Review

APPLICABILITY OF DTA AND KINETIC DATA RELIABILITY OF NON-ISOTHERMAL CRYSTALLIZATION OF GLASSES *

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ABSTRACT

This article presents a survey of recent points of view on the principles of correct analysis of DTA measurements, and discusses the relationship between isothermal and non-isothermal kinetics and the applicability of individual methods of kinetic data evaluation. The thermophysics of the glassy state is also considered with regard to possible kinds of relaxation processes. The practical use and reliability of DTA in studying crystallization processes in glasses is discussed in detail.

INTRODUCTION

The crystallization of glasses is a complex process which may proceed in several stages. These stages, as often cited, can consist of nucleation and crystal growth controlled by either short-range diffusion or interfacial chemical reactions; also by phase separation, structural relaxation and delocalization, long-range diffusion and viscous flow, heat transfer, etc. Under set circumstances, conveniently described by constitutive equations [1,2], the slowest stage acts as the rate-limiting step determining the function $f(\alpha)$ in the assumed simplified rate law $\dot{\alpha} = k(T)f(\alpha)$. In most heterogeneous reactions the rate-controlling process takes place at the interface (either sharp or diffusional) between phases. The speed at which the interface moves is then responsible for the overall reaction rate and gives rise to various types of mathematical modelling. It has been shown [3,4] that certain analytical functions apply in the simple form of two power exponents $(1 - \alpha)^n \alpha^m$ or $(1 - \alpha)^n [-\ln(1 - \alpha)]^p$ (analogous with homogeneous kinetics, where m and p are equal to zero). From a kinetic point of view the interfacial area plays the same role as that of concentration in homogeneous reactions [5]. Prob-

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lems of the location and possible lack of statistical distribution of discrete activated states along such interfaces may, however, rule out the validity of an Arrhenius-type rate constant, $k(T)$ [6]. Similarly, a narrow range of temperature is necessary to satisfy the nucleation–growth frequency [7] which contradicts the requirement of a broad temperature interval, needed to compensate for the mathematical consequence of kinetic data interdependence, called the kinetic compensation effect [8].

It is obviously easy to criticize the present kinetic procedures for not sufficiently characterizing the reality of crystallization processes. However, the substitution of this phenomenological model by another kinetic procedure, which would equally easily yield certain numerical parameters, is difficult. It is because we want, although cannot always achieve, a comparison between them. Finding an optimal compromise between our inability to fully express the crystallization mathematically and the real extent of our efforts to obtain a certain, even if often oversimplified, picture, is the most difficult point of solid-state kinetics in general. Therefore, for the sake of realizability, we do our modelling in terms of geometrically well-defined species [9], although there is often little coincidence with visual, complementary observations (morphology) [4].

Evaluating the quantitative dependence between the particular glass behaviour under isothermal conditions and general crystallization theory is difficult in itself and, thus, its combination with non-isothermal measurements is often felt to be another unsolvable complication. Kinetic studies carried out under constant heating are often considered a delicate field as far as obtaining reliable physical data is concerned and are the frequent subject of criticism, particularly from those studying classical isothermal procedures. It is worth noting that many drawbacks are justly criticized, for example, the effect of self-heating of samples during crystallization which, however, equally appears in isothermal measurements but which is seldom the object of experimental detection. On the contrary, non-isothermal DTA provides direct evidence of the extent of such temperature deviations. DTA may thus provide us with all the necessary data for describing crystallization dynamics which, however, are conditioned by our ability to solve the rather complex relationship between the measured (ΔT_{DTA}) and desired (ΔH) quantities [4]. The wide use of DTA for the determination of kinetic data is mostly based on an oversimplified plot of ln ΔT_{DTA} vs. $1/T$ [10] to determine E or on describing the peak symmetry [11] for determining the power exponent. Uncritical applications of such mathematical treatment to the most complicated case of studying solid-state reactions can be compared to the application of this kinetic procedure to evaluate any arbitrarily drawn peak. This is by no means possible in comparable caloric studies, where further experimental (calibration constant) and material (C_p data) specifications are inevitable [12]. It is understandable that the kinetic use of DTA has become the target of severe criticism [13–16].

Because there is too much contradictory information in the literature, it is worth analysing the problem of the reliability of DTA-obtained kinetic data in more detail. Particular interest can be paid to the following three points:

(i) a glassy sample and its investigation,

(ii) theoretical background of DTA, and

(iii) non-isothermal kinetic analysis.

The listing of problems is important, since it can be considered that the field of non-isothermal kinetics has developed within two more or less characteristic branches of science; namely, thermal analysis, where non-iso-thermal kinetics serves as an analytical treatment, and material science, exhibiting more practical applications. The excellent article by Yinnon and Uhlmann [17], critically reviewing the applicability of non-isothermal methods, can be shown as an example of confusing the physical meaning of time and temperature derivatives of the extent of crystallization [18,19], which was discussed less recently and already rejected on pages of thermoanalytical journals [2,20], and again well analysed by Kemeny and Gramasy [21].

ISOTHERMAL VERSUS NON-ISOTHERMAL KINETICS

There is no basic difference between the kinetic description of isothermal and non-isothermal reactions [1–4,12]. In both cases the same constitutive equations are applicable, i.e., $\dot{\alpha} = \hat{\dot{\alpha}}(\alpha, T)$, $\dot{T} = \hat{\dot{T}}(\alpha, T)$, differing only in the expression for $\dot{T}$, i.e., zero or constant (the effect of thermal history, mechanical treatment or heat self-production can equally be included). This isokinetic hypothesis means that we can use the same assumption which has the practical result of achieving different extents of crystallization assuming an equivalent time interval [2]. This is similar to the difference accounted for in the construction of T–T–T (transformation–temperature–time) and C–T (coding–transformation) diagrams [22].

