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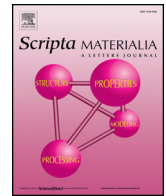
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## Determination of the intrinsic diffusivities from the diffusion couple experiment in multicomponent systems



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## ABSTRACT

A new method, which allows determination of intrinsic diffusivities values on the Kirkendall plane in multicomponent systems, is presented. The approach is based on the zero contribution of drift flux to the total flux value of  $i$ -th component, when calculated relatively to the Kirkendall plane position. The method allows precise determination of intrinsic diffusivities without limitations of Boltzmann-Matano based methods e.g. in situations when uphill diffusion occurs. The approach is validated on a number of theoretical and experimental systems. The results indicate that the method have a very high potential in application for multicomponent systems, including high entropy alloys.

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The discovery of Kirkendall effect [1] and its subsequent mathematical description provided by Darken [2], up to this day remain as one of the most influential developments in the history of diffusion. The concept of a drift velocity  $v^{drift}$ , which arises from the differences between fluxes of respective components, significantly changed our perception of the mechanisms and possible consequences of mass transport processes. One of the most challenging and important tasks in diffusion studies is the estimation of diffusion coefficients, which is essential for understanding of such processes as crystallization, diffusive phase transformations, selective oxidation and many more. In the case of binary systems, most commonly used approaches are based either on the Boltzmann-Matano method (BM) [3], or its developments: Wagner method [4], Sauer-Fraiese method [5] and other [6]. Most of them are based on the mass conservation law written for the interdiffusion coefficient  $\bar{D}$  common for both diffusing species:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left( \bar{D} \frac{\partial c_i}{\partial x} \right), \quad i = 1, 2, \quad (1)$$

with the interdiffusion coefficient being defined by following relation:

$$\bar{D} = \Omega_1 c_1 D_2 + \Omega_2 c_2 D_1, \quad (2)$$

where  $\Omega_i$  are partial molar volumes of components and  $D_i$  denotes their intrinsic diffusion coefficients. Applying of the Boltzmann parameter  $\lambda$

in a form of:

$$\lambda = \frac{x - x^M}{\sqrt{t}} = \frac{x}{\sqrt{t}}, \quad (3)$$

where  $x^M$  denotes position of the Matano plane, allows to obtain relation for the value of interdiffusion coefficient. For the legacy Boltzmann-Matano method it takes form:

$$\bar{D}(c_i^*) = -\frac{1}{2t} \left( \frac{dx}{dc_i} \right)_{c_i^*} \left[ x^* (c_i^* - c_i^-) - \int_{x^*}^{x^-} (c_i - c_i^-) dx \right], \quad (4)$$

where superscript \* describes parameters at a considered position and  $c_i^-$  denotes the initial concentration at the left side of Matano plane. Modifications of the BM method, such as Heumann's approach [7], allow estimating the values of the intrinsic diffusivities in the binary systems.

In ternary and higher systems, the situation is much more complicated. One possibility is to use one of the BM-based method in a quasi-binary approach, such as one presented by Kirkaldy et al. [8], or recent development of Wagner's method presented by Santra et al. [9], which allows to estimate the intrinsic diffusion coefficients. An alternate way is to use the concept of average effective interdiffusion coefficients introduced by Sohn and Dayananda [10,11]. However, both types of analysis have significant disadvantages. In the case of BM-based methods, the biggest one is the necessity of quasi binary approach. It significantly limits the choice of possible compositions and increases number of experiments necessary to determine diffusion coefficients for all components. Another serious limitation is the requirement of monotonicity of concentration profiles, meaning absence of up-hill diffusion effects. This even further limits the choice of possible end-members of diffusion couple and drastically lowers the accuracy of

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these methods if even small up-hill effects are present (what is very common). The approach proposed by Dayananda et al. requires an extremely precise experiment planning and sometimes a great number of diffusion couples [11,12]. Even then, the estimation of intrinsic diffusion coefficients is far more difficult than the estimation of interdiffusion ones and in most cases not even possible [9]. Also, for number of components higher than 3, the amount of necessary experimental data makes use of these methods unrealistic.

