

Diffusion-Controlled Solid-State Reactions of Spherical Particles, A General Model for Multiphase Binary Systems

Vincenzo Buscaglia^{*,†} and Chiara Milanese[‡]

Institute for Energetics and Interphases (IENI), Department of Genoa, National Research Council, Via De Marini 6, I-16149 Genoa, Italy and Department of Physical Chemistry, University of Pavia, Viale Taramelli 16, I-27100 Pavia, Italy

Received: December 3, 2004; In Final Form: March 31, 2005

The formal treatment of the diffusion-controlled growth of n binary compounds with narrow homogeneity range during the reaction of a sphere of reactant A immersed in reactant B is presented and discussed. Both constituents are assumed to be mobile. The reaction products are assumed to grow simultaneously as uniform and compact concentric layers with ideal contact at the interfaces as well as at the external surface of the sphere. The kinetic equations follow from the coupling between chemical reactions and partitioning of the diffusion flux at phase boundaries. The results for the formation of two and three compounds are presented. The influence of the initial radius of the sphere, of the relative magnitude of the kinetic constants, and of the volume variation is discussed in detail.

1. Introduction

Solid-state reactions involving particles of spherical or approximately spherical shape play an important role in synthetic and ceramic processes: production of binary oxides, nitrides, carbides, and borides by solid–gas or solid–solid reaction (e.g., the carbothermal reduction process), synthesis of ternary and more complex oxides starting from mixtures of solid reactants (oxides, hydroxides, carbonates), self-propagating high-temperature synthesis (SHS or combustion synthesis) of innumerable compounds, and reaction sintering of ceramics and ceramic-matrix composites.^{1–3} Reactions involving spherical granules are also of interest in geology and geochemistry. A well-known example is provided by the development of corona microstructures in partially transformed metamorphic rocks.⁴

As long as one of the reactants is not completely consumed and there are no limitations in the supply of the components such as in thin film couples, all the intermediate compounds between the end members are generally observed, according to the relevant phase diagram. In the simplest case of a binary or pseudobinary diffusion couple A–B, the different compounds grow as plane and parallel layers. The overall reaction rate at high temperature is often controlled by solid-state diffusion through the reaction layers,^{1–3} as widely verified for metal–gas reactions (oxidation, nitridation, carburization, sulfidation),^{2,5} many oxide–oxide reactions (formation of spinels, ferrites, silicates, etc.),^{1,3,6–8} and growth of intermetallic compounds.^{3,9–11}

The diffusion-controlled growth of n reaction layers in multiphase diffusion couples with plane slab geometry was theoretically treated by several authors, with fundamental contributions from Kidson,¹² Wagner,¹³ and Pawel.¹⁴ Rafaja et al.¹⁵ have extended the theory to elucidate the influence of the

finite geometry of the couples on the growth of compounds with large deviation from stoichiometry. Recently, a general treatment of the diffusional growth of compounds with a narrow homogeneity range in a multiphase binary system was given by Buscaglia and Anselmi-Tamburini.¹⁶ In any case, one-dimensional diffusion was considered (plane slab geometry) because of the simpler form of the equations.

In contrast, diffusional growth of compounds on the surface of spherical particles is far less studied despite its practical importance. Diffusion equations, even for quasi steady-state (QSS) conditions, are more complex than those for the plane geometry, and consequently, analytical solutions were reported only for the growth of a single concentric shell.^{17–20} Among these solutions, the most general equation was proposed by Valensi¹⁹ and Carter²⁰

$$[1 + (z - 1)\alpha]^{2/3} + (z - 1)(1 - \alpha)^{2/3} = z + 2(1 - z)\frac{k_{VC}t}{R^2} \quad (1)$$

where α is the converted fraction, R the initial sphere radius, t the time, and k the kinetic constant. This equation accounts also for the volume change by making use of the equivalent volume z , i.e., the volume of product per unit volume of the reactant sphere. In contrast, the Ginstling and Brounshtein equation¹⁸

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = 2\frac{k}{R^2}t \quad (2)$$

holds for constant volume transformations ($z = 1$). The general equations describing the diffusion-controlled reaction of a spherical particle of component A to form a single concentric shell of product AB by reaction with component B were set up and numerically solved by Frade and Cable²¹ in their reexamination of the basic theoretical models for the kinetics of solid-state reactions. Their results were compared with the equations

* Author to whom correspondence should be addressed. E-mail: v.buscaglia@ge.ieni.cnr.it. Telephone: +39-010-6475708. Fax: +39-010-6475700.

[†] Institute for Energetics and Interphases (IENI).

[‡] University of Pavia.

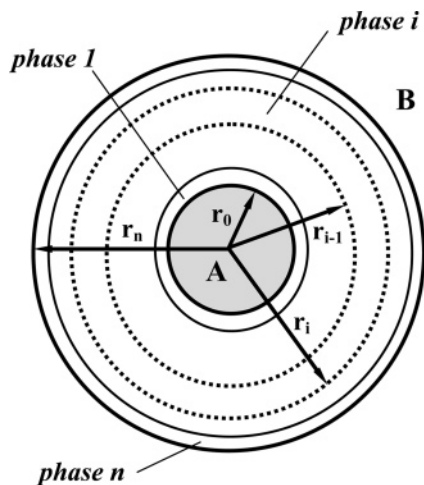


Figure 1. Model for the reaction of a sphere of component A with a homogeneous matrix of component B with formation of n intermediate phases, each corresponding to a distinct concentric layer.

of Ginstling and Brounshtein¹⁸ and Valensi–Carter.^{19–20} It was shown that these QSS models correctly describe the kinetics of the process when component A has a low solubility in the reaction product, i.e., the reaction product possesses a narrow homogeneity range.

As far as we know, theoretical treatments for the diffusion-controlled growth of multiple reaction products on spherical particles were never reported in the literature. The broad practical importance of powder reactions makes the solution of this problem of quite general interest in the fields of solid-state chemistry, materials science, and geochemistry. Indeed, formation of more than one intermediate reaction product is a general rule rather than an exceptional case. Simulation of complex processes involving reactivity and diffusion in the solid state, like combustion synthesis,²² would cover a greater number of systems if formation of multiple reaction product were included.

The aim of the present study is to develop a general model for the diffusion-controlled growth of n intermediate binary phases with narrow homogeneity range on a spherical particle. The paper is organized as follows. In Section 2, the theoretical framework of the kinetic model is developed. In Section 3, the application of the model to the formation of two and three concentric shells of products is discussed in detail. In Section 4, main results and conclusions are summarized.

