

A Model for the Prediction of Reaction Diffusion Paths in Multicomponent Systems with Limited Solubility

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A numerical method to compute the reaction diffusion process in multicomponent systems exhibiting limited solubility in their compounds has been developed. The method combines a description of local thermodynamic equilibrium at the moving interfaces with a phenomenological description of the diffusion process in every phase, taking their specific solubility features into account. There is no formal restrictions on the number of components or phases. The algorithm software can be used for the systematic study of the influence of different system variables such as free energies of formation and mobilities on the stable diffusion path, as well as for the prediction of the actual diffusion path in technologically important contacts. As an example calculations in a hypothetical ternary system are shown.

(Received July 4, 2001; Accepted October 30, 2001)

Keywords: solid state reaction, diffusion path, compound formation, multicomponent systems, model

1. Introduction

In technological applications contacts between chemically incompatible materials are often encountered. Examples are mutual contacts between metals, semiconductors and insulators in electronic devices,¹⁻³⁾ or combinations of a variety of materials in composite structures.⁴⁻⁶⁾ If no thermodynamic equilibrium prevails in the initial contact, a combination of chemical reactions and mutual diffusion usually leads to the build-up of a sequence of new phases. In many cases, the homogeneity range of the compounds involved is small. The knowledge of the final phase sequence, which can be represented by a diffusion path on the isothermal section in the corresponding phase diagram, is of crucial importance for the evaluation of the material combination's applicability.

If the contacted materials belong to a binary system, the stable diffusion path can be directly deduced from the isothermal section of the corresponding phase diagram. However, for higher order systems this is not the case.⁷⁾ Out of the infinite number of plausible diffusion paths, only one is stable.⁸⁾ The stable phase sequence is dictated by the thermodynamic as well as the kinetic properties of the phases involved. Up to now, a general theoretical method to calculate the stable phase sequence is not known. The available empirical methods for predicting stable diffusion paths, like the method of Van Loo *et al.*,⁹⁾ are only applicable to specific cases. As a consequence, a systematic experimental verification of the chemical interactions in the contact is still necessary.

The numerical treatment of diffusion phenomena in multicomponent alloys is rather well established.¹⁰⁾ Software tools, such as DICTRA,¹¹⁾ can be used for the numerical simulation of boundary movement and the calculation of concentration profiles. The simulations are based on the solution of mass flux equations

$$J_i = - \sum_j D_{ij} \nabla C_j, \quad (1)$$

where J_i is the mass flux of component i in $\text{g}\cdot\text{at}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. D_{ij} is a so-called intrinsic diffusion coefficient and C_j is the concentration of component j in $\text{g}\cdot\text{at}\cdot\text{m}^{-3}$. The diffusion coefficients contain partial derivatives of the chemical potentials with respect to the concentrations (see *e.g.*¹²⁾). For nearly stoichiometric compounds, the multiplication of a very low concentration gradient (∇C_j) with an accordingly high value for these partial derivatives creates a numerically unstable situation. Therefore, the presently available numerical treatments of diffusion problems are not suitable for the systems discussed in this paper. Moreover, the concentration dependence of the chemical potentials remains unknown for most of these compounds, due to difficulties in thermodynamic modelling.¹³⁾ Therefore, the real driving force for diffusion, which is the gradient of the chemical potential, should be used for compounds with limited solubility instead of the concentration gradient.

Recently Lee¹⁴⁾ has developed a simulation software for multicomponent and multi-layered phase diffusion. His method is also based on the calculation of concentration profiles and the formation of a new phase at an interface is deduced from the evaluation of the highest driving force of formation, a concept which is also used in prediction of the first reaction compound in thin film systems.¹⁵⁾

In this study, a calculation method is presented for the prediction of stable diffusion paths in multicomponent systems. The method is valid when

- the homogeneity range of the phases involved is restricted to a few at%,
- the process is diffusion controlled; thermodynamic equilibrium is established locally at the interfaces
- the thickness of the contacted materials is large enough to exclude specific thin-film effects and the interfaces exhibit planar morphology,
- and single phase fields occur in the stable diffusion paths.

