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COMPARISON OF CRYSTALLIZATION KINETICS DETERMINED BY ISOTHERMAL AND NON-ISOTHERMAL METHODS

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ABSTRACT

Theoretical results for nucleation and growth controlled transformations indicate that a non-isothermal generalization is only possible along the lines of the isokinetic hypothesis, i.e., the invariance of the rate equation under any thermal conditions. The alternative formalism, i.e., the general use of the isothermal law and the corresponding modification of the rate equation under non-isothermal conditions, is found to be incorrect. Different methods for the evaluation of kinetic parameters are compared, taking into account even thermal lag corrections.

It is illustrated by experimental results for oxide, chalcogenide and metallic glasses that all of the non-isothermal methods that yield kinetic parameters in good agreement with the appropriate isothermal results are easily derived from the usual rate equation.

INTRODUCTION

The crystallization of different glassy materials has been extensively investigated by various non-isothermal methods. It is evident that the kinetics of crystallization are important from the points of view of both fundamental and applied research. The theory and practice of this evaluation, however, are far from being universally accepted.

The general question of whether the usual rate equation is applicable to non-isothermal studies [1–5] is also relevant for crystallization. Apparently unrelated to this problem, many researchers [6–10] freely applied the equations derived for the isothermal case by Johnson and Mehl, Avrami, Kolmogorov and Yerofeev to non-isothermal conditions. When the time derivative of these JMAKY kinetics were calculated, new methods were suggested [11–13] for the calculation of kinetic parameters that are significantly different from those generally applied. Despite a detailed criticism of

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these attempts [14–32], the exact mathematical equivalence of the modified rate equation and the use of isothermal laws under non-isothermal conditions were not generally recognized [33,34].

In this paper, some results on the theory of nucleation and growth controlled transformation are reviewed to show that a non-isothermal generalization is only possible along the lines recommended by the isokinetic hypothesis, i.e., the invariance of the rate equation. If this treatment is to be believed, however, it must be shown that those evaluation methods which claim good experimental verification are consistent with this framework even if originally suggested on the basis of now obsolete theories.

THEORY OF NUCLEATION-GROWTH KINETICS UNDER GENERAL THERMAL CONDITIONS

Crystallization is a special case of the nucleation and grain growth controlled solid-state transformation processes, the theory of which is well known [35–38]. If an embryo of the transformed phase nucleates at moment τ and grows thereafter isotropically in three dimensions with a linear momentary growth rate $Y(t')$ in moment t', then its volume v at moment t (where $\tau < t' < t$) is

$$v(\tau, t) = \frac{4\pi}{3}\left[\int_\tau^t Y(t')\mathrm{d}t'\right]^3 \tag{1}$$

When the possible overlap of the grains is neglected, the so-called extended volume V_{ext} is calculated:

$$V_{\text{ext}} = V\left[N_0 v(0, t) + \int_0^t I(\tau) v(\tau, t)\mathrm{d}\tau\right] \tag{2}$$

where N_0 is the initial number of nuclei and $I = I(\tau)$ is the nucleation rate per unit volume. As the change of the real transformed volume, $\mathrm{d}V_t$, and that of the extended volume, $\mathrm{d}V_{\text{ext}}$, is related by

$$\mathrm{d}V_t = \left(1 - \frac{V_t}{V}\right)\mathrm{d}V_{\text{ext}} \tag{3}$$

the basic nucleation-growth equation for the transformed fraction $\alpha = V_t/V$ is

$$-\ln(1-\alpha) = \frac{4\pi}{3}\left\{N_0\left[\int_0^t Y(t')\mathrm{d}t'\right]^3 + \int_0^t I(\tau)\left[\int_\tau^t Y(t')\mathrm{d}t'\right]^3 \mathrm{d}\tau\right\} \tag{4}$$

This equation is evidently valid under any thermal conditions. Up to this point no assumptions have been made regarding the origin of the time dependence of I and Y, so it could easily include also the implicit time dependences $Y[T(t')]$ and $I[T(\tau)]$. An important limitation of this equation, however, stems from the use of eqn. (3), which describes a completely random overlap of growing crystallites. Surface crystallization is a clear case where this assumption must not be valid. Owing to the possible absence of overlap, this case is also easily treated even under general thermal conditions.

