

A new methodology for the simulation of solid state phase transition kinetics by combination of nucleation and nuclei growth processes

Kristīne Krūkle-Bērziņa · Andris Actiņš ·
Agris Bērziņš

Received: 12 December 2011 / Accepted: 22 March 2012 / Published online: 5 April 2012
© Springer Science+Business Media, LLC 2012

Abstract A new methodology for the simulation of solid state phase transition kinetics has been developed by combining the influence of nucleation rate, nuclei growth rate and the power p characterizing the contact area between the growing particles. The equations used in this methodology were well known, and have been used previously for creating some of the most popular solid-state kinetic equations. The developed methodology made possible calculations of separate rate constants for two processes affecting the rate of phase transition—nucleation (described with K_1) and nuclei growth (described with K_2). Similar phase transitions were also approximated with the well-known single constant Avrami–Erofeev equation, but we successfully calculated both constants according to the new methodology, which allowed a separate evaluation of these two processes and explained the different induction periods. The effects of empirically adjusted constants on theoretically calculated kinetic curves were thus determined.

Keywords Nucleation · Nuclei growth · Phase transition · Kinetic model · Induction period

1 Introduction

The study of solid state phase transition kinetics may be complicated by various factors that can affect and limit the rates of these processes. These factors also depend on the type of solid state reaction. The most common types are decomposition processes, reactions between solid components and phase transformations [1, 2]. Various models for solid state reactions have been put forward and analysed on the basis of

K. Krūkle-Bērziņa (✉) · A. Actiņš · A. Bērziņš
Faculty of Chemistry, University of Latvia, Riga, Latvia
e-mail: kristine.krukle-berzina@lu.lv

transformation. These mechanisms are defined by rate limiting steps, such as nucleation, nuclei growth, phase interface movement or diffusion [1–4].

2 Theoretical background

Nucleation is typically described by the Eq. (1):

$$\frac{dN}{dt} = k_N(N_o - N) \quad (1)$$

Where N is the number of nuclei at time t , k_N is the nucleation rate constant, and N_o is the number of potential nucleation sites (since a phase α to phase β conversion can only start at crystal imperfections, known as nucleation sites) [1,5]. However, this equation is valid for isolated analysis of nucleation alone, when nuclei growth is not involved.

The Eq. (1) describes a single step nucleation. The concept of multistep nucleation is also known, assuming that for the generation of new nuclei several distinct steps may be necessary. In those cases nucleation is described by the Eq. (2), where β is the number of successive events necessary for growth of nuclei, and k_i is a rate constant [1,6].

$$\frac{dN}{dt} = \frac{N_o \cdot k_i^\beta}{\beta!} \beta t^{\beta-1} \quad (2)$$

The second rate determining factor is the growth of nuclei. The volume of nuclei at the time $v(t)$ can be described with the Eq. (3):

$$v(t) = \sigma [r(t, t_o)]^\lambda \quad (3)$$

where σ is a shape factor, r is the radius of nuclei at time t , and λ is the number of growth dimensions. The total volume occupied by all nuclei can be assessed by combining both nucleation and nuclei growth rate in the Eq. (4):

$$V(t) = \int_0^t v(t) \left(\frac{dN}{dt} \right)_{t=t_o} dt \quad (4)$$

If nucleation rate follows the Eq. (2), and nuclei growth rate is constant, then this is a power law (P) type of a model. In the case when some of the possible nucleation sites are eliminated by the growth of existing nuclei, nucleation would not follow Eqs. (1) or (2) [7]. In such a case the reaction rate follows the Avrami–Erofeev or JMAEK model [7,8].

Reactions in solid state also can be described by geometric contraction models, which assume that nucleation happens rapidly on the crystal surface, and depending on the shape of the particle, one of the phase boundary controlled reaction models (R) applies [3,4].

If diffusion is the rate limiting step, then the reaction rate decreases proportionally with the thickness of the product layer, through which diffusion must happen.

