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Application of thermal analysis methods to nucleation and growth transformation kinetics, Part II

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Abstract

The general theory of transformation kinetics is largely confined to isothermal reactions. Several attempts have however been made to apply that theory to non-isothermal nucleation and growth transformations as well. Unfortunately, this has lead to some confusion and misunderstandings when thermal analysis experiments, such as DSC and DTA, associated with Kissinger- or Ozawa-like relationships, are used for the extraction of the kinetic parameters of the non-isothermal transformations. The present Part II of this paper widens the scope of the discussed issues, assesses the correct way of applying the theory of isothermal kinetics to non-isothermal transformations, stresses the sources of confusion and points to the mathematical and physical errors that commonly appear in the literature. It is shown that only 'site saturated' transformations, i.e. those where the nucleation rate is zero, can be properly analyzed. The general non-isothermal equation for the fraction transformed is proven to be the sound and sole foundation for the correct deduction of the transformation kinetic parameters.

Keywords: Non-isothermal integral equation; Non-isothermal nucleation and growth phase transformation kinetics; Rule of additivity; Thermoanalytical techniques

1. Introduction

In Part I of this paper [1], attention has been brought to the apparent "confusion that has arisen during the years about the application of the Kissinger [2] (and Ozawa [3]) methods, or the Avrami formalism [4,5], to non-isothermal nucleation and growth transformation kinetics" [1]. There are two reasons for that confusion. (a) There is a frequent overruling of the limitations involved in the application of the isothermal Avrami rate equation to non-isothermal kinetics, as clearly stated by Henderson [5]. The essential limitation is that the use of the Avrami equation for non-isothermal kinetics must be restricted to the so-called 'site saturation' transformations solely. (b) As there is an explicit time t dependence of the temperature T in the growth function G, the differentiation of the integral on $G(T(t))$ is not straightforward. The often used relation $\mathrm{d}/\mathrm{d}t \int_0^t G(T(t))\mathrm{d}\tau = G(T(t))$ when differentiating the basic non-isothermal equation for the fraction transformed ζ,(T,t) namely: $\xi(T,t) = 1 - \exp[-gN_0 \left\{\int_0^t G(T(\tau))\mathrm{d}\tau\right\}^n]$ is incorrect [1].The general theory of transformation kinetics is largely confined to isothermal reactions. Several attempts have been made to apply that theory to non-isothermal transformation as well. However, as explicitly mentioned in a classical text by Christian [6]: "the difficulties in treating non-

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isothermal reactions are mainly due to the independent variations of growth and nucleation rate with temperature.... The problem is tractable only when the instantaneous transformation rate can be shown to be a function solely of the amount of transformation and the temperature.'' This leads to the concept of additivity, or the one of a *true kinetic equation*, discussed in Section 2 below.

It is the purpose of this paper to complete the reassessment [1] of the applicability of the commonly used thermal analysis methods to non-isothermal nucleation and growth transformation kinetics.

2. Theoretical

Two distinctive approaches have been used during the years for the formulation of non-isothermal transformation kinetics. In this paper, as in Part I, the discussion is restricted to nucleation and growth transformations.

2.1. The integral equation formulation

The general non-isothermal transformation kinetic equation for the *fraction* transformed is:

$$\xi(T,t) = 1 - \exp\left[-g\int_0^t I(T(t'))\times\left\{\int_{t'}^{t} G(T(\tau))\mathrm{d}\tau\right\}^n \mathrm{d}t'\right] \tag{1}$$

$I(T(t))$ and $G(T(t))$ are the nucleation and the growth rates, T the temperature and g a geometrical factor that depends on the dimensionality of growth [4,7,8]. For an interface-controlled growth n is an integer; for a diffusion-controlled growth n takes either integer or half-integer values [6]. In the so-called 'site saturation' [9] case, when heterogeneous nucleation takes place at randomly distributed pre-existing nucleation sites N_0, the nucleation rate being therefore zero, Eq. (1) is reduced to:

$$\xi(T,t) = 1 - \exp\left[-gN_0\left\{\int_0^t G(T(\tau))\mathrm{d}\tau\right\}^n\right] \tag{2}$$

The growth function is generally assumed to be of Arrhenius type, e.g. to exhibit an exponential dependence on temperature. If the heating rate β in thermal analyses is maintained constant, the growth function integral can therefore be written as:

$$\int_0^t G(T(\tau))\mathrm{d}\tau = G_0\int_0^t \exp\left[-\frac{E_\mathrm{g}}{RT(\tau)}\right]\mathrm{d}\tau = G_0\int_{T_0}^{T}\exp\left[-\frac{E_\mathrm{g}}{RT}\right]\frac{\mathrm{d}T}{\beta} \tag{3}$$

where T_0 is the temperature at time t=0, G_0 the pre-exponential factor of the growth function and E_g the activation energy for growth solely.

