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MASS TRANSPORT FROM A SPHERICAL BODY INTO A MULTICOMPONENT FLUID STREAM

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ABSTRACT

This paper analyses mass transfer from a spherical body, either liquid or porous solid, to an n-component fluid stream in uniform flow around the body. The steady-state mass transport rates are calculated from the Maxwell-Stefan diffusion equations (for non-ideal liquid mixtures, in their generalized form) using a matrix method of solution. Proper account is taken of the diffusional interactions between species transfers. The corresponding thermal transport phenomena is also considered in the analysis, which should find application in droplet evaporation, drying, catalytic reactions etc.

Introduction

Mass transfer from (or to) spherical bodies, either liquid or porous solid, is important in many engineering contexts: evaporation of liquid drops into gaseous streams, sublimation, drying, dissolution of solid particles, catalytic reactors etc (for surveys of published literature, see [1 - 4]).

The analyses of the diffusion process when only two components are involved start with the Fick's law formulation

$$J_{1r} = - c \, \mathcal{D}_{12} \frac{dy_1}{dr} \tag{1}$$

For multicomponent ($n \geq 3$) systems, Newbold and Amundson [3], in their analysis of droplet evaporation, adopt simple non-interacting formulations for the diffusion fluxes of the transferring species:

$$J_{ir} = - c \, \mathcal{D}_{i,eff} \frac{dy_i}{dr}, \qquad i = 1,2,\ldots n \tag{2}$$

It has been recognized in recent years that the description of the transport phenomena in multicomponent systems must take account of interactions between species transfers [5]. Such interactions may lead to phenomena such as osmotic diffusion (transfer of a component in the absence of a composition driving force for that species), diffusion barrier (no transfer of a component even though a driving force exists for its transfer) and reverse diffusion (diffusion of a species against its composition gradient). Clearly the formulation (2) will fail to describe such interaction phenomena unless we allow the effective diffusion coefficient $\mathcal{D}_{i,eff}$ to assume zero or negative values.

The correct description of n-component mass transport processes is by use of a matrix of diffusion coefficients of dimension $n-1 \times n-1$ [6,7,8]. Thus the constitutive relations for the molar diffusion fluxes take the form

$$J_{ir} = -c \sum_{k=1}^{n-1} D_{ik} \frac{dy_k}{dr}, \qquad i = 1,2,\ldots n-1 \tag{3}$$

Only n-1 composition gradients are considered for the composition gradient of the nth species is not independent and is given by

$$\frac{dy_n}{dr} = -\sum_{k=1}^{n-1} \frac{dy_k}{dr} \tag{4}$$

Also, the nth molar diffusion flux is determined from the requirement that the n diffusion fluxes sum to zero:

$$\sum_{k=1}^{n} J_{ir} = 0 \tag{5}$$

It is our object here to consider mass transfer from a spherical body to a multicomponent fluid stream, in uniform flow around the body, using the mass transfer formulation (3). We restrict ourselves to isobaric processes under steady-state conditions. The transfer process is considered to be uni-(r)-directional. First, the gaseous stream analysis is carried out; modification to include non-ideal liquid mixtures is considered towards the end of the paper. The method of analysis and solution is similar to the 'planar' treatment of Krishna and Standart [9].

Mathematical Analysis

Consider a spherical body immersed in a gaseous flowing stream. Let r_o represent the radius of the sphere, either liquid or porous solid. The gas composition at the surface of the sphere is y_{io} which is assumed to be constant during the transfer process. In real situations the surface composition is determined by the thermodynamic equilibrium condition at the fluid-body interface. The interface condition is therefore

$$\text{at } r = r_o, \quad y_i = y_{io}, \qquad i = 1,2,\ldots n \tag{6}$$

The bulk gas phase composition is taken as $y_{i\infty}$ and the transition from the interface compositions (y_o) to the bulk compositions (y_∞) is assumed to take place over the radial distance r_o to r_∞(> r_o). The mass transport is assumed to take place by molecular diffusion over the thickness $r_\infty - r_o$; thus we use a 'spherical film' model for mass transfer. The second boundary condition is therefore expressed as

$$\text{at } r = r_\infty, \quad y_i = y_{i\infty}, \qquad i = 1,2,\ldots n \tag{7}$$