The method nevertheless can be used to study reaction diffusion processes in systems of practical importance¹⁶⁾ and allows to predict precipitation or the appearance of a peri-

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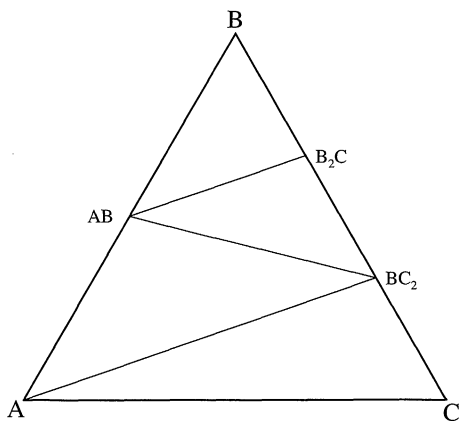


Fig. 1 Isothermal section of a hypothetical A-B-C system. Several diffusion paths can be considered belonging to the A|B₂C contact. They can be represented on the isothermal section as a series of tie-lines connecting A with B₂C.

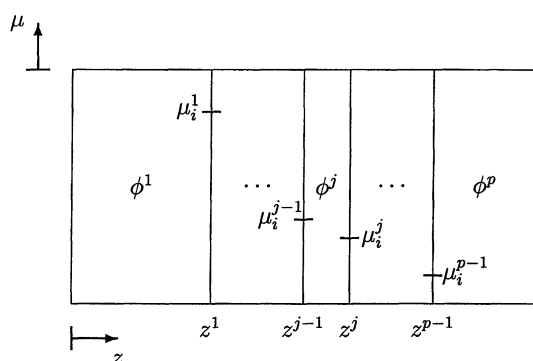


Fig. 2 Schematic representation of the modelled reaction diffusion process in a contact between two materials that belong to a c component system ($i = 1, 2, \dots, c$), resulting in a sequence of p phases and $(p - 1)$ corresponding interfaces.

odic phase structure.¹⁷⁾ Here the calculation method is applied to a contact A|B₂C in the hypothetical A-B-C system, an isothermal section of which is represented in Fig. 1. Several diffusion paths can be considered, like *e.g.* the paths A|AB|BC₂|B₂C and A|BC₂|AB|B₂C. It will be shown that the stable diffusion path may be calculated when certain thermodynamic and kinetic parameters are known or can be estimated.

2. Flux Equations

Figure 2 is a schematic representation of the reaction diffusion process and the variables used in its modelling. The original contact is made between the end phases ϕ^1 and ϕ^p that belong to a c -component system. During reaction diffusion a sequence of p phases ϕ^j ($j = 1, 2, \dots, p$) is formed, leading to $(p - 1)$ planar interfaces. The position of each interface j ($j = 1, 2, \dots, p - 1$) is characterised by its coordinate z^j . The chemical potentials μ_i^j define the thermodynamic properties of the components i ($i = 1, 2, \dots, c$) at each interface j ($j = 1, 2, \dots, p - 1$).

In each phase, an expression for the flux is needed for every component. The same nomenclature as in Fig. 2 will be used throughout the text: subscripts refer to components, superscripts to phases or the interfaces between them.

2.1 Flux equations in the Kirkendall reference frame

Onsager¹⁸⁾ has derived a general phenomenological equation

$$J_i^j = \sum_{k=1}^c L_{ik}^j \nabla(-\mu_k^j) \quad (i = 1, 2, \dots, c; j = 1, 2, \dots, p) \quad (2)$$

that relates the mass fluxes in an isothermal isobaric system to the gradients of the chemical potentials, which are the driving forces for diffusion. The L_{ik} are the so-called phenomenological coefficients. In non-ionic systems, this equation may be simplified (see *e.g.*¹²⁾) if the fluxes are expressed in the Kirkendall reference frame, which is attached to a fixed lattice site, so that

$$(J_i^j)_K = -(L_{ii}^j)_K \nabla \mu_i^j \quad (3)$$

with

$$(L_{ii}^j)_K = M_i^j C_i^j = \frac{M_i^j x_i^j}{V^j} \quad (4)$$

M denoting the mobility of the component in $\text{m g-at} (\text{N s})^{-1}$, x its mole fraction and V the molar volume in the specified phase in $\text{m}^3 (\text{g-at})^{-1}$, which is assumed to be equal for all components in a phase by the model. In ionic systems, interaction coefficients L_{ik} ($i \neq k$) arise through the correlated movement of charged species in order to preserve electroneutrality, as shown by Kirkaldy *et al.*¹⁴⁾ Even in non-ionic systems, eq. (3) is not entirely correct. Manning^{19,20)} demonstrated that cross-effects also occur due to the correlated movement of vacancies through the lattice. From a practical point of view of predicting diffusion paths, we can neglect these effects and still calculate accurate results compared to experimental reproducibility.¹²⁾

