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Review
Analysis of the kinetics of phase transformations

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A common basis of reaction-rate theories is discussed for isothermal and non-isothermal transformations. As a result compatible recipes have been obtained for the extraction of kinetic parameters from isothermally and non-isothermally conducted experiments. It follows that so-called Kissinger-like methods for non-isothermal kinetic analysis, originally derived for homogeneous reactions, can also be applied to heterogeneous reactions, and that these methods constitute (only) a special case of the general analysis proposed. The recipes presented are illustrated by a series of examples taken from recent research on solid-state transformations; among other things, isothermal and non-isothermal analyses of the same transformation are compared and use of the notion of "effective activation energy", that varies during the course of an overall transformation, is discussed.

1. Introduction

This paper has arisen out of my interest over a period of 20 years in solid-state transformations. At irregularly spaced moments of time it was felt necessary to determine kinetic parameters of phase transformations studied. To this end, annealing experiments were conducted in either an isothermal or a non-isothermal fashion. What may be called "standard procedures" were employed to evaluate the kinetic data, as activation energies; reaction-rate theory itself was normally not the focus of attention.

Nevertheless, over the years some knowledge on kinetic analysis has accumulated, which led to the growing awareness that this is one area where ill-considered statements are made and analyses are applied inconsiderately, by many. Three examples of this are:

(i) "non-isothermal analyses are inferior to isothermal analyses";

(ii) application of the so-called Kissinger analysis to solid-state transformations;

(iii) adoption of homogeneous reaction-rate theory for solid-state transformations.

Whilst not wishing to imply that the results presented in such contexts are necessarily wrong, the present assertion is that a balanced discussion and, apparently, profound insight is often lacking.

The present paper has been devised to summarize my personal, current view on the basis of kinetic analyses of, in particular solid-state, transformations, thereby producing recipes for the extraction of kinetic data. It emanates from an earlier paper [1] and it is tributary to, especially, references [2–4]. Hence, the paper is not original. However, I believe that the treatment given here can be useful for those interested in determining kinetic parameters. I hope that this, at some places, possibly provocative and thus somewhat unusual contribution assists in avoiding delusive notions.

2. Thermal history and the stage of transformation

For the analysis of solid-state transformation kinetics a physical property (e.g. hardness, specific volume/length, electrical resistivity, enthalpy, magnetization) of the material subject to investigation can be traced as a function of time and temperature. Then the degree of transformation (fraction transformed), f, can be defined, for example, as

$$f \equiv (p - p_0)/(p_1 - p_0) \qquad 0 \leq f \leq 1 \qquad (1)$$

where p is the physical property measured during the course of transformation and p_0 and p_1 correspond with the values of p at the start and finish of the transformation, respectively. In non-isothermal analysis, p_0 and p_1 cannot normally be considered as constants (Fig. 1).

For thermally activated transformations, the thermal history of a specimen determines its stage of transformation. Consider the temperature–time, T–t, diagram depicted in Fig. 2. A specimen experiencing a thermally activated phase transformation proceeds from "State 1 (t_1, T_1)" to "State 2 (t_2, T_2)" via either path a or path b. Clearly, although the time to proceed from State 1 to State 2 is the same for both paths, the higher temperatures operating along path b cause a stage of transformation in State 2 for path b which is more advanced than that reached along path a. The stage of transformation in State 2 depends, in general, on the path followed: for non-isothermal analysis, t and T are not state variables for the stage of transformation.

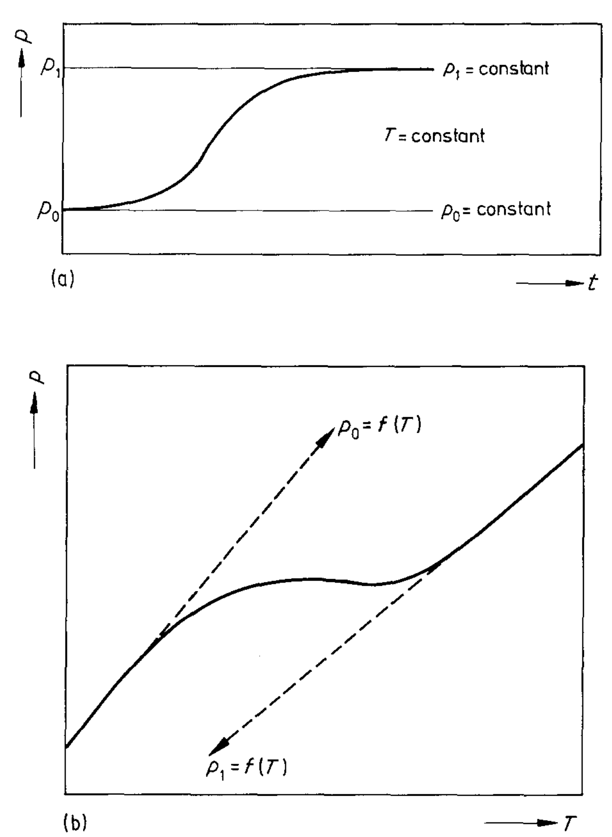

Figure 1 Schematic presentation of the behaviour of the physical property, p, sensitive to the stage of transformation, during (a) isothermal analysis and (b) non-isothermal analysis.

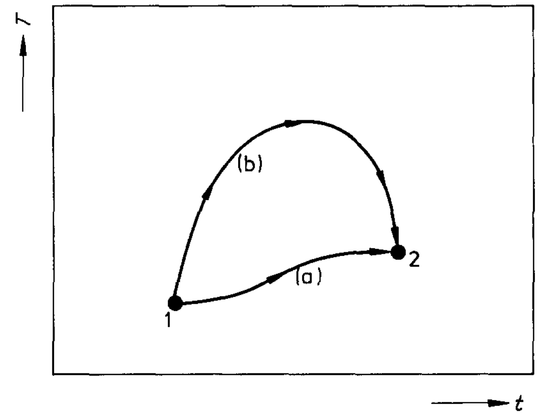

Figure 2 Temperature (T)–time (t) diagram. A specimen experiencing a thermally activated phase transformation proceeds from "State 1 (t_1, T_1)" to "State 2 (t_2, T_2)" via either path a or path b. The stage of transformation in "State 2" depends on the path followed. Hence, in general t and T are not state variables for the stage of transformation.

Thus it appears appropriate to introduce a variable, β, that is fully determined by the path followed in the temperature–time diagram: $T(t)$ prescribes β. Hence, the fraction transformed is fully settled by the state variable β

$$f = F(\beta) \tag{2}$$

Equation 2 does not impose constraints on the type of transformation considered: the relation between f and β, i.e. F, has not been specified; it is only claimed that, given the path followed in the T–t diagram, f is known.

If the transformation mechanism is invariable for the region in the T–t diagram considered, it is tempting to interpret β as proportional to the number of atomic jumps, because T determines the atomic mobility and t defines the duration of the process considered. Against this background the following postulate is given

isothermal annealing

$$\beta = k(T)t \tag{3a}$$

nonisothermal annealing

$$\beta = \int k(T)\,\mathrm{d}t \tag{3b}$$

with k as the rate constant; note that $k(T)$ depends on t in Equation 3b. Next, an Arrhenius-type equation is adopted for the rate constant

$$k = k_0 \exp(-E/RT) \tag{3c}$$

implying that the temperature dependence of the transformation, in the region of the T–t diagram considered, can be described by an (effective, cf. Section 4 and Appendix 2) activation energy, E; k_0 and R denote the pre-exponential factor and the gas constant, respectively. Use of an Arrhenius-type equation for rate constants is universally accepted and relies on compatible analyses of experimental data of transformation kinetics, but rigorous theoretical justification for its applicability is lacking.

