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A NOTE ON THE FILM AND PENETRATION MODELS FOR MULTICOMPONENT MASS TRANSFER

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Abstract—With the aid of the film-penetration model for multicomponent mass transfer, it is shown that the predictions for the limiting cases of the film and penetration theories will differ not only in magnitudes of the transfer rates but also possibly in directions of transfer

INTRODUCTION

Chemical engineering interest in multicomponent mass transport phenomena is relatively recent and most of the theoretical and experimental work has been carried out in the last two decades With the advent of the theory of Irreversible Thermodynamics, correct flux expressions for multicomponent diffusion in non-ideal mixtures have become available The mathematical difficulties associated with the solution of the coupled differential equations describing n-component diffusion were overcome by Toor[1] and Stewart and Prober[2] who independently put forward a linearized theory which essentially requires the assumption that the matrix of diffusion coefficients $[D]$ remains constant along the diffusion path With this assumption the diffusion process is describable by a set of coupled *linear* differential equations which are amenable to solution by use of matrix techniques The matrix procedure has been verified for gaseous ternary diffusion[3] and is widely used for experimental determinations of $[D]$ for liquid mixtures[4]

Many interesting mass transfer characteristics of multicomponent systems have been pointed in the literature[4, 5] For example, recent experimental measurements of ternary point efficiencies during distillation of ethanol—*tert* butanol—water have shown that it is possible to obtain negative efficiencies[6], a practical consequence of coupled diffusion phenomena pointed out by Toor[5] in 1957 This interesting phenomena of transfer of a component against its concentration driving force arises out of coupling between the diffusing species As pointed out by Cussler in his book[4], there are many consequences of n-component diffusion which are yet to be appreciated Apart from being of intrinsic interest, diffusion coupling phenomena has been harnessed for accelerating transfers[7]

In the present communication we focus attention on the film and penetration theories for multicomponent mass transfer These two basic, idealized, mass transfer models, together with their many variants, form the bases for many design correlations used widely in chemical engineering practice The extensions of these models to multicomponent systems are already available in the literature (see for example[1, 2, 8, 9]) The objective in this paper is to compare the predictions of these two basic models and to point out the possibility that the predictions by these two approaches give not only different magnitudes of the transfer rates but also give different directions of transfer

Our analysis is via the film-penetration model of Toor and Marchello[10], suitably generalized to n-component systems

ANALYSIS

For a non-reacting n-component system the equations of continuity for the n diffusing species takes the form

$$\frac{\partial c_i}{\partial t} = -\nabla\ N_i, \qquad i = 1, 2, \quad n \tag{1}$$

where N_i represents the molar flux of species i with respect to a stationary coordinate frame of reference Thus flux can be further expressed as a sum of the diffusive and bulk flow contributions

$$N_i = J_i + c_i u, \qquad i = 1, 2, \quad n \tag{2}$$

in which u represents the net velocity of the diffusing mixture In our development we shall neglect the bulk flow contribution, this neglect can be justified for small transfer rates[11] If we further assume unidirectional transfers, we may write the eqns (1) as

$$\frac{\partial c_i}{\partial t} = -\frac{\partial N_i}{\partial z} = -\frac{\partial J_i}{\partial z}, \qquad i = 1, 2, \quad n-1 \tag{3}$$

where we write only the $n-1$ independent differential equations

Now for n-component diffusion, the generalization of Fick's law gives

$$J_i = -\sum_{k=1}^{n-1} D_{ik} \frac{\mathrm{d}c_k}{\mathrm{d}z}, \qquad i = 1, 2, \quad n-1 \tag{4}$$

Combination of eqns (3) and (4) with the assumption that the elements D_{ik} are independent of composition (and hence of z and t) gives a set of $n-1$ coupled linear differential equations which may conveniently be represented in matrix notation as

$$\frac{\partial (c)}{\partial t} = [D] \frac{\partial^2 (c)}{\partial z^2} \tag{5}$$

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The film-penetration boundary conditions are

$$t = 0, \quad (c) = (c_\delta) \tag{6}$$

$$z = 0, \quad t > 0, \quad (c) = (c_o) \tag{7}$$

$$z = \delta, \quad t > 0, \quad (c) = (c_\delta) \tag{8}$$

where the concentrations at the ends of the diffusion path, (c_o) and (c_δ), are assumed independent of t

