Pergamon

Int. J. Heat Mass Transfer. Vol. 40, No. 10, pp. 2373–2377, 1997
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0017–9310/97 $17.00+0.00

PII: S0017-9310(96)00308-0

The Fick and Lagrange equations as a basis for the Maxwell–Stefan diffusion equations

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(*Received* 20 *March* 1996 *and in final form* 13 *August* 1996)

Abstract—Diffusion in multicomponent systems is described by equations derived by Maxwell in 1866 from the kinetic theory of gases and, independently, by Stefan in 1871 on the basis of hydrodynamic laws. These equations are called the Maxwell–Stefan equations. Their modern derivation is a matter of irreversible thermodynamics, or of statistical mechanics. In the present paper, the Maxwell–Stefan equations are obtained from the equation adopted by Fick in 1855 for diffusion in binary systems. In addition, it is demonstrated that the Maxwell–Stefan equations can also be derived from the classical Lagrange equations valid for a system of bodies undergoing energy dissipation. The energy dissipation in such a system is assumed to obey the dissipation function proposed by Lord Rayleigh in 1873. © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

The mass transfer processes in many operations, such as condensation and evaporation of mixtures, or heterogeneous chemical reactions, often govern the kinetics of the overall process. An accurate modelling of the mass transfer thus becomes necessary and must be undertaken, particularly in multicomponent systems, using the Maxwell–Stefan equations [1–3]. These equations were developed by Maxwell [4] in 1866 from the kinetic theory of gases and by Stefan [5] in 1871 from the laws of hydrodynamics.

Maxwell [4] originally considered a binary mixture exposed to an action of external forces. One of the results he arrived at are the equations for diffusion of each component. Interactions between the components appearing in the equations are proportional to the relative average velocities of the components. The proportionality coefficients are identical for both components and include their partial densities.

Stefan [5] gave an illustrative explanation for the interaction between the components, at first for a binary mixture, but in the same paper he extended the considerations to multicomponent systems. According to Stefan, the diffusion of a particular component in a mixture of gases is viewed as follows:

“In einem Gasgemenge erfährt jedes einzelne Theilchen eines einfachen Gases, wenn es sich bewegt, von jedem anderen einfachen Gase einen Widerstand, welcher der Dichte dieses anderen Gases und der relativen Geschwindigkeit der beiden gegeneinander proportional ist.”*

In a multicomponent mixture, the resulting interaction of a particular component with its neighbours is obtained by summing the binary interactions of this component. Thus, the Stefan view of the diffusion process is analogous to the Dalton law which expresses the total pressure of an ideal gas mixture as the sum of the partial pressures of the components.

In a publication that appeared in 1877, in the 9th edition of the Encyclopaedia Britannica, Maxwell [6] discussed diffusion in a multicomponent gas mixture on the basis of hydrodynamic laws and gave, like Stefan in the above-mentioned paper, the following equation for the movement of component 1:

$$\rho_1 \frac{\mathrm{d}u_1}{\mathrm{d}t} + \frac{\partial p_1}{\partial y} - f_1\rho_1 + A_{12}\rho_1\rho_2(u_1 - u_2) + A_{13}\rho_1\rho_3(u_1 - u_3) + \&c. = 0. \quad (1)$$

Here, ρ is the mass density, u the velocity with respect to a stationary co-ordinate system, p the pressure and f the external force acting per unit mass in the y direction. The subscripts 1, 2 and 3 indicate the different components of the mixture, $\mathrm{d}u/\mathrm{d}t$ represents the substantive change of the velocity, whereas A_{12}, A_{13} denote interaction coefficients. In eqn (1), y is used instead of x, and A instead of C in the original Maxwell equation. The last term, &c., as borrowed from Maxwell's publication, stands for the sum of all the remaining binary interaction terms, that is,

$$\&c. = A_{14}\rho_1\rho_4(u_1 - u_4) + A_{15}\rho_1\rho_5(u_1 - u_5) + , \ldots, .$$

For steady state diffusion with a negligible convective change of the velocity u_1, and without the action of external forces, eqn (1) reduces to

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* “In a gas mixture, any single particle of a simple gas, if it moves, experiences from any other simple gas a resistance, which is proportional to the density of that other gas and the relative velocity of the gases”.