For any shape where the volume is expressed as the product of a geometrical factor and the cube of a characteristic distance, the calculation easily yields

$$1-(1-\alpha)^{1/3}=\int_0^t k[T(t')]\mathrm{d}t' \tag{5}$$

which is a clear example of nth order chemical reaction kinetics. Having established that the classical methods of kinetic parameter evaluation are to be used in this instance, we might return to our central problem: evaluation of kinetic parameters based on eqn. (4).

The two terms in eqn. (4) determine the two limiting processes of major interest under isothermal conditions when $Y=\text{constant}$:

(a) the growth of frozen-in nuclei ($N_0 \neq 0$) without thermal nucleation ($I=0$):

$$[-\ln(1-\alpha)]^{1/3}=kt \tag{6}$$

(b) homogeneous thermal nucleation ($N_0=0$, $I=\text{constant} \neq 0$):

$$[-\ln(1-\alpha)]^{1/4}=kt \tag{7}$$

It is worth noting that in a number of instances, e.g., for the time-dependent transient nucleation where $I(\tau)=I_0\mathrm{e}^{-\tau/\tau_0}$ or for the diffusion-limited growth where the characteristic distance is proportional to $t^{1/2}$, a form analogous to eqns. (6) and (7):

$$[-\ln(1-\alpha)]^{1/n}=kt \tag{8}$$

holds as an acceptable approximation [39], where the exponent n gives an indication of the mode of transformation. This is the physical background of the wide applicability of the JMAKY equation under isothermal conditions.

The same treatment is also applicable to the non-isothermal case taking into account that now

$$Y(t')=Y_0\mathrm{e}^{-E_g/RT(t')} \tag{9}$$

The generalization of case (a) is very easy, yielding

$$[-\ln(1-\alpha)]^{1/3}=\int_0^t k[T(t')]\mathrm{d}t' \tag{10}$$

where

$$k(T)=Z_g\mathrm{e}^{-E_g/RT} \tag{11}$$

$$Z_g=Y_0(4\pi N_0/3)^{1/3} \tag{12}$$

For case (b) the calculation has already been carried out [40,41] by evaluating the double integral in eqn. (4) by the usual methods, where $T = T_0 + \beta t$

$$I(\tau) = Z_n e^{-E_n/RT(\tau)} \tag{13}$$

The result is

$$[-\ln(1-\alpha)]^{1/4} = \bar{Z}(Z_n, Z_g, E_n, E_g)\frac{\bar{E}}{\beta R}\left(\frac{RT}{\bar{E}}\right)^2 e^{-\bar{E}/RT} = \int_0^t \tilde{k}[T(t')]\mathrm{d}t' \tag{14}$$

where

$$\bar{E} = (E_n + 3E_g)/4 \tag{15}$$

$$\tilde{k} = \bar{Z}e^{-\bar{E}/RT(t)} \tag{16}$$

It should be clear from eqns. (10) and (14) that the non-isothermal equivalent of the widely used isothermal JMAKY relation [eqn. (8)] is

$$[-\ln(1-\alpha)]^{1/n} = \int_0^t k[T(t')]\mathrm{d}t' \tag{17}$$

as also shown by Henderson [42,43] and Meisel and Cote [44]. Some particular points following from the preceding analysis are worth noting:

(A) The time derivatives of eqns. (8) and (17) are the same, i.e., the rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = n\bar{Z}(1-\alpha)[-\ln(1-\alpha)]^{\frac{n-1}{n}} e^{-\bar{E}/RT} \tag{18}$$

bears the same form for both isothermal and dynamic cases.

(B) The isothermal transformed fraction can naturally be written either as

$$\alpha = 1 - e^{-(kt)^n} \tag{19a}$$

or as

$$\alpha = 1 - e^{-kt^n} \tag{19b}$$

as the two equations use only a different definition of the activation energy. If

$$k = k_0 e^{-E/RT} \tag{20a}$$

and

$$k_* = k_{0*} e^{-E_*/RT} \tag{20b}$$

then

$$E_* = nE \tag{21}$$

However, the frequently used [45,46] differential form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_* n(1-\alpha)t^{n-1} \tag{22}$$

is not valid [51,52], as

$$-\ln(1-\alpha) = \left\{\int_0^t k[T(t')]\mathrm{d}t'\right\}^n \neq \int_0^t k_*[T(t')]t'^{n-1}\mathrm{d}t' \tag{23}$$

This fact was originally observed by De Bruijn et al. [40] and was recently re-emphasized by Louis and Garcia-Cordovilla [47–49] and by Kasap and Yuhasz [108]. The correct form of eqn. (22) where the rate equation is formulated as a function of T and α only is expressed as [51,52]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = nk_*^{1/n}(1-\alpha)[-\ln(1-\alpha)]^{\frac{n-1}{n}} \tag{24}$$

Later we shall return to establish that this freedom in defining the activation energy does not influence the comparison of isothermally and non-isothermally determined kinetic parameters.