Following Toor[1], we find the modal matrix, $[\mathscr{P}]$, of $[D]$ which has the property that

$$[\mathscr{P}]^{-1}[D][\mathscr{P}] \equiv [\hat{D}] \tag{9}$$

where $[\hat{D}]$ represents a diagonal matrix with elements $\hat{D}_1, \hat{D}_2, \quad \hat{D}_{n-1}$ which are the eigenvalues of [D] Premultiplication of eqns (5)–(8) by $[\mathscr{P}]^{-1}$ reduces the set of $\underline{n-1}$ coupled differential equations to an uncoupled set of $\underline{n-1}$ equations each with its own characteristic diffusion coefficient $\hat{D}_i$ Each one of these uncoupled equations is entirely equivalent to the binary system considered by Toor and Marchello[10] The solution to each of the uncoupled equations may therefore be written straightforwardly Thus the average rates of transfer of the pseudo-species, defined by

$$(\hat{N}) = [\mathscr{P}]^{-1}(N) \tag{10}$$

is given for short time convergence by

$$\hat{N}_i = 2\left(\frac{\hat{D}_i}{\pi t'}\right)^{1/2}\left(1 + 2\sqrt{\pi} \sum_{\mathcal{N}=1}^{\infty} i\,\mathrm{erfc}\, \frac{\mathcal{N}\delta}{\sqrt{(\hat{D}_i t')}}\right)\Delta\hat{c}_i \equiv \hat{k}_i \Delta\hat{c}_i, \quad i = 1, 2, \quad n-1 \tag{11}$$

and equivalently in terms of a long time convergent series

$$\hat{N}_i = \frac{\hat{D}_i}{\delta}\left(1 + \frac{2}{\pi^2}\frac{\delta^2}{\hat{D}_i t'}\left(\frac{\pi^2}{6} - \sum_{\mathcal{N}=1}^{\infty} \exp\left(-\mathcal{N}^2\pi^2\frac{\hat{D}_i t'}{\delta^2}\right)\right)\right)\Delta\hat{c}_i$$

$$\equiv \hat{k}_i \Delta\hat{c}_i, \quad i = 1, 2, \quad n-1 \tag{12}$$

In eqns (11) and (12), $\hat{k}_i$, represent the time averaged mass transfer coefficients for the $\underline{n-1}$ pseudo-species, both eqns (11) and (12) of course give the same value for $\hat{k}_i$

The real fluxes N_i may be recovered by the inverse transformation given by eqn (10) giving

$$(N) = [k](\Delta c) \tag{13}$$

where the matrix of mass transfer coefficients $[k]$ is given by

$$[k] = [\mathscr{P}][\hat{k}][\mathscr{P}]^{-1} \tag{14}$$

As an alternative to the evaluation of the mass transfer coefficients by use of eqn (14) we may apply Sylvester's theorem giving

$$[k] = \sum_{i=1}^{n-1} \hat{k}_i \frac{\prod_{\substack{j=1 \\ j \neq i}}^{n-1} \{[D] - \hat{D}_j[I]\}}{\prod_{\substack{j=1 \\ j \neq i}}^{n-1} \{\hat{D}_i - \hat{D}_j\}} \tag{15}$$

where Π represents a product of $\underline{n-2}$ factors Equations (14) and (15) are exactly equivalent

We now consider the consequence of the above analysis in the limiting cases of the film ($t' \to \infty$) and penetration ($t' \to 0$) theories Thus from the film theory we have

$$\hat{k}_i = \hat{D}_i/\delta, \quad i = 1, 2, \quad n-1 \tag{16}$$

and for the penetration theory

$$\hat{k}_i = 2\left(\frac{\hat{D}_i}{\pi t'}\right)^{1/2} \tag{17}$$

Since the penetration theory predicts a square root dependence of the mass transfer coefficients k_{ij} on the molecular diffusion coefficients, it can be concluded that coupling effects arising due to the presence of non-zero cross coefficients D_{ij} ($i \neq j$) will have a smaller influence on the k_{ij} than the predictions of the film theory In order to highlight an interesting difference in the predictions of the two theories we consider a specific numerical example of diffusion in the system acetone (1)–benzene (2)–methanol (3) For this system, a typical non-ideal mixture encountered in the petrochemical industry, sizable cross-coefficients have been measured[12] The elements D_{ij} vary with composition Over the range of compositions, the structure of the matrix $[D]$ is typically

$$[D] = D_{11}\begin{bmatrix} 1\,0 & 0\,2 \\ -0\,15 & 0\,57 \end{bmatrix}, \qquad D_{11} = 3\,72 \times 10^{-9}\ \mathrm{m^2/s} \tag{18}$$

where we have nornalized the elements of $[D]$ with respect to the coefficient D_{11}

Figure 1 compares the predictions of the film, penetration and film-penetration models for the transfer flux of benzene for the case $\Delta c_1/\Delta c_2 = 4$ The film theory predicts a constant invariant flux for benzene, $N_2/(D_{11}\Delta c_2/\delta) = -0\,03$ On the other hand the penetration theory predicts a positive value for this flux decreasing with time but always remaining positive The

