# ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations

CrossMark

Sergey Vyazovkin [a,*], Konstantinos Chrissafis [b], Maria Laura Di Lorenzo [c], Nobuyoshi Koga [d], Michèle Pijolat [e], Bertrand Roduit [f], Nicolas Sbirrazzuoli [g], Joan Josep Suñol [h]

[a] Department of Chemistry, University of Alabama at Birmingham, 901 S. 14th Street, Birmingham, AL 35294, USA
[b] Solid State Physics Department, School of Physics, Aristotle University of Thessaloniki, Macedonia, Thessaloniki 541 24, Greece
[c] Istituto per i Polimeri, Compositi e Biomateriali (CNR), c/o Comprensorio Olivetti, Via Campi Flegrei 34, Pozzuoli, NA 80078, Italy
[d] Department of Science Education, Graduate School of Education, Hiroshima University, 1-1-1 Kagamiyama, Higashi-Hiroshima 739-8524, Japan
[e] École Nationale Supérieure des Mines, Laboratoire Georges Friedel, CNRS UMR 5307, Centre SPIN, Saint-Étienne 42023, France
[f] AKTS Inc., Advanced Kinetics and Technology Solutions, TECHNOArk 1, Siders 3960, Switzerland
[g] Université Nice Sophia Antipolis, Laboratoire de Physique de la Matière Condensée, Equipe Fluides et Matériaux Complexes, CNRS UMR 7336, Parc Valrose Nice Cedex 2 06108, France
[h] Departament de Física, Universitat de Girona, Girona, Catalonia 17071, Spain

## ARTICLE INFO

## ABSTRACT

The present recommendations have been developed by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC). The recommendations offer guidance for obtaining kinetic data that are adequate to the actual kinetics of various processes, including thermal decomposition of inorganic solids; thermal and thermo-oxidative degradation of polymers and organics; reactions of solids with gases; polymerization and crosslinking; crystallization of polymers and inorganics; hazardous processes. The recommendations focus on kinetic measurements performed by means of thermal analysis methods such as thermogravimetry (TG) or thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). The objective of these recommendations is to assist a non-expert with collecting adequate kinetic data by properly selecting the samples and measurement conditions.

## Foreword

The previous project by the ICTAC Kinetics Committee was focused on producing recommendations for performing efficient kinetic computations [1]. The development of the present recommendations was initiated by the chairman of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee, Sergey Vyazovkin. The initiative was first introduced during the kinetics workshop at the 15th ICTAC Congress (Osaka, Japan, 2012) and further publicized during the kinetics symposium at the 37th NATAS Conference (Bowling Green, USA, 2013). The present team of authors was collected immediately after the NATAS conference and included individuals having extensive expertise in kinetic treatment of thermal analysis data. The team was led by Vyazovkin, who is listed as the first author followed by other team members listed in the alphabetical order. The specific contributions were as follows: 1. Introduction (Vyazovkin); 2. Thermal decomposition of inorganic solids (Koga); 3. Thermal and thermo-oxidative degradation of polymers and organics (Chrissafis); 4. Reactions of solids with gases (Pijolat); 5. Polymerization and crosslinking (Sbirrazzuoli); 6. Crystallization of polymers (Di Lorenzo); 7. Crystallization of inorganics (Suñol); 8. Hazardous processes (Roduit). The draft document was sent to a number of expert reviewers with a request to provide comments. The comments were received from nineteen individuals. The authors tried their best to implement all reviewers' suggestions while keeping the document consistent with its major objective, which was to provide a newcomer to the field of the thermal analysis kinetics with pragmatic guidance for efficiently collecting experimental kinetic data for most common thermal processes.

* Corresponding author. Tel.: +1 205 975 9410; fax: +1 205 975 0070.
E-mail address: vyazovkin@uab.edu (S. Vyazovkin).

## 1. Introduction

The use of efficient techniques [1] for performing kinetic computations does not guarantee obtaining good kinetic results. It is also necessary to have good kinetic data. The question is what constitutes good kinetic data? The most general answer is very simple: the data are good as long as they adequately represent the process kinetics. Unfortunately, the reasons that can make kinetic data inadequate to the process kinetics are numerous and specific to the process. Because it is not practically possible to provide recommendations for every existing process, the present recommendations follow a simple track. First, they address typical problems that can violate the aforementioned adequacy for any type of a process. Then, they address the problems that are specific to the most commonly studied types of processes, both physical and chemical. It is, therefore, believed that the present set of recommendations should be sufficient to cover the majority of typical cases as well as to extend them to other types of processes.

Let us first define what kinetic data are. Generally, any physical property whose change is measured as a function of time can be a source of kinetic data. In the area of thermal analysis, kinetic data are collected most commonly by measuring changes in either heat (calorimetry) or mass (thermogravimetry). Regardless of the physical property, the measured changes are converted to dimensionless value, called the extent or degree of conversion, $\alpha$. For any physical property that is linearly proportional to the progress of a process, $\alpha$ is defined as:

$$\alpha = \frac{\xi_i - \xi}{\xi_i - \xi_f}$$

where $\xi$ is current, $\xi_i$ is initial, and $\xi_f$ is final value of the measured property. The resulting $\alpha$ value varies from 0 to 1. Before the process starts and the respective physical property begins to change (i.e., $\xi = \xi_i$), $\alpha$ is 0. When the process ends and the physical property stops changing (i.e., $\xi = \xi_f$), $\alpha$ is 1. Any intermediate value of $\alpha$ represents the process progress at a given moment of time and is determined via a fractional change in the property measured. For example, if the progress is measured as a change in mass using thermogravimetry (TG), $\alpha$ is determined as a ratio of the current mass change to the total mass change that has occurred throughout the process. Respectively, when the progress is measured as a change in heat using differential scanning calorimetry (DSC), $\alpha$ is evaluated as a ratio of the current heat change to the total heat released or absorbed in the process. Note, when TG or DSC curves reveal the presence of distinct steps, one should consider treating these steps as individual processes, for which $0 < \alpha < 1$. Another note of caution is that in some specific cases $\alpha$ may be greater than zero before the beginning of the experiment. This is due to the aging process that takes place since the moment the material was created until the beginning of the thermal analysis experiment. Aging is especially important for autocatalytic reactions and may affect their course dramatically. If $\alpha$ represents the process progress, its first derivative with respect to time, $d\alpha/dt$, represents the process rate. For the purpose of the present recommendations, the kinetic data are a dependence of $\alpha$ or $d\alpha/dt$ on time. When the runs are performed under non-isothermal conditions, the kinetic data are customarily presented in the form of a dependence of $\alpha$ or $d\alpha/dt$ on temperature.