A very interesting approach to the problem of determination of intrinsic diffusivities in multicomponent systems was presented by Wierzbza et al. [13]. The so called “Generalized Boltzmann-Matano method” (GBM), was intended to allow determination of intrinsic diffusion coefficients for the compositions from the Kirkendall plane position. The idea was to apply the Boltzmann parameter to the mass conservation law in which the total flux was given in a form for laboratory reference frame:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left( D_i \frac{\partial c_i}{\partial x} + c_i v^{drift} \right), \quad i = 1, 2, \dots, r. \quad (5)$$

After analogous procedure as in legacy BM method, the relation for intrinsic diffusion coefficients takes from:

$$D_i(c_i^K) = -\frac{1}{2t} \left( \frac{dx}{dc_i} \right)_{c_i^K} \left[ 2x^K (c_i^K - c_i^-) - \int_{x^-}^{x^K} (c_i - c_i^-) dx \right], \quad (6)$$

where superscript  $K$  denotes values of position and concentrations at Kirkendall plane. Knowing the values of intrinsic diffusion coefficients at Kirkendall plane and self diffusion coefficients at the ends of the couple, it is possible to make a 3-point, parabolic interpolation of intrinsic diffusivities values for the whole composition range (if the data from other diffusion couples from the same system is available, the polynomial of higher degree can be used, as the number of interpolated points will increase). The approach, while very tempting, has however some limitations. One of them is the already mentioned requirement of monotonicity of concentration profiles. Also, the analysis of the Eq. (6) shows that in the case when the Kirkendall plane is on the positive side of Matano position, the values of diffusion coefficients can reach negative values (depending on the  $dx/dc$  derivative sign), making the results not physically valid.

In the proposed approach we base on the fundamental Darken postulate [2,14]. If the Eq. (5) is formulated for the moving Kirkendall plane, it is clear that the interdiffusion flux is simplified to diffusion flux in materials reference frame (as the plane is moving with the Kirkendall's velocity):

$$\tilde{J}(x^K(t)) = J^d(x^K(t)) = -D_i(c_i^K) \frac{\partial c_i}{\partial x} \Big|_{x^K(t)}. \quad (7)$$

As a result we can say that all fluxes flowing through the moving Kirkendall plane can be attributed strictly to the diffusion processes and the drift is nonexistent for such reference frame. It means that the mass balance equation formulated for Kirkendall plane can be written as:

$$\int_{-\infty}^{x^K(t^*)} c_i(t^*, x) dx - \int_{-\infty}^{x^K(t_0)} c_i(t_0, x) dx = \int_{t_0}^{t^*} D_i(c_i^K) \frac{dc_i}{dx} \Big|_{x^K(t)} dt = Q_i^{Tot}, \quad (8)$$

where  $Q_i^{Tot}$  denotes the total amount of  $i$ -th component moved through the Kirkendall plane and  $t_0$  denotes the start of diffusion process. It should be noted that concentration at the Kirkendall plane,  $c_i^K$ , is constant for the whole time of experiment [15,16] and initial position of the Kirkendall plane is identical to the position of Matano plane:

$$x^K(t = 0) = x^M(t). \quad (9)$$

Now, it is possible to apply the Boltzmann parameter to the mass balance equation. While using it in a form given in Eq. (3) would not affect the correctness of solution (the relative movement of both Matano

and Kirkendall planes has parabolic character), the choice of  $x^K$  as the reference position is in this particular case more intuitive and consistent with the applied formalism:

$$\lambda = \frac{x - x^K}{\sqrt{t}} \Rightarrow d\lambda = \frac{dx}{\sqrt{t}}. \quad (10)$$

As a result we obtain the following relation:

$$Q_i^{Tot} = \int_{t_0}^{t^*} -\frac{D_i(c_i^K)}{\sqrt{t}} \frac{dc_i}{d\lambda} dt = -2D_i(c_i^K) \sqrt{t} \frac{dc_i}{d\lambda} \Big|_{t_0}^{t^*}. \quad (11)$$

After substitution of the Boltzmann parameter we arrive with the final equation for intrinsic diffusion coefficient at the position of Kirkendall plane:

$$D_i(c_i^K) = \frac{1}{2t^*} \left( \frac{dc_i}{dx} \Big|_{x^K(t^*)} \right)^{-1} \left[ \int_{-\infty}^{x^K(t^*)} c_i(t^*, x) dx - \int_{-\infty}^{x^K(t^*)} c_i^- dx \right]. \quad (12)$$

