

# Kinetics of phase transformations for constant heating rate occurring close to the thermodynamic transition

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## Abstract

The kinetics of phase transformations has been re-examined by considering the case when this is controlled by phase growth, with nearly instantaneous nucleation. In this case, the phase transformation is likely to occur at temperatures relatively close to the true thermodynamic transformation temperature  $T_i$ , and the growth rate vanishes on approaching this temperature. The actual solutions for nucleation and growth thus deviate from the classical laws proposed to describe the dependence of fraction transformed on temperature and rate of change in temperature. Similarly, the Kissinger equation becomes a poor description for the dependence of the transformation peak temperature on the rate of change in temperature. Nevertheless, the Avrami–Nakamura approach can still be used to derive formulae for these cases. Alternative solutions were thus obtained both by numerical integration and also in the form of nearly correct approximate formulae. These formulae account for sudden deviations on approaching the transition temperature.

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## 1. Introduction

First order phase transitions  $\alpha \rightarrow \beta$  can be detrimental or of outmost importance to many materials due to effects on important applications (e.g. electrical properties) or because they might cause collapse due to excessive lattice mismatch between the  $\beta$  and  $\alpha$  phases. For example, the  $\beta \rightarrow \alpha$  transition in some ion conducting ceramics (e.g.  $\text{Bi}_2\text{O}_3$ - or  $\text{La}_2\text{Mo}_2\text{O}_9$ -based materials) spoils their applicability as solid electrolytes [1,2], or limits the working temperatures. In addition, repeated cycling between high and low temperatures might lead to failure, even for low differences between the lattice parameters of the high and low temperature phases.

The Johnson–Mehl–Avrami (JMA) theory [3,4] is often used to describe the fraction transformed for experiments

performed at constant temperature. The corresponding Avrami–Nakamura models [5,6] have been proposed to analyze experiments performed on heating with variable temperature and were successfully used to analyze the crystallisation in glass–ceramic materials. However, the models for non-isothermal conditions are based on the assumption that the relevant kinetic constant is nearly described by a typical Arrhenius dependence, which might be invalidated near the thermodynamic transition, as discussed below.

Detailed models have been proposed mainly for homogeneous nucleation in glass–ceramic systems [7], and also for phase transformations, with inclusion of the effects of strain misfit energy, as described by [8]:

$$I = I_0 \exp\left[\frac{-E_N}{RT}\right] \exp\left[\frac{-\Delta G^*}{RT}\right] \quad (1)$$

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where  $I_0$  is a pre-exponential factor,  $E_N$  is the energy of migration, and the thermodynamic barrier

$$\Delta G \propto \frac{\gamma^3}{(\Delta G_v - \Delta G_s)^2} \quad (2)$$

is dependent on the interfacial energy  $\gamma$ , the free energy of transformation per unit volume  $\Delta G_v = \Delta G/V_m$  ( $V_m$  being the molar volume), and the strain misfit energy  $\Delta G_s$ . Eqs. (1) and (2) thus show that the temperature dependence of the rate of nucleation is far from simple. Most models are thus derived on assuming simplified conditions such as separate stages of nucleation and growth, or nearly instantaneous nucleation at temperatures which are close to the true transition temperature.

The temperature dependence of the growth rate also deviates from the Arrhenius dependence on approaching the phase transition temperature  $T_t$ . Though more complex formulae have been proposed for glass–ceramic systems [8,9], the following formulae is often used to describe the temperature dependence of growth rate:

$$U = U_0 \exp \left[ \frac{-E_g}{RT} \right] \left\{ 1 - \exp \left[ \left( \frac{\Delta H}{R} \right) (T^{-1} - T_t^{-1}) \right] \right\} \quad (3)$$

$U_0$  being a pre-exponential factor,  $E_g$  the activation energy and  $\Delta H$  the enthalpy change. Eq. (3) will be assumed for solid–solid transformations, and will be used to emphasize the deviations from commonly assumed kinetic models.

## 2. Temperature dependence of the fraction transformed

Nucleation may be a rather complex process [10,11], mainly before reaching a steady state regime [12–14]. However, ready nucleation is likely to occur at internal interfaces or other discontinuities, such as grain boundaries, edges, corners, dislocations, etc. For example, kinks are often active sites for growth and may yield nearly one-dimensional growth of plate-like particles by lateral movement of ledges. In these conditions, nucleation may occur readily at temperatures which are close to the true transition temperature, and the present analysis is thus based on the assumption that nucleation is nearly instantaneous.