2. Theory

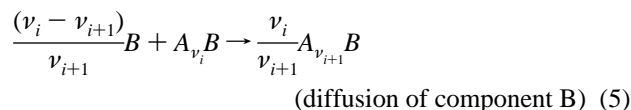
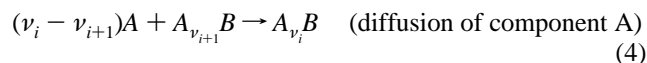
In the following, reaction is assumed to occur, at constant temperature, around a spherical particle (of radius R) of a solid reactant A (phase 0) immersed in a continuous matrix of reactant B (phase $n + 1$, either solid, liquid, or gaseous) with good contact over its entire surface. Reaction is assumed to result in the formation of n intermediate phases with a narrow homogeneity range. The different phases are also assumed to grow simultaneously and to produce compact multiple concentric layers, each corresponding to a different compound (Figure 1). The stoichiometry of each compound is normalized to 1 mol of B, and therefore, the i th phase is denoted as $A_{\nu_i}B$. The reaction rate is supposed to be governed by solid-state diffusion through the product layers. Local thermodynamic equilibrium is assumed inside the reaction layers as well as at the interfaces. Ideal contact at the phase boundaries is considered, without formation of pores and/or cracks.

The area for diffusion through a spherical shell increases as the square of the radius. As a consequence, the flux is not constant through a spherical shell even in steady-state conditions, and this is the most important difference in comparison to one-dimensional diffusion in a plane slab. Thus, it is convenient to refer to the mass rate, Q , i.e., the total amount of matter which flows per unit time (mol s^{-1}). For the spherical shell of phase i (see Figure 1) with inner radius r_{i-1} and outer radius r_i , the mass rate through the shell is constant in steady-state conditions and is given by,²³

$$Q_i = 4\pi k_i \frac{r_{i-1}r_i}{r_i - r_{i-1}} \quad (3)$$

where the constant k_i ($\text{mol s}^{-1} \text{cm}^{-1}$) has the meaning of a rational rate constant. In the simplest case of a constant diffusion coefficient D and a linear concentration profile, it is $k = D(c_i - c_{i-1})$, where c_i is the concentration at $r = r_i$ and c_{i-1} is the concentration at $r = r_{i-1}$. More generally, when both components are mobile, matter transport will be described by two distinct terms, $Q_{A,i}$ and $Q_{B,i}$. In the following, the reaction kinetics is evaluated within the quasi steady-state (QSS) approximation, i.e., eq 3 is assumed to describe the transport of matter that determines the growth of the reaction products. As demonstrated by Frade and Cable,²¹ this is a good approximation provided that the homogeneity range of the reaction products is reasonably narrow. In addition, the mutual solubility of A and B has to be negligibly small or, as an alternative, the dissolution has to be slow in comparison to the growth rate of the product layers, a situation often encountered in the formation of intermetallic compounds. If mutual solubility is not negligible, the overall reaction kinetics cannot be correctly described by a QSS approach unless the reactants are preventively saturated.

Let us consider the system $A/A_{\nu_1}B/\dots/A_{\nu_i}B/\dots/A_{\nu_n}B/B$. For sake of generality, both species A and B are assumed to be mobile without coupling between the diffusion fluxes. However, the introduction of coupling conditions does not affect the general result of the proposed analysis. The movement of each phase boundary implies formation and consumption of the adjacent phases, and this can be related to interface reactions. For the generic boundary between phases i and $i + 1$ ($i = 1, \dots, n - 1$) the following reactions can be considered



Reactions at the first ($A/A_{\nu_1}B$) and at the last ($A_{\nu_n}B/B$) phase boundary directly involve pure components A and B, respectively.



Only a fraction of the flux arriving at a phase boundary reacts at the interface (as described by reactions 4–7), whereas the remaining part goes in the next layer (flux partitioning). The displacement velocity of a phase boundary can thus be defined by the difference between the flux arriving at and the flux leaving the interface. Following the same approach as in a former paper,¹⁶ the growth rate ($\text{cm}^3 \text{s}^{-1}$) of the i th phase can

be obtained from the mass balance at phase boundaries ($i - 1$)/ i and i /($i + 1$) and results

$$\frac{dV_i^T}{dt} = -\frac{V_i}{v_{i-1} - v_i}(|Q_{A,i-1}| + v_{i-1}|Q_{B,i-1}|) + \frac{V_i(v_{i-1} - v_{i+1})}{(v_{i-1} - v_i)(v_i - v_{i+1})}(|Q_{A,i}| + v_i|Q_{B,i}|) - \frac{V_i}{v_i - v_{i+1}}(|Q_{A,i+1}| + v_{i+1}|Q_{B,i+1}|) \quad (8)$$

where V_i^T and V_i are the total volume and the molar volume of A_vB , respectively. The module, $|Q_i|$, of the mass rate terms has been introduced to account for diffusion of A and B in opposite directions. The stoichiometry coefficient v_i , which multiplies the term $Q_{B,i}$, takes into account that the number of moles of A_vB formed for each mole of B is v_i times greater than the number of moles formed for each mole of A. When $i = 1$, the first term on the right hand side of eq 8 does not exist. Likewise, for $i = n$, the last term is missed. This is a consequence of the negligible solubility (or negligible diffusivity) in the terminal phases. The mass rate terms in eq 8 can be rewritten as

$$\Theta_i = (|Q_{A,i}| + v_i|Q_{B,i}|) = 4\pi k_i \frac{r_{i-1}r_i}{r_i - r_{i-1}} \quad (9)$$

where the rational rate constant now accounts for diffusion of both components. It is essential to recognize that the kinetic constant in eqs 3 and 9 is a fundamental physical property of the given phase and it is independent of the geometry of the system. The general expression of the rational rate constant k_i can be obtained from the diffusion flux equation in a chemical potential gradient (the Nernst–Einstein equation) and, for compounds with narrow homogeneity range, takes the form¹⁶

$$k_i = \frac{v_i(v_{i-1} - v_{i+1})}{(v_{i-1} - v_i)(v_i - v_{i+1})} (D_{A,i} + v_i D_{B,i}) \frac{|\Delta G_i^0|}{V_i R_g T} \quad (10)$$

where $D_{A,i}$ and $D_{B,i}$ are the self-diffusion coefficients of A and B, respectively, $|\Delta G_i^0|$ is the absolute value of the variation of Gibbs free energy for the formation of 1 mol of A_vB from the adjacent phases, T the temperature, and R_g the gas constant. The terms $D_{A,i}$ and $D_{B,i}$ have to be considered as average values. Indeed, self-diffusion coefficients generally depend on the activity of the components, and consequently, they vary moving through the layer because growth occurs in a chemical potential gradient. The advantage of using eq 10 is that the calculation of the mass rate (eq 9) does not require the knowledge of the concentration profile, which is very difficult or even impossible to be measured in the case of compounds with small deviation from stoichiometry. The rational rate constant k_i is related to the rate constant of the second kind,¹³ k_i^{II} , which is widely used to describe the parabolic growth of reaction layers in diffusion couples with the plane slab geometry, by the eq¹⁶