Over the diffusion path, r_o to r_∞, the equations of continuity for the n species reduce to

$$\frac{d}{dr}(r^2 N_{ir}) = 0, \qquad i = 1,2,\ldots n \tag{8}$$

which shows that

$$r^2 N_{ir} = r_o^2 N_{io} = r_\infty^2 N_{i\infty}, \qquad i = 1,2,\ldots n \tag{9}$$

The fluxes N_{ir} refer to a stationary coordinate reference frame and are related to the diffusion fluxes J_{ir} by

$$N_{ir} = J_{ir} + y_i N_{tr}, \qquad i = 1,2,\ldots n \tag{10}$$

where N_{tr} is the mixture total flux

$$N_{tr} = \sum_{k=1}^{n} N_{ir} \tag{11}$$

A convenient representation of the constitutive relations for n-component isobaric-isothermal diffusion is the Maxwell-Stefan formulation

$$\frac{dy_i}{dr} = \sum_{\substack{k=1\\k\neq i}}^{n} \frac{y_i N_{kr} - y_k N_{ir}}{c\,\mathcal{D}_{ik}} = \sum_{k=1}^{n} \frac{y_i J_{kr} - y_k J_{ir}}{c\,\mathcal{D}_{ik}}, \qquad i = 1,2,\ldots n-1 \tag{12}$$

If suitably averaged values for the total molar concentration c and the diffusion coefficients $\mathcal{D}_{ik}$ are used, the relations (12) will be applicable to non-isothermal transport processes as well.

In proceeding with the analysis, it is convenient to define the following parameters (see [9]):

(i) dimensionless distance coordinate in the spherical film,

$$\eta = 1 - r_o/r \tag{13}$$

(ii) 'zero flux' mass transfer coefficients for the constituent binary pairs in the mixture,

$$\mathcal{k}_{ik} = c\,\mathcal{D}_{ik}/r_o, \qquad i,k = 1,2,\ldots n \quad i \neq k \tag{14}$$

(iii) a matrix of dimensionless 'rate factors' with elements given by

$$\Phi_{ii} = \frac{N_{io}}{\mathcal{k}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{N_{ko}}{\mathcal{k}_{ik}}, \qquad i = 1,2,\ldots n-1 \tag{15}$$

$$\Phi_{ij} = -N_{io}(1/\mathcal{k}_{ij} - 1/\mathcal{k}_{in}), \qquad i,j = 1,2,\ldots n-1 \quad i\neq j \tag{16}$$

(iv) a column matrix (ζ) with elements

$$\zeta_i = -N_{io}/\mathcal{k}_{in}, \qquad i = 1,2,\ldots n-1 \tag{17}$$

(v) a matrix of inverted diffusion coefficients, $[A_o]$, with elements given by

$$A_{oii} = \frac{y_{io}}{\mathcal{D}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{y_{ko}}{\mathcal{D}_{ik}}, \qquad i = 1,2,\ldots n-1 \tag{18}$$

$$A_{oij} = -y_{io}(1/\mathcal{D}_{ij} - 1/\mathcal{D}_{in}), \qquad i,j = 1,2,\ldots n-1 \quad i\neq j \tag{19}$$

With the above definitions, equations (12) may be written in compact <u>n-1</u> dimensional matrix notation as

$$\frac{d(y)}{d\eta} = [\Phi](y) + (\zeta) \tag{20}$$

with boundary conditions

$$\begin{aligned} &\text{at } \eta = 0, && (y) = (y_o) \\ &\text{at } \eta = 1 - r_o/r_\infty \equiv 1-\kappa, && (y) = (y_\infty) \end{aligned} \tag{21}$$