Eq. (3) implies that an exponential integral has to be evaluated when solutions to Eq. (1) are sought. The commonly used approximations to the exponential integral are those proposed by either Doyle [10]:

$$\int_{T_0}^{T}\exp\left[-\frac{E_\mathrm{g}}{RT}\right]\mathrm{d}T = 10^{-2.315}\ln 10\frac{E_\mathrm{g}}{R}\exp\times\left[-1.052\frac{E_\mathrm{g}}{RT}\right] \equiv C\frac{E_\mathrm{g}}{R}\exp\left[-1.052\frac{E_\mathrm{g}}{RT}\right] \tag{4}$$

or by Murray and White (MW) [11]:

$$\int_{T_0}^{T}\exp\left[-\frac{E_\mathrm{g}}{RT}\right]\mathrm{d}T = \frac{R^3T^2}{E_\mathrm{g}^3}\exp\left[-\frac{E_\mathrm{g}}{RT}\right] \tag{5}$$

Both Doyle and MW approximations may be introduced either directly into the general basic Eq. (2) or after having taken its first derivative with time. For reasons explained in section B below, many authors consider the transformation *rate*, rather than the transformed *fraction*, to be the basic variable. It is therefore of interest to examine (in sub-section A.b below) what happens if either the Doyle or the MW approximations are introduced after having taken the time derivative of Eq. (2).

Case A.a, direct insertion into Eq. (2):

(A.a.1) If introduced directly into Eq. (2), the Doyle approximation leads to the *Ozawa* relationship [3], as has been shown in Part I of this paper [1]:

$$\ln\beta + C' = -1.052\frac{E_\mathrm{g}}{RT_\mathrm{m}} \tag{6}$$

This result has been obtained by assuming in the calculations that 1.052 $nE_g/RT_m \gg 2$. (T_m is the temperature at which a peak is observed when heating rate β is practised in a thermal analysis experiment).

(A.a.2) If the MW approximation is introduced directly into Eq. (2), one obtains the following relationship between the heating rates and the peak temperatures. (See mathematical details in the Appendix A):

$$-\frac{E_g}{RT_m} = \ln\frac{\beta}{T_m^2} + C \qquad (7)$$

which is identical to the one proposed by *Kissinger* [2]. This result is obtained by assuming in the calculations that the entities: $E_g\beta/T_m$, $E_g\beta/RT_m$, nE_g/T_m and $2nE_g/RT_m$ are all $\gg 2$.

Case A.b, insertion of the approximations into Eq. (8), the first time derivative of Eq. (2), gives the following rate equation:

$$\frac{d\xi(T(\tau))}{dt} = -\exp\left[-gN_0\left\{\int_0^t G(T(\tau))d\tau\right\}^n \times\left(-ngN_0\left\{\int_0^t G(T(\tau))d\tau\right\}^{n-1}\right)\right] \times\left[\int_0^t \frac{dG(T(\tau))}{dt}d\tau + G(T(t))\right] \qquad (8)$$

Eq. (8) contains a term which cannot be evaluated straightforwardly, namely:

$$\left[\int_0^t \frac{dG(T(\tau))}{dt}d\tau + G(T(t))\right] \qquad (9)$$

Due to that difficulty, or eventually to other reasons, many authors simply substitute $G(T(t))$ to the term (9), probably assuming (misleadingly) that $d/dt \int_0^t G(T(t))\, d\tau = G(T(t))$. Eq. (8) then erroneously reads:

$$\frac{d\xi(T(\tau))}{dt} = -\exp\left[-gN_0\left\{\int_0^t G(T(\tau))d\tau\right\}^n \times\left(-ngN_0\left\{\int_0^t G(T(\tau))d\tau\right\}^{n-1}\right)\right] G(T(t)) \qquad (10)$$

(A.b.1) Nevertheless, if introduced directly into Eq. (10), the MW approximation surprisingly leads, without need for any numerical assumption, to the correct *Kissinger* relationship [2], despite the fact that Eq. (10) is erroneous.

