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Remarks upon the contribution of J. Stefan to the understanding of diffusion processes

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INTRODUCTION

Following his molecular theory of gases, Maxwell [1] arrived in 1866 at an equation describing the movement of a component by diffusion caused by a concentration gradient in a mixture. Concerning this publication by Maxwell, Stefan [2] noted: "Das Studium der Maxwell'schen Abhandlung ist nicht leicht".† He felt prompted to give an illustrative explanation of the diffusion processes in the light of hydrodynamic laws. Stefan clearly recognized that diffusion can give rise to a convective movement in the mixture. He also derived an equation for the calculation of the total transport rate of a component caused by diffusion in a mixture with a concentration gradient.

Onsager and Fuoss [3] seem to be the first who clearly distinguished between the different transport mechanisms and suggested a calculation of the total transport of a component as a sum of diffusion and convection movement. At about the same time as Onsager and Fuoss, Kuusinen [4] discussed the concept of diffusion to some extent. According to his opinion, the diffusion process is seen as a movement of a component relative to the average velocity of the mixture. Disregarding the clear formulation of the diffusion process, new elements in a physical sense compared with Stefan's view of diffusion are scarce in Kuusinen's publication. Later on, the same questions were considered by Darken [5] and Hartley and Crank [6], who gave a precise explanation of the diffusion process and of the diffusion-caused convection in mixtures using markers in diffusion space and coordinate transformation.

According to Kuusinen [4], Darken [5] and Hartley and Crank [6], the total flow rate $\dot{n}_j$ of a component j in a binary mixture with a concentration gradient should be calculated by

$$\dot{n}_j = J_j + Y_j\dot{n}. \qquad (1)$$

In this equation, Y_j is the mole fraction of the component j, $\dot{n}$ is the sum of all flow rates in the diffusion space and J_j is the flow rate by pure diffusion, see Fig. 1.

For a binary mixture consisting of the components j and k, the total flow rate $\dot{n}$ of the mixture is given by

† 'Maxwell's considerations are not simple.'

NOMENCLATURE

A_{jk}	resistance coefficient	u	absolute velocity
c	molar concentration	y	coordinate (diffusion path).
D_{jk}	diffusion coefficient		
J	diffusion flow rate	Greek symbol	
M	molar mass	ϑ	temperature.
$\dot{n}$	total flow rate		
p	pressure	Subscripts	
$\mathcal{R}$	universal gas constant	j	component j
t	time	k	component k
T	absolute temperature	jk	binary pair.

$$\dot{n} = \dot{n}_j + \dot{n}_k. \tag{2}$$

The total flow rates $\dot{n}_j$ and $\dot{n}_k$ of the components should be calculated according to

$$\left.\begin{aligned} \dot{n}_j &= c_j u_j \\ \dot{n}_k &= c_k u_k \end{aligned}\right\} \tag{3}$$

with c_j and c_k as the molar concentrations, and u_j and u_k as the absolute velocities of the components.

The transport rate J_j by pure diffusion obeys Fick's law

$$J_j = -D_{jk} c \frac{\partial Y_j}{\partial y}. \tag{4}$$

Here D_{jk} is the diffusion coefficient, c is the molar concentration of the mixture and y is the diffusion path.

Equation (1) is now generally accepted and is used as a basic expression for the description of transport processes caused by diffusion [7–9]. The derivations of this equation by Darken [5] and by Hartley and Crank [6] using some inventive means are also accepted. However, if one considers Stefan's studies about diffusion more thoroughly and follows his line of reasoning, one becomes convinced that equation (1) must already be known to Stefan. The reason why he did not derive such an equation is probably due to the fact that he was primarily interested in a final form of an equation for the flow rate in order to estimate the diffusion coefficient.

The aim of this note is to show—in honour of Stefan—that equation (1) can very easily be derived, without any additional assumptions, following the line of consideration already taken by Stefan. It will begin with equations given by Stefan [2, 10]. All his simplifications will also be valid in this note. The considerations should be restricted to one-dimensional diffusion in a binary mixture of ideal gases obeying Dalton's law. The temperature in the diffusion space should be the same everywhere and the diffusion process is caused only by a concentration gradient. The concentration of the mixture and the total pressure should be considered as constant.