On assuming nearly instantaneous nucleation the JMA model for the dependence of fraction transformed  $\alpha$  on time  $t$ , at constant temperature, reduces to [3,4]:

$$-\ln(1 - \alpha) \approx f_0 N_0 (Ut)^m \quad (4)$$

where  $N_0$  is the number of nuclei and  $f_0$  is a geometrical factor (e.g.  $4\pi/3$  for spherical particles of the new phase), and  $m$  is the dimensionality of growth for the case of phase boundary controlled growth. The value of the Avrami coefficient increases for cases when nucleation and growth

occur simultaneously:

$$-\ln(1 - \alpha) f_0 I U^m t^{m+1} \quad (5)$$

To examine the kinetics with variable temperature one must take into account the temperature dependence of the growth rate (Eq. (3)), and perform a change of independent variable  $dt = dT/\beta$ , where  $\beta = dT/dt$  is the rate of change in temperature. By maintaining the value of  $\beta$  throughout the experiment, and using typical Avrami–Nakamura methods [5,6] one obtains:

$$-\ln(1 - \alpha) = f_0 N_0 \left( \frac{U_0}{|\beta|} \right)^m [F(T)]^m \quad (6)$$

where

$$F(T) = \int_{T_t}^T \exp \left[ \frac{-E_g}{(RT')} \right] dT' - \exp \left[ \frac{-\Delta H}{RT_t} \right] \int_{T_t}^T \exp \left[ \frac{\Delta H - E_g}{RT'} \right] dT' \quad (7)$$

Note that  $\Delta H > 0$  for the  $\alpha \rightarrow \beta$  transition occurring at  $T > T_t$ , and  $\Delta H < 0$  for the  $\beta \rightarrow \alpha$  at  $T > T_t$ .

Eq. (6) shows the expected effects of the rate of change in temperature on the fraction transformed, for a selected value of final temperature  $T_f$ , i.e.:

$$\ln[-\ln(1 - \alpha(T_f))] = A_1(T_f) - m \ln |\beta| \quad (8)$$

where  $A_1(T_f) = \ln [f_0 N_0 (U_0 F(T_f))^m]$  corresponds to the conversion attained when the rate of change in temperature is unity. This confirms a method commonly used to evaluate the dimensionality of growth for glass crystallisation [15].

The integrals in Eq. (7) can be solved numerically or by using a suitable approximation for the integrals in Eq. (7), such as [6]:

$$\int_{T_t}^T \exp \left[ \frac{-E_g}{RT'} \right] dT' = \left( \frac{RT^2}{E_g} \right) \exp \left[ \frac{-E_g}{RT} \right] - \left( \frac{RT_t^2}{E_g} \right) \exp \left[ \frac{-E_g}{RT_t} \right] \quad (9)$$

This corresponds to a widely used approximation [16,17] of the so-called Arrhenius integral:

$$p(\theta) = \int_0^\theta \exp \left( \frac{-1}{\theta} \right) d\theta \approx \theta^2 \exp \left( \frac{-1}{\theta} \right) \quad (10)$$

where  $\theta = RT/E_a$  is a dimensionless temperature, with a generic activation energy  $E_a$ . Eqs. (9) and (10) are nearly true for sufficiently low values of  $RT/E_g$ , and the deviations from these models increase with the values of  $\theta$ . In those cases, one may use corrections both for the activation energy and pre-exponential factor [6], or a generic correction [6,17,18]:

$$p(\theta) = f(\theta) \theta^2 \exp \left( \frac{-1}{\theta} \right) \quad (11)$$

For example, integration by parts yields [6,17]:

$$\begin{aligned} f(\theta) &= 1 - 2!\theta + 3!\theta^2 - 4!\theta^3 + \dots \\ &= 1 - 2\theta + 6\theta^2 - 24\theta^3 + \dots \end{aligned} \quad (12)$$

and the first order approximation reduces to the solution proposed by Coats and Redfern [18], with  $f(\theta) = 1 - 2\theta$ . Several reviews (e.g. [16,17]) compared these solutions and also other generic approximations, such as  $p(\theta) = \theta^k \exp(A - B/\theta)$ .