Equation (3) can be applied for expressing the fluxes in the intermediate phases ϕ^j ($j = 2, 3, \dots, p - 1$). In the case of nearly stoichiometric compounds (C_i^j and x_i^j practically constant), it follows from Fick's second law that

$$\frac{\partial C_i^j}{\partial t} = -\nabla J_i^j \approx 0. \quad (5)$$

Therefore, the flux of each component can be assumed to be constant within each intermediate phase. Using an averaged mobility, defined as

$$M_i^j = \frac{\int_{z^{j-1}}^{z^j} M_i d\mu_i}{\mu_i^j - \mu_i^{j-1}} \quad (6)$$

eq. (3) may be rearranged to

$$(J_i^j)_K = -(L_{ii}^j)_K \frac{\Delta \mu_i}{\Delta z} \bigg|_{j-1}^j = -(L_{ii}^j)_K \frac{\mu_i^j - \mu_i^{j-1}}{z^j - z^{j-1}} \quad (j = 2, 3, \dots, p - 1). \quad (7)$$

The fluxes in the intermediate phases can thus be described as a function of the position and the respective chemical potentials at the interfaces.

Equation (7) is not applicable to the end phases ϕ^1 and ϕ^p , since they are only bounded by one interface in the contact. Hence, another approach should be used for expressing the fluxes. Considering that their layer thickness is substantial

in bulk diffusion couples, diffusion in the end phases can be assumed to behave as in a half-infinite diffusion couple. Further assuming that the concentrations at the interface (1 and $p - 1$) are kept constant, eq. (5) yields a differential equation that can be solved analytically if the diffusion coefficients are constant. This is the case in composition regions where the activity of component i is linear with respect to its mole fraction, *i.e.* for Henrian or Raoultian behaviour. For a solution Ref. 21) may be consulted. Expressions for the fluxes in the end phases ϕ^1 and ϕ^p , valid at the interfaces 1 and $(p - 1)$ can also be derived.²¹⁾

$$(J_i^1)_K = \sqrt{\frac{M_i^1 RT}{pt}} \frac{1}{V^1} (x_i^{-\infty} - x_i^1) \quad (8)$$

$$(J_i^p)_K = \sqrt{\frac{M_i^p RT}{pt}} \frac{1}{V^p} (x_i^p - x_i^\infty). \quad (9)$$

where the mole fractions at infinity are equal to 0 for minority elements (*e.g.* for a phase AB in the system A-B-C, C would be a minority element) in the end phase, or equal to 1 when the end phase is a pure component.

A similar solution procedure can be developed for the case where Henrian or Raoultian behaviour is not observed ($0 < x_i^j < 1$) (see Appendix A). The resulting flux equations then are

$$(J_i^1)_K = \sqrt{\frac{M_i^1}{\pi RT t}} \frac{x_i^1}{V^1} (\mu_i^{-\infty} - \mu_i^1) \quad (10)$$

$$(J_i^p)_K = \sqrt{\frac{M_i^p}{\pi RT t}} \frac{x_i^p}{V^p} (\mu_i^p - \mu_i^\infty) \quad (11)$$

where the chemical potentials at infinity correspond to the state of i in the 'pure' end material. The determination of their values is discussed in Section 4 of this paper. Equations (10) and (11) are again only valid at the interfaces 1 and $(p - 1)$.

2.2 Recalculation of the flux equations to a general fixed reference frame

Relations (7), (8) to (11) define all fluxes (see Fig. 2) as expressed in the Kirkendall reference frame. As the position and movement of this frame depend on the relative values of the respective mobilities, a different Kirkendall reference frame generally exists in every participating phase. As a consequence, a recalculation to a general fixed reference frame is needed, in order to relate fluxes in different phases with one another. The first step in the recalculation involves the expression of the flux equations in a volume-fixed reference frame, which, contrary to the Kirkendall reference frame, can be defined on a macroscopic level. In the case of equal partial molar volumes of all components within a phase, this frame is equal to the number-fixed reference frame, and is defined by

$$\sum_i (J_i^j)_V = 0 \quad (12)$$

in each phase j . Appropriate recalculation formulae that relate the fluxes in the volume-fixed frame to the fluxes in the Kirkendall reference frame are available in literature (see for

example¹²⁾). The general relation is

$$(J_i^j)_V = \sum_{k=1}^c (\delta_{ik} - x_k^j) (J_k^j)_K \quad (13)$$

where δ_{ik} denotes the Kronecker-delta. The recalculation of the fluxes induces cross-effects that give rise to cross-coefficients L_{ik} in eq. (2).