$$k_i^{\text{II}} = k_i \tilde{V}_i = k_i \frac{(v_{i-1} - v_{i+1})V_i}{(v_{i-1} - v_i)(v_i - v_{i+1})} \quad (11)$$

where \tilde{V}_i is the reaction volume, i.e., the volume of A_vB resulting from the transport of one mole of A atoms through the reaction product. Equations 10–11 hold also for $i = 1$ and $i = n$, taking into account that $v_0 = \infty$ (pure A) and $v_{n+1} = 0$ (pure B). The initial ($t = 0$) volume of the A sphere and the volumes of the

different phases at time t are related by the geometric constraint

$$V_0^T(t=0) = \frac{4}{3}\pi R^3 = V_0^T(t) + \sum_{i=1}^n \frac{V_i^T(t)}{z_i} \quad (12)$$

where z_i is the volume of phase i formed per unit volume of reactant A. This parameter is directly related to the stoichiometry of the given phase by

$$z_i = \frac{V_i}{v_i V_0} \quad (13)$$

where V_0 is the molar volume of component A. Introducing the definition of the volume of a spherical shell, r_n can be calculated as

$$r_n^3(t) = z_n \left\{ R^3 - r_0^3(t) - \left[\sum_{i=1}^{n-1} \frac{r_i^3(t) - r_{i-1}^3(t)}{z_i} \right] + \frac{r_{n-1}^3(t)}{z_n} \right\} \quad (14)$$

As a result, the radii r_0, r_1, \dots, r_n are not all independent, and in particular, the external radius of the sphere at time t , $r_n(t)$, can be obtained from the other n geometrical parameters. Differentiation of eq 14 leads to

$$\left[\sum_{i=0}^{n-1} r_i^2 \frac{dr_i}{dt} \left(\frac{1}{z_i} - \frac{1}{z_{i+1}} \right) \right] + r_n^2 \frac{dr_n}{dt} \frac{1}{z_n} = 0 \quad (15)$$

where it has been assumed $z_0 = 1$. Substitution of eqs 9, 14, and 15 in eq 8 produces, after some manipulations, the n independent kinetic equations

$$4\pi r_0^2 \frac{dr_0}{dt} = -\frac{1}{z_1} \sum_{j=1}^2 A_{1j} \Theta_j - \sum_{m=2}^{n-1} \frac{1}{z_m} \sum_{j=m-1}^{m+1} A_{mj} \Theta_j - \frac{1}{z_n} \sum_{j=n-1}^n A_{nj} \Theta_j \quad (16a)$$

$$4\pi r_i^2 \frac{dr_i}{dt} = 4\pi r_0^2 \frac{dr_0}{dt} + \sum_{j=1}^2 A_{1j} \Theta_j + \sum_{m=2}^i \sum_{j=m-1}^{m+1} A_{mj} \Theta_j \quad i = 1, \dots, n-1 \quad (16b)$$

where

$$\begin{aligned} \text{for } j = (m-1) \quad A_{m(m-1)} &= -\frac{V_m}{(v_{m-1} - v_m)} \\ \text{for } j = m \quad A_{mm} &= \frac{V_m(v_{m-1} - v_{m+1})}{(v_{m-1} - v_m)(v_m - v_{m+1})} = \tilde{V}_m \\ \text{for } j = (m+1) \quad A_{m(m+1)} &= -\frac{V_m}{(v_m - v_{m+1})} \end{aligned} \quad (17)$$

Although an equation similar to 16b can be written also for r_n , the use of eq 14 is more convenient. By introducing the reduced variables

$$x_i = \frac{r_i}{R} \quad (18)$$

the definition of Θ_i (eq 9) can be rewritten as

$$\Theta_i = 4\pi R k_i \frac{x_i x_{i-1}}{x_i - x_{i-1}} = 4\pi R k_i X_i \quad (19)$$

where X_i is the geometric factor for the i th shell. Insertion of eq 18 and 19 in eqs 16 gives, after rearrangement,

$$R^2 x_0^2 \frac{dx_0}{dt} = -\frac{1}{z_1} \sum_{j=1}^2 A_{1j} k_j X_j - \sum_{m=2}^{n-1} \frac{1}{z_m} \sum_{j=m-1}^{m+1} A_{mj} k_j X_j - \frac{1}{z_n} \sum_{j=n-1}^n A_{nj} k_j X_j \quad (20a)$$

$$R^2 x_i^2 \frac{dx_i}{dt} = \left(1 - \frac{1}{z_1}\right) \sum_{j=1}^2 A_{1j} k_j X_j + \sum_{m=2}^i \left(1 - \frac{1}{z_m}\right) \sum_{j=m-1}^{m+1} A_{mj} k_j X_j - \sum_{m=i+1}^{n-1} \frac{1}{z_m} \sum_{j=m-1}^{m+1} A_{mj} k_j X_j - \frac{1}{z_n} \sum_{j=n-1}^n A_{nj} k_j X_j \quad i = 1, \dots, n-1 \quad (20b)$$

The kinetic equations are greatly simplified in the case of a constant volume reaction, being $z_1 = z_2 = \dots = z_n = 1$. It is worth noting that the equations have an R^2 scale factor. This means that the model will become independent of the initial radius of the sphere if t/R^2 is selected as variable. In other words, once the kinetic equations have been integrated for a sphere with initial radius R_1 , the solution for a sphere with initial radius R_2 can be simply obtained by multiplying the time scale by a factor R_2^2/R_1^2 . This is a general property of diffusion-controlled reactions in spherical geometry.

