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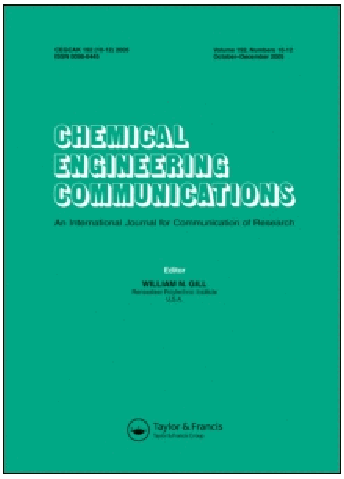

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THE MAXWELL-STEFAN FORMULATION OF IRREVERSIBLE THERMODYNAMICS FOR SIMULTANEOUS HEAT AND MASS TRANSFER

G. L. Standart [a]; R. Taylor [a]; R. Krishna [a]
[a] Department of Chemical Engineering, Separation Processes Laboratory, University of Manchester, Institute of Science and Technology, Manchester, Great Britain

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THE MAXWELL-STEFAN FORMULATION OF IRREVERSIBLE THERMODYNAMICS FOR SIMULTANEOUS HEAT AND MASS TRANSFER

G. L. STANDART†, R. TAYLOR and R. KRISHNA*

Separation Processes Laboratory,
Department of Chemical Engineering,
University of Manchester, Institute of Science and Technology,
Manchester M60 1QD, Great Britain

We consider constitutive relations for diffusion and simultaneous heat conduction in an n-component non-ideal fluid mixture. Using the ideal gas treatment of Hirschfelder, Curtiss and Bird as a basis, we develop the generalization of the Maxwell-Stefan diffusion equations. The application of the second law of thermodynamics is shown to impose non-negativity constraints on the defined diffusion coefficients, $Đ_{ik}$. The practical usefulness of the Generalized Maxwell-Stefan formulation is demonstrated by a few examples.

INTRODUCTION

A correct description of multicomponent diffusion in non-ideal fluid mixtures is of importance in many areas of chemical engineering. That the mass transport characterists of systems with three or more species can be markedly different from a binary system has been recognised for some time [1,2] and experimental work on distillation [3], extraction [4,5], and absorption [6,7] have demonstrated the importance of taking diffusional interactions into account.

Constitutive relations for n-component diffusion are complicated by many factors. Thus one can describe diffusion in terms of various quantities which define the concentration; mass fractions (ω_i), molar fractions (x_i), volume fractions (ϕ_i), mass densities (ρ_i) or molar densities (c_i). Furthermore, several diffusion equations for any of these quantities may be written down, depending on whether the diffusion fluxes ($\mathbf{j}_i$) are defined relative to the mass average velocity ($\mathbf{u}^0$), the molar average velocity ($\mathbf{u}^*$), the volume average velocity ($\mathbf{u}^V$) or the "solvent" velocity ($\mathbf{u}_n$). De Groot and Mazur [8] discuss all these possibilities in detail and relations are available for transforming from one set of diffusion coefficients to another set [8,9].

The existence of a large number of diffusion formulations makes the task of a practising chemical engineer extremely difficult. Ideally one would wish the constitutive relations to fulfill the following requirements:

(i) the set of defined diffusion coefficients should be independent to the choice of reference velocity for diffusion,

(ii) the diffusion coefficients should allow interpretation in terms of the molecular collision processes in the fluid and

(iii) the formulation should provide some guidelines for predicting the n-component

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† Deceased.

*Address correspondence to R. Krishna who is now at: Koninklijke/Shell-Laboratorium, Amsterdam, Badhuisweg 3, 1031 CM Amsterdam-N, The Netherlands.

George L. Standart Commemorative Issue

behaviour in terms of the constituent binary pairs much as the NRTL and Wilson equations do in the description of phase equilibria.

Now, for diffusion in n-component ideal gas mixtures in the absence of temperature and pressure gradients and external forces, the Maxwell-Stefan relations:

$$\nabla x_i = \sum_{\substack{j=1 \\ j \neq 1}}^{n} \frac{x_i \mathbf{N}_j - x_j \mathbf{N}_i}{c\, \mathscr{D}_{ij}} \qquad i = 1,2,\ldots n-1 \tag{1}$$

satisfy the above three conditions. Thus the diffusion coefficients $\mathscr{D}_{ij}$ $(= \mathscr{D}_{ji})$ are independent of the choice of reference velocity frame and can be predicted from the kinetic theory of gases. Also, equations (1) allow the calculation of the fluxes $\mathbf{N}_i$ in an n-component system from information on the coefficients of the binary pairs $\mathscr{D}_{ij}$.

