# A REMARK ON THE APPLICABILITY OF DTA AND THE RELIABILITY OF NON-ISOTHERMAL DETERMINATION FOR THE CRYSTALLIZATION KINETICS OF GLASSES

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The most decisive phenomena arising either from specific DTA measurements (heat inertia, temperature deviation, self-heating) or from non-isothermal kinetic treatment (overlapping models, characteristics determinations) are discussed.

Most commercially produced DTA instruments can be described in terms of a double-non-stationary calorimeter in which the termal behaviours of the sample and of the reference material, usually placed in thermally insulated cells, are compared. From the balance of thermal fluxes, the DTA equation can be established between the measured quantity, i.e. the difference between the averaged temperatures of the specimens $\Delta T_{DTA}$, and the required reaction rate, $\dot{\alpha}$ ($= d\alpha/dt$), 2]:

$$\dot{\alpha} = -\Delta T_{DTA} \frac{K_{DTA}}{\Delta H} - \Delta \dot{T}_{DTA} \frac{C_{pS}}{\Delta H} - \varnothing \frac{\Delta C_p}{\Delta H} + \frac{\Delta K}{\Delta H} \tag{1}$$

Similar analysis yields the DSC equation, but now valid for the compensation thermal flux $\Delta \dot{Q}$ supplied to the specimens [1, 2]:

$$\dot{\alpha} = \Delta \dot{Q} \frac{1}{\Delta H} + \varnothing \frac{\Delta C_p}{\Delta H} - \Delta T_{mantle} \frac{\Delta \Lambda}{\Delta H} \tag{2}$$

However, the originally assumed difference $\Delta T_{DTA}$ now serves as a regulated quantity only to be as close to zero as possible. For well-tuned measuring conditions, the effects of the last two terms in each caloric equation can be neglected (i.e. the heating rate $\varnothing$, the change in thermal capacity $\Delta C_p$, the change in heat transfer $\Delta K$ and the change in heat conductivity $\Delta \Lambda$), and the temperature difference between the sample and the surrounding mantle, $\Delta T_{mantle}$, is constant and can therefore be included in the baseline. A primitive proportionality holds between the DSC recording and the rate of reaction, whilst the similar DTA relationship contains an additional term arising from thermal inertia. It is evident

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that the common plot of the logarithm of the peak deflection *vs.* the reciprocal temperature can be used only in the case of DSC, while for DTA it should be corrected, employing the modified form of the $\ln (K_{\text{DTA}} \Delta T_{\text{DTA}} + C_p \Delta \dot{T}_{\text{DTA}})$ *vs.* $(1/T)$ dependence, however, this has rarely been applied in practice [3]. Consequently, a simple derivation of the extent of reaction by simply relating the partial *vs.* total areas of a DTA peak is misleading, unless the actual *s*-shaped background of a peak is encountered. It can easily be found that the maximum deviation between the as-scanned and corrected peaks lies within its inflections. This certainly means difficulty in the simple application of evaluation methods based on a fixed extent of reaction taken for multiple DTA peaks measured at different $\varnothing$. On the other hand, the popular Kissinger method remains valid, because $\ddot{\alpha} = 0$, $\Delta \ddot{T} = 0$ and $\Delta T_{\text{DTA}} \geqslant \dot{\alpha}_{max}$, if, of course, there is no change in the thermal capacity of the investigated material, which is often fulfilled during the crystallization of glasses [3].

The applicability of individual methods of kinetic data evaluation should not be generally overemphasized. These methods rank into two groups, involving single or multiple non-isothermal runs, and can be based on two different procedures, requiring either the threefold input data $\alpha$, $\dot{\alpha}$, $T$ for the primitive rate law, or the twofold data $\alpha$, $T$ for the integrated form of the rate equation. The latter method is presumably less laborious, but also less sensitive as concerns both the experimental errors ($\dot{\alpha}$ is avoided) and the model relation distinguishability. In particular, the analytical forms of $\int d\alpha / f(\alpha) = g(\alpha)$ overlap each other for different rate-controlling processes, which in particular makes it impossible to distinguish the power exponents in the nucleation-growth $(J-M-A-Y-K)$ equation. Practical evaluation through integral methods is comparatively easy and thus popular, but requires certain assumptions about the behaviour of the exponent integral arising from the Arrhenius rate constant $k(t)$. Methods based on a fixed extent of crystallization $\alpha_i$ for a series of traces taken at different heating rates $\varnothing$ permit a plot of $\ln (T_i^2 / \varnothing)$ *vs.* $(1/T_i)$. A generally valid equation for $\varnothing$ at $\ddot{\alpha} = 0$ has been derived [4], although limited to a simplified case of a one-parameter model $(1 - \alpha)^n$:

$$\varnothing = -k(T) (df(\alpha)/d\alpha)_T / (d \ln k(T)/dT + (d \ln f(\alpha)/dT) )_A \qquad (3)$$