It should be stressed that the extent of crystallization, α, itself is not a state function of temperature and time (i.e., $\alpha \neq \hat{\alpha}(T, t)$) like its derivative $\dot{\alpha}$. Therefore, any additional term of the type $(d\hat{\alpha}/dT)_t$, sometimes required to correct the non-isothermal rate [17,18,20,23], is unjustified and thus invalid [3,24]. This, in fact, is a long-discussed puzzle introduced by McCallum and Tanner as early as 1970 [25], recently reapplied to the JMAYK (Johnson–Mehl–Avrami–Yerofeev–Kolmogorov) equation ($[-\ln(1 - \alpha)] = k'_{(T)}t^p$) [17–19,23] and thus appropriately recriticized [2,21].

The simplest description of crystallization kinetics is usually made in terms of only two macroscopic variables, α and T. However, phase separation, β, as a general property of most glasses, may also be encountered in practice, although this is not yet appreciated in kinetic models [4,26] because of the experimental difficulty in the parallel determination of its numerical values. Furthermore, two mutually independent functions, f(α) and $k(T)$,

are used for analytically expressing the rate equation and are considered as experimentally verified. This is not generally true, as shown, e.g., for coupled processes [27]. The success of this approach depends further on a proper analytical expression of individual functions [28] which is usually based on long-established models of isothermal reactions and their consequent integration and derivation [4,12]. Henderson [29] excellently discussed all possible problems connected with the transfer of isothermally derived models to non-isothermal conditions. It was pointed out, however, that the formal theory of crystallization must not be generally isokinetic. Šesták [4,26,30] and De Bruijn et al. [31] mathematically analysed the integration procedure of the basic nucleation–growth equation under non-isothermal conditions and showed that the temperature dependence thus obtained is similar to that obtained on classical isothermal treatment. The same apparent activation energy and characteristic power exponents can, in principle, be determined which differ only in the value of the pre-exponential factor, depending on the process itself and the numerical approximation employed.

For a general relaxation process the exponential form of the Arrhenius rate constant, expressing the probability of successfully moving from an initial glassy-liquid to a final crystalline state, should be valid for all thermally activated crystallization processes, where either diffusion and/or interfacial chemical reactions are effective. The term $k(T)$ is then composed of the pre-exponential factor, Z, describing the frequency of attempts to overcome an energy barrier E, called the activation energy. If non-activated heat transfer becomes the rate-controlling process instead of $k(T)$, the non-exponential heat transfer coefficient, $\Lambda(T)$, should be considered. For a narrow temperature interval of reaction, E and Z are found to be interdependent, considered [28] to be virtually the mathematical consequence of a functional correlation of the type 1 vs. $1/T$ [8]. This compensation effect can be avoided by using $k(T)$ related to a reference point, conveniently called the isokinetic temperature [8], T_i. Then $k(T) = Z \exp[-E/R(T - T_i)]$ which assumes the form of the Vogel–Fultcher–Tamman equation already recommended for describing the crystallization of glasses [18,29].

PRINCIPLES OF CORRECT ANALYSIS OF DTA-BASED DATA

Average commercially produced DTA apparatuses can be described in terms of a double non-stationary calorimeter [4,32], in which the thermal behaviour of the sample and reference materials, usually placed in thermally insulated cells, is compared. From the balance of thermal fluxes the DTA equation can be established [32–35] which relates the measured quantity, i.e., the difference between the reference and sample temperatures, $T_0 - T_s =$

ΔT_{DTA}, versus the required reaction rate, $\dot{\alpha}$:

$$\dot{\alpha} = -\Delta T_{\mathrm{DTA}}\frac{K_{\mathrm{DTA}}}{\Delta H} - \Delta \dot{T}_{\mathrm{DTA}}\frac{C_{\mathrm{pS}}}{\Delta H} - \phi\frac{\Delta C_{\mathrm{p}}}{\Delta H} + \frac{\Delta K}{\Delta H}$$

Similar analysis yields the DSC equation, which now applies to the compensation thermal flux, $\Delta \dot{Q}$, supplied to specimens [4,32]

$$\dot{\alpha} = \Delta \dot{Q}\frac{1}{\Delta H} + \phi\frac{\Delta C_{\mathrm{p}}}{\Delta H} - \Delta T_{\mathrm{mantle}}\frac{\Delta \Lambda}{\Delta H}$$

where, however, the originally assumed difference, ΔT_{DTA}, now serves as a regulated quantity only in the sense of being as close to zero as possible. For well-established measuring conditions the effect of the last two terms of both caloric equations can be neglected (i.e., heating rate, ϕ, change in thermal capacity, ΔC_{p}, change in heat transfer, ΔK, and in heat conductivity, $\Delta \Lambda$, and the temperature difference between the sample and surrounding mantle,
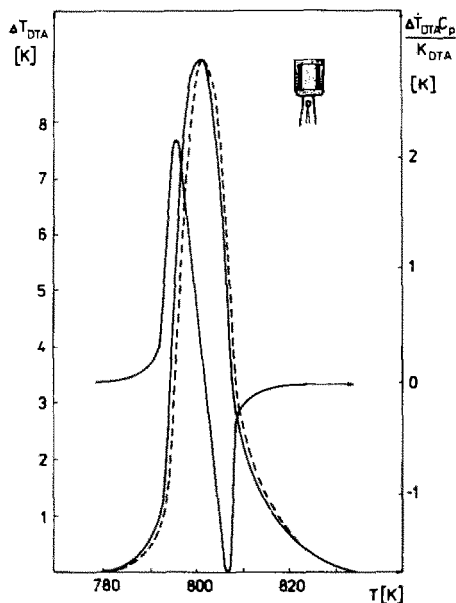