(C) It is evident from eqn. (17) that the isothermal form of the JMAKY relation [eqn. (8)] is *not* valid under non-isothermal conditions. The relationship derived [eqn. (17)] clearly shows that α depends on the whole $T(t)$ path. In this way the theory of nucleation and growth controlled transformation is completely incompatible with the existence of an $\alpha = \hat{\alpha}(t, T)$ function that would predict α if only the end-point (t, T) is specified, i.e., with the assumption that we shall call the alternative formalism.

The fact that the transformed fraction is a path function does not give any problems when α is determined for a properly defined thermal route. For example, with linear heating [50–52]

$$T = T_0 + \beta t$$

Equation (17) yields

$$g(\alpha) = [-\ln(1-\alpha)]^{1/n} = \frac{\bar{Z}\bar{E}}{\beta R}p(E/RT) \tag{25}$$

where $p(E/RT)$ denotes the exponential integral. Equation (25) is no doubt a functional relationship, i.e., for linear heating the $\alpha = \hat{\alpha}_{\mathrm{lh}}(\beta, T)$ function exists.

In this way the theory of nucleation and growth controlled transformations makes an unambiguous choice between the two methods of kinetic parameter evaluation. The usual method is based on the isokinetic hypothesis, i.e., on the invariance of the rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{26}$$

under any thermal conditions. The transformed fraction is

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha'}{f(\alpha')} = \int_0^t k[T(t')]\mathrm{d}t' \tag{27}$$

which yields $g(\alpha) = kt$ only under isothermal conditions. This hypothesis, even if not exactly valid [43] (causing here only a deviation of $\bar{Z}$ from its isothermally calculated value), is a reasonable approximation also in our case.

The alternative formalism is based on the existence of an $\alpha = \hat{\alpha}(T, t)$ function. A significant modification of the rate equation is calculated under non-isothermal conditions [1–5]. The preceding analysis therefore excludes the applicability of this formalism to nucleation and growth controlled transformations. The exact mathematical equivalence of the modified rate equation and the use of the isothermal law under non-isothermal conditions [6–10] will be shown in a separate paper [34].

EVALUATION OF KINETIC PARAMETERS FROM THERMOANALYTICAL EXPERIMENTS

The evaluation of linear heating experiments is based on eqn. (25), where two different approximations of the exponential integral, namely the Doyle approximation

$$l_{\text{Doyle}}(E/RT) = \ln p(E/RT) \approx -5.33 - 1.05\frac{E}{RT} \pm 3\% \tag{28}$$

and the asymptotic equation

$$p\left(\frac{E}{RT}\right) = \mathrm{e}^{-E/RT}\left(\frac{RT}{E}\right)^2\left[1 - \frac{2RT}{E} + o\left(\frac{RT}{E}\right)^2\right] \tag{29}$$

will be used. The first term in eqn. (29) means typically a few per cent accuracy of $p(E/RT)$. It should be understood, however, that the use of eqn. (28) for estimating $p(E/RT)$ itself is irrelevant, as the 3% error in the exponent has very serious consequences, as shown in Table 1.