The resolution of the above kinetic equations requires numerical integration. However, integration cannot start at $t = 0$ with zero thickness of the reaction layers because, in such a case, the activity gradients as well as the diffusion fluxes are not defined. From the physical point of view, this means that, at the very early stages, the reaction rate will be controlled by purely chemical processes at the interfaces, which proceed at a finite rate in any case. However, it is possible to define the starting conditions for integration by choosing a suitable time $t_0 > 0$, corresponding to $(r_i - r_{i-1}) \ll R$ for all reaction layers. In this case, the growth of the reaction layers will conform very closely to that observed for the plane slab geometry.^{13,16} Therefore, the thickness Δy_i of the different layers can be calculated from the general solution for a plane slab (eq 16 in ref 16)

$$\frac{(r_i - r_{i-1})^2}{2t_0} \cong \frac{\Delta y_i^2}{2t_0} = k_i \left[v_i \sum_{j=1}^{i-1} \frac{\Delta y_j}{V_j \Delta y_i} + \frac{v_i}{V_i} + \sum_{j=i+1}^n \frac{v_j \Delta y_j}{V_j \Delta y_i} \right] \quad i = 1, \dots, n \quad (21)$$

and the different radii follows immediately from $\Delta y_i = r_i - r_{i-1}$ and from eq 14. Comparison between eq 21 and the solution obtained by numerical integration of eq 20 for $n = 2$ and $n = 3$ shows that, up to a thickness of about 0.20 R , the total thickness of the reaction products is nearly the same for a sphere of radius R and for a plane slab of depth $2R$, in agreement with

the result reported by van Loo³ for the formation of a single product layer. For values larger than $\approx 0.2R$, the total thickness of the reaction layers is progressively larger for the sphere in comparison to the planar geometry.

In the above theoretical treatment, it has been implicitly assumed that the equilibrium condition at the interfaces is independent of the radius of the sphere. However, if the interface has a high curvature (as in the case of nanosized particles), the chemical potential of the compounds and, in turn, the Gibbs free energy term in eq 10, will deviate from the values typical of nearly flat interfaces (Gibbs–Thompson effect). The curvature effect is limited to the expression of the kinetic constant (eq 10), and therefore, the kinetic equation 20 still holds for small particles. Obviously, the effect of curvature on k_i should be taken into account during integration. In general, the influence of the curvature can be neglected for particles larger than a few tens of nanometers. In the case of very small particles, the applicability of the present model becomes critical for a second reason. For diffusion in a planar geometry, transition from diffusion-controlled kinetics to interface-controlled growth will be observed for a critical thickness of the reaction layer. The value of the critical thickness is system dependent and the lack of data about the rate of interfacial reactions prevents an accurate estimation. As a general indication, transition to interface-controlled kinetics is expected when the thickness of the reaction layer is $\ll 1 \mu\text{m}$. As a result, diffusion-controlled growth will not be a general rule for nanometer-range particles.

3. Some Detailed Results

The simplest, but of large practical importance, cases of formation of two and three intermediate phases, corresponding to the sequences $A/A_{v1}B/A_{v2}B/B$ and $A/A_{v1}B/A_{v2}B/A_{v3}B/B$, respectively, are discussed in detail. For $n = 2$, eq 20 rewrites as

$$R^2 x_0^2 \frac{dx_0}{dt} = -\frac{(z_2 A_{11} + z_1 A_{21})k_1 X_1 + (z_2 A_{12} + z_1 A_{22})k_2 X_2}{z_1 z_2} \quad (22a)$$

$$R^2 x_1^2 \frac{dx_1}{dt} = \frac{[z_2(z_1 - 1)A_{11} - z_1 A_{21}]k_1 X_1 + [z_2(z_1 - 1)A_{12} - z_1 A_{22}]k_2 X_2}{z_1 z_2} \quad (22b)$$

and the external radius of the sphere is

$$r_2 = \left\{ \frac{1}{z_1} [z_1 z_2 R^3 + (z_1 - z_2)r_1^3 + z_2(1 - z_1)r_0^3] \right\}^{1/3}$$

For constant volume ($z_1 = z_2 = 1$), using the expressions 13 and 17, eq 22 takes the simpler form

$$R^2 x_0^2 \frac{dx_0}{dt} = -V_0 k_1 X_1$$

$$R^2 x_1^2 \frac{dx_1}{dt} = \frac{V_0}{v_1 - v_2} (v_2 k_1 X_1 - v_1 k_2 X_2)$$

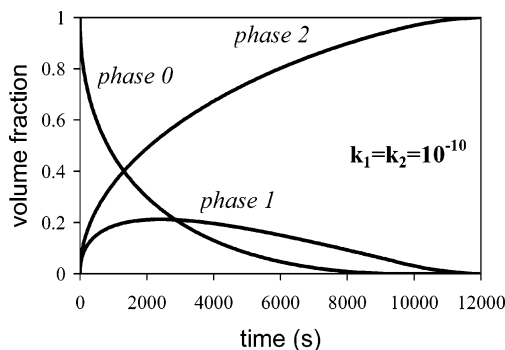


Figure 2. Reaction kinetics for a sphere of radius 100 μm , $\nu_1 = 1$, $\nu_2 = 0.5$, $V_0 = 10 \text{ cm}^3 \text{ mol}^{-1}$, $k_1 = k_2 = 10^{-10} \text{ mol cm}^{-1} \text{ s}^{-1}$, constant volume.

and $x_2 = 1$. For $n = 2$, an analytical solution of eq 21 exists, and the starting conditions for integration correspond to:

$$\frac{(r_1 - r_0)^2}{2t_0} \cong \frac{\Delta y_1^2}{2t_0} = \frac{1}{\nu_1^2} \left\{ (\nu_1 - \nu_2)(\nu_1 k_1^{\text{II}} - \nu_2 \gamma^2 k_2^{\text{II}}) + \frac{1}{2} \nu_2 [\gamma^2 k_2^{\text{II}} (2\nu_1 - \nu_2) + \nu_1 k_1^{\text{II}} \pm D] \right\}$$

$$\frac{(r_2 - r_1)^2}{2t_0} \cong \frac{\Delta y_2^2}{2t_0} = \frac{1}{2\nu_1 \gamma^2} [(2\nu_1 - \nu_2) \gamma^2 k_2^{\text{II}} + \nu_1 k_1^{\text{II}} \pm D]$$

where

$$D = \sqrt{(\nu_1 k_1^{\text{II}} - \gamma^2 k_2^{\text{II}} \nu_2)^2 + 4\nu_1^2 \gamma^2 k_1^{\text{II}} k_2^{\text{II}}}$$