The validity of equations (1) to describe ternary ideal gas diffusion has been verified experimentally (see for example [10–12]).

In the present communication we consider the generalization of the Maxwell-Stefan equations (1) to non-ideal mixtures allowing for temperature and pressure gradients and external forces. Though such a generalization has been considered in the literature [13–15], not all of its aspects seems to have been explored. In particular, we employ the second law of thermodynamics to obtain certain important restrictions on the transport coefficients.

We use the ideal gas treatment of Hirschfelder, Curtiss and Bird (hereafter HCB) [16] as a starting point for our development.

THEORETICAL DEVELOPMENT

HCB show (their eq. (7.3–27)) that the correct mass transfer driving force for ideal gases for mass or molar variables is

$$\mathbf{d}'_i \equiv \nabla x_i + \left(x_i - \frac{\rho_i}{\rho}\right) \nabla \ln p - \frac{\rho_i}{p\rho}\left(\rho \tilde{\mathbf{F}}_i - \sum_{j=1}^{n} \rho_j \tilde{\mathbf{F}}_j\right) \tag{2}$$

where x_i is the mole fraction of constituent i, ρ_i is its mass density with $\rho \equiv \Sigma \rho_i$, the mixture mass density, p is the pressure and $\tilde{\mathbf{F}}_i$ is the external force acting on unit mass of i. Clearly

$$\sum_{i=1}^{n} \mathbf{d}'_i = 0 \tag{3}$$

It is more common in irreversible thermodynamics to use a slight modification of this driving force by multiplying $\mathbf{d}'_i$ by the common factor p/cRT ($\equiv 1$ for ideal gases), where c is the mixture molar density, R is the gas constant and T is the absolute temperature, when we can write

$$\mathbf{d}_i \equiv \frac{p}{cRT}\mathbf{d}_i' = \frac{1}{cRT}\left[c_i \nabla_{T,p}\mu_i + (\phi_i - \omega_i)\nabla p - \rho_i\{\tilde{\mathbf{F}}_i - \sum_{j=1}^{n}\omega_j\tilde{\mathbf{F}}_j\}\right] =$$

$$= \frac{1}{cRT}\left[\rho_i \nabla_{T,p}\mu_i + (\phi_i - \omega_i)\nabla p - \rho_i\{\tilde{\mathbf{F}}_i - \sum_{j=1}^{n}\omega_j\tilde{\mathbf{F}}_j\}\right]$$

$$= \frac{\rho_i}{cRT}\left[\tilde{\Lambda}_i - \frac{1}{\rho}\nabla p + \sum_{j=1}^{n}\omega_j\tilde{\mathbf{F}}_j\right] \tag{4}$$

where the tilded quantities are specific (i.e. per unit mass) values obtained by dividing the corresponding molar quantities by the constituent molecular weight, M_i, as the constituent mass density is

$$\rho_i = c_i M_i = c x_i \ m_i \tag{5}$$

Further μ_i is the specific chemical potential; ϕ_i is the constituent volume fraction:

$$\phi_i \equiv c_i \bar{V}_i = \rho_i \tilde{\bar{V}}_i \tag{6}$$

where $\bar{V}_i$ is the partial molar volume and $\tilde{\bar{V}}_i$ is the partial specific volume of constituent i.

$\tilde{\Lambda}_i$ in equation (4) is the (specific) mass transfer driving force obtained by conventional irreversible thermodynamic arguments (HCB eq. 11.1–27),

$$\tilde{\Lambda}_i \equiv \nabla_T \tilde{\mu}_i - \tilde{\mathbf{F}}_i = \nabla_{T,p}\tilde{\mu}_i + \tilde{\bar{V}}_i \nabla p - \tilde{\mathbf{F}}_i \tag{7}$$