Still, if the phases occurring in the reaction diffusion process have different integral molar volumes, each of them will have its own volume-fixed reference frame. Therefore the total volume of the diffusion couple usually alters during the reaction diffusion process: the sample expands or shrinks.²²⁾ The difference in integral molar volumes induces a bulk velocity v_B^j in each phase j . The bulk velocities of neighbouring phases can be related through mass balance requirements at the interface between them:

$$\frac{1}{V^{j+1}} v_B^{j+1} = \frac{1}{V^j} v_B^j + \left(\frac{1}{V^{j+1}} - \frac{1}{V^j} \right) \frac{\partial z^j}{\partial t} \quad (j = 1, 2, \dots, p - 1). \quad (14)$$

In our model, a general fixed reference frame is arbitrarily chosen to be attached to the left edge of the contact, as indicated in Fig. 2. A recalculation of the fluxes between the volume-fixed reference frame and the general (laboratory-fixed) reference frame 'L' is now possible by making use of the bulk velocities. These can be obtained for all phases through eq. (14), knowing that v_B^1 is equal to zero in the presently chosen frame. The resulting relation is

$$(J_i^j)_L = (J_i^j)_V + \frac{x_i^j}{V^j} v_B^j. \quad (15)$$

After recalculating the fluxes in eqns. (7), and (8) to (11) by means of (13) and (15), new flux expressions are obtained having the same reference frame. The total number of variables in these expressions is $(c + 1)(p - 1)$, consisting of $(p - 1)$ interface co-ordinates and $c(p - 1)$ chemical potentials. The remaining quantities in the flux equations can be regarded as parameters (*cfr.* Section 4).

3. Interface Conditions

Two types of relations exist between the $(c + 1)(p - 1)$ variables at the interfaces. Local thermodynamic equilibrium imposes a set of $(p - 1)$ double conditions on the chemical potentials, one at either side of each interface:

$$\sum_{i=1}^c x_i^j \mu_i^j = \Delta G_f^0(\phi^j) \quad (j = 1, 2, \dots, p - 1) \quad (16)$$

where ΔG_f^0 denotes the Gibbs energy of formation of the specified phase, using the same reference states as for the corresponding chemical potentials.

As for the relation between the bulk velocities in Section 2.2, the mass balance requirement additionally applies for the individual fluxes at both sides of every interface. Therefore, the fluxes have to be expressed in the

same reference frame, being the general fixed frame defined by eq. (15). Conservation of mass yields the following set of relations

$$(J_i^{j+1})_L - (J_i^j)_L = (C_i^{j+1} - C_i^j) \frac{\partial z^j}{\partial t} \quad (i = 1, 2, \dots, c-1; j = 1, 2, \dots, p-1) \quad (17)$$

Only $(c-1)$ independent relations of this type exist at every interface, since the fluxes within each phase are interrelated through eq. (13). Expressions (16) and (17) define a set of $(c+1)(p-1)$ equations in $(c+1)(p-1)$ variables, thus allowing the calculation of a solution for the presently modelled problem.

4. Parameters

Values for the parameters that occur in the equations (the Gibbs energy of formation, the molar volume and the composition of each phase, the chemical potentials of the components forming the pure compounds in the end phases, and the mobilities of the elements in every phase) are required to solve the equations.

