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EFFECT OF HIGH TRANSFER RATES ON THE DIFFUSION BEHAVIOUR OF MULTICOMPONENT SYSTEMS

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ABSTRACT

The effect of finite transfer rates on the diffusion behaviour of multicomponent systems is examined with the aid of two illustrative examples in steady state ternary gas diffusion. It is shown that the corrections due to finite transfer rates of the individual species on the transfer coefficients, and hence transfer rates, are significant even when the diffusing species are dilute or when equimolar counter diffusion prevails.

Introduction

For molecular diffusion in a fluid mixture with n components the differential equations of continuity in molar units are given by [1]

$$\frac{\partial c_i}{\partial t} + \underset{\sim}{\nabla} \cdot \underset{\sim}{N}_i = R_i, \qquad i = 1,2,..n \qquad (1)$$

where R_i is the rate of production of i due to chemical reaction and $\underset{\sim}{N}_i$ is the molar flux of i with respect to a stationary coordinate frame of reference:

$$\underset{\sim}{N}_i = c_i \underset{\sim}{u}_i, \qquad i = 1,2,..n \qquad (2)$$

The velocity of the diffusing mixture may be defined in various ways [2]; here we choose the molar average velocity defined by

$$c\,\underset{\sim}{u} = \sum_{i=1}^{n} c_i \underset{\sim}{u}_i; \quad \underset{\sim}{u} = \sum_{i=1}^{n} y_i \underset{\sim}{u}_i \qquad (3)$$

The total mixture flux is obtained by summing equations (2) over the n constituent species and we obtain in view of equation (3):

$$\underset{\sim}{N}_t = \sum_{i=1}^{n} \underset{\sim}{N}_i = c \, \underset{\sim}{u} \tag{4}$$

The molar diffusion flux of species i relative to the molar average velocity of the mixture is

$$\underset{\sim}{J}_i = c_i(\underset{\sim}{u}_i - \underset{\sim}{u}) = \underset{\sim}{N}_i - y_i \underset{\sim}{N}_t, \qquad i = 1,2,..n \tag{5}$$

but in view of equations (2) to (4) only n-1 of the J_i are independent for

$$\sum_{i=1}^{n} \underset{\sim}{J}_i = 0 \tag{6}$$

With the molar diffusion fluxes $\underset{\sim}{J}_i$ as defined in (5), the continuity equations (1) may be written as

$$\frac{\partial c_i}{\partial t} + \underset{\sim}{\nabla} \cdot c_i \underset{\sim}{u} + \underset{\sim}{\nabla} \cdot \underset{\sim}{J}_i = R_i, \qquad i = 1,2,..n \tag{7}$$

In the solution of many diffusion problems, with or without chemical reaction, it is customary in the literature to neglect the term involving $\underset{\sim}{u}$, the 'convective' term, in equations (7). This neglect is justified for cases in which we have equimolar counter diffusion or when a single species diffuses through a large excess of 'solvent'. For diffusion in systems of three or more species - multicomponent systems - the neglect of the convective term is open to question and is the subject for examination in this paper.

We take as an example steady state diffusion in n - component ideal gas mixtures in the absence of chemical reaction and study the diffusion behaviour under conditions of finite transfer rates leading to non-vanishing mixture flux $\underset{\sim}{N}_t$.

Analysis

For isothermal, isobaric diffusion in ideal gas mixtures the convenient constitutive relations to use are the Maxwell-Stefan equations, which for uni-(z)-directional transport are given by

$$\frac{dy_i}{dz} = \sum_{\substack{k=1 \\ k\neq i}}^{n} \frac{y_i N_k - y_k N_i}{c \, \mathcal{D}_{ik}} = \sum_{\substack{k=1 \\ k\neq i}}^{n} \frac{y_i J_k - y_k J_i}{c \, \mathcal{D}_{ik}}, \qquad i = 1,2,..n-1 \tag{8}$$

where only the n-1 independent equations are considered. The molar fluxes N_i are independent of z for steady state conditions (see equations (1)) whereas the diffusion fluxes J_i vary along the diffusion path. We assume here that the compositions at either end of the diffusion path, of length δ, are known:

$$\begin{array}{l} \text{at} \quad z = 0, \quad y_i = y_{io}, \\ \text{at} \quad z = \delta, \quad y_i = y_{i\delta}, \end{array} \qquad i = 1,2,\ldots n \tag{9}$$

The n-1 independent composition differences

$$\Delta y_i \equiv y_{io} - y_{i\delta}, \qquad i = 1,2,..n-1 \tag{10}$$

may be viewed as the driving forces for diffusion.