The problems that violate the adequacy of the kinetic data to the process kinetics can be related to the two aspects of kinetic measurements: sample and instrument. This categorization naturally follows from the way kinetic data are collected (Fig. 1). A process is confined to the sample so that the sample parameters necessarily affect the process conditions. On the other hand, the sample is exposed to a set of conditions controlled by the instrument. That is, the adequacy of kinetic data can be violated when either sample or instrument defined conditions are controlled poorly. The instrument defined conditions are the temperature, the rate of temperature change (i.e., the heating or cooling rate), the gas atmosphere and its flow rate, and the pressure. The sample defined conditions involve sample form and size as well as a sample holder (pan or crucible). Typical samples used in thermal analysis are solids or low volatility liquids. Solid samples can be prepared in several forms such as: a single chunk or crystal, powder, and film. Sample holders are cylindrical thin wall pans made of metal (aluminum, steel, copper, gold, and platinum) or nonmetal (glass, quartz, and alumina). The volume is usually around 20–100 μL. The pan size limits the sample size, which normally is from a few to tens of milligram. Samples can be run in the pans that are either completely open, or hermetically closed, or covered by a lid with a pinhole.

By taking a closer look into the nature of kinetic data, it is easy to understand how sample and instrument related problems can invalidate collecting of adequate kinetic data. According to the general rate Eq. (1) of a single-step process:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \tag{1}$$

the overall rate, $d\alpha/dt$, is a function of $\alpha$ as well as of two other variables: the temperature ($T$) and the pressure ($P$). The dependence of the process rate on temperature is represented by the rate constant $k(T)$ that is typically represented by the Arrhenius equation. The dependence on $\alpha$ is defined by the reaction model, $f(\alpha)$, which can take a variety of mathematical forms (Table 1). The pressure dependence is also expressed in various mathematical forms [1]. Experimentally measured rate is adequate to the actual process kinetics only when the process variables ($\alpha$, $T$, and $P$) are controlled accurately and precisely. It should be emphasized that for most of real life processes Eq. (1) is a rather large oversimplification of reality than the rule to obey. Real processes tend to include more than a single step. Ways to deal with multi-step processes have been addressed in the previous set of recommendations [1].

A specific point of concern is the pressure control. Although pressure controlled instruments are commercially available, most of the commonly manufactured instruments operate under ambient pressure of a flowing inert or reactant gas, which is adequate to majority of kinetic studies. However, one should be aware that the pressure dependence of the process rate may dramatically affect the kinetics of processes that involve gaseous reactants and/or products. For instance, the rate of oxidation and reduction depends on the partial pressure of the respective gaseous oxidant and reductant. In decomposition of energetic
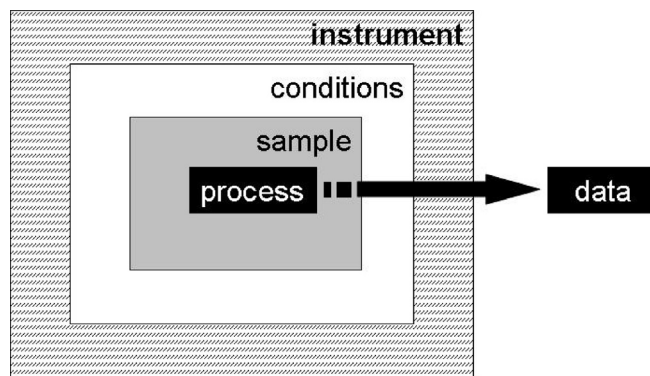


**Fig. 1.** Although the data are expected to represent adequately the process, they are unavoidably affected by the sample, conditions, and instrument that may distort the adequacy of the representation.

**Table 1**
Some of the kinetic models used in the solid-state kinetics.

|   | Reaction model | Code | $f(\alpha)$ | $g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1}\,d\alpha$ |
|---|---|---|---|---|
| 1 | Power law | P4 | $4\alpha^{3/4}$ | $\alpha^{1/4}$ |
| 2 | Power law | P3 | $3\alpha^{2/3}$ | $\alpha^{1/3}$ |
| 3 | Power law | P2 | $2\alpha^{1/2}$ | $\alpha^{1/2}$ |
| 4 | Power law | P2/3 | $2/3\alpha^{-1/2}$ | $\alpha^{3/2}$ |
| 5 | Mampel (first order) | F1 | $1-\alpha$ | $-\ln(1-\alpha)$ |
| 6 | Avrami–Erofeev | A4 | $4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$ | $[-\ln(1-\alpha)]^{1/4}$ |
| 7 | Avrami–Erofeev | A3 | $3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$ | $[-\ln(1-\alpha)]^{1/3}$ |
| 8 | Avrami–Erofeev | A2 | $2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$ | $[-\ln(1-\alpha)]^{1/2}$ |
| 9 | Contracting sphere | R3 | $3(1-\alpha)^{2/3}$ | $1-(1-\alpha)^{1/3}$ |
| 10 | Contracting cylinder | R2 | $2(1-\alpha)^{1/2}$ | $1-(1-\alpha)^{1/2}$ |
| 11 | One-dimensional diffusion | D1 | $1/2\alpha^{-1}$ | $\alpha^2$ |
| 12 | Two-dimensional diffusion | D2 | $[-\ln(1-\alpha)]^{-1}$ | $(1-\alpha)\ln(1-\alpha)+\alpha$ |
| 13 | Three-dimensional diffusion (Jander) | D3 | $3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$ | $[1-(1-\alpha)^{1/3}]^2$ |
| 14 | Three-dimensional diffusion (Ginstling–Brounshtein) | D4 | $3/2[(1-\alpha)^{-1/3}-1]^{-1}$ | $1-2/3\alpha-(1-\alpha)^{2/3}$ |

