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Diffusing uphill with James Clerk Maxwell and Josef Stefan

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The primary objective of this article is to highlight a number of situations of importance in chemical engineering in which one of the components in a mixture is transported uphill of its own composition gradient. The proper appreciation and modeling of uphill diffusion requires the use of chemical potential gradients as driving forces. Furthermore, due account needs to be taken of coupling effects, that is, the influence of the driving force of any component in the mixture on the transport fluxes of all partner species in the mixture. The Maxwell–Stefan formulation, that has its roots in theory of irreversible thermodynamics, affords the most general, and convenient, approach for modeling diffusion in fluid mixtures, electrolytes, alloys, glasses, and porous adsorbents.

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Introduction

Fick's law, that relates the diffusion flux to the composition gradient,

$$J_i = -c_t D_i \left(\frac{dx_i}{dz}\right) \tag{1}$$

is widely used in chemical engineering practice for the design of separation equipment [1•,2•,3]. The Fick diffusivity is usually positive definite, that is, $D_i > 0$, and the flux of species i is directed down its composition gradient. However, there are a number of examples for which Eq. (1) fails, even at a qualitative level, to describe the diffusion phenomena. Lars Onsager was amongst the first to recognize the limitations of Fick's law. In his classic paper published in 1945 entitled *Theories and Problems of Liquid Diffusion*, Onsager [4] wrote *The theory of liquid diffusion is relatively undeveloped... It is a striking symptom of the common ignorance in this field that not one of the phenomenological schemes which are fit to describe the general case of diffusion is widely known*. In the Onsager formalism for n-component mixture diffusion, the diffusion fluxes J_i are postulated to be linearly dependent on the chemical potential gradients, $d\mu_i/dz$, of each of the species present in the mixture.

A persuasive demonstration of the need to use $d\mu_i/dz$ as driving force, is available in the classic experiments reported in 1949 by Darken [5•]. In one of Darken's experiments, two austenite bars of different compositions (0.48% C, 3.8% Si, 95.72% Fe), and (0.45% C, 0.05% Si, 99.50% Fe) are welded together and maintained at 1323 K for a period of 13 days. The bars are then quenched and the C composition profiles determined; the results are shown in Figure 1. We note that C has diffused from the left-hand bar (with high Si content) to the right-hand bar (with low Si content). The high C content near the surface of the austenite bar on the right, imparts the required 'hardness' to steel. The process of hardening of steel by 'carburizing' is reliant on uphill transport of carbon from the high-Si bar to the low-Si bar, despite the fact that the initial compositions of carbon are practically the same in the two adjoining bars. In Table 3 of Darken's paper, the activity of carbon, defined by $a_1 = \gamma_1 x_1$, is calculated for the compositions A (0.315% C), and B (0.586% C); see Figure 1. The activity at A, $a_{1A} = 0.3$, while the activity at B, $a_{1B} = 0.29$. This implies that carbon diffuses down its activity gradient. In other words, the thermodynamic non-ideality effects are the root cause of uphill diffusion. Three quotes from the Darken paper [5•], summarize the foregoing arguments and serve as tramlines for the ensuing discussions and analysis:

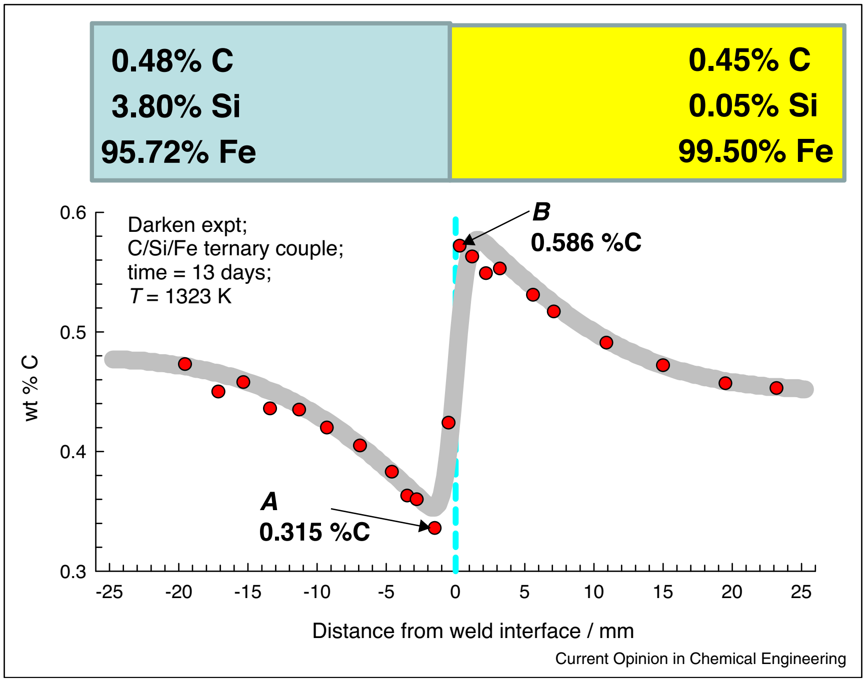
"*the driving force in an isothermal diffusion process may be regarded as the gradient of the chemical potential,*",