Data regarding the Gibbs energies of formation of the compounds are required for the calculation of the isothermal section and to calculate local thermodynamic equilibrium at every interface. If available, literature values can be used. If not, a set of consistent Gibbs energies can be obtained by thermodynamic optimisation of the system using the Calphad approach.^{13,23)} Since the systems which are studied in this work exhibit limited solubility, simple temperature dependent expressions can be adopted for the Gibbs energy of formation,¹³⁾

$$\Delta G_f^0(\phi^j) = A^j + B^j T. \quad (18)$$

If solubility is neglected, an isothermal section in a c -component system is completely filled with c -phase equilibria, as illustrated in Fig. 1. This feature considerably simplifies the calculation of isothermal sections. A new algorithm for the calculation of isothermal sections of any complexity, if the solubility is neglected, has been proposed.²⁴⁾ The need for accurate Gibbs energy descriptions is twofold. Firstly, they are used in the calculation of isothermal sections, which reveal the plausible diffusion paths connecting the end phases in the contact. Referring to the isothermal section in Fig. 1, nine theoretical diffusion paths can be defined for the A|B₂C contact, involving three to six phases (*e.g.* A|AB|B₂C, A|AB|BC₂|B₂C or A|C|BC₂|AB|B|B₂C).

Secondly, the optimised Gibbs energy values are used in the reaction diffusion model to express the conditions of local thermodynamic equilibrium at the interfaces.

For most of the compounds, approximate molar volumes can be calculated using crystallographic data on the dimensions of the unit cell at room temperature.²⁵⁾ If no such data are available, usually an estimation can be made based on the molar volumes of the pure components or those of the compounds having the nearest stoichiometry.

Concerning the composition of the phases, distinction must be made between the thermodynamic and the kinetic calculations. While expressing thermodynamic equilibrium as in

eq. (16), the mole fractions corresponding to the pure compounds can be directly used, since the Gibbs energy values in the equation refer as well to the pure state. In the calculation of the diffusion process, however, the fluxes of minority elements can play an important role and should be included. Therefore their mole fractions should be known in the eqns. (7), (8) and (9). In a steady-state situation, which is the present case, it is assumed that the maximum solubility is reached for each minority element in every phase. The mole fractions of the other components are therefore recalculated using the following approximation,

$$x_i^j \rightarrow x_i^j (1 - \sum_k x_k^j) \quad (j = 1, 2, \dots, p) \quad (19)$$

with k for the minority elements and i for the other components. In the eqns. (10) and (11), the chemical potentials at the outer edge of the end materials are needed. The compounds are assumed to be pure at the edge, and the chemical potentials are accordingly approximated by the average value of the chemical potentials in all c -component phase equilibria involving the compound in the isothermal section of the phase diagram. Referring to Fig. 1, the chemical potentials of A and B in pure AB are thus approximated by taking the average of the respective values in the equilibria A-AB-BC₂, AB-B₂C-BC₂ and AB-B-B₂C. Although this choice may seem arbitrary, it corresponds to an average position in the stability field of the phase.

In the case of multicomponent diffusion processes, very little data on mobility are available. Therefore, an estimation of the respective mobilities is usually required. As shown in another paper,¹⁶⁾ approximate mobility values can also be generated by simulating experimentally determined diffusion paths by using the solution method.

5. Mathematical Solution

The solution of a general diffusion problem involves the substitution of the flux eqns. (1) in the time-dependent mass balance eqns. (5), leading to a set of differential eqns. that require numerical solving. In the present paper, a steady-state situation is calculated, having constant fluxes throughout each phase and constant chemical potentials at the interfaces. From the flux eqns. (7) and (8) to (11), as well as the mass balance requirement (17), the classical time-dependence of steady-state diffusive growth can be deduced, as

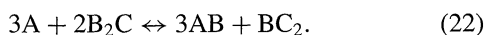
$$z^j \sim \sqrt{t} \quad (20)$$

$$J_i^j \sim \frac{1}{\sqrt{t}}. \quad (21)$$

These relations lead to the possibility of eliminating t in eq. (17), hence replacing the differential by a plain term in z^j . As a consequence, the set of $(c+1)(p-1)$ equations in $(c+1)(p-1)$ variables, as defined by the eqns. (16) and (17), becomes free of differentials and partly non-linear.

Still, no general method exists that guarantees obtaining one or more solutions for such a set of equations. However, since the present set contains several linear equations, solutions can be obtained rather easily. In this study, the Newton-Raphson iteration technique for solving a set of non-

linear equations has been applied.²⁵⁾ The convergence of this method is highly dependent on the starting values for the unknown variables. Therefore, a simplified linear version of the set of eqns. (16) and (17) is used to generate a suitable set of starting values. In this approach, the mass balance requirement is approximated by considering the global chemical reaction in the contact. Referring to Fig. 1, starting values for interface velocities in the phase sequence A|AB|BC₂|B₂C would thus be generated that reproduce the relative volume changes, dictated by the global chemical reaction



Based on these values, a series of appropriate starting sets is constructed in order to find all solutions.

