



**HAL**  
open science

## Implementation and application of some nonlinear models of diffusion/reaction in solids

Jean-Baptiste Leblond, Jean-Michel Bergheau, Rémi Lacroix, Didier Huin

► **To cite this version:**

Jean-Baptiste Leblond, Jean-Michel Bergheau, Rémi Lacroix, Didier Huin. Implementation and application of some nonlinear models of diffusion/reaction in solids. *Finite Elements in Analysis and Design*, 2017, 132, pp.8 - 26. 10.1016/j.finel.2017.04.004 . hal-01522592

**HAL Id: hal-01522592**

**<https://hal.sorbonne-universite.fr/hal-01522592>**

Submitted on 15 May 2017

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Implementation and application of some nonlinear models of diffusion/reaction in solids

Jean-Baptiste Leblond<sup>1</sup>\*, Jean-Michel Bergheau<sup>2</sup>, Rémi Lacroix<sup>3</sup>,  
Didier Huin<sup>4</sup>

<sup>1</sup>*Sorbonne Universités, Université Pierre et Marie Curie (UPMC), CNRS, UMR 7190, Institut Jean Le Rond d'Alembert, Tour 65-55, 4 place Jussieu, 75252 Paris Cedex 05, France*

<sup>2</sup>*Université de Lyon, ENISE, CNRS, UMR 5513, Laboratoire de Tribologie et Dynamique des Systèmes, 58 rue Jean Parot, 42023 Saint-Etienne Cedex 02, France*

<sup>3</sup>*ESI-France, Immeuble Le Récamier, 70 rue Robert, 69006 Lyon, France*

<sup>4</sup>*ArcelorMittal Global R&D, Maizières Automotive Products, Voie Romaine, 57283 Maizières-lès-Metz Cedex, France*

---

## Abstract

Feulvarch *et al.* (2009) defined an extended class of nonlinear models of diffusion/reaction in solids, applicable to both problems of diffusion of heat with phase change, and problems of diffusion of chemical elements with formation of simple, “stoichiometric” precipitate phases. They also presented an efficient finite element implementation of this class of models, based on a two-field formulation coupled with an implicit time-integration. This paper extends this earlier work in various ways. First it is shown that the class defined encompasses more elaborate models of diffusion of chemical elements with formation of complex, “non-stoichiometric” precipitate phases, consisting of solid solutions of “stoichiometric” constituents in variable proportions. Second, a more economical finite element implementation based on a one-field formulation - thus halving the number of nodal unknowns - is proposed. The keypoint in the new algorithm lies in an improved treatment of boundary conditions. Third, applications of this new algorithm pertaining to problems of internal oxidation of steel sheets are presented. Four distinct, practically significant situations are considered: (i) the case of a single, highly oxidizable element, with a reference to the seminal analytical solution of Wagner (1959); (ii) the case of a complex system involving 5 oxidizable elements and 9 *a priori* possible oxides; (iii) the case of a single oxidizable element but with formation of a non-stoichiometric oxide; (iv) a 2D case involving preferred diffusion along grain boundaries.

*Keywords:* Diffusion/reaction models; heat diffusion with phase change; diffusion and precipitation of chemical elements; finite element method; one-field formulation; internal oxidation

---

\* Corresponding author.

## 1 Introduction

An extended class of nonlinear models of diffusion/reaction in solid matrices has been defined by Feulvarch *et al.* (2009). These authors showed that this class does not only encompass the classical equation of heat diffusion with phase change, but also less standard models of diffusion of chemical elements with formation of precipitate phases, defined in their simplest form by Wagner (1959) in the case of internal oxidation of steels, and later gradually extended to more complex cases by Fortunier *et al.* (1995), Huin *et al.* (2005) and Brunac *et al.* (2010). The common feature of these models is that in the diffusion equations, the unknown quantities appearing in the left-hand side (LHS) involving a time-derivative, and the right-hand side (RHS) involving the divergence of a flux, are different, unlike in a simple heat diffusion equation. These two unknowns are however related since that in the RHS is a well-defined, given function of that in the LHS - the converse being not true, the function in question being not necessarily invertible. For instance, for heat diffusion with phase change, the unknown in the LHS is the enthalpy per unit volume and that in the RHS is the temperature: the temperature is a well-defined function of the enthalpy, but the enthalpy is not a well-defined function of the temperature in the case of phase change at a fixed temperature.

Feulvarch *et al.* (2009) have also presented an innovative finite element algorithm for numerical solution of the boundary-value problem for this class of models. The two major features of this algorithm are: (i) a two-field formulation involving both unknowns appearing in the LHS and the RHS; and (ii) an implicit time-integration. The advantages of the new algorithm are as follows:

- In the case of heat diffusion with phase change:
  - Since it considers the *enthalpy* (which makes it similar, if not identical, to so-called *enthalpic methods* developed by Mundim and Fortes (1989); Droux (1991); Gremaud (1991); Pham (2000); Nedjar (2002), among others), it offers a natural and unified treatment of phase changes occurring both at some fixed, given temperature and over some finite temperature range.
  - Since it also considers the *temperature*, it permits to evaluate the thermal gradient directly from the temperature field, rather than by using the derivative of the function connecting the temperature to the enthalpy plus the enthalpy gradient. This is an advantage in the case of a phase change occurring at a fixed temperature, because the latter method is then hampered by the spatial discontinuity of the derivative of the function connecting the temperature to the enthalpy.
  - Its implicit scheme for time-integration warrants a good numerical stability.
- In the case of diffusion of chemical elements with formation of precipitate phases:
  - Its use of finite elements makes the meshing, in the case of 2D and 3D problems, much easier than in the approach of Huin *et al.* (2005) and Brunac *et al.* (2010) based on finite differences.
  - Its implicit time-integration also permits to use large time-steps without any apparent degradation of the results; this again represents an advantage over the approach of Huin *et al.* (2005) and Brunac *et al.* (2010) based on explicit time-integration, which required careful (but nevertheless often inefficient) control of the time-step.

The main drawback of Feulvarch *et al.* (2009)'s two-field algorithm, however, is that the number of degrees of freedom (DOF) per node is twice that in a more customary one-field approach. This is *not* a serious shortcoming for problems of heat diffusion with phase change because the number of DOF per node is small anyway, be it 1 or 2. But it *is* a drawback for problems of diffusion of chemical elements with formation of precipitate phases, which frequently involve 5 or more elements: increasing the number of DOF per node means making the simulations longer, and more importantly the convergence of the iterative procedure at each time-step harder, if not impossible.

In order to obviate this difficulty, Feulvarch *et al.* (2009) tentatively proposed to eliminate the nodal DOF pertaining to the RHS so as to retain only those pertaining to the LHS. But this suggestion raises an insurmountable difficulty tied to boundary conditions (BC) of Dirichlet type. It so happens that in the class of problems considered, these BC involve the unknowns in the RHS, not the LHS. For instance, in problems of heat diffusion with phase change, Dirichlet BC involve the temperature, not the enthalpy. If Dirichlet BC are treated by a standard penalty method, the elimination of the nodal DOF pertaining to the RHS leads, in the “reduced” nonlinear system on the nodal DOF pertaining to the LHS, to very large off-diagonal terms of the tangent-matrix which prevent convergence of the iterations.

The aim of this paper is to pursue the work of Feulvarch *et al.* (2009) in several directions. Attention will essentially be focussed on elaborate models of diffusion of chemical elements with formation of precipitate phases, but the case of heat diffusion with phase change will also be considered incidentally, to provide a simple illustration of the main ideas.

We shall focus here on three features:

- First, we shall show that the class of models defined by Feulvarch *et al.* (2009) encompasses more complex models of diffusion of chemical elements with formation of precipitate phases than considered up to now. Fortunier *et al.* (1995), Huin *et al.* (2005) and Brunac *et al.* (2010) all assumed that the precipitate phases were “stoichiometric” in the sense that their chemical composition was defined unambiguously: MnO, Al<sub>2</sub>O<sub>3</sub>, etc. But more complex, “non-stoichiometric” phases are often encountered in the metallurgical industry, in the form of solid solutions of stoichiometric constituents with well-defined chemical composition, but in variable, *a priori* unknown proportions: for instance (FeO)<sub>x</sub>(MnO)<sub>1-x</sub>, with  $0 \leq x \leq 1$ . An extended model incorporating such phases will be defined and shown to still fit within Feulvarch *et al.* (2009)'s theoretical framework.
- Second, an innovative one-field finite element algorithm solving the difficulties of Feulvarch *et al.* (2009)'s two-field approach, while retaining its advantages, will be proposed. The key point in the new algorithm lies in a special treatment of Dirichlet BC permitting to eliminate the nodal DOF pertaining to the RHS. This treatment is possible only for a special subclass of Feulvarch *et al.* (2009)'s class of models; but all examples of models considered by Feulvarch *et al.* (2009) and in this paper fall within this subclass.
- Third, we shall present some applications of the new numerical algorithm, implemented in the SYSWELD<sup>®</sup> finite element code developed by ESI-Group. The examples chosen all pertain to problems of internal oxidation of steel sheets, of practical interest in the metallurgical industry. Most of them are 1D but may involve complex physical

situations and/or raise drastic numerical difficulties, owing to severe nonlinearities. The final example involves a 2D problem. (Considering fully 3D problems would not raise any other problem than the heaviness and cost of the simulations).

The paper is organized as follows:

- Section 2 briefly presents, as a prerequisite, Feulvarch *et al.* (2009)’s class of nonlinear models of diffusion/reaction in solids.
- Section 3 recalls, as a first, elementary but illuminating example, the heat diffusion equation with phase change and shows how it fits into Feulvarch *et al.* (2009)’s theoretical framework.
- Section 4 presents, as a more elaborate example, a model of diffusion of chemical elements with formation of precipitate phases, extending those studied by Fortunier *et al.* (1995), Huin *et al.* (2005) and Brunac *et al.* (2010) through consideration of non-stoichiometric phases. The proof of the fact that this extended model still belongs to the class defined by Feulvarch *et al.* (2009) will require a careful mathematical investigation of the “problem of local thermodynamic equilibrium”, defining the unknowns in the RHS of the diffusion equations as functions of the unknowns in the LHS.
- Section 5 presents an innovative algorithm for numerical solution of the boundary value problem by the finite element method, considering nodal DOF pertaining to the sole LHS of the diffusion equations.
- Section 6 considers, as a first application, the case of 1D, isothermal internal oxidation of a steel sheet containing a single, highly oxidizable alloying element (very low solubility product of the oxide). This problem was solved analytically almost 60 years ago by Wagner (1959), whose solution quickly became a cornerstone of the science of internal oxidation. This reference solution is used to critically assess the algorithm proposed, in some “numerically tough” case.
- Section 7 considers a still 1D, but nevertheless much more complex problem of anisothermal internal oxidation, involving 5 chemical elements, 9 *a priori* possible precipitate phases, and a variable (prescribed) temperature.
- Section 8 comes back to a simpler case involving isothermal diffusion of only two elements and precipitation of a single oxide, but a non-stoichiometric one.
- Finally Section 9 considers a 2D problem of isothermal internal oxidation again involving only two diffusing elements and a single oxide, but with enhanced diffusion along grain boundaries.

## 2 Feulvarch *et al.* (2009)’s class of nonlinear models of diffusion/reaction

### 2.1 Field equations

The models considered by Feulvarch *et al.* (2009) involve two  $n$ -vector-valued functions of position and time,  $\mathbf{u} \equiv (u_i)_{1 \leq i \leq n}$  and  $\mathbf{v} \equiv (v_i)_{1 \leq i \leq n}$ , satisfying the following field equations

in the domain  $\Omega$  considered:

$$\begin{cases} \frac{\partial u_i}{\partial t} = \operatorname{div}(k_i \mathbf{grad} v_i) & (1 \leq i \leq n) \\ \mathbf{v} = \phi(\mathbf{u}) \end{cases} \quad \text{in } \Omega \quad (1)$$

with the initial condition

$$\mathbf{u}(t = 0) = \mathbf{u}^0 \quad \text{in } \Omega \quad (2)$$

where  $\mathbf{u}^0$  is a given function. In the “diffusion” equations (1)<sub>1</sub> the “diffusivities”  $k_i$  may depend on position and time (for instance *via* some dependence upon the temperature). Also,  $\phi(\mathbf{u})$  is a given function of  $\mathbf{u}$ , which may have an additional dependence upon position and time (again for instance *via* some dependence upon the temperature). *This function may not be invertible*, that is, it may be impossible to express  $\mathbf{u}$  as  $\mathbf{u} = \phi^{-1}(\mathbf{v})$ .

## 2.2 Boundary conditions

The boundary  $\partial\Omega$  of the domain  $\Omega$  is the union of disjoint parts  $\partial_M\Omega$ ,  $\partial_N\Omega$  over which BC of mixed- (Dirichlet/Neumann) and Neumann-type, respectively, are enforced.

The BC on  $\partial_M\Omega$  are of the following type, where  $J$  denotes a given subset of the set  $\{1, 2, \dots, n\}$  and  $\bar{J} = \{1, 2, \dots, n\} - J$  the complementary subset:

$$\begin{cases} v_i = v_i^{\text{presc}} & \text{if } i \in J \\ \mathbf{grad} v_i \cdot \mathbf{n} = 0 & \text{if } i \in \bar{J} \end{cases} \quad \text{on } \partial_M\Omega \quad (3)$$

where the prescribed values  $v_i^{\text{presc}}$  may depend on position and time, and  $\mathbf{n}$  denotes the unit outward normal vector to  $\partial\Omega$ . Note that the BC (3)<sub>1</sub> involves the unknown  $\mathbf{v}$  appearing in the RHS of the diffusion equations (1)<sub>1</sub>, not that,  $\mathbf{u}$  appearing in the LHS as would seem natural; this will create difficulties, as will be apparent in the sequel.

The BC on  $\partial_N\Omega$  are of more standard, “zero-flux type”:

$$\mathbf{grad} v_i \cdot \mathbf{n} = 0 \quad (1 \leq i \leq n) \quad \text{on } \partial_N\Omega. \quad (4)$$

More complex BC could of course be considered; for instance, the subset  $J$  of  $\{1, 2, \dots, n\}$  could depend upon position on  $\partial_M\Omega$ , nonzero fluxes could be prescribed on  $\partial_N\Omega$ , etc. The simple BC (3), (4) are adopted here for simplicity and because they will suffice for the practical examples considered.

## 2.3 Additional properties

The treatment of BC within the numerical algorithm proposed in this paper will rely on some additional properties of the function  $\phi(\mathbf{u})$  restricting the class of problems considered. To define these properties, it is necessary to introduce the following notations:

$\mathbf{w} \equiv (w_i)_{1 \leq i \leq n}$  denoting some arbitrary  $n$ -vector,  $\mathbf{w}^J$  and  $\mathbf{w}^{\bar{J}}$  are the vectors composed of those components  $w_i$  with index  $i$  in  $J$  and  $\bar{J}$ , respectively.

The first property then reads as follows:

( $\mathcal{P}_1$ ): *The equation*

$$\mathbf{v} \equiv (\mathbf{v}^J, \mathbf{v}^{\bar{J}}) = \phi(\mathbf{u}) \equiv \phi(\mathbf{u}^J, \mathbf{u}^{\bar{J}}) \quad (5)$$

where  $\mathbf{v}^J$  and  $\mathbf{u}^{\bar{J}}$  are given while  $\mathbf{v}^{\bar{J}}$  and  $\mathbf{u}^J$  are unknown, unambiguously defines  $\mathbf{v}^{\bar{J}}$  as a function of  $\mathbf{v}^J$  and  $\mathbf{u}^{\bar{J}}$ ,

$$\mathbf{v}^{\bar{J}} \equiv \phi^J(\mathbf{v}^J, \mathbf{u}^{\bar{J}}). \quad (6)$$

It may seem at first sight that property ( $\mathcal{P}_1$ ) must automatically be satisfied, the function  $\phi^J(\mathbf{v}^J, \mathbf{u}^{\bar{J}})$  being obtainable by the following procedure: use equation (5) for the component  $\mathbf{v}^J$  to relate it to  $\mathbf{u}^J$  and  $\mathbf{u}^{\bar{J}}$ ; invert the relation with respect to  $\mathbf{u}^J$  to relate it to  $\mathbf{v}^J$  and  $\mathbf{u}^{\bar{J}}$ ; finally re-use equation (5) for the component  $\mathbf{v}^{\bar{J}}$  to relate it to  $\mathbf{v}^J$  and  $\mathbf{u}^{\bar{J}}$ . The failure of this reasoning, however, lies in the fact that the relation connecting  $\mathbf{v}^J$  to  $\mathbf{u}^J$  and  $\mathbf{u}^{\bar{J}}$  may not be invertible. Thus property ( $\mathcal{P}_1$ ) is *not* automatically fulfilled, and does represent an extra condition imposed upon the type of problems considered.

The second property is as follows:

( $\mathcal{P}_2$ ): *Equation (5) also unambiguously defines  $\mathbf{u}^J$  as a function of  $\mathbf{v}^J$  and  $\mathbf{u}^{\bar{J}}$ ,*

$$\mathbf{u}^J \equiv \psi^J(\mathbf{v}^J, \mathbf{u}^{\bar{J}}). \quad (7)$$

Again, property ( $\mathcal{P}_2$ ) is *not* an automatic consequence of the hypotheses made.

For the treatment of BC proposed below to be applicable, fulfillment of property ( $\mathcal{P}_1$ ) will reveal compulsory, whereas that of property ( $\mathcal{P}_2$ ) will reveal useful but not indispensable.

### 3 Basic example: heat diffusion with phase change

The classical equation of diffusion of heat with phase change reads

$$\frac{\partial H}{\partial t} = \text{div}(\lambda \mathbf{grad} T) \quad (8)$$

where  $H$  is the enthalpy per unit volume of the material,  $\lambda$  the thermal conductivity and  $T$  the temperature. The temperature is a well-defined function of the enthalpy:

$$T \equiv \phi(H) \quad (9)$$

but the converse is not necessarily true. Indeed in the case of phase change occurring at a fixed temperature,  $H$  may, at this specific temperature, take all values in a given interval, depending on the respective proportions of the phases. Equations (8) and (9) are of type (1), with  $n \equiv 1$ ,  $\mathbf{u} \equiv H$ ,  $\mathbf{v} \equiv T$  and  $k_1 \equiv \lambda$ .

Classical Dirichlet-type BC are also of type (3) (with  $J \equiv \{1\}$  and  $\bar{J} \equiv \emptyset$ ), since they involve the temperature, not the enthalpy.