materials, the gaseous products are frequently reactive toward the decomposing substance leading to autocatalytic acceleration of the reaction rate. The rate of reversible decompositions can demonstrate a strong dependence on the partial pressure of the gaseous products. If the partial pressure of the gaseous reactant and/or product is not controlled, it is equivalent to assuming that $h(P)$ remains constant throughout an experiment. If a reaction is pressure dependent, this condition can be satisfied by supplying a large excess of a gaseous reactant in solid–gas reactions and/or by effectively removing reactive gaseous products in reversible and autocatalytic reactions. The actual constancy of $h(P)$ can be readily checked by performing a few runs at significantly different flow rates. For a solid–gas reaction, one should vary the flow rate of reactive gas e.g., oxygen in a reaction of oxidation. For reactions producing reactive gaseous product, one should vary the flow rate of the purge gas. If the kinetic data i.e., the curves of $\alpha$ or $d\alpha/dt$ vs. time do not demonstrate any systematic shifts with increasing the flow rate, the assumption, $h(P) = $ constant, holds. A systematic change may take place at low flow rates but cease at the higher values; therefore, revealing the threshold flow rate at which the condition, $h(P) = $ constant, is fulfilled. If it is not fulfilled, the unaccounted variation of $h(P)$ may reveal itself through a variation of kinetic parameters with the temperature and/or conversion as frequently is the case of reversible decompositions studied not far from equilibrium [2]. As a note of caution, the flow rate should be varied within the limits specified by the instrument manufacturer.

The good instrumental control of $\alpha$ means accurate measurements of the values that give rise to $\alpha$ i.e., the mass in TG and heat in DSC. In either case, the accuracy is accomplished via proper calibration. The heat calibration of DSC is accomplished by measuring the heats of some reference process, typically the heats of melting of certain metals (indium, zinc, aluminum, etc.). The TG analytical balance (thermobalance) is usually capable of self-calibration, although some models may require the use of reference masses. The regular mass calibration is, however, insufficient for collecting accurate TG data because it is normally done at an ambient temperature. Such calibration does not account for the temperature variability of the upward buoyant (Archimedes) force. It equals the sample volume times the density of surrounding gas times the acceleration of gravity. As temperature rises, the density of the gas surrounding the sample decreases; therefore, reducing the buoyancy force so that the sample mass appears increasingly heavier (Fig. 2). The resulting systematic error must be eliminated by first performing a blank TG run with an empty sample pan and then subtracting the resulting blank TG curve from the TG curve measured by having placed a sample in

this pan (Fig. 2). Both runs must obviously be conducted under identical conditions. Another key to accurately measuring masses, especially when the sample is prone to oxidation, is efficiently removing air before performing TG measurements. It is accomplished by closing TG with the sample inside and purging the whole setup with an inert gas for at least 20–30 min before starting the actual heating program.

A good control of the sample (i.e., process) temperature may provide a significant challenge that is only partially addressed by proper temperature calibration of the instrument. The sample temperature is determined by the conditions of heat transfer between the furnace and sample. The instrument controls the heat supply to the sample. Below 800 °C [3], this occurs primarily by heat conductance i.e., through direct contact between the sample and the sample pan as well as the sample and the gas atmosphere. When the furnace temperature changes, the sample temperature lags behind because it takes some time for heat from the furnace to become transferred into the sample. The time and the resulting temperature lag increase with increasing the rate of temperature change (i.e., heating or cooling rate) as well as with decreasing the thermal diffusivity (which is proportional to the thermal conductivity) of the gas atmosphere, pan material, and sample substance. The temperature lag is accounted for by temperature calibration. The latter is typically accomplished by measuring the phase transition temperature in reference materials. Melting
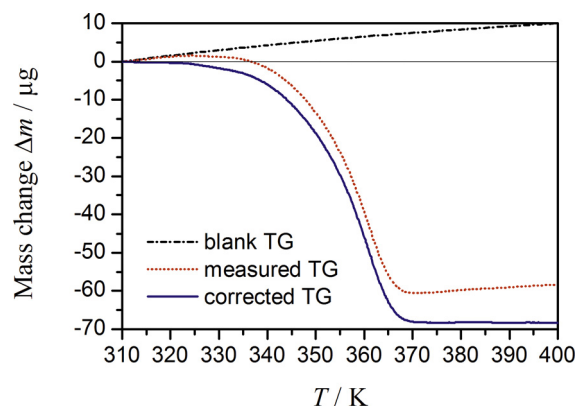


**Fig. 2.** TG curves for an empty Pt pan (blank TG) and 555 mg sample of calcium oxalate monohydrate placed in this pan (measured TG). Corrected TG is obtained by subtracting blank TG from measured TG. The TG curves recorded using a suspended TG (TGA-50, Shimadzu) under heating rate of 0.5 K min⁻¹ in flowing $N_2$ (80 cm³ min⁻¹).

temperatures of metals are used most commonly for calibration of DSC as well as of TG instruments capable of measuring the differential thermal analysis (DTA) or DSC signal. Otherwise, the temperature calibration of TG instruments is done by heating ferromagnetic materials (e.g., alumel, nickel, cobalt, etc) in a sample pan while placing a magnet under or above the furnace [4]. The temperature of the mass jump detected at the ferromagnetic to paramagnetic transition is then identified with the well defined Curie temperature of the material. An alternative is to use a dropping weight (platinum coil) connected to the balance beam by a fusible link, which is a thin wire made of melting point metal standard [5].

The temperature calibration is done under, and thus, holds for certain heat transfer conditions: heating rate, gas atmosphere, pan material, and sample substance. For this reason, the calibration should be performed under the conditions that are very close to the conditions of the actual kinetic measurements. In particular, this means that when nonisothermal kinetic measurements are conducted at several heating rates, the calibration must be performed in the whole range of the heating rates used. Using sample pans of the same material and size as in calibration are an easy condition to satisfy. Maintaining the same gas atmosphere is more difficult when the sample decomposes producing large quantities of gases whose thermal conductivity is significantly poorer that that of the purge gas. The thermal conductivity of a gas decreases with increasing the square root of its molecular mass. That is, the formation of heavy gas products (e.g., $CO_2$, $NO_2$, organic gases) may become a concern, especially when the calibration was performed in a highly conductive purge gas as helium. It is generally advisable to minimize the amount and rate of the gaseous products generation by respectively keeping the sample mass smaller and the reaction rate slower as well as to maximize the efficiency of the gaseous products removal by maintaining sufficiently fast flow rate of a purge gas. It is also difficult to satisfy the last condition i.e., to calibrate the instrument by using substances whose thermal conductivity is similar to that of the sample of interest. As mentioned earlier, typical calibrants are metals that conduct heat much faster than inorganic and, especially, organic and polymeric samples. Slower heat transfer within the material sample can potentially lead to a significant temperature lag unaccounted by calibration.