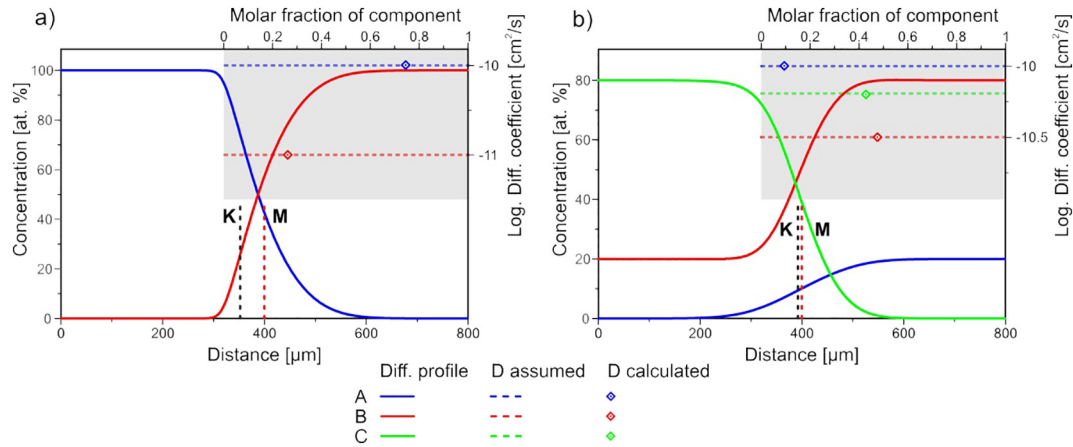
It should be noted that a well defined position of Kirkendall plane is necessary to successfully apply the presented approach to experimental results, therefore a marker experiments are required. In the case of ternary and higher system the intrinsic diffusion coefficients, as defined in Eq. (12), are equal to the values of diagonal matrix of intrinsic diffusion coefficient, given for the Kirkendall reference frame and written using Onsager formalism. More detailed discussion on the relation between Onsager and Darken formalisms is provided in [17–19].

To check the correctness of the presented approach, a series of tests was conducted, basing on the numerically simulated diffusion profiles. All simulations were conducted using MATLAB software with use of the Darken method and methodology described elsewhere [14,19]. All simulations were conducted for diffusion time of 100 h. The assumed diffusion couples were 800  $\mu\text{m}$  thick with constant distance between nodes equal to 1  $\mu\text{m}$ , what implicates position of Matano plane at 399.5  $\mu\text{m}$ . During the first test a simple A-B binary couple was simulated using the constant values of intrinsic diffusion coefficients. In this case the partial molar volumes were assumed to be identical for both components. The most important parameters for this and subsequent diffusion couples, namely: Kirkendall plane position, concentrations at the Kirkendall plane, calculated intrinsic coefficients and error of their determination, are summarized in the Table 1. As it can be seen in the Fig. 1a, the values of intrinsic diffusion coefficients at Kirkendall plane position determined using proposed approach are practically identical to the input values. The next test was conducted using a 3-component

**Table 1**

Kirkendall plane position, atomic fractions and calculated intrinsic diffusion coefficients at the Kirkendall plane, and error of their determination for the simulated diffusion couples.

	$x^K$ [ $\mu\text{m}$ ]	$N_i^K$ [at. %]	$D_i^K$ [ $\text{cm}^2/\text{s}$ ]	Error [%]
<b>Test 1 Fig. 1a</b>				
A	352.3	74.2	$1.00 \times 10^{-10}$	0.07
B		25.1	$1.00 \times 10^{-11}$	0.02
<b>Test 2 Fig. 1b</b>				
A		9.4	$1.00 \times 10^{-10}$	0.03
B	392.2	47.6	$3.17 \times 10^{-11}$	0.11
C		42.9	$6.31 \times 10^{-11}$	-0.04
<b>Test 3 Fig. 2a</b>				
A		28.4	$1.33 \times 10^{-10}$	-0.05
B	385.4	16.4	$2.21 \times 10^{-12}$	0.37
C		55.3	$8.98 \times 10^{-13}$	0.06
<b>Test 4 Fig. 2b</b>				
A		39.3	$1.13 \times 10^{-12}$	1.98
B	417.0	35.1	$7.85 \times 10^{-13}$	-0.16
C		25.6	$1.33 \times 10^{-10}$	0.00



**Fig. 1.** Diffusion profiles (solid lines) calculated for constant intrinsic diffusivities (shown in the right upper corner): a) binary system, b) ternary system. The Kirkendall and Matano planes are marked by the vertical dotted lines (K and M respectively).

system (Fig. 1b), also with constant values of intrinsic diffusion coefficients. Similarly to the previous case, the calculated values are in full agreement with the input ones.

