Letter to the Editor

Josef Stefan and his evaporation–diffusion tube—the Stefan diffusion problem

ABSTRACT

In 1871, Josef Stefan published a diffusion model that later became one of the fundamental models of transport phenomena, the Stefan–Maxwell (sometimes called the Maxwell–Stefan) diffusion relation. In his last paper on diffusion, which appeared in 1889, Stefan treated the evaporation–diffusion process in a vertical tube with a moving interface, and gave a complete analytical solution to this problem. This process – known as the Stefan diffusion problem – is frequently referred to in the literature. However, Stefan's own solution to this problem is not mentioned, and its existence seems to be unknown in scientific circles. The present note reproduces the Stefan's treatment of that evaporation–diffusion process.

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1. Statement of the problem

Stefan's solution to the evaporation–diffusion problem was published in 1889 in the *Sitzungsberichte der kaiserlichen Akademie der Wissenschaften Wien* (hereafter referred to as *Sitzungsberichte*) (Stefan, 1889) and reprinted in *Annalen der Physik* (Stefan, 1890) in 1890, both in German. Fig. 1 illustrates the physical situation. A vertical tube was partly filled with a liquid, which in turn evaporated and the vapour flowed out of the tube at the open end. The tube portion above the liquid level contained a (binary) mixture consisting of the surrounding gas (air) and the vapour, generated on the liquid–gas interface. Due to evaporation, the liquid level fell, and the process was unsteady, even if all other parameters were kept constant. Under these conditions, Stefan derived equations for calculating the concentration distribution along tube length and the evaporation rate of the liquid.

In the period from 1871 to 1890 Stefan published several papers on diffusion, altogether some 240 pages, without figures, exclusively in the *Sitzungsberichte*. This journal was not widely distributed across libraries at that time as other journals; in addition, Stefan scarcely communicated with colleagues from abroad, and these facts taken together may explain, why Stefan's ideas were not widely known in scientific circles as rapidly as they should have. So, his treatment of the evaporation–diffusion process remained undiscovered and eventually forgotten. In 1997, Slattery and Mhetar (Slattery and Mhetar, 1997) published a solution to this problem, independently and without knowledge of the existence of Stefan's work. The problem was thus solved twice, and needs not be treated again anymore. However, considering Stefan's fundamental contributions to the area of diffusion, it seems justifiable to present his original solution to a wider circle of researchers interested in diffusion processes.

2. The Stefan solution

Stefan started by applying the momentum and continuity equations to diffusion in the gaseous area above the liquid level,

Fig. 1. The gas mixture and its components were treated as ideal gases, and the total pressure and temperature were constant throughout the whole system. The origin of the coordinate x is the plane of the upper tube end, and the position of the liquid level is denoted by L.

The gas mixture contained two components, and the Stefan equations describing the diffusion process are:

$$\frac{\partial p_1}{\partial x} + A_{12}\rho_1\rho_2(u_1 - u_2) = 0, \quad \frac{\partial p_2}{\partial x} + A_{21}\rho_1\rho_2(u_2 - u_1) = 0, \tag{1}$$

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial(\rho_1 u_1)}{\partial x} = 0, \quad \frac{\partial \rho_2}{\partial t} + \frac{\partial(\rho_2 u_2)}{\partial x} = 0. \tag{2}$$

Here p, ρ and u denote the pressure, the mass density, and the absolute velocity, respectively; the indices 1 and 2 refer to the mixture components 1 (vapour) and 2 (gas); t is the time, while A_{12} and A_{21} represent the resistance coefficients. Eqs. (1) and (2) were derived by Stefan in his first paper on diffusion (Stefan, 1871), in 1871, and successfully used in the treatment of the same problem, but for a non-moving interface.