"*for a system with more than two components it is no longer necessarily true that a given element tends to diffuse toward a region of lower concentration even within a single phase region*", and

"*departure from the behavior of an ideal solution may be so great that the concentration gradient and the chemical potential gradient, or activity gradient, may be of different sign, thus giving rise to uphill diffusion*".

The primary objective of this article is to highlight the importance of uphill transport in a wide variety of systems and scenarios that are of practical importance in the chemical, petrochemical and related industries. The first task is set up a convenient framework for describing multicomponent diffusion that can be applied for the solution of practical problems.

Figure 1



Experimental data of Darken [5•] for inter-diffusion between the left and right austenite bars consisting of C/Si/Fe mixtures. The wt% of each component is measured on either side of the Matano plane, measured at $t = 13$ days after the start of the experiment are shown.

The Maxwell–Stefan diffusion formulation

The approach we adopt stems from the pioneering works of James Clerk Maxwell [6] and Josef Stefan [7••], who analyzed diffusion in ideal gas mixtures. The Maxwell–Stefan (M–S) formulation is essentially a "friction formulation" in which the force acting on species i is balanced by friction with each of the partner species in the mixture [8••,9••] (a more detailed derivation is provided in the Supplementary material accompanying this publication):

$$-\frac{1}{RT}\frac{d\mu_i}{dz} = \sum_{j=1_{j\neq i}}^{n} \frac{x_j(u_i - u_j)}{Đ_{ij}}; \quad i = 1, 2, \ldots n \tag{2}$$

The pair diffusivity $Đ_{ij}$ can be interpreted as an inverse "drag coefficient" between species i and species j. Eq. (2) is consistent with the theory of irreversible thermodynamics; the Onsager reciprocal relations demand the symmetry constraint $Đ_{ij} = Đ_{ji}$. We define the fluxes $J_i \equiv c_i(u_i - u)$ with respect to the molar average mixture velocity, $u = x_1u_1 + x_2u_2 + \cdots x_nu_n$; in terms of the diffusion fluxes, J_i, the M–S formulation for n-component diffusion takes the form

$$-\frac{x_i}{RT}\frac{d\mu_i}{dz} = \sum_{j=1_{j\neq i}}^{n} \frac{x_jJ_i - x_iJ_j}{c_tĐ_{ij}}; \quad i = 1, 2, \ldots n \tag{3}$$

For mixtures of ideal gases, the Maxwell–Stefan formulation is entirely consistent with the kinetic theory of gases, and the pair diffusivities $Đ_{ij}$ can be identified with the diffusivity in the *binary* gas mixture of species i and species j.

Uphill diffusion in binary mixtures caused by phase splitting

For a binary mixture, Eq. (3) reduces to yield the following expression for the diffusion flux of species 1 in the mixture with species 2

$$J_1 = -c_tĐ_{12}\frac{x_1}{RT}\frac{d\mu_1}{dz} = -c_tĐ_{12}\frac{x_1}{RT}\left(\frac{\partial \mu_1}{\partial x_1}\right)\frac{dx_1}{dz} \tag{4}$$

Comparing with Eq. (1), we note that the Fick diffusivity is related to the M–S diffusivity

$$D_{12} = Đ_{12}\Gamma; \quad \Gamma \equiv \frac{x_1}{RT}\left(\frac{\partial \mu_1}{\partial x_1}\right) \tag{5}$$

For thermodynamically ideal mixtures, $\Gamma = 1$, and the Fick diffusivity can be identified with the M–S diffusivity. For mixtures of liquids, alloys, and glasses the tendency for phase separation has a strong influence on the Fick diffusivity, causing it to attain negative values and, as a consequence, the phenomenon of uphill transport. To demonstrate this possibility, let us consider diffusion in a binary alloy mixture consisting of Fe (= component 1) and Cr (= component 2). Let us combine n_{Fe} atoms of Fe and n_{Cr} atoms of Cr in a face centered cubic (FCC) lattice