Fig. 1. The effect of heat inertia. A typical macro-DTA recording [38] (— — — —) using a Netzsch apparatus (recording sensitivity of 0.1 mV/250 mm with Pt–Pt/13% Rh thermocouple or 0.4 mV/250 mm using the measuring head modified by Pallaplat thermocouples, heating rate 10 K min^{-1} (0.166 K s^{-1}), sample weight 0.15 g (metallic glass ribbons 7 mm wide and 30 μm thick, of composition Co–Ni–Fe–Si–B) wound [38] inside the Pt-cell (2 g, $r = 12$ mm); the remaining void was filled with powdered Al_2O_3 and/or Ag. The corrected DTA peak is also shown (———), according to the DTA equation (apparatus constant 20 mJ K^{-1} s^{-1}) with a manual scanning of minimum 26 points followed by computer evaluation (Video Genie, Basic). The S-shaped curve illustrates the actual profile of the DTA peak background [which is subtracted from the originally recorded DTA peak (— — —) to obtain the corrected peak (———)].

ΔT_{mantle}, are constant and can thus be included in the baseline) [32]. A simple proportionality between the DSC recording and the rate of reaction holds, whilst the similar DTA relationship contains an additional term arising from thermal inertia [4,32,35]. It is evident that the usual plot of the logarithm of peak deflection versus the reciprocal temperature can only be used in the case of DSC, while for DTA, a modified form should be used: $\ln(K_{\text{DTA}}\Delta T_{\text{DTA}} + C_p\Delta\dot{T}_{\text{DTA}})$ vs. $1/T$, which has, however, rarely been applied in practice [30,36]. Consequently, a simple derivation of the extent of reaction by simply relating the partial vs. total areas of a DTA peak is misleading unless an actual S-shaped background to the peak is found [37] (cf. Fig. 1). It can easily be verified that the maximum deviation between the as-scanned and corrected peaks occurs at the inflection point. This certainly causes difficulty for simply applying evaluation methods based on the fixed extent of reaction taken for multiple DTA peaks measured at different ϕ values. On the other hand, the popular Kissinger method [11] remains valid because at $\ddot{\alpha} = 0$, $\Delta\ddot{T} = 0$ and $\Delta T_{\text{max}} \equiv \alpha_{\text{max}}$ providing, of course, there is no change in the thermal capacity of the material investigated, which is often fulfilled during the crystallization of glasses.

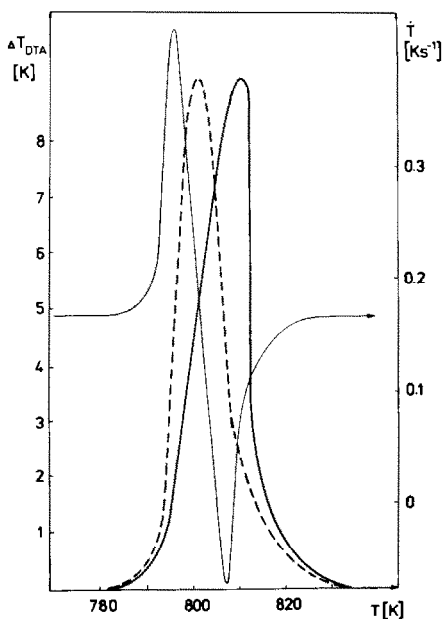In contradiction to DSC, during any DTA experiment the heating rate is

Fig. 2. The effect of actual temperatures. The originally recorded DTA peak (cf. Fig. 1, — — — —) is redrawn to the scale of real temperatures, $T = T_{\text{real}}$ (i.e., $T_{\text{real}} = T_{\text{linear}} + \Delta T_{\text{DTA}}$, ————) [38]. The S-shaped curve illustrates the course of the instantaneous values of heating rate (if the temperature deviations due to the DTA peak are accounted for in the ideally constant heating rate of 0.166 K s^{-1}).

actually changed because of DTA deflection, which is also a direct measure of the deviation between actual and predetermined temperatures. At the moment when completely controlled thermal conditions of the sample are reached, the DTA peak disappears demonstrating well the contradiction between non-stationary DTA measurements and the steady (equilibrium-like) conditions assumed in non-isothermal kinetics. From the actual course of real heating rate, as illustrated in Fig. 2, it follows that a certain shift in peak temperatures will occur when the original peak is redrawn on the actual (i.e., $T_{real} = T_{lin} + \Delta T_{DTA}$) temperature axis. The best solution to avoid such disagreement between a DTA and a non-isothermal kinetic analysis may be found through a double-derivative equation of the form [4,39]

$$\frac{\ddot{\alpha}T^2}{\dot{\alpha}\dot{T}} = \frac{df(\alpha)/d\alpha}{f(\alpha)} \frac{T^2\dot{\alpha}}{\dot{T}} + \frac{E}{R}$$

valid for true instantaneous values of α and T and their derivatives ($\dot{\alpha}$, $\ddot{\alpha}$, $\dot{T}$) detected for the entire sample. This is in contrast to the convenient parameters used so far, where T and ϕ ($= \dot{T}$) are replaced by their extrapolated ideal values. Practical applicability is, however, very difficult, even though a computer-aided evaluation is available [39] and the possible scatter of derivatives can be smoothed by spline fitting [38].