3. The transformation rate

From Equation 2 it follows that

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\mathrm{d}F(\beta)}{\mathrm{d}\beta}\frac{\mathrm{d}\beta}{\mathrm{d}t} \tag{4a}$$

Because, in the general case of non-isothermal annealing, f and β (cf. Equation 2), are not uniquely determined by the time and the temperature corresponding to that time, total differentials for f and β with T and t as variables are not allowed. For example $\mathrm{d}\beta/\mathrm{d}t$ can*not* be expressed on the basis of Equations 3a and c as

$$\begin{aligned}\frac{\mathrm{d}\beta}{\mathrm{d}t} &= \left(\frac{\partial\beta}{\partial t}\right)_T + \left(\frac{\partial\beta}{\partial T}\right)_t \frac{\mathrm{d}T}{\mathrm{d}t}\\ &= k + t\frac{\mathrm{d}k}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t}\\ &= k + \frac{E}{RT^2}\beta\frac{\mathrm{d}T}{\mathrm{d}t}\end{aligned}$$

The erroneous reasoning leading to the above expression for $\mathrm{d}\beta/\mathrm{d}t$, and to similar expressions for $\mathrm{d}f/\mathrm{d}t$, has been applied at several places in the literature; e.g. [5].

In the above sense, a physically sound expression for $\mathrm{d}\beta/\mathrm{d}t$ is obtained by accepting the formalism of Equation 3a in the non-isothermal case but for an infinitesimal lapse of time: $\mathrm{d}\beta = k\,\mathrm{d}t$, which leads to Equation 3b. Then it immediately follows that the postulate given by Equations 3a and b implies that the formulae for the transformation rate in the isothermal and non-isothermal cases are identical

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\mathrm{d}F(\beta)}{\mathrm{d}\beta}\frac{\mathrm{d}\beta}{\mathrm{d}t}$$

$$= k(T)\frac{\mathrm{d}F(\beta)}{\mathrm{d}\beta} \qquad (4b)$$

Hence, β, or f, and T are state variables for the transformation rate. This realization introduces the notion of "additivity": after the transformation has progressed at temperatures different from T' and a degree of transformation equal to f_0 has been attained, the course of subsequent transformation at temperature, T', is identical to that followed as if the degree of transformation f_0 would have been produced by isothermal transformation at T' (Fig. 3).

Additionally, the separation of variables T and β (or f) achieved in Equation 4b leads in a straightforward manner to the following integral equation for the time, $t_{f'}$, needed to attain a certain fraction transformed, f', in a non-isothermal annealing experiment (see Appendix 1):

$$\int_0^{t_{f'}} \frac{\mathrm{d}t}{t_{f'}^{\mathrm{iso}}(T)} = 1 \qquad (5)$$

where $t_{f'}^{\mathrm{iso}}$ denotes the time required to transform the fraction f' isothermally at the temperature T. In words: conceiving a non-isothermal transformation as composed of a series of isothermally conducted steps, the total time required follows by adding relative durations of time spent at each temperature and equating this sum to one (cf. Fig. 3).

4. Transformation mechanisms

In principle, one can distinguish homogeneous and heterogeneous reactions. For homogeneous reactions the probability for the transformation to occur is the same for all locations in the virginal system considered. As a result the transformation rate decreases monotonically from $t = 0$ onwards. Heterogeneous reactions, as transformations where nucleation and growth play a role, in general exhibit a maximal transformation rate at some $t > 0$.

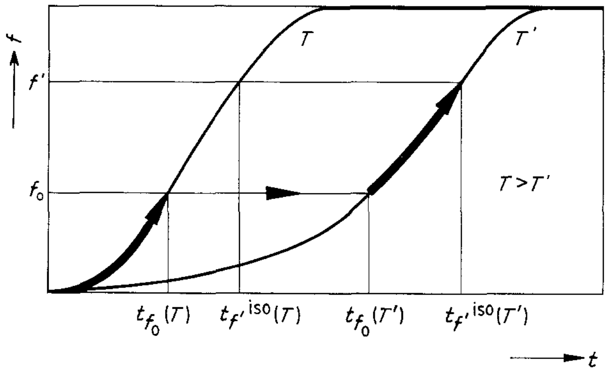

Figure 3 Illustration of the "additivity principle". The total time, $t_{f'}$, needed to attain a fraction transformed, f', by annealing first at a temperature, T, during t_{f_0} and then at a temperature T', is written as (see figure): $t_{f'} = t_{f_0}(T) + [t_{f'}^{\mathrm{iso}}(T') - t_{f_0}(T')]$. Then, according to Equation 5

$$\frac{t_{f_0}(T)}{t_{f'}^{\mathrm{iso}}(T)} + \frac{[t_{f'}^{\mathrm{iso}}(T') - t_{f_0}(T')]}{t_{f'}^{\mathrm{iso}}(T')} = \frac{t_{f_0}(T)}{t_{f'}^{\mathrm{iso}}(T)} + \frac{[t_{f'} - t_{f_0}(T)]}{t_{f'}^{\mathrm{iso}}(T')} = 1$$

Solid-state transformations are normally of the heterogeneous type. (An example to the contrary is the process of structural relaxation in amorphous solids, for which homogeneous reaction kinetics are adopted. Note, however, that crystallization of an amorphous solid is a heterogeneous process; cf. Section 9.3.) Then it is striking to observe that in the recent literature, extensive elaborations of homogeneous reaction kinetics for application to solid-state transformations can still be found (e.g. see [6]). This also means that a procedure as the so-called Kissinger analysis and variants thereof for determination of activation energies, which have been derived on the basis of homogeneous reaction kinetics [7, 8], cannot, in general, be applied without further ado to most solid-state transformations; for a derivation of the generalized version of such methods, see Section 6.

The prescription for f implying dependence only on the state variable β according to Equation 2 is fully compatible with, for example, (i) the well known result for homogeneous reactions

$$(1 - f)^{1-m} = 1 - \beta(1 - m) \qquad m > 1 \qquad (6a)$$

$$\ln(1 - f) = -\beta \qquad m = 1 \qquad (6b)$$

where m is order of reaction, and (ii) the Johnson–Mehl–Avrami (JMA) equation for heterogeneous (solid-state) reactions

$$f = 1 - \exp(-\beta^n) \qquad (7)$$

where n denotes the JMA exponent (note that Equation 7 is identical to Equation 6b for $n = 1$).

Hence it follows for the transformation rate in case (i) above of homogeneous reactions

$$\frac{\mathrm{d}f}{\mathrm{d}t} = k(T)[1 - \beta(1 - m)]^{[m/(1-m)]}$$

$$= k(T)(1 - f)^m \qquad (8)$$

and in case (ii) above of heterogeneous reactions

$$\frac{\mathrm{d}f}{\mathrm{d}t} = nk(T)\beta^{n-1}\exp(-\beta^n)$$

$$= nk(T)[\ln(1 - f)^{-1}]^{[(n-1)/n]}(1 - f) \qquad (9)$$

As discussed in Section 2, the equations of state for the degree of transformation are identical for the cases of isothermal and non-isothermal annealing if they are expressed in terms of β; if f has to be expressed in terms of T and t, β should be substituted in accordance with Equations 3a and b, respectively.