In view of the Gibbs-Duhem relation

$$\sum_{i=1}^{n} \rho_i \nabla_{T,p}\tilde{\mu}_i = 0 \tag{8}$$

and the Euler relation

$$\sum_{i=1}^{n} \rho_i \tilde{\bar{V}}_i = 1 \tag{9}$$

(both also valid in molar units) we find

$$\sum_{i=1}^{n} \mathbf{d}_i = 0 \tag{10}$$

(as well as eq. (3)). Thus for the conventional IT driving forces for mass transfer we find

$$\sum_{i=1}^{n} \rho_i \tilde{\Lambda}_i = \nabla p - \sum_{i=1}^{n} \rho_i \tilde{\mathbf{F}}_i \tag{11}$$

which sum only vanishes at mechanical equilibrium (cf HCB eq. 11.1–3). What we have essentially done in eqs. (4) is to apportion (subtract) the fraction ρ_i/ρ ($\equiv \omega_i$) of this deviation from each $\rho_i\tilde{\Lambda}_i$ to obtain the $\mathbf{d}_i$ for the general non-ideal solution case. While it is always dangerous to generalize from a specific to the general case, we believe that $\mathbf{d}_i$ in eq. (4) is the correct driving force for mass transfer for non-ideal solutions not only because it reduces to the correct kinetic theory value for ideal gases (eq. (2)) and the correct conventional IT value for mechanical equilibrium, but also because the deviation between $cRT\mathbf{d}_i$ and $\rho_i\tilde{\Lambda}_i$ depends only on quantities occurring in the equations of motion and the constituent mass fraction, which quantities are the same for any fluid. In other words, eq. (4) is more than an arbitrary definition of convenience, as implied by Lightfoot [14, p. 161] and Slattery [15, p. 466].

It remains to show that the driving force $\mathbf{d}_i$ is compatible with the conventional IT expression for the volumetric rate of entropy production by heat and mass transfer (HCB eq. 11.2–18)

$$\sigma = -\frac{1}{T}\left[\frac{\nabla T}{T} \cdot \mathbf{q} + \sum_{i=1}^{n} \mathbf{j}_i \cdot \tilde{\Lambda}_i\right] \geq 0 \tag{12}$$

where $\mathbf{q}$ is the "pure" heat flux and $\mathbf{j}_i$ is the constituent diffusive mass flux

$$\mathbf{j}_i \equiv \rho_i(\mathbf{u}_i - \mathbf{u}^0) \tag{13}$$

with respect to the mass average velocity $\mathbf{u}^0$ defined as

$$\rho \mathbf{u}^0 \equiv \sum_{i=1}^{n} \rho_i \mathbf{u}_i \tag{14}$$

where $\mathbf{u}_i$ is the constituent velocity. Since

$$\sum_{j=1}^{n} \mathbf{j}_i = 0 \tag{15}$$

we can write eq. (12) as (HCB eq. 11.2–43)

$$\sigma = -\frac{1}{T^2}\nabla T \cdot q - cR\sum_{i=1}^{n} \mathbf{d}_i \cdot (\mathbf{u}_i - \mathbf{u}^0). \tag{16}$$

Indeed as noted by Lightfoot (p. 162), the expression for σ is unchanged if any arbitrary reference velocity $\mathbf{u}^a$ is chosen in place of $\mathbf{u}^0$, in view of eq. (10): thus we have a natural generalisation of the Prigogine theorem [17] for this driving force, valid outside mechanical equilbrium of the fluid.

Various choices of reference velocities $\mathbf{u}^a$ are possible [8]; here we choose the molar average velocity $\mathbf{u}^*$ because of the widespread use of molar units in chemical engineering. Also, it is convenient to use the molar diffusion flux $\mathbf{J}_i$ defined by

$$\mathbf{J}_i \equiv c_i\,(\mathbf{u}_i - \mathbf{u}^*) \tag{17}$$

which allows us to write equation (16) as

$$\sigma = -\frac{1}{T^2}\nabla\, T\cdot\mathbf{q} - R\sum_{i=1}^{n}\frac{\mathbf{d}_i}{x_i}\cdot\mathbf{J}_i \geq 0 \tag{18}$$