APPLICABILITY OF EVALUATION METHODS

The value of individual methods of kinetic data evaluation should not be over-emphasized [12]. These methods rank into two groups, using single or multiple non-isothermal runs, and can be based on two different procedures, requiring either three-fold input data (α, $\dot{\alpha}$, T) for the primitive rate law, or two-fold data (α, T) for the integrated form of rate equation. The latter method is presumably less laborious, but is also less sensitive regarding both experimental errors ($\dot{\alpha}$ is avoided) and model relation distinguishibility [40,41]. In particular, the analytical forms of $\int d\alpha/f(\alpha) = g(\alpha)$ overlap each other for different rate-controlling processes [4] which, as shown first by Šesták [42], makes it practically impossible to distinguish the power exponents, p, in the JMAYK equation [40–43]. The actual evaluation through integral methods is comparatively easy but it requires certain assumptions about the behaviour of the exponent-integral [4]. Broido and Williams [44] diagnosed exactly which integral methods yield the most accurate data by dinstinguishing the accuracy of individual polynomials hidden in exponent-integral approximations. For instance, with the most common plots: $\ln g(\alpha)$ vs. $\ln T$, ΔT or $1/T$, the last plot is more accurate than the second and first, which are still within the accepted limit of ± 10 refl.% of E. For the JMAYK equation, however, often less sensitive double-logarithmic plots result. Tang and Chaudhri [45] have shown that the plot of $\{\ln(1 - \alpha) - p \ln[-\ln(1 - \alpha)]\}$

vs. α within the range $0.25 < \alpha < 0.75$ is almost constant [17] and thus the least applicable for manipulating the original equation to find two parameters on a single strain-line fitting. A slightly more sensitive way is the use of the expressions $[\ln\{(1-\alpha)[-\ln(1-\alpha)]^p\}]$ [5] and/or $[n\ln(1-\alpha) - m\ln\alpha]$. A more detailed critical examination of the various methods which are currently used to analyse dynamic experimental data is recently surveyed in refs. 4, 17, 29 and 43–45.

Among the most convenient methods are those which are based on the fixed extent of crystallization, α_i, which, for a series of traces taken at different heating rates, ϕ, allows a plot of $\ln(T_i^2/\phi)$ vs. $(1/T_i)$ to be made (e.g., an Ozawa [46] or Chen [47] plot). Similar to the above approach is the method of Kissinger [11], fitting a straight line to $\ln(\phi/T_{max})$ vs. $(1/T_{max})$ for the maximum reaction rate, $\dot{\alpha}_{max}$. Despite its extensive discussion [17,21,23,29,45], the work of Comel et al. [48] is worth noting as they derived a generally valid equation for ϕ at $\ddot{\alpha} = 0$ (although limited to a simplified case of a one-parameter model):

$$\phi = -k(T)[\mathrm{d}f(\alpha)/\mathrm{d}\alpha]_T/[\mathrm{d}\ln k(T)/\mathrm{d}T] + [\mathrm{d}\ln f(\alpha)/\mathrm{d}T]_\alpha).$$

Eliminating ϕ and transferring the equation into the general equation of the rate for α_{max} (assuming that $f(\alpha) = (1-\alpha)^n$ is not T-dependent) it follows that [48]

$$(\dot{\alpha}_\phi)_{max} = -[\mathrm{d}\ln k(T)/\mathrm{d}T]_\alpha/[\mathrm{d}\ln f(\alpha)/\mathrm{d}\alpha]_T$$

which finally gives

$$(\dot{\alpha}_\phi)_{max} = -(E/RT_{max}^2)(1-\alpha)/n$$

Considering the two-parameter model ($m \neq 0$, $n \neq 0$) the validity of the above equation can be similarly generalized to hold for [49]

$$(\dot{\alpha}_\phi)_{max} = -(E/RT_{max}^2)[\alpha(1-\alpha)]/[\alpha(m+n)-m]$$

These equations are valid more generally even for any point α_i and demonstrate that the slope, $\dot{\alpha}_i$, of a kinetic curve is really related to the kinetic parameters E, m and n [50]. Consequently, it can be shown that the value of α_{max} varies with ϕ, as dealt with in detail by Tang and Chaudhri [45]. The temperature of maximum reaction rate, T_{max}, is then dependent upon the heating rate applied as given by Comel et al. [48] for $m = 0$, $n > 0$ in the form of the equation

$$\mathrm{d}\phi/\mathrm{d}T_{max} = k(T)(R + 2nRT_{max})/E \qquad \text{(for } m = 0,\ n > 0)$$

which is close to the classical Kissinger plot derived for unimolecular reactions. For a generalized case of $m \neq 0$, $n \neq 0$ a rather complicated relationship can be obtained, where the simple constant n is replaced by the sum $(m + n)$ and the whole term assumes the form of a series multiplied by n/m and α. Fătu and Segal [50] applied a similar analysis assuming the case

when the reaction rate is itentionally kept constant. Such isokinetic conditions seem advantageous for either the determination of E without taking into account the analytical form of $f(\alpha)$ or for the establishment of $f(\alpha)$ from the shape of the isokinetic curve, with the ability to distinguish between one- (n) and two- (n, m) parameter models. Such conditions are experimentally difficult to achieve; the closest approach is quasi-isothermal derivatography introduced by the Pauliks [51].

In conclusion, the mathematical procedures themselves should also be noted as responsible for a possible discrepancy in the reported kinetic data obtained with various assumptions, where a straight-line fitting is carried out. Popular logarithmization is a typical example, where the required Gaussian normal distribution is deformed, e.g., when $(1 - \alpha)$ increases ten-fold, the transformed quantity, $\ln(1 - \alpha)$, decreases only twice and thus originally independent errors also change. It follows that the quality of the resulting data depends on the type of regression analysis applied (i.e., linear regression or linear regression with weights or even non-linear regression with one non-linear parameter [4]). On using the Hotelling χ^2-test, Archangelski et al. [52] showed that kinetic data are also statistically non-equivalent, and recommended a hypothesis test to distinguish their significance or non-significance [4].