and $\gamma = V_1/V_2$. It can be easily shown that only the solutions with the negative sign have a physical meaning. An example of the reaction kinetics for $n = 2$ is reported in Figure 2 for a sphere with radius of 100 μm and $k_1 = k_2 = 10^{-10} \text{ mol cm}^{-1} \text{ s}^{-1}$. The value of the rate constant is roughly determined by the magnitude of the interdiffusion coefficient $D_A + \nu D_B$ in eq 10. A chemical diffusion coefficient of the order of $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ is typical of intermetallic compounds and oxides at a temperature of 1000 $^\circ\text{C}$ or higher.^{6–11} Therefore, Figure 2 provides a significant example of the time scale in a realistic process. As previously mentioned, given the solution for a sphere of radius R_1 , the solution for a sphere of radius R_2 can be simply obtained by multiplying the time scale by the ratio R_2^2/R_1^2 . The growth rate of the core of component A (phase 0) is always negative because the core is progressively consumed ($dx_0/dt < 0$). In contrast, the growth rate, dV_2^T/dt , of phase 2 (phase n in the general case) is expected to be always positive, because the sphere is gradually converted in the final reaction product $A_{\nu_2}B$ ($A_{\nu_n}B$ in the general case). For the phase $A_{\nu_1}B$ (phases 1, ..., $n - 1$ in the general case), the growth rate dV_1^T/dt can change its sign from positive (growth) to negative (consumption) as the reaction proceeds (see Figure 2). As a result, the volume of phase 1 has a maximum corresponding to the condition $dV_1^T/dt = 0$

$$\frac{1}{4\pi R^3} \frac{dV_1^T}{dt} = x_1^2 \frac{dx_1}{dt} - x_0^2 \frac{dx_0}{dt} = 0 \quad (23)$$

Substituting eq 22 in eq 23 and solving for k_1/k_2 gives

$$\frac{k_1}{k_2} = \frac{x_2(x_1 - x_0)}{x_0(x_2 - x_1)} \quad (24)$$

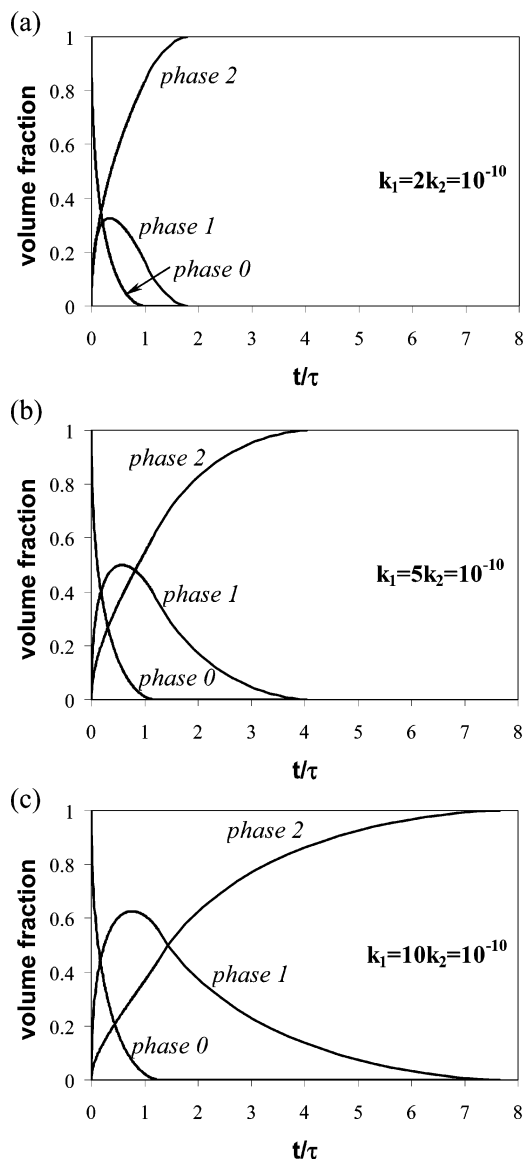


Figure 3. Reaction kinetics for a sphere of radius 100 μm , $\nu_1 = 1$, $\nu_2 = 0.5$, $V_0 = 10 \text{ cm}^3 \text{ mol}^{-1}$, constant volume; (a) $k_1 = 2k_2 = 10^{-10} \text{ mol cm}^{-1} \text{ s}^{-1}$; (b) $k_1 = 5k_2 = 10^{-10} \text{ mol cm}^{-1} \text{ s}^{-1}$; (c) $k_1 = 10k_2 = 10^{-10} \text{ mol cm}^{-1} \text{ s}^{-1}$. The abscissa is the ratio between the time and the reference time τ required for complete transformation of the sphere in phase 2 when $k_1 = k_2$ (Figure 2).

Therefore, for constant volume ($x_2 = 1$), the shape of the kinetic curves (volume fraction vs time) is uniquely determined by the ratio k_1/k_2 , whereas the sphere radius and the absolute value of the kinetic constants defines the time scale of the reaction. The influence of the ratio k_1/k_2 on the kinetic curves is shown in Figures 3 and 4. For the abscissas, the dimensionless time t/τ has been used, where τ is the time required for complete transformation of the sphere when $k_1 = k_2$ (Figure 2). When $k_1 \gg k_2$, the formation of compound $A_{\nu_1}B$ is rather fast, but full transformation of $A_{\nu_1}B$ in $A_{\nu_2}B$ takes a much longer time (Figure 3). From a practical point of view, this means that production of pure $A_{\nu_2}B$ without traces of $A_{\nu_1}B$ might be difficult to achieve. On the contrary, when $k_2 \gg k_1$ (Figure 4), the time required for full transformation to $A_{\nu_2}B$ is comparable to that corresponding to the condition $k_1 = k_2$ (Figure 2). In any case, the overall reaction is largely controlled by the value of k_2 despite the relative magnitude of the kinetic constants. The volume fraction of phase 1 in Figure 4c is small and nearly constant over a broad