This is why the form of the rate equation proposed by Matusita et al. [53]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K(1-\alpha)\beta^n \exp\left(-1.05\frac{E}{RT}m\right)$$

is considered to be too rough an approximation to be recommended. The actual evaluation methods proposed [53], however, utilize only $\ln(\mathrm{d}\alpha/\mathrm{d}t)$

TABLE 1

Effect of a 3% error in the Doyle equation for calculating $p(E/RT)$

$l_{\text{Doyle}}(E/RT) = -5.33 - 1.05(E/RT)$; with an error of ±3%, and $E/RT = 40$

	+3%	Equation	−3%
$\ln p(E/RT)$	−48.75	−47.33	−45.91
$p(E/RT)$	6.74×10^{-22}	2.79×10^{-21}	1.15×10^{-20}
p/p_{equation}	0.241	1	4.14

and ln g(α) and in this way are also easily derived in the correct formalism: when the logarithm of eqn. (25) is connected with eqn. (28), then

$$\ln[-\ln(1-\alpha)] \approx n \ln \frac{Z}{\beta} - 1.05\frac{nE}{RT} + C \tag{30}$$

results. If the logarithm of eqn. (18) is combined with either eqn. (28) or (29), then the result is [54]

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \ln \frac{Z^n}{\beta^{n-1}} - \frac{nE}{RT} + \sigma\left(1-\alpha, \ln \frac{T}{T_0}\right) \tag{31}$$

It is evident that these plots might reveal only nE. If n and E are to be determined separately from a single thermogram, then the three-term version of eqn. (29) is applied to yield

$$\ln\left[\frac{-\ln(1-\alpha)^{1/n}}{T^2}\right] = \ln\left[\frac{ZR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{32}$$

The separate determination of n and E in this way requires a very high precision if the variation of terms whose order of magnitude is ln T (found to be almost negligible with the usual precision) is to be significantly established in addition to terms of the order of $1/T$.

As the typical variations are $\partial(1/T)/1/T = \partial T/T \approx 10\%$ and $\partial \ln T/\ln T \lesssim 2\%$, and the precision of α itself can hardly surpass 2%, the fulfillment of this requirement is far from trivial. This is why multi-thermogram methods, usually based on temperature shifts caused by a variation of the heating rate, β, play a dominant role. It is a basic advantage of these methods that the determination of activation energy (as it is defined here) is independent of the transformation mechanism [50,55–59]. The connection of eqn. (25) with eqn. (28) for any g(α) and for any α_0 fixed transformed fraction yields

$$\ln \frac{\beta}{Z} = C_1 - 1.05\frac{E}{RT_{\alpha_0}} \tag{33}$$

while the use of eqn. (29) results in

$$\ln \frac{\beta}{ZT_{\alpha_0}^2} = C_2 - \frac{E}{R}\frac{1}{T_{\alpha_0}} \tag{34}$$

where C_1 and C_2 are independent of β and T_{α_0}, which denotes the temperature where the transformed fraction is α_0. If Z = constant it is incorporated in the C coefficient and then these equations are the Ozawa and the Kissinger plots, respectively, which are seen here to be only different approximations of $p(E/RT)$ and are thus equivalent [60]. It is also easily verified that the transformed fraction at the maximum transformation rate, α_m, is independent of β and is thus useful for the determination of activation energy without integrating the thermoanalytical curve. The usual criticism that the thermal lag between $\mathrm{d}\alpha/\mathrm{d}t$ and the measured ΔT invalidates this method will be treated in the Appendix and will be shown to be inapplicable to modern thermoanalytical instruments. Using

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{Z}{\beta}\mathrm{e}^{-E/RT}\mathrm{f}(\alpha) \tag{35}$$

the maximum condition is

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha_\mathrm{m}} = 0 = \left[\mathrm{e}^{-E/RT}\frac{\mathrm{df}(\alpha)}{\mathrm{d}\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}T} + \frac{E}{RT^2}\mathrm{e}^{-E/RT}\mathrm{f}(\alpha)\right]$$

where the substitution of eqn. (35) and rearrangement yields

$$\frac{ZE}{R\beta}\left(\frac{RT}{E}\right)^2 \mathrm{e}^{-E/RT}\frac{\mathrm{df}(\alpha)}{\mathrm{d}\alpha}\bigg|_{\alpha_\mathrm{m}, T_\mathrm{m}} + 1 = 0$$

which is reduced with the help of the first term approximation in eqn. (29) to

$$\mathrm{g}(\alpha)\frac{\mathrm{df}(\alpha)}{\mathrm{d}\alpha}\bigg|_{\alpha_\mathrm{m}} + 1 = 0$$

This relationship, besides proving that α_m is independent of β for any process described by eqns. (26) and (27), is also applicable to the direct determination of α_m with

$$\mathrm{f}(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{\frac{n-1}{n}} \text{ (see eqns. 18 and 26)} \tag{36}$$

$$\mathrm{g}(\alpha) = [-\ln(1-\alpha)]^{1/n} \text{ (see eqns. 25 and 27)} \tag{37}$$

functions, yielding

$$\alpha_\mathrm{m} = 1 - \frac{1}{e} = 0.63 \tag{38}$$

These results, which were also derived previously [42,61–63], show that statements sometimes found in the literature that "the linearity of the Kissinger plot shows the applicability of the first-order kinetics" [106] or "the Ozawa plot is valid for chemical reactions only" [107] are not substantiated and the shift of α_m with β which is also sometimes discussed [23a] must be insignificantly small.