Finally property ( $\mathcal{P}_1$ ) is trivially satisfied: prescribing the value of  $\mathbf{v}^J \equiv T$  suffices to fix that of  $\mathbf{v}^{\bar{J}}$  since the latter vector does not exist ( $\bar{J} \equiv \emptyset$ ). On the other hand property ( $\mathcal{P}_2$ ) is *not* satisfied, since prescribing the value of  $\mathbf{v}^J \equiv T$  may not suffice to fix that of  $\mathbf{u}^J \equiv H$ . (For instance, a prescribed temperature of 0°C in a mixture of liquid water and ice is compatible with any proportions of the phases, and therefore does not suffice to fix the enthalpy of this mixture).

#### 4 Complex example: diffusion of chemical elements with formation of precipitate phases

The model presented in this Section is similar to that developed in the works of Fortunier *et al.* (1995); Huin *et al.* (2005); Brunac *et al.* (2010), with the important novelty, however, that the possibility of non-stoichiometric precipitate phases is accounted for.

##### 4.1 General hypotheses and notations

The material considered consists of a “matrix” phase containing mobile, dissolved chemical elements plus a number of immobile, “precipitate” phases (Figure 1). The fractions of elements dissolved in the matrix are assumed to be small (hypothesis of *dilute solution*), and so are also the fractions of precipitate phases. The “representative volume elements” (RVE) considered are large enough to contain the matrix phase plus all types of precipitate phases. Local variations of chemical composition within each RVE are disregarded.

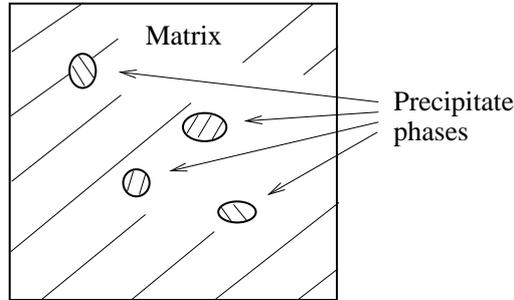


Fig. 1. Schematic “representative volume element” considered by the model

There are  $n_e$  chemical elements denoted with a Latin index  $i = 1, \dots, n_e$ . The atomic mass of element  $i$  is denoted  $m_i$ , its total mass fraction (in all possible phases of the RVE)  $F_i$ , and its mass concentration or dissolved fraction (in the sole matrix phase)  $C_i$ . Its total molar fraction and molar concentration are therefore  $F_i/m_i$  and  $C_i/m_i$ .

There are  $n_p$  precipitate phases denoted with a Greek index  $\lambda = 1, \dots, n_p$ . Each phase  $\lambda$  is made of  $n_c(\lambda)$  stoichiometric constituents denoted with an additional Greek index  $\alpha = 1, \dots, n_c(\lambda)$ . (The phase is stoichiometric if  $n_c(\lambda) = 1$ , non-stoichiometric if  $n_c(\lambda) \geq 2$ ). The molar mass of constituent  $(\lambda, \alpha)$  of phase  $\lambda$  is denoted  $M_{\lambda\alpha}$ , and its mass fraction in the RVE  $P_{\lambda\alpha}$ . Its molar fraction is thus  $P_{\lambda\alpha}/M_{\lambda\alpha}$ . The stoichiometric coefficient of

element  $i$  in constituent  $(\lambda, \alpha)$  of phase  $\lambda$ , that is the number of atoms of the element in a molecule of the constituent, is denoted  $N_{\lambda\alpha i}$ .

Counting all atoms of element  $i$  in the RVE (in the matrix phase plus all precipitate phases), one gets the obvious balance equation

$$\frac{F_i}{m_i} = \frac{C_i}{m_i} + \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} N_{\lambda\alpha i} \frac{P_{\lambda\alpha}}{M_{\lambda\alpha}} \quad (i = 1, \dots, n_e). \quad (10)$$

#### 4.2 Diffusion equations

The *activity*  $a_i$  of element  $i$  in the matrix phase is classically defined by

$$a_i \equiv \gamma_i C_i \quad (i = 1, \dots, n_e) \quad (11)$$

where  $\gamma_i$  is *Henry's coefficient*. This (positive) coefficient depends upon the material and the temperature but not on the concentrations of other elements (that is, *interaction coefficients* between elements are disregarded).

The flux-vector of element  $i$  within the matrix phase is classically assumed to be proportional to the opposite of the gradient of its activity. Writing then the rate of the total number of atoms of element  $i$  within the RVE as minus the integral of this flux over its boundary, and using the divergence theorem, one gets the diffusion equations

$$\frac{\partial F_i}{\partial t} = \operatorname{div} \left( \frac{D_i}{\gamma_i} \mathbf{grad} a_i \right) \quad (i = 1, \dots, n_e) \quad (12)$$

where  $D_i$  is the diffusion coefficient of the element. (Note that the RHS here reduces to  $\operatorname{div}(D_i \mathbf{grad} C_i)$  when  $\gamma_i$  is uniform). This diffusion coefficient again depends on the material and the temperature.

#### 4.3 Laws of mass action

The precipitate phase  $\lambda$  being assumed to be an *ideal* solid solution of its constituents, the *activity*  $A_{\lambda\alpha}$  of constituent  $(\lambda, \alpha)$  in this phase is simply identical to its partial molar fraction within it:

$$A_{\lambda\alpha} \equiv \frac{P_{\lambda\alpha}/M_{\lambda\alpha}}{S_\lambda} \quad , \quad S_\lambda \equiv \sum_{\beta=1}^{n_c(\lambda)} \frac{P_{\lambda\beta}}{M_{\lambda\beta}} \quad (13)$$

( $S_\lambda$  is the sum of the molar fractions of the constituents of phase  $\lambda$ ). Note that this definition implies that the sum of the activities of the constituents of a given phase must always be unity:

$$\sum_{\alpha=1}^{n_c(\lambda)} A_{\lambda\alpha} = 1 \quad (\lambda = 1, \dots, n_p). \quad (14)$$

The laws of mass action, expressing the hypothesis of local thermodynamic equilibrium between the various phases within the RVE, may then be stated as follows:

- If phase  $\lambda$  is present, then for each of its constituents,

$$\frac{\prod_{i=1}^{n_e} a_i^{N_{\lambda\alpha i}}}{A_{\lambda\alpha}} = K_{\lambda\alpha} \quad (\alpha = 1, \dots, n_c(\lambda))$$

where  $K_{\lambda\alpha}$  is the *solubility product* of constituent  $(\lambda, \alpha)$ . This equation expresses the equality, within the RVE, of the chemical potentials of this constituent and the atoms dissolved in the matrix which produce it and *vice versa*. The solubility product depends upon the constituent and the temperature.

- But phase  $\lambda$  may be absent, if the activities of the elements dissolved in the matrix are too small for the chemical reaction producing it to occur. To find the condition satisfied then, it suffices to note that if the phase is *present*, then necessarily, by equations (14) and the above laws of mass action,  $\sum_{\alpha=1}^{n_c(\lambda)} \left( \prod_{i=1}^{n_e} a_i^{N_{\lambda\alpha i}} \right) / K_{\lambda\alpha} = 1$ . Thus the condition of *absence* of phase  $\lambda$  reads

$$\sum_{\alpha=1}^{n_c(\lambda)} \frac{\prod_{i=1}^{n_e} a_i^{N_{\lambda\alpha i}}}{K_{\lambda\alpha}} < 1.$$

These laws may be summarized as follows: for each of the phases,

$$\left\{ \begin{array}{l} * \text{ either } S_\lambda = 0 \quad \text{and} \quad \sum_{\alpha=1}^{n_c(\lambda)} \frac{\prod_{i=1}^{n_e} a_i^{N_{\lambda\alpha i}}}{K_{\lambda\alpha}} \leq 1 \\ * \text{ or } \quad S_\lambda > 0 \quad \text{and} \quad \frac{\prod_{i=1}^{n_e} a_i^{N_{\lambda\alpha i}}}{A_{\lambda\alpha}} = K_{\lambda\alpha} \quad \text{for every } \alpha = 1, \dots, n_c(\lambda) \end{array} \right. \quad (\lambda = 1, \dots, n_p). \quad (15)$$

(The limit-case where  $S_\lambda = 0$  and  $\sum_{\alpha=1}^{n_c(\lambda)} \left( \prod_{i=1}^{n_e} a_i^{N_{\lambda\alpha i}} \right) / K_{\lambda\alpha} = 1$  corresponds to the special circumstance where phase  $\lambda$  is still absent but just about to appear).

It is important to note the following qualitative consequence of this law. Let us say that a given constituent  $(\lambda, \alpha)$  is *a priori excluded* if it contains at least one element which happens to be absent, that is if there is an  $i$  for which  $N_{\lambda\alpha i} > 0$  and  $F_i = 0$ . (Of course, such a constituent is necessarily absent). Then:

*If a given phase  $\lambda$  is present ( $S_\lambda > 0$ ), then all of its constituents  $(\lambda, \alpha)$  which are not a priori excluded are necessarily present ( $P_{\lambda\alpha} > 0$ ).*

Equivalently, if a given phase  $\lambda$  is present ( $S_\lambda > 0$ ) but contains a constituent  $(\lambda, \alpha)$  which is not ( $P_{\lambda\alpha} = 0$ ), then this constituent is *a priori excluded*. To establish this, consider such a phase and constituent. Then  $A_{\lambda\alpha} = 0$  so that, by equation (15)<sub>2</sub>,  $\prod_{i=1}^{n_e} a_i^{N_{\lambda\alpha i}} = 0$ . There must thus be some  $i$  for which  $N_{\lambda\alpha i} > 0$  and  $a_i = 0$ , implying  $C_i = 0$ . Now consider any other constituent  $(\mu, \beta)$  containing element  $i$  ( $N_{\mu\beta i} > 0$ ). If phase  $\mu$  is absent, then  $P_{\mu\beta} = 0$ ; if it is present, then  $\prod_{j=1}^{n_e} a_j^{N_{\mu\beta j}} = 0$  since the product contains the term  $a_i^{N_{\mu\beta i}} = 0$ , so that by equation (15)<sub>2</sub>,  $A_{\mu\beta} = 0$ , implying again  $P_{\mu\beta} = 0$ . Thus all constituents containing element  $i$  are necessarily absent. It then follows from the balance equation (10), with  $C_i = 0$ , that  $F_i = 0$  also, which means that constituent  $(\lambda, \alpha)$  is *a priori excluded*.

#### 4.4 Analysis of the problem of local thermodynamic equilibrium

The topic of this Subsection is the mathematical analysis of the *problem of local thermodynamic equilibrium* which may be stated as follows:

*For given non-negative values of the total fractions of elements  $F_i$ , find non-negative values of the fractions of constituents  $P_{\lambda\alpha}$  - principal unknowns of the problem - and the concentrations of elements  $C_i$  - ancillary unknowns deduced from the  $P_{\lambda\alpha}$  and the given  $F_i$  through equations (10) -, obeying the laws of mass action (15).*

The reader uninterested in mathematical developments may safely skip the present Subsection 4.4 and move to the next one 4.5, retaining only the following conclusions:

- for any given non-negative values of the total fraction of elements, there always exists a solution to the problem of local thermodynamic equilibrium;
- this solution is unique in general, but may be non-unique in some exceptional cases involving special values of the solubility products of constituents;
- however the concentrations of elements at thermodynamic equilibrium are unique even if the fractions of constituents are not.

The treatment to follow basically stands as an extension of that of Leblond (2005) for stoichiometric precipitate phases to possibly non-stoichiometric ones - with the exception of Subsubsection 4.4.6 devoted to the property of uniqueness of the concentrations of elements, which was overlooked by Leblond (2005).

##### 4.4.1 Preliminaries

In order to simplify a number of heavy expressions to follow, we momentarily set the Henry coefficients  $\gamma_i$ , the atomic masses  $m_i$  and the molar masses  $M_{\lambda\alpha}$  to unity. (This is equivalent to redefining the total fractions and concentrations of elements as  $F'_i = F_i/m_i$  and  $C'_i = C_i/m_i$ ,  $i = 1, \dots, n_e$ , and the fractions and solubility products of constituents as  $P'_{\lambda\alpha} = P_{\lambda\alpha}/M_{\lambda\alpha}$  and  $K'_{\lambda\alpha} = K_{\lambda\alpha}/\prod_{i=1}^{n_e}(\gamma_i m_i)^{N_{\lambda\alpha i}}$ ,  $\lambda = 1, \dots, n_p$ ,  $\alpha = 1, \dots, n_c(\lambda)$ ). Standard notations will be resumed in Subsection 4.5 below.

Since, as noted above, equations (10) define the  $C_i$  as (linear) functions of the  $P_{\lambda\alpha}$  (and the given  $F_i$ ), *we essentially concentrate in the present Subsection 4.4 on the principal unknowns  $P_{\lambda\alpha}$  - with the exception of Subsubsection 4.4.6 below.*

Also, an important remark is that all the  $F_i$  may be assumed to be positive; indeed if one  $F_i$  is zero, all constituents  $(\lambda, \alpha)$  containing it ( $N_{\lambda\alpha i} > 0$ ) are *a priori* excluded, so it suffices to simply discard element  $i$  and all constituents containing it from the problem of local thermodynamic equilibrium. *The hypothesis of positivity of all  $F_i$  will therefore be made in the entire present Subsection 4.4.*

Then, for a given set of positive  $F_i$ , let  $\mathcal{C}$  denote the set of “admissible points”  $\mathbf{P} \equiv (P_{\lambda\alpha})_{1 \leq \lambda \leq n_p, 1 \leq \alpha \leq n_c(\lambda)}$ . These points are defined by the “admissibility conditions”  $P_{\lambda\alpha} \geq 0$  ( $\lambda = 1, \dots, n_p$ ,  $\alpha = 1, \dots, n_c(\lambda)$ ) and  $C_i \geq 0$  ( $i = 1, \dots, n_e$ ). Each of these conditions

defines a closed half-space in the space of points  $\mathbf{P}$ . Each such half-space being convex,  $\mathcal{C}$  is itself *closed* and *convex*. Moreover each  $P_{\lambda\alpha}$  is bounded from below, and also from above since for every  $(\lambda, \alpha)$ , one can find an  $i$  such that  $N_{\lambda\alpha i} > 0$  (each constituent contains at least one element) so that  $N_{\lambda\alpha i} P_{\lambda\alpha} \leq C_i + \sum_{\mu=1}^{n_p} \sum_{\beta=1}^{n_c(\mu)} N_{\mu\beta i} P_{\mu\beta} = F_i$  implying that  $P_{\lambda\alpha} \leq F_i/N_{\lambda\alpha i}$ . Hence  $\mathcal{C}$  is bounded. Since it is closed, it is *compact*.

The boundary  $\partial\mathcal{C}$  of  $\mathcal{C}$  consists of those points of this set for which (i) at least one  $P_{\lambda\alpha}$  is zero, or (ii) at least one  $C_i$  is zero. Let  $\partial_1\mathcal{C}$  and  $\partial_2\mathcal{C}$  denote those parts of  $\partial\mathcal{C}$  defined by conditions (i) and (ii), respectively. Obviously,  $\partial_1\mathcal{C} \cup \partial_2\mathcal{C} = \partial\mathcal{C}$ . (In contrast  $\partial_1\mathcal{C} \cap \partial_2\mathcal{C} \neq \emptyset$  generally, but this is unimportant).

The analysis to follow will make a fundamental use of the function  $G$  defined on  $\mathcal{C}$  by

$$\begin{aligned} G(\mathbf{P}) &\equiv \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} P_{\lambda\alpha} \ln K_{\lambda\alpha} + \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} P_{\lambda\alpha} \ln A_{\lambda\alpha} + \sum_{i=1}^{n_e} C_i (\ln C_i - 1) \\ &= \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} P_{\lambda\alpha} \ln K_{\lambda\alpha} + \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} P_{\lambda\alpha} \ln P_{\lambda\alpha} - \sum_{\lambda=1}^{n_p} S_\lambda \ln S_\lambda + \sum_{i=1}^{n_e} C_i (\ln C_i - 1) \end{aligned} \quad (16)$$

where equation (13) has been used. This function, which is continuous on the compact set  $\mathcal{C}$ , physically represents the *Gibbs energy* per unit volume of the material. The existence and uniqueness of the state of thermodynamic equilibrium will be studied by showing that this state corresponds to the minimum of  $G$ .

Let us calculate the first and second derivatives of  $G$  using equations (10), (13)<sub>2</sub> and (16)<sub>2</sub>:

$$\begin{aligned} \frac{\partial G}{\partial P_{\lambda\alpha}}(\mathbf{P}) &= \ln K_{\lambda\alpha} + \ln P_{\lambda\alpha} + 1 - \frac{\partial S_\lambda}{\partial P_{\lambda\alpha}} \ln S_\lambda - \frac{\partial S_\lambda}{\partial P_{\lambda\alpha}} + \sum_{i=1}^{n_e} \ln C_i \frac{\partial C_i}{\partial P_{\lambda\alpha}} \\ &= \ln K_{\lambda\alpha} + \ln P_{\lambda\alpha} - \ln S_\lambda - \sum_{i=1}^{n_e} N_{\lambda\alpha i} \ln C_i; \end{aligned} \quad (17)$$

$$\begin{aligned} \frac{\partial^2 G}{\partial P_{\lambda\alpha} \partial P_{\mu\beta}}(\mathbf{P}) &= \frac{1}{P_{\lambda\alpha}} \frac{\partial P_{\lambda\alpha}}{\partial P_{\mu\beta}} - \frac{1}{S_\lambda} \frac{\partial S_\lambda}{\partial P_{\mu\beta}} - \sum_{i=1}^{n_e} \frac{N_{\lambda\alpha i}}{C_i} \frac{\partial C_i}{\partial P_{\mu\beta}} \\ &= \frac{\delta_{\lambda\mu} \delta_{\alpha\beta}}{P_{\lambda\alpha}} - \frac{\delta_{\lambda\mu}}{S_\lambda} + \sum_{i=1}^{n_e} \frac{N_{\lambda\alpha i} N_{\mu\beta i}}{C_i} \end{aligned} \quad (18)$$

where the  $\delta_{ij}$  are Kronecker's symbols. It follows from equation (18) that for any vector  $\mathbf{X} \equiv (X_{\lambda\alpha})_{1 \leq \lambda \leq n_p, 1 \leq \alpha \leq n_c(\lambda)}$ ,

$$\begin{aligned} \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} \sum_{\mu=1}^{n_p} \sum_{\beta=1}^{n_c(\mu)} \frac{\partial^2 G}{\partial P_{\lambda\alpha} \partial P_{\mu\beta}}(\mathbf{P}) X_{\lambda\alpha} X_{\mu\beta} &= \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} \frac{X_{\lambda\alpha}^2}{P_{\lambda\alpha}} - \sum_{\lambda=1}^{n_p} \frac{1}{S_\lambda} \left( \sum_{\alpha=1}^{n_c(\lambda)} X_{\lambda\alpha} \right)^2 \\ &\quad + \sum_{i=1}^{n_e} \frac{1}{C_i} \left( \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} N_{\lambda\alpha i} X_{\lambda\alpha} \right)^2. \end{aligned} \quad (19)$$

- To study the first two terms in the RHS here, let us set  $Y_{\lambda\alpha} \equiv X_{\lambda\alpha}/P_{\lambda\alpha}^{1/2}$  and  $Z_{\lambda\alpha} \equiv P_{\lambda\alpha}^{1/2}$ .