NOMENCLATURE

A	interaction (resistance) coefficient
a	activity coefficient
c	volumetric molar concentration
D	diffusion coefficient in binary mixture
$Đ$	diffusion coefficient in multicomponent mixture
E	mechanical energy
F	dissipation function due to Lord Rayleigh
f	force per unit of mass, also fugacity
G	Gibbs free energy
J	diffusion flux per unit area
L	Lagrangian
M	molar mass
N	amount of substance
$\dot{n}$	total molar flux per unit area
Q	generalized force
q	generalized co-ordinate
$\mathscr{R}$	universal gas constant
t	time
T	temperature
u	mean velocity
V	volume
$\tilde{v}$	partial molar volume
y	co-ordinate
Y	molar fraction of component.

Greek symbols

α	kinetic (interaction) coefficient
μ	chemical potential
ρ	volumetric mass density.

Subscripts

j	component j
jk	binary pair $j-k$
k	component k
kin	kinetic energy
pot	potential energy
s	particular degree of freedom
$1, 2, \ldots$	component $1, 2, \ldots$.

$$-\frac{\partial p_1}{\partial y} = \sum_{k=1}^{n} A_{1k}\rho_1\rho_k(u_1-u_k), \tag{2}$$

where the subscript k refers to an arbitrary component of the n mixture components.

Replacing the subscript 1 in eqn (2) by a subscript j, regarding the relationship between the mass density and the molar concentration, further assuming both the total pressure and the temperature in the mixture to be constant and the mixture itself to be ideal, the relationship

$$-c\frac{\partial Y_j}{\partial y} = \sum_{k=1}^{n} \frac{c_j c_k (u_j-u_k)}{Đ_{jk} c} = \sum_{k=1}^{n} \frac{Y_k \dot{n}_j - Y_j \dot{n}_k}{Đ_{jk}} \tag{3}$$

describing the diffusion of an arbitrary component j is obtained. Here, Y_j, Y_k, c_j and c_k are the molar fractions and concentrations of the components j and k, $\dot{n}_j$ and $\dot{n}_k$ are the corresponding total fluxes, and c is the molar concentration of the mixture. The quantity $Đ_{jk}$, representing the ratio

$$Đ_{jk} \equiv \frac{\mathscr{R}T}{A_{jk}M_j M_k c}, \tag{4}$$

assumes the nature of a binary diffusion coefficient in a multicomponent mixture [7].

Equation (3) is regarded as the most useful expression of the Maxwell–Stefan equation at both constant pressure and temperature of an ideal mixture. For a mixture of n components, there are $n-1$ such independent equations.

In the current literature, the Maxwell–Stefan equation is usually derived from the postulates of irreversible thermodynamics, e.g. ref. [8]. Elementary considerations of transport processes within the molecular theory leading to the Maxwell–Stefan equation are for example given in refs. [9–11], and approximations of higher-orders in refs. [12, 13]. This equation has meanwhile been generalized to include co-operative phenomena arising from gradients of different physical properties, such as concentration, temperature, etc., e.g. refs. [14, 15]. The generalizations are mostly based on the well-known hypothesis proposed in 1931 by Onsager [16, 17], who is, as noted in numerous references, considered to be the founder of a theory of transport processes occurring in systems undergoing irreversible transformations. Onsager's theory starts from the entropy balance with a source term corresponding to a slightly modified expression for energy dissipation proposed by Lord Rayleigh and leads to a linear relationship between forces and fluxes.

It is noteworthy, however, that the transport theory of irreversible processes based on the entropy balance has been worked out prior to the Onsager publication, probably for the first time, by Jaumann [18] in 1911, and refined by Lohr [19] in 1917. The transport equations developed and analysed by Jaumann include the entropy generation associated with several processes occurring simultaneously. Thus, they account for the interactive phenomena in a mutually non-homogeneous system. Although the Jaumann theory has been overlooked, or simply ignored, it is, however, not only of historical interest, but also because of its completeness.