In addition to the difference in the thermal diffusivity of the calibrant and sample, the temperature calibration does not account for the sample self-heating/cooling due to the thermal effect of the process. That is, the slow exchange of the process heat with the surroundings can make the sample temperature deviate significantly from the furnace temperature. It can also cause significant temperature gradients inside the sample. These effects can be reduced by adjusting the sample size and its form. To secure quick and uniform distribution of heat, and thus, to minimize the temperature gradients inside the sample, the latter should form a thin (not thicker than a few hundred micron) uniform layer on the pan bottom. The small thickness of the sample is critical considering that the sample is likely to be the slowest heat conductor in whole experimental assembly. The temperature gradient inside the sample, $\Delta T$, i.e., the difference between the temperature in the middle of a sample and the temperature on its surface, which is equal to the furnace temperature, can be approximately estimated as follows. Assuming that a sample is shaped as a flat layer of the height $h$, the time for heat transfer from the surface to the middle is

$$t = \frac{h^2}{4\lambda}$$

where $\lambda$ is the sample thermal diffusivity. If the furnace temperature changes at the rate $\beta$, the temperature gradient is estimated to be:

$$\Delta T = \frac{\beta h^2}{4\lambda}$$

To minimize the errors in evaluation of the kinetic parameters, it is recommended to select the sample thickness and heating (cooling) rate so that the temperature gradient does not exceed a few degrees (for details see Section 8, Fig. 18).

The flat shape is naturally assumed by liquids unless they are highly viscous, in which case they should be pressed against the pan bottom. If solid is readily soluble in some solvent, it can be prepared in the form of a thin layer by dropping the solution in the pan and heating it to vaporize the solvent. When using this technique, one needs to make sure that the solvent is stable on heating because some solvents may decompose and form highly reactive radical species. In this case, the traces of the residual solvent left after vaporization may affect dramatically decomposition of the resulting solid. Poorly soluble materials such as certain semi-crystalline polymers can be heated to some temperature between the temperatures of the glass transition and melting and then pressed against the pan bottom once softened. Similar procedure can be applied to melted samples. In either case, care should be exercised because many substances start to decompose close to their melting temperatures. If dissolution and softening are not an option, a solid sample can be prepared by mechanical action such as grinding, milling, sawing, etc. Once the sample is reduced to fine powder, it can be spread thin on the pan bottom.

The sample temperature deviations associated with self-heating/cooling are effectively reduced by accelerating exchange of the process heat with the surroundings as well as by decreasing the total amount of process heat and the rate of heat release or consumption. The heat exchange with the surroundings is accelerated by using high diffusivity pan materials and purge gases. For most common pan materials, the thermal diffusivity decreases approximately 200 times in the following sequence: Al, Pt, $Al_2O_3$, steel, quartz, and glass. Regularly used gases (nitrogen, argon, air, and oxygen) conduct heat about as fast as Pt. However, the thermal diffusivity of helium is about twice that of Al. The use of helium as a purge or carrier gas can be considered as a way to improve the rate of heat transfer in TG runs. In DSC, the use of helium is undesired because it causes a decrease in the instrument sensitivity. The rate of heat release or consumption can be readily reduced by decreasing the temperature of isothermal run or the heating rate of a nonisothermal one. The total amount of heat is decreased by decreasing the sample mass. It is generally advisable to keep the sample mass as small as possible. The sensitivity of modern thermal analysis instruments is such that one rarely needs more than a few mg of a sample. The only practical concern with using small masses is the representativeness of the samples in the case of composite materials, in which some minor component amounts to a very small mass fraction. In such a case, the actual amount of such component in a small sample can fluctuate significantly between the samples due its non-uniform distribution throughout the material. Then, the minimum sample size should be figured out based on the material structure and composition.

The aforementioned methods allow one to lower the temperature gradients within the sample as well as to minimize deviations of the sample (process) temperature from the reference (furnace) temperature. While smaller, the sample temperature deviations, and gradients would still be present as long as a process is accompanied by a thermal effect. Therefore, one should always be advised to check the sample temperature against the reference one. Modern thermal analysis instrumentation allows one to access both temperatures. A deviation between the sample and reference temperature is acceptable when it does not exceed a few degrees (see Section 8,

Fig. 18 and related discussion). The smaller the deviation the better the sample temperature represents the process temperature, and thus, the more adequate kinetic data are. It is the best practice to use the sample temperature in kinetics calculations. The computational methods that permit directly using the sample temperature are described in the previous set of recommendations [1].

As discussed earlier, keeping the process rate slower has clear benefits in terms of maintaining accurate control of the process temperature. Slower process rate is accomplished by using lower temperatures in isothermal runs and slower temperature changes in nonisothermal runs.

Reliable determination of the Arrhenius parameters requires one to conduct runs at three or more temperatures or heating rates. It must be kept in mind that the use of only three temperature programs would result in the Arrhenius or a similar linear plot that has only three points on it. In statistical terms, such a plot can be accepted as linear with 95% confidence only when its respective correlation coefficient, $r$ is more than 0.997 ($r^2 = 0.994$), which is frequently not the case. That is why four–five runs at different temperatures or heating rates should normally be carried out. A statistical argument can be raised that the precision of estimated Arrhenius parameters can be increased by performing replicate measurements at only two (the lowest and highest) heating rates or temperatures. However, the absence of intermediate points between the two extremes would not allow the Arrhenius type plots to reveal possible nonlinearity that is an important source of kinetic information [6–10]. Therefore, the use of multiple (no less than four) heating rates or temperatures offers an extra benefit.