The n-1 linear differential equations (8) may be solved using matrix analysis to give the diffusion fluxes at $z = 0$ as [3,4]

$$(J_o) = [k_o][\Phi]\{\exp[\Phi] - \lceil I \rfloor\}^{-1}(\Delta y) \tag{11}$$

where all the matrices are of dimension n-1 and the matrices $[k_o]$ and $[\Phi]$ are defined in Table 1. The calculation of the molar fluxes N_i from the n-1 diffusion fluxes J_{io} requires an additional determinancy condition. If conditions of equimolar counter diffusion:

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

are specified then

$$N_i = J_{io}, \qquad i = 1,2,\ldots n \tag{13}$$

On the other hand if we have diffusion of n-1 species through an inert or stagnant nth component:

$$N_n = 0 \tag{14}$$

then the fluxes N_i may be calculated from

$$N_i = \sum_{k=1}^{n} (\delta_{ik} + y_{io}/y_{no})\, J_{ko}, \qquad i = 1,2,..n-1 \tag{15}$$

The total fluxes N_i may therefore be written generally as

$$(N) = [\beta][k_o][\Phi]\{\exp[\Phi] - \lceil I \rfloor\}^{-1}(\Delta y) \tag{16}$$

where the elements of $[\beta]$ are given for equimolar counter diffusion by

$$\beta_{ik} = \delta_{ik}, \qquad i,k = 1,2,..n-1 \tag{17}$$

and for the stagnant nth component case, equations (14) and (15):

$$\beta_{ik} = \delta_{ik} + y_{io}/y_{no}, \qquad i,k = 1,2,..n-1 \tag{18}$$

The matrix

$$[\Xi] \equiv [\Phi]\{\exp[\Phi] - \lceil I \rfloor\}^{-1} \tag{19}$$

gives the effect of finite rates of mass transfer on the coefficients $[k_o]$

TABLE 1

Definitions of Parameters

Zero flux mass transfer coefficients of the binary pairs in mixture:

$$\mathcal{k}_{ik} = c\,\mathcal{D}_{ik}/\delta$$

Matrix of dimensionless mass transfer rate factors, $[\Phi]$, with elements

$$\Phi_{ii} = \frac{N_i}{\mathcal{k}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{N_k}{\mathcal{k}_{ik}}, \qquad i = 1,2,..n-1$$

$$\Phi_{ij} = -N_i\left(\frac{1}{\mathcal{k}_{ij}} - \frac{1}{\mathcal{k}_{in}}\right), \qquad i,j = 1,2,..n-1$$

Matrix of inverted mass transfer coefficients, $[B_o]$, with elements

$$B_{oii} = \frac{y_{io}}{\mathcal{k}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{y_{ko}}{\mathcal{k}_{ik}}, \qquad i = 1,2,..n-1$$

$$B_{oij} = -y_{io}\left(\frac{1}{\mathcal{k}_{ij}} - \frac{1}{\mathcal{k}_{in}}\right), \qquad i,j = 1,2,..n-1$$

Matrix of zero flux multicomponent mass transfer coefficients, $[k_o]$, with elements given by the inverse of the matrix $[B_o]$,

$$[k_o] = [B_o]^{-1}$$

Explicitly for a binary system:

$$B_o = 1/\mathcal{k}_{12} \; ; \quad k_o = \mathcal{k}_{12}$$

For a ternary system the four elements of $[k_o]$ are given explicitly as

$$k_{o11} = \mathcal{k}_{13}(y_{1o}\mathcal{k}_{23} + (1 - y_{1o})\mathcal{k}_{12})/S$$

$$k_{o12} = y_{1o}\mathcal{k}_{23}(\mathcal{k}_{13} - \mathcal{k}_{12})/S$$

$$k_{o21} = y_{2o}\mathcal{k}_{13}(\mathcal{k}_{23} - \mathcal{k}_{12})/S$$

$$k_{o22} = \mathcal{k}_{23}(y_{2o}\mathcal{k}_{13} + (1 - y_{2o})\mathcal{k}_{12})/S$$

where

$$S = y_{1o}\mathcal{k}_{23} + y_{2o}\mathcal{k}_{13} + y_{3o}\mathcal{k}_{12}$$

and hence on the diffusion behaviour of the system. When all the transfer rates N_i are vanishingly small, it may be verified that the matrix $[\Xi]$ reduces to the identity matrix; there are no corrections to the transfer facility for this case. The effect of finite transfer rates is to alter the composition profiles themselves and hence the facilities for transfer offered by the system. Bird, Stewart and Lightfoot [1] give an excellent discussion on the effect of finite transfer rates in two-component mixtures.