(A.b.2) However, if the Doyle approximation is introduced directly into Eq. (10), one obtains the following relationship between the heating rates and the peak temperatures, without any additional numerical assumption either:

$$\ln\beta + C' = -1.052\frac{nE_g}{RT_m} \qquad (11)$$

which *differs from the Ozawa* relationship, Eq. (6). The fact that Eq. (11) is not identical to Eq. (6) might be due to the use of the incorrect Eq. (10).

2.2. The true kinetic equation formalism

The condition for additivity implies that the kinetic equation applied to non-isothermal transformations should be isokinetic (in the Avrami sense [4]), or expressed by a true kinetic equation, as discussed by Cahn [9] and mentioned by Graydon [12]. A reaction that involves two distinctive time–temperature parameters, such as in nucleation associated with growth reactions, will however not necessarily be additive. Moreover, the formal theory of transformations itself is not generally isokinetic. But, if the nucleation sites saturate early in the transformation, or the nucleation rate is zero (‘site saturation’), and if the growth rate is a function of the instantaneous temperature only, the reaction will be additive indeed [9]. That condition can be expressed by Eq. (12) below, that shows that the instantaneous transformation rate is expressed at a product of two functions, one of temperature, the other of fraction transformed:

$$\frac{d\xi(T,t)}{dt} = K(T)f[\xi(T,t)] \qquad (12)$$

There is another restriction implied by the requirement of additivity. As stated by Christian [6], the kinetics of a transformation in which the nucleation sites saturate can be describe by an Eq. (12) type, only if the number of initial nuclei N_0 is not only constant, but also independent of the temperature. This is an additional restriction for the application of non-isothermal kinetics.

When dealing with the general transformation *rate* Eq. (12) in non-isothermal kinetics, one has to choose the expressions for the right-hand side terms. There are different ways to do that, as detailed in the following sub-sections.

(B.a.) Several authors have started kinetic treatments by using Eq. (12) as an initial stage (Ref. [12], as an example). It is then assumed that the function $f[\xi(T,t)]$ is independent of the thermal history and that the temperature dependence of the rate of transformation is exponential. The Doyle approximation then leads to the *Ozawa* relationship, Eq. (6), while the MW approximation results in the *Kissinger* relationship, Eq. (7).

(B.b.) In Ref. [12], the second condition mentioned is the one that requires the rate of transformation temperature dependence to be exponential. This is indeed the case when the transformation rate is deduced from the isothermal Avrami kinetic equation [13]:

$$\xi(T,t) = 1 - \exp[-K(T)t^n] \tag{13}$$

$K(T)$ is defined as an effective overall reaction rate. As shown by Avrami [4] and Cahn [9], Eq. (13) is isokinetic, e.g. fulfills the additivity condition. It should be stressed again and again that, in non-isothermal conditions, Eq. (13) is valid only for 'site saturation' transformations [5].

The time derivative of Eq. (13) reads:

$$\begin{aligned}\frac{\mathrm{d}\xi(T,t)}{\mathrm{d}t} &= nK(T)^{1/n}[1-\xi(T,t)] \\ &\quad\times\left\{\ln\left[\frac{1}{1-\xi(T,t)}\right]\right\}^{n-1/n} \\ &\equiv K(T)f[\xi(T,t)] \end{aligned} \tag{14}$$

Eq. (14) is sometimes referred to as the Johnson–Mehl–Avrami (JMA) transformation *rate* equation [5]. In that case, there is no exponential integral to be approximated. $K(T)$ is legitimately interpreted as a function of an overall activation energy E_a for the considered reaction. This has also been the case for the equation chosen by Kissinger, though he dealt with solid⇒solid+gas reactions [14]. It should be however stressed that the overall activation energy for any considered transformation is not identical to the energy for growth of the new phase. If there is no nucleation, and the transformation is activated solely by growth of a new phase, i.e. through a moving interface or a diffusion mechanism, then, and only then are both the energies E_g and E_a equivalent, as there are no separate nucleation E_n and growth E_g energies to be considered. The general activation energy E_a for a nucleation and growth transformation is a contribution of both E_n and E_g.

