Interdiffusion under the Chemical Potential Gradient; Comparison of Onsager and Darken Models

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Abstract. The generalized Darken method of interdiffusion in multicomponent systems (GDM) enables obtaining an exact expression for the evolution of component distributions for arbitrary initial distributions and time dependent boundary conditions. In this work we studied the consequences of the more general formulae for the diffusional flux (Planck's equation) which permits to take into account thermodynamical driving forces.

This paper is based on our studies of diffusion couples in the Cu-Fe-Ni system at 1273 K. The Cu-Fe-Ni system was chosen because it is a single phase in a wide range of compositions and because its thermodynamic properties are fairly well known. However, the solid solutions in this system are not ideal and consequently the diffusivities depend on composition. The driving force for the diffusion in such ternary system is the gradient of the chemical potential which can be calculated from the concentration profiles and using the known thermodynamical data of the system. Consequently the diffusional flux can be expressed as a function of the concentration gradients of all elements in the system, of the thermodynamical terms and of the mobilities. The diffusion paths are discussed in the light of the ternary interdiffusion coefficients and the self diffusivities with the use of generalized Darken method. A comparison of the Onsager and Darken models is presented. The results show the prospect for the future application of the GDM in the modelling of stress affected diffusion in ternary and higher solid solutions.

The generalized Darken’s method

A key problem in multicomponent diffusion is the prediction of the diffusion path between the two terminal alloys. For the predictive calculations, the data for the intrinsic diffusivities and/or self diffusion coefficients and their concentration dependence have to be known. Moreover the thermodynamic data for the system have to be known for the calculation of the chemical potentials for each component.

The generalised Darken method (GDM) allows a complete quantitative description of the complex diffusional transport process and for the unlimited number of elements. It allows calculation of the diffusion paths when the interdiffusion coefficients are concentration dependent. The details of this model for the closed system [1] and the more general description of interdiffusion that incorporates the equation of motion can be found elsewhere [2-3]. In this paper the formulation of the initial-boundary-value problem for the interdiffusion in a closed system is presented. It differs from that presented recently [4,5] with the expression for the mass flux.

Physical laws: 1) the law of the mass conservation of an i-th element:

\[
\frac{\partial c_i}{\partial t} = - \frac{\partial J_i}{\partial x} \quad (i=1,...,r).
\]
Following Darken drift flow idea we postulate that the flux of an $i$-th element is a sum of the diffusional flux and drift flux:

$$J_i = J_{id} + c_i v$$

(2)

2) *Postulate of the constant mixture concentration*, i.e., the equation of state, which tells that the sum of concentrations of all elements at any position and for every time is constant.

**Data**: 1) self diffusivities:$D_1^*, ..., D_r^*$, 2) activities of the components: $a_i = a_i(N_1, ..., N_r)$, where $N_i$ is the mole fraction of component $i$, 3) time of the process duration: $t^*$ and 4) initial conditions.

**Initial and boundary conditions**: 1) the initial positions of the left and right ends of the system: $\lambda_1(0) = -A_1, \lambda_2(0) = A_2$, where indices “1” and “2” denote the left and right end of the system; 2) the initial distribution of the elements $c_i(0, x) = \hat{c}_i(x)$; 3) fluxes of the components through the boundary are excluded – the system is closed: $(\hat{c}_1, \hat{v}_1)(t, \pm A) = 0$.

**Unknowns**: 1) the concentrations of all elements as a function of time and position $c_i(t, x)$ and the drift velocity $v_i(t, x)$.

In the original Darken’s treatment [6] and GDM [2] the diffusional flux was postulated to be a Fickian flow. Often, the more general formulae of diffusional flow can be transformed to Fick’s I law. In a multicomponent system the diffusional flux of the $i$-th element may be expressed by the phenomenological flux equation:

$$J_{id} = B_i c_i F_i,$$

(3)

where $B_i$ is mobility of the $i$-th component and $F_i$ denotes a local force, e.g. the gradient of the chemical potential ($F_i = -\partial \mu_i / \partial x$). The chemical potential of the $i$-th component is a function of $(r-1)$ independent mole fractions $\mu_i(N_1, ..., N_{r-1})$ and consequently its space derivative becomes:

$$\frac{\partial \mu_i}{\partial x} = \sum_{j=1}^{r-1} \frac{\partial \mu_j}{\partial N_j} \frac{\partial N_j}{\partial x}.$$