Equations (20) may be solved for the conditions (21) to give the composition profiles within the film as [9]

$$(y - y_o) = \{\exp[\Phi]\eta - {}^{\ulcorner}I_{\lrcorner}\}\{\exp\{[\Phi](1-\kappa)\} - {}^{\ulcorner}I_{\lrcorner}\}^{-1}(y_\infty - y_o) \tag{22}$$

which may be differentiated to give the composition gradient at the interface,

$$\left.\frac{d(y)}{d\eta}\right|_{\eta=0} = [\Phi]\{\exp\{[\Phi](1-\kappa)\} - {}^{\ulcorner}I_{\lrcorner}\}^{-1}(y_\infty - y_o) \tag{23}$$

The composition gradient at the interface may also be obtained from equations (12), (18) and (19) as

$$\left.\frac{d(y)}{d\eta}\right|_{\eta=0} = -\frac{r_o}{c}[A_o]\,(J_o) \tag{24}$$

Equation (24) may be rewritten as

$$(J_o) = -\frac{c\,[A_o]^{-1}}{r_o}\left.\frac{d(y)}{d\eta}\right|_{\eta=0} = -\frac{c\,[D_o]}{r_o}\left.\frac{d(y)}{d\eta}\right|_{\eta=0} \tag{25}$$

Comparison of equation (25) with equations (3) shows that the Maxwell-Stefan formulation is consistent with the generalized Fick's law formulation. Further, the Maxwell-Stefan formulation also gives a means for estimating the matrix of multicomponent diffusion coefficients from binary diffusivities,

$$[D_o] \equiv [A_o]^{-1} \tag{26}$$

Combining equation (23) and (25) we get the final expression for the diffusion fluxes at the interface as

$$(J_o) = \frac{c\,[D_o]}{r_o}[\Phi]\{\exp\{[\Phi](1-\kappa)\} - [I]\}^{-1}(y_o - y_\infty) \tag{27}$$

It is convenient to define a matrix of 'finite flux' mass transfer coefficients, $[k_y^\bullet]$, by the matrix relation

$$(J_o) = [k_y^\bullet](y_o - y_\infty) \tag{28}$$

which gives in view of equation (27),

$$[k_y^\bullet] = \frac{c\,[D_o]}{r_o}[\Phi]\{\exp\{[\Phi](1-\kappa)\} - [I]\}^{-1} \tag{29}$$

The matrix factor

$$[\Xi] \equiv [\Phi]\{\exp\{[\Phi](1-\kappa)\} - [I]\}^{-1} \tag{30}$$

reduces to the identity matrix for vanishing rates of transfer, i.e.

$$\lim_{\substack{N_{io}\to 0,\\ i=1,2,..n}} [\Xi] = [I] \tag{31}$$

and when this happens, the matrix of mass transfer coefficients reduces to

$$\lim_{\substack{N_{io}\to 0,\\ i=1,2,..n}} [k_y^\bullet] = \frac{c\,[D_o]}{r_o} \equiv [k_y] \tag{32}$$

and therefore the matrix $[k_y]$ may be termed as the matrix of 'zero flux' mass transfer coefficients. The factor $[\Xi]$ corrects this 'zero flux' matrix of coefficients for conditions of finite transfer rates.

As an extension of binary transport concepts a matrix of Sherwood numbers may be defined as

$$[Sh] \equiv \frac{[k_y^\bullet]\ d\ [D_o]^{-1}}{c} \tag{33}$$

where d is the diameter of the spherical body. Equations (29), (30) and (33) give the matrix of Sherwood numbers as

$$[Sh] = 2\ [\Xi] \tag{34}$$

which reduces to twice the identity matrix for vanishing rates of transfer, N_i (cf. equation (31)). For two-component systems, equation (34) simplifies to

$$Sh = 2\ \frac{\Phi}{e^{\Phi(1-\kappa)} - 1} \quad \text{with} \quad \Phi = \frac{N_1 + N_2}{k_{12}} \tag{35}$$