6. Stability Criteria

The set of non-linear equations discussed above usually leads to multiple solutions. Moreover, solutions are calculated for each possible diffusion path according to the isothermal section. Hence, many mathematical solutions are obtained for the unknowns. As discussed in the introduction, only one of these will occur in practice. This stable solution has to meet certain requirements, which are twofold in the steady-state situation. The first criterion is physical and straightforward. A calculated solution is physically possible if all phases, except the original starting materials, grow as a function of time. Therefore, the criterion for physical feasibility becomes

$$z^{j+1} - z^j > 0 \quad (j = 1, 2, \dots, p-2) \quad (23)$$

with the co-ordinates expressed in the general fixed frame, as indicated in Fig. 2. However, a solution that is physically possible can still not occur in practice due to the chemical instability of one or more interfaces. An interface is chemically stable if the values of the chemical potentials lie in a range where none of the phases, that form a stable phase equilibrium in the isothermal section with those actually present at the interface, are thermodynamically stable. As an example, the interface BC₂|AB can be considered in the A|BC₂|AB|B₂C diffusion path on Fig. 1. If for instance the calculated chemical potential of A at this interface is positive, pure A is thermodynamically stable and will ultimately form between BC₂ and AB, hence altering the diffusion path. A similar reasoning applies for the possible stability of B₂C. Mathematically, the following condition must be fulfilled:

$$\sum_{i=1}^c x_i^k \mu_i^j < \Delta G_f^0(\phi^k) \quad (j = 1, 2, \dots, p-1) \quad (24)$$

where k stand for all the values for which ϕ^k forms a stable phase equilibrium with ϕ^j and ϕ^{j+1} .

If both criteria (23) and (24) are satisfied, the stable diffusion path has been obtained. Solutions that are physically possible, but do not meet the second criterion, are still relevant for the interpretation of the stable diffusion path. They can indicate the occurrence of a precipitation if the same phase becomes stable at two consecutive interfaces, or of a periodic layered structure in the diffusion path, as is discussed in a subsequent paper.¹⁷⁾

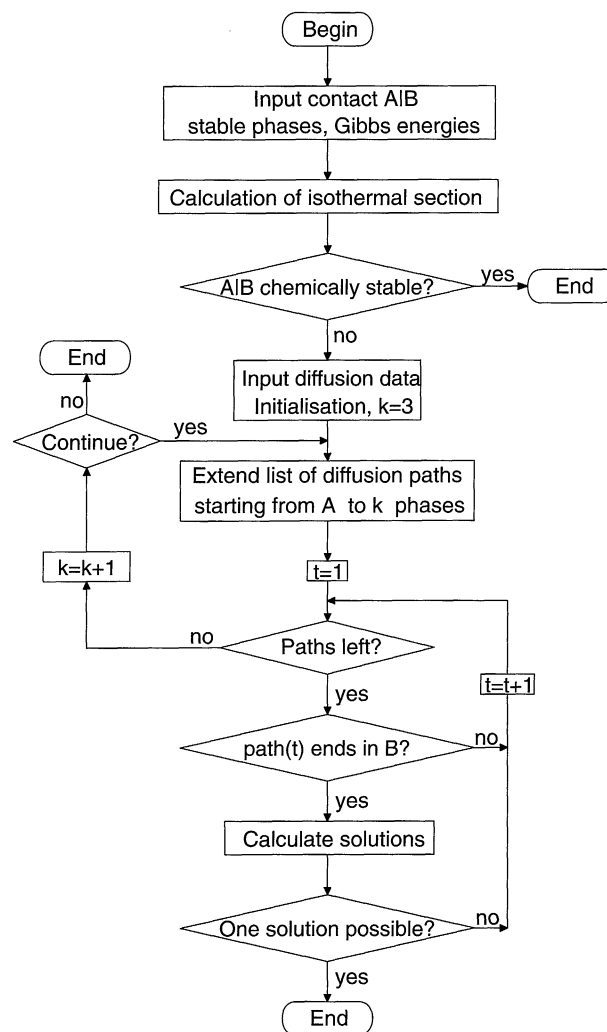


Fig. 3 Flow chart of the general algorithm for the prediction of stable diffusion paths in multicomponent systems with limited solubility. k and t are counters, respectively denoting the number of phases in the investigated diffusion paths and the number of the actually investigated path.