For the paper (Stefan, 1889) in question, Stefan used molar densities instead of mass densities, and we will follow his nomenclature. Starting with the state equations for ideal gases,

$$\left.\begin{array}{ll} p_1 = c_1 \Re T, & p_2 = c_2 \Re T \\ c_1 + c_2 = c, & p_1 + p_2 = p \end{array}\right\}, \tag{3}$$

Eqs. (1) and (2) may be written as

$$D_{12}\frac{\partial c_1}{\partial x} + c_1 c_2(u_1 - u_2) = 0, \quad D_{21}\frac{\partial c_2}{\partial x} + c_1 c_2(u_2 - u_1) = 0, \tag{4}$$

$$\frac{\partial c_1}{\partial t} + \frac{\partial(c_1 u_1)}{\partial x} = 0, \quad \frac{\partial c_2}{\partial t} + \frac{\partial(c_2 u_2)}{\partial x} = 0 \tag{5}$$

where

$$D_{12} = \frac{\Re T}{A_{12}M_1 M_2}, \quad D_{21} = \frac{\Re T}{A_{21}M_1 M_2} \tag{6}$$

are the diffusion coefficients, $D_{12} = D_{21}$.
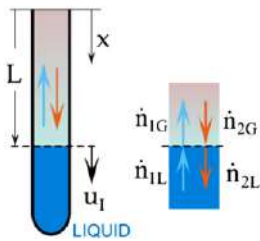
Fig. 1. Schematic of Stefan's evaporation–diffusion tube.

Adding Eq. (4) gives

$$\frac{\partial(c_1+c_2)}{\partial x} = \frac{\partial c}{\partial x} = 0, \quad c = c_1+c_2 = const \qquad (7)$$

where

$$p = c\Re T; \quad p,T = const : c = const. \qquad (8)$$

Summing Eq. (5) and including Eq. (7) gives,

$$\frac{\partial(c_1+c_2)}{\partial t} + \frac{\partial(c_1u_1+c_2u_2)}{\partial x} = 0, \quad c_1u_1+c_2u_2 = cu = const. \qquad (9)$$

To solve eqs. (4) and (5), Stefan used the boundary condition that evaporation was taking place at the moving liquid–gas interface. In order to take into account the movement of the interface and to connect these equations, Stefan invoked the continuity requirements at a moving interface with phase change; I have sketched these requirements according to his wording (see enlargement in Fig. 1). As the components are not consumed while passing the interface, their fluxes ($\dot{n}_1,\dot{n}_2$) are the same on both sides of the interface, so,

$$\left.\begin{array}{l}\dot{n}_{1L} = \dot{n}_{1G} \; c_{1L}(u_{1L}-u_I) = c_{1G}(u_{1G}-u_I) \\ \dot{n}_{2L} = \dot{n}_{2L} \; c_{2L}(u_{2L}-u_I) = c_{2G}(u_{2G}-u_I)\end{array}\right\} \qquad (10)$$

where u_I denotes the velocity of the interface; the indices L, G and I stand for liquid, gas, and interface, respectively.

Adding Eq. (10),

$$c_{1L}(u_{1L}-u_I)+c_{2L}(u_{2L}-u_I) = c_{1G}(u_{1G}-u_I)+c_{2G}(u_{2G}-u_I), \qquad (11)$$

and considering that the interface is impermeable to gas (component 2) and the liquid does not move, so $c_{2L}=0$, $u_{1L}=0$, hence

$$c_{1G}u_{1G}+c_{2G}u_{2G} = -(c_{1L}-c_G)u_I. \qquad (12)$$

The interface velocity u_I measures the time change of the interface position, thus

$$u_I = \frac{dL}{dt}. \qquad (13)$$

Taken together, Eqs. (12) and (13) state the flow continuities across the interface as obtained by Stefan:

$$c_1u_1+c_2u_2 = -(c_L-c)\frac{dL}{dt}, \qquad (14)$$

where, for reason of simplicity we have omitted some indices, and set:

$$c_{1L} = c_L, \quad c_{1G} = c_1, \quad u_{1G} = u_1$$
$$c_{2G} = c_2, \quad u_{2G} = u_2, \quad c_G = c.$$

Note that Eq. (14) is obtained from the boundary conditions at the interface, but due to Eq. (9) it is valid in the whole diffusion space.