Eq. (10) yields reasonably accurate results at least for  $\theta < 0.05$ , which corresponds to values of activation energy  $>167$  kJ/mol, with typical temperatures in the order of 1000 K. In addition, the second term in the right side of Eq. (9) is often neglected for experiments performed on heating from room temperature. However, this should not be assumed for cases when the phase transformations occurs in a relatively short temperature interval, close to the thermodynamic transition. The lower integration limit was thus retained in Eq. (7) and this was combined with Eq. (6) to obtain:

$$-\ln(1 - \alpha) \approx f_o N_o \left[ \frac{U_o R}{E_g |\beta|} \right]^m T^{2m} \left\{ \varepsilon_1 \exp \left[ \frac{-E_g}{RT} \right] - \varepsilon_2 \right\}^m \quad (13)$$

or

$$\begin{aligned} \ln \left[ \frac{-\ln(1 - \alpha)}{T^{2m}} \right] &\approx \ln \left\{ f_o N_o \left[ \frac{U_o R}{E_g |\beta|} \right]^m \right\} \\ &+ m \ln \left\{ \varepsilon_1 \exp \left[ \frac{-E_g}{RT} \right] - \varepsilon_2 \right\} \end{aligned} \quad (14)$$

with

$$\varepsilon_1 = 1 - \left( \frac{1 - \Delta H}{E_g} \right)^{-1} \exp \left[ \left( \frac{\Delta H}{R} \right) (T^{-1} - T_t^{-1}) \right] \quad (15)$$

$$\varepsilon_2 = \left[ 1 - \left( 1 - \frac{\Delta H}{E_g} \right)^{-1} \right] \left( \frac{T_t}{T} \right)^2 \exp \left[ \frac{-E_g}{RT_t} \right] \quad (16)$$

Eq. (14) thus shows that the actual behaviour may deviate from a widely assumed isokinetic model proposed to describe the kinetics of crystallisation [16]:

$$\ln \left[ \frac{-\ln(1 - \alpha)}{T^{2m}} \right] \approx \ln \left\{ f_o N_o \left[ \frac{U_o R}{E_g |\beta|} \right]^m \right\} - \frac{m E_g}{RT} \quad (17)$$

Note that this model was based on the assumption that the temperature dependence of growth rate follows the Arrhenius law. The deviations described by Eq. (14) are even sharper than for other cases of phase transformations with temperature dependent equilibrium states, namely for cases when the temperature dependence of phase boundaries implies changes in the maximum amount of transformed material (e.g. [19]).

### 3. Transformation peak versus rate of change in temperature

A commonly used method to obtain the activation energy of glass crystallisation and similar processes is the Kissinger equation [20] which describes the dependence of crystallisation peak temperature  $T_p$  on the rate of change in temperature:

$$\ln \left( \frac{\beta}{T_p^2} \right) = \text{Const.} - \frac{E}{RT_p} \quad (18)$$

The applicability of Kissinger equation has been discussed in the literature (e.g. [21]), and must also be revised in the present case. Note that the actual temperature dependence of the growth rate deviates strongly from a simple Arrhenius law, on approaching the thermodynamic transition. Nevertheless, one may still resort to a typical condition  $[d^2\alpha/dT^2]_{T=T_p} = 0$  to obtain the peak of transformation rate. On differentiating Eqs. (6) and (7), with  $d^2\alpha/dT^2 = 0$ , and on rearranging one thus obtained:

$$\begin{aligned} \ln \left( \frac{|\beta|}{T_p^2} \right) &= m^{-1} \ln \left\{ f_o N_o \left( \frac{U_o R}{E_g} \right)^m \right\} \\ &- \left( \frac{E_g}{R} \right) T_p^{-1} + \ln(|\varepsilon_3|), \end{aligned} \quad (19)$$

where the deviations from Kissinger equation are accounted by:

$$\varepsilon_3 = \frac{\{1 - \exp[(\Delta H/R)(1/T_p - 1/T_t)]\}^2}{\{1 - (1 - \Delta H/E_g) \exp[(\Delta H/R)(1/T_p - 1/T_t)]\}} \quad (20)$$

The actual deviations from the Kissinger equation are also different from those expected for cases when equilibrium states are temperature dependent [19]. In those cases, the maximum amount of transformed phase varies with the actual temperature range and thus also with the rate of change in temperature.

