THE CALCULATION OF BINARY CONCENTRATION PROFILES FROM DIFFUSION-COEFFICIENT AND LATTICE-CONSTANT DATA

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Abstract

A method is presented for calculating concentration profiles for the case that the diffusion coefficients and/or the partial molar volumes are concentration-dependent. With some numerical examples it is shown that even slight concentration dependencies in the partial volumes contribute substantially to the resulting profiles. The calculations are performed for the boundary conditions of the infinite diffusion couple. It is shown that the evaluation of diffusion coefficients by the classical Boltzmann–Matano analysis may cause considerable errors.

1. Introduction

It is well known that the classical Boltzmann–Matano analysis \(^{1,2}\)) for the evaluation of concentration-dependent diffusion coefficients can, in principle, be applied only to systems with constant partial molar volumes. Many attempts have been made to generalize this analysis for binary \(^{3-9}\)), and recently also for ternary \(^{10,11}\)) systems with partial volumes which depend on concentration.

On the other hand no attention has been paid to the question of the extent to which the concentration distributions resulting from a diffusion process are influenced by the actual variation of the molar volume (or lattice constant) nor to the question how such distributions can be calculated, the diffusion coefficient once being known. Because of the limited physical meaning of the chemical diffusion coefficients and their rather involved determination these nevertheless seem to be very reasonable questions. The main purpose of this article is to give a method for the calculation of concentration profiles in infinite diffusion couples and then to illustrate the influence of the molar volume by a few numerical examples. In addition, a derivation of the appropriate equations is given in a first appendix, a second one being devoted to the question of how the origin is to be defined in expanding or shrinking diffusion couples and to the meaning of the Matano planes in this context.
2. Basic equations and numerical procedure

Consider an infinite binary diffusion couple with concentrations $C_i^L$ at the left side and $C_i^R$ at the right side ($i = 1, 2$), the concentration jump at $t = 0$ being located at $x = x_0$. As will be shown in appendix A we then have the following general relationship between the diffusion coefficient $D(C_i)$ and the concentration distribution of component 1:

$$\frac{dC_i}{dt} = \frac{-1}{2D} \left\{ (1 - C_i \frac{V_i}{c_i^L}) \int \lambda \frac{dC_i}{c_i^L} + C_i \frac{V_i}{c_i^L} \int \lambda \frac{dC_i}{c_i^L} \right\},$$

with $V_i$ the partial molar volume of component $i$; this equation is essentially the same as that derived by Saue and Freise \(^3\)\(^-\)\(^5\), and reduces to the well-known Boltzmann-Matano equation \(^2\) when the partial molar volumes are constant. The concentrations are expressed in moles per unit volume, and are supposed to be functions of $x - x_0$.

The plane $x = x_0$ can be identified with the Matano plane (i) as is usual; when the partial molar volumes are constant this may be very satisfactory but when they are not, each component has its own Matano plane, whose location depends on time (and even on the concentration unit); see appendix B.

Therefore we prefer to fix the $x$-axis at the left end of the couple, so that the plane $x = x_0$ in (2) lies at a constant distance from this end (ii). It will be shown in appendix B that (i) and (ii) require the same assumption about the concentration distributions and that $x_0$ coincides with the welding interface at $t = 0$ so that it can be replaced by the coordinate $x_0$.

From eq. (1) it is obvious that the concentration distributions resulting from diffusion processes are influenced by the behaviour of the partial volumes in the concentration interval $C_i^L - C_i^R$. These volumes are related to the molar volume $V$ (which, in turn, is directly related to the lattice constants when the vacancy fraction is negligible) by

$$V_i = V + (1 - N_i) \frac{dV}{dN_i},$$

where $N_i$ denotes the atom fraction of component $i$.

What we want to show now is

(a) how to calculate diffusion profiles when the diffusion coefficient and molar volume are known, taking into account the non-constancy of the partial volumes;

(b) how these profiles are influenced by small changes in the lattice parameters at concentrations between those of the pure components (fig. 2);
(c) what values of the diffusion coefficients result from these profiles on applying the usual Boltzmann-Matano analysis, thus neglecting the volume effects.