To arrive at the final form of the differential equation for diffusion in the mixture, Eq. (4) for component 1 is written as:

$$D_{12}\frac{\partial c_1}{\partial x}+c_1u_1c_2-c_1c_2u_2 = 0, \qquad (15)$$

and the term c_2u_2 removed with the help of Eq. (14):

$$D_{12}\frac{\partial c_1}{\partial x}+c_1u_1+\frac{c_L-c}{c}c_1\frac{dL}{dt} = 0. \qquad (16)$$

Differentiating Eq. (16) with respect to x and combining with Eq. (5) for component 1 gives the relation known as the Stefan diffusion equation:

$$\frac{\partial c_1}{\partial t} = D_{12}\frac{\partial^2 c_1}{\partial x^2}+\frac{c_L-c}{c}\frac{\partial c_1}{\partial x}\frac{dL}{dt}. \qquad (17)$$

The boundary conditions which must be satisfied by Eq. (17) are:

$$\left.\begin{array}{l}x = 0 : c_{10} = 0 \\ x = L : c_1 = c_{1I}\end{array}\right\}. \qquad (18)$$

At $x=0$, the equation is satisfied automatically; it must but also be satisfied at the interface, $x=L$ for $c_1=c_{1I}$, thus:

$$\frac{\partial c_{1I}}{\partial t} = D_{12}\frac{\partial^2 c_{1I}}{\partial x^2}+\frac{c_L-c}{c}\frac{\partial c_{1I}}{\partial x}\frac{dL}{dt}, \quad x = L. \qquad (19)$$

At this stage of the derivation, Stefan noted that there was an additional condition at the interface that also must be satisfied, namely the continuity of fluxes of the species. He stated this condition without explanation; for this reason some steps of his reasoning are sketched here analytically.

Since the concentration c_{1I} depends only on temperature (saturation concentration of vapour), it is independent of time t when the temperature is constant. Given this assumption, Eq. (19) becomes

$$\frac{\partial c_{1I}}{\partial t} = 0, \quad D_{12}\frac{\partial^2 c_{1I}}{\partial x^2}+\frac{c_L-c}{c}\frac{\partial c_{1I}}{\partial x}\frac{dL}{dt} = 0, \quad x = L. \qquad (20)$$

Integrating the second equation in Eq. (20) with respect to x,

$$D_{12}\frac{\partial c_{1I}}{\partial x}+\frac{c_L-c}{c}c_{1I}\frac{dL}{dt} = \varphi(t), \quad x = L, \qquad (21)$$

and comparing with Eq. (19), yields:

$$\varphi(t) = \frac{\partial c_{1I}}{\partial t} = -(c_1u_1)_I, \quad x = L. \qquad (22)$$

The molar flux $(c_1u_1)_I$ can be obtained from Eq. (14),

$$(c_1u_1)_I = -(c_L-c_{1I})\frac{dL}{dt}, \quad x = L, \qquad (23)$$

and inserted in Eq. (22) to get:

$$\varphi(t) = (c_L-c_{1I})\frac{dL}{dt}, \quad x = L. \qquad (24)$$

Finally, combining Eqs. (21) and (24) gives the additional boundary condition relation:

$$D_{12}\frac{\partial c_1}{\partial x}-\frac{c-c_{1I}}{c}c_L\frac{dL}{dt} = 0, \quad x = L. \qquad (25)$$