Particular values of temperatures and heating rates should be selected so that a process of interest is studied in a reasonably wide temperature range. Note that the quality of kinetic evaluations increases with increasing the width of the range of the reciprocal temperatures. That is, when a process occurs at higher temperature, one would need to perform runs in wider temperature range than when process takes place at lower temperature. Typically, the temperature range should not be less than 20–40 °C. This condition is easy to satisfy in nonisothermal runs because a single run normally covers a rather wide temperature range. As a rule of thumb, doubling the heating rate causes the kinetic curve to shift to higher temperature by 10–15 °C. Typically, one can cover sufficient temperature range by varying the heating rates so that the fastest one is about 10–15 times larger than the slowest. Most commonly, the heating rates are selected to be within the range 1–20 °C min$^{-1}$. The initial and final temperature of a nonisothermal run should be selected with regard of the actual temperature range of the process. The idea is to measure reliably the baseline signal before the process starts and after it ends. It is a good routine to start heating ∼50 °C below the temperature at which the process starts and finish it ∼50 °C above the temperature at which it ends.

Conducting good isothermal runs can be more challenging because of the unavoidable heat-up period. This is the time during which the sample reaches the preset isothermal temperature. Depending on the instrument response time and sample size, it may take up to a few minutes before the sample stabilizes at the preset temperature. Inevitably the sample transforms during the heat-up period. Thus, by the time the isothermal measurements start to be taken, the $\alpha$ value is already not zero. The size of the effect depends on the process type. For a process with an induction period, aging may shorten its length. It can be even more dramatic for decelerating processes (reaction-order type processes) [1], whose rate is the fastest at the lowest conversion. Since the reaction during the heat-up period cannot be eliminated, it must be minimized by selecting the maximum isothermal temperature so that the total process time is significantly longer than the heat-up time. For example, if the heat-up time is about 1 min, an appropriate maximum temperature should be such that the process proceeds to completion in about 1 h. The heat-up and completion time can be estimated from a trial run conducted at some reasonable temperature. The latter is best determined from quick nonisothermal measurements. It typically lies in the temperature range of the initial process stages ($0.05 \leq \alpha \leq 0.10$) under nonisothermal conditions. Once the total process time is determined at a trial temperature, it can be scaled to a desired time by a simple rule: changing temperature by 10 °C increases the process rate two–three times. Note that this rule is approximate and works for the processes that occur at moderately high temperatures (100–300 °C) and have the activation energy in the range 100–200 kJ mol$^{-1}$. For processes taking place at significantly larger temperatures, the rate increase per 10 °C would be markedly smaller. The rule obviously suggests that once the maximum temperature selected so that a process completes in 1 h, at 20 °C lower temperature this process would run for about 4–9 h. The problem with using low temperatures is that, as the process approaches completion, its rate may become too slow to detect reliably when it is finished. Similarly, if a process has an induction period, it may be difficult to detect its beginning. Although isothermal kinetics data usually are easier to analyze and interpret, obtaining good isothermal data typically take more time and effort than in case of nonisothermal runs.

When selecting the temperature range for kinetic experiments, one should be mindful of possible phase transitions that a reactant may undergo within that range. For example, a solid compound can melt. The respective rates and Arrhenius parameters for solid and for liquid state decomposition can differ significantly [11], although there may be cases [12] when they remain practically identical. Significant changes in the reactivity may also occur due to the morphological solid–solid phase transitions, the phenomenon known as the Hedvall effect [13,14]. Therefore, combining kinetic data collected in the temperature ranges below and above the phase transition temperature may lead to estimating questionable kinetic parameters. Since the aforementioned phase transitions are undetectable by TG, it is recommended that TG measurements be always complimented by a DSC (or DTA) run that would allow such transitions to be revealed.

## 2. Thermal decomposition of inorganic solids

The thermal decomposition of inorganic solids refers to reactions of the type: A(s) → B(s) + C(g). The kinetics of the thermal decomposition of solids is heterogeneous and as such it differs from classical homogenous kinetics in two aspects [15,16]. One is a non-uniform distribution of reactive sites in the reactant A(s). The other is possible interactions between A(s) and C(g) as well as between B(s) and C(g) that can control the kinetics of the decomposition of A(s) and formation of B(s) and C(g). Considering the diversity of the reaction situations, a number of physico-geometrical reaction models, $f(\alpha)$, have been derived for reactions under isothermal conditions [17]. Some of these models are shown in Table 1. The models are usually derived under oversimplified assumptions that a solid reactant is single crystal of a well defined geometry. Any possible changes that occur in the reactant as well as an effect of the generated products are typically ignored [18]. If the application of the simplified models is quite limited in the case of isothermal kinetics, it may be even more problematic when decomposition takes place under nonisothermal conditions.

Further complexities arise when studying the kinetics of polycrystalline solids. In this case, the simplified kinetic models are directly applicable only when the reactant particles are all of practically the same size and shape so that they all have the same degree of the reactant conversion throughout the decomposition. Such a condition is hard to realize in practice. Large variability in the particle size and shape may affect significantly the overall

kinetics of decomposition [19]. The occurrence of a temperature gradient inside a solid sample is another problem unaccounted for by the simplified kinetic models. The problem is caused by non-uniform heating of individual solid particles as well as by self-cooling or self-heating due to the thermal effect of decomposition [20] (the issue is discussed in more detail in Section 8). In addition, a gradient in the partial pressure of C(g) can arise inside the sample due to the gross diffusion of the gas as it is removed from the reaction system [21], which is yet another issue unaccounted for by the simplified kinetic models. The occurrence of the aforementioned gradients further increases the variability of the degree of conversion among the sample particles.

The kinetics of thermal decomposition of solids is most commonly studied by TG that allows one to track changes in sample mass as a function of time and temperature. Modern TG instruments feature high performance and large variety of temperature control modes. However, the reliability of kinetic data is not determined by instrument performance alone. When measuring the kinetics of processes that involve solid and gas phases the temperature and partial pressure uniformity must be maintained within the sample during the course of the entire process.

It is important to note that TG does not directly measure either the sample temperature or the partial pressure of the evolved gas in the sample assembly. The sample temperature is measured in close proximity of the sample (suspended TG instrument) or on the bottom of a sample pan (supported TG instrument) without considering any possible temperature gradients within the sample. The measurements are usually performed in a flow of an inert purge gas. Once the thermal decomposition of the sample starts, the steady state conditions are perturbed by the reaction heat and the evolution of a product gas. These perturbations cause gradients in temperature and partial pressure of the evolved gas within the sample. When the sample is a powder, these gradients give rise to the variability of the degree of conversion among the sample particles.