Thus for equimolar counter diffusion in a binary system we have

$$\Phi = 0; \quad \Xi = 1 \tag{20}$$

and so

$$N_1 = k_{12}\,\Delta y_1 \tag{21}$$

For transfer of species 1 through stagnant 2:

$$N_1 = \frac{k_{12}}{1 - y_{1o}} \frac{\Phi}{\exp\Phi - 1} \Delta y_1 \; ; \quad \Phi = N_1/k_{12} \tag{22}$$

For magnitudes of Φ less than 0.2 the correction $\Phi/(\exp\Phi - 1)$ is about 0.9 and therefore for dilute species transfer

$$N_1 = k_{12}\,\Delta y_1 \tag{23}$$

is a good approximation; neglect of the convective term is often justified in many engineering applications involving binary systems.

We now turn our attention to a ternary system and to start with consider diffusion of two species through a stagnant third component. The numerical values are summarized in Table 2. To study the effect of finite transfer rates on the system, the fluxes given by equation (16) are obtained by two different methods:

(i) we assume that since the diffusing species are dilute (maximum composition $y_1 + y_2$ at any position is 0.3), we may approximate the correction factor matrix $[\Xi]$ by the identity matrix, i.e. we take the finite flux matrix

$$[k_o^\bullet] = [k_o] \tag{24}$$

(ii) in this calculation the fluxes are evaluated exactly with the correction factor matrix evaluated from equation (19) using Sylvester's theorem; explicit expressions for $[\Xi]$ are available in [3]. The finite flux coefficients $[k_o^\bullet]$ are calculated from

$$[k_o^\bullet] = [k_o][\Xi] \tag{25}$$

TABLE 2

Illustrative Example:
Diffusion of Acetone (1) and Benzene (2) through Stagnant Helium (3)

<u>Boundary Conditions</u>: $z = 0,\ y_{1o} = 0.10;\ y_{2o} = 0.00$

$z = \delta,\ y_{1\delta} = 0.06;\ y_{2\delta} = 0.24$

<u>Diffusion Coffficients of binary pairs in the ternary mixture</u>:

$$\mathcal{D}_{12} = 4\ \mathrm{mm}^2/\mathrm{s};\quad \mathcal{D}_{13} = 41\ \mathrm{mm}^2/\mathrm{s};\quad \mathcal{D}_{23} = 39\ \mathrm{mm}^2/\mathrm{s}$$

<u>Results of the calculation of</u> $[k^\bullet_o]$ <u>and</u> N_1, N_2 $(N_3 = 0)$ <u>using the equation</u>:

$$(N) = [\beta]\,[k^\bullet_o]\,(\Delta y)$$

	$\frac{N_1}{c/\delta}$ mm^2/s	$\frac{N_2}{c/\delta}$ mm^2/s	$\frac{k^\bullet_{o11}}{c/\delta}$ mm^2/s	$\frac{k^\bullet_{o12}}{c/\delta}$ mm^2/s	$\frac{k^\bullet_{o21}}{c/\delta}$ mm^2/s	$\frac{k^\bullet_{o22}}{c/\delta}$ mm^2/s
$[\Xi] = \ulcorner I \lrcorner$ neglect effect of finite transfer rates	-3.86	-4.99	41.00	19.24	0.00	20.80
$[\Xi]$ calculated from equation (19)	-1.77	-8.12	74.40	15.65	-26.79	29.36

TABLE 3

Equimolar Counter Diffusion in the System: $CO_2(1)$-$H_2O(2)$-$H_2(3)$

<u>Boundary conditions</u>: $y_{1o} = 0.5;\ y_{2o} = 0.0;\ y_{1\delta} = 0.2;\ y_{2\delta} = 0.8$

<u>Diffusivities</u>: $\mathcal{D}_{12} = 0.922\ \mathrm{cm}^2/\mathrm{s};\ \mathcal{D}_{13} = 2.7064\ \mathrm{cm}^2/\mathrm{s};\ \mathcal{D}_{23} = 3.4576\ \mathrm{cm}^2/\mathrm{s}$

<u>Fluxes</u> N_1, N_2 calculated from $(N) = [k^\bullet_o](\Delta y);\quad N_3 = -N_1 - N_2$

	$\frac{N_1}{c/\delta}$ cm^2/s	$\frac{N_2}{c/\delta}$ cm^2/s	$\frac{k^\bullet_{o11}}{c/\delta}$ cm^2/s	$\frac{k^\bullet_{o12}}{c/\delta}$ cm^2/s	$\frac{k^\bullet_{o21}}{c/\delta}$ cm^2/s	$\frac{k^\bullet_{o22}}{c/\delta}$ cm^2/s
$[\Xi] = \ulcorner I \lrcorner$	-0.027	-1.57	3.265	1.258	-0.793	1.671
$[\Xi]$ from eqn. (19)	-0.069	-1.51	3.438	1.375	-1.040	1.503

Since the fluxes N_i are not known in advance of calculating the transfer coefficients $[\mathrm{k}_o^\bullet]$, it is clear a trial and error procedure is involved in the second procedure involving (25). Iterations may be started by assuming that equation (24) holds and then repeated resubstitution assures convergence on the N_i.