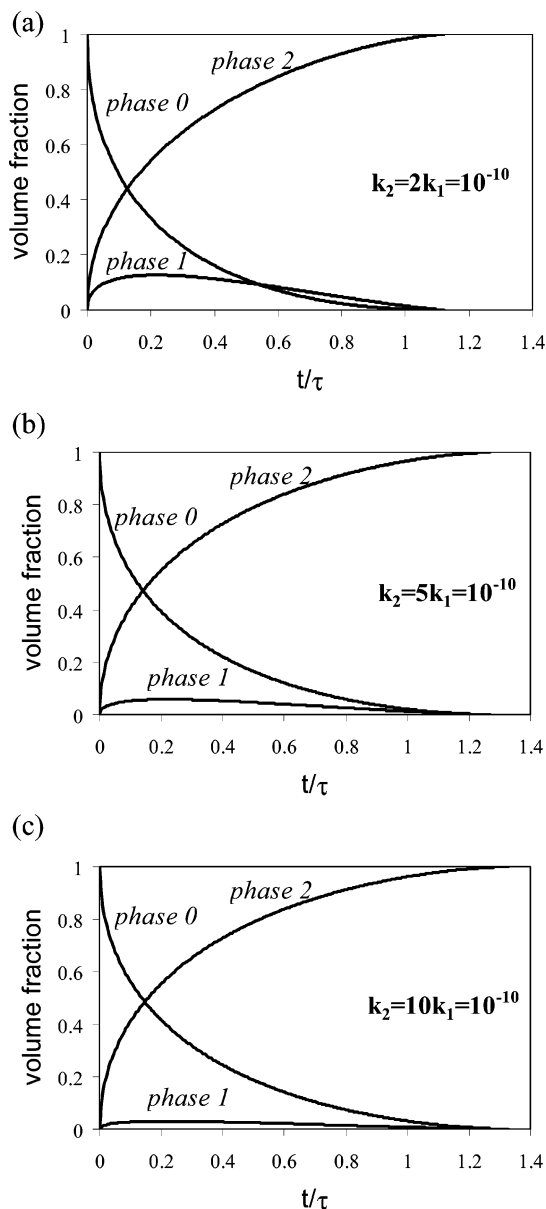


Figure 4. Reaction kinetics for a sphere of radius 100 μm , $\nu_1 = 1$, $\nu_2 = 0.5$, $V_0 = 10 \text{ cm}^3 \text{ mol}^{-1}$, constant volume; (a) $k_2 = 2k_1 = 10^{-10} \text{ mol cm}^{-1} \text{ s}^{-1}$; (b) $k_2 = 5k_1 = 10^{-10} \text{ mol cm}^{-1} \text{ s}^{-1}$; (c) $k_2 = 10k_1 = 10^{-10} \text{ mol cm}^{-1} \text{ s}^{-1}$. The abscissa is the ratio between the time and the reference time τ required for complete transformation of the sphere in phase 2 when $k_1 = k_2$ (Figure 2).

time interval. This means that, for $k_2 \gg k_1$, a pseudo steady-state condition is achieved for formation of phase 1.

In the case of variable volume, there is an additional degree of freedom, and the appearance of the kinetic curves will be also determined by the value of z_1 and z_2 . An example is reported in Figure 5. With increasing volume variation, the initial formation rate of $A_{\nu_2}B$ increases, while the maximum of $A_{\nu_1}B$ moves at shorter time. These effects are related to the increase of the molar volumes when $z > 1$, as described by eq 13. A useful application of eq 24 is for checking the accuracy of the numerical integration algorithm and the correctness of the simulation.

The calculation of the kinetic constants k_1 and k_2 can be carried out by fitting a set of experimental data by the model equations. However, the application of eq 24 gives immediately the ratio of the kinetic constants without the need of a detailed analysis. Moreover, if the Gibbs free energy of formation of

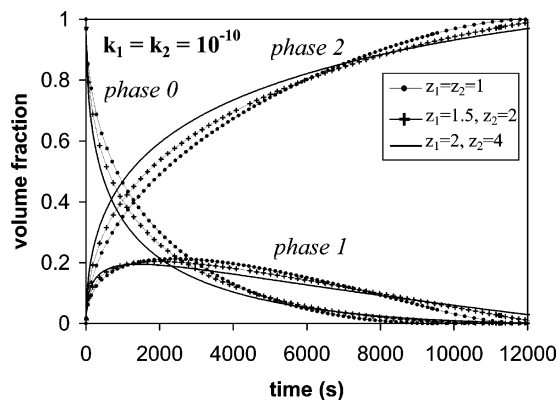


Figure 5. Reaction kinetics for a sphere of radius 100 μm , $\nu_1 = 1$, $\nu_2 = 0.5$, $V_0 = 10 \text{ cm}^3 \text{ mol}^{-1}$, $k_1 = k_2 = 10^{-10} \text{ mol cm}^{-1} \text{ s}^{-1}$; (●) $z_1 = z_2 = 1$; (+) $z_1 = 1.5$, $z_2 = 2$; (---) $z_1 = 2$, $z_2 = 4$.

the two compounds involved in the reaction is known, eq 24 in combination with eq 10 provides the ratio of self-diffusion coefficients of the rate-determining species in the reaction products. The present model can be applied also to predict the kinetics of powder reactions using values of the kinetic constants calculated from diffusion and thermodynamic properties of the different compounds.

When the core of component A (phase 0) is completely consumed ($t = t_1$), the reaction proceeds by transformation of $A_{\nu_1}B$ to $A_{\nu_2}B$ by reaction with residual component B. With reference to the diagonal term of eq 8 and remembering that $\nu_3 = 0$, the growth rate of phase 2 can be written as

$$\frac{dV_2^T}{dt} = \frac{\nu_1 V_2}{\nu_2(\nu_1 - \nu_2)}(|Q_{A,2}| + \nu_2|Q_{B,2}|) \quad (25)$$

where the volume of $A_{\nu_2}B$ is

$$V_2^T = \frac{4}{3}\pi(z_2 R^3 - z_{12} r_1^3) \quad (26)$$

where z_{12} is the volume of phase 2 formed for unit volume of phase 1. Substitution of eqs 26 and 9 in eq 25 gives the kinetic equation

$$-r_1^2 \frac{dr_1}{dt} = \frac{\nu_1 V_2}{\nu_2(\nu_1 - \nu_2)} \frac{k_2}{z_{12}} \frac{r_2 r_1}{r_2 - r_1} = \tilde{V}_2 \frac{k_2}{z_{12}} \frac{r_2 r_1}{r_2 - r_1} \quad (27)$$

Integration between $t = t_1$ (disappearance of A) and the generic time t gives

$$[r_1^3(1 - z_{12}) + z_2 R^3]^{2/3} + (1 - z_{12})(R_1^2 - r_1^2) - [R_1^3(1 - z_{12}) + z_2 R^3]^{2/3} = 2(1 - z_{12}) \frac{k_2 \tilde{V}_2}{z_{12}} (t - t_1) \quad (28)$$

where R_1 is the value of r_1 when $t = t_1$. For constant volume ($z_1 = z_2 = z_{12} = 1$), integration of eq 27 yields

$$\frac{2}{3} \left(\frac{r_1}{R} \right)^3 - \left(\frac{r_1}{R} \right)^2 + \left(\frac{R_1}{R} \right)^2 \left[1 - \frac{2}{3} \left(\frac{r_1}{R} \right) \right] = 2 \tilde{V}_2 \frac{k_2}{R^2} (t - t_1) \quad (29)$$

Equations 28 and 29 were used to calculate the volume fraction of phases 1 and 2 for $t > t_1$ in Figures 2–5. It can be easily shown that eq 28 represents a generalized form of the

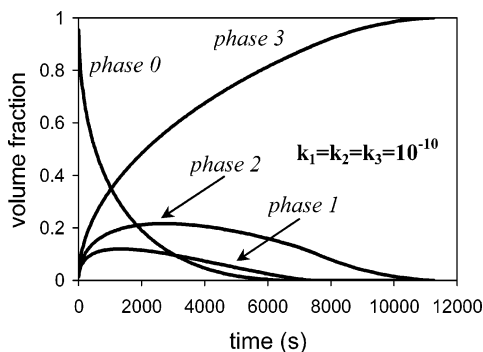


Figure 6. Reaction kinetics for a sphere of radius 100 μm , $\nu_1 = 2$, $\nu_2 = 1$, $\nu_3 = 0.5$, $V_0 = 10 \text{ cm}^3 \text{ mol}^{-1}$, $k_1 = k_2 = k_3 = 10^{-10} \text{ mol cm}^{-1} \text{ s}^{-1}$, constant volume.