### 4. Dimensionless treatment

In order to minimize the number of relevant parameters one may use dimensionless variables, thus simplifying the relevant models for the dependence of fraction transformed on temperature and rate of change in temperature, and the dependence of the transformation peak temperature on the rate of change in temperature. The chosen dimensionless variables were:

$$\theta = \frac{TR}{E_g} \quad (21)$$

$$\theta_t = \frac{T_t R}{E_g} \quad (22)$$

$$\beta^* = \frac{\beta E_g}{[RT_t^2 U_o (f_o N_o)^{1/m}]} \quad (23)$$

$$h = \frac{\Delta H}{RT_t} \quad (24)$$

On inserting these variables in Eqs. (14)–(16) one thus obtains:

$$m^{-1} \ln \left[ -\ln(1-\alpha) \left( \frac{\theta_t}{\theta} \right)^{2m} \right] \approx -\ln(\beta^*) + \ln \left\{ \varepsilon_1 \exp \left( \frac{-1}{\theta} \right) - \varepsilon_2 \right\} \quad (25)$$

$$\varepsilon_1 = 1 - (1 - \theta_t h)^{-1} \exp \left[ h \left( \frac{\theta_t}{\theta} \right) - 1 \right] \quad (26)$$

$$\varepsilon_2 = [1 - (1 - \theta_t h)^{-1}] \left( \frac{\theta_t}{\theta} \right)^2 \exp \left( \frac{-1}{\theta_t} \right) \quad (27)$$

Thus, the kinetics can be expressed in terms of three dimensionless parameters only. These parameters correspond to the dimensionless transition temperature  $\theta_t = T_t R / E_g$ , the dimensionless heating rate  $\beta^* = \beta E_g / [RT_t^2 U_o (f_o N_o)^{1/m}]$ , and the dimensionless enthalpy  $h = \Delta H / RT_t$ .

Eqs. (19) and (20) can also be expressed in dimensionless terms as follows:

$$\ln \left[ |\beta^*| \left( \frac{\theta_t}{\theta_p} \right)^2 \right] = -\frac{1}{\theta_p} + \ln(|\varepsilon_3|), \quad (28)$$

$$\theta_p = \frac{T_p R}{E_g} \quad (29)$$

$$\varepsilon_3 = \frac{\{1 - \exp(-h + h\theta_t/\theta_p)\}^2}{\{1 - (1 - h\theta_t) \exp(-h + h\theta_t/\theta_p)\}} \quad (30)$$

## 5. Predictions

Fig. 1 shows finite difference solutions of Eqs. (6) and (7) (symbols) and the corresponding predictions of Eq. (14), with  $\varepsilon_1$  and  $\varepsilon_2$  described by Eqs. (15) and (16) (solid lines), for the  $\alpha \rightarrow \beta$  transformation with  $T_t R / E_g = 0.02$ ,  $\beta^* = \beta E_g / [RT_t^2 U_o (f_o N_o)^{1/m}] = 10^{-21}$  and  $\Delta H / RT_t = 1, 10$  and  $10^2$ . Note that the actual range of values of dimensionless parameter  $\beta^* = \beta E_g / [RT_t^2 U_o (f_o N_o)^{1/m}]$ , in Fig. 1 corresponds to typical values of  $RT_t$ ,  $E_g$ ,  $N_o$  and  $U$  in the order of 10 kJ/mol, 500 kJ/mol,  $10^{-2} \mu\text{m}^{-3}$  and  $10^{-2} \mu\text{m/s}$ , with dimensionality  $m=3$  and  $f_o$  close to unity. Eq. (17) (dashed line) is also shown to demonstrate its limitations, mainly for temperatures close to the transformation temperature  $T_t$ . The transient regime becomes shorter with increasing values of  $\Delta H / RT_t$ , which allows a quick decay of the thermodynamic barrier  $\exp [(\Delta H/R)(T^{-1} - T_t^{-1})]$  in the growth rate (Eq. (3)), on heating above  $T_t$ . The most relevant range of values of fraction transformed ( $0.01 < \alpha < 0.99$ ) corresponds