To develop the Maxwell-Stefan formulation, it is convenient to employ the guide of the kinetic theory to write

$$\sigma = -\frac{1}{T^2}\nabla\, T\cdot\mathbf{q} - \frac{cR}{n}\sum_{i=1}^{n}\sum_{j=1}^{n}\mathbf{d}_i\cdot(\mathbf{u}_i - \mathbf{u}_j). \tag{19}$$

as we wish to introduce the constituents' velocity difference $(\mathbf{u}_i - \mathbf{u}_j)$. We shall in fact take this expression as the basis for developing our constitutive relations rather than the conventional eq. (12). Again however we shall use the kinetic theory results as guides as far as possible and take $\mathbf{d}_i$ and $\mathbf{q}$ as dependent and $(\mathbf{u}_j - \mathbf{u}_i)$ and $\nabla\, T$ as independent variables with the linear dependence for ideal gases (HCB eqs. 7.4–48, 64; 8.1–3, 11.2–54)

$$\mathbf{d}'_i = \sum_{\substack{j=1\\ j\neq 1}}^{n}\frac{x_i x_j}{\mathscr{D}_{ij}}\left\{(\mathbf{u}_j - \mathbf{u}_i) + \left[\frac{D_j^T}{\rho_j} - \frac{D_i^T}{\rho_i}\right]\frac{\nabla\, T}{T}\right\} \tag{20}$$

$$\mathbf{q} = -\lambda\nabla\, t - cRT\sum_{\substack{i,j\\=1\\ j\neq 1}}^{n}\frac{x_i x_j}{\mathscr{D}\,_{ij}}\left[\frac{D_i^T}{\rho_i}\right](\mathbf{u}_j - \mathbf{u}_i)$$

$$= -\lambda\nabla\, T + \frac{cRT}{2}\sum_{\substack{i,j\\=1\\ j\neq 1}}^{n}\frac{x_i x_j}{\mathscr{D}_{ij}}\left[\frac{D_j^T}{\rho_j} - \frac{D_i^T}{\rho_i}\right](\mathbf{u}_j - \mathbf{u}_i). \tag{21}$$

To modify eq. (20) to apply to non-ideal solutions, we may multiply by p/cRT and write

$$\mathbf{d}_i = \sum_{\substack{j=1\\ j\neq 1}}^{n}\frac{x_i x_j}{\text{Đ}_{ij}}\left\{(\mathbf{u}_j - \mathbf{u}_i) + \frac{D_j^T}{\rho_j} - \frac{D_i^T}{\rho_i}\frac{\nabla\, T}{T}\right\} \tag{22}$$

where

$$\text{Đ}_{ij} \equiv cRT\mathscr{D}_{ij}/p \tag{23}$$

but with the heat flux it is desirable to proceed more cautiously and to write

$$\mathbf{q} = -\lambda \nabla T + \frac{zcRT}{2} \sum_{\substack{i,j\\=1\\j\neq 1}}^{n} \frac{x_i x_j}{\text{Đ}_{ij}} \left[\frac{D_j^T}{\rho_j} - \frac{D_i^T}{\rho_i} \right] (\mathbf{u}_j - \mathbf{u}_i) \tag{24}$$

where z is a common factor to be determined.

To determine z it suffices to consider the special case of an isobaric binary system not subject to external forces when we can express σ in terms of independent quantities as (see equations 4,8,15,17,18).

$$\sigma = -\frac{1}{T} \left[\frac{1}{T} \nabla T \cdot \mathbf{q} + \mathbf{J}_1 \cdot \left(\frac{1}{x_2} \nabla_{T,p} \mu_1 \right) \right] \tag{25}$$

In the standard Onsager formulation we can write

$$\mathbf{J}_1 = -L_{11} \left(\frac{1}{x_2} \nabla_{T,p} \mu_1 \right) - L_{10} \frac{\nabla T}{T} \tag{26}$$

$$\mathbf{q} = -L_{01} \frac{1}{x_2} \nabla_{T,p} \mu_1) - L_{00} \frac{\nabla T}{T} \tag{27}$$

and from eqs. (13,15,22) we readily find (in molar units)

$$\mathbf{J}_1 = -c\text{Đ}_{12} \left[\frac{x_1}{RT} \nabla_{T,p} \mu_1 - \frac{x_1 x_2}{\text{Đ}_{12}} \left[\frac{D_2^T}{\rho_2} - \frac{D_1^T}{\rho_1} \right] \frac{\nabla T}{T} \right] \tag{28}$$

while from eqs. (4,21,24) we obtain

$$\begin{aligned} \mathbf{q} &= -\lambda \nabla T + cRT \frac{x_1 x_2}{\text{Đ}_{12}} \left[\frac{D_2^T}{\rho_2} - \frac{D_1^T}{\rho_1} \right] (\mathbf{u}_2 - \mathbf{u}_1) \\ &= -\left[\lambda + zcR \frac{x_1 x_2}{\text{Đ}_{12}} \left[\frac{D_2^T}{\rho_2} - \frac{D_1^T}{\rho_1} \right]^2 \right] \nabla T + zcx_1 \left[\frac{D_2^T}{\rho_2} - \frac{D_1^T}{\rho_1} \right] \nabla_{T,p} \mu_1 \end{aligned} \tag{29}$$