The results of the calculations of the fluxes N_i in Table 2 using the two procedures above show that neglect of the effect of finite transfer rates leads to extremely large % errors even though the system is very dilute in species 1 and 2. Moreover, the approximation

$$N_1 \simeq k_{13}\Delta y_1 = 1.64\,\frac{c}{\delta} \tag{26}$$

gives the wrong direction of transfer. In actual fact the direction of transfer of species 1 is opposite to that dictated by its constituent driving force Δy_1, i.e.

$$N_1\,\Delta y_1 = (-1.77)(0.1) < 0 \tag{27}$$

Equation (27) signifies the phenomenon of reverse diffusion and Toor [5] has discussed this and other diffusional interaction phenomena possible in ternary systems, which are typical of multicomponent behaviour.

The diffusional interaction effects are quantified by the presence of the cross coefficients k_{o12} and k_{o21} in the matrix of mass transfer coefficients. When these cross coefficients are large the interaction effects will be large. The magnitudes of the cross coefficients increase with increasing differences in the values of the diffusion coefficients of the binary pairs $\mathcal{D}_{ik}$. When all the binary pairs have equal facilities for transfer:

$$\mathcal{D}_{ik} = \mathcal{D}\ ;\ k_{ik} = c\,\mathcal{D}_{ik}/\delta = c\,\mathcal{D}/\delta = k \qquad |\text{special}| \tag{28}$$

the matrix $[\mathrm{k}_o]$ reduces to

$$[\mathrm{k}_o] = k \ulcorner I \lrcorner \qquad |\text{special}| \tag{29}$$

and the matrix of correction factors degenerates to

$$[\Xi] = \frac{\Phi}{\exp\Phi - 1} \ulcorner I \lrcorner \quad \text{where} \quad \Phi = \frac{N_t}{k} \tag{30}$$

and the system will have all the characteristics of simple two-component systems. All the classical approximations used for binary systems may be used for the general multicomponent case when (28) holds.

It is interesting to note that when the constituent binary diffusivities are unequal the matrix of correction factors $[\Xi]$ does not reduce to the identity matrix when conditions of equimolar counter diffusion exist. This result is in contrast to that obtained for a two-component system (equation (20)). One might therefore expect that finite flux corrections would be important for systems with widely differing transfer facilities for the constituent binary pairs. The calculations in Table 3 for diffusion in the system $CO_2 - H_2O - H_2$ show that this expectation is fulfilled and the assumption (24) leads to a large error in the calculation of the flux of species 1, which again suffers reverse diffusion.

The general conclusion to be drawn from the above study is that when the species making up the multicomponent mixture are of different size and nature, diffusional interaction effects can be important and when this is so the finite flux corrections on the transfer coefficients and transfer rates cannot be ignored. The neglect of the convective term in equations (7) is not generally justified for a multicomponent system even when such an omission is reasonable for a binary system under the same circumstance.

Nomenclature

$[\mathcal{B}_o]$	matrix of inverted mass transfer coefficients
c	total molar density of fluid mixture
$\mathcal{D}_{ik}$	diffusion coefficient of the binary pair i-k in mixture
$[I]$	identity matrix with elements δ_{ik}
$\underset{\sim}{J}_i$	molar diffusion flux of _i_ relative to molar average velocity
$\mathcal{k}_{ik}$	mass transfer coefficient of pair i-k in mixture
$[k_o]$	matrix of zero flux mass transfer coefficients
$[k_o^\bullet]$	matrix of finite flux mass transfer coefficients
n	number of species in multicomponent mixture
$\underset{\sim}{N}_i$	molar flux of _i_ in stationary coordinate reference frame
$\underset{\sim}{N}_t$	total mixture molar flux in stationary coordinate reference frame
S	summation parameter
t	time
$\underset{\sim}{u}_i$	velocity of species _i_ in diffusing mixture
$\underset{\sim}{u}$	molar average velocity of mixture
y_i	mole fraction of species _i_ in mixture
z	distance coordinate along diffusion path

Greek Letters

$[\beta]$	matrix with elements given by equation (17) or (18)
δ	length of diffusion path
δ_{ik}	Kronecker delta
$[\Xi]$	matrix of correction factors
$[\Phi]$	matrix of dimensionless mass transfer rate factors

Matrix Notation

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

Subscripts

o	parameter or coefficient calculated at $z = 0$
δ	parameter or coefficient calculated at $z = \delta$

Superscripts

$\bullet$	coefficient corresponding to finite transfer rates

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