To confirm the method's ability to deal with the systems in which uphill diffusion effects are present and diffusivities are concentration-dependent, a 3-component system in which intrinsic diffusion coefficient were given as a parabolic functions of concentrations was simulated. As it is visible in the Fig. 2a, a significant uphill diffusion effect occurred in the simulated profile. Again, the presented method allows to extract the values of intrinsic diffusion coefficients at Kirkendall plane with excellent precision and despite the lack of monotonicity. It would not be possible with use of any BM derived method. The final test was conducted on the theoretical 3-component system in which diffusion coefficients were again concentration dependent and uphill effects occurred, but this time additionally different molar volumes were assumed for all components: 5, 7 and 10 [cm<sup>3</sup>/mol] for components A, B and C respectively. The results presented in the Fig. 2b clearly show that the presented approach allows calculating the exact values of intrinsic diffusivities.

To further examine the correctness of the developed approach, a two experimental concentration profiles available in literature were examined. Following systems were selected: Ni-Au [20] and Co-Fe-Ni [21], as in both cases the data concerning the position of Kirkendall plane was available. Similarly as it was proposed in GBM method [13], it was assumed that the appropriate choice of diffusion coefficients values for the end-members of diffusion couples should allow to interpolate the values of intrinsic diffusion coefficients for the whole composition range of

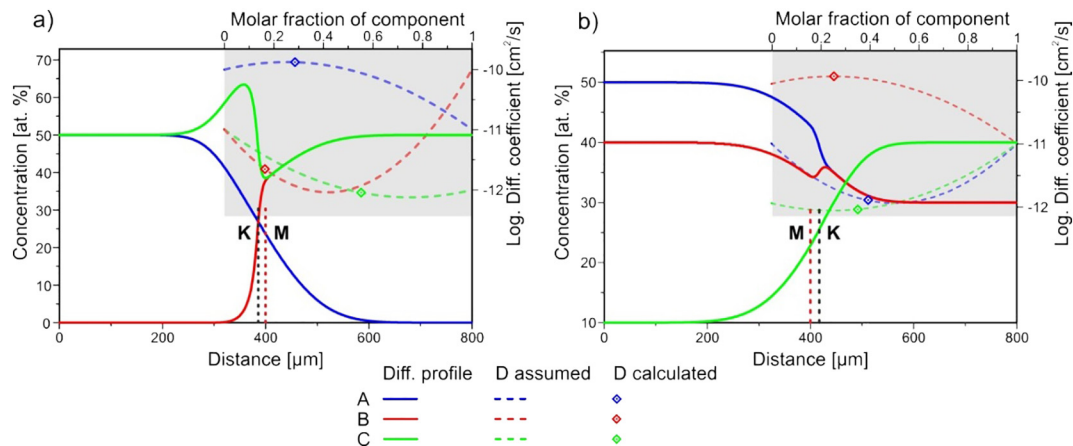
interest. In the case of Ni-Au system, it was assumed that on the respective ends of diffusion couple, the diffusion coefficients of both components can be estimated using the self diffusion coefficient of the main element. In the case of Co-Fe-Ni, a similar approach as presented in [22] was used. It should be noted that when e.g., a diffusion couple consisting of two alloys from different metallic systems is considered, a preferred option would be to use the intrinsic diffusion coefficients determined for each component in each system (assuming that the data is available).

The results together with the values calculated and used for the interpolation of  $D_i$  (data taken from [23–26]) are summarized in the Table 2. The comparison of obtained theoretical results with