The maximum reaction rate is calculated as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}\bigg|_{\max} = \frac{nZ}{e}\mathrm{e}^{-E/RT_\mathrm{m}} \tag{39}$$

which is clearly different from the result derived for fixed nth-order chemical kinetics, cf. eqn. (26), where $\mathrm{f}(\alpha) = (1-\alpha)^n$ and

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}\bigg|_{\max} = -\frac{E}{RT_\mathrm{m}^2}(1-\alpha)/n$$

These results, i.e., for transformations described by eqns. (18) and (25) under linear heating conditions: (a) $\alpha_m = 0.63$ (independent of β, n or any other parameters), (b) T_m is independent of n [which follows directly from eqn. (25) by applying point (a)] and (c) the maximum reaction rate is directly proportional to the characteristic exponent, n, are also fully confirmed by a detailed numerical simulation [64].

A comparison of isothermal and non-isothermal temperature shift methods is appropriate here. As eqn. (26) is established to be valid in both cases, the relation

$$\ln \left.\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right|_{\alpha_0} = \ln Z\mathrm{f}(\alpha_0) - \frac{E}{RT} \tag{40}$$

is applicable. In addition, the condition for the maximum isothermal rate is

$$kt_m = \left(\frac{n-1}{n}\right)^{1/n} \tag{41}$$

which is independent of T, i.e., α_m is used in eqn. (40) under any circumstances. On the other hand the relationship evident from eqn. (8):

$$\ln t_{\alpha_0} = C + \frac{E}{RT} \tag{42a}$$

is also valid with t_m. All of these relationships predict the same activation energy that is obtained by eqns. (33) and (34) under non-isothermal conditions. It is evident that a different activation energy can also be defined by eqn. (19b). By this definition the isotherms

$$\ln t_m = \tilde{C} + E_*/nRT \tag{42b}$$

result, but owing to eqn. (24) the relationships (33) and (34) also yield E_*/n in this instance.

This section should be concluded by emphasizing that peak methods, in addition to being so useful and convenient, also give a significant loss of information. With the availability of cheap microcomputers it is advisable to evaluate the full thermoanalytical curve to establish that the same activation energy is really associated with any transformed fraction value, the assumed transformation mechanism is in fact valid and the same characteristic exponent is determined from different heating rate experiments. If these cross-checks are carried out succesfully then a series of different heating rate curves can give as reliable a characterization as a series of different temperature isotherms, while α and $\mathrm{d}\alpha/\mathrm{d}t$ might be determined with better accuracy even faster and the problems of the initial transient and the difficult determination of the incubation time are better avoided. This means that *non-isothermal measurements can be used even for the determination of the mechanism of crystallization, in contrast to the belief that it is restricted to isothermal methods only.*

EXPERIMENTAL RESULTS FOR THE CRYSTALLIZATION KINETICS OF DIFFERENT GLASSES

This paper does not attempt to cover the vast literature on crystallization. Some results on oxide, chalcogenide and metallic glasses are mentioned to reveal how and why the general methods outlined in the previous section are modified under special circumstances and to investigate whether the same kinetic parameters are indeed to be determined from isothermal and non-isothermal experiments.

Oxide glasses

A basic feature of oxide glasses is the separation of temperature ranges for nucleation and growth. Thermal experiments detecting heat evolution naturally observe the growth of pre-existing nuclei. If the glasses were heated uniformly in the nucleation temperature range and investigated later with different heating rates in the growth regime only, then the evaluation methods in the previous section can be used without any modifications. As the samples are usually heated at the same rate in both regimes they are not even equivalent before crystallization and therefore a modification arises [63].