Then the sum of these first two terms is equal to

$$\begin{aligned} & \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} Y_{\lambda\alpha}^2 - \sum_{\lambda=1}^{n_p} \frac{\left(\sum_{\alpha=1}^{n_c(\lambda)} Y_{\lambda\alpha} Z_{\lambda\alpha}\right)^2}{\sum_{\alpha=1}^{n_c(\lambda)} Z_{\lambda\alpha}^2} \\ &= \sum_{\lambda=1}^{n_p} \frac{1}{\sum_{\alpha=1}^{n_c(\lambda)} Z_{\lambda\alpha}^2} \left[ \left(\sum_{\alpha=1}^{n_c(\lambda)} Y_{\lambda\alpha}^2\right) \left(\sum_{\alpha=1}^{n_c(\lambda)} Z_{\lambda\alpha}^2\right) - \left(\sum_{\alpha=1}^{n_c(\lambda)} Y_{\lambda\alpha} Z_{\lambda\alpha}\right)^2 \right]. \end{aligned}$$

The term [...] here is non-negative by the Cauchy-Schwartz inequality, so that the entire sum  $\sum_{\lambda=1}^{n_p} \dots$  is non-negative.

- The third term in the RHS of equation (19) is also trivially non-negative.

These results, applicable in the interior  $\mathcal{C} - \partial\mathcal{C}$  of the convex set  $\mathcal{C}$ , show that the Hessian matrix of  $G$  is positive semidefinite over this interior, which implies that the function  $G$  is *convex* over it and hence, by continuity, over the entire set  $\mathcal{C}$ .

#### 4.4.2 If $G$ is minimum somewhere, the laws of mass action are satisfied there

*Lemma 1.* If  $G$  is minimum at  $\mathbf{P} \in \mathcal{C}$ , then  $\mathbf{P} \notin \partial_2\mathcal{C}$ , that is, all the  $C_i$  are positive there.

(This does not exclude the possibility that  $\mathbf{P} \in \partial_1\mathcal{C}$ , that is, that some  $P_{\lambda\alpha}$  may be zero).

*Proof.* Consider a point  $\mathbf{P} \in \partial_2\mathcal{C}$ , where one  $C_i$  is zero; we must show that  $G$  is not minimum there. Since, by equation (10),  $F_i = \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} N_{\lambda\alpha i} P_{\lambda\alpha} > 0$ , there must be a pair  $(\lambda, \alpha)$  such that  $N_{\lambda\alpha i} > 0$  and  $P_{\lambda\alpha} > 0$ . Consider some small negative variation  $\delta P_{\lambda\alpha} = -\epsilon$ ,  $\epsilon \rightarrow 0^+$ , of this  $P_{\lambda\alpha}$ . By equation (10), each  $C_j$  then varies by the amount  $\delta C_j = -N_{\lambda\alpha j} \delta P_{\lambda\alpha} = N_{\lambda\alpha j} \epsilon$ ; these amounts are non-negative so that the  $C_j$  remain non-negative, implying that  $\mathbf{P}$  remains in  $\mathcal{C}$ . In the RHS of equation (16)<sub>2</sub>, the variations of the first three sums are  $O(\epsilon)$  since  $P_{\lambda\alpha} > 0$ . In the last sum, the term  $C_i (\ln C_i - 1)$ , which is initially zero, varies by the amount  $\delta C_i (\ln \delta C_i - 1) = N_{\lambda\alpha i} \epsilon \ln \epsilon + O(\epsilon)$ , whereas the other terms  $C_j (\ln C_j - 1)$  vary by  $O(\epsilon)$  or  $N_{\lambda\alpha j} \epsilon \ln \epsilon + O(\epsilon)$ , depending on whether  $C_j$  is positive or zero. Thus the variation  $\delta G$  of  $G$  is globally of the form  $c\epsilon \ln \epsilon + O(\epsilon)$  with  $c \geq N_{\lambda\alpha i} > 0$ . It follows that  $\delta G < 0$  so that  $G$  is not minimum at  $\mathbf{P}$ .

*Lemma 2.* If  $G$  is minimum at  $\mathbf{P} \in \mathcal{C}$  and  $\lambda \in \{1, \dots, n_p\}$  is an index such that  $S_\lambda > 0$  there, then  $P_{\lambda\alpha} > 0$  for every  $\alpha \in \{1, \dots, n_c(\lambda)\}$ .

*Proof.* Assume that at the point  $\mathbf{P}$ ,  $G$  is minimum and  $S_\lambda > 0$  but  $P_{\lambda\alpha} = 0$  for some pair  $(\lambda, \alpha)$ . Consider some small positive variation  $\delta P_{\lambda\alpha} = \epsilon$ ,  $\epsilon \rightarrow 0^+$ , of this  $P_{\lambda\alpha}$ . For such a variation the  $C_i$  decrease, but since they are initially positive by Lemma 1, they remain so provided that  $\epsilon$  is chosen small enough, implying that  $\mathbf{P}$  again remains in  $\mathcal{C}$ . In the RHS of equation (16)<sub>2</sub>, the first sum varies by  $O(\epsilon)$ , the second by  $\delta P_{\lambda\alpha} \ln \delta P_{\lambda\alpha} = \epsilon \ln \epsilon$ , the third by  $O(\epsilon)$  (since  $S_\lambda > 0$ ) and the fourth by  $O(\epsilon)$  (since  $C_i > 0$  for every  $i$ ). Thus the variation  $\delta G$  of  $G$  is globally of the form  $\epsilon \ln \epsilon + O(\epsilon) < 0$ , implying that  $G$  cannot be minimum at  $\mathbf{P}$ , in contradiction with the hypothesis made.

It now becomes necessary to introduce a few extra notations:

- $\mathcal{C}'$  will denote the subset of  $\mathcal{C}$  consisting of those points  $\mathbf{P} \in \mathcal{C}$  satisfying two conditions: all the  $C_i$  are positive, and if, for any  $\lambda \in \{1, \dots, n_p\}$ ,  $S_\lambda$  is positive, then all the  $P_{\lambda\alpha}$  ( $\alpha = 1, \dots, n_c(\lambda)$ ) are positive. Note that Lemmas 1 and 2 then reduce to the following statement: if  $G$  is minimum at  $\mathbf{P} \in \mathcal{C}$ , then necessarily  $\mathbf{P} \in \mathcal{C}'$ .
- For any  $\lambda \in \{1, \dots, n_p\}$ ,  $\mathbf{X}_\lambda \equiv (X_{\lambda\alpha})_{1 \leq \alpha \leq n_c(\lambda)}$  will denote an arbitrary  $n_c(\lambda)$ -vector.
- For any vector  $\mathbf{X}_\lambda$ ,  $D_{\mathbf{X}_\lambda} G$  will denote, if it exists, the directional derivative of the function  $G$  in the direction  $\mathbf{X}_\lambda$ , defined as  $\lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} [G(\mathbf{P} + \epsilon \overline{\mathbf{X}}_\lambda) - G(\mathbf{P})]$  where  $\overline{\mathbf{X}}_\lambda$  is the “completed” vector whose  $(\mu, \alpha)$ -component is  $X_{\lambda\alpha}$  if  $\mu = \lambda$  and 0 if  $\mu \neq \lambda$ .

Let us now study the directional derivatives of  $G$  at an arbitrary point  $\mathbf{P}$  of the subset  $\mathcal{C}'$ . Let  $\lambda$  denote an arbitrary index in  $\{1, \dots, n_p\}$ .

- *Case where  $S_\lambda > 0$ .* The positivity of all  $C_i$  and  $P_{\lambda\alpha}$  then implies, by equation (17)<sub>2</sub>, that the derivatives  $\partial G / \partial P_{\lambda\alpha}$  exist. Thus  $G$  is differentiable with respect to the set of variables  $P_{\lambda\alpha}$ , the directional derivative  $D_{\mathbf{X}_\lambda} G$  exists for all vectors  $\mathbf{X}_\lambda$ , and is given by

$$D_{\mathbf{X}_\lambda} G(\mathbf{P}) = \sum_{\alpha=1}^{n_c(\lambda)} \frac{\partial G}{\partial P_{\lambda\alpha}}(\mathbf{P}) X_{\lambda\alpha}. \quad (20)$$

Note that this expression is linear in the vector  $\mathbf{X}_\lambda$ .

- *Case where  $S_\lambda = 0$ .* Then the derivatives  $\partial G / \partial P_{\lambda\alpha}$  do *not* exist because of the indeterminate form  $\ln P_{\lambda\alpha} - \ln S_\lambda = \ln(P_{\lambda\alpha}/S_\lambda)$  in the RHS of equation (17)<sub>2</sub>; that is,  $G$  is *not* differentiable with respect to the set of variables  $P_{\lambda\alpha}$ . However, consider a vector  $\mathbf{X}_\lambda$  having  $X_{\lambda\alpha} \geq 0$  for all  $\alpha$  and  $\sum_{\alpha=1}^{n_c(\lambda)} X_{\lambda\alpha} = 1$ , and variations of the  $P_{\lambda\alpha}$  of the form  $\delta P_{\lambda\alpha} = \epsilon X_{\lambda\alpha}$ ,  $\epsilon \rightarrow 0^+$ , so that  $\delta S_\lambda = \sum_{\alpha=1}^{n_c(\lambda)} \delta P_{\lambda\alpha} = \epsilon$ . For sufficiently small values of  $\epsilon$ , the  $C_i$  remain positive and by equation (16)<sub>2</sub>, the variation  $\delta G$  of  $G$  is given by

$$\begin{aligned} \delta G &= \sum_{\alpha=1}^{n_c(\lambda)} \frac{\partial}{\partial P_{\lambda\alpha}} \left[ \sum_{\mu=1}^{n_p} \sum_{\beta=1}^{n_c(\mu)} P_{\mu\beta} \ln K_{\mu\beta} + \sum_{i=1}^{n_e} C_i (\ln C_i - 1) \right] \delta P_{\lambda\alpha} + O(\epsilon^2) \\ &\quad + \sum_{\alpha=1}^{n_c(\lambda)} \delta P_{\lambda\alpha} \ln(\delta P_{\lambda\alpha}) - \delta S_\lambda \ln \delta S_\lambda \\ &= \sum_{\alpha=1}^{n_c(\lambda)} \left[ \ln K_{\lambda\alpha} + \sum_{i=1}^{n_e} \ln C_i \frac{\partial C_i}{\partial P_{\lambda\alpha}} \right] \epsilon X_{\lambda\alpha} + \sum_{\alpha=1}^{n_c(\lambda)} \epsilon X_{\lambda\alpha} \ln(\epsilon X_{\lambda\alpha}) - \epsilon \ln \epsilon + O(\epsilon^2) \\ &= \sum_{\alpha=1}^{n_c(\lambda)} (Q_{\lambda\alpha} + \ln X_{\lambda\alpha}) \epsilon X_{\lambda\alpha} + O(\epsilon^2) \end{aligned}$$

where

$$Q_{\lambda\alpha} \equiv \ln K_{\lambda\alpha} - \sum_{i=1}^{n_e} N_{\lambda\alpha i} \ln C_i. \quad (21)$$

Thus the directional derivative  $D_{\mathbf{X}_\lambda} G$  exists and is given by

$$D_{\mathbf{X}_\lambda} G(\mathbf{P}) = \sum_{\alpha=1}^{n_c(\lambda)} (Q_{\lambda\alpha} + \ln X_{\lambda\alpha}) X_{\lambda\alpha}. \quad (22)$$

Note however that  $D_{\mathbf{X}_\lambda} G$  is no longer a linear function of the vector  $\mathbf{X}_\lambda$ , as a consequence of the fact that the derivatives  $\partial G / \partial P_{\lambda\alpha}$  do not exist. (The fact that  $D_{\mathbf{X}_\lambda} G$

nevertheless exists basically results from the cancellation of the terms in  $\epsilon \ln \epsilon$  in the above calculation of  $\delta G$ ).

We may now state

*Theorem 1.* If  $G$  is minimum at  $\mathbf{P} \in \mathcal{C}$ , the laws of mass action (15) are satisfied there.

*Proof.* Consider a point  $\mathbf{P} \in \mathcal{C}$  where  $G$  is minimum,  $\mathbf{P} \in \mathcal{C}'$  by what precedes, and an arbitrary index  $\lambda \in \{1, \dots, n_p\}$ .

- *Case where  $S_\lambda > 0$ .* Since all  $P_{\lambda\alpha}$  are positive ( $\mathbf{P} \in \mathcal{C}'$ ), one may consider small but otherwise arbitrary variations of these quantities around  $\mathbf{P}$ . One then concludes from the assumed existence of a minimum of  $G$  at  $\mathbf{P}$  that at this point, the directional derivative  $D_{\mathbf{X}_\lambda} G$  must necessarily be zero for all vectors  $\mathbf{X}_\lambda$ ; equivalently all derivatives  $\partial G / \partial P_{\lambda\alpha}$  must be zero. By equations (13)<sub>1</sub> and (17)<sub>2</sub>, this condition reads

$$\ln K_{\lambda\alpha} + \ln A_{\lambda\alpha} - \sum_{i=1}^{n_e} N_{\lambda\alpha i} \ln C_i = 0 \quad \Leftrightarrow \quad \frac{\prod_{i=1}^{n_e} C_i^{N_{\lambda\alpha i}}}{A_{\lambda\alpha}} = K_{\lambda\alpha} \quad (\alpha = 1, \dots, n_c(\lambda))$$

which is one possible form of the laws of mass action, see equation (15)<sub>2</sub> (with  $a_i \equiv C_i$  since  $\gamma_i = 1$ ).

- *Case where  $S_\lambda = 0$ .* Then all  $P_{\lambda\alpha}$  are zero. Consider an arbitrary vector  $\mathbf{X}_\lambda$  having  $X_{\lambda\alpha} \geq 0$  for all  $\alpha$  and  $\sum_{\alpha=1}^{n_c(\lambda)} X_{\lambda\alpha} = 1$ , and small non-negative variations of the  $P_{\lambda\alpha}$  of the form  $\delta P_{\lambda\alpha} = \epsilon X_{\lambda\alpha}$ ,  $\epsilon \rightarrow 0^+$ . One then deduces from the existence of a minimum of  $G$  at  $\mathbf{P}$  that at this point, the directional derivative  $D_{\mathbf{X}_\lambda} G$  given by equation (22) must necessarily be non-negative. Thus the condition

$$M_\lambda \equiv \text{Min}_{\mathbf{X}_\lambda} D_{\mathbf{X}_\lambda} G(\mathbf{P}) \geq 0 \quad (23)$$

where the minimum is taken over all vectors  $\mathbf{X}_\lambda$  such that  $X_{\lambda\alpha} \geq 0$  for all  $\alpha$  and  $\sum_{\alpha=1}^{n_c(\lambda)} X_{\lambda\alpha} = 1$ , must be met. The calculation of the minimum implied in the definition of  $M_\lambda$  is carried out in Appendix A, with the result that

$$M_\lambda = -\ln \left( \sum_{\alpha=1}^{n_c(\lambda)} \frac{\prod_{i=1}^{n_e} C_i^{N_{\lambda\alpha i}}}{K_{\lambda\alpha}} \right). \quad (24)$$

It follows from this result that condition (23) reduces to

$$\sum_{\alpha=1}^{n_c(\lambda)} \frac{\prod_{i=1}^{n_e} C_i^{N_{\lambda\alpha i}}}{K_{\lambda\alpha}} \leq 1$$

which is the other possible form of the laws of mass action, see equation (15)<sub>1</sub> (with  $a_i \equiv C_i$ ).

*4.4.3 If the laws of mass action are satisfied somewhere,  $G$  is minimum there*

*Lemma 3.* If the laws of mass action (15) are satisfied at  $\mathbf{P} \in \mathcal{C}$ , then  $\mathbf{P} \notin \partial_2 \mathcal{C}$ .

*Proof.* Equivalently, we must show that if at some point  $\mathbf{P} \in \mathcal{C}$ , one  $C_i$  is zero ( $\mathbf{P} \in \partial_2 \mathcal{C}$ ), the laws of mass action (15) are not satisfied. For such a  $\mathbf{P}$  and  $i$ , by equation (10),  $F_i = \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} N_{\lambda\alpha i} P_{\lambda\alpha} > 0$ , so that there must be a pair  $(\lambda, \alpha)$  such that  $N_{\lambda\alpha i} > 0$  and  $P_{\lambda\alpha} > 0$ . Hence phase  $\lambda$  is present ( $S_\lambda > 0$ ) but the law of mass action  $(\prod_{j=1}^{n_e} C_j^{N_{\lambda\alpha j}}) / A_{\lambda\alpha} = K_{\lambda\alpha}$  is not satisfied, because the LHS is zero (the product contains the term  $C_i^{N_{\lambda\alpha i}} = 0$ ) whereas the RHS is not.

*Lemma 4.* If the laws of mass action (15) are satisfied at  $\mathbf{P} \in \mathcal{C}$  and  $\lambda \in \{1, \dots, n_p\}$  is an index such that  $S_\lambda > 0$  there, then  $P_{\lambda\alpha} > 0$  for every  $\alpha \in \{1, \dots, n_c(\lambda)\}$ .

*Proof.* This lemma is a consequence of the remark made at the end of Subsection 4.3 above. Indeed since all  $F_i$  are assumed here to be positive, no constituent  $(\lambda, \alpha)$  is *a priori* excluded; hence if  $S_\lambda > 0$ , then necessarily  $P_{\lambda\alpha} > 0$  for all  $\alpha$ .

Lemmas 3 and 4 may be summarized as follows: if the laws of mass action (15) are satisfied at  $\mathbf{P} \in \mathcal{C}$ , then necessarily  $\mathbf{P} \in \mathcal{C}'$ .

*Theorem 2.* If the laws of mass action (15) are satisfied at  $\mathbf{P} \in \mathcal{C}$ ,  $G$  is minimum there.