With the Onsager Reciprocal Relations:

$$L_{01} = L_{10} \tag{30}$$

we see readily using equations (24, 26–29) that we must take

$$z \equiv 1. \tag{31}$$

It is convenient to introduce the multicomponent thermal diffusion factor

$$\alpha_{ij} \equiv \frac{1}{\text{Đ}_{ij}}\left[\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j}\right] \tag{32}$$

(undefined for $i = j$) when we can write eq. (22,24) more compactly as

$$\mathbf{d}_i = \sum_{\substack{j=1 \\ j\neq 1}}^{n} \frac{x_i x_j}{\text{Đ}_{ij}} (\mathbf{u}_j - \mathbf{u}_i) - \sum_{\substack{j=1 \\ j\neq 1}}^{n} x_i x_j \alpha_{ij} \frac{\nabla T}{T} \tag{22'}$$

$$\mathbf{q} = -\lambda \nabla T - \frac{cRT}{2} \sum_{\substack{i,j \\ =1 \\ j\neq 1}}^{n} x_i x_j \alpha_{ij} (\mathbf{u}_j - \mathbf{u}_i) \tag{24'}$$

Alternatively on eliminating $(\mathbf{u}_j - \mathbf{u}_i)$ using eq. (22)

$$\mathbf{q} = -\lambda \nabla T - cRT \sum_{\substack{i,j \\ =1 \\ j\neq 1}}^{n} \frac{x_i x_j}{\text{Đ}_{ij}} \left[\frac{D_i^T}{\rho_i}\right] (\mathbf{u}_j - \mathbf{u}_i)$$

$$= -\lambda \nabla T - cRT \sum_{i=1}^{n} \frac{D_i^T}{\rho_i} \mathbf{d}_i + cR \sum_{\substack{i,j \\ =1 \\ j\neq i}}^{n} \frac{x_i x_j}{\text{Đ}_{ij}} \left[\frac{D_i^T}{\rho_j}\right]\left[\frac{D_j^T}{\rho_i} - \frac{D_i^T}{\rho_i}\right] \nabla T$$

$$= -\left[\lambda + \frac{cR}{2} \sum_{\substack{i,j \\ =1 \\ j\neq i}}^{n} x_i x_j \text{Đ}_{ij} \alpha_{ij}^2\right] \nabla T - cRT \sum_{i=1}^{n-1} \alpha_{in} \text{Đ}_{in} \mathbf{d}_i \tag{33}$$

where the thermal conductivity in eq. (24) is that in the absence of diffusion and that in eq. (33) is that in the absence of mass transfer driving forces ("uniform composition").

If we substitute eqs. (22′,24′) in the second law relation (19), we find after some manipulation

$$\sigma = \lambda \left[\frac{\nabla T}{T}\right]^2 + \frac{cR}{2} \sum_{\substack{i,j \\ =1 \\ j\neq i}}^{n} \frac{x_i x_j}{\text{Đ}_{ij}} (\mathbf{u}_j - \mathbf{u}_i)^2 \geq 0 \tag{34}$$

in agreement with the HCB result for ideal gases (eq. 11.2–44). This formulation of the second law condition may be considered "natural", as it represents a reduction to a sum of squares for σ so the corresponding independent "driving forces"

$$\frac{\nabla T}{T} \text{ and } c x_i x_j (\mathbf{u}_j - \mathbf{u}_i) = x_i \mathbf{J}_j - x_j \mathbf{J}_i = x_i \mathbf{N}_j - x_j \mathbf{N}_i \tag{35}$$

of the Maxwell-Stefan approach may also be considered the natural ones, where $\mathbf{J}_i$ is the molar diffusive flux and $\mathbf{N}_i$ is the total molar constituent convective flux (i.e. with respect to a fixed coordinate frame).