7. Algorithm

The flow chart of the general algorithm for predicting stable diffusion paths is given in Fig. 3. First, the thermodynamic description of the system is set up by calculating the isothermal section, based on the optimised Gibbs energies of all stable phases as input parameters. The actual calculation of the isothermal section is performed by a separate algorithm.²⁴⁾ If the contacted materials are chemically incompatible, the diffusion path calculation proceeds in a recursive way. Starting with a k -value of three, the plausible diffusion paths involving k phases connecting both end materials are identified from the isothermal section. For these diffusion paths, solutions are calculated and evaluated using the new reaction diffusion model. Several attempts are made for finding different solutions. For each attempt a different set of starting values is used. If no stable solution is found, the list of diffusion paths is renewed by extending the previously listed paths with one more phase ($k \rightarrow k+1$). Calculations are repeated for the new set of diffusion paths. The algorithm terminates if the stable diffusion path has been found, or if no diffusion paths involving a higher number of phases are left. The user may

	A	AB	BC ₂	B ₂ C
$v(rel)$		-12.78	12.89	19.45
$\mu(A)$	0.000		-663	-1338
$\mu(B)$	-2000		-1337	-1000
$\mu(C)$	-3476		-832	-1000
$v(bulk)$	0.000	0.000	0.000	0.000
$J(A)$	0.103	6.48	0.051	0.051
$J(B)$	0.051	-6.42	-8.57	-2.09
$J(C)$	-0.051	-0.051	8.52	2.04

Fig. 4 Calculated stable diffusion path for the A|B₂C contact in the A-B-C system of Fig. 1. Input data are $-1000 \text{ J (g-at)}^{-1}$ for the Gibbs energy of formation of every compound, $10^{-18} \text{ m s (N g-at)}^{-1}$ for every mobility and $10^{-5} \text{ m}^3 \text{ (g-at)}^{-1}$ for all molar volumes. The maximum solubility of all minority elements is 0.1 at%. The values for v are in $10^{-9} \sqrt{t} \text{ m s}^{-1}$; for μ in J/mole and for J in $10^{-4}/\sqrt{t} \text{ mole (m}^2 \cdot \text{s)}^{-1}$.

interrupt the calculations if he considers the number of phases in the calculated paths to become too high.

8. Example

A typical output from the program is given in Fig. 4 for the A|B₂C contact in the system shown in Fig. 1. The output consists of a schematic drawing of the stable phase sequence. The interface velocities and the chemical potentials at the interfaces are given, followed by the bulk velocity and the fluxes in all phases, expressed in a general fixed reference frame that is attached to the left edge of the contact. In this example the bulk velocity is zero in every phase since it was assumed that all phases have equal molar volumes.

Often the exact values of several parameters in a reaction diffusion problem are unknown, and thus estimations have to be made. It is therefore important to gain some insight into the influence on the stable diffusion path of possible errors in the estimated values. Especially for mobilities very few experimental data are available in multicomponent systems. It is therefore useful to be able to analyse their influence on the stability of a diffusion path. Such an analysis is possible using the software. General trends can be deduced, providing important information for estimating unknown parameters. As an example the trend is deduced for the influence of the mobility values. While those of minority elements tend to influence the chemical stability at the interfaces, the main effect of the mobilities of the other components consists in changing the global rate of the reaction diffusion process. An example is shown in Fig. 5, where the global rate is displayed for the A|AB|BC₂|B₂C diffusion path of Fig. 4, as a function of the mobilities in the AB and the BC₂ phases. The figure indicates that the phase in which the mobilities have the lowest values

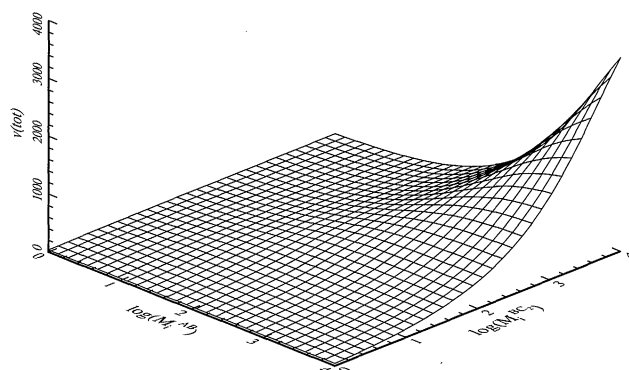


Fig. 5 Global rate $v(tot)$ of the reaction diffusion process, expressed as the relative velocity difference between the BC₂|B₂C and the A|AB interface of the A|AB|BC₂|B₂C diffusion path, shown in Fig. 5. The same input data have been used, except for the relative mobilities in AB and BC₂. $v(tot)$ is in $10^{-9} \sqrt{t} \text{ m s}^{-1}$, M in $10^{-18} \text{ m s (N g-at)}^{-1}$.

is rate determining for the process.