*Proof.* Consider a point  $\mathbf{P} \in \mathcal{C}$  where the laws of mass action (15) are satisfied,  $\mathbf{P} \in \mathcal{C}'$  by what precedes, and another arbitrary point  $\mathbf{P}' \in \mathcal{C}$ . Let  $h(t)$  denote the function defined on the interval  $[0, 1]$  by the formula

$$h(t) \equiv G(\mathbf{P} + t\mathbf{X}) \quad , \quad \mathbf{X} \equiv \mathbf{P}' - \mathbf{P}. \quad (25)$$

This function is convex since the function  $G$  is convex and  $\mathbf{P} + t\mathbf{X}$  is a linear function of  $t$ . Now, for every index  $\lambda \in \{1, \dots, n_p\}$ , let  $\mathbf{X}_\lambda$  denote the  $n_c(\lambda)$ -vector of components  $(X_{\lambda\alpha})_{1 \leq \alpha \leq n_c(\lambda)}$  and  $\overline{\mathbf{X}}_\lambda$  the completed vector whose  $(\mu, \alpha)$ -component is  $X_{\lambda\alpha}$  if  $\mu = \lambda$  and 0 if  $\mu \neq \lambda$ . Then  $\mathbf{X} = \sum_{\lambda=1}^{n_p} \overline{\mathbf{X}}_\lambda$  so that  $h(t) = G(\mathbf{P} + \sum_{\lambda=1}^{n_p} t\overline{\mathbf{X}}_\lambda)$  and consequently<sup>1</sup>

$$h'(t=0) = \sum_{\lambda=1}^{n_p} D_{\mathbf{X}_\lambda} G(\mathbf{P}). \quad (26)$$

One must now, for every index  $\lambda \in \{1, \dots, n_p\}$ , distinguish two cases.

- *Case where  $S_\lambda > 0$ .* Then the law of mass action (15)<sub>2</sub> implies that  $(\prod_{i=1}^{n_e} C_i^{N_{\lambda\alpha i}}) / A_{\lambda\alpha} = K_{\lambda\alpha}$  for all  $\alpha$ . The calculations presented in Subsubsection 4.4.2 above show that this is equivalent to  $(\partial G / \partial P_{\lambda\alpha})(\mathbf{P}) = 0$  for all  $\alpha$  or  $D_{\mathbf{Y}_\lambda} G(\mathbf{P}) = 0$  for every vector  $\mathbf{Y}_\lambda$ . Thus in particular  $D_{\mathbf{X}_\lambda} G(\mathbf{P}) = 0$ .
- *Case where  $S_\lambda = 0$ .* Then all  $P_{\lambda\alpha}$  are zero. Furthermore, by the law of mass action (15)<sub>1</sub>,  $\sum_{\alpha=1}^{n_c(\lambda)} (\prod_{i=1}^{n_e} C_i^{N_{\lambda\alpha i}}) / K_{\lambda\alpha} \leq 1$ . The calculations of Subsubsection 4.4.2 above show that this is equivalent to  $D_{\mathbf{Y}_\lambda} G(\mathbf{P}) \geq 0$  for every vector  $\mathbf{Y}_\lambda$  such that  $Y_{\lambda\alpha} \geq 0$  for all  $\alpha$  and  $\sum_{\alpha=1}^{n_c(\lambda)} Y_{\lambda\alpha} = 1$ ; but this remains true even if the sum  $\sum_{\alpha=1}^{n_c(\lambda)} Y_{\lambda\alpha}$  is not unity, since

<sup>1</sup> Use is made here of the fact that the RHS of equation (16)<sub>2</sub>, with  $\mathbf{P} + t\mathbf{X}$  instead of  $\mathbf{P}$ , is a sum of  $n_p$  terms which admit directional derivatives in the directions  $\mathbf{X}_\lambda$ , plus a sum of  $n_e$  terms which are differentiable with respect to  $\mathbf{X}$ .

$D_{k\mathbf{Y}_\lambda}G(\mathbf{P}) = kD_{\mathbf{Y}_\lambda}G(\mathbf{P})$  for every scalar  $k$  by the very definition of the directional derivative. Now for every  $\alpha$ ,  $X_{\lambda\alpha} = P'_{\lambda\alpha} - P_{\lambda\alpha} = P'_{\lambda\alpha} \geq 0$ . Hence  $D_{\mathbf{X}_\lambda}G(\mathbf{P}) \geq 0$ .

It follows from these elements that  $D_{\mathbf{X}_\lambda}G(\mathbf{P}) \geq 0$  for every  $\lambda$ , so that  $h'(0) \geq 0$ . Since the function  $h$  is convex, this implies that  $h(1) \geq h(0)$ , or equivalently  $G(\mathbf{P}') \geq G(\mathbf{P})$ . Hence the function  $G$  is minimum at  $\mathbf{P}$ .

#### 4.4.4 Existence of a solution to the problem of local thermodynamic equilibrium

The results of Subsubsections 4.4.2 and 4.4.3 imply that looking for a solution of the problem of local thermodynamic equilibrium, defined by the laws of mass action (15), is equivalent to looking for a minimum of  $G$ . Since this function is continuous on the compact set  $\mathcal{C}$ , it reaches its minimum over this set. Hence there exists a solution to the problem of local thermodynamic equilibrium.

#### 4.4.5 Is the solution of the problem of local thermodynamic equilibrium unique?

The uniqueness of the solution of the problem of local thermodynamic equilibrium is not guaranteed. A simple example of non-uniqueness, involving only stoichiometric precipitate phases, was provided by Leblond (2005). But he also showed that lack of uniqueness is an exceptional circumstance arising only for special values of the solubility products.

#### 4.4.6 Uniqueness of the concentrations of elements at thermodynamic equilibrium

Even if, in some exceptional case, the vector  $\mathbf{P}$  of fractions of constituents at thermodynamic equilibrium happens not to be unique, the corresponding vector  $\mathbf{C} \equiv (C_i)_{1 \leq i \leq n_e}$  of concentrations of elements is unique. This stems from the following theorem:

*Theorem 4.* Assume that  $G$  reaches its minimum at distinct points  $\mathbf{P} \neq \mathbf{P}'$ . Then the vectors  $\mathbf{C}$  and  $\mathbf{C}'$  of concentrations of elements at  $\mathbf{P}$  and  $\mathbf{P}'$  are identical.

*Proof.* First, note that both  $\mathbf{P}$  and  $\mathbf{P}'$  lie in  $\mathcal{C}'$  by Lemmas 1 and 2. Note then that the function  $G$  takes the same value at these two points so that, since it is convex, it is constant and minimum over the entire segment  $[\mathbf{P}, \mathbf{P}'] = \{\mathbf{P} + t\mathbf{X}, t \in [0, 1]\}$  where  $\mathbf{X} \equiv \mathbf{P}' - \mathbf{P}$ . Introduce then the function  $h$  defined by equation (25); it is constant over the interval  $[0, 1]$  so that the function  $h''$  is uniformly zero.

Now let  $E$  and  $E'$  denote the sets of indices  $\lambda$  of phases present at points  $\mathbf{P}$  ( $S_\lambda > 0$ ) and  $\mathbf{P}'$  ( $S'_\lambda > 0$ ) respectively - note that these sets do not necessarily coincide - and  $\bar{E}$  and  $\bar{E}'$  the complementary subsets in  $\{1, \dots, n_p\}$ . Then for every  $\lambda$  and  $\alpha$ ,  $X_{\lambda\alpha} = 0$  if  $\lambda \in \bar{E} \cap \bar{E}'$  (because  $P_{\lambda\alpha} = P'_{\lambda\alpha} = 0$ ); thus the only possibly nonzero components  $X_{\lambda\alpha}$  are those with index  $\lambda \in E \cup E'$ . Also, let  $\mathbf{P}'' \equiv \frac{1}{2}(\mathbf{P} + \mathbf{P}')$  denote the midpoint of the segment  $[\mathbf{P}, \mathbf{P}']$ ; at this point phase  $\lambda$  is absent if  $\lambda \in \bar{E} \cap \bar{E}'$  ( $S''_\lambda = \frac{1}{2}(S_\lambda + S'_\lambda) = 0$  since  $S_\lambda = S'_\lambda = 0$ ), and present if  $\lambda \in E \cup E'$  ( $S''_\lambda = \frac{1}{2}(S_\lambda + S'_\lambda) > 0$  since  $S_\lambda \geq 0$ ,  $S'_\lambda \geq 0$ , and  $S_\lambda > 0$  or  $S'_\lambda > 0$ ).

It follows from these elements and equation (19) that

$$\begin{aligned} h''\left(\frac{1}{2}\right) &= \sum_{\lambda \in E \cup E'} \sum_{\alpha=1}^{n_c(\lambda)} \sum_{\mu \in E \cup E'} \sum_{\beta=1}^{n_c(\mu)} \frac{\partial^2 G}{\partial P_{\lambda\alpha} \partial P_{\mu\beta}}(\mathbf{P}'') X_{\lambda\alpha} X_{\mu\beta} \\ &= \sum_{\lambda \in E \cup E'} \sum_{\alpha=1}^{n_c(\lambda)} \frac{X_{\lambda\alpha}^2}{P''_{\lambda\alpha}} - \sum_{\lambda \in E \cup E'} \frac{1}{S''_{\lambda}} \left( \sum_{\alpha=1}^{n_c(\lambda)} X_{\lambda\alpha} \right)^2 + \sum_{i=1}^{n_e} \frac{1}{C_i} \left( \sum_{\lambda \in E \cup E'} \sum_{\alpha=1}^{n_c(\lambda)} N_{\lambda\alpha i} X_{\lambda\alpha} \right)^2. \end{aligned}$$

Following the discussion after equation (19), the condition  $h''(1/2) = 0$  then implies that in the RHS the sum of the two first terms, and the third term, must separately be zero. For the third term this implies that

$$\sum_{\lambda \in E \cup E'} \sum_{\alpha=1}^{n_c(\lambda)} N_{\lambda\alpha i} X_{\lambda\alpha} = 0 \quad \text{for every } i = 1, \dots, n_e.$$

Now take the difference of the balance equations (11) written at points  $\mathbf{P}$  and  $\mathbf{P}'$ ; since the  $F_i$  are the same in both cases one gets

$$\begin{aligned} 0 &= C'_i - C_i + \sum_{\lambda=1}^{n_p} \sum_{\alpha=1}^{n_c(\lambda)} N_{\lambda\alpha i} (P'_{\lambda\alpha} - P_{\lambda\alpha}) \\ \Rightarrow C_i - C'_i &= \sum_{\lambda \in E \cup E'} \sum_{\alpha=1}^{n_c(\lambda)} N_{\lambda\alpha i} X_{\lambda\alpha} \quad (i = 1, \dots, n_e) \end{aligned}$$

where account has been taken of the fact that  $X_{\lambda\alpha} = 0$  if  $\lambda \in \bar{E} \cap \bar{E}'$ . The last double sum here is zero by what precedes, so that  $C_i = C'_i$  for every  $i$ .

#### 4.5 Connection with Feulvarch et al. (2009)'s class of models

We now come back to the general notations defined in Subsections 4.1 and 4.2: the  $\gamma_i$ ,  $m_i$  and  $M_{\lambda\alpha}$  are no longer assumed to be unity.

The diffusion equations (12) are of type (1)<sub>1</sub> with  $n \equiv n_e$ ,  $\mathbf{u} \equiv \mathbf{F} \equiv (F_i)_{1 \leq i \leq n_e}$  (the vector of total fractions of elements),  $\mathbf{v} \equiv \mathbf{a} \equiv (a_i)_{1 \leq i \leq n_e} \equiv (\gamma_i C_i)_{1 \leq i \leq n_e}$  (the vector of activities of elements) and  $k_i \equiv D_i/\gamma_i$ . Also,  $\mathbf{a}$  is a well-defined function of  $\mathbf{F}$ , as required by equation (1)<sub>2</sub>, since it has been shown in Subsection 4.4 that for any given value of  $\mathbf{F}$ , (i) the problem of local thermodynamic equilibrium defined by the laws of mass action (15) always admits a solution, and (ii) the values of the concentrations  $C_i$ , and whence of the activities  $a_i$ , are the same for all possible solutions, in the case of multiple ones.

Dirichlet and Neumann BC are also of type (3) or (4):

- Dirichlet conditions involve the activities  $a_i$  of elements, not their total fractions  $F_i$ . (The activity of some element on the bounding surface of the solid is fixed when atoms of this element dissolved in the matrix are in quick chemical equilibrium with those in gaseous form in the surrounding atmosphere; on the other hand there is no practical way to fix the total fractions of elements).

- Neumann conditions, as a rule, involve zero prescribed fluxes. (There is no practical way to prescribe nonzero given fluxes).

To see whether the additional property ( $\mathcal{P}_1$ ) defined in Subsection 2.3 applies, consider a given subset  $J$  of  $\{1, \dots, n_e\}$  and the complementary subset  $\bar{J}$ . Assume that at some point and instant, the activities  $a_i, i \in J$  and total fractions  $F_i, i \in \bar{J}$  are imposed, whereas the  $a_i, i \in \bar{J}$  and  $F_i, i \in J$  are unknown. The laws of mass action (15) may then be rewritten as follows, “incorporating” the known activities into the solubility products: for each of the phases,

$$\left\{ \begin{array}{l} * \text{ either } S_\lambda = 0 \quad \text{and} \quad \sum_{\alpha=1}^{n_c(\lambda)} \frac{\prod_{i \in \bar{J}} a_i^{N_{\lambda\alpha i}}}{K'_{\lambda\alpha}} \leq 1 \\ * \text{ or } \quad S_\lambda > 0 \quad \text{and} \quad \frac{\prod_{i \in \bar{J}} a_i^{N_{\lambda\alpha i}}}{A_{\lambda\alpha}} = K'_{\lambda\alpha} \quad \text{for every } \alpha = 1, \dots, n_c(\lambda) \end{array} \right. \quad (\lambda = 1, \dots, n_p) \quad (27)$$

where

$$K'_{\lambda\alpha} \equiv \frac{K_{\lambda\alpha}}{\prod_{i \in J} a_i^{N_{\lambda\alpha i}}} \quad (\lambda = 1, \dots, n_p, \alpha = 1, \dots, n_c(\lambda)). \quad (28)$$

Equations (27), together with the balance equations (10) written for indices  $i \in \bar{J}$  only, define a “reduced” problem of local thermodynamic equilibrium with unknowns  $P_{\lambda\alpha}, \lambda = 1, \dots, n_p, \alpha = 1, \dots, n_c(\lambda)$  and  $a_i, i \in \bar{J}$ , possessing the same properties as the original one. Hence this problem unambiguously defines the  $a_i, i \in \bar{J}$  as functions of the  $F_i, i \in \bar{J}$ . This means that property ( $\mathcal{P}_1$ ) is satisfied.

Remarkably, property ( $\mathcal{P}_2$ ) of Subsection 2.3 also applies (unlike in the case of heat diffusion with phase change, see Section 3). Indeed once the  $P_{\lambda\alpha}, \lambda = 1, \dots, n_p, \alpha = 1, \dots, n_c(\lambda)$  have been determined by solving the reduced problem of local thermodynamic equilibrium, it suffices to now re-use the balance equations for  $i \in J$ , where the  $C_i$  are known from the  $a_i$ , to get the unknown  $F_i, i \in J$ .

In conclusion, the model defined in Subsections 4.1 to 4.3 does not only fit into Feulvarch *et al.* (2009)’s class, but also verifies the additional properties ( $\mathcal{P}_1$ ) and ( $\mathcal{P}_2$ ) of Subsection 2.3.

## 5 One-field algorithm for numerical solution of the boundary value problem

We now come back to the general class of problems and notations defined in Section 2.

### 5.1 Definition of nodal variables - Spatial and temporal discretizations

We consider a finite-element mesh of the domain  $\Omega$ . The nodes of this mesh are denoted with an index  $p$ , and quantities at node  $p$  are denoted with an upper symbol  $^{(p)}$ ; for

instance  $N^{(p)}(\mathbf{x})$  is the shape function associated to node  $p$ . ( $N^{(p)}(\mathbf{x}) = N_e^{(p)}(\mathbf{x})$  if the point  $\mathbf{x}$  lies in element  $e$ ,  $N_e^{(p)}(\mathbf{x})$  denoting the shape function of node  $p$  in element  $e$ ).

We consider first the LHS of the diffusion equations (1)<sub>1</sub>. In the spirit of the *enthalpic methods* developed for problems of heat diffusion with phase change by Mundim and Fortes (1989); Droux (1991); Gremaud (1991); Pham (2000); Nedjar (2002), among others, we introduce a first set of nodal variables consisting of the values  $u_i^{(p)}$  of the functions  $u_i$  at the various nodes  $p$ .

The diffusion equations (1)<sub>1</sub> obviously entail spatial continuity of the functions  $v_i$ , but permit spatial discontinuities of the functions  $u_i$ , especially in the case of multimaterial problems since the function  $\phi(\mathbf{u})$  may then have an extra, *discontinuous* dependence upon position. The natural way of accounting for such discontinuities would be to introduce, at each node lying on some interface between different materials and for each index  $i = 1, \dots, n$ , several variables  $u_i^{(p)}$  - one for each material containing the node. We do not follow this approach which would increase the number of DOF per node in an unreasonable way, and stick to only one variable  $u_i^{(p)}$  per node  $p$  and index  $i$ . This means ruling out multimaterial problems here. It will however be shown in a future paper that such problems may be handled with minimal adjustments of the method, without increasing the number of DOF per node.

There is no real need for a spatial interpolation of the functions  $u_i$  - the hypothesis that their time-derivatives vary little in the immediate vicinity of each node will suffice. On the other hand a temporal discretization of these functions will be necessary. Assume that all quantities at time  $t$ , denoted with an upper index <sup>0</sup>, are known and that all quantities at time  $t + \Delta t$ , denoted without any index, are to be evaluated from there. To do so, we shall use a fully implicit Euler (first-order) scheme resulting in the following approximate expression of the derivatives  $\partial u_i^{(p)}/\partial t$  at time  $t + \Delta t$ :

$$\frac{\partial u_i^{(p)}}{\partial t} \simeq \frac{u_i^{(p)} - u_i^{0(p)}}{\Delta t} \quad (i = 1, \dots, n). \quad (29)$$

The implicit Euler scheme is preferred to the explicit one because it is known to tolerate much larger time-steps, for problems of the type considered.

We now consider the RHS of the diffusion equations (1)<sub>1</sub>. There are several options to discretize this RHS. A natural one would be to use equation (1)<sub>2</sub> to express  $\mathbf{grad} v_i$  as  $\sum_{j=1}^n \frac{\partial \phi_i}{\partial u_j} \mathbf{grad} u_j$ , plus a spatial interpolation of the functions  $u_j$ . But such an approach would be hampered by (i) difficulties arising from the possible spatial discontinuities of the derivatives  $\partial \phi_i / \partial u_j$ , and (ii) the necessity of the extra calculation of the second-derivatives  $\partial^2 \phi_i / (\partial u_j \partial u_k)$  to evaluate the tangent-matrix.

