Historical perspectives

Jožef Stefan and the dissolution-diffusion phenomena – Not only a historical note

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ABSTRACT

In a series of papers published from 1871 to 1889, Jožef (Josef) Stefan dealt with several diffusion processes, including also multicomponent systems. In his last paper on diffusion, which appeared in 1889, he studied the dissolution-diffusion process with a moving interface, and gave an analytical solution to this problem. However, Stefan's dissolution-diffusion analysis is not mentioned in literature, and its existence seems to be unknown in scientific community. The present paper summarizes the main Stefan ideas on dissolution of solids governed by diffusion of solute in the adjacent solvent phase thus making his results accessible to wider scientific circles.

Contents

1. Introduction

Dissolution of solids in liquids and gases is encountered both in nature and many technical processes. The dissolution of cooking salt and sugar in processes of everyday life, minerals in rain water, drugs in leaving organisms, direct solid–vapor phase transition (sublimation of water ice at low temperature) might serve as examples. According to the wide field of dissolution occurrence and application, it is not surprising that mechanisms behind the dissolution phenomena have attracted the attention of scientists for centuries. Dokoumetzidis and Macheras (2006) provided a comprehensive review in this area, starting with the paper by Noyes and Whitney (1897). Regarding the historical boundaries stated in the title of their publication, Dokoumetzidis and Macheras' review is complete and provides important historical insights into the understanding and modeling of dissolution phenomena. However, it would be of interest to push back the lower time boundary and

supplement the review by including the contributions of Jožef Stefan (1835–1893) to the understanding of dissolution phenomena.[1]

In the period from 1870 to 1890, Stefan conducted several experiments on diffusion in gases and liquids under various initial and boundary conditions and published a series of papers, altogether some 240 pages (Mitrovic, in press). In his last paper on diffusion (Stefan, 1889), which appeared 8 years prior to the (Noyes and Whitney, 1897) publication, Stefan gave a detailed description of the dissolution process governed by diffusion of the solute in the adjacent solvent phase. Consequently, the widely accepted view that the paper by Noyes and Whitney marks the beginning of the modeling of dissolution-diffusion phenomena appears thus to be incorrect. This fact, however, is not only of historical interest.

Stefan's analysis of the dissolution-diffusion phenomena, which was published in the *Sitzungsberichte der kaiserlichen Akademie der Wissenschaften Wien* (hereafter referred to as *Sitzungsberichte*) in

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[1] Josef Stefan was a professor in mathematical physics at the University Vienna. His name is tightly connected with several transport phenomena like diffusion, thermal radiation, Stefan-problem in heat transfer (solidification). He was the Doktorvater (supervisor) of only 3 PhD students: Josef Loschmidt, Ludwig Boltzmann and Marian von Smoluchowski. All of them became later world-renown scientists.

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Nomenclature

Latin letters

A	resistance coefficient
B	constant
c	molar density
D	diffusion coefficient
f	interaction force, function
j	diffusion flux
K	constant
L	position of interface, penetration depth
M	molar mass
$\dot{n}$	molar flux
p	pressure
R	resistance force
$\Re$	gas constant
t	time
T	temperature
u	velocity
v	molar volume
X	body force
x,y,z	coordinates
z	dummy variable

Greek letters

α	constant
β	parameter
ξ	acceleration
ρ	mass density

Indices

I	interface
L	liquid
S	solid
1	component 1
2	component 2
12	binary pair 1-2
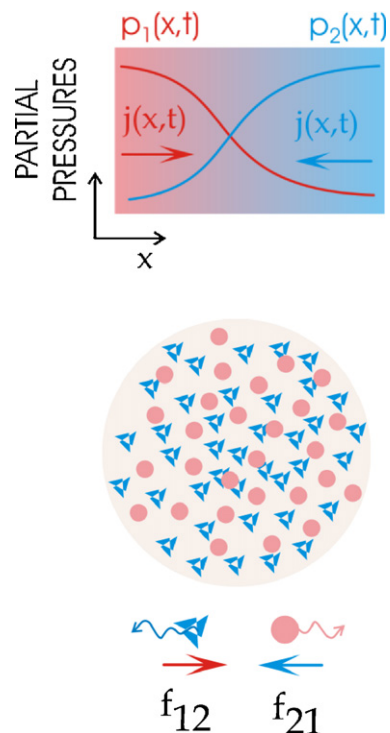
Fig. 1. Distribution of partial pressures and directions of the diffusion fluxes in an isobaric binary gas system (above), illustration of the resistance force (below).