The aim of the present paper is twofold. Firstly, it will be shown that the Maxwell–Stefan equation can be derived from the well-known Fick equation valid for binary mixtures. A simple rearrangement of the Fick equation enables its extension to multicomponent mixtures. Furthermore, it should be demonstrated that the Maxwell–Stefan equation can also be deduced directly from the classical Lagrange equation describing the movement of a system of bodies, if the energy dissipation within the system is assumed to obey the Rayleigh dissipation function.

For reasons of simplicity, the considerations are restricted to ordinary isothermal and steady-state one-dimensional diffusion without action of external forces. Interaction phenomena which can arise from gradients of different physical quantities are thus excluded.

The present considerations may perhaps appear to be old-fashioned in comparison with recent works, some of which are cited here. However, the publication seems to be justified because of the simplicity of the method used.

DERIVATION OF THE MAXWELL–STEFAN EQUATION FROM THE FICK EQUATION

We consider an inhomogeneous binary mixture composed of components j and k. The ordinary diffusion of each component in such a mixture usually obeys the Fick [20] equation, that relates the diffusion flux J of one component, for example of component j, to the corresponding concentration*,

$$J_j = -D_{jk} c \frac{\partial Y_j}{\partial y}. \tag{5}$$

The symbols in this equation correspond to those of eqn (3), D_{jk} is consequently the diffusion coefficient in a binary system.

As Fick noted in his paper [20], the diffusion of one component causes a countercurrent movement of the other one at an equal volumetric flow rate. This verbal statement of Fick is now usually expressed by the relationship

$$\sum_{j=j}^{k} \tilde{v}_j J_j = \tilde{v}_j J_j + \tilde{v}_k J_k = 0, \tag{6}$$

which, according to current terminology, shows that the Fick diffusion occurs relative to the volume-average velocity. In eqn (6), $\tilde{v}_j$ and $\tilde{v}_k$ are the partial molar volumes of the components.

To derive the Maxwell–Stefan equation from the Fick eqn (5), we combine the latter with the Stefan equation,

$$\dot{n}_j = J_j + Y_j \dot{n}, \tag{7}$$

that relates the diffusion flux J_j to the total flux $\dot{n}_j$ of the component j and the total flux $\dot{n}$ of the mixture [7]. Equations (5) and (7) yield:

$$-c\frac{\partial Y_j}{\partial y} = \frac{\dot{n}_j - Y_j \dot{n}}{D_{jk}}. \tag{8}$$

The flux $\dot{n}_j$ is now multiplied by $Y_j + Y_k = 1$, and the total flux $\dot{n}$ is replaced by $\dot{n} = \dot{n}_j + \dot{n}_k$. The numerator on the right-hand side of eqn (8) can thus be written as

$$\begin{aligned} \dot{n}_j - Y_j \dot{n} &= \dot{n}_j (Y_j + Y_k) - Y_j (\dot{n}_j + \dot{n}_k) \\ &= \dot{n}_j \sum_{k=j}^{k} Y_k - Y_j \sum_{k=j}^{k} \dot{n}_k = \sum_{k=j}^{k} (Y_k \dot{n}_j - Y_j \dot{n}_k). \end{aligned} \tag{9}$$

Combining eqns (8) and (9), we arrive at the expression

$$-c\frac{\partial Y_j}{\partial y} = \sum_{k=j}^{k} \frac{Y_k \dot{n}_j - Y_j \dot{n}_k}{D_{jk}} = \frac{Y_k \dot{n}_j - Y_j \dot{n}_k}{D_{jk}}, \tag{10}$$

which is the Fick equation for a binary mixture written in the common form of the Maxwell–Stefan equation. According to this equation, the spatial change of the fraction Y_j is only caused by the interactions between the molecules of different species, the interactions between the molecules of the same component are thus disregarded by this relationship.

The eqn (10) is similar to the equation describing the movement of a body within an isolated system of bodies. As discussed in many sources of classical mechanics, for example in ref. [21], the momentum change of such a body is caused by its interactions with all the other bodies of the system.