Irrespective of the application of either isothermal or non-isothermal analyses it should be realized that there is no generally valid theoretical justification for use of the JMA equation, as given by Equation 7, to describe solid-state transformations. In heterogeneous transformations the transformation rate can be controlled by more than one activation energy. In such a case applicability of the postulate for β (Equation 3), in principle, is questionable. In practice, Equation 3 can still be used in many cases because one of the operating mechanisms can be (made) dominant, or the activation energy determined may be conceived as an effective value presenting some weighted mean of the separate activation energies of the occurring mechanisms (e.g. see Appendix 2). Also, the activation energy can vary as a function of the degree of transformation, because a change of governing mechanism can occur upon progressing transformation; if the effective activation energy can be traced as a function of the degree of transformation (see Sections 5 and 6), in this way revealing data on the phase transformation studied can be obtained (see Section 9.3).

5. Recipe for isothermal analysis

Without recourse to any kinetic model, i.e. $F(\beta)$ (cf. Equation 2) need not be known, a value for the activation energy can be obtained from the lengths of time between two fixed stages of transformation f_1 and f_2, measured at a number of temperatures (f_1 can, but need not be, taken equal to its initial value: 0) (Fig. 4). It follows (cf. Equation 3a) $k(t_{f_2} - t_{f_1}) = \beta_{f_2} - \beta_{f_1} =$ constant (because $f_2 - f_1 = F(\beta_{f_2}) - F(\beta_{f_1}) =$ constant; cf. Equation 2) and thus

$$\ln(t_{f_2} - t_{f_1}) = \frac{E}{RT} - \ln k_0 + \ln(\beta_{f_2} - \beta_{f_1}) \tag{10}$$

Hence, the activation energy can be determined from the slope of the straight line obtained by plotting $\ln(t_{f_2} - t_{f_1})$ versus $1/T$ (see Section 9.1). A value for k_0 can only be obtained if β_{f_1} and β_{f_2} are known, implying adoption of a specific kinetic model (i.e. $F(\beta)$ has to be prescribed; see Section 9.2 and Table I).

This procedure allows determination of change in the activation energy as the transformation proceeds by suitable choices of a series of f_1 and f_2 values (cf. discussion at the end of Section 4).

6. Recipe for non-isothermal analysis

In accordance with common practice for non-isothermal annealing experiments, in the sequel only the case of a constant heating rate, $\Phi = dT/dt$, is considered (so-called isochronal annealing). Then β (cf. Equation 3b) can be approximately written as (see Appendix 3)

$$\beta = \frac{T^2}{\Phi}\frac{R}{E}k \tag{11}$$

Without recourse to any specific kinetic model, a value for the activation energy can be obtained from the temperatures $T_{f'}$ corresponding to a fixed stage of transformation f' measured for a number of heating rates (Fig. 5). It follows (cf. Equation 11) $(T_{f'}^2/\Phi)$. $(R/E)k = \beta_{f'} =$ constant (because $f' = F(\beta_{f'}) =$ constant; cf. Equation 2) and thus [1]

$$\ln\frac{T_{f'}^2}{\Phi} = \frac{E}{RT_{f'}} + \ln\frac{E}{Rk_0} + \ln\beta_{f'} \tag{12}$$

Hence, the activation energy can be determined from the slope of the straight line obtained by plotting $\ln(T_{f'}^2/\Phi)$ versus $1/T_{f'}$. A value for k_0 can be obtained if $\beta_{f'}$ is known, implying adoption of a specific model (i.e. $F(\beta)$ has to be prescribed; see Section 9.2 and Table II).

This procedure allows determination of change in the activation energy as the transformation proceeds by choosing a series of progressive f' values.

Hence, in retrospect, methods of kinetic analysis for the non-isothermal case on the basis of Equation 12 are full pendants of those derived from Equation 10 for the isothermal case.

7. Non-isothermal analysis versus isothermal analysis

To give preference to either isothermal or non-isothermal analysis should depend on the case considered. In particular, if a series of overlapping transformations occurs, the degree of overlap in an isothermal experiment can be larger than the degree of overlap in a non-isothermal experiment. This can be illustrated as follows.

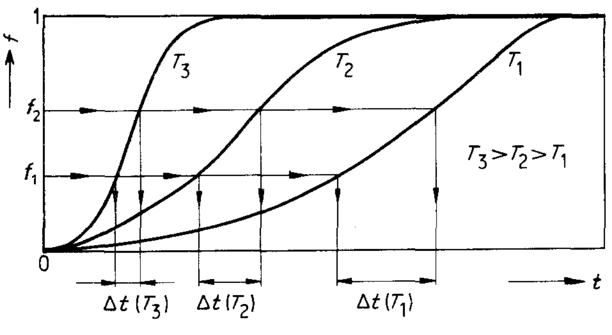

Figure 4 The lengths of time, Δt, between two fixed stages of transformation, f_1 and f_2, for isothermal transformations at T_1, T_2 and T_3 (see also Fig. 1a). The activation energy can be determined from the slope of the straight line obtained by plotting $\ln(\Delta t)$ versus $1/T$ (cf. Equation 10).

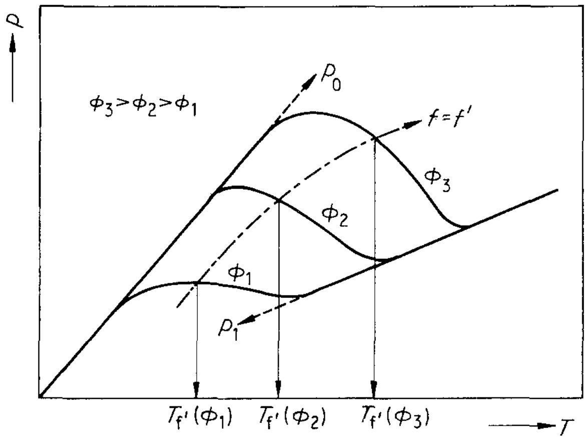

Figure 5 The temperatures, $T_{f'}$, corresponding to a fixed stage of transformation, f', for non-isothermal transformations with heating rates Φ_1, Φ_2 and Φ_3 (see also Fig. 1b). The activation energy can be determined from the slope of the straight line obtained by plotting $\ln(T_{f'}^2/\Phi)$ versus $1/T_{f'}$ (cf. Equation 12).

Consider three consecutive, more or less overlapping transformations, 1, 2 and 3, with activation energies E_1, E_2 and E_3, obeying $E_1 < E_2 < E_3$. For the first stage of transformation 2 there is overlap with the end stage of transformation 1; for the final stage of transformation 2 there is overlap with the first stage of transformation 3. Because in the non-isothermal experiment the first and final stages of a transformation occur at relatively low and relatively high temperatures, respectively, and realizing $E_1 < E_2 < E_3$, it follows that, depending on the heating rate applied in the non-isothermal experiment and the temperature applied in the isothermal experiment and (the differences between) the activation energies involved, the dominance of transformation 2 in the beginning and end stages of this transformation can be more pronounced in the non-isothermal experiment, compared to the isothermal experiment. This can be formulated differently: the range of heating rates for non-isothermal kinetic analysis can be less restricted by overlaps with previous and next transformations than the range of temperatures for isothermal kinetic analysis of the separate transformation considered (see Section 9.2).