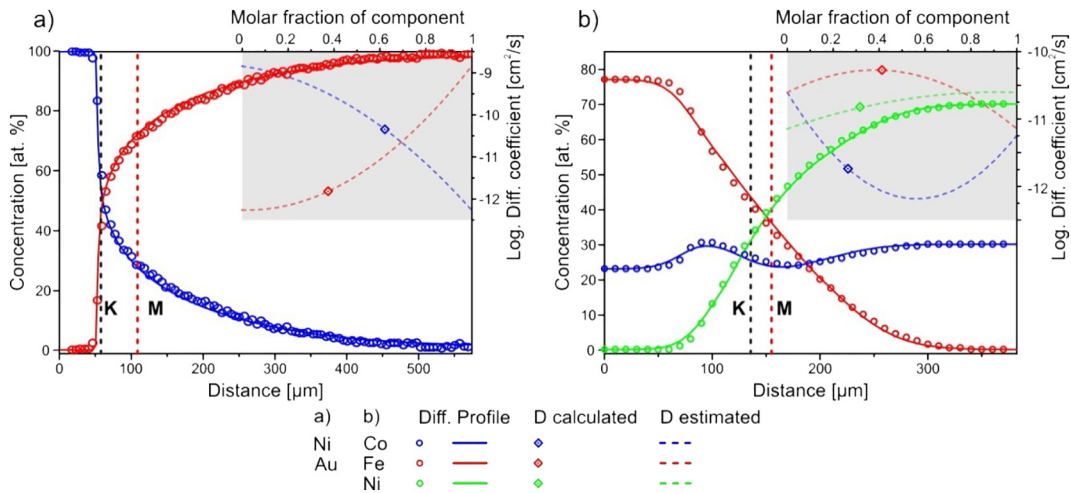
**Table 2**

Kirkendall and Matano planes position, atomic fraction and calculated intrinsic diffusion coefficients at the Kirkendall plane and for the end members of diffusion couples for the studied Ni-Au and Co-Fe-Ni diffusion couples.

	$x^K$ [μm]	$x^M$ [μm]	$N_i^K$ [at. %]	$D_i^K$ [cm <sup>2</sup> /s]	$D_i(\text{left end})$ [cm <sup>2</sup> /s]	$D_i(\text{right end})$ [cm <sup>2</sup> /s]
Ni-Au Fig. 3a						
Ni	58	109	62.3	$4.53 \times 10^{-11}$	$1.44 \times 10^{-9}$	$5.46 \times 10^{-13}$
Au			37.7	$1.55 \times 10^{-12}$	$5.46 \times 10^{-13}$	$1.44 \times 10^{-9}$
Co-Fe-Ni Fig. 3b						
Co			26.4	$1.82 \times 10^{-12}$	$3.67 \times 10^{-11}$	$5.71 \times 10^{-12}$
Fe	136	155	41.4	$5.31 \times 10^{-11}$	$5.63 \times 10^{-11}$	$7.15 \times 10^{-12}$
Ni			32.2	$1.48 \times 10^{-11}$	$7.89 \times 10^{-12}$	$2.48 \times 10^{-11}$



**Fig. 2.** Diffusion profiles (solid lines) calculated for composition-dependent intrinsic diffusivities (shown in the right upper corner): a) equal partial molar volumes, b) different partial molar volumes. The Kirkendall and Matano planes are marked by the vertical dotted lines (K and M respectively).



**Fig. 3.** Comparison of experimental (circles) and simulated (solid lines) diffusion profiles for: a) Ni-Au [20] and; b) Co-Fe-Ni system [21]. Values of used intrinsic diffusivities are presented in the right upper corner. The Kirkendall and Matano planes are marked by the vertical dotted lines (K and M respectively).

the literature data is presented in the Fig. 3. As it can be seen, for both investigated systems the quality of the fit is excellent and in the case of Co-Fe-Ni system the determined values of diffusion coefficients allow to describe the uphill effect present on Co concentration profile.

Of course the presented method also has certain limitations, although not nearly as restrictive as the currently used ones. The calculated values are heavily influenced by the precision of determination of Kirkendall plane position. Deviation of the 1 μm for the typical diffusion zone of hundreds of micrometers usually results in an error of ~5% for the diffusion coefficient values. The problems may also occur when one of the diffusion coefficients in the system is much smaller than the rest, as it may reduce the precision of calculations for this particular element. Another drawback is that the intrinsic diffusion coefficient values can be determined only at the Kirkendall plane, although as it was presented in the Fig. 3, it is not a problem for most of the systems. What is more, for a certain types of diffusion couples in which the diffusion coefficients can be treated as constant values (e.g. when the gradients of concentrations are relatively small [27]), the presented approach can easily serve as a method for estimation of their values.

To summarize, a new method for determination of intrinsic diffusion coefficients from the marker experiments was developed. The method bases on the key Darken postulate that the fluxes flowing through the moving Kirkendall plane do not depend from the drift velocity and the atomic transport is strictly dependent on the intrinsic diffusivities only. The method allows calculating the values of intrinsic diffusion coefficients at the position of Kirkendall plane for arbitrary number of components, even when the uphill diffusion effects occur. Obtained results can be also used to determine Onsager matrix of kinetic coefficients [17–19]. The proposed approach should be extremely useful for estimation of intrinsic diffusion coefficients in multicomponent systems, what considering the growing interest in diffusion studies of e.g. high-entropy alloys seems to be a high-priority topic.

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