The number of nuclei is described as [68]

$$N_0 = N_1 + N_2 + N_3 \tag{43}$$

where N_1 is the number of bulk nuclei initially present, N_2 is that of nucleated during heating in the appropriate temperature range and N_3 is the number of surface nuclei treated separately. If $N_1 \gg N_2$ ("nucleated glass") then $N_0 \approx N_1$ is independent of β and the usual equations can be used. If $N_1 \ll N_2$ ("as-quenched glass"), then

$$N_2 = \int_{t_1}^{t_2} I[T(t')]\mathrm{d}t' = \frac{1}{\beta}\int_{T_1}^{T_2} I(T)\mathrm{d}T = \frac{\tilde{N}}{\beta} \tag{44}$$

where T_1 and T_2 are the lower and higher limits of the nucleation temperature range, respectively, and crystallization is observed at $T > T_2$. Under these circumstances

$$N_0 \approx N_2 = \frac{\tilde{N}}{\beta} \tag{45}$$

and through eqn. (12)

$$Z \approx \beta^{-1/n} \tag{46}$$

is obtained, which modifies eqns. (30)–(34) to

$$\ln[-\ln(1-\alpha)] = -(n+1)\ln\beta - 1.05n\frac{E}{RT} + C \tag{47}$$

$$\ln \frac{\mathrm{d}\alpha}{\mathrm{d}t} = -n \ln \beta - \frac{nE}{RT} + \sigma(1 - \alpha_1 \ln T) \tag{48}$$

$$\ln \beta = \tilde{C}_1 - \frac{n}{n+1} 1.05 \frac{E}{RT_{\alpha_0}} \tag{49}$$

$$\frac{1}{n} \ln \frac{\beta^{n+1}}{T_{\alpha_0}^{2n}} = C_2 - \frac{E}{R} \frac{1}{T_{\alpha_0}} \tag{50}$$

Surface nucleation was shown to follow fixed-order chemical kinetics [eqn. (5)] and therefore an apparent order $n = 1$ is expected here.

The applicability of these relationships was carefully tested for $LiO_2 \cdot 2SiO_2$ glasses [53,69–73]. It was verified that $\ln[-\ln(1-\alpha)]$vs. $\ln \beta$ with $T =$ constant yields ca. 3 and ca. 4 for the nucleated and as-quenched glass, respectively [eqn. (30) with $Z =$ constant and eqn. (47)] [53]. It was also established that the activation energies determined from eqns. (33) and (49) are in good agreement with that of viscous flow. Similar agreement is also reported for the surface nucleated case [72,73], where the exponent $n = 1$ is observed. (Correspondence of the activation energies of surface and bulk crystallization was also verified for metallic glasses [74].) These results are also substantiated by independent observations [75,76]. Equations (30)–(34) are also found to be applicable to the crystallization of $CaO{-}SiO_2$ based glasses [77,78] and good agreement with isothermal values was reported for GeO_2 and $3BaO \cdot 5SiO_2$ also [79].

In the original publications [53,68,69–73,75–79], eqns. (30)–(34) and (47)–(50) were derived by an irregular procedure, either assuming the validity of the JMAKY kinetics [eqn. (8)] under non-isothermal conditions, or using the extremely rough $e^{I_{\mathrm{Doyle}}(E/RT)} \Rightarrow p(E/RT)$ approximation. These doubtful procedures do in fact lead to some ambiguous results, e.g., to the suggestion of an evaluation method for DDTA curves [8] that is not yet derived from correct principles [29] and to a modified exponent in eqn. (50) where $T_{\alpha_0}^2$ is calculated instead of the correct $T_{\alpha_0}^{2n}$. This latter problem is irrelevant, however, as the variation of β is dominant and in fact both methods, eqns. (49) and (50), yield to a good approximation the same $[n/(n+1)](E/R)$ value [73].

It is emphasized here that eqns. (30)–(34) and (47)–(50) have now calculated from correct premises [63] and found to be experimentally applicable in some instances. The basic reason for the modification apparent in eqns. (47)–(50) should, however, be understood: it is only a correction due to the unequal heating rates applied in the nucleation range, resulting in samples with unequal kinetic parameters.