The temperature dependence of the rate of transformation $K(T)$ is expressed by an exponential, Arrhenius-type relationship [15]:

$$K(T) = K_0\exp\left[-\frac{E_g}{RT}\right] \tag{15}$$

It can be shown [17] that $K(T)$ is proportional to $I(T)^{1/n+1}G(T)^{1/n}$. Hence, assuming an Arrhenian temperature dependence of $K(T)$ implies therefore that both $I(T)$ and $G(T)$ also vary in an Arrhenian manner with temperature [16]. Such a dependence is not always the case: in many cases, the temperature dependence of the nucleation frequency is far from Arrhenian [6]. When a broad range of temperature is considered, the temperature dependence of the crystal growth is not Arrhenian either [16]. As already mentioned by De Bruijn et al. [19], using the derivative of Eq. (13), after insertion of Eq. (14), for analyzing non-isothermal experiments, is incorrect. Such a procedure, however, results in the correct kinetic parameters if, and only if, reactions with growth of a constant number of nuclei are considered, i.e. in the 'site saturation' case.

Many authors have used this approach for the interpretation of thermal analysis experiments. Henderson [5] has obtained an Eq. (12) – like relationship, by defining a *rate* equation based upon the isothermal Avrami kinetic Eq. (13):

$$\begin{aligned}\frac{\mathrm{d}\xi(T)}{\mathrm{d}t} &= nK(T)^{1/n}(1-\xi(T)) \\ &\quad\times\{\ln(1-\xi(T))^{-1}\}^{n-1/n}\end{aligned} \tag{16}$$

and then derived a *modified Kissinger* relationship for the dependence of the peak temperatures in thermal analysis experiments on the heating rates:

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E_g}{nRT_m} + C \tag{17}$$

The slope of a plot of $\ln(\beta/T_m^2)$ versus $1/T_m$ yield the value of E_g/n. An additional equation will be needed for the separate evaluation of n and E_g [17].

Matusita et al. [18] have studied the kinetics of non-isothermal crystallization processes. They tackle the issue by deriving a relation between the radius r of the forming crystallites and the temperature and obtain the following *rate* equation (with the Doyle approximation for the exponential integral):

$$\frac{\mathrm{d}\xi(T)}{\mathrm{d}t} = C\frac{(1-\xi(T))}{\beta^{(n-1)}}\exp\left[-\frac{1.052mE_g}{RT}\right] \quad (18)$$

derived from the more general expression:

$$-\ln(1-\xi(T)) = \frac{gN_0}{\beta^n}\exp\left[-\frac{1.053mE_g}{RT}\right] \quad (19)$$

where $n{=}m{+}1$ for a quenched glass containing no nuclei and $n{=}m$ for the site saturation case, i.e. a glass containing a sufficiently large number of nuclei ($m{=}3$, 2 or 1 for three-, two- or one-dimensional growth, respectively). The *Matushita* et al. relationship between the peak temperatures in thermal analysis experiments and the heating rates is then derived (using the Doyle approximation for the exponential integral):

$$n\left(\frac{\beta^n}{T_m^2}\right) = -1.052m\frac{E_g}{RT_m} + C' \quad (20)$$

A critical review of additional applications of thermoanalytical techniques to the study of crystallization in glass-forming liquids, by Piloyan and Borchart, Coats, Redfern and Sestak, Takhor, Augis and Bennet, is given in Ref. [16].

(B.c.) The starting *rate* equation can be the derivative of Eq. (2) into which either the Doyle or the MW approximations have been introduced prior to derivation. Let us examine both cases.