The relation (34) requires that

$$\lambda \geq 0 \qquad Đ_{ij} \geq 0 \tag{36}$$

This non-negativity constraint on the coefficients λ and $Đ_{ij}$ is a generalization of the HCB result for ideal gases (eq. (11.2–46). Also, since the $Đ_{ij}$ have been defined in terms of the $\mathbf{d}_i$, which are reference frame independent, the coefficients $Đ_{ij}$ are also independent of the choice of the reference velocity frame. Further we note that although any unsymmetric part of $Đ_{ij}$ cancels in eq. (34), we must utilize the Onsager reciprocal relations to conclude that

$$Đ_{ij} = Đ_{ji} \tag{37}$$

in eqs. (22′,24′) (Cf Coleman & Truesdell [18]). (We had also to assume these relations to obtain eq. (31)). Note also that with the relations (37), the thermal diffusion factors α_{ij} are antisymmetric but otherwise unrestricted.

DISCUSSION

Equations (4,22′,24′) are the constitutive relations we have sought and represent the generalization of the Maxwell-Stefan relations (1) for non-ideal mixtures in the presence of simultaneous heat transfer. We consider various special cases below and demonstrate the superiority of the generalized Maxwell-Stefan (GMS) formulation over the Fickian formulation.

Let us consider the simple case of a binary mixture of species 1 and 2, in the absence of temperature and pressure gradients and with no external body forces acting on the system.

Equations (4,22′,35) reduce to

$$\begin{aligned} \mathbf{J}_1 &\equiv \mathbf{N}_1 - x_1 (\mathbf{N}_1 + \mathbf{N}_2) = - c Đ_{12} \mathbf{d}_1 = \\ &= - c\, Đ_{12} \frac{x_1}{RT} \nabla_{T,p} \mu_1 = - c\, Đ_{12} \frac{x_1}{RT} \frac{\partial \mu_1}{\partial x_1} \nabla x_1 \\ &= - c\, Đ_{12} \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1}\right) \nabla x_1 \end{aligned} \tag{38}$$

where γ_1 is the activity coefficient in solution. For ideal gas mixtures we have

$$Đ_{ij} = \mathscr{D}_{ij} \tag{39}$$

which is identical to the Fick's law diffusivity. For non-ideal solutions we usually define the Fick's law diffusivity by

$$\mathbf{J}_1 \equiv -c\,\mathscr{D}_{12} \nabla x_1 \tag{40}$$

and therefore we see from equation (38) that

$$\mathscr{D}_{12} = Đ_{12} \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1}\right) \tag{41}$$

Though both $\mathscr{D}_{12}$ and $Đ_{12}$ are functions of composition, the GMS diffusion coefficient $Đ_{12}$ shows a much more predictable composition dependence and lends itself to interpretation in terms of molecular collision processes taking place in the fluid [19,20].

For an n-component system if we define the following coefficients

$$B_{ii} = \frac{x_i}{Đ_{in}} + \sum_{\substack{k=1 \\ k\neq 1}}^{n} \frac{x_k}{Đ_{ik}} \qquad i = 1,2\ldots n-1 \tag{42}$$

and

$$B_{ij} = -x_i \left[\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}}\right] \qquad \begin{matrix} i,j = 1,2,\ldots n-1 \\ i \neq j \end{matrix} \tag{43}$$

we may easily derive the following relation for the matrix of Fick's law diffusivities, defined by

$$(\mathbf{J}) = -c\,[D] \nabla (x), \tag{44}$$

as [21]

$$[D] = [B]^{-1} [\Gamma]. \tag{45}$$

Here the elements of the matrix $[\Gamma]$ are given as

$$\Gamma_{ij} \equiv \delta_{ij} + \frac{x_i}{x_j} \frac{\partial \ln \gamma_i}{\partial \ln x_j} , \qquad i,j = 1,2,\ldots n-1 \tag{46}$$

Equation (45) is the matrix analogue of equation (38) and again provides a method for predicting the Fickian matrix $[D]$ as shown by Kosanovich and Cullinan [22,13]. Their work shows the distinct superiority of the GMS $Đ_{ik}$ over the Fickian D_{ik} in describing non-ideal mass transport. Future experimental work on multicomponent diffusion in liquids must recognise this and diffusion data must be reported in terms of the GMS coefficients.

