen from eqns (52) and (53) Since the contribution to the mass fluxes of Δq is to be divided by $\bar{\lambda}$, it may be concluded that this contribution to the mass fluxes will be small in most practical cases

The condition (55) requires the differences in the partial molar enthalpies in the vapour and liquid phases for each component in the mixture to be equal to one another In practice these differences could be large when the components making up the mixture are highly non-ideal and have widely different molecular weights In this case eqn (55) will not hold and the matrices $[\beta^x]$, $[\beta^y]$ will not be diagonal

RESULTS AND DISCUSSION

Combining eqns (26), (40), (52) and (53) we obtain the final working relations incorporating the film model analysis for non-equimolar distillation Thus for the liquid phase we have

$$(N) = [\beta^x][k_{xb}][\theta]\{\exp[\theta] - \lceil I \rfloor\}^{-1}(x_b - x_I) + (x_b)\frac{\Delta q}{\bar{\lambda}_x} \tag{56}$$

and for the vapour phase, if assumed to ideal

$$(N) = [\beta^y][k_{yb}][\Phi]\exp[\Phi]\{\exp[\Phi] - \lceil I \rfloor\}^{-1}(y_I - y_b) + (y_b)\frac{\Delta q}{\bar{\lambda}_y} \tag{57}$$

In order to illustrate the effect of unequal molar heats of vaporizations on the transfer fluxes we consider distillation of the mixture pentane-2 (1), ethanol (2), and water (3) We take $\Delta q = 0$ and the interfacial compositions are assumed to be known In practice the interfacial conditions will be determined by determined by the continuity relations for mass energy, eqns (6) and (42) Table 1 summarizes the physical conditions chosen for this system and also the calculation of the transfer fluxes using eqns (57), these fluxes must of course be identical to those calculated using eqn (56) for the transport process in the liquid phase

The numerical calculations show that the transfer rate of pentane-2 assuming equimolar transfer is significantly lower than that calculated using the proper interfacial energy balance relations This result is to be expected because the molar latent heat of pentane-2 is much lower compared to the other species in the mixture Water has the highest molar latent heat and the assumption of equimolar transfer overestimates its transfer rate In azeotropic drying applications, the transfer efficiency of water will actually be lower than that calculated assuming equimolar diffusion

Table 1 Distillation of the system pentane-2 (1), ethanol (2), and water (3) Effect of non-equimolar behaviour on the interfacial transfer fluxes

	Equimolar transfer	Nonequimolar transfer
$[k^{\bullet}_{yb}]$, kmol/(s)-(m²)(Δy)	$\begin{bmatrix} 4\ 62 & 1\ 95 \\ 0\ 74 & 3\ 54 \end{bmatrix} \times 10^{-2}$	$\begin{bmatrix} 4\ 55 & 1\ 95 \\ 0\ 73 & 3\ 47 \end{bmatrix} \times 10^{-2}$
$[\beta^y]$	$\begin{bmatrix} 1\ 0 & 0\ 0 \\ 0\ 0 & 1\ 0 \end{bmatrix}$	$\begin{bmatrix} 1\ 41 & 0\ 031 \\ 0\ 105 & 1\ 008 \end{bmatrix}$
N_1, kmol/(s)(m²)	$-2\ 09 \times 10^{-3}$	$-2\ 99 \times 10^{-3}$
N_2, kmol/(s)(m²)	$-2\ 27 \times 10^{-3}$	$-2\ 46 \times 10^{-3}$
N_3, kmol/(s)(m²)	$4\ 36 \times 10^{-3}$	$3\ 98 \times 10^{-3}$

Boundary conditions Interface $y_{1I} = 0\ 60$, $y_{2I} = 0\ 10$, $y_{3I} = 0\ 30$ Bulk vapour $y_{1b} = 0\ 62$, $y_{3b} = 0\ 16$, $y_{3b} = 0\ 22$

Vapour phase diffusion coefficients of binary pairs (estimated from [24]) $\mathcal{D}_{y12} = 0\ 727 \times 10^{-5}$ m²/s, $\mathcal{D}_{y13} = 1\ 44 \times 10^{-5}$ m²/s, $\mathcal{D}_{v23} = 2\ 09 \times 10^{-5}$ m²/s

Film thickness $\delta = 1\ 0 \times 10^{-5}$ m, *Temperature* $T = 346$ K, *Pressure* $p = 1$ bar

Partial molar enthalpies (units MJ/kmol) Liquid phase $\bar{H}_1{}^x = 15\ 5$, $\bar{H}_2{}^x = 10\ 1$, $\bar{H}_3{}^x = 5\ 0$ Vapour phase $\bar{H}_1{}^y = 38\ 0$, $\bar{H}_2{}^y = 50\ 6$, $\bar{H}_3{}^y = 47\ 0$

Another point to note in the calculations in Table 1 is that diffusional interaction effects are important in the system under consideration, this fact is reflected in the large values of the cross coefficients relative the main ones in the matrix $[k^{\bullet}_{yb}]$ Such interaction effects will have the effect of making the individual component transfer efficiencies significantly different [22]