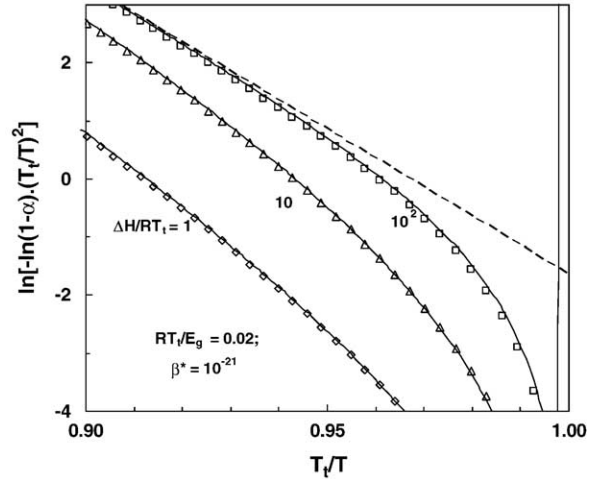


Fig. 1. Temperature dependence of fraction transformed calculated for  $T_t R / E_g = 0.02$ ,  $\beta E_g / [RT_t^2 U_o (f_o N_o)^{1/m}] = 10^{-21}$ , and  $\Delta H / RT_t = 1, 10$  and  $10^2$ . The symbols shows finite difference solutions, solid lines represent Eq. (14), and dashed line is Eq. (17).

to  $\ln(-\ln(1-\alpha))$  in the range from  $-4.6$  to  $1.6$ . Increasing the heating rate parameter also displaces the relevant conditions of phase transformations to higher temperatures (Fig. 2), thus contributing to overcome the transient regime (Figs. 1 and 3).

Fig. 1 also shows that Eq. (14) provides reasonably correct solutions. These formulae are nearly indistinguishable from the corresponding finite difference solutions, at least for sufficiently small  $RT_t / E_g$  (Figs. 4 and 5). Though the errors tend to increase with  $RT_t / E_g$ , one may expect reliable solutions, at least for  $RT_t / E_g < 0.05$ , and thus for  $E_g > 20RT_t$ , or  $> 134$  kJ/mol, at 800 K. The examples simulated in Fig. 4 were computed for conditions close to  $RT_t / E_g = 0.01$ ,  $f_o N_o = 10^{-2} \mu\text{m}^{-3}$ ,  $m=3$ , and growth rate  $U_o \exp[-E_g/(RT_t)] = 10^{-2} \mu\text{m/s}$ , yielding  $\beta^* = \beta E_g / [RT_t^2 U_o (f_o N_o)^{1/m}] = 1.73 \times 10^{-43}$ . Similarly, for  $RT_t / E_g = 0.05$ ,  $f_o N_o = 10^{-2} \mu\text{m}^{-3}$ ,  $m=3$  and  $U_o \exp[-E_g/(RT_t)] = 10^{-2} \mu\text{m/s}$  one

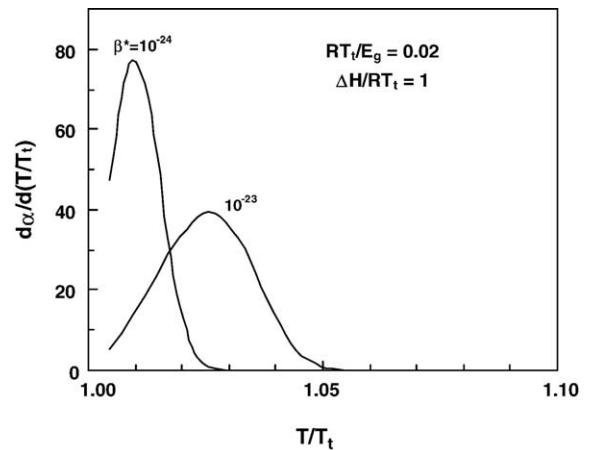


Fig. 2. Transformation peaks for  $T_t R / E_g = 0.02$ ,  $\beta E_g / [RT_t^2 U_o (f_o N_o)^{1/m}] = 10^{-24}$  and  $10^{-23}$ ,  $\Delta H / RT_t = 1$ .