(4)

Using: 1) the Nernst-Einstein relation between the self diffusion and mobility and 2) the relation between the chemical potential and the activity, the diffusional flux (3) can be expressed:

$$J_{id} = -D_i^* \frac{c_i}{c} \sum_{j=1}^{r-1} \frac{\partial \ln a_j}{\partial N_j} \frac{\partial N_j}{\partial x} = -\sum_{j=1}^{r-1} D_y^* \frac{\partial c_j}{\partial x},$$

(5)

where $D_y^*$ is the interdiffusion coefficients:

$$D_y^* = D_i^* \frac{c_i}{c} \frac{\partial \ln a_i}{\partial N_i}.$$

(6)

When necessary thermodynamic data are available, the interdiffusion coefficients as a function of the concentrations can be evaluated.
The inverse method – calculations of the self diffusivities

Let \( c_i^*(D, x) \) be a solution of the GDM – the calculated concentration of the \( i \)-th component for the time \( t^* \), position \( x \) and for the \( D = (D_1, \ldots, D_r) \) – \( r \) parameters which define the self diffusivities \( D_i^* \). Let us define function \( \text{err} \), given by formula:

\[
\text{err} (D_1, \ldots, D_r) = \int_A \sum_{i=1}^{r} \left( c_i(x) - c_i^*(D, x) \right)^2 dx,
\]  

(7)

where \( c_i(x) \) is the experimentally determined concentration profile of the \( i \)-th element for the time \( t^* \). We are looking for such parameters \( D_1, \ldots, D_r \) that minimize function \( \text{err} \), eq. (7). Determined numbers approximate self diffusivities \( D_i^* \). A single diffusion annealing experiment at a fixed temperature at any time \( t^* \) allows calculation of the constant self diffusivities for the unrestricted number of elements in the system.

Interdiffusion in the Cu-Fe-Ni system

The diffusion couples investigated in the present work (Fe-Ni-Cu system at 1273 K) are shown in Table 1.

<table>
<thead>
<tr>
<th>Diffusion couple</th>
<th>Composition, wt %</th>
<th>Time, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td>14Ni-86Cu</td>
<td>75.9Ni-24.1Fe</td>
</tr>
<tr>
<td>V2</td>
<td>48Ni-52Cu</td>
<td>19.7Ni-80.3Fe</td>
</tr>
<tr>
<td>V3</td>
<td>58.1Ni-41.9Cu</td>
<td>75.9Ni-24.1Fe</td>
</tr>
<tr>
<td>V4</td>
<td>58.1Ni-41.9Cu</td>
<td>49.6Ni-50.4Fe</td>
</tr>
<tr>
<td>V5</td>
<td>58.1Ni-41.9Cu</td>
<td>Fe</td>
</tr>
<tr>
<td>V6</td>
<td>Cu</td>
<td>49.6Ni-50.4Fe</td>
</tr>
<tr>
<td>V7</td>
<td>48Ni-52Cu</td>
<td>49.6Ni-50.4Fe</td>
</tr>
<tr>
<td>V8</td>
<td>Cu</td>
<td>19.7Ni-80.3Fe</td>
</tr>
<tr>
<td>V9</td>
<td>33Ni-67Cu</td>
<td>49.6Ni-50.4Fe</td>
</tr>
<tr>
<td>V10</td>
<td>33Ni-67Cu</td>
<td>1Ni-99Fe</td>
</tr>
</tbody>
</table>

Table 1. Diffusion couple experiments in the Fe-Ni-Cu system at 1273 K.

Using equations (6) and (7) and the method described in the previous section, the self diffusivities and interdiffusion coefficients have been calculated. The computed self diffusivities are presented in Table 2 and graphically in Figure 1, where the diffusivities are plotted as a function of the concentration of copper*. The results presented here show agreement with those presented by van Loo et al. [7] in the Cu-Fe-Ni system and with values in the binary systems Fe-Ni [8] and Cu-Ni [9-12]. The activities in equation (6) are based on the calculated isoactivity curves by van Loo et al. [7]. As a general tendency, the mobility of each component increases as the copper content increases (Fig. 1). The difference in the mobilities in high-copper and low-copper alloys is about 1 order of magnitude.