2.1. Numerical procedure

Equation (1) is very well suited to elementary numerical procedures; we used a first-order predictor–corrector method \(^{13}\) in combination with the trapezoidal rule for the integrals. Writing for (1)

\[ C' = f(C, \lambda), \]

we find the predictor and corrector at the step \( \lambda_n \) to \( \lambda_{n+1} = \lambda_n + h \) to be

\[ C_{n+1}^* = C_n + hf(C_n, \lambda_n), \]

\[ C_{n+1} = C_n + \frac{h}{2} \left\{ f(C_n, \lambda_n) + f(C_{n+1}^*, \lambda_{n+1}) \right\}. \]

This simple procedure yields accurate results when the integration interval described below is divided in 2000–3000 steps; the use of more sophisticated methods, like the predictor–corrector method after Milne, in combination with Simpson's rule \(^{13}\) appears to be hardly profitable.

The main difficulty now consists in fitting the boundary conditions

\[ \lambda = -\infty, \quad C = C_L; \]
\[ \lambda = \infty, \quad C = C_R. \]

The solution for constant \( D \) and \( V_1 \) of (1) is, with \( \eta = \lambda / 2\sqrt{D} \) and \( b \) a constant:

\[ C = C_L + b (1 + \text{erf} \, \eta), \]

\[ \frac{dC}{d\lambda} = \frac{b}{(\pi D)^{1/2}} \exp (-\eta^2). \]

This is also a good approximation for the tails of the real solution, e.g. for \( |\eta| > 4 \) which can be easily verified by integration beyond these values: Thus we start at \( \eta = -4 \), that is \( \lambda = -8 \sqrt{D(C_L)} \), where \( C \) and \( C' \) are given by (7) with some arbitrary value of \( b \); boundary values of the integrals in (1) can be found from the value of \( C' \) since the partial volumes are practically constant in the region \( \eta < -4 \). After integration up to \( \eta = 4 \), that is \( \lambda = 8 \sqrt{D(C_R)} \) the curve is fitted to another tail after (7) yielding a value of \( C(\infty) \) which will generally deviate from the desired value \( C_R \).

Repeating this procedure and interpolating between the results at \( \eta = 4 \) in order to get better \( b \)-values, we always found a correct solution within 3–10 integrations. The reliability of the results has been tested in various ways: by
changing the integration interval, by changing the number of steps and by backward integration from the upper integration limit arrived at.

The input of diffusion coefficient and molar volume is accomplished by a least-square fitting of polynomials to the known data; it is convenient to introduce the molar volume as a function of $C_1$, being the independent variable in (1). The appropriate formulas for the partial volumes can be found from (3), noting that $N_1 = C_1 V$; then the diffusion coefficient can simply be introduced as a function of the atom fraction which is now known for any value of $C_1$.

3. Results and discussion

3.1. Calculated concentration profiles

Given the boundary conditions (6) and a hypothetical diffusion coefficient (fig. 1), concentration profiles have been calculated for a number of different molar volumes (fig. 2). Computations of this kind yield an indication about the magnitude of volume effects in binary diffusion and thus about the necessity of taking these into account. Of course the numerical method is also applicable to systems with constant molar volumes.

3.1.1. The molar volumes

The molar volumes (fig. 2) originate from hypothetical lattice parameters

$$ a = a_2 + N_1 (a_1 - a_2) + p N_1 (1 - N_1) $$

for f.c.c. systems with negligible vacancy fraction. The lattice parameters $a_1$ and $a_2$ of the pure elements are chosen to be 3.5 and 4.0414 kX, corresponding
Fig. 2. Linear molar volume (curve 0) and molar volumes from lattice constants after eq. (8) for f.c.c. systems; the values of p are ±0.147 and ±0.294.

to molar volumes of 6.5 and 10 cm³/mole, values close to the Au-Ni system. The parameter p in (8) has such values that maximum departures from linearity,

\[ \Delta = \frac{a - a_{1n}}{a_{1n}} \]  

(9)
of −2, −1, 0, 1 and 2% result, values which are often encountered in metallic systems and often exceeded in non-metallic ones. Finally, a molar volume has been added which is linear in the atom fraction so that the partial molar volumes are concentration-independent in this case.