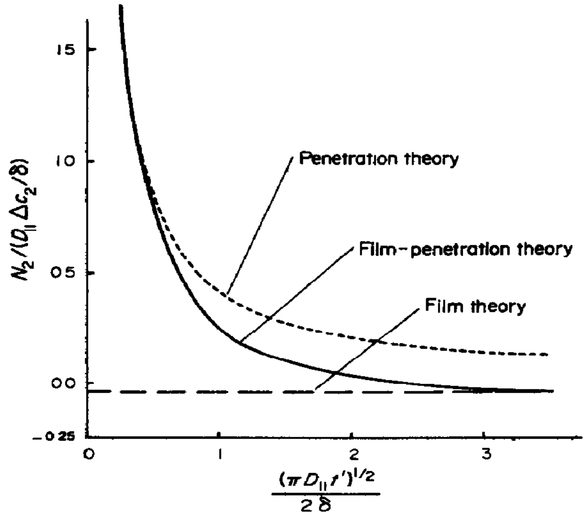

Fig 1 Comparison of film, penetration and film-penetration theories for diffusion in the system acetone–benzene–methanol Figure shows the normalized flux of benzene, $N_2/(D_{11}\Delta c_2/\delta)$, as a function of a characteristic time parameter, $(\pi D_{11}t')^{1/2}/2\delta$, for the case of $\Delta c_1 = 4\Delta c_2$

film-penetration theory predicts a positive flux for short times and negative flux for long exposure times

The reason for the different directions of transfer of benzene anticipated by the film and penetration theories is as follows From the film model, eqns (15) and (16), we obtain the matrix of mass transfer coefficients as

$$\begin{bmatrix} k_{11} & k_{12} \\ k_{21} & k_{22} \end{bmatrix} = \frac{D_{11}}{\delta} \times \begin{bmatrix} 1\ 0 & 0\ 2 \\ -0\ 15 & 0\ 57 \end{bmatrix} \tag{19}$$

Therefore the flux of benzene is given by

$$\begin{aligned} N_2 = k_{21}\Delta c_1 + k_{22}\Delta c_2 &= \frac{D_{11}}{\delta}\{-0\ 15\Delta c_1 + 0\ 57\Delta c_2\} \\ &= \frac{D_{11}\Delta c_2}{\delta} \times (-0\ 03) \end{aligned} \tag{20}$$

which shows that the direction of transfer of benzene is opposite to that dictated by its driving force Δc_2 (reverse diffusion)

On the other hand the penetration model, described by eqns (15) and (17), gives the matrix of mass transfer coefficients as

$$\begin{bmatrix} k_{11} & k_{12} \\ k_{21} & k_{22} \end{bmatrix} = 2\left(\frac{D_{11}}{\pi t'}\right)^{1/2} \begin{bmatrix} 1\ 005 & 0\ 113 \\ -0\ 085 & 0\ 761 \end{bmatrix} \tag{21}$$

Due to the square root dependence of k_{ij} on the D_{ij}, the penetration theory gives a reduced coupling effect, the ratio $k_{21}/k_{22} = -0\ 085/0\ 761$ is lesser than that predicted by the film theory and insufficient to drive the benzene molecule against its concentration driving force Δc_2

The film-penetration theory predicts a smooth transition from the penetration theory prediction for short contact times to the film theory prediction for large contact times, t'

CONCLUDING REMARKS

We have developed a film-penetration model for multicomponent mass transfer in this paper and compared the predictions of the film and penetration theories For a typical non-ideal mixture, acetone–benzene–methanol, we have shown that it is possible to obtain not only different magnitudes of transfer of benzene predicted by the film and penetration theories but also different directions of transfer

The resulting analysis clearly underlines the differences between a simple two-component system characteristics and the characteristics displayed by a non-ideal multicomponent mixture Apart from providing a better insight into the transfer mechanisms of $\underline{n}$-component mixtures, the analysis presented here should provide a means of discriminating between transfer models Thus, by performing mass transfer experiments with non-ideal ternary mixtures in distillation, absorption, extraction and other equipment, a clearer picture of the transfer mechanism in industrial contactors may be obtained

NOTATION

c_i	molar concentration of species $\underline{i}$ in mixture
c	molar concentration of mixture of $\underline{n}$ species
D_{ik}	Fick's law diffusivities for multicomponent mixture
$[D]$	matrix of diffusion coefficients with elements D_{ik}
$\hat{D}_i$	eigenvalues of $[D]$
$[\hat{D}]$	diagonal matrix of eigenvalues $\hat{D}_i$
$[I]$	identity matrix with elements δ_{ik}
J_i	molar diffusion flux of species $\underline{i}$ with respect to molar average reference velocity
k_{ik}	mass transfer coefficients in multicomponent mixture
$[k]$	matrix of multicomponent mass transfer coefficients with elements k_{ij}
$\hat{k}_i$	eigenvalues of $[k]$
$[\hat{k}]$	diagonal matrix of eigenvalues $\hat{k}_i$
n	number of species in multicomponent mixture
N_i	molar flux of $\underline{i}$ with respect to stationary reference frame
$[\mathcal{P}]$	modal matrix of $[D]$ defined by eqn (9)
t	time
t'	contact time
z	distance along diffusion path

Greek symbols

δ	film thickness
δ_{ik}	Kronecker delta

Operational symbols

Δ	difference operator
Σ	summation operator
Π	product operator

Matrix notation

[ ]	square matrix of dimension $\underline{n-1} \times \underline{n-1}$
( )	column matrix of dimension $\underline{n-1}$
⌈ ⌋	diagonal matrix with $\underline{n-1}$ non-zero elements

Subscripts

i, j, k	indices
0	parameter at $z = 0$
δ	parameter at $z = \delta$

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