THERMOPHYSICS OF GLASSY SAMPLES

Glasses obtained by a suitable rapid cooling of melts are in a constrained thermodynamic state which tends to transform to the nearest, more stable state on reheating. The well-known dependence of a sample's extensive property vs. temperature then best illustrates the possible processes which can take place during the temperature change [4]. A most convenient diagram is that of ΔH vs. T which can be derived using the lever rule from a concentration section of an ordinary phase diagram [24,53,54] (see Fig. 3). Upon reheating, the unstable glassy state first undergoes glass transition followed by separation of the closest metastable crystalline phase [54]. On attaining a temperature at which another non-crystalline phase of the first melt may appear, the formation of stable crystals is initiated. If considering a more complex case, for example the existence of another metastable phase, the sequence of processes becomes more complicated, since the metastable phase is probably produced first to precipitate later into the more stable phases. This, in fact, gives us an idea of what kind of equilibrium background [24] is to be considered for the processes. Thus, the partial reaction steps, experimentally observed as individual peaks, are classified to fit the scheme chosen in accordance with the type of phase diagram related to the sample composition. It is evident that the majority of crystallization processes are of an invariant type [4,24,55], i.e., the equilibrium background changes
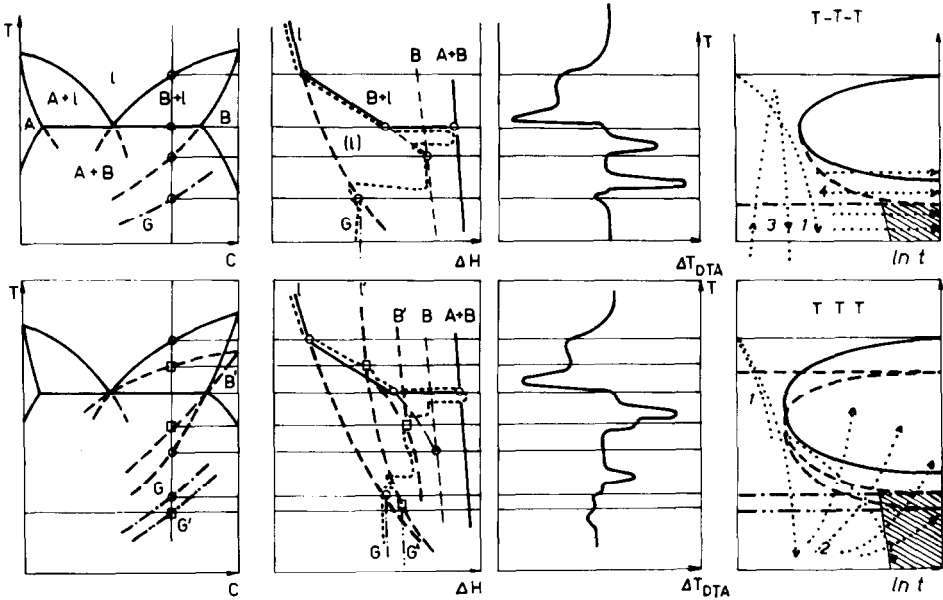
Fig. 3. An illustrative method for distinguishing the possible processes taking place on heating glass. The first column shows a hypothetical binary phase diagram with stable (————), extrapolated metastable (— — —) and glassy (·–·–·) states marked. The vertical line (□, ○) of characteristic temperatures shows the composition in question. The second column gives the dependence of enthalpy change vs. temperature derived from the preceding phase diagram by means of the lever rule. (······) The possible course of consequent processes taking place on normal heating of the glassy state (G) through the metastable (B, B′) and stable (A + B) crystalline states into a liquid (l). The boundary lines (— — —, ————) actually express the limiting metastable and stable cases attainable under extreme conditions of the ultrafast or ultraslow cooling or heating, respectively. The temperature derivative of this course ($d\Delta H/dT$) resembles the DSC and/or DTA (ΔT_{DTA}) recording, each peak corresponding to the individual processes exhibited by steps in the ΔH vs. T plot. The last column shows the corresponding, hypothetical T-T-T (transformation–temperature–time) diagram with the stable and metastable crystal areas again bounded (———— and — — —, respectively). The thin hirozontal lines correspond to the characteristic points (melting, glass transformation) and the shaded area illustrates the existing region of quenched-in nuclei. (······›) Indicate either preparation method (1) [chill block melt-spinning and/or twin roller quenching (with two resulting separate cooling rates, the bottom raw)] or annealing procedures in the isothermal (4) and flash (heat pulse: (3)) modes or reheating under different heating rates (2). The T-T-T diagram is important as it introduces the time factor which in the otherwise equilibrium-like plot of ΔH vs. T cannot be included, although the point of the departure of the glassy state is dependent upon the experimentally attained rate of cooling/reheating. The above representation can be modified for any more complicated (or multicomponent) system as, e.g., shown in the bottom row with a polymorphic transformation of the B ⇌ B′ type and two glassy regions (G and G′).

stepwise from unstable/metastable to metastable/stable states. Beside the prediction of consecutive and/or coupled reactions, it has an important consequence for the equality of isothermal and non-isothermal degrees of

crystallization [4,24] and thus the applicability of previously described kinetic models.

An equally hypothetical model, but also very useful for gaining an overall picture of reactions which may occur during crystallization, is a diagram of the Gibbs (free) energy for the various phases vs. composition [56]. Dependent on concentration, the transition of unstable/metastable into metastable/stable crystalline phases can proceed by one of the following reactions [4,56,57]:

(i) polymorphic crystallization (i.e., supersaturated alloy formation without any change in concentration);

(ii) primary crystallization (increase in concentration until a metastable equilibrium is achieved);

(iii) eutectic crystallization (i.e., a simultaneous, often discontinuous, crystallization of two stable phases).