3.1.2. Results obtained with a constant diffusion coefficient

The figs 3a and b show two effects originating from the non-constancy of the molar volume. First of all it is seen that the concentration differences resulting from slight variation in intermediate molar volumes are certainly observable, though not dramatically so; secondly it appears that the \( C_1-\lambda \) curves are fairly symmetrical (for this constant \( D \)) while the \( N_1-\lambda \) curves appear to be less influenced by the differences in intermediate molar volumes. It seems noteworthy that asymmetrical atom fraction profiles result even for constant diffusion coefficient and constant (but unequal) partial volumes; it therefore seems to be a matter of taste as to what concentration unit should be used for the representation of diffusion results: mole fraction or molar concentration.

3.1.3. Other results

Calculations have also been performed with diffusion coefficients given by
Fig. 3. Molar-concentration and atom-fraction distributions for the constant diffusion coefficient in combination with the molar volumes of fig. 3.

\[ D = D_2 + N_1 (D_1 - D_2) + N_1 (1 - N_1) (q_0 + q_1 N_1 + q_2 N_1^2) \]  

(10)

The numerical procedure described above remains very satisfactory even when the diffusion coefficients vary over one or more decades, although fitting the boundary conditions takes more preliminary integrations as the diffusion coefficient varies more drastically. The magnitude of the volume effects is hardly affected by the shape of the diffusion coefficient; fig. 4 may serve as an example for this. Similar results were obtained with other lattice constants and smaller concentration gaps.

3.2. Diffusion coefficients obtained from the classical Boltzmann–Matano analysis

It seemed interesting to see what diffusion coefficients result from the calculated profiles on applying the classical Boltzmann–Matano analysis, thus
Fig. 4. Concentration profiles for the variable diffusion coefficient; the concentrations on the horizontal lines are those of the pure components, both on the atom-fraction and on the molar-concentration scale.

Fig. 5. Matano coefficients from the concentration profiles of components 1 and 2 for the linear lattice parameter.

neglecting the volume effects. An estimate of the resulting errors has been given by Sauer and Freise 3). Errors in the diffusion coefficients up to 15% were observed on applying this analysis to the concentration profiles shown in figs 3 and 4. In fig. 5 it is shown that even for the nearly linear molar volume, obtained from the linear lattice constant these errors are not yet wholly negligible and that the coefficients obtained from the profiles of the two components are not equal. Of course the errors diminish with the total concentration difference 3); therefore the values reported here can be considered as upper limits for the majority of all metallic systems.

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Appendix A

Derivation of eq. (1)

The main difficulty in deriving the appropriate equations arises from the fact that Fick's first law is not valid for the fluxes \( (J_i)_x \) through planes situated at constant values of \( x \) when the partial molar volumes depend on concentration \(^{14}\). Unfortunately it is these fluxes we have to use in the accumulation equation

\[
\left( \frac{\partial C_i}{\partial t} \right)_x = - \frac{\partial (J_i)_x}{\partial x}, \quad i = 1, 2. \tag{A1}
\]

We therefore have to reduce these fluxes to those in another reference frame; the volume-fixed frame \( v \), defined by \(^{14}\)

\[
V_1 (J_1)_v + V_2 (J_2)_v = 0, \tag{A2}
\]

is very appropriate. With the aid of the general thermodynamic relations

\[
V_1 C_1 + V_2 C_2 = 1 \tag{A3}
\]

and

\[
V_1 \, dC_1 + V_2 \, dC_2 = 0 \tag{A4}
\]

it follows that the partial diffusion coefficients

\[
(D_i)_v = (J_i)_v \left/ \frac{\partial C_i}{\partial x} \right. \tag{A5}
\]

are equal to each other and to the chemical diffusion coefficient, defined by \(^{15,7}\)

\[
D = C_1 \, V_1 (D_2)_v + C_2 \, V_2 (D_1)_v. \tag{A6}
\]