We therefore introduce instead a second set of nodal variables consisting of the values  $v_i^{(p)}$  of the functions  $v_i$  at the various nodes  $p$ . Following the standard finite-element procedure (Zienkiewicz *et al.*, 2005), these functions and their gradients are interpolated spatially using shape functions:

$$v_i(\mathbf{x}) \simeq \sum_p N^{(p)}(\mathbf{x}) v_i^{(p)} \quad , \quad \mathbf{grad} v_i(\mathbf{x}) \simeq \sum_p \mathbf{grad} N^{(p)}(\mathbf{x}) v_i^{(p)} \quad , \quad \forall \mathbf{x} \in \Omega. \quad (30)$$

On the other hand no time-discretization of these functions is required.

The vectorial functions  $\mathbf{u} \equiv (u_i)_{1 \leq i \leq n}$  and  $\mathbf{v} \equiv (v_i)_{1 \leq i \leq n}$  are connected through equation (1)<sub>2</sub>. In order to enforce this relation, Feulvarch *et al.* (2009) proposed to use, within a two-field approach involving both functions as unknowns, a weak formulation. The simpler approach adopted here consists in *writing equation (1)<sub>2</sub> pointwise, at every node p*:

$$\mathbf{v}^{(p)} \equiv (v_1^{(p)}, \dots, v_n^{(p)}) = \boldsymbol{\phi}(\mathbf{u}^{(p)}) \equiv \boldsymbol{\phi}(u_1^{(p)}, \dots, u_n^{(p)}) \quad \text{for every } p. \quad (31)$$

This means calculating the temperature as a function of the enthalpy, in the case of heat diffusion with phase change, or solving the laws of mass action, in the case of diffusion of chemical elements with formation of precipitate phases, at the nodes instead of the integration points. This procedure basically amounts to eliminating the unknown nodal variables  $v_i^{(p)}$  in the system of equations to be solved, that is to using a one-field formulation with sole nodal variables  $u_i^{(p)}$ , instead of a two-field one.

## 5.2 Finite element equations

In order to simplify the presentation, we first assume that the BC are exclusively of Neumann-type; this means, in reference to the notations introduced in Subsection 2.2, that  $\partial_M \Omega = \emptyset$  and  $\partial_N \Omega = \partial \Omega$ . The treatment of mixed (Dirichlet/Neumann) BC will be explained in Subsection 5.3 below.

Following the standard finite element procedure (Zienkiewicz *et al.*, 2005), we multiply both sides of equation (1)<sub>1</sub> by the shape function  $N^{(p)}$  of node  $p$  and integrate over  $\Omega$ , accounting for the approximations (29) and (30)<sub>2</sub>.

- The LHS then becomes  $\int_{\Omega} \frac{\partial u_i}{\partial t} N^{(p)} d\Omega$ . Assuming that the derivative  $\partial u_i / \partial t$  varies little in the immediate vicinity of node  $p$  where  $N^{(p)}$  is nonzero, we replace it with  $\partial u_i^{(p)} / \partial t$ , extract it from the integral, and finally use approximation (29); the final result is:  $\frac{u_i^{(p)} - u_i^{0(p)}}{\Delta t} \int_{\Omega} N^{(p)} d\Omega$ .
- The RHS becomes  $\int_{\Omega} \text{div}(k_i \mathbf{grad} v_i) N^{(p)} d\Omega$ , or equivalently upon integration by parts (account being taken of equation (4) applicable on the whole of  $\partial \Omega$ ) plus use of approximation (30)<sub>2</sub>:  $-\sum_q \int_{\Omega} k_i \mathbf{grad} N^{(p)} \cdot \mathbf{grad} N^{(q)} v_i^{(q)} d\Omega$ .

The net result is the following set of “finite element equations”:

$$R_i^{(p)} \equiv \left( \int_{\Omega} N^{(p)} d\Omega \right) \frac{u_i^{(p)} - u_i^{0(p)}}{\Delta t} + \sum_q \left( \int_{\Omega} k_i \mathbf{grad} N^{(p)} \cdot \mathbf{grad} N^{(q)} d\Omega \right) v_i^{(q)} = 0 \quad (32)$$

for every  $i = 1, \dots, n$  and  $p$ . Equations (32) form a nonlinear system on the sole unknowns  $u_i^{(p)}$ , the  $v_i^{(p)}$  being expressed in terms of them *via* equations (31). The components of the tangent-matrix of this system are given by

$$\frac{\partial R_i^{(p)}}{\partial u_j^{(q)}} = \left( \int_{\Omega} N^{(p)} d\Omega \right) \frac{\delta_{pq} \delta_{ij}}{\Delta t} + \left( \int_{\Omega} k_i \mathbf{grad} N^{(p)} \cdot \mathbf{grad} N^{(q)} d\Omega \right) \frac{\partial v_i^{(q)}}{\partial u_j^{(q)}}. \quad (33)$$

Note that this tangent-matrix is non-symmetric, the term  $k_i$  having no counterpart for the index  $j$ , and the term  $\partial v_i^{(q)}/\partial u_j^{(q)}$  for the index  $p$ .

### 5.3 Treatment of mixed boundary conditions

We now consider the more general case where mixed (Dirichlet/Neumann) BC are enforced on a non-empty part  $\partial_M\Omega$  of  $\partial\Omega$ , equations (3). Attention is restricted to the subclass of Feulvarch *et al.* (2009)'s class of models obeying property  $(\mathcal{P}_1)$  of Subsection 2.3.

A first remark is that within the one-field approach adopted here, penalty methods classically used to impose Dirichlet BC are not usable since these BC do not pertain to the unknowns  $u_i^{(p)}$  themselves but to the  $v_i^{(p)}$  which are functions of them, see equation (31).

A second remark is that the finite element equations (32) apply to (i) nodes lying in the interior of  $\Omega$  or on that part  $\partial_N\Omega$  of  $\partial\Omega$  over which the Neumann BC (4) are imposed; and (ii) nodes lying on  $\partial_M\Omega$  but *only for indices  $i \in \bar{J}$  for which the Neumann BC (3)<sub>2</sub> is imposed*. They are *not* applicable to nodes lying on  $\partial_M\Omega$  and indices  $i \in J$  for which the Dirichlet BC (3)<sub>1</sub> is imposed, because they disregard the flux resulting from enforcement of this BC. (For instance, in the case of heat diffusion with phase change, prescribing the temperature somewhere requires inputting or extracting a suitable amount of heat there).

A third remark pertains to the unknowns involved in the second term of the RHS of equation (32). All values of the  $v_i^{(q)}$  - that is, at all nodes  $q$  and for all indices  $i$  - appear in this second term. For a node  $q$  lying in the interior of  $\Omega$  or on  $\partial_N\Omega$ , these values depend on those of the  $u_i^{(q)}$  at the same node according to equation (31). For a node  $q$  lying on  $\partial_M\Omega$ , there are two cases: if  $i \in J$ ,  $v_i^{(q)}$  is prescribed and known according to equation (3)<sub>1</sub>; and if  $i \in \bar{J}$ , it depends on the values of the  $u_j^{(q)}$ ,  $j \in \bar{J}$  according to equation (6) resulting from the assumed property  $(\mathcal{P}_1)$ . (Note that the vector  $\mathbf{v}^J$  in this equation is known from the BC (3)<sub>1</sub>). Thus all unknown quantities  $v_i^{(q)}$  in the second term of the RHS of equation (32) are expressible in terms of (i) the nodal unknowns  $u_j^{(q)}$  at nodes  $q$  lying in the interior of  $\Omega$  or on  $\partial_N\Omega$ ; (ii) the nodal unknowns  $u_j^{(q)}$  at nodes  $q$  lying on  $\partial_M\Omega$ , but *only for indices  $j \in \bar{J}$* .

The last two remarks suggest a simple strategy: exclude from the system to be solved all equations and nodal unknowns corresponding to nodes  $p$  lying on  $\partial_M\Omega$  and indices  $i \in J$ . Equations (32) are then written at nodes  $p$  lying in the interior of  $\Omega$  or on  $\partial_N\Omega$ , and at nodes  $p$  lying on  $\partial_M\Omega$  but only for indices  $i \in \bar{J}$ ; and their unknowns are the values of the  $u_i^{(p)}$  for the same nodes  $p$  and indices  $i$ . The system is thus complete and non-redundant.

This method is thus based on *elimination* rather than *penalization*. It must be stressed, however, that such an elimination is possible only for the subclass of models obeying property  $(\mathcal{P}_1)$ . Were this property not obeyed, it would not be possible, at a node  $p$  lying on  $\partial_M\Omega$ , to express the  $v_i^{(p)}$ ,  $i \in \bar{J}$  in terms of the sole  $u_j^{(p)}$ ,  $j \in \bar{J}$ ; the  $u_j^{(p)}$ ,  $j \in J$  would also be involved and thus could not be eliminated from the system.

With regard to the nodal unknowns  $u_i^{(p)}$  at nodes  $p$  lying on  $\partial_M\Omega$  and for indices  $i \in J$ ,

there are two possibilities. If property ( $\mathcal{P}_2$ ) of Subsection 2.3 *is* satisfied, like in the case of diffusion of chemical elements with formation of precipitate phases, these unknowns can, as a bonus, be deduced from equation (7) once the system on other unknowns has been solved. If property ( $\mathcal{P}_2$ ) is *not* satisfied, like in the case of heat diffusion with phase change, there is no way to calculate them. But this has no impact upon the unambiguousness of the rest of the solution of the problem.

#### 5.4 Comparison with Feulvarch *et al.* (2009)'s algorithm

The main novelty brought by the present algorithm, as compared to that proposed by Feulvarch *et al.* (2009), lies in the halving of the number of DOF per node resulting from the replacement of a two-field formulation by a single-field one. As already mentioned in the Introduction, such a halving is *not* decisive for problems of heat diffusion with phase change for which this number is small anyway, but it *is* for problems of diffusion of chemical elements with formation of precipitate phases, which frequently involve numerous elements. Without even mentioning the fact that some finite element codes place limits on the number of DOF per node, halving this number means halving the system of linear equations to be solved at each iteration, thus decreasing the CPU time spent in inversion of the tangent matrix by a factor of roughly 4; but more importantly, it facilitates the convergence of the iterations, thus permitting to solve more difficult problems. For the problem envisaged in Section 9 below for instance, the new algorithm results in a shorter CPU time, due to less adjustments of the time-steps in order to get convergence, than that of Feulvarch *et al.* (2009); and for the problem of Section 7, it simply permits to obtain results, a thing which the earlier algorithm could never do.

## 6 Application 1: Wagner's problem of internal oxidation of a single, very oxidizable element

### 6.1 Presentation of the problem

Wagner (1959) has provided an analytic solution to an archetypal 1D problem of isothermal internal oxidation of a steel sheet containing initially no oxygen (O) but a given concentration of some oxidizable element (A) fixed by the grade of the steel. The problem involves (i) inward diffusion of element O, with diffusion coefficient  $D_O$ , from the surface of the sheet at  $x = 0$  where the value of its mass concentration  $C_O$  is fixed at some value  $C_O^{\text{surf}}$ ; (ii) outward diffusion of element A, with diffusion coefficient  $D_A$ , from the deep regions of the sheet at  $x = +\infty$  where its mass concentration  $C_A$  is fixed at some value  $C_A^{\text{core}}$ ; and (iii) precipitation of a single oxide of chemical formula  $OA_\nu$ , where  $\nu$  is a rational number. The solubility product of this oxide is considered to be so small (element A so highly oxidizable) that the two chemical elements cannot coexist in their dissolved forms. As a consequence, oxidation occurs only on an *oxidation front*, the position of which is denoted  $\xi(t)$ . In the region  $0 \leq x < \xi(t)$ ,  $C_O$  is nonzero but  $C_A$  is zero; in the region

$\xi(t) < x < +\infty$  the converse is true.

The equations of the problem admit a solution wherein the total mass fractions  $F_O$ ,  $F_A$  and mass concentrations  $C_O$ ,  $C_A$  of the elements O and A, and the mass fraction  $P$  of the oxide  $OA_\nu$ , all depend on the single variable  $x/\sqrt{t}$  where  $t$  denotes time. The position  $\xi(t)$  of the oxidation front is therefore looked for in the form

$$\xi(t) = 2\gamma\sqrt{D_O t} \quad (34)$$

where  $\gamma$  is a positive constant to be determined. The concentration  $C_O$  in the region  $0 \leq x < \xi(t)$  and the concentration  $C_A$  in the region  $\xi(t) < x < +\infty$  obey standard diffusion equations since  $\partial P/\partial t$  is zero in both regions. (This derivative is nonzero only at the position  $x = \xi(t)$ , where it is infinite). These concentrations are thus expressible in terms of the classical erf function.

The value of the constant  $\gamma$  is then deduced from the relation connecting the left-hand flux of O and the right-hand flux of A at  $x = \xi(t)$ ,  $-\nu \frac{D_O}{M_O} \frac{\partial C_O}{\partial x}[\xi(t)^-, t] = \frac{D_A}{M_A} \frac{\partial C_A}{\partial x}[\xi(t)^+, t]$  where  $M_O$  and  $M_A$  denote the atomic masses of O and A; this relation arises from the fact that all O and A atoms arriving there, from the left and the right respectively, are consumed in creation of  $OA_\nu$  molecules. The equation defining  $\gamma$  reads (Wagner, 1959):

$$\frac{\exp(\gamma^2) \operatorname{erf} \gamma}{\sqrt{\phi} \exp(\gamma^2 \phi) \operatorname{erfc}(\gamma\sqrt{\phi})} = \nu \frac{M_A}{M_O} \frac{C_O^{\text{surf}}}{C_A^{\text{core}}} \quad , \quad \phi \equiv \frac{D_O}{D_A}. \quad (35)$$

Finally  $\partial P/\partial t$ , and by integration  $P$ , may be deduced from the left- and right-hand fluxes of O and A at  $x = \xi(t)$  plus the velocity  $\dot{\xi} = \gamma\sqrt{D_O/t}$  of the oxidation front. It is found that  $P$  is *uniform* within the oxidized zone  $0 \leq x < \xi(t)$  and given by (Wagner, 1959):

$$P = C_A^{\text{core}} \frac{M_P}{\nu M_A} \frac{\exp(-\gamma^2 \phi)}{\gamma\sqrt{\pi\phi} \operatorname{erfc}(\gamma\sqrt{\phi})} \quad (36)$$

where  $M_P$  is the molar mass of the precipitate  $OA_\nu$ . Note that  $P$  is not simply proportional to  $C_A^{\text{core}}$  as one would intuitively expect, since the parameter  $\gamma$  itself depends on  $C_A^{\text{core}}$  in a complex way; this is because the diffusion of elements leaves time for a gradual *enrichment in element A* near the sheet's surface, due to the "consumption" of this element at  $x = \xi(t)$ .

Wagner (1959)'s work was extended in several directions. Rapp (1965) first summarized and discussed the theory. Wagner's various restrictive assumptions were then relaxed, so as to extend the validity of the model, by various authors, including Kirkaldy (1969); Laflamme and Morral (1978); Ohriner and Morral (1979); Whittle *et al.* (1981); Christ *et al.* (1986); Stott and Wood (1988); Fortunier *et al.* (1995); Gesmundo and Gleeson (1995); Gesmundo *et al.* (1996); Huin *et al.* (1997); Gesmundo *et al.* (1997, 1998); Gesmundo and Niu (1999); Niu and Gesmundo (2001), among others. A critical discussion of improved variants of Wagner's model was also provided by Douglass (1995). But no fully explicit analytical solution was ever found for any situation more complex than that envisaged by Wagner (1959), although a semi-analytical solution - reducing the problem to the numerical integration of an ordinary nonlinear second-order differential equation on a

single unknown function - may be found in the work of Huin *et al.* (2005), for a situation analogous to that of Wagner but with a finite, nonzero solubility product of the oxide.

## 6.2 Numerical results

As a numerical example, we consider the case of the system O/Al/Al<sub>2</sub>O<sub>3</sub> at a temperature of 800°C. The diffusion and precipitation constants of this system, taken from (Oikawa, 1982) and the (Thermodata, 2005) data bank, are displayed in Table 1 except for the Henry coefficients  $\gamma_i$  which are considered to be unity. (Note that Dirichlet boundary conditions on activities of elements are then equivalent to conditions on their concentrations). The solubility product of Al<sub>2</sub>O<sub>3</sub> is sufficiently small for Wagner (1959)'s solution to be applicable.

$M_O$ (g)	$M_{Al}$ (g)	$M_{Al_2O_3}$ (g)	$D_O$ ( $\mu\text{m}^2\text{s}^{-1}$ )	$D_{Al}$ ( $\mu\text{m}^2\text{s}^{-1}$ )	$K_{Al_2O_3}$ (ppm <sup>5</sup> )
15.999	26.982	101.961	8.009	$5.559 \times 10^{-4}$	$2.1425 \times 10^{-18}$

Table 1

Diffusion and precipitation constants of the system O/Al/Al<sub>2</sub>O<sub>3</sub>

The initial mass concentration of Al imposed by the grade of the steel,  $C_{Al}^{\text{core}}$ , is 1,200 ppm, and the mass concentration of O enforced on the surface of the sheet (by some external atmosphere),  $C_O^{\text{surf}}$ , is  $9.231 \times 10^{-3}$  ppm.

Figures 2, 3 and 4 display the calculated mass concentrations of O and Al and mass fraction of Al<sub>2</sub>O<sub>3</sub> respectively, as functions of position, at times  $t = 1, 15$  and  $60$  s. One sees that the concentration of O is nonzero in the oxidized zone but zero outside, whereas the converse is true for the concentration of Al, in agreement with Wagner (1959)'s solution. Also, the fraction of Al<sub>2</sub>O<sub>3</sub> is quite uniform within the oxidized zone, again in agreement with the theoretical prediction. This peculiar feature of Wagner (1959)'s solution, which implies spatial and temporal discontinuities of the fraction of Al<sub>2</sub>O<sub>3</sub> at the oxidation front, makes the numerical simulation of the problem a difficult challenge, since the finite element method is based in essence on an assumption of continuity of the unknowns represented through their nodal values.<sup>2</sup> One may note in this context that the fraction of Al<sub>2</sub>O<sub>3</sub> found numerically in fact varies *smoothly*, although quickly, in the vicinity of the oxidation front, as a consequence of the finite element method's hypotheses of continuity.