8. Maximal transformation rate and Kissinger-like analyses

For the maximal reaction rate, it holds (cf. Equation 4)

$$\frac{\mathrm{d}^2 f}{\mathrm{d}t^2} = \frac{\mathrm{d}^2 F(\beta)}{\mathrm{d}\beta^2}\left(\frac{\mathrm{d}\beta}{\mathrm{d}t}\right)^2 + \frac{\mathrm{d}F(\beta)}{\mathrm{d}\beta}\frac{\mathrm{d}^2\beta}{\mathrm{d}t^2} = 0 \qquad (13)$$

In the case of *isothermal* annealing $\mathrm{d}^2\beta/\mathrm{d}t^2 = 0$ and, consequently, the maximal reaction rate occurs always at exactly the same value of β (and thus f) prescribed by $\mathrm{d}^2F(\beta)/\mathrm{d}\beta^2 = 0$. (For the kinetic models corresponding to Equations 6 and 7 we obtain $\beta = 0$ and $\beta^n = (n-1)/n$, respectively. Here it should be realized that β should be ≥ 0 and hence for the kinetic model according to Equation 6 the isothermal transformation rate is maximal at $\beta = 0$ for all m).

In the case of *non-isothermal* annealing it follows that (Equations 3b and c)

$$\left(\frac{\mathrm{d}\beta}{\mathrm{d}t}\right)^2 \bigg/ \frac{\mathrm{d}^2\beta}{\mathrm{d}t^2} = \frac{k}{\Phi}\frac{RT^2}{E} \qquad (14a)$$

and thus, for isochronal annealing, using the (approximate) Equation 11

$$\left(\frac{\mathrm{d}\beta}{\mathrm{d}t}\right)^2 \bigg/ \frac{\mathrm{d}^2\beta}{\mathrm{d}t^2} = \beta \qquad (14b)$$

Therefore, it can be concluded that the maximal reaction rate occurs always at *about* the same value of β (and thus f) prescribed by (Equations 13 and 14b)

$$\beta\frac{\mathrm{d}^2F(\beta)}{\mathrm{d}\beta^2} + \frac{\mathrm{d}F(\beta)}{\mathrm{d}\beta} = 0 \qquad (15)$$

Hence, the temperature, T_i, where the reaction rate is maximal, i.e. the temperature corresponding to a point of inflection on the curve of f versus t (or T), occurs to a very good approximation at the same value for f for variable heating rate. (Assuming that Equation 14b holds exactly, the general solution of the differential Equation 15 (independent of a specific kinetic model) reads: $F(\beta_{T_\mathrm{i}}) = c_1 \ln \beta_{T_\mathrm{i}} + c_2$, where β_{T_i} is β at $T = T_\mathrm{i}$ and c_1 and c_2 are constants. This result is not of practical use. For both kinetic models considered here (see Equations 6 and 7) it is deduced from Equation 15 by straightforward substitution that $\beta_{T_\mathrm{i}} = 1$. Then it follows for the degree of transformation at maximal non-isothermal transformation rate, $f_{T_\mathrm{i}} = F(\beta_{T_\mathrm{i}})$, for transformation kinetics according to Equation 6: $f_{T_\mathrm{i}} = 1 - 1/e (m = 1)$ and $f_{T_\mathrm{i}} = 1 - m^{1/(1-m)} (m > 1)$; and for transformation kinetics according to Equation 7: $f_{T_\mathrm{i}} = 1 - 1/e$.)

In the past a family of constant heating-rate procedures has been proposed for the determination of kinetic parameters as activation energies. These methods, called here Kissinger-like methods (e.g. see 7, 8, 4, 9), can be considered as special cases of the one presented in Section 6: Equation 12 is applied for that stage of transformation where the transformation rate is maximal; i.e. $T_{f'}$ is substituted by T_i in Equation 12 (see below Equation 15). As follows from the present treatment, the derivations of these Kissinger-like methods suffer from two unnecessary limitations: (i) a specific kinetic model is adopted; (ii) the dependence on heating rate of only the temperature where the reaction rate is maximal is analysed. For example, in the paper usually referred to [7], the analysis is based on the assumption of homogeneous reactions, whereas most solid-state transformations are heterogeneous (cf. Section 4), and therefore this analysis cannot be applied apropos of nothing in the latter case. This has often been overlooked; a recent example is in reference [10]. In fact, the general proof for all Kissinger-like methods has been presented above: use of T_i for $T_{f'}$ in Equation 12 is justified because the value of f' at the point of inflection on the curve of f versus t (or T) indeed is practically independent of the heating rate; see Equation 15 and its discussion.

It follows from Equation 15 that for both kinetic models (Equations 6 and 7) $\beta = 1$ and hence $\beta_{T_\mathrm{i}} \cong 1$, implying that the last term at the right-hand side of Equation 12 vanishes. Then, in the application of Kissinger-like methods, after the activation energy has been determined from the slope of the straight line obtained by plotting $\ln(T_\mathrm{i}^2/\Phi)$ versus $1/T_\mathrm{i}$, the pre-exponential factor, k_0, can be directly calculated from the intercept of the ordinate at $1/T_\mathrm{i} = 0$ (see Section 9.2 and Table II).

For determination of f', and thus $T_{f'}$, or T_i in the case of Kissinger-like analyses, the reference states p_0 and p_1 (cf. Equation 1), within the temperature region where the transformation occurs, are normally obtained by linear extrapolation from the temperature regions where the parent and product phases are stable (see Fig. 1); i.e. $\mathrm{d}p_0/\mathrm{d}T$ and $\mathrm{d}p_1/\mathrm{d}T$ are taken to be constant. (Note: In a dilatometer the actual signal recorded is proportional to the quantity p (specific volume/length), not f, and T_i can be taken only approximately equal to the temperature corresponding to the inflection point on the curve of p versus t (or T) [9], while in an apparatus for differential scanning calorimetry the actual signal recorded is proportional to $\mathrm{d}p/\mathrm{d}T$ (heat capacity; p denotes enthalpy), not $\mathrm{d}f/\mathrm{d}T$, and T_i can be taken only approximately equal to the temperature equal to the temperature corresponding to the extremum in the curve of $\mathrm{d}p/\mathrm{d}T$ versus t(or T)).Because $\mathrm{d}p_0/\mathrm{d}T$ and $\mathrm{d}p_1/\mathrm{d}T$ will generally be different, and variable, significant errors may occur in the value calculated for f' according to Equation 1, in particular if f', or $1-f'$, is small. An error calculation can only be made if a certain kinetic model is assumed: Appendix 4 provides such an error calculation for the Kissinger-like method.

9. Examples

Three cases of kinetic analysis of solid-state transformations, taken out of recent research in which I have been involved, are discussed in this section. The examples chosen serve various purposes: demonstration of the "classical" case of isothermal analysis; application and benefit of non-isothermal analysis; comparison of isothermal and non-isothermal analyses, and, finally, the use of the concept of "effective activation energy" allowing establishment of the dominant transformation mechanism as a function of time and/or temperature.

9.1. Isothermal analysis: formation of Guinier–Preston zones in AlMg alloys

Ageing at temperatures between, say, 290 and 350 K of AlMg alloys containing more than 10 at% Mg in solid solution leads to the development of Guinier–Preston (GP) zones in the aluminium-rich matrix [11]. The progress of GP-zone formation at a certain ageing temperature can be traced by measuring, as a function of ageing time, the amount of heat consumed for dissolving the GP-zones on heating the aged specimen. This can be done by performing differential scanning calorimetry (DSC). An example of a result thus obtained is shown in Fig. 6 [11]. Considering Fig. 6 and with a view to Equation 1, the degree of transformation for the process of GP-zone formation can be given as (see also Fig. 1a)

$$f(t) = \frac{\Delta H_{\mathrm{meas}}(t)}{\Delta H_{\mathrm{meas}}(t = \infty)}$$

where $-\Delta H_{\mathrm{meas}}(t)$ and $-\Delta H_{\mathrm{meas}}(t=\infty)$ are the heats of dissolution after ageing times t and ∞, respectively.