If $\varnothing$ is eliminated and the equation is transformed into the general equation of the rate for $\alpha_{max}$, assuming that $f(\alpha)$ is not $T$-dependent:

$$(\dot{\alpha}_{\varnothing})_{max} = -(d \ln k(T)/dT)_\alpha / (d \ln f(\alpha)/d\alpha)_T \qquad (4)$$

which finally gives

$$(\dot{\alpha}_{\varnothing})_{max} = -(E/RT_{max}^2) (1-\alpha)/n \qquad (5)$$

If this is extended for a two-parameter model $(1 - \alpha)^n \alpha^m$, the validity of the above equation can be generalized as follows:

$$(\dot{\alpha}_{\varnothing})_{max} = -(E/RT^2_{max})(\alpha(1-\alpha))/(\alpha(m+n)-m) \tag{6}$$

Both equations are valid for any point $\alpha_i$ and demonstrate that the slope $\dot{\alpha}_i$ of a kinetic curve is really related to the kinetic parameters $E$, $m$ and $n$. The temperature of maximum reaction rate $T_{max}$ is then dependent upon the heating rate applied, e.g.

$$d\varnothing/dT_{max} = k(T)(R + 2nRT_{max})/E \quad \text{(for } m = 0, \ n > 0) \tag{7}$$

which is close to the classical Kissinger plot derived originally for unimolecular reactions.

A relatively large deflection of a sharp DTA exotherm is typical evidence of a time-located heat production, as indicative for most crystallization processes [1]. Under limiting conditions, the heat transfer from the reaction zone may become a rate-controlling process, in which the reaction rate is assumed to depend upon the multiple of two functions $f(\alpha)$ and $\Lambda(T)$, but where $\Lambda(T)$ is introduced instead of the original $k(T)$, as a non-activated heat-exchange coefficient proportional to the temperature. An extreme example of such terminal conditions is an adiabatic process which can be assumed when the self-generated production of heat catalyses a very sharp crystallization process, where the heat exchange between the crystallizing glass, the sample holder and its surroundings is comparatively negligible with respect to the narrow duration of the reaction. The reaction rate then becomes directly proportional to the temperature change $\dot{T}$ displayed by the sample.

In conclusion, we can say that experimental arrangements relating to the thermophysics of glassy samples are often underestimated, although they may serve as the basis for any consequent evaluation of crystallization dynamics and mechanism [1, 3]. Corrections due to the effect of heat inertia and the temperature deviations during the crystallization indicated as a DTA peak are also generally neglected, although no satisfactory proofs are available to demonstrate a possible misfit of current kinetic treatments.

If there is a discrepancy between the various kinetic data evaluated on the basis of DTA measurements, it should not generally apply that neither DTA nor non-isothermal kinetics is a justifiable target of blame or rejection as an a priori source of error. Formal two even sometimes one parameter kinetic models seem suitable enough to satisfy the geometrical characterization of a DTA peak as regards the formal crystallization kinetics. A proper distinction between individual crystallization models, however, is rather difficult because of insensitive or overlapping

mathematical procedures, particularly due to the frequent double logarithmization. The utilization of isothermal kinetic models under non-isothermal conditions is acceptable [5], as the errors produced in this way are negligible in comparison with normal experimental inadequacies. Non-Arrhenius behaviour is not yet appreciated enough, although in some special cases it may govern the entire process of crystallization. However, the present rather trivial non-gradient treatment for kinetic data evaluation from DTA measurements is in contradiction with the sophisticated state of computer science and with the general theory of data evaluation for truly non-equilibrium conditions.

## References

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**Zusammenfassung** — Die entscheidensten Phänomene werden diskutiert, die entweder bei spezifischen DTA-Messungen (Wärmeträgheit, Temperaturabweichungen, Selbsterhitzung) oder bei der nicht-isothermen kinetischen Behandlung (überlappende Modelle, Charakteristikbestimmungen) auftreten.

**Резюме** — Обсуждены основные эффекты, проявляющиеся при специфических ДТА измерениях (тепловая инерционность, температурные отклонения, самонагрев) или же при неизотермической кинетической обработке (модельные дублирования, характеристические определения).