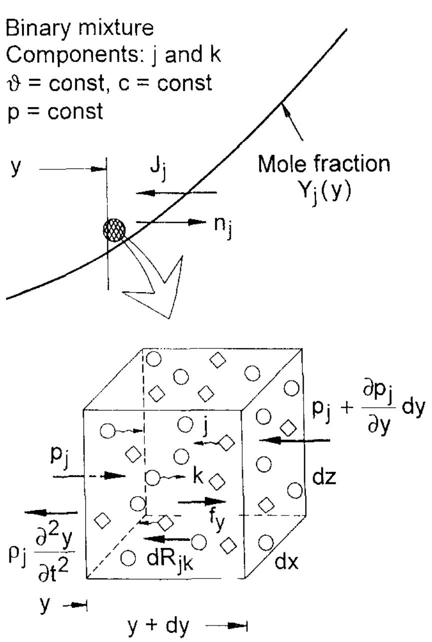

Fig. 1. Differential volume for deriving the momentum equation. The direction of the flow rate $\dot{n}_j$ is arbitrary.

DERIVATION IN THE LIGHT OF STEFAN'S THEORY

The movement of the component j by diffusion in a mixture is governed by the momentum equation and the equation of continuity. Referring to the sketch in Fig. 1, the momentum equation in the y direction can be written as follows:

$$\left(\rho_j \frac{\partial^2 y}{\partial t^2} - f_j \rho_j + \frac{\partial p_j}{\partial y}\right) dV = dR_{jk}. \tag{5}$$

Here t is the time, ρ_j is the density, f_j is the field force per unit mass and p_j is the partial pressure of component j. The term dR_{jk} denotes the resistance force exerted by all particles of component k upon all particles of component j, both being in the volume element dV.

The resistance force dR_{jk} is assumed to depend linearly on the relative velocity of the components $u_j - u_k$, on the total number of the particles j, i.e. on the mass $\rho_j\, dV$ of the component j in the volume dV, and on the number of the particles k per unit volume, i.e. on the density ρ_k. Therefore, the resistance force dR_{jk} may be expressed as

$$dR_{jk} = A_{jk} \rho_j \rho_k (u_j - u_k)\, dV \tag{6}$$

where the quantity A_{jk} assumes the part of a resistance coefficient.

In most cases the diffusion processes take place very slowly. The inertia term, therefore, should not necessarily be regarded. If the same is also assumed for the field force, $f_j = 0$, the momentum equation (5), together with equation (6), simplifies to

$$-\frac{\partial p_j}{\partial y} = A_{jk} \rho_j \rho_k (u_j - u_k) = A_{jk} M_j M_k c_j c_k (u_j - u_k) \tag{7}$$

where M_j and M_k are the molar masses of the mixture components j and k.

Equation (7) was derived by Stefan [10]. In order to show that this equation expresses the same as the transport equation (1), we will use the identity

$$c_j c_k(u_j - u_k) = c_k \dot{n}_j - c_j \dot{n}_k \tag{8}$$

and introduce an intrinsic diffusion coefficient D_{jk},

$$\frac{\mathscr{R}T}{A_{jk} M_j M_k c} \equiv D_{jk}. \tag{9}$$

With expressions (8) and (9), the momentum equation (7) can be rearranged and written as follows:

$$c_k \dot{n}_j = -D_{jk} \frac{c}{\mathscr{R}T} \frac{\partial p_j}{\partial y} + c_j \dot{n}_k. \tag{10}$$

The term $c_j \dot{n}_k$ in this equation should be determined using the equation of continuity. For component j, the continuity equation reads:

$$\frac{\partial c_j}{\partial t} + \frac{\partial}{\partial y}(c_j u_j) = 0. \tag{11}$$

Writing a similar equation for component k, adding it to equation (11) and considering that the molar concentration c of the mixture, $c = c_j + c_k$, is constant, $\partial c/\partial t = 0$, we obtain

$$\frac{\partial}{\partial y}(c_j u_j + c_k u_k) = 0$$

or

$$c_j u_j + c_k u_k = \text{const} = cu \tag{12}$$

with u as the molar average velocity of the mixture.†

Combining equations (10) and (12), setting $cu = \dot{n}$ and $p_j = y_j p$ with $p = c\mathscr{R}T$, and regarding equations (3), we arrive at the following relationship:

$$\dot{n}_j = -D_{jk} c \frac{\partial Y_j}{\partial y} + Y_j \dot{n}. \tag{13}$$

This expression is identical to equation (1). It states that the diffusion flow rate of a component j is seen as a difference of the total flow of this component and the flow of the mixture as the whole. Because equation (13) follows directly from equations used by Stefan, and bearing in mind Stefan's contributions to the understanding of diffusion processes in general, it becomes obvious to name relationship (13) the Stefan equation.

† The cases $u_j = 0$, $u_k = 0$, have already been considered by Stefan [10].

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