With the parameters indicated above, equation (35) predicts that  $\gamma \simeq 8.25 \times 10^{-4}$ . (The fact that  $\gamma$  is much smaller than unity means that the precipitation of Al<sub>2</sub>O<sub>3</sub> slows down the diffusion of O into the sheet by a very important factor, which is an illustration of the extreme nonlinearity of the problem). It follows that at times  $t = 1, 15$  and  $60$  s the oxidation front is, by equation (34), at the positions  $\xi \simeq 0.0047, 0.0181$  and  $0.0362 \mu\text{m}$ .

<sup>2</sup> The "finite element equations" (32) were arrived at by assuming small variations of the functions  $\partial u_i / \partial t$ , that is of  $\partial F_O / \partial t$  and  $\partial F_{Al} / \partial t$  in the present context, in the vicinity of the node considered; this hypothesis breaks down here at the precipitation front since the moving discontinuity of  $P$  there entails similar discontinuities of  $F_O$ ,  $F_{Al}$  and their time-derivatives.

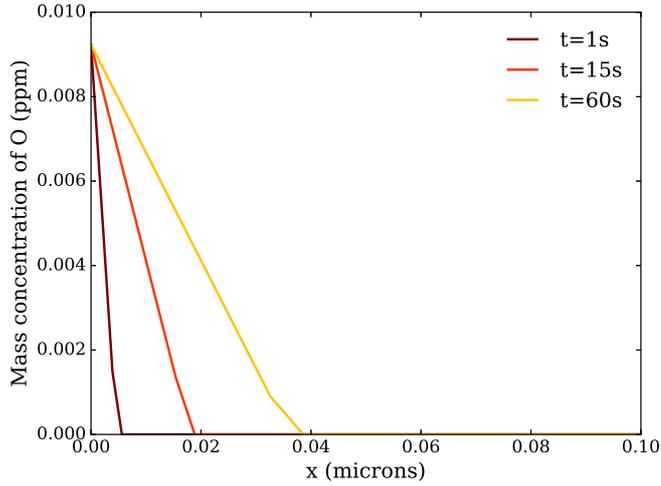


Fig. 2. Wagner's problem - Distribution of mass concentration of O at several instants

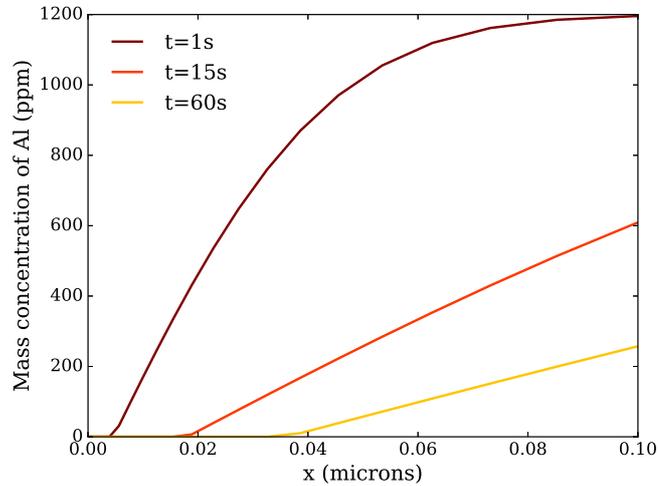


Fig. 3. Wagner's problem - Distribution of mass concentration of Al at several instants

Furthermore equation (36) predicts that  $P \simeq 14,395$  ppm within the oxidized zone. These predictions are quite compatible with the computed results, see Figure 4 where the theoretical predictions are provided in the form of dotted lines. This illustrates the quality of the numerical results, in spite of the difficulty of the problem.

## 7 Application 2: a complex case involving many chemical elements and precipitate phases

We now consider a much more complex case involving diffusion of 5 elements, O, Mn, Si, Al and Cr, and possible precipitation of 9 oxides, MnO,  $Mn_2SiO_4$ ,  $SiO_2$ ,  $Cr_2O_3$ ,  $Al_2O_3$ ,  $Al_2MnO_4$ ,  $MnSiO_3$ ,  $FeAl_2O_4$  and  $Fe_2SiO_4$ . It should be noted, however, that if  $p$  oxides are present, the laws of mass action (15) expressing their equilibrium with the surrounding matrix provide  $p$  independent equations on the 5 unknown concentrations of elements in the matrix, so that  $p$  cannot be larger than 5. (On the surface  $p$  cannot be larger than 4 since there are only 4 *a priori* free concentrations of elements, that of O being fixed). Thus

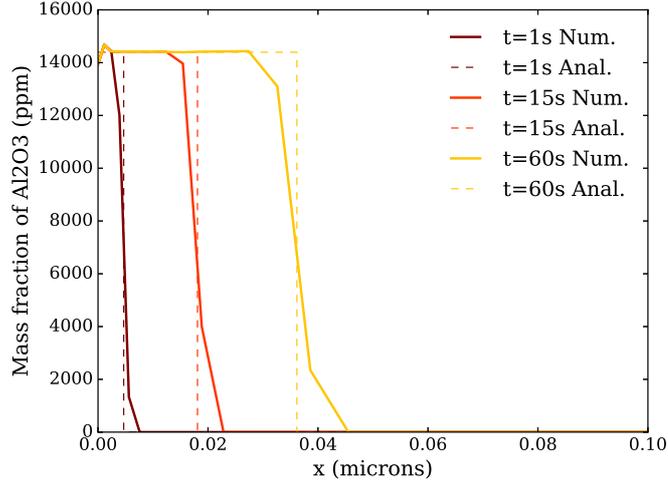


Fig. 4. Wagner's problem - Distribution of mass fraction of  $\text{Al}_2\text{O}_3$  at several instants and comparison with the analytical solution

among the 9 *a priori* possible precipitate phases, no more than 5 (4 on the surface) may be present simultaneously; but of course the determination of the set of actually existing phases at each point and each instant is an integral part of the solution of the problem.

The phases  $\text{FeAl}_2\text{O}_4$  and  $\text{Fe}_2\text{SiO}_4$  involve Fe, the element the matrix is made of. This element is considered not to participate in the diffusion process (the matrix is considered to be unaffected by the diffusion of alloying elements within it) and is therefore disregarded in the simulation. For this reason it will be noted hereafter between parentheses in the phases involving it,  $(\text{Fe})\text{Al}_2\text{O}_4$  and  $(\text{Fe})_2\text{SiO}_4$ , and will not be accounted for in the physical constants (molar mass and solubility product) of these phases.

The calculation is also more involved because the temperature is assumed to vary according to some specified law, and most of the diffusion and precipitation parameters vary accordingly; furthermore the concentration of oxygen prescribed on the surface of the sheet also varies, because it is governed by chemical equilibrium between oxygen atoms dissolved in the Fe matrix and present in gaseous form in the surrounding atmosphere, which depends upon temperature.

The parameters of the problem, except for the Henry coefficients which are again considered to be unity, are as follows:

- Atomic masses of elements:

$M_O$ (g)	$M_{Mn}$ (g)	$M_{Si}$ (g)	$M_{Al}$ (g)	$M_{Cr}$ (g)
15.999	54.938	28.086	26.982	51.996

Table 2

Atomic masses of elements

- Molar masses of precipitate phases:
- Diffusion coefficients of elements: the diffusion coefficients below, taken from Oikawa

$M_{MnO}$ (g)	$M_{Mn_2SiO_4}$ (g)	$M_{SiO_2}$ (g)	$M_{Cr_2O_3}$ (g)	$M_{Al_2O_3}$ (g)
70.937	201.958	60.084	151.989	101.961
$M_{Al_2MnO_4}$ (g)	$M_{MnSiO_3}$ (g)	$M_{(Fe)Al_2O_4}$ (g)	$M_{(Fe)_2SiO_4}$ (g)	
172.898	131.031	117.960	92.082	

Table 3

Molar masses of precipitate phases

(1982), are expressed in  $\mu\text{m}^2\text{s}^{-1}$  as functions of the absolute temperature  $T$  in K:

$$\left\{ \begin{array}{l} D_O = 2.44 \times 10^5 \exp(-11078/T) \\ D_{Mn} = 7.56 \times 10^7 \exp(-26983/T) \\ D_{Si} = 7.35 \times 10^7 \exp(-26439/T) \\ D_{Al} = 5.15 \times 10^8 \exp(-29566/T) \\ D_{Cr} = 7.60 \times 10^8 \exp(-28183/T). \end{array} \right. \quad (37)$$

- Solubility products of oxides: the solubility products below, taken from the Thermodata (2005) data bank, are expressed in  $(\text{ppm})^n$  where  $n$  is the number of atoms per molecule of the oxide considered, as functions of the absolute temperature  $T$  in K:

$$\left\{ \begin{array}{l} K_{MnO} = 25.213 \exp(-24937/T) \\ K_{Mn_2SiO_4} = 88.788 \exp(-107922/T) \\ K_{SiO_2} = 36.841 \exp(-50680/T) \\ K_{Cr_2O_3} = 69.009 \exp(-76216/T) \\ K_{Al_2O_3} = 65.739 \exp(-114208/T) \\ K_{Al_2MnO_4} = 91.827 \exp(-144934/T) \\ K_{MnSiO_3} = 62.308 \exp(-78841/T) \\ K_{(Fe)Al_2O_4} = 74.028 \exp(-123856/T) \\ K_{(Fe)_2SiO_4} = 60.696 \exp(-75191/T). \end{array} \right. \quad (38)$$

- Dependence of the oxygen concentration on the sheet's surface upon the parameters of the external atmosphere and the temperature: see Appendix A of (Huin *et al.*, 2005).
- Core concentrations of oxidizable elements imposed by the grade of the steel:

$$C_{Mn}^{\text{core}} = 12,350 \text{ ppm} ; C_{Si}^{\text{core}} = 1,250 \text{ ppm} ; C_{Al}^{\text{core}} = 2,700 \text{ ppm} ; C_{Cr}^{\text{core}} = 500 \text{ ppm}. \quad (39)$$

- Thermal history:  $T$  varies linearly between the instants indicated in Table 4 below.

Figure 5 displays the mass concentrations of the various elements as functions of position, for various times. The distributions of oxygen on the one hand, oxidizable elements on the other hand, are roughly similar to those obtained in the much simpler case of the Wagner problem (see Figures 2 and 3); in particular the concentrations of all oxidizable

$t$ (s)	0	130	172	232	250
$T$ (K) – 273.15	20	800	800	500	500

Table 4  
Thermal history

elements in the matrix go down near the surface, which is a clear indication that they are all involved in formation of oxides. There is however a notable difference with respect to Wagner’s problem: here the solution does *not* depend on the single variable  $x/\sqrt{t}$ , as a result of the variations of the temperature in time which generate similar variations of most of the parameters of the problem. The more complex dependence of the solution upon  $x$  and  $t$  is apparent for instance in the dependence of the surface concentrations (at  $x = 0$ ) upon time. This is true for all elements but especially O and Cr; for O the explanation obviously lies in the dependence of  $C_{\text{O}}^{\text{surf}}$  upon the time-varying temperature, see Appendix A of (Huin *et al.*, 2005); for Cr it is to be found in the combined effects of the variations of  $C_{\text{O}}^{\text{surf}}$  and the solubility product  $K_{\text{Cr}_2\text{O}_3}$ .

Figure 6 shows the mass fractions of the oxides MnO, Mn<sub>2</sub>SiO<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>MnO<sub>4</sub> and MnSiO<sub>3</sub> as functions of position, for various times. (Note that the scale on the vertical axis, indicated in the upper-left corner of each subfigure, just above the diagram, is different for each oxide). The distributions of the oxides SiO<sub>2</sub>, (Fe)Al<sub>2</sub>O<sub>4</sub> and (Fe)<sub>2</sub>SiO<sub>4</sub> are not shown, because SiO<sub>2</sub> appears only at a single point and a single instant, with a low fraction, and (Fe)Al<sub>2</sub>O<sub>4</sub> and (Fe)<sub>2</sub>SiO<sub>4</sub> are never formed. Again, the lack of dependence of the solution upon the single variable  $x/\sqrt{t}$  is apparent, for instance in the distribution of Al<sub>2</sub>MnO<sub>4</sub> which exhibits a time-varying maximum, see Subfigure 6(e). Also, it is worth noting that on the surface, only MnO, Mn<sub>2</sub>SiO<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>MnO<sub>4</sub> are formed (see Subfigures 6(a), 6(b), 6(c), 6(e)), in agreement with the property mentioned above that only 4 precipitate phases can coexist here. The upper limit of 5 precipitate phases in the interior of the sheet is also respected since only Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>MnO<sub>4</sub> and MnSiO<sub>3</sub> coexist there (see Subfigures 6(d), 6(e), 6(f)).

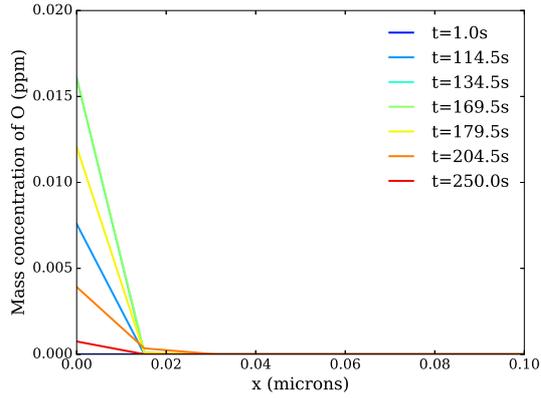
## 8 Application 3: a case involving a non-stoichiometric oxide

We come back to a case involving isothermal diffusion of two elements only, O and Mn, and precipitation of a single oxide, but a non-stoichiometric one, ((Fe)O) <sub>$x$</sub> (MnO) <sub>$1-x$</sub>  with  $0 \leq x \leq 1$ . The laws of mass action are given by equations (15), with the activities  $A_{(\text{Fe})\text{O}} \equiv x$ ,  $A_{\text{MnO}} \equiv 1 - x$  of the constituents (Fe)O, MnO being given by equation (13). The determination of these activities at each point and instant is an integral part of the solution of the problem, thereby increasing its numerical difficulty.

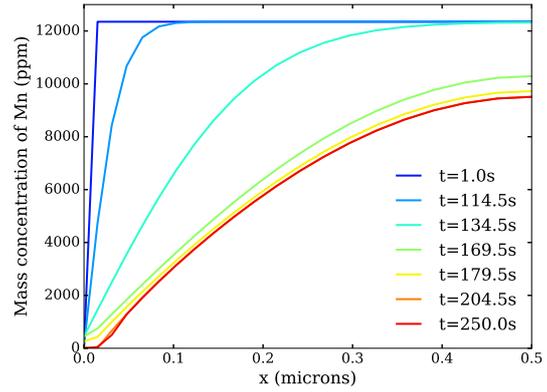
Remarks about element Fe and constituent (Fe)O similar to those of Section 7 apply here.

Table 5 provides the diffusion and precipitation constants of the system, except again for the Henry coefficients which are considered to be unity.

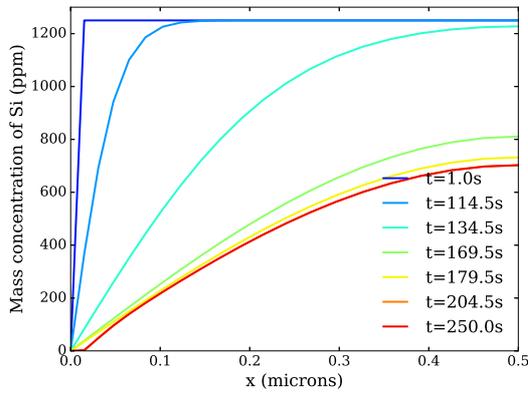
The initial mass concentration of Mn imposed by the grade of the steel,  $C_{\text{Mn}}^{\text{surf}}$ , is 12,350



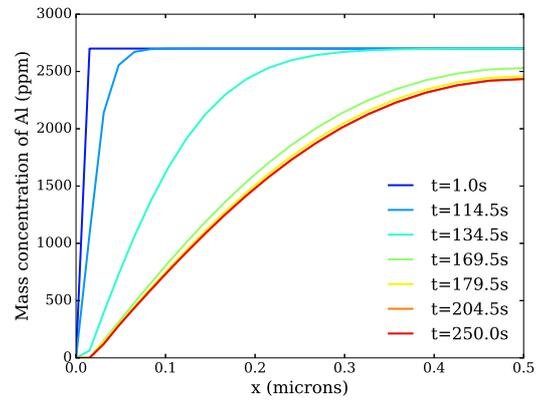
(a) Oxygen



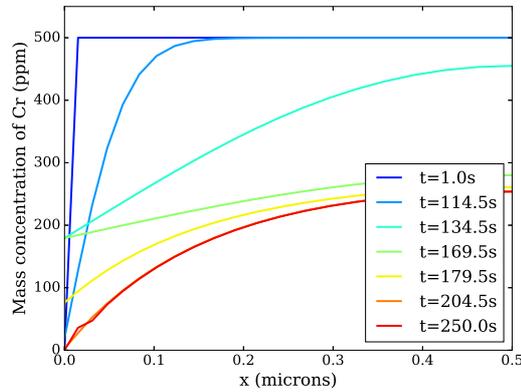
(b) Manganese



(c) Silicon



(d) Aluminium



(e) Chromium

Fig. 5. Complex anisothermal case - Distribution of mass concentrations of elements at several instants

ppm. Two values of the mass concentration of O enforced on the surface of the sheet,  $C_O^{\text{surf}}$ , are considered:  $9.231 \times 10^{-3}$  ppm and 0.88 ppm.

If the phase  $((\text{Fe})\text{O})_x(\text{MnO})_{1-x}$  exists, the activity  $x$  of the constituent (Fe)O is simply proportional to  $C_O$  ( $x = C_O/K_{(\text{Fe})\text{O}}$  by equation (15)<sub>2</sub>), so there is no need to display it.