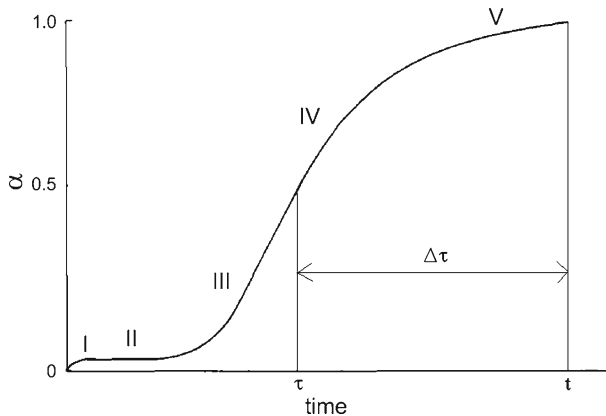


Fig. 1 Generalized α — t plot showing the characteristic experimental curve, where τ indicates the time when an individual nuclei form, t is the point where the calculation is done, and $\Delta\tau$ denotes nuclei growth over the time τ

Depending on the mechanism of diffusion, various diffusion models have been developed [1,4].

Experimental data points can also be described by order-based rate laws (F), which were originally developed for homogeneous reactions in gas or liquid phase, but were later adopted also for solid state reactions [9,10]. The aforementioned mathematical models are listed in the literature [1,7,11].

Generally, the kinetic curve in the coordinate system of α versus time can be described according to the Fig. 1, where I is the initial reaction phase, sometimes associated with the reaction of impurities or unstable superficial material, II is the induction period, III is the acceleration range, IV is the deceleration range and V denotes the reaction completion [1]. Each mathematical model has a different applicability of specific regions of the curve, thus for each model there is a typical curve shape, as represented in the literature [11]. While the definition of rate acceleration or deceleration region depends mostly on the selected model, the most variable part of experiments is the induction period. This period can be influenced by:

- a) thermal inertia;
- b) some other changes in sample delaying the onset of the reaction;
- c) a slow start of the main reaction.

The last interpretation matches the true induction period t_i [1]. Although the induction time is not typically included in mathematical models, it is possible to incorporate a mathematically reasoned induction period in a reaction model.

3 A mathematical expression of the theoretical model

As said before, the nucleation rate can be described with Eq. (1). The nucleation rate decreases with time, because the number of remaining potential nucleation sites at time $(N_o - N)$ also decreases. If we look at the phase transition expressed as:

$$\alpha_{(s)} \rightarrow \beta_{(s)}$$

then the value of $N_o - N$ is proportional to W_α (residual mass fraction of phase α) if nucleation sites are equally distributed in the whole volume, so the Eq. (1) can be written also as Eq. (5), where k_1 is the nucleation rate constant:

$$\frac{dN}{dt} = k_1 W_\alpha(\tau) \tag{5}$$

By assuming that nuclei growth rate would be isotropic and proportional to the phase boundary area, at low conversion degree values this phase boundary area is equal to the total surface of all growing particles. However, there is a possibility that two growing nuclei can come into contact, blocking further growth at this contact area. Such a contact area, which must increase with conversion degree, is determined by the residual phase α mass fraction. The total effect of these processes can be described by the Eq. (6), which includes dependence of nuclei growth rate on the surface area of growing phase β and the residual mass fraction of phase α to the power p , which describes the influence of contact area between the β phase crystals.

$$\frac{dm}{dt} = k'_2 S_\beta W_\alpha^p(\tau) \tag{6}$$

The surface area of a growing spherical particle can be expressed from its density and mass:

$$\frac{dm}{dt} = k_2 (m_i(\tau))^{2/3} W_\alpha^p(\tau) \tag{7}$$

By integration of this equation, the following expressions can be obtained:

$$\frac{dm}{(m_i(\tau))^{2/3}} = k_2 W_\alpha^p(\tau) dt \tag{8}$$

$$3dm^{1/3} = k_2 W_\alpha^p(\tau) dt \tag{9}$$

$$m^{1/3} = \frac{k_2}{3} \int_{\tau}^t W_\alpha^p(\tau) dt + \text{const} \tag{10}$$