If we now identify the component j in a multicomponent mixture as a particular body of the mechanical system, we recognize that the movement of this species is governed by its binary interactions within the mixture. Thus, the change of the fraction Y_j of the component j will depend on all these interactions. Considering the binary interactions as independent from each other, that is, as being caused by a change of the potential of each component of the mixture relative to the component j, we may sum up all the binary interactions according to the right-hand side of eqn (10) to obtain the derivative $\partial Y_j / \partial y$ in a multicomponent mixture, $k = 1, 2, \ldots, n$. Such a procedure immediately leads to the Maxwell–Stefan equation, noted above as eqn (3). By doing this, the question whether the binary interactions in the actually binary and in the multicomponent system are the same needs to be considered. In cases where these interactions are different from each other, the diffusion coefficient D_{jk} in eqn (10) has to be replaced by Đ_{jk}.

The expansion of the Fick equation to the Maxwell–Stefan equation illustrated here is an "*a posteriori*"

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* A relationship as expressed by eqn (5) does not exist in Fick's publication. Fick [20] only mentioned that the diffusion process is analogous to heat conduction obeying the Fourier law and derived an equation for the instationary concentration distribution, which is now known as the Fick second law. Fick's balance equation, however, leads immediately to eqn (5). In this context, it should be mentioned that Fick originally used in his derivations the gradient of the partial density instead of the mole fraction of the component.

derivation and the associated explanations do hardly allow new insights into the diffusion process.

THE LAGRANGE EQUATION AS A BASIS FOR THE MAXWELL–STEFAN EQUATION

In this section, we show how the Maxwell–Stefan equation can be derived from the Lagrange equation when the energy dissipation in the system obeys the Rayleigh dissipation function. The Lagrange equation of classical mechanics describes the movement of a system of material points from the laws of energy conversion. For a non-conservative system with a dissipation of mechanical energy, this equation takes the form [22]

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_s}\right)-\frac{\partial L}{\partial q_s}+\frac{\partial F}{\partial \dot{q}_s}=Q_s, \tag{11}$$

where t is the time, F is the Rayleigh dissipation function, q is the generalized coordinate, $\dot{q}_s = \mathrm{d}q_s/\mathrm{d}t$ is the corresponding generalized velocity, and L the so-called Lagrangian that expresses the difference between the kinetic and the potential energy of the system,

$$L = E_{\text{kin}} - E_{\text{pot}}. \tag{12}$$

The subscript s in eqn (11) refers to a particular degree of freedom of the system, Q_s is the corresponding generalized force, which is not contained in L, or F. The number of equations is determined by the number of degrees of freedom. To apply the Lagrange equation to diffusion in a multicomponent mixture, we consider the components of the mixture as subsystems of a mechanical system. The diffusion movement of the components is assumed to be very slow so that the kinetic energy may be neglected, $E_{\text{kin}} = 0$.

The potential energy E_{pot} of the system is a complex function of the system configuration, that is, of the distribution of the components in the mixture. An estimation of this energy thus requires the knowledge of the micro-state of the system considered which is a matter of molecular mechanics. However, from a macroscopic point of view, the potential energy E_{pot} of a mechanical system, or of its parts, being capable of a total conversion into other forms of energy, is identical to the Gibbs free energy G of a thermodynamic system, $E_{\text{pot}} = G$. The Gibbs free energy of a system in the state of equilibrium can be determined from the macroscopic state quantities according to thermodynamic relations.

The Lagrange eqn (11) is valid for the total system and its parts as well. Thus, we may apply this equation to each mixture component which is considered as a subsystem subject to actions of forces arising from the remaining subsystems of the total system. Without the action of additional forces ($Q_s = 0$), the Lagrange eqn (11) applied to one-dimensional diffusion of an arbitrary component j ($q_s = y$, $\dot{q}_s = u_j$) becomes

$$\frac{\partial G_j}{\partial y}+\frac{\partial F_j}{\partial u_j}=0 \tag{13}$$

where u_j is the average velocity of the component j in the y direction with respect to a stationary co-ordinate system.

The dissipation function F introduced by Rayleigh [23] represents half the rate at which the mechanical energy is dissipated. It thus balances the conversion of the potential into the kinetic energy occurring in a dissipative system, and vice versa. Adapted to our purpose, the dissipation function F for the diffusing component j takes the form

$$F_j = \frac{1}{2}\sum_{k=1}^{n}\alpha_{jk}(u_j-u_k)^2, \tag{14}$$

wherein the kinetic coefficients α_{jk} of the binary interactions depend, as Rayleigh pointed out, on the configuration of the system, but not on the velocities u_j and u_k.