1889, is not mentioned in literature. This journal was not widely distributed at that time among libraries as other journals. In addition, the physics of the dissolution-diffusion phenomenon Stefan formulated for the first time was not that simple, and, notwithstanding the reprinting of the paper in *Annalen der Physik* (Stefan, 1890) in 1890, the Stefan ideas got forgotten. This may be viewed as a loss of an important scientific contribution. It is thus the aim of this paper to present the main results of Stefan's work on dissolution and to make it accessible to broader scientific circles.

2. The basis of Stefan's diffusion theory

Stefan derived the diffusion equations for gas mixtures starting from the basic principles of classical mechanics. For a binary system these equations have the form (x-direction, component 1):

$$\left(\rho_1 X_1 - \frac{\partial p_1}{\partial x} \right) dxdydz - R_{12} = \rho_1 \xi_1 dxdydz, \tag{1}$$

where ρ_1, P_1, X_1, and ξ_1 denote, respectively, the mass density, the partial pressure, the body force, and the average acceleration; R_{12} is the resistance force (Fig. 1).

The resistance force R_{12} accounts for the interaction of the species in the mixture and was expressed as

$$R_{12} = A_{12}\rho_1\rho_2(u_1 - u_2)dxdydz, \tag{2}$$

where ρ_2 is the mass density of the companion gas, and A_{12} is a constant that depends on the nature of the gases; u_1 and u_2 are the absolute average velocities of the components.

Inserting (2) in (1) gives

$$\rho_1 \xi_1 = \rho_1 X_1 - \frac{\partial p_1}{\partial x} - A_{12}\rho_1\rho_2(u_1 - u_2). \tag{3}$$

By the same reasoning, it follows for the component 2:

$$\rho_2 \xi_2 = \rho_2 X_2 - \frac{\partial p_2}{\partial x} - A_{21}\rho_1\rho_2(u_1 - u_2) \tag{4}$$

where, by Newton principle, $R_{12} = R_{21}$ and $A_{12} = A_{21}$.

3. The Stefan analysis of dissolution-diffusion processes

Stefan started the dissolution-diffusion investigations by stating the process conditions as follows: constant system temperature, constant system pressure, negligible accelerations of the components, and absence of body forces. Then his Eqs. (3) and (4) become:

$$\frac{\partial p_1}{\partial x} + A_{12}\rho_1\rho_2(u_1 - u_2) = 0$$
$$\frac{\partial p_2}{\partial x} + A_{21}\rho_1\rho_2(u_1 - u_2) = 0 \tag{5}$$

As the movement of the components must satisfy the continuity requirements, these equations must be supplemented by the equations of continuity:

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial(\rho_1 u_1)}{\partial x} = 0$$
$$\frac{\partial \rho_2}{\partial t} + \frac{\partial(\rho_2 u_2)}{\partial x} = 0 \tag{6}$$

where t denotes the time.

The above equations have been originally derived for gaseous systems. In order to apply them in a dissolution-diffusion process, Stefan (1889, 1890) provided first a brief comment on diffusion in liquids and considered then the dissolution of solids in liquids, which is controlled by diffusion of the solute in the adjacent liquid

phase. While doing so he assumed that the partial pressures p_1 and p_2 of the gas components in Eqs. (5) and (6) may be expressed in case of liquid mixtures as

$$p_1 = K_1 c_1 \quad p_2 = K_2 c_2, \tag{7}$$

where the quantities K_1 and K_2 shall be independent of the molar concentrations c_1 and c_2 in the mixture.

Stefan did not state the physics behind the relations (7). One could speculate about his thoughts on this point and connect his ideas with the concept of the osmotic pressure Π ($\Pi = \Re Tc = Kc$; $K = const$ for ideal solution at $T = const$), which was well-established at that time (see e.g. Findlay, 1919). By contrast, he gave a detailed analysis of the diffusion of the solute in a liquid, as follows next.