When the self diffusivities are known, the diffusion paths can be predicted from the generalized Darken method. For calculations the following data were used: atomic masses of Fe, Ni and Cu, thickness of diffusional couple (1÷2 mm), constant alloy concentration \( c = 0.144 \text{ mol/cm}^3 \), activities of

* For calculations on the base of GDM the diffusion coefficients are plotted as a function of the average concentration of copper in the diffusion couple.
the components [7], annealing times and self diffusivities (Table 2). Self diffusivities have been computed from the experimentally measured concentrations of the all elements in the diffusion couple before and after diffusional annealing. In computations presented here we have assumed that the self diffusivities do not depend on the composition (are constant in the diffusion couple). One should note that such a simplification does not exclude composition dependent interdiffusivity – see eq. (6).

Table 2. The calculated self diffusivities of components in the Fe-Ni-Cu system at 1273 K.

<table>
<thead>
<tr>
<th>Symbol of diffusion couple</th>
<th>( D_{\text{Cu}}^* ) ( \times 10^{-14} )</th>
<th>( D_{\text{Fe}}^* ) ( \times 10^{-15} )</th>
<th>( D_{\text{Ni}}^* ) ( \times 10^{-15} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td>1.08 ( \times 10^{-14} )</td>
<td>2.43 ( \times 10^{-15} )</td>
<td>2.32 ( \times 10^{-15} )</td>
</tr>
<tr>
<td>V2</td>
<td>5.00 ( \times 10^{-15} )</td>
<td>2.39 ( \times 10^{-15} )</td>
<td>2.11 ( \times 10^{-15} )</td>
</tr>
<tr>
<td>V3</td>
<td>2.89 ( \times 10^{-15} )</td>
<td>1.52 ( \times 10^{-15} )</td>
<td>2.09 ( \times 10^{-15} )</td>
</tr>
<tr>
<td>V4</td>
<td>1.35 ( \times 10^{-15} )</td>
<td>4.60 ( \times 10^{-15} )</td>
<td>3.70 ( \times 10^{-15} )</td>
</tr>
<tr>
<td>V5</td>
<td>1.17 ( \times 10^{-15} )</td>
<td>1.91 ( \times 10^{-15} )</td>
<td>8.44 ( \times 10^{-16} )</td>
</tr>
<tr>
<td>V6</td>
<td>1.09 ( \times 10^{-14} )</td>
<td>2.42 ( \times 10^{-15} )</td>
<td>2.38 ( \times 10^{-15} )</td>
</tr>
<tr>
<td>V7</td>
<td>8.75 ( \times 10^{-16} )</td>
<td>1.60 ( \times 10^{-15} )</td>
<td>1.38 ( \times 10^{-15} )</td>
</tr>
<tr>
<td>V8</td>
<td>1.33 ( \times 10^{-14} )</td>
<td>8.25 ( \times 10^{-15} )</td>
<td>2.76 ( \times 10^{-15} )</td>
</tr>
<tr>
<td>V9</td>
<td>1.06 ( \times 10^{-14} )</td>
<td>2.42 ( \times 10^{-15} )</td>
<td>2.31 ( \times 10^{-15} )</td>
</tr>
<tr>
<td>V10</td>
<td>3.00 ( \times 10^{-15} )</td>
<td>2.37 ( \times 10^{-15} )</td>
<td>1.40 ( \times 10^{-15} )</td>
</tr>
</tbody>
</table>

Figure 1. The self diffusion coefficients as a function of the concentration of copper.

If one knows the diffusivities, it is possible to calculate the diffusion paths. Thus, concentrations of the components can be predicted from the GDM. Figure 2 shows diffusion paths for the selected diffusion couples. The experimentally measured and computed diffusion paths show good agreement.

When interdiffusion coefficients \( D_{\text{ij}}^* \) are known, the diffusion path can be expressed in terms of error functions [13-14]. Figure 3 shows comparison of the computed diffusion paths using the GDM and another models. In a case of the error function based solutions for the modelling of diffusion paths the constant interdiffusion coefficients were employed. In Figure 3 are shown: 1) The calculated diffusion path based on Dayananda model [13,15]. In this case the following interdiffusion coefficients calculated on the base of Boltzmann-Matano method were used:

\[
D_{\text{CA}}^* = 1.69 \times 10^{-15} \text{ m}^2\text{s}^{-1}, \\
D_{\text{CF}}^* = 1.41 \times 10^{-17} \text{ m}^2\text{s}^{-1},
\]
Figure 2. Comparison of experimental data and computed values on the base of GDM.