In the Eq. (10), the mass of a single nucleus (formed at the time τ) is obtained at time t (see the Fig. 1). As noted previously, the growth starts only when nuclei with mass m_o are formed, thus we can calculate an integration constant, because when $t = \tau$, then $m = m_o$, so the constant equals to $m_o^{1/3}$:

$$m_{(t-\tau)} = m_o \left(1 + \frac{k_2}{3m_o^{1/3}} \int_{\tau}^t W_\alpha^p(\tau) dt \right)^3 \tag{11}$$

If the constant k_2 is combined with $m_o^{1/3}$, then a constant K_2 is obtained:

$$m_{(t-\tau)} = m_o \left(1 + \frac{K_2}{3} \int_{\tau}^t W_{\alpha}^p(\tau) dt \right)^3 \quad (12)$$

In order to calculate the mass increase of all nuclei formed at the time $d\tau$, the Eq. (12) describing the growth of these nuclei should be multiplied by the Eq. (5), which describes the amount of nuclei formed at a given time:

$$dM(\tau) = k_1 m_o \left(1 + \frac{K_2}{3} \int_{\tau}^t W_{\alpha}^p(\tau) dt \right)^3 W_{\alpha}(\tau) d\tau \quad (13)$$

The mass increase of all particles formed between $t = 0$ to t , expressed in the Eq. (13), should be integrated. A new constant $K_1 = k_1 \cdot m_o$ is thus created.

$$1 - W_{\alpha} = \alpha = \int_0^t dM(\tau) = K_1 \int_0^t \left(1 + \frac{K_2}{3} \int_{\tau}^t W_{\alpha}^p(\tau) dt \right)^3 W_{\alpha}(\tau) d\tau \quad (14)$$

By solving this integral equation, the dependence of α on time can be obtained. The method for solving the Eq. (14) is presented further.

4 Calculation methods

The Eq. (14) was solved according to the Runge–Kutta method of numerical integration [12], and for this purpose the Eq. (15) describing nucleation and the Eq. (17) describing nuclei growth were introduced. The starting conditions were $W_{\alpha(t=0)} = 1$, and each formed nucleus was assumed to have a mass of m_o . In these equations ΔN was replaced with $\Delta M/m_o$, because $\Delta M = \Delta N \cdot m_o$, obtaining:

$$\Delta M = K_1 \cdot W_{\alpha}(\tau) \Delta t \quad (15)$$

where ΔM is the total mass of nuclei formed over Δt , and τ is the moment of formation.

A non-dimensional mass multiplication parameter Z was inserted into the Eq. (7), where $Z = m/m_o$, resulting in the Eq. (16):

$$\Delta Z = K_2 Z_{\tau-\Delta t}^{2/3} W_{\alpha}^p(\tau) \Delta t \quad (16)$$

The growing particle mass multiplication parameter Z over Δt , relative to the initial nuclei mass can be calculated at time t , according to the Eq. (17):

$$Z_{t-\tau} = Z_{\tau-\Delta t} + \Delta Z \quad (17)$$

Table 1 Tables used for calculations representing nucleation and nuclei growth

<i>i</i>	<i>j</i>				
	1	2	3	...	<i>z</i>
A					
1	ΔM_1	0	0	0	0
2	ΔM_1	ΔM_2	0	0	0
3	ΔM_1	ΔM_2	ΔM_3	0	0
...	ΔM_1	ΔM_2	ΔM_3	...	0
<i>z</i>	ΔM_1	ΔM_2	ΔM_3	...	ΔM_n
B					
1	Z_{11}	0	0	0	0
2	Z_{12}	Z_{22}	0	0	0
3	Z_{13}	Z_{23}	Z_{33}	0	0
...	$Z_{1\dots}$	$Z_{2\dots}$	$Z_{3\dots}$...	0
<i>z</i>	Z_{1z}	Z_{2z}	Z_{3z}	...	Z_{zz}

This process can be simulated by using two Table 1A and B, of which the former represents the amount of formed nuclei, calculated according to the Eq. (15), and the latter represents a mass multiplication factor of growing nuclei calculated according to the Eq. (17). Each table consists of rows *i* (numbered from 1 to *z*) and columns *j* (numbered from 1 to *z*), both representing time. Changing column or row by one means changing time by Δt . The values in the table cells were calculated in such a way that changing *j* means changing τ , and changing *i* means changing *t*. If we look at the example shown in the Table 1, then the amount of nuclei formed (in the Table 1A) in time τ (corresponding to the first column *j*) did not depend on changes in the time *t* (corresponding to any of the rows *i*), if $i > j$. However, by changing the time *t* (corresponding to any of the rows *i*), the mass multiplication factor *Z* in the Table 1B was increased.