(B.c.1.) If the MW approximation is used, Eq. (2) transforms to:

$$\begin{aligned}\xi(T) &= 1-\exp\left[-\frac{gN_0G_0^n}{\beta^n}\right]\left\{\int_{T_0}^{T}\exp\left[-\frac{E_g}{RT}\right]\mathrm{d}T\right\}^n\\ &= 1-\exp\left[-\frac{gN_0G_0^nR^{3n}T^{2n}}{\beta^nE_g^{3n}}\exp\left[-\frac{nE_g}{RT}\right]\right]\end{aligned} \quad (21)$$

N_0 is taken here as temperature independent. The rate equation is then:

$$\begin{aligned}\frac{\mathrm{d}\xi(T(t))}{\mathrm{d}t} &= (1-\xi(T(t)))C\exp\left[-\frac{nE_g}{Rt}\right]\\ &\quad\times\left(2+\frac{E_g}{RT}\right)\frac{T^{2n-1}}{\beta^{n-1}}\end{aligned} \quad (22)$$

where $C = gnN_0G_0^nR^{3n}/E_g^{3n}$

(B.c.2.) If the Doyle approximation is used, Eq. (2) transforms to:

$$\begin{aligned}\xi(T) &= 1-\exp\left[-\frac{gN_0G_0^nE_g^n10^{-2.315n}(\ln 10)^n}{\beta^nR^n}\right.\\ &\quad\left.\times\exp\left[-\frac{nE_g}{RT}\right]\right]\end{aligned} \quad (23)$$

The rate equation is then:

$$\begin{aligned}\frac{\mathrm{d}\xi(T(t))}{\mathrm{d}t} &= (1-\xi(T(t)))\frac{C'}{\beta^{n-1}}\\ &\quad\times\exp\left[-1.052\frac{nE_g}{RT}\right]\frac{1}{T^2}\end{aligned} \quad (24)$$

where $C' = gnN_0G_0^nE_g^{n+1}/R^{n+1}1.052(10^{-2.315}\ln 10)^n$.

Eqs. (22) and (24) afford evidence that the basic non-isothermal kinetic Eq. (2) fulfills the additivity requirement. These are true kinetic equations, in the sense that the temperature dependence is separable from the fraction transformed function, though that dependence is now not purely exponential. That restriction seems therefore not to be necessary for the correct treatment of non-isothermal transformation kinetics.

3. Discussion

3.1. Derivation of the kinetic parameters

The interpretation of all experimental thermal analysis methods is based on the formal non-isothermal transformation kinetics formalisms as derived in Section 2. The common thrust is to manipulate the various equations, in order to extract two parameters (heating rate β versus peak temperature T_m) which, when plotted against each other, enable the evaluation of the activation energy E_a and the reaction order n. This is how the above derived Kissinger, modified Kissinger, Ozawa, modified Ozawa and Matusita et al. relationships have been used in the literature.

In the Matusita et al. approach, the n-value and the activation energy E_g can be obtained from the plot of $\ln[-\ln(1-x)]$ against $\ln\beta$ at a specific temperature, after solving Eq. (19).

An analogue approach is taken when the non-isothermal integral Eq. (2) serves as the expression of the correct, unrestricted kinetic starting equation. Eq. (21) can easily be transformed to (MW approximation):

$$\ln[\ln(1-\xi(T))] = \ln(-C') - n\left(\ln\beta + 1.052\frac{E_g}{RT_m}\right) \tag{25}$$

where $C' = gN_0G_0^nE_g^{n+1}/R^{n+1}1.052(10^{-2.315}\ln 10)^n$

In the same way, Eq. (23) is equivalent to (Doyle approximation):

$$\ln[\ln(1-\xi(T))] = \ln(-C) + n\left(\ln\frac{T_m^2}{\beta} - \frac{E_g}{RT_m}\right) \tag{26}$$

where $C = gN_0G_0^nR^{3n}/E_g^{3n}$

Extraction of the activation energy for growth and the reaction order is made by using a double set of equations: either the Ozawa relationship with Eq. (26), or the Kissinger relationship with Eq. (25).

It is important to note that Eqs. (25) and (26) are based on straight non-isothermal kinetic foundations, without any additional physical or mathematical assumptions, except the Doyle or MW approximations to the exponential integral. The questions what differences in n and E_g values are obtained with each of the methods described above, and which are the ones that correctly represents the true physical situation, still remain open. The fact that many authors report values for the order parameter n which are not in agreement with the nature of the transformation (values not being integers or half integers, as required by the theory) may hint to the fact that those reports have overruled the restrictions mentioned in this paper. The studied transformation though must be single-phased without secondary crystallization, must not proceed with activation of mixed nucleation modes and exclude any geometrical anisotropy in crystal growth.