Valensi–Carter equation.^{19–20} The radius $R_{1,0}$ of the equivalent sphere completely composed of phase 1 is

$$R_{1,0}^3 = \frac{z_2}{z_{12}} R^3 \quad (30)$$

and, accordingly, the reacted fraction α is

$$\alpha = 1 - \left(\frac{r_1}{R_{1,0}} \right)^3 \quad (31)$$

Substituting $R_1 = R_{1,0}$ in eq 28 and making use of eq 31 gives

$$[1 + (z_{12} - 1)\alpha]^{2/3} + (z_{12} - 1)(1 - \alpha)^{2/3} = z_{12} + 2(1 - z_{12}) \frac{k_2 \tilde{V}_2}{R_{1,0}^2 z_{12}} t$$

which is equivalent to eq 1. Likewise, it can be shown that eq 29 represents a generalized form of the Ginstling and Brounshstein equation.¹⁸ The time interval elapsed between the disappearance of the A core (instant t_1) and the complete transformation to phase 2 (instant t_2) can be obtained by setting $r_1 = 0$ in eqs 28–29 and results

$$t_2 - t_1 = \frac{z_2^{2/3} R^2 + (1 - z_{12}) R_1^2 - [R_1^3(1 - z_{12}) + z_2 R^3]^{2/3}}{2(1 - z_{12})} \frac{z_{12}}{k_2 \tilde{V}_2}$$

in the case of variable volume and

$$t_2 - t_1 = \left(\frac{R_1}{R} \right)^2 \left[1 - \frac{2}{3} \left(\frac{R_1}{R} \right) \right] \frac{R^2}{2k_2 \tilde{V}_2}$$

in the case of constant volume.

An example of application of the model when $n = 3$ is reported in Figure 6. As anticipated in the foregoing discussion, the volume fraction of either phases 1 and 2 has a maximum. For the maximum of $A_{\nu_1}B$, eq 24 still holds unchanged, whereas for the maximum of $A_{\nu_2}B$ it is

$$\frac{k_2}{k_3} = \frac{x_3(x_2 - x_1)}{x_1(x_3 - x_2)} \quad (32)$$

Even in this case, the ratio of the kinetic constants can be easily obtained from the volume fractions corresponding to the maxima. The extension of eqs 24 and 32 to the formation of n intermediate compounds is straightforward. When reactant A

is completely consumed, the system falls again in the case $n = 2$ discussed above.

While the migration velocity of the phase boundaries for a planar reaction couple is proportional to the inverse of the thickness of the reaction layer (parabolic rate law), a different situation is encountered for a sphere. If the interface velocity is defined as $\dot{r}_i = dr_i/dt$ ($i = 0, \dots, n - 1$, see Figure 1), then \dot{r}_i will not be, in general, a monotonic decreasing function of time. Let us consider, for sake of simplicity, the case of a single reaction product ($n = 1$) and constant volume. The velocity of the inner interface can be described (eq 27) as

$$-\dot{r}_0 \approx \frac{R}{r_0(R - r_0)}$$

Thus, the interface velocity (module) will have a minimum for an intermediate value of the thickness $R - r_0$ between 0 and R . The velocity will be very high at the beginning of reaction ($r_0 \rightarrow R$) as well as when the core of the reactant disappears ($r_0 \rightarrow 0$). As a result, the very last stage of the process will be driven by an interface reaction, like the initial instants.

A common practice in the kinetic analysis of solid-state (heterogeneous) reactions is the use of the laws of homogeneous kinetics (concentration vs time) to model the evolution of the volume fraction of the different phases. This practice, however, is erroneous and lacks any theoretical justification. For instance, the kinetic curves of Figures 2–6 closely resemble the concentration vs time functions typical of first-order consecutive homogeneous reactions,²⁴ but this similarity is only apparent. The similarity is determined by the finite geometry of the moieties (particles, grains, inclusions) involved in the heterogeneous reaction. At an early stage, all the product phases have a positive growth rate. At some later stage, the phases close to the core are preferentially consumed with the advantage of the final reaction product. In light of the present results, some solid-state geochemical reactions, previously reported as first-order consecutive reactions, probably deserve a reinvestigation as diffusion-controlled processes.

Powder reactions can be influenced by many parameters, like average particle size, particle size distribution, particle shape, contact area between particles, impurity segregation at surfaces or at interfaces, vaporization, surface diffusion, etc. To avoid the complexity related to the inclusion of all these effects, rather ideal boundary conditions have been adopted in the present model. The main advantage of the proposed approach is that the influence of some important variables, like the diameter of the particles, the molar volumes, and the kinetic constants, on the reaction kinetics can be precisely defined. On the other hand, the model has two major limitations. First, in a system where both the reactants are in solid form, the proposed equations will correctly apply if only a constant chemical potential of one of the reactants over the entire surface of other is provided either by gas-phase transport (high vapor pressure) or rapid surface diffusion. If these conditions are not fulfilled, formation of the reaction products will preferentially occur at the contact points. However, if $R_B \ll R_A$, the number of contact points is very large, and the assumption that reactant B completely envelops the A particles should be closely verified. Second, the influence of elastic stresses has not been taken into account. For a specimen with an infinite plane surface, the reaction layer(s) can in principle collapse on the retreating reactant surface without stress generation if the reaction takes place uniformly over the surface. For specimens with finite dimensions, constraints are imposed on the system, and this can produce cracks and voids at the interfaces or within the reaction layers. In turn, the loss of

adherence and void formation affects the reaction kinetics. The situation is even worse if reaction involves large volume variations. Large plastic deformations of the reaction products are thus required to ensure good contact with the reactant. However, stress relief by plastic deformation is only effective at relatively high temperature.²