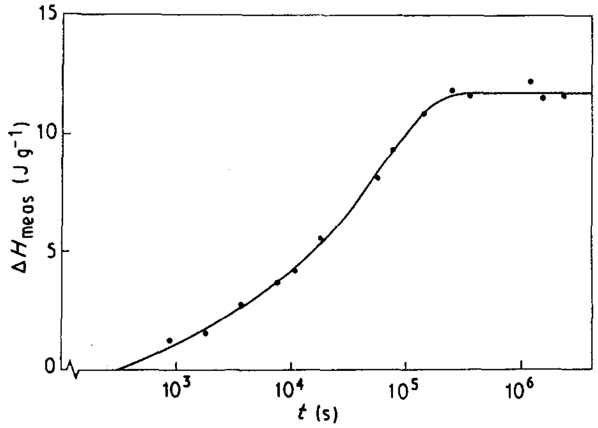

Figure 6 Enthalpy change for Guinier–Preston zone dissolution (an endothermal transformation) for liquid-quenched AlMg (16.1 at% Mg) aged at 333 K, as a function of ageing time.

Now the procedure outlined in Section 5 on the basis of Equation 10 can be applied. Data for f were obtained for GP-zone formation at room temperature (≈ 293), 313 and 333 K. The determination of the activation energy, E, was performed with $f_1 = 0.2$ and $f_2 = 0.5$ and with $f_1 = 0.5$ and $f_2 = 0.8$ (cf. Equation 10 and Fig. 4). Values of f_1 smaller than, say, 0.2 and values of f_2 larger than, say, 0.8, should not be applied because the corresponding values for t_{f_1} and t_{f_2} (cf. Equation 10) are relatively sensitive to error propagation as a consequence of relatively small values for $\mathrm{d}f/\mathrm{d}t$ for small f and small $1-f$. The values thus determined for the activation energy read [11]

$$f_1 = 0.2 \text{ and } f_2 = 0.5\text{: } E = 133\,\mathrm{kJ\,mol^{-1}}$$

$$f_1 = 0.5 \text{ and } f_2 = 0.8\text{: } E = 136\,\mathrm{kJ\,mol^{-1}}$$

In view of the experimental inaccuracy, the difference between both values for E should be considered as insignificant. Apparently the transformation mechanism is invariable for the region concerned in the $T-t$ diagram (cf. Section 2). Interpretation of the result is not straightforward. It seems likely that the value found for E should be conceived as an effective value combining contributions of nucleation and growth of the GP-zones (cf. Appendix 2 and [11]).

9.2. Isothermal analysis and non-isothermal analysis; tempering of iron–carbon martensite and austenite

Iron–carbon austenite can be described as an fcc lattice of iron atoms containing carbon atoms in

TABLE I Kinetic parameters for *isothermal* tempering of martensitic iron–carbon steel (1.18 wt% C) [12]

Process	Annealing temperature (K)	E (kJ mol^{-1})	JMA analysis n	E_{JMA} (kJ mol^{-1})	τ (years)	Technique
ε/η	388–424	**116**	0.6	114	~ 4.5	dilatometry
γ	450–476	**130**	1.1–1.2	~ 130	~ 3×10^5	dilatometry
γ	443–531	**127**	1.1–1.5	~ 127	~ 1×10^5	magnetometry

In the text of this paper α' = martensite, α = ferrite, γ = austenite, ε/η = transition carbide and θ = cementite ("equilibrium" carbide). The symbols ε/η and γ in this table denote precipitation of the transition carbide ($\alpha' \rightarrow \varepsilon/\eta + \alpha$) and decomposition of retained austenite ($\gamma \rightarrow \theta + \alpha$). The activation energy, E, has been obtained by application of Equation 10. Symbols n, E_{JMA} and τ are the JMA exponent, the activation energy and the relaxation time at 293 K, respectively, as obtained by fitting the JMA equation (Equation 7) to the isothermal data.

TABLE II Kinetic parameters for *non-isothermal* tempering of martensitic iron–carbon steel (1.1 wt % C) [12]

Process	$\langle T_{f'}(10\,\mathrm{K\,min^{-1}})\rangle$ (K)	$\langle T_i(10\,\mathrm{K\,min^{-1}})\rangle$ (K)	E (kJ mol^{-1})	τ	Technique
Segregation ($f' = 0.5$)	329		**83**	~ 2 h	Dilatometry
Local enrichment ($f' \cong 0.5$)	354		**79**	~ 9 h	Calorimetry
ε/η		415	**111**	~ 2 yr	Calorimetry
ε/η		414	**126**	~ 7 yr	Dilatometry
γ		544	**132**	~ 6×10^3 yr	Calorimetry
θ		580	**203**	~ 2×10^{12} yr	Dilatometry

In the text of this paper α' = martensite, α = ferrite, γ = austenite, ε/η = transition carbide and θ = cementite ("equilibrium" carbide). The symbols ε/η, γ and θ in this table denote precipitation of the transition carbide ($\alpha' \rightarrow \varepsilon/\eta + \alpha$), decomposition of retained austenite ($\gamma \rightarrow \theta + \alpha$) and conversion of transition carbide into "equilibrium" carbide ($\varepsilon/\eta + \alpha \rightarrow \theta$). The average values for the temperatures corresponding with a fixed stage of transformation, f', and with the point of inflection are indicated by $\langle T_{f'} \rangle$ and $\langle T_i \rangle$, respectively. The activation energy, E has been obtained by application of Equation 12. The symbol τ denotes the relaxation time at 293 K.

octahedral interstices. Quenching a completely austenitic specimen from a relatively high temperature, say 1100 K, to room temperature leads to a martensitic specimen composed of martensite (α') and some retained austenite (γ). Iron–carbon martensite can be described as a bct lattice of iron atoms containing carbon atoms in, predominantly *c*-type, octahedral interstices. Such a martensitic specimen is highly unstable: ageing at room temperature and heating lead to a series of phase transformations which are gathered under the heading "tempering" [12].

9.2.1. Isothermal analysis

Isothermal changes of specific length of iron–carbon martensitic specimens are shown in Figs 7 and 8 for two temperatures. As follows from Fig. 8, the successive stages of tempering (denoted by arrows in the figures) overlap. Only for very limited ranges of temperature, is isothermal kinetic analysis possible for only a couple of the successive processes.

A remedy to severe overlap by successive processes, as exhibited in curves of property, p, versus time, t, can be selection of another property, p, which is relatively much more or even only sensitive to the separate process to be studied. In this way the decomposition of retained austenite ($\gamma \rightarrow \theta + \alpha$) in the iron–carbon martensitic specimen could be analysed by means of magnetometry at temperatures where this is impossible by means of dilatometry (cf. Table I and Fig. 8).

The data gathered in Table I were obtained by isothermal analysis according to Equation 10 with $f_1 = 0.2$ and $f_2 = 0.8$ [12].