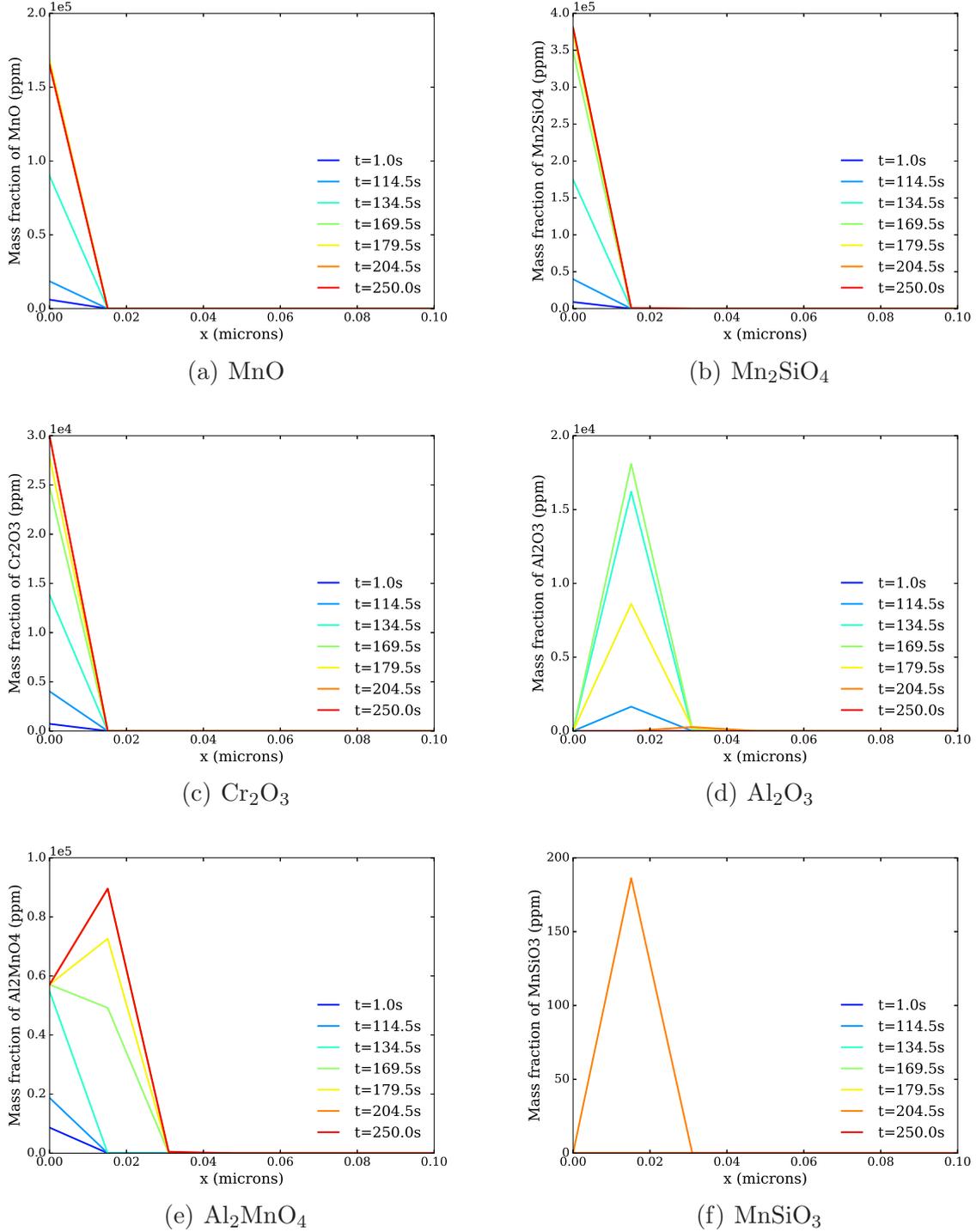


Fig. 6. Complex anisothermal case - Distribution of mass fractions of oxides  $MnO$ ,  $Mn_2SiO_4$ ,  $Cr_2O_3$ ,  $Al_2O_3$ ,  $Al_2MnO_4$ ,  $MnSiO_3$  at several instants

Figures 7, 8 and 9 show, in the two cases, the mass concentration of O, the mass concentration of Mn and the mass fraction of the phase  $((Fe)O)_x(MnO)_{1-x}$ , respectively, as functions of position, at times  $t = 1, 15$  and  $60$  s. Several points are noteworthy here:

- With regard to the distributions of the mass concentration of O (Figure 7), there are several differences between the two cases. First, the orders of magnitude of this concen-

$M_O$ (g)	$M_{Mn}$ (g)	$M_{(Fe)O}$ (g)	$M_{MnO}$ (g)
15.999	54.938	15.999	70.937
$D_O$ ( $\mu\text{m}^2\text{s}^{-1}$ )	$D_{Mn}$ ( $\mu\text{m}^2\text{s}^{-1}$ )	$K_{(Fe)O}$ (ppm)	$K_{MnO}$ (ppm <sup>2</sup> )
8.009	$9.06 \times 10^{-4}$	1.706	7.19

Table 5

Diffusion and precipitation constants of the system O/Mn/((Fe)O)<sub>x</sub>(MnO)<sub>1-x</sub>

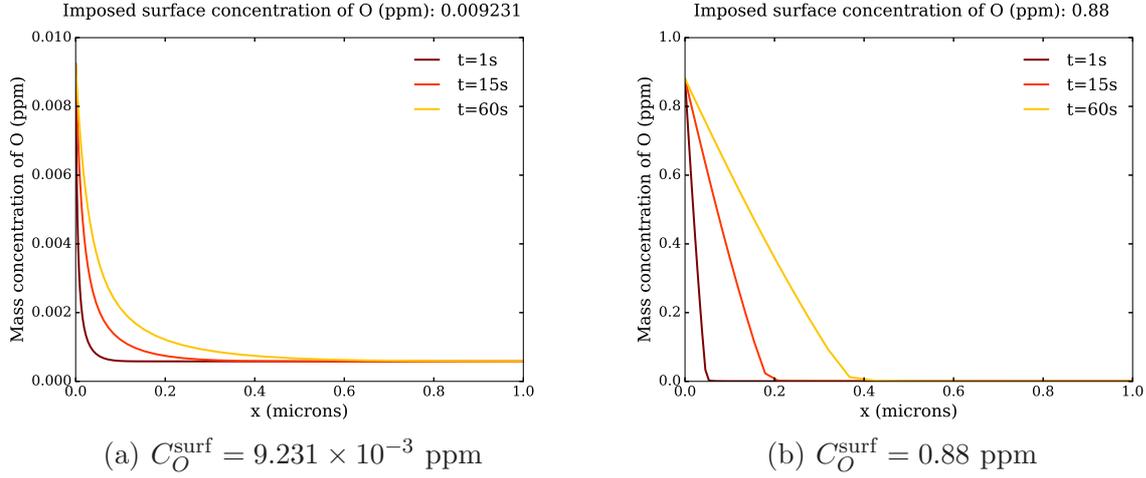


Fig. 7. System O/Mn/((Fe)O)<sub>x</sub>(MnO)<sub>1-x</sub> - Distribution of mass concentration of O at several instants

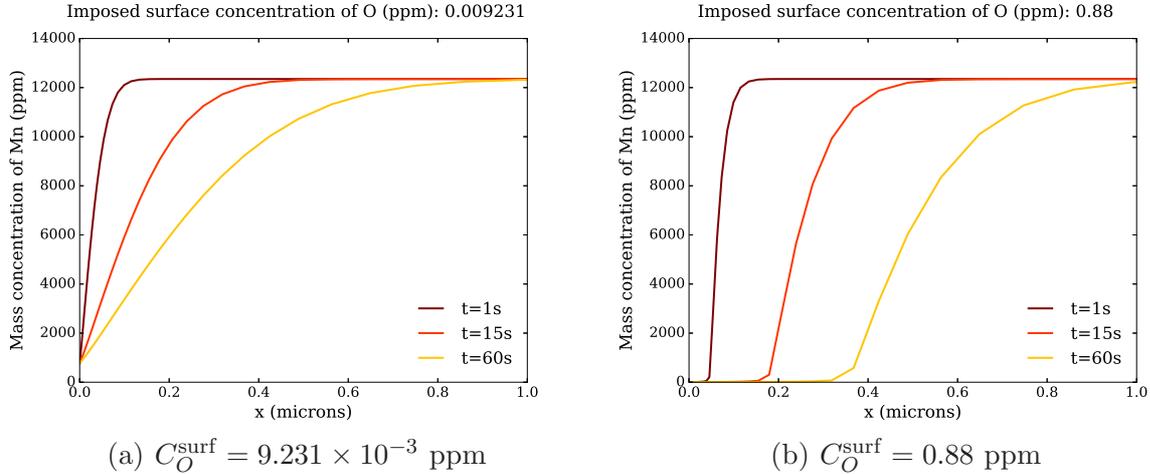


Fig. 8. System O/Mn/((Fe)O)<sub>x</sub>(MnO)<sub>1-x</sub> - Distribution of mass concentration of Mn at several instants

tration are different, as an obvious consequence of the widely different values imposed on the sheet's surface. Second, the shapes of the distributions are also different, the decrease being strongly nonlinear for the smaller value of  $C_O^{\text{surf}}$  but almost linear for the larger value. Third, the decrease is less quick in the latter case, suggesting a thicker oxidized zone.

- Inspection of the distributions of the mass concentration of Mn (Figure 8) confirms the last conclusion, the main difference between the two cases being a depletion in dissolved Mn atoms near the surface (due to “pumping” by oxides) more important,

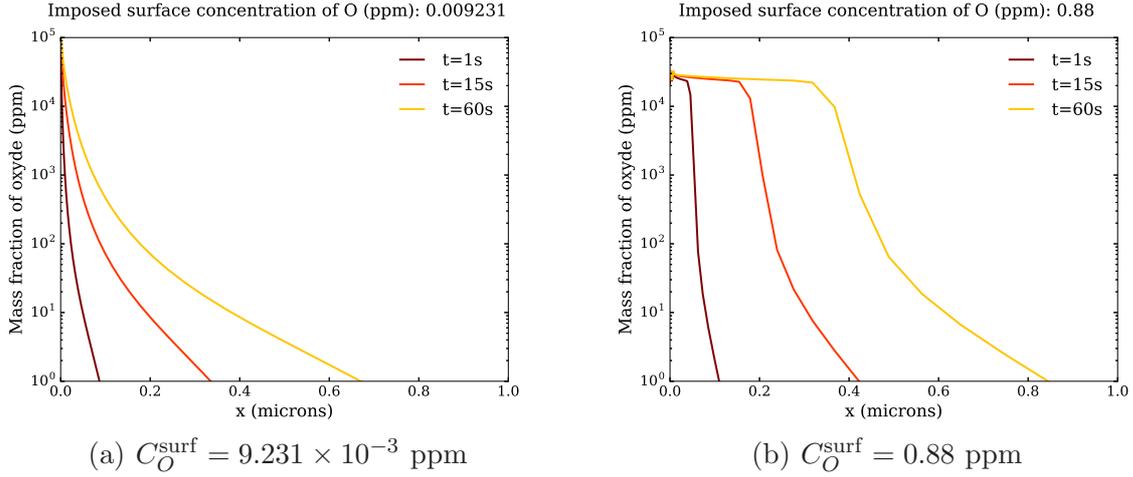


Fig. 9. System O/Mn/ $((\text{FeO})_x(\text{MnO})_{1-x})$  - Distribution of mass fraction of  $((\text{FeO})_x(\text{MnO})_{1-x})$  at several instants

and occurring deeper in the sheet, for the larger value of  $C_O^{\text{surf}}$ .

- Figure 9, showing the distributions of the mass fraction of the phase  $((\text{FeO})_x(\text{MnO})_{1-x})$ , again confirms that the thickness of the oxidized zone is (much) larger for the larger value of  $C_O^{\text{surf}}$ . However the value of this fraction on the sheet's surface is higher for the lower value of  $C_O^{\text{surf}}$ ; in fact in this case the situation could almost be characterized as “external oxidation”.

## 9 Application 4: preferred diffusion along grain boundaries

We finally study a 2D problem of internal oxidation wherein individual grains are explicitly meshed, in order to account for the preferred diffusion of elements in grain boundaries. Subfigure 10(a) shows the whole square geometry considered, and Subfigure 10(b) a zoom on a few grains. Note the refinement of the mesh in the grains near the grain boundaries, aimed at resolving the high concentration gradients that may be anticipated there. The length of the side of the square is  $100 \mu\text{m}$ , the size of the grains varies between  $10 \mu\text{m}$  and  $30 \mu\text{m}$  (fine grain structure), and the grain boundaries are  $1 \mu\text{m}$  thick.

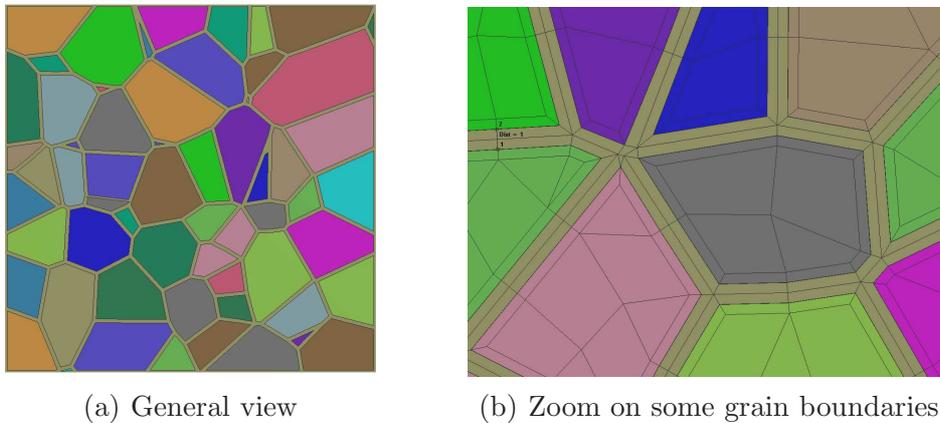


Fig. 10. Mesh of a 2D polycrystal

The system considered is O/Mn/MnO at a temperature of  $800^{\circ}\text{C}$ . The diffusion coefficients of O and Mn are enhanced by an arbitrary factor of  $10^3$  in the grain boundaries, in order to simulate their role of diffusion shortcuts (due to the local mismatch of atomic lattices which creates vacancies available for diffusion of alloying elements).

The diffusion and precipitation constants in the grains are displayed in Table 6, except once again for the Henry coefficients which are considered to be unity. The initial mass concentration of Mn imposed by the grade of the steel is 12,350 ppm and the mass concentration of O enforced on the surface of the sheet is 0.88 ppm.

$M_O$ (g)	$M_{Mn}$ (g)	$M_{MnO}$ (g)	$D_O$ ( $\mu\text{m}^2\text{s}^{-1}$ )	$D_{Mn}$ ( $\mu\text{m}^2\text{s}^{-1}$ )	$K_{MnO}$ (ppm $^2$ )
15.999	54.938	70.937	8.009	$9.060 \times 10^{-4}$	7.190

Table 6

Diffusion and precipitation constants of the system O/Mn/MnO

Figure 11 displays the distributions of the mass concentrations of O and Mn at three instants. Again one observes the gradual penetration of O into the sheet from the surface located at the top of the square, and the gradual depletion of Mn near this surface, due to precipitation of MnO. Both of these phenomena are more marked in the grain boundaries than in the grains.

Figure 12 displays the distribution of the mass fraction of MnO at the same instants as before. The oxide gradually “invades” the material from the surface, and this again occurs preferentially along grain boundaries.

## 10 Conclusion

The aim of this work was to extend the previous one of Feulvarch *et al.* (2009) on numerical implementation of a class of nonlinear models of diffusion/reaction in solids. In this class, the unknowns appearing in the LHS of the diffusion equations involving a time-derivative, and in the RHS involving spatial derivatives, are different, the latter unknowns being functions of the former. The class encompasses interesting cases like diffusion of heat with phase change, and diffusion of chemical elements with formation of precipitate phases. In the present work emphasis was placed on the second, more complex case.

The first task was to show that Feulvarch *et al.* (2009)’s class encompasses more complex models of diffusion of chemical elements with formation of precipitate phases than considered in previous publications (Fortunier *et al.*, 1995; Huin *et al.*, 2005; Brunac *et al.*, 2010). In all of these, the hypothesis was made of “stoichiometric” precipitate phases, of well-defined chemical composition. In Section 4 of this paper we introduced the possibility of “non-stoichiometric” phases, consisting of solid solutions of stoichiometric constituents of well-defined chemical composition but in variable, *a priori* unknown proportions, as commonly encountered in the metallurgical industry. It was shown that the resulting extended model still fits within Feulvarch *et al.* (2009)’s framework. The proof required a careful examination of the mathematical properties of the model, in order to show that

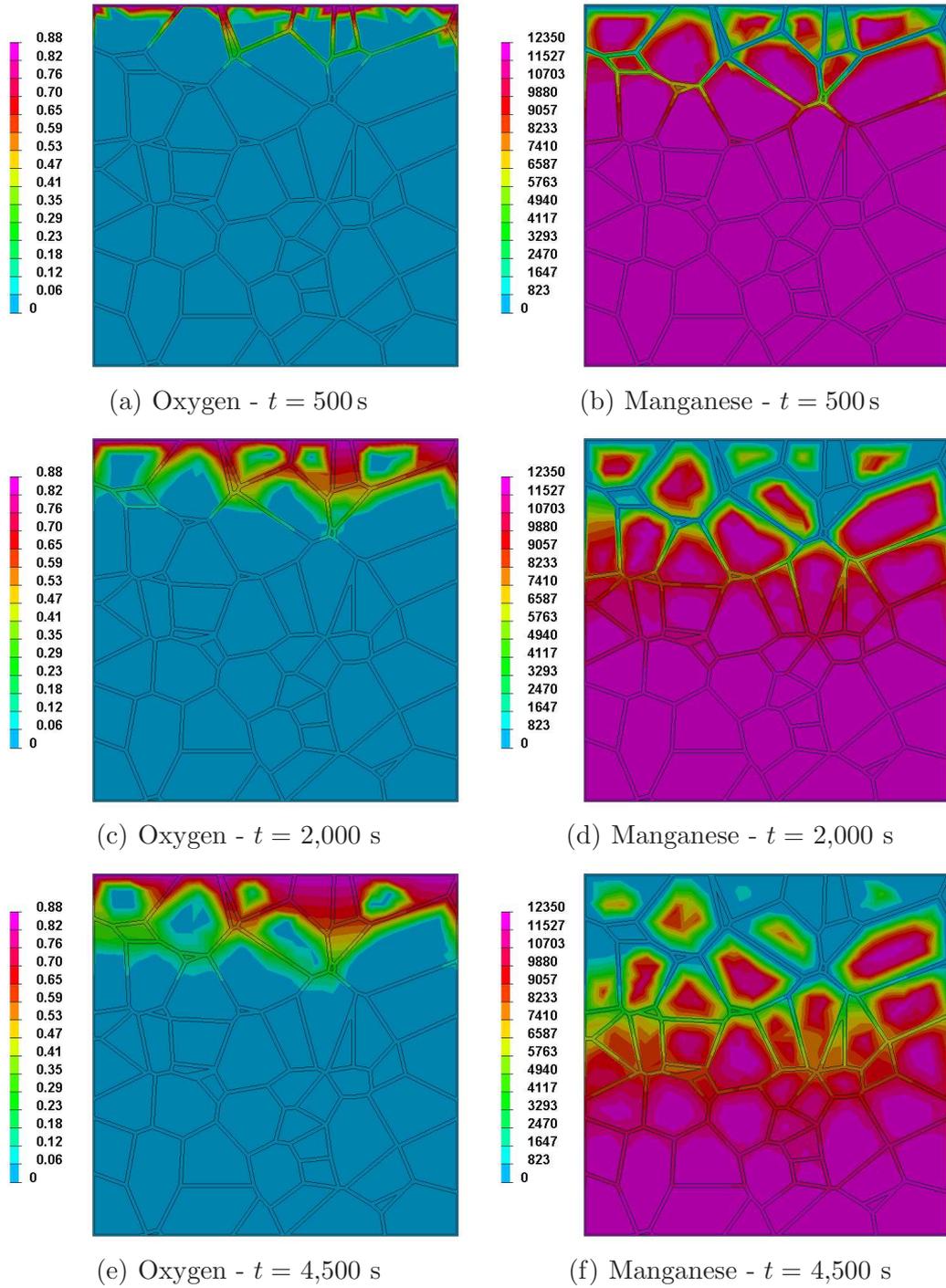


Fig. 11. Distributions of mass concentrations of O and Mn (in ppm) at several instants - Case 1, identical solubility products of MnO in the grains and the grain boundaries

the concentrations of chemical elements dissolved in the matrix phase are well-defined, unambiguous functions of their total fractions. This result was proved by establishing that: (i) one may always find some fractions of the constituents of the phases satisfying the laws of mass action defining local thermodynamic equilibrium; (ii) even though, in exceptional cases, these laws may not define these fractions in a unique way, the concentrations of elements corresponding to two possible solutions are identical.