For collecting adequate kinetic data, it is preferable to maintain the conditions that secure a moderate decomposition rate and immediate removal of the evolved gas. The major controlling factors are the sample mass, gas atmosphere, and heating conditions (e.g., temperature and/or heating rate). These factors are not independent, and the ranges of their variability are limited by the instrumental and procedural reasons as well as by the properties of the solid reactant and the reaction parameters. Accordingly, it always takes some preliminary optimization of reaction conditions to enable obtaining adequate kinetic data.

To secure proper function of a TG instrument, it must be placed on an anti-vibration table. Additionally, noises caused by electricity must be eliminated. The configuration of the instrument (supported vs. suspended) must be known in order to understand how the sample temperature is measured. Furthermore, the points of gas flow delivery and its directions need to be known for efficient realization of the removal of the reaction product gases and purging the balance system. Once the measurement conditions are selected after considering a number of factors described below, it is advisable to recalibrate the instrument under this selected set of conditions prior to performing the actual kinetic measurements. A blank run on an empty pan should also be performed under this set of conditions in order to eliminate properly the buoyancy effect from TG curves (Fig. 2). Alternatively, instead of using an empty pan one may consider conducting a blank measurement on a sample pan loaded with the same volume of a thermally stable material (e.g., $Al_2O_3$) as that used for the actual sample.

Detailed characterization of the solid reactant and reaction products, including their crystallographic characteristics, is a fundamental requirement for any kinetic study. The reaction pathway and possible formation of intermediates during the reaction must also be carefully investigated using a range of analytical techniques. Because the direct application of Eq. (1) assumes that the reaction rate is limited by a single reaction step (rate-determining step), any possible overlap of multiple reaction steps must be known before conducting any kinetic analysis. This basic information about the sample and the decomposition reaction is vital for successful kinetic measurements and subsequent kinetic analysis [22]. Furthermore, careful microscopic observations of changes in the sample morphology during the reaction greatly aid when interpreting the kinetic results in terms of physico-geometrical reaction models [23,24].

TG measurements are performed on samples placed in a sample pan. The pan should be selected so that the pan material (e.g., Pt, Ag, Al, $Al_2O_3$ ceramics, silica glass, and others) does not react with the sample or catalyze the reaction. The material must be thermally stable within the temperature range of measurements and have high thermal conductivity. The preferred shape of the sample pans is cylindrical with a small ($<1$) height to diameter ratio that secures effective removal of the evolved gases formed during the reaction. On the other hand, a closed pan with a pierced lid can be used for studying the thermal decomposition process under quasi-isobaric conditions. For measurements using a suspended TG, a metal wire and mesh can be used to support a large block sample such as a single crystal or pellet. Regardless of the sample form, a single crystal or powder, a smaller sample mass is preferred because it generates a smaller amount of gas and heat during the reaction, and thus, reduces the partial pressure and temperature gradients. When using a fine powder sample, the sample mass must be reduced so that the sample particles are spread on the pan bottom in a thin layer, ideally as thin as possible. In principle, when all sample particles react uniformly i.e., without any variability in the degree of conversion between them, the experimentally measured mass loss curves should be independent of the sample mass after being converted to the form conversion vs. time or temperature. However, this is seldom to observe in practice. More commonly, the shape and position of the TG curves vary with the sample mass and the thickness of the sample particle layer [25]. It should be noted that the influence of the sample mass on the TG curves may vary depending on the reaction type (Fig. 3). For a reaction in which the interactions between the gaseous product and either the solid reactant or the solid product are not significant during the thermal decomposition, the mass loss curves vary rather moderately with the sample mass (Fig. 3a). On the other hand, a significant systematic variation in the mass loss curves for samples of different masses is observed when the gaseous product reacts with the solid product (Fig. 3b).

In practice, a sample mass that gives rise to a mass loss of about 1 mg is usually a good choice for the first run. To confirm the appropriateness of the selected sample mass, the second run is performed under the same measurement conditions using about half the original sample mass. If there is a significant difference between the mass loss curves for the first and second runs, further reduction of the sample mass may be necessary. When obtaining a series of kinetic measurements at several constant temperatures or heating rates, the sample mass should be kept practically the same within the series.

TG measurements are usually carried out in the flow of an inert gas, such as nitrogen and argon. It is recommended that the gas be passed through a drying tube with a desiccant before entering into the instrument. For samples very sensitive to oxidation, the residual oxygen in a TG instrument can be removed by repeated evacuating and filling with an inert gas passed through an oxygen getter material placed in the flow path of the inert gas.