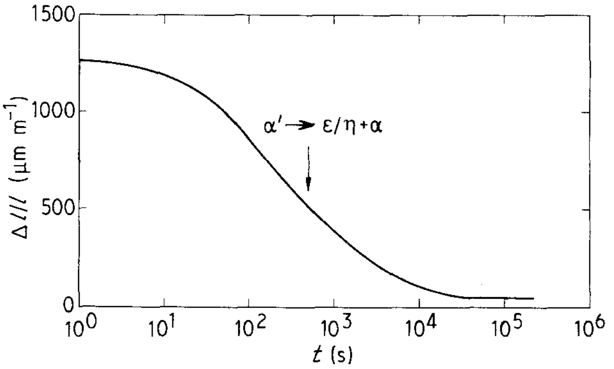

Figure 7 Relative length change, $\Delta l/l$, of martensitic iron–carbon steel (1.18 wt % C) as a function of annealing time, t, at 403 K. The precipitation of ε/η carbide leads to length contraction (α' = martensite; α = ferrite).

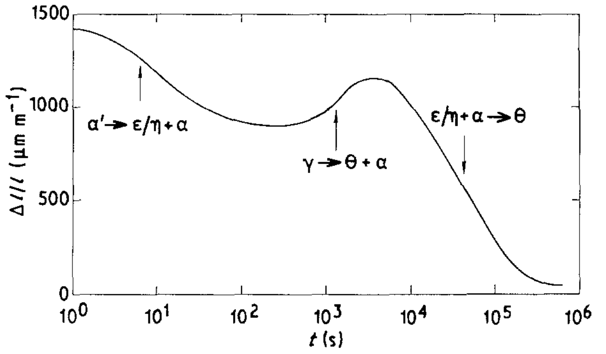

Figure 8 Relative length change, $\Delta l/l$, of martensitic iron–carbon steel (1.18 wt % C) as a function of annealing time, t, at 508 K. Clearly, the observed increase of length due to the decomposition of retained austenite, γ, is severely affected by pronounced overlap with the previous (precipitation of ε/η carbide) and next (conversion of ε/η carbide into cementite, θ) transformations (α' = martensite; α = ferrite).

A more constrained approach to isothermal analysis involves fitting of the JMA equation (Equation 7) to the isothermal data. A well-known procedure is plotting of $\ln[\ln(1-f)^{-1}]$ versus $\ln t$; from the slope of the straight line obtained (cf. Equations 3a and 7), a value of n can be derived, while a value for k follows from the part cut from the ordinate. Next a plot of $\ln k$ versus $1/T$ yields values for the pre-exponential factor, k_0, and the activation energy, E (cf. Equation 3c). Finally a relaxation time $\tau = 1/k$ can be calculated for the transformation considered during isothermal annealing (for JMA kinetics, τ corresponds to the time needed to transform a fraction $1 - 1/e \triangleq 63\%$). For the processes dealt with, τ was calculated at room temperature (293 K). Obviously, the values for τ can be subject to large (extrapolation) errors. Results from this JMA analysis have been included in Table I. To distinguish the value of the activation energy arrived at in the JMA analysis from that derived above (using Equation 10) without imposing JMA behaviour, the JMA result has been indicated as E_{JMA} in the table. The overall agreement between both sets of activation energy values could be considered as support for the assumption of JMA behaviour. On the other hand, the range observed for the JMA exponent for the decomposition of retained austenite, on varying the temperature, could hint at the inadequacy of the JMA description for this transformation.

9.2.2. Non-isothermal analysis

Changes in specific length (to be considered as integral parameter p; cf. Fig. 1b) and heat capacity (to be considered as differential parameter $\mathrm{d}p/\mathrm{d}T$) induced in iron–carbon martensitic specimens by non-isothermal annealing employing a constant heating rate are shown in Fig. 9a and b. The successive stages of tempering have been indicated by arrows in the figures.

The kinetics of the processes occurring on tempering were established by determining either the temperature $T_{f'}$, corresponding to a fixed stage of transformation f' (see Equation 12), or the temperature T_i, corresponding to either a point of inflection on the curve of p versus T (dilatometry) or a peak maximum on the curve of $\mathrm{d}p/\mathrm{d}T$ versus T (calorimetry: DSC) (see discussion below Equation (15) and the note Section 8), both as a function of heating rate, Φ. The results have been compiled in Table II [12]. For each heating rate two to four experiments were performed; the average values for $T_{f'}$ and T_i have been indicated in the table. The activation energies, E, were determined on the basis of Equation 12. The pre-exponential factor, k_0, was also determined: for the analysis based on the point of inflection on the curve of f versus T, this was done by ignoring the last term at the right-hand side of Equation 12 (which is a justified procedure if, for example, JMA kinetics hold: $\beta(T_i) \simeq 1$; see discussion below Equation 15); for the analysis based on the temperature corresponding to a fixed stage of transformation, f', this was done by taking in Equation 12 for $\ln \beta_{f'}$, an estimate obtained by adopting JMA kinetics and substituting f' for f and 1 for n in Equation 7. From the values obtained for k_0 and E, a relaxation time $\tau = 1/k$ (see Section 9.2.1) can be calculated for the transformation considered during isothermal annealing. For the processes dealt with, values for τ at room temperature (293 K) were calculated and have also been included in Table II. It should be emphasized that the values obtained for k_0 and thus τ can be subject to large extrapolation errors (see above). The estimates arrived at for τ at room temperature provide an order of magnitude for the ageing time needed for a particular process to occur effectively during ageing at room temperature.

For interpretation of the kinetic data gathered in Tables I and II the reader is referred to Reference 12.

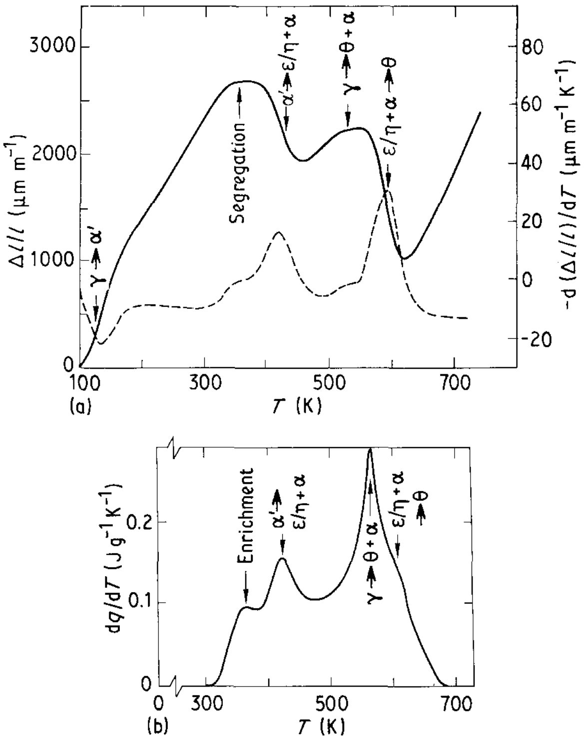

Figure 9 (a) Relative length change, $\Delta l/l$ (——) and its derivative with respect to temperature, $\mathrm{d}(\Delta l/l)/\mathrm{d}T$ (– – – –), of martensitic iron–carbon (1.1 wt % C) as a function of temperature, T, on non-isothermal annealing applying a heating rate of 20 K min^{-1}. The consecutive transformations have been indicated (α' = martensite; α = ferrite; γ = austenite; ε/η = transition carbide; θ = cementite; "segregation" denotes the segregation of a minor amount of carbon atoms (a few tenths of an atomic per cent) to lattice defects). (b) Rate of heat generation, $\mathrm{d}q/\mathrm{d}T$, of martensitic iron–carbon (1.1 wt % C) as a function of temperature, T, on non-isothermal annealing applying a heating rate of 20 K min^{-1}. The consecutive transformations have been indicated (cf. (a); "enrichment" denotes the development of carbon enrichments in the martensite matrix, a process involving most of the carbon atoms).