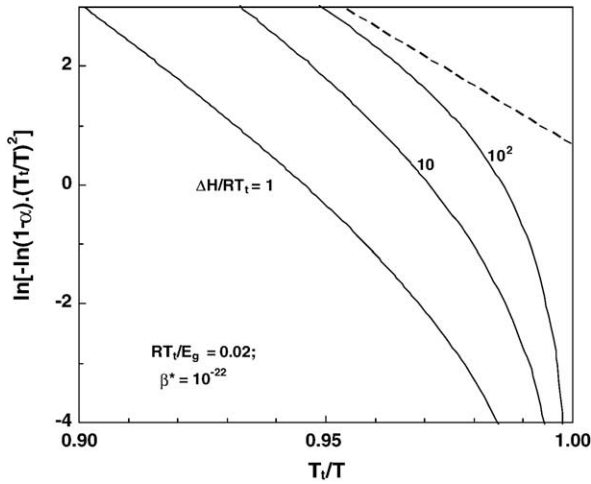


Fig. 3. Temperature dependence of fraction transformed calculated for  $T_f R/E_g = 0.02$ ,  $\beta E_g/[RT_t^2 U_o(f_o N_o U_o)^{1/m}] = 10^{-22}$ , and  $\Delta H/RT_t = 1, 10$  and  $10^2$ . The dashed line is Eq. (17).

obtains  $\beta^* = \beta E_g/[RT_t^2 U_o(f_o N_o)^{1/m}] = 1.6 \times 10^{-10}$ , i.e. in the range selected for Fig. 5.

The dependence of the peak temperature on the heating rate parameter (Fig. 6) also shows the deviations from a simple Kissinger equation (dashed line). The symbols show finite difference solutions and the solid line represents Eq. (19), where  $\varepsilon_3$  is described by Eq. (20). Though deviations from linearity should thus be a clear indication of the failure of the Kissinger equation, the actual range of results may be too narrow to distinguish this. In fact, the range of values of heating rate  $\beta$  often reduces to about one order of magnitude (e.g. 5–50 K/min) and, in this case, the actual amplitude of  $\beta^*$  values also reduces to one order of magnitude. One should thus use the widest possible range of values of heating rate to avoid

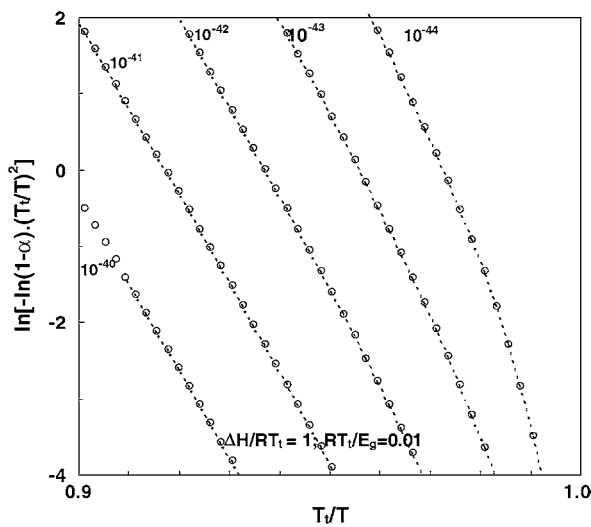


Fig. 4. Temperature dependence of fraction transformed for  $T_f R/E_g = 0.01$ ,  $\Delta H/RT_t = 1$  and  $\beta E_g/[RT_t^2 U_o(f_o N_o U_o)^{1/m}] = 10^{-40}, 10^{-41}, 10^{-42}, 10^{-43}, 10^{-44}$ . The symbols are finite difference solutions and solid lines represent Eq. (14).

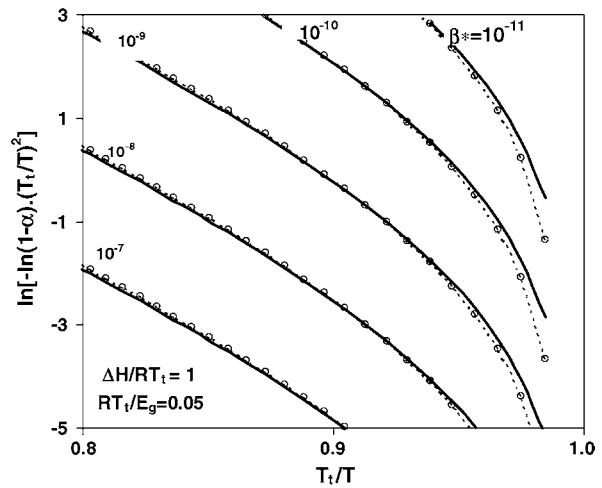


Fig. 5. Temperature dependence of fraction transformed for  $T_f R/E_g = 0.05$ ,  $\Delta H/RT_t = 1$  and  $\beta E_g/[RT_t^2 U_o(f_o N_o U_o)^{1/m}] = 10^{-7}, 10^{-8}, 10^{-9}, 10^{-10}, 10^{-11}$ . The symbols are finite difference solutions and solid lines represent Eq. (14).