Deviations from the ideal behavior can also arise from the Kirkendall porosity.²⁵ If the number of sinks, like edge dislocations, is not large enough to allow for a sufficiently high annihilation rate, the local vacancy concentration can increase to very high levels and pores can be formed. Höglund and Ågren,²⁶ as well as Masumura et al.,²⁷ have shown that the maximum tendency to pore formation is expected at a certain location of the diffusion couple. High levels of porosity will strongly reduce the area available for diffusion, and eventually, the diffusion couple will fracture under negligible stress. In the case of spherical particles, an extreme level of porosity can determine the formation of hollow spheres, as reported by Aldinger.²⁸

4. Summary

The formal treatment of the diffusion-controlled growth of multiple compounds during the solid-state reaction of a spherical particle was presented and discussed. The theory is given for the reaction between two elements resulting in the formation of compounds with narrow homogeneity range. In general, the model can be applied to reactions between an element and a binary compound or between two binary compounds. The reaction products are assumed to grow simultaneously as uniform and compact concentric shells with ideal contact at the interfaces as well as at the external surface of the sphere. Both elements are assumed to be mobile. The growth process is described in terms of chemical reactions and partitioning of the diffusion flux at phase boundaries. Diffusion in the terminal phases has to be negligible, i.e., limited mutual solubility or very low diffusivity. Differently, the terminal phases have to be preventively saturated. In these conditions, diffusional matter transport in each intermediate phase can be considered to occur in quasi steady-state conditions and can be described by means of a rational rate constant independent of the geometry of the system and of the nature of the terminal phases. The rational rate constant is directly related to the diffusional properties of the given phase and to its thermodynamic stability. Therefore, proper values of the rate constants can be obtained from diffusion and thermochemical data available in the literature. The time evolution of the volume fraction of the different phases was generated by numerical integration of the kinetic equations. As a result, the influence of the initial radius of the reactant sphere, of the relative magnitude of rate constants, and of the volume variations was simulated. The shape of the resulting kinetic curves is essentially determined by the relative magnitude of the rate constants and, to a lesser extent, by the volume variations associated with the reaction. The time needed to achieve a given fractional conversion scales with the square of the initial sphere radius.

Application of the present analysis to the study of reactions involving spherical particles should take into account some limitations related to the boundary conditions of the model. The main problem arises from the assumed ideal contact at phase boundaries. Development of voids or cracks as well as a nonuniform supply of one of the reactants can determine strong spatial variations of the reaction rate, and consequently, the proposed model will be invalid. However, a careful selection of the experimental conditions can minimize the influence of adverse factors.

Finally, caution should be exercised in applying the proposed model to very small particles ($\ll 1 \mu\text{m}$). First, for nanosized particles, the kinetics could be controlled by interfacial reactions rather than by solid-state diffusion. Second, in the analysis employed in the present paper, the influence of the radius of curvature on the chemical potential of the compounds has been neglected. The curvature effect is expected to lead to a variation of the kinetic rate constant with the size of the particle.

References and Notes

- (1) Schmalzried, H. *Chemical Kinetics of Solids*; VCH: Weinheim, Germany, 1995.
- (2) Kofstad, P. *High-Temperature Corrosion*; Elsevier: London, U.K., 1988.
- (3) Van Loo, F. J. J. *Prog. Solid. St. Chem.* **1990**, *20*, 47.
- (4) Kretz, R. *Metamorphic Crystallization*; J. Wiley & Sons: Chichester, U.K., 1994.
- (5) Lengauer, W. *J. Alloys Compd.* **1995**, *229*, 80.
- (6) Pettit, F. S.; Randklev, E. H.; Felten, E. J. *J. Am. Ceram. Soc.* **1966**, *49*, 199.
- (7) Kotula, P. G.; Carter, C. B. *J. Am. Ceram. Soc.* **1998**, *81*, 2877.
- (8) Buscaglia, V.; Buscaglia, M. T.; Giordano, L.; Martinelli, A.; Viviani, M.; Bottino, C. *Solid State Ionics* **2002**, *146*, 257.
- (9) Barge, T.; Gas, P.; d'Heurle, F. M. *J. Mater. Res.* **1995**, *10*, 1134.
- (10) van Dal, M. J. H.; Huibers, D. G. G. M.; Kodentsov, A. A.; van Loo, F. J. J. *Intermetallics* **2001**, *9*, 409.
- (11) Milanese, C.; Buscaglia, V.; Maglia, F.; Anselmi-Tamburini, U. *Acta Mater.* **2003**, *51*, 4837; *J. Phys. Chem. B* **2002**, *106*, 5859; *Acta Mater.* **2002**, *50*, 1393.
- (12) Kidson, G. V. *J. Nucl. Mater.* **1961**, *3*, 21.
- (13) Wagner, C. *Acta Metall.* **1969**, *17*, 99.
- (14) Pawel, R. E. *J. Electrochem. Soc.* **1979**, *126*, 1111.
- (15) Rafaja, D.; Lengauer, W.; Ettmayer, P. *Acta Mater.* **1996**, *44*, 4835.
- (16) Buscaglia, V.; Anselmi-Tamburini, U. *Acta Mater.* **2002**, *50*, 525.
- (17) Jander, W. *Z. Anorg. Allg. Chem.* **1927**, *163*, 1.
- (18) Ginstling, A. M.; Brounshtein, B. I. *J. Appl. Chem. USSR (Engl. Transl.)* **1950**, *23*, 1327.
- (19) Valensi, G. *C. R. Acad. Sci. Fr.* **1936**, *202*, 309.
- (20) Carter, R. E. *J. Chem. Phys.* **1961**, *34*, 2010; Carter, R. E. *J. Chem. Phys.* **1961**, *35*, 1137.
- (21) Frade, J. R.; Cable, M. *J. Am. Ceram. Soc.* **1992**, *75*, 1949.
- (22) Maglia, F.; Anselmi-Tamburini, U.; Gennari, S.; Spinolo, G. *J. Phys. Chem. B* **2002**, *106*, 6121.
- (23) Crank, J. *The Mathematics of Diffusion*; Oxford University Press: Oxford, U.K., 1956; p 84.
- (24) Levenspiel, O. *Chemical Reaction Engineering*; J. Wiley & Sons: New York, 1972.
- (25) Philibert, J. *Atom Movements Diffusion and Mass Transport in Solids*; Les Editions de Physique: Les Ulis, France, 1991; p 220.
- (26) Höglund, L.; Ågren, J. *Acta Mater.* **2001**, *49*, 1311.
- (27) Masumura, R. A.; Rath, B. B.; Pande, C. S. *Acta Mater.* **2002**, *50*, 4535.
- (28) Aldinger, F. *Acta Metall.* **1974**, *22*, 923.