9.2.3. Comparison of isothermal analysis and non-isothermal analysis

In the case of severe overlapping of successive transformations in the curve of property, p, versus time, t, in isothermal analysis, p_0 and p_1 (cf. Fig. 1a) cannot be determined accurately, if at all. This is a major drawback of the isothermal analysis. The determination of T_i in the non-isothermal analysis is essentially less sensitive to errors in p_0 and p_1. As a consequence, the series of tempering processes could be much more completely subjected successfully to non-isothermal kinetic analysis (cf. Tables I and II).

As follows from a comparison of activation energy values reported in Tables I and II for the precipitation of the transition carbide ($\alpha' \to \varepsilon/\eta + \alpha$) and for the decomposition of retained austenite ($\gamma \to \theta + \alpha$), the results obtained by isothermal analysis are similar to those obtained by non-isothermal analysis. This is just one example demonstrating the equivalence of isothermal analysis and non-isothermal analysis. The type of analysis to be preferred, in practice, should depend on the specific transformation(s) to be studied (see also Section 7).

9.3. Change of effective activation energy during overall transformation: solid-solution formation and solid-state amorphization in Ni/Ti multilayers

A multilayer is an alternating stack of sublayers of element A and sublayers of element B. Upon annealing a multilayer composed of crystalline nickel and crystalline titanium sublayers, titanium dissolves in nickel and an amorphous phase develops both at the Ni/Ti interfaces and along the grain boundaries in the nickel and titanium sublayers [13]. The processes of titanium dissolution and "solid-state amorphization" overlap strongly.

Solid-state amorphization and solid-solution formation are both associated with production of heat (i.e. loss of enthalpy). An example of a non-isothermal DSC scan, recorded with $\Phi = 10\ \mathrm{K\ min^{-1}}$, is shown in Fig. 10 for a Ni/Ti multilayer [14]. The structural interpretation of the heat effects was achieved by performing X-ray diffraction analysis. Thus the large overlapping heat effects below 700 K could be ascribed to dissolution of titanium in nickel and to amorphization. Amorphization was found to continue up to 735 K; the sharp peak at 735 K in the DSC curve is due to crystallization of the amorphous phase. Consequently, the first major peak in the DSC curve (at about 580 K) is assigned to solid-solution formation.

To perform non-isothermal kinetic analysis on the basis of Equation 12 the enthalpy has been adopted as property p. The degree of transformation, f, has been defined as the ratio of the enthalpy change measured up to a certain temperature in the DSC experiment (i.e. the area enclosed by the solid line ($= \mathrm{d}H/\mathrm{d}t$) and the base line (given by $\mathrm{d}H/\mathrm{d}t = 0$) in Fig. 10 up to a certain temperature (or, alternatively, time; $\phi \equiv \mathrm{d}T/\mathrm{d}t = \text{constant}$)) and the total enthalpy change (similarly measured from Fig. 10). This definition of f parallels the one applied in Section 9.1 in an isothermal analysis.

For specific stages of the combined process of solid-solution formation and solid-state amorphization, the effective activation energy of the overall process was determined by applying the method based on Equation 12. This activation energy has been plotted as a function of temperature (i.e. as a function of the degree of transformation) in Fig. 10 (dashed line). Initially the effective activation energy gradually increases from about $160\ \mathrm{kJ\ mol^{-1}}$ up to approximately $200\ \mathrm{kJ\ mol^{-1}}$. Then, right after the first main peak in the DSC curve, it abruptly decreases to about $140\ \mathrm{kJ\ mol^{-1}}$, at which value it remains fairly constant up to the onset of crystallization. Dissolution of titanium in nickel has an activation energy that is larger than $200\ \mathrm{kJ\ mol^{-1}}$; whereas amorphization in Ni/Ti is associated with an activation energy of about $140\ \mathrm{kJ\ mol^{-1}}$ [14]. Upon heating, the contribution of the process with the higher activation energy (dissolution of titanium in nickel), becomes increasingly relatively important and, accordingly, the effective activation energy increases. However, saturation of the solid solution is achieved at a stage where amorphization is still possible and, consequently, on passing through that stage the effective activation energy then drops to the value corresponding to amorphization. The rarity of such an observation should be realized: the effective activation energy, in general increases when the temperature rises (see the reasoning two sentences above).

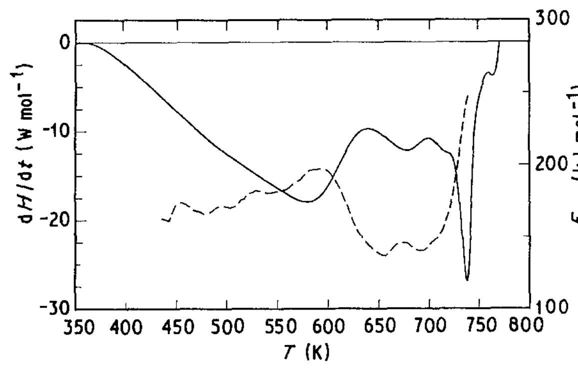

Figure 10 (——) The enthalpy-change rate, $\mathrm{d}H/\mathrm{d}t$ (see left ordinate), for a heating rate of $10\ \mathrm{K\ min^{-1}}$, for an $\mathrm{Ni_{22}Ti_{78}}$ multilayer of average composition-modulation period equal to 22.11 nm (DSC scan). (– – –) The change of the effective activation energy, E_{eff} (see right ordinate), during the course of the overall transformation (combined solid-solution formation and amorphization followed by crystallization of the amorphous phase).

The activation energy for crystallization of the amorphous phase can easily be determined by application of Equation 12, utilizing the corresponding peak temperature in the DSC curve as T_i which is taken for $T_{f'}$ in Equation 12 (see discussion below Equation 15). For discussion of the result obtained, $271 \pm 13\ \mathrm{kJ\ mol^{-1}}$, see [14].

Appendix 1. Additivity of relative time

Defining $l(\beta) \equiv \mathrm{d}F(\beta)/\mathrm{d}\beta$, Equation 4b can be written as

$$\frac{\mathrm{d}f}{\mathrm{d}t} = k(T)\, l(\beta) \qquad \text{(A1)}$$

Equation A1 will be integrated such that f changes from 0 to f' (and correspondingly β changes from 0 to β'; cf. Equation 2).