We therefore have for both components

\[
(J_i)_x = -D \frac{\partial C_i}{\partial x} + U_v \, C_i \tag{A7}
\]

and after substitution in (A1)

\[
\left( \frac{\partial C_i}{\partial t} \right)_x = \frac{\partial}{\partial x} \left( D \frac{\partial C_i}{\partial x} - U_v \, C_i \right), \tag{A8}
\]

where \( U_v \) denotes the velocity of the volume-fixed reference planes, the mean volume velocity, still relative to the left end of the couple.

Summation of the eqs (A8) after multiplication by \( V_i \) yields \(^{14}\) with the aid of (A3) and (A4) and after conversion to \( \lambda \) (eq. (2)):
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\[ U_v \sqrt{t} = g(\lambda) = \int_{-\infty}^{\lambda} \sum V_i \frac{d}{d\lambda} \left[ D \frac{dC_i}{d\lambda} \right] d\lambda, \quad (A9) \]

where use is also made of the fact that \( U_v \) vanishes at the left end of the couple since both \( (J_i)_x \) and the concentration gradients in (A7) vanish. With the boundary conditions (6) it follows from (A8) and (A9) that

\[ \frac{1}{2} \int \lambda \, dC_i = -D \frac{dC_i}{d\lambda} + C_i \, g(\lambda), \quad i = 1, 2. \quad (A10) \]

The elimination of \( g \) from eq. (A10) yields (1) where (A3) and (A4) have been used for eliminating \( C_2 \).

Appendix B

The origin of the x-axes in expanding diffusion couples

At the right end of a couple where the concentration gradients vanish, the mean volume velocity (see app. A) equals the velocity with which the couple expands or shrinks, so that it is implicitly assumed that the total length varies proportionally to \( \sqrt{t} \) (A9):

\[ l = l_0 + \int_0^t U_v(\infty, t) \, dt = l_0 + 2 \, g(\infty) \sqrt{t}. \quad (B1) \]

The Matano plane \( x_i^M \) of component \( i \) is usually defined by

\[ \int \frac{c_i^R}{c_i^L} (x - x_i^M) \, dC_i = 0. \quad (B2) \]

Performing the integration in (A10) up to \( C_i^R \) for a fixed time \( t \) yields

\[ \int \frac{c_i^R}{c_i^L} (x - x_o) \, dC_i = 2 \, C_i^R \, g(\infty) \sqrt{t}. \quad (B3) \]

Subtraction of (B2) from (B3) yields

\[ (x_i^M - x_o) = 2 \, g(\infty) \sqrt{t} \frac{C_i^R}{C_i^R - C_i^L}, \quad (B4) \]

so that the assumption that the concentrations are functions of

\[ \lambda = \frac{x - x_o}{\sqrt{t}} \quad (B5) \]

implies that the displacements of Matano planes relative to \( x_o \) (and thus to
the left end of the couple) are proportional to $\sqrt{t}$ and are therefore located at constant values of $\lambda$. Hence the assumption that $C_i = C_i(\lambda)$ implies that the concentrations are also functions of

$$\lambda_i = \frac{x - x_i^M}{\sqrt{t}} = \lambda + \text{const.},$$  
(B6)

as stated in sec. 2. Applying (B4) with $C_i^R = 0$ shows that the Matano plane of a component which was absent in the right half of the couple at $t = 0$ remains at $x = x_0$ for all $t$. From the boundary conditions and the application of (B3) for $t = 0$ it is seen that the plane $x = x_0$ in (B5) coincides with the plane where the concentration jump occurs at $t = 0$, so that the coordinates $x_0^1$ in (2) and $x_0$ are indeed identical. Finally, it must be noted that there is no asymmetry in this analysis; from (B1) it is obvious that the $x$-axes could have been fixed to the right end of the couple as well 3).

REFERENCES

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