Because of the finite cooling rate of rapidly quenched thin sections of (usually metallic) samples, they are regarded as partially annealed (cf. T–T–T diagrams in Fig. 3). Assuming the last stage of their uncontrolled cooling, which effects the experimentally detectable differences in their physical properties, Ratajczak and Stobiecki [58] classify the resulting relaxation processes in three different categories:

(i) reversible changes, where the reproducible changes of the measured property proceed in one direction on rising and in the opposite direction on decreasing the annealing temperature [59];

(ii) crossover effects indicative of switches from one annealing regime to another, where the observed change of the measured property does not follow either extrapolated course, but often exhibits an intermediate (local) extreme [57];

(iii) logarithmic kinetics, if the property change varies linearly with the logarithm of isothermal annealing time.

The above effects are of particular importance in the modern field of flash annealing of metallic glasses by ultrafast heat pulses [60,61] which can replace the traditional furnace treatment (cf. Fig. 3).

The model recently proposed by Gibbs et al. [62] is worth noting. Activation energies of a relaxation-causing process, which are ready to contribute to the experimentally detectable changes of a physical property, are distributed over a certain spectrum and the corresponding characteristic annealing functions can be substituted by a step function. For as-received samples all types of relaxation processes are possible. After pre-annealing for a certain time and at a given temperature most structural distortions are removed leaving a more narrow distribution of the available activation energies, which is consistent with the latter stages of logarithmic kinetics.

A deeper knowledge of the crystallization-preceding stages of nucleation has become very important, including time-dependent (transient) nucleation [63] as well as the athermal behaviour of quenched-in nuclei [57,58]. Other-

wise, the generally understandable process of glass crystallization is excellently covered by Köster and Herold [57] and Scott [59], including pertinent structural considerations concerning metallic glasses.

USE OF DTA TO STUDY CRYSTALLIZATION OF GLASSES

First, we have to assume that an ordinary DTA arrangement can never satisfy all the demands arising from specific characteristics of the glassy state and the non-isothermal nature of its investigation. DTA itself has developed along two more or less separate directions. Micro-DTA, where possible temperature gradients are maximally decreased so that it has become a useful tool for precisely detecting characteristic temperatures. On the other hand, macro-DTA allows the effective measurement of integral changes needed in calorimetry. Kinetics ranks somewhere in between, with respect to the extremely delicate nature of this type of investigation [55].

A relatively large deflection in a sharp DTA exotherm is a typical sign of time-located heat production, which is indicative of some crystallization processes. Under limiting conditions the heat transfer from the reacting zone may become a rate-controlling process in which the reaction rate is assumed to depend upon the product of two functions, $f(\alpha)$ and $\Lambda(T)$, but where $\Lambda(T)$, introduced instead of the original $k(T)$, is a non-activated heat exchange coefficient proportional to temperature. An extreme example of such terminal conditions is an adiabatic process which can be assumed to exist when the self-generated production of heat catalyses a very sharp crystallization process, where the heat exchange between crystallizing glass, sample holder and its surroundings is negligible compared to the narrow duration of the reaction. Then the reaction rate becomes directly proportional to the temperature change, $\dot{T}$, displayed by the sample.

An essential point is, however, the bulky behaviour of glass which is often violated when the glassy sample is mechanically pre-treated, thus causing extra lines of metastable surface-catalysed phases to be included in the ΔH vs. T diagram [64]. Glassy samples of shapes, like fibres [65] and/or very thin metallic ribbons, should also be treated with increased attention as the process of filling a DTA cell can introduce not only additional interfaces (cracks), but also unpredictable mechanical tension which may affect the crystallization dynamics. For a preliminary evaluation, the tendency of the glass towards volume and surface crystallization, an ordinary DTA experiment can be modified in such a way as to compare the finely and roughly pulverized samples placed as DTA specimens via possible changes on the otherwise monotonous baseline.

A simple but very useful method was described by Marotta et al. [66,67] for evaluating the effect of temperature on the annealing time of bulk nucleation. The number of nuclei formed during pretreatment can be related

to the difference between the crystallization peak temperature of an as-quenched sample and that of a previously heat-treated one. The plot of these temperature differences against pre-annealing temperature gives a nucleation-like curve exhibiting a maximum at the maximum nucleation rate.

The best experimental approach, however, is to investigate a compact glassy sample, best prepared by directly quenching the melt in the DTA cell [68,69]. For example, Šesták and Strnad [69] analysed a DTA peak for the bulk crystallization of $70SiO_2 \cdot 10Al_2O_3 \cdot 20ZnO$ glass cast directly into a cylindrical DTA holder and obtained a very good coincidence between the front part of the DTA curve and that calculated on the basis of the JMAYK and DTA equations using known data for nucleation and growth measured by an independent optical technique [30,69].

Such simulation of a DTA peak does not account, however, for plausible temperature gradients arising from heat transfer within the sample. The existence of such gradients is obvious and is often the reason for the above-mentioned large decrease in size of the DTA sample. On the other hand, it may contradict the requirement of a negligible sample surface compared to its volume. A quantitative estimate of the maximum extent of temperature gradients can be found to be proportional to $\Delta H \rho \phi / (\lambda)^{-1/2}$ multiplied either by $\delta / \sqrt{2}$ or r for the layer thickness δ or cylinder radius r, respectively [70]. Another approach [71] gives a temperature error, ϑ, due to the difference between the heat released during crystallization and the heat escaping along a temperature gradient between the sample and its holder: $\vartheta = (\Delta H \rho \dot{G} \delta) / \lambda$ [72], where ρ, $\dot{G}$ and λ are the density, crystal growth rate and thermal conductivity, respectively.