Each cell of the Table 1A was filled according to the following rules:

- 1) $\Delta M_{(i,j)} = 0$, if $j > i$
- 2) $\Delta M_{(i,j)} = \text{Eq. (15)}$, if $j = i$
- 3) $\Delta M_{(i,j)} = \Delta M_{(i-1,j)}$, if $j < i$

Each cell of the Table 1B was filled according to the following rules:

- 1) $Z_{(i,j)} = 0$, if $j > i$
- 2) $Z_{(i,j)} = 1$, if $j = i$
- 3) $Z_{(i,j)} = \text{Eq. (17)}$, if $j < i$

The conversion degree was obtained from the Eq. (18), by calculating the sum of products of $\Delta M_{(i,j)}$ and $Z_{(i,j)}$ for each given time, according to the row *i*:

$$1 - W_{\alpha,t} = M_{\alpha,t} = \sum_{j=1}^z (\Delta M_{(i,j)} \cdot Z_{(i,j)}) \tag{18}$$

In that way, the corresponding conversion degree for the given constants K_1 , K_2 and p was found for the time t .

After describing the experimental process with such a mathematical procedure, a least squares method in *Excel Solver* was used for optimizing the equation constants K_1 , K_2 and p , in order to minimize the divergence between experimental and theoretical conversion degree values at given times.

5 Discussion

The developed methodology produced a kinetic curve with a sigmoid shape, as shown in the Fig. 2. From the kinetic curve shown in the Fig. 2 it was concluded that a phase transition with an induction period can be described analytically. Similar curves could also be obtained with the Avrami–Erofeev equation [7,8].

The major differences between the well-known Avrami–Erofeev equation and our provided method can be outlined as:

1. The number of nuclei appearing in a volume V was obtained in the Avrami equation [13] by:

$$N = V \dot{N} d\tau, \quad (19)$$

where \dot{N} is the rate constant of nucleation. The reduction of nucleation sites due to growth of nuclei was not included in this equation, and this shortcoming was circumvented by further analysing an extended volume—the volume of the new phase that would form if the entire sample was not yet transformed. However, in the provided equation we used the real volume from the very beginning, and the nucleation rate was described with the Eq. (5), including a decrease of nucleation rate with an increasing mass fraction of the product.