Figure 3. Comparison of computed diffusion paths on the base of GDM and another models, for diffusion couple V2.

The diffusion path calculated on the base of Morral-Thompson model [16]. In this case we have obtained the following interdiffusion coefficients:

\[ D_{\text{CuNi}}^{\text{NR}} = 1.5 \times 10^{-15} \text{ m}^2\text{s}^{-1}, \]
\[ D_{\text{FeNi}}^{\text{NR}} = 4.3 \times 10^{-16} \text{ m}^2\text{s}^{-1}, \]
\[ D_{\text{CuFe}}^{\text{NR}} = 2.75 \times 10^{-16} \text{ m}^2\text{s}^{-1}, \]
\[ D_{\text{FeNi}}^{\text{MR}} = 2.25 \times 10^{-15} \text{ m}^2\text{s}^{-1}. \]

3) The calculated diffusion path on the base of Dayananda model of average diffusivities [14]. For calculations of diffusion path two sets of constant interdiffusion coefficients were used, one set for each side of the Matano plane. These coefficients represent average values over the respective composition ranges along the diffusion path. For composition range \( c_i \in [c_i(-\infty), c_i(x_0)] \), where \( x_0 \) is the position of the Matano plane, we have obtained the following interdiffusion coefficients:

\[ \bar{D}_{\text{CuNi}}^{\text{NI}} = 5.83 \times 10^{-15} \text{ m}^2\text{s}^{-1}, \]
\[ \bar{D}_{\text{FeNi}}^{\text{NI}} = 1.37 \times 10^{-15} \text{ m}^2\text{s}^{-1}, \]
\[ \bar{D}_{\text{CuFe}}^{\text{NI}} = 9.22 \times 10^{-16} \text{ m}^2\text{s}^{-1}, \]
\[ \bar{D}_{\text{FeNi}}^{\text{NI}} = 9.11 \times 10^{-16} \text{ m}^2\text{s}^{-1} \]

and on the other side of the Matano plane, for composition range \( c_i \in [c_i(x_0), c_i(+\infty)] \):

\[ \bar{D}_{\text{CuNi}}^{\text{NI}} = 1.16 \times 10^{-15} \text{ m}^2\text{s}^{-1}, \]
\[ \bar{D}_{\text{FeNi}}^{\text{NI}} = 1.42 \times 10^{-16} \text{ m}^2\text{s}^{-1}, \]
\[ \bar{D}_{\text{CuFe}}^{\text{NI}} = 9.16 \times 10^{-16} \text{ m}^2\text{s}^{-1}, \]
\[ \bar{D}_{\text{FeNi}}^{\text{NI}} = 7.6 \times 10^{-16} \text{ m}^2\text{s}^{-1}. \]

4) The calculated profiles on the base of GDM (the self diffusion coefficients \( D^* \), are shown in Table 2).

The agreement between the calculated on the base of GDM and experimental diffusion paths is clearly visible. The satisfactory agreement was also obtained in the case of Dayananda model with average interdiffusion coefficients. Hence, the average values for the interdiffusion coefficients determined over concentrations on both sides of the Matano plane can be successfully employed in the error function solutions for Cu-Fe-Ni system. In the case of constant interdiffusion coefficients (Boltzmann-Matano analysis and Morral-Thompson model) the agreement between the experimental and calculated diffusion paths is not satisfactory.
Summary

The quantitative analysis of the transport in nonideal and multicomponent system requires a combined thermodynamic and kinetic approach. The gradients of the chemical potentials (or the gradients of the activities) of each component can be evaluated from experimental concentration profiles when the thermodynamic data of the system are known.

The generalized Darken method of interdiffusion allows a quantitative description of complex diffusional transport process for an unlimited number of elements. It allows to calculate the diffusion paths and other diffusion related effects when interdiffusion coefficients, intrinsic diffusivities and/or self diffusivities are concentration dependent. The equations describing the interdiffusion process in such a general case where the components’ diffusivities vary with composition were shown.

The diffusion paths are discussed with the use of the generalized Darken method. A comparison of the Onsager and Darken models shows the great potential of GDM in the future applications. Our results show the prospect for the GDM in the modelling of stress affected diffusion in multicomponent system using the more general formulae of the driving force for the diffusion: \( F_i = -\partial \mu_i / \partial x + \sigma \), where \( \sigma \) is a stress. This phenomenon deserves further studies.

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