Metallic glasses

For metallic glasses the difference between the glass transition temperature, T_g, and that of crystallization, T_{cr}, is very small; in many instances T_g

is not even observed, being overlapped by T_{cr}. Under these circumstances a separate temperature regime for nucleation cannot be defined. A general equation for the activation energy was suggested by Von Heimendahl and co-workers [80–82]

$$\bar{E} = \frac{aE_n + bmE_g}{a + bm} \tag{51}$$

where $a = 0$ for quenched-in nuclei and $a = 1$ for a constant isothermal nucleation rate, m is the number of growth dimensions and $b = 1$ for linear and 1/2 for parabolic growth. The activation energies of nucleation, E_n, and growth, E_g, were separately determined by transmission electron microscopy, and $\bar{E}$ predicted by eqn. (51) was in good agreement with that determined by the usual methods. As a high value is obtained for E_n, it is evident that changes in the concentration of the quenched-in nuclei significantly influence $\bar{E}$. The effect of quenching rate on crystallization has been experimentally verified for a series of Fe–B glasses [89]. This fact makes the

TABLE 2

Comparison of activation energies determined by isothermal and non-isothermal methods

	Isothermal			Non-isothermal		
	Eqn.	Ref.	E(kJ mol^{-1})	Eqn.	Ref.	E(kJ mol^{-1})
$Fe_{80}P_{13}C_7$	42	83	435	34	83	448
$Fe_{29}Ni_{49}P_{14}B_6Si_2$	42	84	426	33	87	429
$Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$	42	86	286	33	87	270
$Fe_{40}Ni_{40}P_{14}B_6$	42	85	376	33	87	367
	42	84	385			
$Fe_{75}B_{25}$	42	27	250	33 [a]	27	250
$Fe_{80}B_{20}$	42	89	239	34	89	240
	19a	93	240–245	34	93	243
$Fe_{67}Co_{18}Si_1B_{14}$ [b]	42	96	231	34	96	244
			360			355
$Co_{84\,8}P_{15\,2}$	42	94	195	34	94	213
$Co_{81\,6}P_{18\,4}$	42	94	190	34	94	221
$Ni_{85}P_{15}$	19 [a]	44	221	34	44	227
$Pd_{80}Ge_{20}$	42	90	212	34	90	218
$(Au_{85}Cu_{15})_{77}Si_8Ge_{14}$	42	91	250	34	91	240
$Zr_{75}Pt_{25}$	40	95	339	34	95	325–345
$Ni_{60}Nb_{40}$ [b,c]	42	92	629	34	92	626
			433			446
$Al_{23}Te_{77}$	40	100	270	34	100	270
$(GeSe_2)_{70}(Sb_2Te_3)_{20}(GeTe)_{10}$	40	99	176	34	99	168

[a] Refined Ozawa plot [59] for different transformed fractions and detailed analysis of the full $d\alpha/dt$ curve [65–67].

[b] Different stages of the transformation evaluated separately.

[c] Transformed fraction determined from electrical resistance.

comparison of results obtained on different ribbons very difficult and can even contribute to the significant dispersion obtained on different batches of nominally similar samples [88]. Despite these difficulties, there are many examples in the literature where an acceptable agreement was observed between activation energies obtained by isothermal and non-isothermal methods (Table 2). It is only remarked here that agreement is found both for metallic and chalcogenide glasses and for a wide variety of *a* and *b* parameters. $n \approx 3$ is observed for $Fe_{75}B_{25}$ and $n \lesssim 3$ is established for $Fe_{80}B_{20}$, which indicates the dominant role of the quenched-in nuclei. On the other hand, $n \gtrsim 4$ is found for $Fe_{40}Ni_{40}P_{14}B_6$, which indicates linear growth with concurrent nucleation, whereas parabolic growth is applicable to $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ [80].

There are only a few instances where the characteristic exponent is determined by non-isothermal methods. Good agreement with the isothermally determined values was reported for Pd–Be [97] and Pd–B [98], where a combination of eqns. (31) and (33) was used, and for $Fe_{75}B_{25}$, where a detailed evaluation of the full $d\alpha/dt$ curve was utilized [27].

This section is concluded by mentioning an interesting piece of evidence on the fundamental problem of non-isothermal evaluation. The basic assumption of the usual formalism (which in our case is a direct consequence of the well established theory of nucleation and growth controlled transformations) is that the rate equation is of the same form for both isothermal and non-isothermal measurements. It was actually tested for $(GeSe_2)_{60}(GeTe)_{40}$ glasses with eqn. (40) and the two sets of measurements were found to merge into a common plot [101]. This result is direct experimental proof of the validity of the isokinetic hypothesis and shows that the alternative formalism, where the rate equation is modified under non-isothermal conditions, is inapplicable.