The difference between a known (artificially introduced) heat pulse and the evaluated DTA response best illustrates the extent of temperature gradients. A rectangular pulse generated by micro-heating the DTA specimen directly shows clearly that the resulting DTA peak, corrected according to the DTA equation, has a shape very similar to that of the original pulse thermal gradients, responsible for the remaining deviations [4,32] at the frontal and decaying sections.

CRYSTALLIZATION KINETICS BY DTA

It should be emphasized again that for practical applications of the most popular Kissinger method [11] apparent values, $E_{app} = E/p$, are obtained [41,43] which are similarly effective for any integral method [40,42,63] based on the JMAYK equation. It is, therefore, essential to compare only the appropriate values of E when they are obtained by different methods. In the literature, a large number of kinetic data exists [42,63,65–67,73–92] showing either good or poor mutual coincidence [4,12]. In the following table three randomly selected examples of heat-inertia uneffected (DSC-based) studies

are shown to illustrate the situation. First, isothermal data obtained by either classically plotting $\ln[-\ln(1-\alpha)]$ vs. $\ln t$ (providing both E and p values, case A), or assuming only the time, t_m, at which maximum rate (peak tip) is attained at a given temperature (plot of $\Delta \ln t_m$ vs. $\Delta(1/T) \equiv E_{app}$ [19,28], case B) or obtaining non-isothermal E_{app} extracted from a Kissinger plot ($\Delta \ln(\phi/T_m)$ vs. $\Delta(1/T_m)$, case C).

Sample	Case A			Case B	Case C
	E	p	E/p	E_{app}	E_{app}
CdGeAs [71]	95.4	2.2	43.1	61.1	42.7
As [18]				50.6	65.2
$Fe_{80}P_{13}C_7$ [93]	104	5	20.8		107

Spayer and Risbud [71] made a thorough comparison of individual E values and reported a good coincidence between data obtained by the Kissinger method (C) and those from analysis by the JMAYK equation (A), but only a fair agreement with the isothermal maximum-rate method (B). This is in contrast to a similar study by Marseglia [19] showing a reciprocal trend with E_{app} by the isothermal maximum-rate method (B) and the heating-rate method (C). Less recently, Scott and Ramachandrarao [93] indicated a good agreement between isothermally (A) and non-isothermally (C) obtained E values; however, they did not consider the reducing effect of p. Colmenero et al. [77] and Marotta and Buri [78] found good agreement between the iso- and non-isothermal-based resulted, the first [77] also discussing the treatment [78] already criticized by Criado [76] as the method ressembling the classical method of Piloyan et al. [10]. Using the Ozawa method [46], Lucci and Battezzati [80] also reported a good agreement between kinetic data obtained in the two different thermal modes. Surveying such results can be continued further, particularly researching the fast-increasing literature on metallic glasses [41,77,79,80,84,89,93].

One of the most important steps remaining is to finally evaluate the experimentally obtained (apparent, E_{app}) values of the activation energy in terms of the nucleation–growth (overall crystallization, E_{CR}) process in order to provide elementary activation energies of nucleation, E_N, growth, E_G, and diffusion, E_D. For example, Lucci and Meneghini [79] investigated metallic glasses in their as-quenched and preheated states and found that E_{app} and p are lowered by the presence of preformed nuclei and tend to reach constant values corresponding to a condition of zero nucleation rate, where E_{app} represents, in fact, the entire activation energy of crystal growth, E_G. From the known correlations between individual E values [4,42,73] the overall activation energy of crystallization is $E_{CR} = (aE_N + bE_G)/(a+b)$ and/or $E_{CR} = (aE_N + bE_D)/(a+b/2)$ [where the denominator equals the power exponent of the JMAYK equation, p, and the coefficients a and b indicate the nucleation rate (zero, $a = 0$; decreasing, $0 < a < 1$; constant,

$a = 1$; and increasing, $a > 1$) and the growth dimensionality ($b = 1$, 2 and 3), respectively]; this, however, is an ambiguous procedure introduced and analyzed by Šesták [42] and Ranganathan and Heimendahl [73], respectively.

To correlate experimental-kinetic and more rigorous thermodynamic data [4], the approach of Miura and Isa [75] can be considered, when assuming the free energy ($\Delta G_N^{\ddagger} \approx E_N$) of critical nucleus formation during homogeneous-like nucleation ($\approx 16\pi\gamma_{SL}^3/3\Delta G_{CR}^2$). For diffusion-controlled crystallization (of glassy metals) we can assume that $E_D \approx E_{CR} - E_N$ (if $E_{app} = E_{CR} \approx \Delta H^{\ddagger}$, the activation enthalpy) and calculate E_N by introducing the value of Gibbs (free) energy for crystallization (ΔG_{CR}) and the solid–liquid surface Gibbs (free) energy ($\gamma_{SL} \approx 0.4\Delta H_{melt} + 10^{-10}N^{1/3}(2.1 + \bar{V}^{2/3}/2)(T - T_{melt})$, where ΔH, N, $\bar{V}$ and T are the enthalpy, Avogadro number, molar volume and temperature, respectively.

Matusita and Sakka [68,81] proposed another approach, including a ratio factor, z/p, in their model for E, where z arises from the z-powered heating rate, ϕ, as the result of an assumption of non-exponential nucleation, proportional to the heating rate only ($N = N_0/\phi$). The activation energy thus calculated on the basis of the pre-assumed rate-controlling process (e.g., bulk crystallization of $Li_2O \cdot SiO_2$ glasses, where $p = 3$ and $z = 4$) under non-isothermal conditions, agrees well with that of viscous flow. For such treatment the ratio z/p is closer to unity than the original values of p so that a better coincidence between iso- and non-isothermal data can be anticipated. The course of these derivations has recently been reinvestigated [82] and also reconsidered on a more rigorous theoretical basis by Ozawa [83].