drawing incorrect conclusions about the applicability of the Kissinger equation and extracting meaningless estimates of the activation energy. Note that the slope varies rapidly on approaching the transition temperature.

One extension of classical models (e.g. Eq. (17)) is its modification to obtain the Avrami coefficient, or the dimensionality of growth  $m$  [15]. This is often obtained from the dependence of fraction transformed on the rate of change in temperature, for a given final temperature  $T_f$ . Fortunately, this rather simple method may still be used for conditions when Eq. (17) becomes rather crude, i.e. close to the thermodynamic transformation temperature  $T_t$ , as described by Eq. (8).

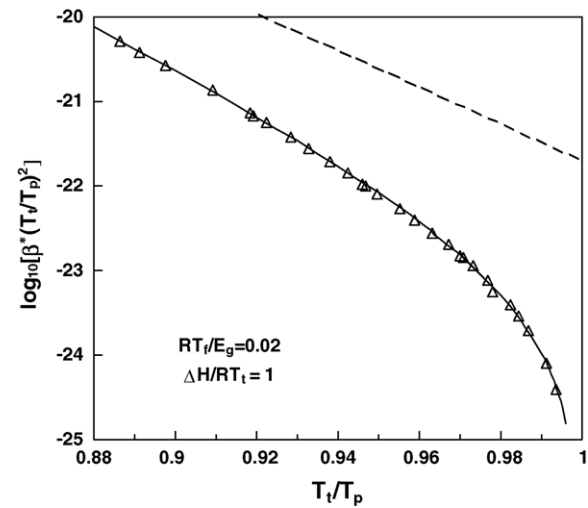


Fig. 6. Dependence of transformation peak temperature on the heating rate for  $T_f R/E_g = 0.02$  and  $\Delta H/RT_t = 1$ . The symbols are finite difference solutions and the solid line represents Eq. (19).



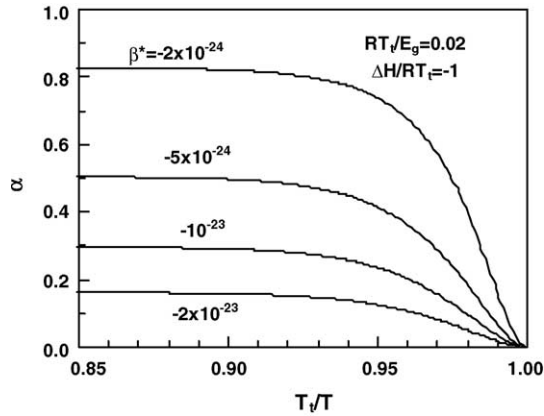


Fig. 7. Temperature dependence of fraction transformed for  $T_t R/E_g = 0.02$ ,  $\Delta H/RT_t = -1$  and  $\beta E_g/[RT_t^2 U_o(f_o N_o U_o)^{1/m}] = -2 \times 10^{-24}$ ,  $-5 \times 10^{-24}$ ,  $-10^{-23}$ ,  $-2 \times 10^{-23}$ .

Augis and Bennet [22] proposed an alternative method to calculate the Avrami coefficient as follows:

$$m = \frac{2.5 RT_p^2}{E \Delta T} \quad (31)$$

where  $E$  is the activation energy obtained by the Kissinger method and  $\Delta T$  is the peak half width. This method might be in error for two different reasons. The first reason is related to deviations from linearity of Kissinger plots, on approaching the transition temperature  $T_t$ ; this is described by Eq. (19), and demonstrated in Fig. 6, yielding crude estimates of the activation energy. The second reason is related to expected changes in peak shape, as revealed by the deviations from the temperature dependence of fraction converted (e.g. Figs. 1, 3 and 5). In fact, other authors [23] also indicated that the Augis and Bennet method can yield incorrect predictions for conditions when the JMA models fail. The actual results show that this includes deviations from the Arrhenius law.