The efficiency of the gas products removal depends on the choice of the purge gas, its direction and flow rate. The direction of
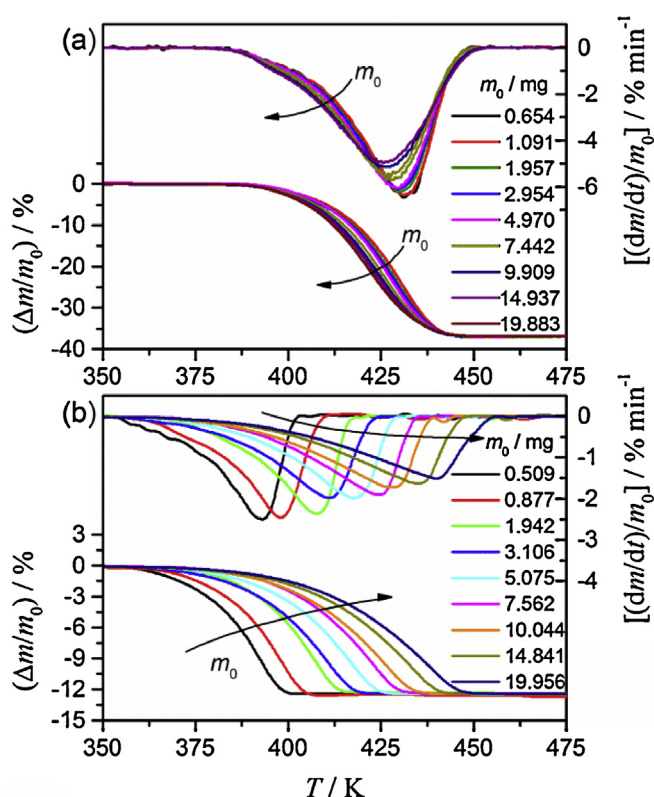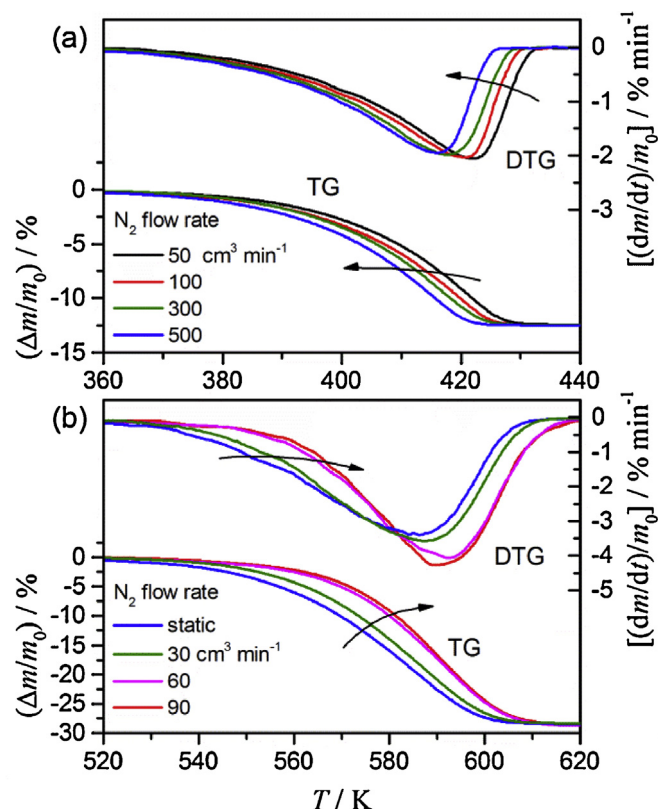
**Fig. 3.** Effect of sample mass on the experimental mass loss curves recorded using a horizontal supported TG (TG–DTA SSC5200, SII) under linear nonisothermal conditions at a heating rate of 5 K min$^{-1}$ in flowing N$_2$ (300 cm$^3$ min$^{-1}$). (a) Thermal decomposition of sodium hydrogen carbonate and (b) thermal dehydration of calcium oxalate monohydrate.

the gas flow is determined by the instrument configuration. The most effective removal of the evolved gases is observed for vertical supported TG instruments when the inert gas flows from the bottom to the top, which is the natural direction of a hot gas flow. In a horizontal TG instrument, the removal effect of the gas flow is more limited, and thus, a larger flow rate must be applied. However, while a larger flow rate of inert gas is preferable for achieving faster removal of the evolved gas, the applicable flow rate is limited by instrumental factors. Typically, an inert gas flow rate close to 100 cm$^3$ min$^{-1}$ is used in the vertical TG instruments. A two–three times faster flow rate is employed in the horizontal TG systems. Regardless of the instrument type, the effect of the flow rate on the experimentally measured mass loss curves varies with the type of decomposition reaction (Fig. 4). For a reversible reaction an increase in the flow rate would promote the removal of the gaseous products, and therefore, would accelerate the reaction shifting its temperature range to lower temperatures (Fig. 4a). However, for reactions that can be catalyzed by gaseous reaction products an increase in the flow rate causes the opposite effect i.e., the temperature range shifts to high temperatures because of more effective removal of the gaseous product [26] (Fig. 4b).

The heating conditions strongly affect the reliability of the mass loss kinetic data, because they directly affect the reaction rate. Classical isothermal measurements are a good approach for maintaining moderate reaction rates, which are preferable for kinetic studies. Although initiation of the reaction before reaching the preset constant temperature (i.e., during the warm-up period) presents a problem with the isothermal measurements, it can be partially resolved with the aid of computational kinetic methods capable of treating data obtained under arbitrary temperature programs [1]. However, isothermal runs tend to be incomplete at

lower temperatures when decomposition proceeds at very slow rates. Thus, the temperature range of isothermal measurements is always quite limited. This range is significantly extended when using nonisothermal measurements at a slow heating rate. Another option is to use the so-called controlled transformation rate measurements [27] in which the rate of gas evolution is maintained at a sufficiently low constant rate so that the self-cooling and self-heating effects due to the reaction enthalpy are reduced.

When nonisothermal measurements are used, it is best to begin the measurements with a slow heating rate (~1 K min$^{-1}$) and use the data obtained as a reference for assessing the quality of data at a higher heating rates. Fast heating rates (tens K min$^{-1}$) should generally be avoided. Within the acceptable range of heating rates, the curves of mass against temperature should demonstrate an almost parallel shift toward higher temperatures with increasing the heating rate. As a rule of a thumb, increasing the heating rate by the same factor should cause a nearly constant temperature shift of TG curves. If significant changes in the slope and shifting behavior of the mass loss curve are observed, the respective heating rate should be recognized as a deviation. Such a deviation is likely to be related to either the sample mass being too large or heating rate being too fast (see also Section 8). During decomposition, the actual heating rate, $\beta$, may deviate from the programmed (user-preset) heating rate, $\beta_{prog}$, due to a deviation of the sample temperature from the reference temperature caused by insufficient rate of heat transfer between the sample and surroundings. These deviations increase with increasing the heating rate and sample mass (Fig. 5a and b). The large deviations in the heating rate



**Fig. 4.** Effect of flow rate of the inert gas on the experimental mass loss curves recorded under linear nonisothermal conditions at a heating rate of 5 K min$^{-1}$. (a) Thermal dehydration of calcium oxalate monohydrate ($m_0$ = 5.0 mg) recorded using a horizontal supported TG (TG–DTA SSC5200, SII) and (b) thermal decomposition of copper(II) carbonate hydroxide (Cu$_2$CO$_3$(OH)$_2$: $m_0$ = 10.0 mg) recorded using a vertical supported TG (TGD9600, ULVAC).

and sample temperature are usually accompanied by the gradients in temperature and partial pressure of the gaseous products as well as in the variability in the degree of conversion among the sample particles. However, these problems are diminished dramatically by keeping the sample mass and the heating rate sufficiently low.

## 3. Thermal and thermo-oxidative degradation of polymers and organics

TG is the most common thermal analysis technique used to study the thermal degradation of polymers and organics. Generally, the thermal degradation kinetics may depend not only on the nature of the material but also on experimental conditions such as sample mass, crucible type, and the type and flow rate of a carrier gas. For this reason, prior to performing kinetic measurements one needs to consider carefully the issues related to the instrument, sample, and conditions to be employed.