The incorporation of the treatment of non-equimolar transfer in $\underline{n}$-component distillation presented in this paper into standard design procedures is straightforward Thus, if we define a matrix of overall mass transfer coefficients in the vapour phase using

$$(J_b{}^y) = [K^{\bullet}_{oyb}](y^* - y_b) \tag{58}$$

where (y^*) represents the $\underline{n-1}$ dimensional column matrix of compositions in equilibrium with the bulk liquid phase, the formula for addition of mass transfer resistances can be obtained, assuming (54), as [23]

$$[K^{\bullet}_{oyb}]^{-1}[\beta^y]^{-1} = [k^{\bullet}_{yb}]^{-1}[\beta^y]^{-1} + [M][k^{\bullet}_{xb}]^{-1}[\beta^x]^{-1} \tag{59}$$

The matrix $[M]$ in eqn (59) represents the equilibrium constants in the vapour–liquid equilibrium relations

$$M_{ij} = \partial y^*_i / \partial x_j, \quad i, j = 1, 2, \quad n - 1 \tag{60}$$

The addition of resistances formula for non-equimolar multicomponent distillation is therefore much more complicated than the simple formula (4) which is true for equimolar diffusion in two component mixtures

For multicomponent distillation on a tray, we may define matrices of number of transfer units

$$[NTU^{\bullet}_{oy}] \equiv \frac{[K^{\bullet}_{oyb}]\mathscr{A}\mathscr{V}}{G_t}, \quad [NTU_y{}^{\bullet}] \equiv \frac{[k^{\bullet}_{yb}]\mathscr{A}\mathscr{V}}{G_t}, \quad [NTU_x{}^{\bullet}] \equiv \frac{[k^{\bullet}_{xb}]\mathscr{A}\mathscr{V}}{L_t} \tag{61}$$

and thus develop the proper generalization of eqn (2) in the form

$$[NTU^{\bullet}_{oy}]^{-1}[\beta^y]^{-1} = [NTU_y{}^{\bullet}]^{-1}[\beta^y]^{-1} + \frac{[M]G_t}{L_t}[NTU_x{}^{\bullet}]^{-1}[\beta^x]^{-1} \tag{62}$$

The matrix of multicomponent Murphree vapour efficiencies can then be obtained from [22]

$$[E_{oy}] = \lceil I \rfloor - \exp\{-[NTU^{\bullet}_{oy}]\} \tag{63}$$

Finally, we may also define for continuous contact distillation operations involving n-component mixtures the matrices of heights of transfer units

$$[HTU_{oy}^{\bullet}] \equiv [K_{oyb}^{\bullet}]^{-1}\frac{G_t}{aA},$$

$$[HTU_y^{\bullet}] \equiv [k_{yb}^{\bullet}]^{-1}\frac{G_t}{aA}, \quad [HTU_x^{\bullet}] \equiv [k_{xb}^{\bullet}]^{-1}\frac{L_t}{aA} \tag{64}$$

which gives the generalization of eqn (3) as

$$[HTU_{oy}^{\bullet}][\beta^y]^{-1} = [HTU_y^{\bullet}][\beta^y]^{-1} + \frac{[M]G_t}{L_t}[HTU_x^{\bullet}][\beta^x]^{-1} \tag{65}$$

Once the overall height of vapour phase transfer units is calculated from eqn (65), the height of a continuous contact distillation column may be obtained by solution of the matrix differential equation

$$\frac{\mathrm{d}(y_b)}{\mathrm{d}Z} = [HTU_{oy}^{\bullet}]^{-1}(y^* - y_b) \tag{66}$$

which represents the exact matrix analogue of the classical binary distillation relationship

$$\frac{\mathrm{d}y_b}{\mathrm{d}Z} = \mathscr{H}\mathscr{T}\mathscr{U}_{oy}^{-1}(y^* - y_b) \tag{67}$$

The matrices of the number of transfer units $[NTU^{\bullet}]$ and the height of transfer units $[HTU^{\bullet}]$ can be estimated from the corresponding parameters of the constituent binary pairs Thus for example if the heights of transfer units of the constituent binary pairs in the vapour phase, $\mathscr{H}\mathscr{T}\mathscr{U}_{yij}$, can be estimated from an appropriate correlation, then the elements of the matrix of zero flux heights of transfer units $[HTU_y]$ can be estimated from the relations (see eqns 34, 35 and 64)

$$HTU_{yii} = y_{ib}\mathscr{H}\mathscr{T}\mathscr{U}_{yin} + \sum_{\substack{j=1 \\ j \neq i}}^{n} y_{jb}\mathscr{H}\mathscr{T}\mathscr{U}_{yij}, \quad i = 1, 2, \quad n-1 \tag{68}$$

and

$$HTU_{yij} = -y_{ib}(\mathscr{H}\mathscr{T}\mathscr{U}_{vij} - \mathscr{H}\mathscr{T}\mathscr{U}_{vin}), \quad \substack{i, j = 1, 2, \quad n-1 \\ i \neq j} \tag{69}$$