DISCUSSION

It can be seen from the preceding sections that DTA-based evaluation of crystallization kinetics is a very sensitive procedure. It evidently belongs to the methods of a formal (phenomenological) treatment and it thus requires further interpretation in terms of the thermodynamics of nucleation–growth processes and the structural and morphological description of the elementary reactions involved. A good example of a thoroughly analysed crystallization process already available is the case of As_2S_3 reported by Henderson and Ast [74], employing viscosity, microscopy and DSC measurements. Crystallization kinetics are satisfactorily described by the JMAYK equation yielding a constant power exponent ($p \approx 4.5$) which is interpreted in such a way that the nucleation rate is an increasing function of time for specific random primary nucleation along the coalescence-caused interfaces throughout the bulk of powdered samples, regardless of the initial powder size. Microscopic examinations reveal a spherulitic growth habitat with plate-like morphology changing at higher temperatures to rod-like growth. Activation energy evaluated from DSC measurements is comparable to that derived from direct

observation, but about half that for viscous flow, the latter being comparable to the activation energy assumed for secondary nucleation. This example by no means aims to discredit the many valuable articles dealing with formal crystallization kinetics. It is just a warning against both self-satisfaction with easily obtainable numerical results and oversimplified explanations of complex crystallization processes within a suppressed "double logarithmic" treatment of usually single-valued data on averaged temperatures [5,12,28,29,43]. For an improved interpretation of such thermometric (DTA and DCC) measurements we can learn a lot from experimental physically detected (complementary for thermoanalysts) magnetic and/or electric properties. Such measurements often exhibit a greater sensitivity in distinguishing partial reactions (e.g., Stobiecki [87] by measuring saturation magnetization determined, for isothermally annealed Fe–B layers, three different crystallization regions associated with either the growth of quenched-in nuclei or grain growth with constant and later decreasing nucleation rates). Upon analysing resistivity measurements [88–92] the authors had to solve the problem of how to express the extent of crystallization when the glassy matrix is partly transformed during the course of annealing and/or if the infinite (starting or final) values of the measured property are not known. It was found that the resistivity measurements of $Ge_{20}Bi_{15}S_{65}$ exhibit the course of crystallization much earlier than that detected by DTA [91] and it was suggested that experimental data should be evaluated without any restrictions of the functions g(α) by fitting individual experimental curves by the least-squares method [92].

In many cases, however, we have to rely on the classical methods of kinetic data evaluation, but being aware of certain precautions. For a series of isothermal measurements we should take into account possible crossover effects [58] which can create discrepancies otherwise difficult to explain in terms of an ordinary kinetic description. This can also disturb the annealing experiments further investigated under the non-isothermal regime. Quenching itself may also be regarded as partially achieved annealing (cf. T–T–T diagram in Fig. 3), namely, considering quenched-in nuclei. The popular logarithmic plotting on the basis of the JMAYK equation may exhibit the kinetic compensation effect [8] for a too narrow temperature interval which, in turn, disagrees with the approximation requirements for $k(T)$ integration [4]. If we were to rely solely on the low sensitivity of ln–ln plots to discriminate between the individual functional forms, the experimental data introduced would have to be of the highest quality which, however, contradicts the general method of DTA experimentation and the errors associated with it, as discussed above. Comparison of a series of non-isothermally obtained traces at different ϕ values (in order to extract the desired kinetic parameters of an assumed single process) can be affected by procedural parameters (sufficiently precise reproducibility of individual runs) as well as by both the extent of DTA temperature deviations (ΔT_{DTA}, cf. Fig. 2) which

unfortunately shifts the peak apex (affecting, e.g., the Kissinger method) and the advance of the heat inertia ($\Delta \dot{T}_{\mathrm{DTA}}$, cf. Fig. 1) which disturbs the slope of a DTA peak in the vicinity of its inflections (affecting, e.g., Piloyan and Ozawa methods).

For the future we can anticipate that the current kinetic treatment based on the evaluation of certain kinetic parameters, E and p (n, m), can possibly be replaced by an equally formal method of mathematical analysis in terms of fitting the whole (or part) of a DTA peak again attempting to obtain certain numerical values characterizing the peak shape. The change of such constants can then be used for the indication not only of switches from one crystallization mode to another, but also of physical processes of heat transfer. The present, rather trivial and so far non-gradient treatment of kinetic data evaluation, however, contradicts the sophisticated stage of computer science and the advanced theory of data evaluation for truly non-equilibrium conditions, which is our case of DTA.

LIST OF SYMBOLS

A, B	components
C_{p}	heat capacity
C	concentration
d	derivative
E	activation energy
H	enthalpy
f(α), g(α)	kinetic models
$k(T)$	Arrhenius rate constant
K	apparatus constant
m, n, p	kinetic power exponents
T	temperature
t	time
r	radius
Z	pre-exponential factor
α	degree of reaction
β	phase separation
λ	heat conductivity
$\Lambda(T)$	heat transfer coefficient
γ	surface energy

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ρ	density
δ	thickness
Δ	difference
ϕ	constant heating rate

Superscripts

$\char`\^{}$	function
$\cdot$	time derivative (e.g., reaction rate, $\dot{\alpha}$, actual heating rate, $\dot{T}$)

Subscripts

app	apparent
CR	crystallization
D	diffusion
DTA	differential thermal analysis
G	growth
i	arbitrary point
max	maximum
N	nucleation
s	sample
0	reference

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