Some papers reported changing values of the Avrami exponent n during ongoing crystallization of metallic glasses [20] analyzed by DSC. This finding is attributed to ''changing populations of pre-existing nuclei''. This seems clearly to be a violation of the requirements for applying any isothermal kinetics formalism, such as the Avrami equation, to non-isothermal transformations.

3.2. Summary of restrictions to the application of thermoanalytic techniques to non-isothermal nucleation and growth transformation kinetics

The main requirement for applying non-isothermal formalism to the study of the kinetics of nucleation and growth transformations is to consider only the 'site saturation'; case, i.e. to deal only with a reaction that exhibits a zero nucleation rate. Even then, the number of pre-existing nuclei has to be temperature independent. These two restrictions ensure fulfilling the additivity condition, and consecutively provide a true kinetic equation for the transformation rate.

Additional physical restrictions exclude any secondary crystallization mechanism, and complete geometrical isotropy of the new phase growth.

The integral equation formalism appears to be the only one that satisfies the previous restrictions, and therefore enables the correct evaluation of the activation energy for growth E_g and the reaction order n. Use of the integral equation formalism does not infer mathematical assumptions, except the Doyle or MW approximations to the exponential integral.

Though the rate Eq. (10) derived from the general integral equation is mathematically incorrect, it is often used for the interpretation of thermoanalytical experiments. It makes use of various numerical approximations, without knowing a priori if these approximations comply with the true physical nature of the investigated transformation. Surprisingly though, this procedure leads to the Kissinger relationship between the peak temperatures in thermal analysis experiments and the heating rates (when the MW approximation is used for the exponential integral). It is however unclear if the Kissinger [2] or the modified Kissinger proposed by Henderson [5] is the correct one to be used for the extraction of the kinetic parameters. Experiments have been undertaken in order to elucidate this point [21].

4. Conclusions

There is a widespread use of thermoanalytical methods for the study of nucleation and growth transformation kinetics. Several relationships between peak temperatures in thermal analysis experiments and heating rates have been described in the text, all aimed to extract the values of the activation energy and the order of the transformation. The detailed physical and mathematical treatment presented in both parts of this paper leads to the conclusion that application of isothermal kinetics models to non-isothermal transformations may lead to errors and confusion, often involving incorrect mathematical derivations and unproved numerical approximations.

The straightforward treatment that starts with the general non-isothermal integral equation for the fraction transformed leads to either the Kissinger (when the exponential integral is approximated by the Murray–White method) or the Ozawa relationships Kissinger (when the exponential integral is approximated by the Doyle method), with no need to 'modify' them, as proposed by several authors. The general non-isothermal integral equation is shown to fulfill the condition of additivity, it has the form of a true kinetic equation. It is also shown that the temperature dependence within the rate equation needs not to be exclusively exponential.

In any case, the main conclusion for applying non-isothermal kinetics models to nucleation and growth transformations is that only transformations with zero nucleation rate, i.e. the 'site saturated' transformations, should be dealt with. The kinetic parameters of such transformations can then be extracted analytically from the general non-isothermal integral equation. The application of isothermal kinetic models (like the Avrami equation, or the JMA rate equation) to non-isothermal nucleation and growth transformations is valid if, and only if attentive care is taken for the full observance of the necessary physical and mathematical restrictions and limitations involved with that method.

Appendix A: Mathematical derivations

(A.a.2)

The MW approximation introduced directly in Eq. (2)

$$\begin{aligned}\xi(t) &= 1-\exp\left[-\frac{gN_0G_0^n}{\beta^n}\right]\left\{\int\limits_{T_0}^{T}\exp\left[-\frac{E_\mathrm{g}}{RT}\right]\mathrm{d}T\right\}^n\\ &= 1-\exp\left[-\frac{gN_0G_0^nR^{3n}T^{2n}}{\beta^nE_\mathrm{g}^{3n}}\exp\left[-\frac{nE_\mathrm{g}}{RT}\right]\right] \qquad \text{(A.1)}\end{aligned}$$