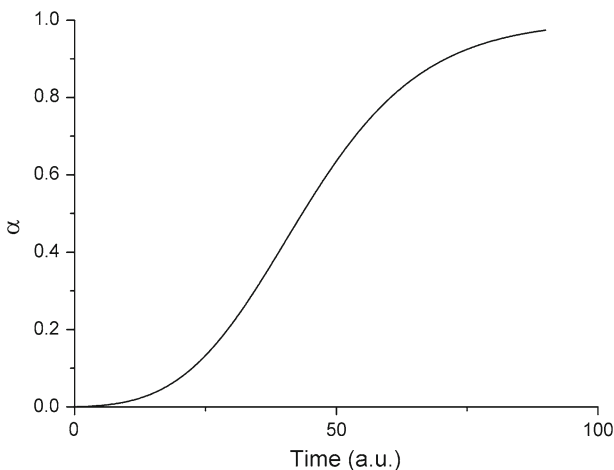


Fig. 2 An example of a calculated kinetic curve

2. With both approaches an increase of volume was obtained by multiplying equations describing nucleation and nuclei growth. In Avrami equation a constant growth rate of particle volume was used, and the extended volume was again obtained due to ignoring any contact areas of growing particles. In our Eq. (6) we used a more realistic mass increase rate, which was proportional to the growing phase surface area, and the mass fraction of initial phase raised to the power p . By using this function, we introduced a rate adjustment due to the predicted contact between growing particles.
3. The starting mass of nuclei m_o was obtained from integrating the Eq. (7), describing the growth of nuclei. Although the size of nuclei and their Gibbs energy diagrams have been characterized in the literature [14], the concept of critical mass has not been introduced neither in Avrami equation, nor in other published equations.
4. A simple equation describing an extended volume with two constants was obtained by a combination of nuclei growth rate and the nucleation rate. For obtaining the real volume, it was multiplied with a volume fraction [13]. Our equation included a correction already from the beginning, and it was different for each nucleation and nuclei growth process.
5. Finally, the Avrami equation was obtained as integral equation, and the nucleation and nuclei growth constants were combined into one constant K . This form of Avrami equation made it impossible to obtain separate growth and nucleation rate constants. However, a second constant n was introduced, characterizing dimensions. Our equation was obtained in differential form, and the product of both constants could not be obtained. Solving of such a differential equation was possible only through numerical integration, which gave both nucleation and nuclei growth constants combined together with the constant p .

In Fig. 3 we show the parameter change effect on simulated theoretical plots with general kinetic parameters $K_1 = 0.00013 \text{ g h}^{-1}$, $K_2 = 0.13 \text{ h}^{-1}$ and $p = 1$. In each case the rest of the parameters were not changed. It can be seen that both constants K_1 and K_2 influenced the shape of the curve. The constant K_2 mainly determined the curvature of the line, while the constant K_1 mainly affected the induction period. The constant p had a slight effect on the curve at the end of the phase transition, when growing nuclei were starting to aggregate, and therefore the growth rates were slower than would be in an ideal case.

When such a numerical integration was performed, the results depended on the calculation time interval. The Fig. 4a shows the differences in calculated conversion degree values, compared with those calculated with $\Delta t = 0.05 \text{ h}$, but the Fig. 4b presents a comparison with those calculated with $\Delta t = 0.3 \text{ h}$. The largest calculated conversion degree difference created by Δt increase from 0.05 to 0.3 h was smaller than 0.004, but when comparing the effect of $\Delta t = 0.05 \text{ h}$ versus $\Delta t = 0.45 \text{ h}$, then the largest difference was approximately 0.006. These errors were negligible in the context of the typical X-ray powder diffraction analysis accuracy, used for phase content determination in real phase transitions.

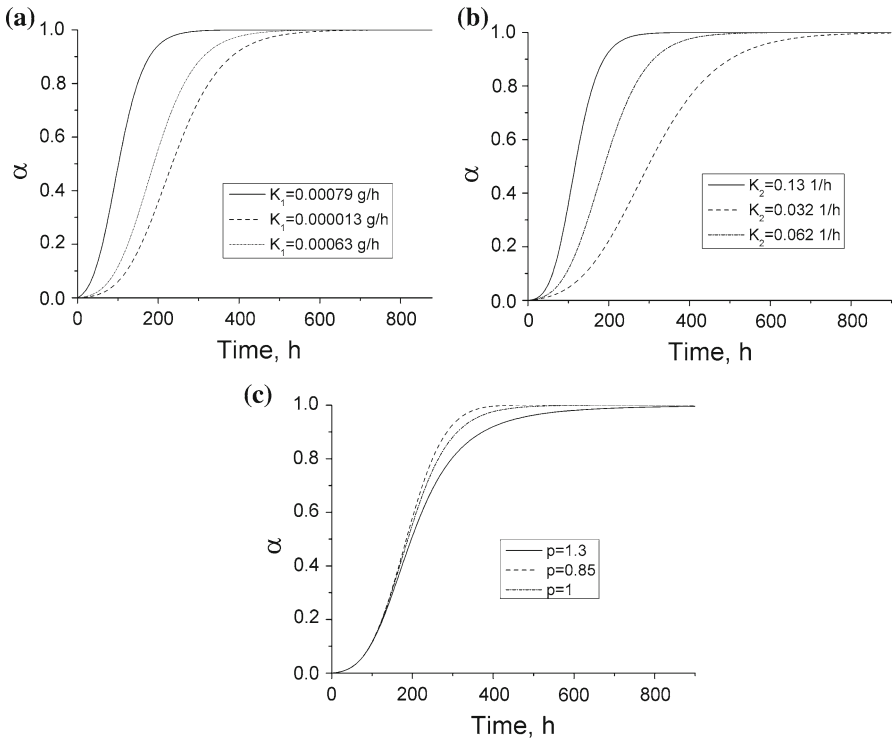


Fig. 3 Effects of **a** K_1 , **b** K_2 and **c** p on the plot of differential equation (14)