The matrix of finite flux heights $[HTU_y^{\bullet}]$ can be obtained in view of eqns (27) and (64) as

$$[HTU_y^{\bullet}] = [\Xi]^{-1}[HTU_y] \tag{70}$$

As the generalized Maxwell–Stefan diffusion coefficients $Đ_{ij}$ canot in general be identified with the liquid phase diffusivity $\mathscr{D}_{xij}$ normally used in correlations for the parameters $\mathscr{N}\mathscr{T}\mathscr{U}_{xij}$ and $\mathscr{H}\mathscr{T}\mathscr{U}_{xij}$, the calculation of the elements of $[HTU_x^{\bullet}]$ using equations analogous to (68), (69) and (70) is not fully justified but would seem adequate for engineering purposes

CONCLUDING REMARKS

A film model for nonequimolar interphase mass transfer processes during distillation of n-component mixtures has been developed It is seen that when the species making up the mixture are widely different in size and nature both diffusional interaction effects and nonequimolar mass transfer effects become important The models presented in this paper can form the basis of improved design procedures for non-ideal distillation separations Towards this end, calculation procedures have been indicated for adapting available binary correlations for multicomponent separations

NOTATION

a	interfacial area per unit volume of continuous contact distillation column
$\mathscr{A}$	interfacial area per unit volume of dispersion on a tray
A	cross sectional area of the column
$[B_{xb}]$	matrix with elements defined by eqns (35a) and (35b)
c	molar density of fluid mixture
$Đ_{ij}$	generalized Maxwell–Stefan diffusion coefficients
$\mathscr{D}_{yij}$	gas phase diffusivity of pair $i-j$
E	energy flux
$\mathscr{E}_{oy}$	Murphree point efficiency for distillation of binary mixture
$[E_{oy}]$	matrix of multicomponent Murphree point efficiencies
G_t	molar flow rate of vapour mixture
$\bar{H}_i$	partial molar enthalpy of species i in fluid mixture
$\mathscr{H}\mathscr{T}\mathscr{U}$	height of transfer unit for binary distillation
$[HTU]$	matrix of heights of transfer units for multicomponent distillation
$\ulcorner I \lrcorner$	identity matrix with elements δ_{ij}
J_i	diffusion flux of species i relative to molar average velocity u
(J)	column matrix, $n-1$ dimensional, of diffusion fluxes
$\mathscr{K}_{ij}$	zero flux mass transfer coefficient for pair $i-j$ in multicomponent mixture
$[k]$	matrix of multicomponent mass transfer coefficients
$[K_0]$	matrix of overall multicomponent mass transfer coefficients
L_t	molar flow rate of liquid mixture
$[M]$	matrix of equilibrium constants, $M_{ij} = \partial y_i^* / \partial x_j$
n	number of components in mixture
N_i	molar flux of species i relative to a stationary frame of reference
N_t	total molar flux of diffusing mixture relative to a stationary frame of reference
$\mathscr{N}\mathscr{T}\mathscr{U}$	number of transfer units for binary distillation
$[NTU]$	matrix of number of transfer units for multicomponent distillation
p	total system pressure
R	gas constant
T	absolute temperature
u	molar average velocity of diffusing mixture
$\mathscr{V}$	volume of dispersion on tray
x_i	mole fraction of species i in liquid mixture
y_i	mole fraction in gaseous phase

z	distance coordinate along diffusion path
Z	distance coordinate along column height

Greek symbols

$[\beta]$	matrix with elements given by eqns (50), (51)
γ_i	activity coefficient of species $\underline{i}$ in solution
$[\Gamma]$	matrix of thermodynamic factors with elements given by eqn (30)
δ	thickness of diffusion "film"
δ_{ij}	Kronecker delta
$[\theta]$	matrix defined by eqn (29)
λ_i	parameters defined by eqns (45)
Λ_i	parameters defined by eqns (48), (49)
μ_i	molar chemical potential of species $\underline{i}$ in mixture
$[\Xi]$	matrix of correction factors defined by eqn (28)
$[\Phi]$	matrix of dimensionless mass transfer rate factors with elements given by eqns (31), (32)

Operational symbols

Δ	difference operator

Matrix notation

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

Subscripts

b	bulk phase parameter or property
I	interfacial parameter or property
n	pertaining to $\underline{n}$th component
o	overall coefficient
t	pertaining to total mixture
x	pertaining to liquid phase
y	pertaining to vapour phase

Superscripts

$*$	equilibrium with adjoining bulk fluid phase
x	pertaining to liquid phase
y	pertaining to vapour phase
$\bullet$	coefficient corresponding to finite transfer rates

Overlines

$\bar{\ }$	averaged property, as in eqns (46), (47)
$\bar{\ }$	partial molar property, as for $\bar{H}_i$

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