Stefan gave the solution of Eq. (17) in the form

$$c_1(x,t) = B\int_0^{x/(2\sqrt{D_{12}t})}\exp(-z^2-2\alpha\beta z)dz, \qquad (26)$$

$$L = 2\alpha\sqrt{D_{12}t}, \quad \beta = \frac{c_L-c}{c}, \qquad (27)$$

where the constants B and α are to be determined from the boundary conditions at $x=L$. Hence, Eq. (26) becomes

$$c_{1I} = B\int_0^{\alpha}\exp(-z^2-2\alpha\beta z)dz, \qquad (28)$$

whereas Eq. (25) with Eq. (28) gives

$$B\exp(-\alpha^2-2\alpha^2\beta) = 2\frac{c-c_{1I}}{c}\alpha c_L. \qquad (29)$$

From Eqs. (28) and (29) it follows

$$\alpha \exp(\alpha^2 + 2\alpha^2 \beta) \int_0^\alpha \exp(-z^2 - 2\alpha\beta z)dz = \frac{1}{2}\frac{c}{c - c_{1I}}\frac{c_{1I}}{c_L}. \tag{30}$$

When α is obtained from Eq. (30), the constant B follows from Eq. (29):

$$B = 2\frac{c - c_{1I}}{c}c_L \alpha \exp(\alpha^2 + 2\alpha^2 \beta). \tag{31}$$

With the constants B and α thus calculated, Eq. (26) gives Stefan's solution to the problem.

Stefan then proceeded to discuss the case when the molar liquid density was much larger than the gas density, namely, $c_L \gg c$, and $\beta = (c_L - c)/c$ becomes very large. He simplified the integral (30),

$$\alpha \exp(2\alpha^2 \beta) \int_0^\alpha \exp(-2\alpha\beta z)dz = \frac{1}{2}\frac{c}{c - c_{1I}}\frac{c_{1I}}{c_L}, \tag{32}$$

and performed the integration to obtain:

$$\frac{\exp(2\alpha^2 \beta) - 1}{\beta} = \frac{c}{c - c_{1I}}\frac{c_{1I}}{c_L}. \tag{33}$$

From this equation the following expression for the position of the interface was deduced[1]

$$L(t)^2 = 2\frac{c}{c_L - c}D_{12}t \ln\left(\frac{c}{c_L}\frac{c_L - c_{1I}}{c - c_{1I}}\right). \tag{34}$$

Stefan compared this expression with an expression he derived in an earlier paper (Stefan, 1873) under the assumption of a constant evaporation rate (fixed interface):

$$L(t)^2 - L_0^2 = 2\frac{M_1 p}{\rho_L \Re T}D_{12}(t - t_0)\ln\frac{p - p_{10}}{p - p_{1I}}. \tag{35}$$

Eq. (34) rests on the assumption $c_{10} = 0$, that is, $p_{10} = 0$. Assuming in this equation $c_L \gg c_{1L}$, $c_L \gg c_{1I}$, it becomes identical with Eq. (35). From such a comparison Stefan concluded that the expression he derived under the condition of constant evaporation rate (non-moving interface) and used in the diffusion experiments was sufficiently accurate.

In the same paper Stefan also treated dissolution of solids in liquids using the same physical model and mathematics he successfully applied for evaporation–diffusion.

3. Conclusion

The aim of this note was to present the original Stefan solution to the evaporation–diffusion process with a moving interface. As far as I am aware, this solution has not been referred to in the literature and remained hidden to the scientific community for more than a century.

Nomenclature

A	resistance coefficient
B	constant
c	molar density
D	diffusion coefficient
L	position of interface
$\dot{n}$	molar flux
p	pressure
t	time
u	velocity
x	coordinate
z	dummy variable
α	constant
β	parameter
ρ	mass density

Indices

G	gas
L	liquid
I	interface
1	component 1
2	component 2
12	interaction 12

Acknowledgement

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[1]In the original papers (Stefan, 1889, 1890), Eq. (21), there is a misprint; in our notation, Stefan's original equation reads: $L(t)^2 = (1/2)(c/c_L)D_{12}t \ln(c/(c - c_{1I}))$.

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