To obtain the change of the free energy $\partial G_j/\partial y$ in eqn (13), we assume a local equilibrium in the non-homogeneous system. We then determine the work gained, if an amount δN_j of the component j is moved along the distance $\mathrm{d}y$ from a region where the chemical potential is μ_j to a neighbouring region where the chemical potential is $\mu_j-(\partial\mu_j/\partial y)\,\mathrm{d}y$. This work coincides with the change of the Gibbs free energy and we get, at constant temperature and pressure in the mixture, the relationship

$$\frac{\partial G_j}{\partial y}=\frac{\partial \mu_j}{\partial y}\delta N_j. \tag{15}$$

Using eqns (14) and (15), eqn (13) can be written as

$$\frac{\partial \mu_j}{\partial y}\delta N_j+\sum_{k=1}^{n}\alpha_{jk}(u_j-u_k)=0. \tag{16}$$

The binary coefficients α_{jk} may be determined on the basis of the reasoning proposed by Stefan [5] in connection with the coefficients A_{jk} in eqn (1). According to him, the interactions between the components depend on the number of particles of the component k in the volume element δV and the concentration c_j of the component j. Since the number of the particles k is proportional to the concentration c_k, we may expect a proportionality of the form $\alpha_{jk} \sim c_j c_k \delta V$, or

$$\alpha_{jk} = A^*_{jk} c_j c_k \delta V \tag{17}$$

with A^*_{jk} as the binary interaction coefficient accounting for the resistance of diffusional movement of the component j with respect to the component k.

Regarding the relationship $\delta N_j = c_j \delta V = Y_j c \delta V$, eqns (16) and (17) yield

$$-Y_j\frac{\partial \mu_j}{\partial y}=\sum_{k=1}^{n}A^*_{jk}\frac{c_j c_k}{c}(u_j-u_k), \tag{18}$$

which, after a multiplication by $c/(\mathscr{R}T)$, gives

$$-\frac{Y_j c}{\mathscr{R}T}\frac{\partial \mu_j}{\partial y}=\sum_{k=1}^{n}\frac{c_j c_k(u_j-u_k)}{Ð_{jk}c}. \tag{19}$$

The diffusion coefficient $Ð_{jk}$ in this equation is given by

$$Ð_{jk}\equiv\frac{\mathscr{R}T}{A^*_{jk}c}, \tag{20}$$

where the coefficient A^*_{jk} is related to A_{jk} in eqn (4) by $A^*_{jk}=A_{jk}M_jM_k$.

Equation (19) is a general expression of the Maxwell–Stefan equation for diffusion of a component j in a multicomponent system. It does not account for the co-operative phenomena that may arise from gradients of different physical quantities.

The chemical potential μ_j is given by

$$\mu_j=\mu_j^0+\mathscr{R}T\ln a_j, \tag{21}$$

where μ_j^0 is the reference potential and a_j is the activity coefficient representing the ratio of the fugacities, $a_j=f_j/f_j^0$, where f_j is the actual fugacity and f_j^0 that in the reference state. For an ideal mixture, we have $f_j=Y_jf_j^0$ and the Maxwell–Stefan relationship (3) is obtained from eqns (19) and (21).

CONCLUSIONS

This paper deals with the diffusion in multicomponent systems. The equations describing the diffusion processes in such systems were derived in 1866 by Maxwell and, independently, in 1871 by Stefan. These equations are called the Maxwell–Stefan equations.

The Maxwell–Stefan equations can, as shown in the paper, be derived from the Fick equation, valid for the diffusion in binary systems. A simple rearrangement of the Fick equation allows its extension to multicomponent systems. This extension is based on an analogy between the diffusion of an arbitrary component in the mixture and the movement of a body within an isolated system of bodies.

In addition, it is demonstrated in the paper that the Maxwell–Stefan equation follows directly from the classical Lagrange equation, valid for a non-conservative system of bodies. The irreversible energy conversion in such a system has been assumed to obey the Rayleigh dissipation function.

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