If we now consider coupled heat and mass transfer in binary systems we have from equations (4,22′)

$$\mathbf{J}_1 = -c\text{Đ}_{12}\left(1 + \frac{\partial \ln\gamma_1}{\partial \ln x_1}\right)\nabla x_1 + k_T\frac{\nabla T}{T} \tag{47}$$

where k_T is the thermal diffusion ratio defined as

$$k_T = \frac{\rho}{c^2 M_1 M_2}\,\frac{D_1^T}{\text{Đ}_{12}} = -\frac{\rho}{c^2 M_1 M_2}\,\frac{D_2^T}{\text{Đ}_{12}} \tag{48}$$

Equation (48) is the generalized form of the HCB relation (8.1–10).

For separation processes involving pressure gradients and external forces, such as centrifugation, osmosis, electrodialysis etc., the GMS relations (4,22′) provide the most convenient point for analysing such problems as shown in [14,24].

For steady-state transport in ideal gas mixtures, equations (1) can be solved exactly by matrix procedures to yield the fluxes $\mathbf{N}_i$ for engineering design calculations [25]. Such exact solutions are in general superior to approximate methods as has been shown experimentally [11]. For mass transport in non-ideal solutions the set of equations (4,22′) have to be combined with the continuity relations and solved numerically in general, although solutions may be obtained by making some approximations [21].

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NOTATION

$[B]$	$n-1 \times n-1$ dimensional matrix of inverted GMS diffusion coefficients with elements given by equations (41, 42)
c	molar density of mixture
c_i	molar density of constituent species i
Đ_{ij}	GMS diffusion coefficient for pair i-j in multicomponent mixture
$\mathcal{D}_{ij}$	Fick's law diffusivity pair i-j
$[D]$	$n-1 \times n-1$ matrix of Fickian diffusion coefficients
D_i^T	thermal diffusion coefficient i in multicomponent mixture
$\mathbf{d}_i'$	generalized mass transfer driving force for ideal gas mixture defined by equation (2)

$\mathbf{d}_i$	generalized mass transfer driving force for ideal gas mixture defined by equation (3)
$\tilde{\mathbf{F}}_i$	external force acting per unit mass of species i
$\mathbf{j}_i$	mass diffusion flux relative to mass average velocity (equation (13))
$\mathbf{J}_i$	molar diffusion flux relative to molar average velocity (equation (17))
k_T	thermal diffusion ratio (equation (47))
L_{ij}	Onsager coefficients
M_i	molecular weight of species i
n	number of components in mixture
N_i	molar flux of species i relative to stationary coordinate reference frame
p	pressure
$\mathbf{q}$	"pure" heat flux
R	gas constant
T	absolute temperature
$\mathbf{u}_i$	velocity of diffusing species i
$\mathbf{u}^0$	mass average velocity of mixture: $\mathbf{u}^0 = \sum^{n} \omega_i \mathbf{u}_i$
$\mathbf{u}^v$	volume average velocity of mixture $\mathbf{u}^v = \sum^{n} \phi_i \mathbf{u}_i$
u^*	molar average velocity of mixture $u^* = \Sigma\, x_i \mathbf{u}_i$
$\bar{V}_i$	partial molar volume of species i
$\tilde{\bar{V}}_i$	partial specific volume of species i
x_i	mole fraction of species i
z	undefined constant

Greek Letters

α_{ij}	multicomponent diffusion factor defined by equation (31)
γ_i	activity coefficient of species i in solution
$[\Gamma]$	matrix of thermodynamic factors defined by equation (45)
δ_{ij}	Kronecker delta
$\tilde{\Lambda}_i$	specific mass transfer driving force defined by equation (7)
μ_i	molar chemical potential of species i
$\tilde{\mu}_i$	specific chemical potential of species i

ρ_i	mass density of species *i* in mixture
ρ	mixture mass density
ϕ_i	volume fraction of species *i* (equation (6))
ω_i	mass fraction of species *i*

Operational Symbols

∇	gradient operator
	dot product
Σ	summation operator

Matrix Notation

$(\ )$	column matrix of dimension $n-1$
$[\ ]$	square matrix of dimension $n-1 \times n-1$
$[\ ]^{-1}$	inverted matrix of dimension $n-1 \times n-1$

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