Taking the first time derivative:

$$\begin{aligned}\frac{\mathrm{d}\xi(T)}{dt} &= \frac{gN_0G_0^nR^{3n}}{\beta^nE_\mathrm{g}^{3n}}T^{2n}\left\{\frac{2n}{T}\exp\left[-\frac{nE_\mathrm{g}}{RT}\right]\right.\\ &\quad\left.+\frac{nE_\mathrm{g}\beta}{RT^2}\exp\left[\frac{nE_\mathrm{g}}{RT}\right]\right\}\exp\left[-\frac{gN_0G_0^nR^{3n}}{\beta^nE_\mathrm{g}^{3n}}T^{2n}\right.\\ &\quad\left.\times\exp\left[-\frac{nE_\mathrm{g}}{RT}\right]\right] \qquad \text{(A.2)}\end{aligned}$$

Taking the second time derivative and equating to zero for $T{=}T_\mathrm{m}$:

$$\begin{aligned}&\frac{ngN_0G_0^nR^{3n}}{\beta^nE_\mathrm{g}^{3n}}T_\mathrm{m}^{2n-2}\exp\left[-\frac{nE_\mathrm{g}}{RT}\right]\left(2-\frac{E_\mathrm{g}\beta}{RT_\mathrm{m}}\right)\\ &\times\left(2+\frac{E_\mathrm{g}\beta}{RT_\mathrm{m}}\right)=\frac{\beta}{T_\mathrm{m}^2}\left(\frac{2nE_\mathrm{g}}{RT_\mathrm{m}}-2+\frac{E_\mathrm{g}\beta}{RT_\mathrm{m}}\right.\\ &\left.\times\left(\frac{nE_\mathrm{g}}{T_\mathrm{m}}-2\right)\right) \qquad \text{(A.3)}\end{aligned}$$

Making now the following approximations:

$$\frac{E_\mathrm{g}\beta}{RT_\mathrm{m}}\gg 2 \quad \frac{nE_\mathrm{g}}{T_\mathrm{m}}\gg 2 \quad \frac{2nE_\mathrm{g}}{RT_\mathrm{m}}\gg 2 \quad \frac{E_\mathrm{g}\beta}{T_\mathrm{m}}\gg 2$$

leads to the final Kissinger relationship:

$$-\frac{E_\mathrm{g}}{RT_\mathrm{m}}=\ln\frac{\beta}{T_\mathrm{m}^2}+\ln C \qquad \text{(A.5)}$$

where C is:

$$\left(\frac{ngN_0G_0^nR^{3n}}{E_\mathrm{g}^{3n}}\right)^{-1}. \qquad \text{(A.6)}$$

(A.b.1)

The Doyle approximation is introduced into (the erroneous) transformation rate Eq. (10)

$$\begin{aligned}\frac{\mathrm{d}\xi(T(\tau))}{\mathrm{d}t} &= -\exp\left[-gN_0\left\{\int\limits_0^t G(T(\tau))d\tau\right\}^n\right.\\ &\quad\left.\times\left(-ngN_0\left\{\int\limits_0^t G(T(\tau))\mathrm{d}\tau\right\}^{n-1}\right)\right]G(T(t)).\end{aligned}$$

The growth function is assumed to be of the Arrhenius type, and then:

$$\int_{0}^{t} G(T(\tau))\mathrm{d}\tau = G_0 \int_{T_0}^{T} \exp\left[-\frac{E_\mathrm{g}}{RT}\right]\frac{\mathrm{d}T}{\beta} \qquad \text{(A7)}$$

where T_0 is the temperature at time t=0.

The first time derivative then reads, after some algebraic manipulations:

$$\frac{\mathrm{d}\xi(T)}{\mathrm{d}t} = \frac{C_2}{\beta^{n-1}}\exp\left[-\frac{C_1}{\beta^n}\exp\left[-1.052\frac{nE_\mathrm{g}}{RT}\right]\right] \times \exp\left[\frac{(-1.052n+0.052)E_\mathrm{g}}{RT}\right] \qquad \text{(A8)}$$

where $C_1 = gN_0G_0^nE_\mathrm{g}^n(10^{2.315}\ln 10)^n/R^n$ and $C_2 = gN_0G_0^nE_\mathrm{g}^{n-1}(10^{2.315}\ln 10)^{n-1}/R^{n-1}$

Taking the second time derivative and equating to zero for T=T_m:

$$-C_1\exp\left[-1.052\frac{nE_\mathrm{g}}{RT_\mathrm{m}}\right]1.052 = C_2\beta(-1.052n+0.052) \qquad \text{(A9)}$$

which finally gives:

$$-1.052\frac{nE_\mathrm{g}}{RT_\mathrm{m}} = \ln\left[\frac{nR}{E_\mathrm{g}}\beta\left(\frac{0.052-1.052n}{1.052(10^{2.315}\ln 10)}\right)\right] = \ln n\beta + C \qquad \text{(A10)}$$

Eq. (A10) is only *similar* to the Ozawa relationship, Eq. (6).