Other results were computed for the inverse  $\beta \rightarrow \alpha$  transformation, on cooling below the thermodynamic transition temperature, i.e.  $T < T_t$  (Figs. 7–9). The values

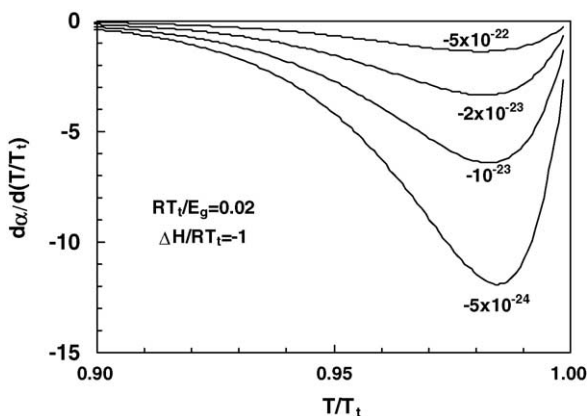


Fig. 8. Transformation peaks calculated for  $T_t R/E_g = 0.02$ ,  $\Delta H/RT_t = -1$  and  $\beta E_g/[RT_t^2 U_o(f_o N_o U_o)^{1/m}] = -2 \times 10^{-24}$ ,  $-5 \times 10^{-24}$ ,  $-10^{-23}$  and  $-2 \times 10^{-23}$ .

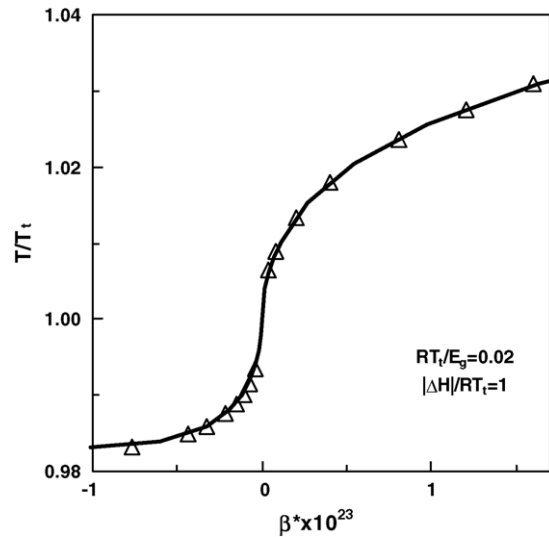


Fig. 9. Dependence of transformation peak temperature on the heating and cooling rate for  $T_t R/E_g = 0.02$  and  $|\Delta H/RT_t| = 1$ . The symbols are finite difference solutions and the solid line represents Eq. (19).

of the relevant parameters  $T_t R/E_g$ ,  $\Delta H/RT_t$  and  $\beta^* = \beta E_g/[RT_t^2 U_o(f_o N_o)^{1/m}]$  are shown in those figures. It is easily recognised that the transformation may be halted for kinetic reasons, before reaching complete transformation. The upper value of the fraction transformed is dependent on the cooling rate. These results also confirm that Eq. (14) gives relatively correct solutions for the  $\beta \rightarrow \alpha$  transformation.

Eq. (14) can also be used to obtain the thermodynamic transition temperature  $T_t$ , by combining the dependence of the transformation peak temperature on the heating or cooling rate (Fig. 9); this corresponds to an inflection point.

## 6. Conclusions

Commonly used kinetic models for nucleation and growth do not provide a correct description of phase transformations near the true thermodynamic transformation temperature  $T_t$ . This occurs because the growth rate vanishes on approaching  $T_t$ . Revised models were thus derived to describe the dependence of fraction transformed on temperature, and the dependence of the peak transformation temperature on the rate of heating or cooling. Dimensionless treatment is suitable to minimize the number of relevant dimensionless parameters. Alternative finite difference solutions were computed to demonstrate the applicability of the revised models, and their limitations. Those revised models are reasonably correct for wide ranges of conditions and only fail for relatively low values of activation energy, i.e. typically for  $E_g < 10RT_t$ .

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