A1.1. Isothermal transformation

It follows from Equation A1 that

$$k(T) \int_0^{t_{f'}^{\mathrm{iso}}(T)} \mathrm{d}t = \int_0^{f'} \frac{1}{l(\beta)}\, \mathrm{d}f \qquad \text{(A2)}$$

where $t_{f'}^{\mathrm{iso}}$ denotes the time required to transform the fraction f' isothermally at the temperature T. Using Equation 2 one obtains

$$k(T)\, t_{f'}^{\mathrm{iso}}(T) = \int_0^{\beta'} \frac{1}{l(\beta)}\, \mathrm{d}F(\beta) \qquad \text{(A3)}$$

and defining the right-hand member of this equation as $L(\beta')$

$$k(T) = L(\beta')/t_{f'}^{\mathrm{iso}}(T) \qquad \text{(A4)}$$

A1.2. Non-isothermal transformation

After substitution of Equation A4 into Equation A1 it follows that

$$\int_0^{t_{f'}} \frac{1}{t_{f'}^{\mathrm{iso}}(T)}\, \mathrm{d}t = \frac{1}{L(\beta')} \int_0^{f'} \frac{1}{l(\beta)}\, \mathrm{d}f \qquad \text{(A5)}$$

Again using Equation 2 results immediately in (see above Equation A4)

$$\int_0^{t_{f'}} \frac{\mathrm{d}t}{t_{f'}^{\mathrm{iso}}(T)} = 1 \qquad \text{(A6)}$$

Appendix 2. Nucleation and growth

A generalized form of the JMA equation accounting for both nucleation and growth reads [2]

$$f = 1 - \exp\left(- C \int_0^t v_\tau(t) I_\tau \mathrm{d}\tau \right) \qquad \text{(A7)}$$

where C is a constant indicating the maximal amount of volume to be transformed and $v_\tau(t)$ denotes the volume at time t of one of the particles of the product phase nucleated at time τ when the nucleation rate per unit volume equalled I_τ. Now, for both v_τ ("growth") and I_τ ("nucleation") Arrhenius-type temperature dependencies are assumed. Interpreting the activation energy for growth as the activation energy for diffusion, E_D, the Arrhenius factor in v_τ contains an activation energy equal to $m_D E_D$, where m_D is related to the dimensionality of the growth (e.g. for isotropic three-dimensional growth, m_D obviously equals 3/2 as the radial growth rate is proportional to the square root of the diffusion coefficient).

In the case of isothermal analysis the temperature-dependent Arrhenius factors in v_τ and I_τ can be put before the integral in Equation A7. Under certain conditions (for the time dependency of the nucleation rate) the remaining integral over τ will reduce to: constant $\times t^n$, with n as the so-called JMA exponent. Then, eventually, the following well-known formulation of the JMA equation for *isothermal* analysis results

$$f = 1 - \exp(-k' t^n) \qquad \text{(A8)}$$

An example of a treatment on this basis (from Equation A7 to Equation A8) is provided by [15].

As follows immediately from the above, the combined rate constant $k'(T)$ can then be written as an Arrhenius factor too, with an effective activation energy, E'_{eff}, which is a weighted linear combination of activation energies of the separate contributing processes (as nucleation and growth); hence, in general (cf. above discussion on $m_D E_D$)

$$E'_{\mathrm{eff}} = \sum_i m_i E_i \qquad \text{(A9)}$$

With a view to Equations 7 and 3a it is concluded that $k^n = k'$. Therefore, if the kinetic analysis has been based on Equations 7, 3a and 3c and the value of the activation energy thus determined has to be considered as an effective one, E_{eff}, it follows that

$$E_{\mathrm{eff}} = \frac{1}{n} E'_{\mathrm{eff}} = \frac{1}{n} \sum_i m_i E_i \qquad \text{(A10)}$$

Appendix 3. The temperature integral

For non-isothermal analysis with constant heating rate $\Phi = \mathrm{d}T/\mathrm{d}t$, the time integral in Equation 3b can be replaced by a temperature integral

$$\beta = \int_0^t k \mathrm{d}t = \frac{k_0}{\Phi} \int_{T_0}^T \exp(-E/RT')\mathrm{d}T' \qquad \text{(A11)}$$

where use has also been made of Equation 3c and T_0 indicates the initial state: $\beta(T_0) = 0$.

The integration over T' cannot be performed analytically. The "temperature integral" sooner or later appears in most more or less complicated procedures presented in the literature for non-isothermal analysis. A series of approximations to the integral have been proposed; ten of these are assessed in [16]. Here we proceed as follows.

Equation A11 can be rewritten as

$$\begin{aligned} \beta &= \frac{k_0}{\Phi} \left\{ \int_0^T \exp(-E/RT')\mathrm{d}T' - \int_0^{T_0} \exp(-E/RT')\mathrm{d}T' \right\} \\ &= \frac{k_0}{\Phi} \left\{ T \int_1^\infty \frac{\exp(-E/RT)z}{z^2} \mathrm{d}z - T_0 \int_1^\infty \frac{\exp(-E/RT_0)z}{z^2} \mathrm{d}z \right\} \qquad \text{(A12)} \end{aligned}$$

where for the two integrals a change of variable has been applied according to $z = T/T'$ and $z = T_0/T'$, respectively. Adopting a usual development for the exponential integral [17] it is obtained

$$\beta = \frac{T^2}{\Phi} \frac{R}{E} k \left(1 - 2\frac{RT}{E} + \ldots \right) \qquad \text{(A13)}$$

where it has been assumed that between the braces in Equation A12 the second term is small compared to the first ($T_0 \ll T$).

For solid-state transformations, $RT/E \ll 1$ normally holds and this results in Equation 11.

Appendix 4. Error terms in the Kissinger-like method

If the degree of transformation, f, as a function of the physical property, p, is given by Equation 1 and if $\mathrm{d}p_0/\mathrm{d}T$ and $\mathrm{d}p_1/\mathrm{d}T$ are constant, it follows for the temperature $T_{i,p}$ where $\mathrm{d}^2p/\mathrm{d}T^2 = 0$

$$\left[\frac{\mathrm{d}^2 f}{\mathrm{d}T^2} \right]_{T_{i,p}} \cong C \left[\frac{\mathrm{d}f}{\mathrm{d}T} \right]_{T_{i,p}} \qquad \text{(A14)}$$

with

$$C = 2\left(\frac{\mathrm{d}p_1}{\mathrm{d}T} - \frac{\mathrm{d}p_0}{\mathrm{d}T} \right) \Big/ (p_1 - p_0) \qquad \text{(A15)}$$

Obviously, if $\mathrm{d}p_1/\mathrm{d}T = \mathrm{d}p_0/\mathrm{d}T$, $[\mathrm{d}^2 f/\mathrm{d}T^2]_{T_{i,p}} = 0$ and $T_{i,p} = T_{i,f}$, where $T_{i,f}$ ($\equiv T_i$) is the temperature of the point of inflection on the curve of f versus T (or t; cf. Section 8).

Adopting Equation A13 and JMA kinetics (cf. Equation 7), one obtains for $RT_i/E \ll 1$, and omitance of terms of order higher than RT_i/E,

$$\ln \frac{T_i^2}{\Phi} = \frac{E}{RT_i} + \ln \frac{E}{Rk_0} + \mathrm{Res}\,1 + \mathrm{Res}\,2 \qquad \text{(A16)}$$

with

$$\mathrm{Res}\,1 \;=\; \frac{C}{n^2}\frac{RT_\mathrm{i}^2}{E} \tag{A17}$$

$$\mathrm{Res}\,2 \;=\; 2\left\{1 - \frac{1}{n^2} + n\ln\left[\frac{T_\mathrm{i}^2}{\Phi}\frac{Rk(T_\mathrm{i})}{E}\right]\right\}\frac{RT_\mathrm{i}}{E} \tag{A18}$$

If it is allowed to neglect both residuals, the Kissinger-like analysis is possible (cf. Equation 12 and Section 8).

It will practically always be justifiable to neglect Res 2. However, no such general statement can be made for Res 1 (note the presence of C in Res 1). For any method of non-isothermal analysis where p is measured as a function of T or t (cf. Equation 1) it is advisable to verify the permissibility of the omittance of Res 1 in each case.

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