Inserting in Eq. (5) the pressures according to (7) and adding gives

$$K_1 \frac{\partial c_1}{\partial x} + K_2 \frac{\partial c_2}{\partial x} = 0. \tag{8}$$

By the assumption that diffusion in liquids occurs at constant volume of the mixture, the relation

$$c_1 v_1 + c_2 v_2 = 1, \tag{9}$$

was obtained and combined with Eq. (8) to get

$$K_1 = K v_1, \quad K_2 = K v_2, \tag{10}$$

$$p_1 = K v_1 c_1, \quad p_2 = K v_2 c_2. \tag{11}$$

Here v_1 and v_2 are the molar volume of the components; K is now a mixture-specific constant.

With the pressures p_1 and p_2 thus introduced, Eq. (5) become

$$\left. \begin{array}{l} K v_1 \dfrac{\partial c_1}{\partial x} + A_{12} M_1 M_2 c_1 c_2 (u_1 - u_2) = 0 \\[2mm] K v_2 \dfrac{\partial c_2}{\partial x} + A_{12} M_1 M_2 c_1 c_2 (u_1 - u_2) = 0 \end{array} \right\} \tag{12}$$

from which, after multiplication by v_1 and v_2, one obtains

$$\left. \begin{array}{l} D_{12} \dfrac{\partial c_1}{\partial x} + v_2 c_1 c_2 (u_1 - u_2) = 0 \\[2mm] D_{21} \dfrac{\partial c_2}{\partial x} + v_1 c_1 c_2 (u_1 - u_2) = 0 \end{array} \right\}, \tag{13}$$

$$D_{12} = \frac{K v_1 v_2}{A_{12} M_1 M_2}, \quad D_{21} = \frac{K v_1 v_2}{A_{21} M_1 M_2}, \quad D_{12} = D_{21}. \tag{14}$$

The continuity equations (6) are valid unchanged,

$$\frac{\partial c_1}{\partial t} + \frac{\partial (c_1 u_1)}{\partial x} = 0, \quad \frac{\partial c_2}{\partial t} + \frac{\partial (c_2 u_2)}{\partial x} = 0, \tag{15}$$

and multiplying first by v_1 and the second by v_2, then adding together, and considering Eq. (9) gives:

$$\frac{\partial}{\partial x}(v_1 c_1 u_1 + v_2 c_2 u_2) = 0 \quad v_1 c_1 u_1 + v_2 c_2 u_2 \neq f(x) \tag{16}$$

For diffusion in a container with impermeable walls which Stefan at first assumed, it is $u_1, u_2 = 0$, and the expression

$$v_1 c_1 u_1 + v_2 c_2 u_2 = 0 \tag{17}$$

holds in the whole diffusion space.

Eliminating $v_2 c_2 u_2$ in Eq. (13) for the component 1 by using Eq. (17) and considering Eq. (9) result in:

$$D_{12} \frac{\partial c_1}{\partial x} + c_1 u_1 = 0 \tag{18}$$

As Stefan noted, this equation represents the Fick equation of diffusion, although such an equation has not been reported by Fick (1855a,b). However, its time-derivative, combined with Eq. (15), results in the so-called second Fick law,

$$\frac{\partial c_1}{\partial t} - D_{12} \frac{\partial^2 c_1}{\partial x^2} = 0, \tag{19}$$
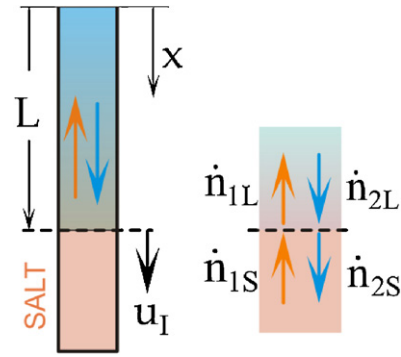

Fig. 2. Schematic of Stefan's dissolution-diffusion process.

An analogous equation immediately follows for the component 2. The condition (17), however, is not satisfied generally, e.g. for systems with permeable walls.