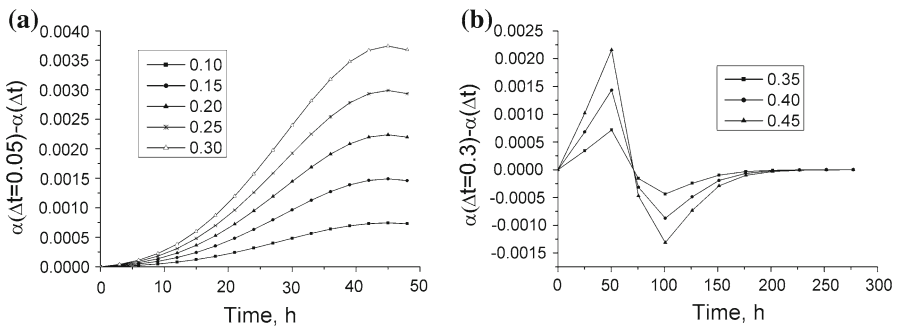


Fig. 4 Differences in calculated conversion degree values for various Δt , comparing **a** $\Delta t = 0.05$ h and **b** $\Delta t = 0.3$ h

6 Conclusions

With this developed methodology it was possible to successfully simulate and analyse phase transitions, where both nucleation and nuclei growth represented rate limiting steps, and a certain induction period was observed. Such phase transitions were described with an equation involving three constants—rate constants of nucleation (K_1) and crystal growth (K_2), and a constant p characterizing the contact area between

the growing particles. For experimental phase transitions these constants would be determined from kinetic data with *Excel Solver*. It was concluded that the value of nucleation rate constant (K_1) affected mostly the early part of the curve, while the crystal growth rate constant (K_2) defined the curvature of the kinetic plot.

Acknowledgments This work has been supported by the European Social Fund within the project “Support for Doctoral Studies at University of Latvia” and by Latvian Academy of Sciences Grant No. 09.1555.

References

1. M.E. Brown, D. Dollimore, A.K. Galwey, *Reactions in the Solid State. Comprehensive Chemical Kinetics*, vol. 22 (Elsevier, Amsterdam, 1980), pp. 41–246
2. R.C. Ropp, *Solid State Chemistry* (Elsevier, Amsterdam, 2003), pp. 129–189
3. S.F. Hulbert, *J. Br. Ceram. Soc.* **6**, 11 (1969)
4. J. Sestik, G. Berggren, *Thermochim. Acta* **3**, 1 (1971)
5. V.V. Boldyrev, *Thermochim. Acta* **100**, 315 (1986)
6. C. Bagdassarian, *Acta Physicochim. URSS* **20**, 441 (1945)
7. A.K. Galwey, M.E. Brown, *Thermal Decomposition of Ionic Solids* (Elsevier, Amsterdam, 1999), pp. 75–115
8. B.V. Erofeev, C.R. Dokl. Acad. Sci. URSS **52**, 511 (1946)
9. K.L. Mampel, *Z. Phys. Chem. Abt. A* **187**, 235 (1940)
10. K.L. Mampel, *Z. Phys. Chem. Abt. A* **187**, 43 (1940)
11. K. Khawami, D.R. Flanagan, *J. Pharm. Sci.* **95**, 472 (2006)
12. J.C. Butcher, *Numerical methods for ordinary differential Equations* (Wiley, Chippenham, 2003), pp. 86–96
13. M. Avrami, *J. Chem. Phys.* **1103**, 7 (1939)
14. A.K. Galwey, G.M. Laverty, *Solid State Ion.* **155**, 38 (1990)