(A.b.2)

The MW approximation is introduced into (the erroneous) transformation rate Eq. (10), the growth function is again assumed to be of the Arrhenius type.

The first time derivative reads:

$$\frac{\mathrm{d}\xi(T)}{\mathrm{d}t} = \frac{C_2}{\beta^{n-1}}\exp\left[-\frac{C_1}{\beta^n}\exp\left[-\frac{nE_\mathrm{g}}{RT}\right]\right]\exp\left[-\frac{nE_\mathrm{g}}{RT}\right] \qquad \text{(A11)}$$

where C_1 and C_2 have the same meaning as in Section A.b.1.

Taking the second time derivative and equating to zero for T=T_m:

$$\exp\left[-\frac{nE_\mathrm{g}}{RT_\mathrm{m}}\right] = \frac{\beta^n}{T_\mathrm{m}^{2n}}\left(\frac{E_\mathrm{g}^{3n}}{gN_0G_0^nR^{3n}}\right) \qquad \text{(A12)}$$

which is exactly the Kissinger relationship (7):

$$-\frac{E_\mathrm{g}}{RT_\mathrm{m}} = \ln\frac{\beta}{T_\mathrm{m}^2} + C'$$

where $C' = E_\mathrm{g}^{3n}/gN_0G_0^nR^{3n}$

Appendix B:

The heating rate versus peak temperature relationships

B.1 Ozawa: (Eq. (6))

$$\ln\beta + C' = -1.052\frac{E_\mathrm{g}}{RT_\mathrm{m}} \qquad \text{(A13)}$$

limitations: 1.052 $nE_\mathrm{g}/RT_\mathrm{m} \gg 2$

B.2 Kissinger (Eq. (7))

$$-\frac{E_\mathrm{g}}{RT_\mathrm{m}} = \ln\frac{\beta}{T_\mathrm{m}^2} + C \qquad \text{(A14)}$$

limitations: $E_\mathrm{g}\beta/T_\mathrm{m}$, $E_\mathrm{g}\beta/RT_\mathrm{m}$, $nE_\mathrm{g}/T_\mathrm{m}$ and $2nE_\mathrm{g}/RT_\mathrm{m}$ are all $\gg 2$

B.3 Modified Ozawa (Eq. (11))

$$\ln\beta + C' = -1.052\frac{nE_\mathrm{g}}{RT_\mathrm{m}} \qquad \text{(A15)}$$

B.3 Modified Kissinger: (Eq. (17))

$$\ln\left(\frac{\beta}{T_\mathrm{m}^2}\right) = -\frac{E_\mathrm{a}}{nRT_\mathrm{m}} + C \qquad \text{(A16)}$$

B.5 Matusita (Eq. (20))

$$n\left(\frac{\beta^n}{T_\mathrm{m}^2}\right) = -1.052m\frac{E_\mathrm{g}}{RT_\mathrm{m}} + C' \qquad \text{(A17)}$$

where n+m+1

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[13] The Avrami rate equation may also be written as:

$$\xi(T,t) = 1 - \exp[-(K(T)t)^n] \tag{a}$$

instead of

$$\xi(T,t) = 1 - \exp[-K(T)t^n] \tag{b}$$

Mention should always be made which equation is used, and care should be taken for the interpretation of the thermal analysis experiments and the extraction of kinetic parameters.

[14] The equation proposed by Kissinger [2] is:

$$\frac{\mathrm{d}\xi(T)}{\mathrm{d}t} = A(1-\xi(T))^n \exp\left[-\frac{E_g}{RT}\right] \tag{c}$$

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[17] When equation (b) in Reference [13] is used, instead of equation (a), the overall (nucleation plus growth) activation energy E_a for nucleation and growth transformations is expressed by:

$$E_a = \frac{E_n + nE_g}{n+1} \tag{d}$$

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