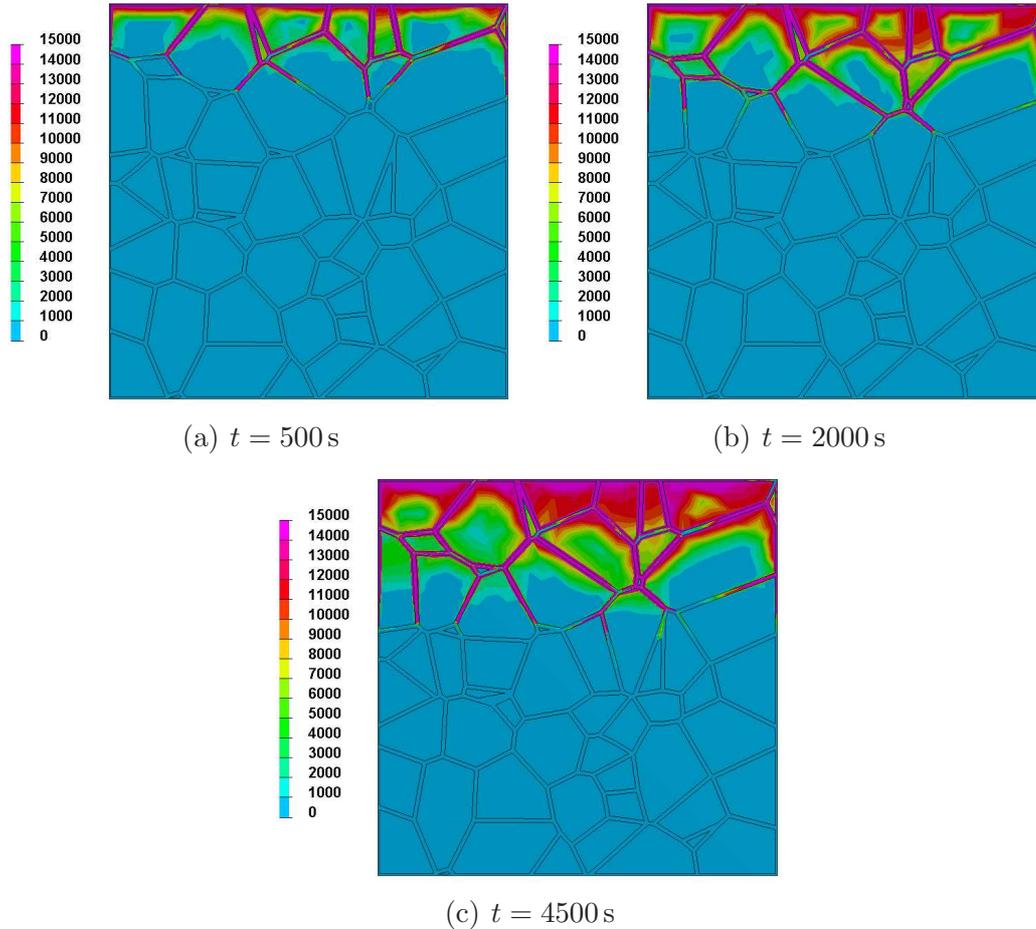


Fig. 12. Distribution of the mass fraction of MnO (in ppm) at several instants - Case 1, identical solubility products of MnO in the grains and the grains boundaries

The second task was to overcome some difficulties encountered by Feulvarch *et al.* (2009) when defining a numerical algorithm of solution by the finite element method. These difficulties were tied to the nature of BC of Dirichlet type. For the type of models considered, Dirichlet BC involve the unknowns in the RHS of the diffusion equations, making it difficult to use a classical penalty method to enforce them within approaches considering the unknowns in the LHS. Feulvarch *et al.* (2009) proposed to use such a method within a two-field approach considering both types of unknowns, but this approach resulted in an unhappy doubling of the number of DOF per node; and elimination of the unknowns in the RHS, although possible, led to very large off-diagonal terms in the tangent-matrix preventing convergence of the iterative procedure required to deal with nonlinearities. These problems were overcome in Section 5 of this paper by showing that for some subclass of Feulvarch *et al.* (2009)'s class of models, encompassing those of practical interest, one may use an economical one-field approach considering the sole unknowns in the LHS, Dirichlet BC being tractable for members of this subclass through elimination rather than penalization.

The third task was to provide examples of application of the new algorithm of solution, duly implemented into the SYSWELD<sup>®</sup> finite element programme developed by ESI-Group. All the examples chosen pertained to problems of internal oxidation of steel sheets, of interest in the metallurgical industry. In spite of their being 1D for the most part, they

all exhibited severe nonlinearities making their numerical solution a difficult challenge.

Section 6 considered the archetypal 1D problem of isothermal internal oxidation of a sheet containing a single oxidizable element reacting with oxygen to form a single oxide of very low solubility product. An analytical solution to this problem was provided in the seminal work of Wagner (1959). In this solution the chemical reaction occurs on some “oxidation front” of measure zero; the fraction of oxides formed is uniform within the growing oxidized zone, and discontinuous across the oxidation front. The numerical solution satisfactorily reproduced the main features of the analytical one and especially the uniformity of the fraction of oxides in the oxidized zone, although it varied quickly but continuously in the elements adjacent to the precipitation front, rather than discontinuously across it.

Section 7 was devoted to a much more complex problem involving 5 diffusing elements and 9 *a priori* possible oxides, and a temperature varying in time, making most parameters of the problem functions of time. The problem was too complex to be amenable to some analytical solution which could serve as a reference, but the numerical solution exhibited reasonable features, and respected in particular the theoretical restrictions imposed by the laws of mass action upon the number of oxides present at a given point and a given instant, both in the interior of the sheet or on its surface.

Section 8 came back to a problem of isothermal internal oxidation involving diffusion of two elements only, O and Mn, and precipitation of a single, but non-stoichiometric oxide,  $(\text{FeO})_x(\text{MnO})_{1-x}$ . This feature increased the difficulty of the numerical determination of the state of local thermodynamic equilibrium through introduction of an extra unknown, the activity  $x$  of the constituent FeO within the solid solution  $(\text{FeO})_x(\text{MnO})_{1-x}$ . Again no analytical solution was available for comparison with the numerical one but the simulation yielded reasonable results.

Section 9 was finally devoted to a problem of internal oxidation involving preferred diffusion along grain boundaries, using a 2D mesh of an ensemble of grains and grain boundaries. The diffusion coefficients of elements were enhanced in the grain boundaries by a factor of  $10^3$  in order to simulate their role of diffusion shortcuts. The results evidenced the selective penetration of oxygen, depletion of oxidizable element and formation of oxides in the grain boundaries.

The work opens various perspectives. Among these, the possibility of accounting for geometry changes arising from precipitation (because of differences of specific volume between the various phases) probably deserves special mention. This perspective implies a coupling of diffusion/reaction and mechanical simulations. A full coupling would imply adding the three displacements to the diffusion/reaction DOF, thus making the simulations much heavier and the convergence of the iterative procedure at each time-step much more uncertain. An alternative approach would consist of a “weak”, “explicit” coupling; in this option the calculation between times  $t$  and  $t + \Delta t$  would consist of first solving the diffusion/reaction equations on this time-interval on the geometrical configuration at time  $t$ , then solving the elasticity equations on the same time-interval and geometrical configuration using the “free strains” determined by the fractions of phases at time  $t + \Delta t$  just calculated, and finally updating the geometrical configuration before proceeding to the next time-step. The advantage of this simpler option would be to perform diffu-

sion/reaction and mechanical calculations in succession instead of simultaneously - thus facilitating convergence of the iterations -, its disadvantage to require small time-steps in order to minimize errors arising from the explicit character of the algorithm. This could permit, among other things, to evaluate mechanical consequences of carburizing and nitriding treatments.

## References

- Brunac J.B., Huin D. and Leblond J.B. (2010). Numerical implementation and application of an extended model for diffusion and precipitation of chemical elements in metallic matrices, *Oxid. Metals*, **73**, 565-589.
- Christ H.J., Christl W., Sockel H.G. (1986). Carburization of high-temperature materials. I. Mathematical model description of the penetration and simultaneous precipitation of a compound of the diffusing element, *Werkst. Korros.*, **37**, 385-390 (in German with English title).
- Douglass D.L. (1995). A critique of internal oxidation in alloys during the post-Wagner era, *Oxid. Metals*, **44**, 81-111.
- Droux J.J. (1991). Three-dimensional numerical simulation of solidification by an improved explicit scheme, *Comput. Meth. Appl. Mech. Engng.*, **85**, 57-74.
- Feulvarch E., Bergheau J.M. and Leblond J.B. (2009). An implicit finite element algorithm for the simulation of diffusion with phase changes in solids, *Int. J. Numer. Meth. Engng.*, **78**, 1492-1512.
- Fortunier R., Leblond J.B., Pont D. (1995). Recent advances in the numerical simulation of simultaneous diffusion and precipitation of chemical elements in steels, in: *Phase Transformations During the Thermal/Mechanical Processing of Steel*, Hawbolt and Yue, eds., the Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Canada, pp. 357-371.
- Gesmundo F., Castello P., Viani F., Roos C. (1998). The effect of supersaturation on the internal oxidation of binary alloys, *Oxid. Metals*, **49**, 237-260.
- Gesmundo F., Gleeson B. (1995). Oxidation of multicomponent two-phase alloys, *Oxid. Metals*, **44**, 211-237.
- Gesmundo F., Niu Y. (1999). The formation of two layers in the internal oxidation of binary alloys by two oxidants in the absence of external scales, *Oxid. Metals*, **51**, 129-158.
- Gesmundo F., Viani F., Niu Y. (1996). The internal oxidation of two-phase binary alloys under low oxidant pressure, *Oxid. Metals*, **45**, 51-76.
- Gesmundo F., Viani F., Niu Y. (1997). The internal oxidation of two-phase binary alloys beneath an external scale of the less-stable oxide, *Oxid. Metals*, **47**, 355-380.
- Gremaud P.A. (1991). Analyse numérique de problèmes de changements de phase liés à des phénomènes de solidification, Ph.D. thesis, Ecole Polytechnique Fédérale de Lausanne, Switzerland (in French).
- Huin D., Flauder P. and Leblond J.B. (2005). Numerical simulation of internal oxidation of steels during annealing treatments, *Oxid. Metals*, **64**, 131-167.
- Huin D., Lanteri V., Loison D., Autesserre P., Gaye H. (1997). Modelling of internal oxidation of several elements, in: *Microscopy of Oxidation - 3*, Newcomb and Little, eds., the Institute of Metals, London, pp. 573-586.

- Kirkaldy J.S. (1969). On the theory of internal oxidation and sulphation of alloys, *Can. Metall. Quart.*, **8**, 35-38.
- Lafamme G., Morral J.E. (1978). Limiting cases of subscale formation, *Acta Metall.*, **26**, 1791-1794.
- Leblond J.B. (2005). Mathematical results for a model of diffusion and precipitation of chemical elements in solid matrices, *Nonlinear Anal. B: Real World Applic.*, **6**, 297-322.
- Mundim M.J. and Fortes M. (1989). Evaluation of finite element method utilised in the solution of solid-liquid phase change problems, in: *Numerical Methods in Thermal Problems*, Lewis and Morgan, eds., Pineridge Press, Swansea, UK, vol. **6**, pp. 90-100.
- Nedjar B. (2002). An enthalpy-based finite element method for nonlinear heat problems involving phase change, *Comput. Struct.*, **80**, 9-21.
- Niu Y., Gesmundo F. (2001). An approximate analysis of the external oxidation of ternary alloys forming insoluble oxides. I: High oxidant pressures, *Oxid. Metals*, **56**, 517-536.
- Ohriner E.K. and Morral J.E. (1979). Precipitate distribution in subscales, *Scripta Metall.*, **13**, 7-10.
- Oikawa H. (1982). Lattice diffusion in iron - A review, *Trans. Iron Steel Inst. Japan*, **68**, 1489-1497.
- Pham Q.T. (2000). Comparison of general-purpose finite element methods for the Stefan problem, *Numer. Heat Transfer B: Fundamentals*, **27**, 417-435.
- Rapp R. (1965). Kinetics, microstructures and mechanism of internal oxidation - Its effect and prevention in high temperature alloy oxidation, *Corros.*, **21**, 382-401.
- Stott F.H., Wood G.C. (1988). Internal oxidation, *Mater. Sc. Technol.*, **4**, 1072-1078.
- Thermodata (2005). Electronic data bank for thermodynamic quantities, available online at the address <http://thermodata.online.fr>.
- Wagner C. (1959). Reaktionstypen bei der oxydation von Legierungen, *Zeitschr. Elektrochemie*, **63**, 772-782 (in German).
- Whittle D.P., Gesmundo F., Bastow B.D., Wood G.C. (1981). The formation of solid solution oxides during internal oxidation, *Oxid. Metals*, **16**, 159-174.
- Zienkiewicz O.C., Taylor R.L. and Zhu J.Z. (2005). *The Finite Element Method Set (Sixth Edition) - Its Basis and Fundamentals*, Butterworth-Heinemann.

## A Appendix: calculation of the minimum $M_\lambda$

The aim of this Appendix is to evaluate the quantity  $M_\lambda$  defined by equations (22) and (23) of the text.

Let us define, for any vector  $\mathbf{X}_\lambda$  such that  $X_{\lambda\alpha} \geq 0$  for all  $\alpha$ , the function

$$f_\lambda(\mathbf{X}_\lambda) \equiv \sum_{\alpha=1}^{n_c(\lambda)} (Q_{\lambda\alpha} + \ln X_{\lambda\alpha}) X_{\lambda\alpha}.$$

Note that  $f_\lambda(\mathbf{X}_\lambda) = D_{\mathbf{X}_\lambda} G(\mathbf{P})$  if  $\sum_{\alpha=1}^{n_c(\lambda)} X_{\lambda\alpha} = 1$ . Thus the problem is to minimize the convex function  $f_\lambda(\mathbf{X}_\lambda)$  over the convex set  $\{\mathbf{X}_\lambda, X_{\lambda\alpha} \geq 0 \text{ for all } \alpha, \sum_{\alpha=1}^{n_c(\lambda)} X_{\lambda\alpha} = 1\}$ ;  $M_\lambda$  will be the value of the minimum.

The minimum is not reached on the boundary of the set, that is at some point  $\mathbf{X}_\lambda$  having some zero component  $X_{\lambda\alpha}$ . Indeed at such a point some other component  $X_{\lambda\beta}$  must be positive, because of the condition  $\sum_{\gamma=1}^{n_c(\lambda)} X_{\lambda\gamma} = 1$ . Considering then variations of  $X_{\lambda\alpha} = 0$  and  $X_{\lambda\beta} > 0$  of the form  $\delta X_{\lambda\alpha} = \epsilon$ ,  $\delta X_{\lambda\beta} = -\epsilon$ ,  $\epsilon \rightarrow 0^+$  (preserving the relation  $\sum_{\gamma=1}^{n_c(\lambda)} X_{\lambda\gamma} = 1$ ), one sees that the resulting variation  $\delta f_\lambda$  of  $f_\lambda$  is of the form  $\epsilon \ln \epsilon + O(\epsilon)$  and hence negative, so that  $f_\lambda$  is not minimum at  $\mathbf{X}_\lambda$ .

Hence the minimum is reached in the interior of the set, and may be deduced from the constrained extremum theorem:  $g_\lambda(\mathbf{X}_\lambda)$  denoting the function defined by

$$g_\lambda(\mathbf{X}_\lambda) \equiv \sum_{\alpha=1}^{n_c(\lambda)} X_{\lambda\alpha} - 1,$$

at a point where the minimum is reached, there is a scalar  $\eta_\lambda$  (a *Lagrange multiplier*) such that

$$\frac{\partial f_\lambda}{\partial X_{\lambda\alpha}}(\mathbf{X}_\lambda) = \eta_\lambda \frac{\partial g_\lambda}{\partial X_{\lambda\alpha}}(\mathbf{X}_\lambda) \quad \text{for every } \alpha = 1, \dots, n_c(\lambda).$$

This is equivalent to

$$Q_{\lambda\alpha} + \ln X_{\lambda\alpha} + 1 = \eta_\lambda \quad \Rightarrow \quad X_{\lambda\alpha} = e^{\eta_\lambda - 1} e^{-Q_{\lambda\alpha}} \quad (\alpha = 1, \dots, n_c(\lambda)).$$

The factor  $e^{\eta_\lambda - 1}$  here must be such that  $\sum_{\alpha=1}^{n_c(\lambda)} X_{\lambda\alpha} = 1$ , implying that

$$X_{\lambda\alpha} = \frac{e^{-Q_{\lambda\alpha}}}{\sum_{\beta=1}^{n_c(\lambda)} e^{-Q_{\lambda\beta}}} \quad (\alpha = 1, \dots, n_c(\lambda)).$$

This equation provides the values of the components  $X_{\lambda\alpha}$  of that point  $\mathbf{X}_\lambda$  where the minimum is reached. Inserting them into the expression of  $f_\lambda(\mathbf{X}_\lambda)$  and using the expression (21) of the quantities  $Q_{\lambda\alpha}$ , one gets equation (24) of the text.