CONCLUSION

A progress report has been given on the investigation of crystallization in the solid state. It was concluded that a non-isothermal generalization of the laws describing nucleation and growth controlled transformations is only possible along the lines of the isokinetic hypothesis. The alternative formalism, where the transformed fraction is invariant and the rate equation is modified under non-isothermal conditions, is in contradiction with both the general theory and the experiments.

Different methods were reviewed for the isothermal and non-isothermal determination of the kinetic parameters. It was established that the usual precision makes the simultaneous determination of all kinetic parameters from a single non-isothermal experiment very problematic. In addition to methods that are capable of determining *nE* only, special attention was paid to the determination of E using temperature shift methods. For a linear heating experiment the transformed fraction at the maximum rate is always $\alpha_m = 1 - 1/e = 0.63$, and is independent of any experimental parameter. The Ozawa and Kissinger methods are thus equivalent and both are generally valid if otherwise identical samples are heated at different rates in their transformation region. In addition to the different quenching rates, the different heating rates in the nucleation region may also result in systematically different samples and then an appropriate correction is necessary.

Experimental results for oxide, chalcogenide and metallic glasses clearly illustrate that identical kinetic parameters can be determined from both isothermal and dynamic experiments in many instances.

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APPENDIX: EFFECT OF EXPERIMENTAL THERMAL LAG ON MAXIMUM RATE METHODS

As the temperature at which the transformation rate is maximal is usually determined by thermal methods, the reliability of this determination was seriously questioned [102] owing to the finite thermal inertia of any measuring system. While it was shown in some recent publications [103–105] that this negative conclusion is exaggerated, the actual calculation is given here to show the real figures.

If we assume the basic DTA equation in the simplified form:

$$\dot{\alpha} = -\Delta T K/\Delta H - \Delta\dot{T} C_p/\Delta H$$

(neglecting terms arising from experimentally unbalanced conditions for non-stationary calorimetry in the twin arrangement), then ΔT can be routinely expanded into a Taylor series around T_0 where ΔT is maximal:

$$\Delta T = \Delta T_0 + \left.\frac{\mathrm{d}\Delta T}{\mathrm{d}T}\right|_{T=T_0}(T - T_0) + \frac{\mathrm{d}^2\Delta T}{\mathrm{d}T^2}\frac{(T-T_0)^2}{2} + \ldots$$

As ΔT is maximal at T_0,

$$\left.\frac{\mathrm{d}\Delta T}{\mathrm{d}T}\right|_{T=T_0} = 0$$

Introducing the notation

$$D_2 = \left.\frac{\mathrm{d}^2\Delta T}{\mathrm{d}T^2}\right|_{T=T_0}$$

$$\Delta\dot{T} = (T - T_0)D_2\beta$$

$$\Delta\ddot{T} = D_2\beta^2$$

the temperature of the maximum transformation rate is determined by

$$\Delta H\ddot{\alpha} = 0 = \left(-K\dot{\Delta}T - C_p\ddot{\Delta}T\right)\Big|_{T=T_\mathrm{m}} = -K(T_\mathrm{m} - T_0)D_2\beta - C_pD_2\beta^2$$

yielding $T_\mathrm{m} = T_0 - C_p\beta/K$.

When the activation energy is determined by plotting $\ln\beta$ vs. $1/T_\mathrm{m}$, then

$$1/T_\mathrm{m} = (1/T_0)/\left(1 - C_p\beta/T_0K\right) \approx 1/T_0\left(1 + C_p\beta/T_0K\right)$$

Parameters typical of, e.g., the Perkin-Elmer DSC-2 are 5 mg $Fe_{75}B_{25}$ ($C_p = 2.5$ mJ K^{-1}), $T_0 = 700$ K, $K = 10$ mJ K^{-1} s^{-1}, $\beta = 0.15$ K s^{-1}, thus $C_p\beta/T_0K = 5 \times 10^{-5}$, which is negligible. Even in typical macro-DTA with a 300 mg sample and $K = 20$–50 mJ K^{-1} s^{-1} the order of magnitude of the correction never exceeds 10^{-3}, which is still negligible.

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