Stefan applied the above equations to case of dissolution-diffusion of solids in liquids, particularly of rock salt in water. Due to solid dissolution, the solid–liquid interface moves (Fig. 2). Eqs. (13) and (15) describe this process (component 1: solid phase, solute in the solution):

$$D_{12} \frac{\partial c_1}{\partial x} + v_2 c_1 c_2 (u_1 - u_2) = 0, \tag{20}$$

$$\frac{\partial c_1}{\partial t} + \frac{\partial (c_1 u_1)}{\partial x} = 0, \tag{21}$$

Because of the interface movement, the continuity requirements for the species transport across the interface must be fulfilled. These requirements are stated as the balance equations (Fig. 2):

$$\left. \begin{array}{l} \dot{n}_{1S} = \dot{n}_{1L} \quad c_{1S}(u_{1S} - u_I) = c_{1L}(u_{1L} - u_I) \\[1mm] \dot{n}_{2S} = \dot{n}_{2S} \quad c_{2S}(u_{2S} - u_I) = c_{2L}(u_{2L} - u_I) \end{array} \right\} \tag{22}$$

where $\dot{n}_1$ and $\dot{n}_2$ denote the molar fluxes of the components 1 (solvent) and 2 (solute), while the indices I, L and S refer to interface, liquid phase and solid phase, respectively.

Multiplying the first of Eq. (22) by v_{1L} and the second one by v_{2L}, and considering that the solid phase does not move, $u_{1S} = 0$, and does not contain any solvent, $c_{2S} = 0$, they become

$$\left. \begin{array}{l} c_{1L} u_{1L} v_{1L} = -c_{1S} u_I v_{1L} + c_{1L} u_I v_{1L} \\[1mm] c_{2L} u_{2L} v_{2L} = c_{2L} u_I v_{2L} \end{array} \right\} \quad \text{at} \quad x = L \tag{23}$$

Adding them together gives

$$c_1 u_1 v_1 + c_2 u_2 v_2 = (-c_S v_1 + c_1 v_1 + c_2 v_2) u_I \quad \text{at} \quad x = L \tag{24}$$

where the index L is omitted.

Replacing $c_2 v_2$ on the right in Eq. (24), according to Eq. (9), and considering that the interface velocity measures the time change of the diffusion path L,

$$u_I = \frac{dL}{dt}. \tag{25}$$

Eq. (24) becomes

$$c_1 u_1 v_1 + c_2 u_2 v_2 = -(c_S v_1 - 1)\frac{dL}{dt}. \tag{26}$$

Inserting now $c_2 u_2 v_2$ from this equation in Eq. (20) and rearranging gives

$$D_{12} \frac{\partial c_1}{\partial x} + c_1 u_1 = -(c_S v_1 - 1) c_1 \frac{dL}{dt}. \tag{27}$$

Combining the derivative of Eq. (27) with respect to x,

$$D_{12} \frac{\partial^2 c_1}{\partial x^2} + \frac{\partial}{\partial x}(c_1 u_1) = -(c_S v_1 - 1)\frac{\partial c_1}{\partial x}\frac{dL}{dt}, \tag{28}$$

with the continuity Eq. (21), leads to the Stefan dissolution-diffusion equation:

$$\frac{\partial c_1}{\partial t} = D_{12}\frac{\partial^2 c_1}{\partial x^2} + (c_S v_1 - 1)\frac{\partial c_1}{\partial x}\frac{dL}{dt}. \tag{29}$$

The boundary conditions to be satisfied by Eq. (29) are:

$$\left.\begin{array}{l} x = 0 : c_{10} = 0 \\ x = L : c_1 = c_{1I} \end{array}\right\}. \tag{30}$$

At $x = 0$, the equation is satisfied automatically; it must but also be satisfied at the interface, $x = L$, thus:

$$\frac{\partial c_1}{\partial t} = D_{12}\frac{\partial^2 c_1}{\partial x^2} + (c_S v_1 - 1)\frac{\partial c_1}{\partial x}\frac{dL}{dt}, \quad x = L \tag{31}$$

At this derivation stage Stefan noted, that there is also an additional condition at the interface that must be satisfied, namely the continuity of fluxes of the species. With $c_1 u_1 = -(c_S - c_1)dL/dt$ according to Eq. (23), this additional boundary condition follows from Eq. (27):

$$D_{12}\frac{\partial c_1}{\partial x} = c_S(1 - c_1 v_1)\frac{dL}{dt}, \quad \text{at} \quad x = L \tag{32}$$