which for vanishing rates of transfer further simplifies to give the classical result

$$Sh = 2 \tag{36}$$

Equation (27) determines the diffusion fluxes J_{io}; the determination of the total fluxes N_{io} requires a further determinancy condition. If conditions of equimolar transfer prevail then we have

$$N_{to} = 0 \tag{37}$$

and therefore (cf. equations (10))

$$N_{io} = J_{io}, \qquad i = 1,2,\ldots n-1 \tag{38}$$

with the nth total flux determined from

$$N_{no} = N_{to} - \sum_{k=1}^{n-1} N_{io} \tag{39}$$

For transfer of n-1 species through a stagnant nth component we have

$$N_{no} = J_{no} + y_{no}\, N_{to} = 0 \tag{40}$$

and the total fluxes are related to the diffusion fluxes by

$$N_{io} = \sum_{k=1}^{n-1} (\delta_{ik} + y_{io}/y_{no})\ J_{ko}, \qquad i = 1,2,\ldots n-1 \tag{41}$$

The calculation of the total fluxes N_{io} from knowledge of the diffusivities of the constituent binary pairs and the composition driving forces by use of equations (27) with (38) or (41) requires a trial and error procedure [9]. A convenient calculation method is to start the iterations by assuming the matrix of correction factors $[\Xi]$ is the identity matrix. This matrix can be revaluated once an estimate of N_{io} is available. Repeated re-substitution may be used to converge on the final values for the total fluxes.

For non-ideal liquid mixtures, the generalized Maxwell-Stefan equations

$$\frac{1}{R\,T}\frac{d\mu_i}{dr} = \sum_{\substack{k=1\\k\neq i}}^{n} \frac{x_i N_{kr} - x_k N_{ir}}{c\,Ð_{ik}}, \qquad i = 1,2,\ldots n-1 \qquad (42)$$

afford a convenient starting point for the analysis. By defining the parameters as below:

$$\Gamma_{ij} = \delta_{ij} + \frac{x_i}{x_j}\frac{\partial \ln\gamma_i}{\partial \ln x_j}, \qquad i,j = 1,2,\ldots n-1 \qquad (43)$$

Krishna [10] has shown that the equations (42) may be written in n-1 dimensional matrix notation as

$$[\Gamma]\frac{d(x)}{d\eta} = [\Phi](x) + (\zeta) \qquad (44)$$

where the remainder of the parameters are as defined by equations (13) - (17), taking the generalized Maxwell-Stefan diffusivities $Ð_{ik}$ in place of the binary gas pair diffusivities $\mathcal{D}_{ik}$.

If we assume that the elements of $[\Gamma]$ and $[\Phi]$ are independent of composition, we may use the solution procedure as outlined in this paper, taking

$$[\Theta] \equiv [\Gamma]^{-1}[\Phi] \qquad (45)$$

in place of the matrix $[\Phi]$ in equation (27).

Thermal Transport Phenomena

A differential energy balance in the film provides the appropriate starting point for the discussions on the accompanying thermal transport phenomena. Thus for r-directional transfer from the spherical body into the multicomponent fluid stream we have

$$\frac{d}{dr}(r^2 E_r) = 0 \qquad (46)$$

where E_r, the total energy flux is given by

$$E_r = q_r + \sum_{k=1}^{n} \bar{H}_{ir} N_{ir} \qquad (47)$$

q_r represents the conductive heat flux in the fluid mixture and is given by Fourier's law as

$$q_r = -k_T \frac{dT}{dr} \qquad (48)$$

where k_T is the thermal conductivity of the fluid mixture. If we define the following parameters:

(i) 'zero flux' heat transfer coefficient in the fluid phase,

$$h = k_T/r_o \tag{49}$$

(ii) dimensionless heat transfer rate factor,

$$\varepsilon = \sum_{k=1}^{n} C_{pi} N_{io}/h \tag{49'}$$

we may solve equations (46) - (48) for the boundary conditions:

$$\begin{aligned} &\text{at } \eta = 0, && T = T_o \\ &\text{at } \eta = 1 - \kappa, && T = T_\infty \end{aligned} \tag{50}$$

to give the conductive heat flux at the interface as

$$q_o = h \frac{\varepsilon}{e^{\varepsilon(1-\kappa)} - 1}(T_o - T_\infty) = h^\bullet (T_o - T_\infty) \tag{51}$$

The total energy flux E_o is determined from equation (47), with the total molar fluxes N_{io} given by the mass transfer analysis.

The Nusselt number, defined by

$$Nu \equiv \frac{h^\bullet d}{k_T}, \tag{52}$$

is therefore given as (cf. equation (51))

$$Nu = 2 \frac{\varepsilon}{e^{\varepsilon(1-\kappa)} - 1} \tag{53}$$

which for vanishing transfer rates ($N_i \to 0$) gives another classical result

$$Nu = 2 \tag{54}$$

Concluding Remarks

We have presented a general analysis of mass and thermal transport processes between a spherical body and a surrounding fluid stream. The analysis, which is based on a film model, allows calculation of the mass and thermal transport rates from information on the transport parameters of the constituent binary pairs. The results have been presented in convenient matrix notation and are seen to be exact matrix analogues of classical binary relations. This single body analysis is easily extendable to include a bed of particles or swarm of droplets of liquid.

Nomenclature

$[A_o]$	matrix whose elements are defined by equations (18) and (19)
c	total molar concentration of fluid mixture
d	diameter of spherical body
$\mathcal{D}_{ik}$	diffusivity of binary i-k in gaseous mixture
$Đ_{ik}$	generalized Maxwell-Stefan diffusivity of pair i-k
D_{ik}	generalized Fick's law diffusivities
$[D]$	matrix of generalized Fick's law diffusion coefficients
E	total energy flux
h	heat transfer coefficient in fluid mixture
$\bar{H}_i$	partial molar enthalpy of species i in fluid mixture
$[I]$	Identity matrix with elements δ_{ik}
J_i	molar diffusion flux of species i
k_{ik}	zero-flux mass transfer coefficient for pair i-j in multicomponent mixture
k_T	thermal conductivity of fluid mixture
$[k_y]$	matrix of zero flux mass transfer coefficients
$[k_y^\bullet]$	matrix of finite flux mass transfer coefficients
n	number of species in multicomponent fluid mixture
N_i	total molar flux of species i
N_t	total mixture molar flux
q	conductive heat flux
r	radial distance parameter
r_o	radius of spherical body
r_∞	radial distance at which the fluid phase attains its bulk phase composition
T	temperature
x_i	mole fraction of species i in liquid mixture
y_i	mole fraction of species i in gaseous mixture

Greek Letters

γ_i	activity of species i in solution
$[\Gamma]$	matrix of thermodynamic factors defined by equations (43)
δ_{ik}	Kronecker delta
ε	heat transfer rate factor defined by (49')

Greek Letters (cont'd)

η dimensionless distance along film

κ ratio of radii r_o/r_∞

μ_i molar chemical potential of species $\underline{i}$

$[\Xi]$ matrix of correction factors

$[\Phi]$ matrix of dimensionless mass transfer rate factors

Matrix Notation

( ) $\underline{n-1}$ dimensional column matrix

[ ] $\underline{n-1}\times\underline{n-1}$ dimensional square matrix

$[\ ]^{-1}$ $\underline{n-1}\times\underline{n-1}$ dimensional inverted matrix

⌜ ⌟ diagonal matrix with $\underline{n-1}$ elements

Subscripts

i,j,k indices

n species $\underline{n}$

o property or parameter at interface between body and fluid

r at any radial distance r from centre of spherical body

∞ property or parameter in the bulk fluid phase

Superscript

$\bullet$ coefficient corresponding to finite transfer rates

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