9. Summary

A method has been developed for the reaction diffusion process in multicomponent systems exhibiting limited solubility. There are no limitations on the number of components and phases. It has been shown that appropriate flux equations can be derived for the intermediate as well as for the end phases. Specific use has been made of the limited solubility feature. After a recalculation of the flux equations for every phase to a general fixed reference frame, the resulting expressions can be compared quantitatively. A set of equations has been formulated, involving the fluxes using the conditions for local thermodynamic equilibrium and conservation of mass at every interface. The number of equations is equal to the number of unknowns, being the co-ordinates and the respective chemical potentials at each interface. A number of parameters appears in these equations, the determination of which has been discussed. For the thermodynamic description, the existing formalism for expressing the Gibbs energy in systems with limited solubility has been adopted. A new algorithm for the calculation of isothermal sections for systems with an unlimited number of components has been used. The set of non-linear equations can be solved using the Newton-Raphson technique. Good starting values for the unknowns are obtained by solving a simplified linear version of the equations. Out of a multitude of numerically possible solutions, the stable solution is isolated by the application of two stability criteria. Only one of the calculated solutions meets both criteria, and hence represents the stable diffusion path.

The applicability of the method was illustrated for a contact in a hypothetical ternary system. It was also shown that the method may be used to study general features of the reaction diffusion process. This is useful as often the exact values of several parameters in a reaction diffusion problem are unknown, and thus estimations have to be made. It is therefore important to gain some insight into the influence on the stable diffusion path of possible errors in the estimated values. Especially for mobilities very few experimental data are available in multicomponent systems. Such an analysis is possible using the presently developed software as was shown in this

paper.

Acknowledgement

B. Halleman acknowledges financial support as a Research Assistant from the National Fund for Scientific Research, Belgium (N.F.W.O.). This work has been partly sponsored by the Ministry of Education under GOA-contract No. 92/96-01.

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Appendix

In composition regions where neither Raoult's nor Henry's law apply, the diffusion coefficients are not constant. An approximate analytical solution can then be obtained by introducing the basic diffusion eq. (3) in Fick's second eq. (5) in the Kirkendall reference frame, yielding

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial z} \left(L_{ii} \frac{\partial \mu_i}{\partial z} \right). \quad (\text{A.1})$$

Using eq. (4) to replace L_{ii} , and assuming M_i as well as C_i not dependent on z , the foregoing expression can again be simplified,

$$\frac{\partial C_i}{\partial t} = M_i C_i \frac{\partial^2 \mu_i}{\partial z^2}. \quad (\text{A.2})$$

In order to solve this equation, C_i on the left hand side should be transformed into μ_i using the relationship

$$C_i = \frac{C}{\gamma_i} \exp \left(\frac{\mu_i}{RT} \right). \quad (\text{A.3})$$

The dependence of the activity coefficient γ_i on t may be neglected since we are dealing with a virtually constant concentration, so that the following differential equation is obtained:

$$\frac{\partial \mu_i}{\partial t} = M_i RT \frac{\partial^2 \mu_i}{\partial z^2}. \quad (\text{A.4})$$

The solution of this diffusion equation is:

$$\mu_i^j(z, t) = \mu_i^\infty + (\mu_i^0 - \mu_i^\infty) \left[1 - \Theta \left(\frac{|z - z^k|}{2\sqrt{M_i RT t}} \right) \right] \quad (j = 1, p; k = 1, p - 1) \quad (\text{A.5})$$

where Θ is the error function.

Equations (10) and (11) are deduced from the above expression. It may be emphasised that this solution is only valid in the case of virtually negligible dependence of C_i on z and t , and of μ_i on t , which is the case for components forming a nearly stoichiometric compound. Moreover, the assumption of a half-infinite phase is still made, requiring the effect of diffusion at the edge of the end phase to be zero.