The integral of the dissolution-diffusion equations (29) that satisfies all of the boundary conditions according to Stefan is:

$$c_1(x, t) = B \int_0^{x/(2\sqrt{D_{12}t})} \exp(-z^2 - 2\alpha\beta z)dz, \tag{33}$$

$$L = 2\alpha\sqrt{D_{12}t}, \quad \beta = c_S v_1 - 1. \tag{34}$$

The boundary conditions deliver the equations for the determination of the constants B and α:

$$\alpha \exp(\alpha^2 + 2\alpha^2\beta)\int_0^\alpha \exp(-z^2 - 2\alpha\beta z)dz = \frac{1}{2}\frac{1}{1 - v_1 c_{1I}}\frac{c_{1I}}{c_S}, \tag{35}$$

$$B = 2(1 - v_1 c_{1I})c_S \alpha \exp(\alpha^2 + 2\alpha^2\beta) \tag{36}$$

The parameter β in Eq. (34) takes into account the expansion of the solid phase due to dissolution.

As far as the author is aware, the differential equation (29) and its integral (33), taken together with the boundary conditions equations (35) and (36) present the first complete closed mathematical analysis of dissolution of solids in liquids. The Stefan papers (Stefan, 1889, 1890) presenting this analysis have not been mentioned in literature. The review paper by Dokoumetzidis and Macheras (2006) was limited to a time period of the last 100 years (1896–2006), starting with Noyes and Whitney (1897), which excludes Stefan's works.

The Noyes and Whitney (1897) ideas have been sufficiently appreciated by Dokoumetzidis and Macheras (2006) and need not be considered again here. However, to provide a linkage of their ideas and those of Stefan (1889) we may quote from Noyes and Whitney (1897):

...the phenomenon may be considered as simply a process of diffusion. That is, we can imagine the sticks of solid substances surrounded by an indefinitely thin film of saturated solution, from which diffusion takes place into all portions of the solvent, this being kept homogeneous by the rotation. If this were the case, the velocity of solution, in accordance with the law of diffusion, would be proportional to the difference between the concentration of the saturated solution and that of the solution present at the moment in question.

This notion is in perfect agreement with the Stefan view of the diffusion-controlled dissolution of solid bodies.

Nernst (1904) and Brunner (1904) treated the same problem and refined the film model of Noyes and Whitney. However, the film model equations reported by Nernst and Brunner are already contained in the first Stefan paper on evaporation-diffusion (Stefan, 1873), published in 1873, and the Stefan original equations may be written as

$$\dot n_1 = c\frac{D_{12}}{L}\ln\frac{c - c_{1L}}{c - c_{10}} \tag{37}$$

$$\dot n_1 = \frac{D_{12}}{L}(c_{10} - c_{1L}), \tag{38}$$

where c denotes the molar concentration of the liquid solution; c_{10} and c_{1L} are the molar concentrations of the solute in the liquid solution at the solid surface and outer boundary of the film of the thickness L, respectively. Eq. (37) includes the Stefan flow, while the simplified Stefan Eq. (38), reported by Nernst and Brunner, follows already from the Fick theory. The most accurate expression for the dissolution rate per unit of solid surface follows from the Stefan dissolution theory,

$$\dot n_1 = c_S\frac{dL}{dt} = \alpha c_S \sqrt{\frac{D_{12}}{t}}, \tag{39}$$

if α is obtained from Eq. (35). Eq. (39) belongs basically to so-called penetration mass transfer models; because of the movement of the solid surface, the dissolution of the solid may be viewed as penetration of the solvent into the solid phase.

Interestingly, none of the authors mentioned above was familiar with the Stefan analysis of the dissolution-diffusion processes. The situation is still unchanged and the Stefan analysis is not mentioned in the literature. The same is true with his both penetration and film models of mass transfer worked out in Stefan (1878) and revisited in Mitrovic (in press).

4. Conclusions

Josef Stefan has thoroughly explored the dissolution kinetics of solid bodies under the assumption that the dissolution phenomena were dominated by diffusion in the adjacent liquid phase and the solid–liquid interface is moving. The corresponding paper was printed in the Sitzungsberichte of the Vienna Academy more than 120 years ago, but the results remained unnoticed so far. In view of their scientific content and their importance for actual research activities, the present contribution revisits the Stefan achievements in the dissolution-diffusion area and makes them accessible to the scientific community.

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