The measurement quality is largely determined by the condition of the instrument. One of the main reasons for poor measurement is pollution of the instrument furnace as well as of the inlet and outlet gas lines. In many cases, the carrier gas does not carry away completely gaseous degradation products so that they can partially condense and accumulate in some parts of the furnace and the gas lines. The resulting pollution can obstruct the normal function of the instrument. Thus, one should regularly check the cleanness of the instrument especially when running samples that produce large quantities of low volatility products.

To make sure that a TG instrument functions properly, it is advisable to check if it produces constant mass signal when measuring a sample whose mass does not change during heating. This can be done by measuring either an empty pan or a calibration metal (e.g., Al, Ag, etc) in an inert gas flow. Since such a sample is expected to maintain its original mass, the TG curve obtained after the baseline subtraction should yield a constant mass within $\pm 0.01\%$ of the initial mass. Once the instrument passes this test, the mass loss measurements observed for actual samples can be assigned uniquely to the process of degradation.

Cleaning a TG instrument should be performed in accord with the manufacturer instructions. Removable gas line components and other parts should be cleaned carefully using the appropriate solvent/cleaning/drying method. A vacuum pump can be used to remove any possible contaminants left in the internal gas line system. The furnace and adjacent parts can be cleaned of carbonaceous residue by heating to about 600–800 °C under oxygen or air. Then, the ability of the instrument to produce a constant mass signal should be checked again.

Another factor that can affect significantly the quality of measurements is the condition of the sample pans (crucibles). Depending on the maximum temperature of the measurement, the following pan materials can be used: (1) Al up to 500 °C, (2) $Al_2O_3$, $ZrO_2$ and Pt up to 1750 °C, (3) tungsten and graphite up to 2400 °C. The most frequently used pans are Al and $Al_2O_3$ due to their relatively low price, good thermal conductivity, and chemical stability. When the same crucible is used repeatedly, it should be cleaned properly before each use. Various methods can be used for the cleaning of the crucibles. For instance, $Al_2O_3$ can be cleaned mechanically with fine sea sand, or by boiling in a suitable solvent (water or acids such as hydrochloric, nitric or aqua regia), rinsing with water and if necessary mechanically cleaned again in an ultrasonic bath. Prior to reuse, the crucibles should be heated to 1200–1500 °C for a couple of hours. Similarly, the platinum crucibles can be cleaned by boiling in appropriate solvents, water or acids like diluted hydrochloric acid, followed by an ultrasonic bath or by mechanical treatment with a fine powder like sea sand. Then, soaking in a diluted hydrochloric or hydrofluoric acid for at least 24 h and boiling for a couple of hours should be followed by rinsing with water and baking the crucibles at 900 °C prior the crucibles reuse [28]. An indirect method for checking pan cleanness is to compare a blank run on a cleaned crucible against a blank run on a similar virgin pan that has never been used for running any samples. If the cleaning is adequate, the resulting TG curves normalized to the initial mass should be identical.

Any study of the thermal degradation kinetics is always performed under the premise that all samples used in the study are practically identical. If this condition holds, repetitive measurements on several samples under the same set of conditions should yield well reproducible results. Sometimes the similarity of samples can be difficult to accomplish on composite materials. Solid fillers and especially nanofillers may have the tendency to form large aggregates. The material can, thus, become highly inhomogeneous so that its samples differ significantly from each other. As a result, the respective TG curves measured on different samples can show significant differences in their shape and temperature region of degradation.

Typically the same polymer can be obtained in a variety of forms that differ in molecular weight, polydispersity, tacticity etc. All these factors may have a significant effect on the degradation process and its kinetics. Also, the thermal degradation process of the same material can give rise to significantly different TG curves depending on the sample form (powder, film, and chunk). In particular, the powder grain size and/or film thickness affect the temperatures of degradation. In Fig. 6, crosslinked high density polyethylene samples of various thicknesses are measured in
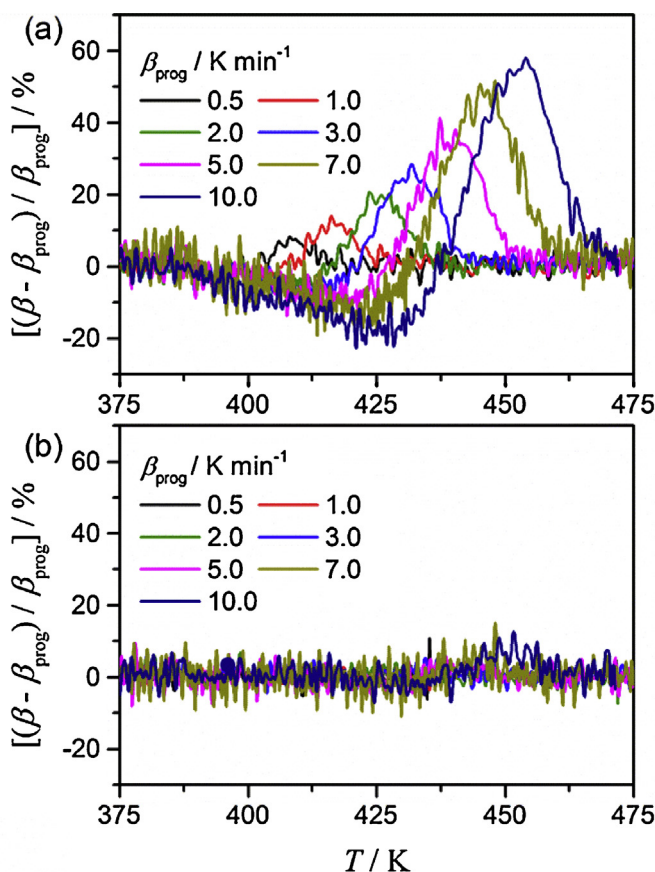


**Fig. 5.** Deviations in the actual heating rate, $\beta$, from the programmed heating rate, $\beta_{prog}$, during the thermal decomposition of sodium hydrogen carbonate (100–170 mesh) recorded using a horizontal supported TG (TG–DTA SSC5200, SII) at different heating rates in flowing $N_2$ (300 cm$^3$ min$^{-1}$). (a) $m_0 = 10.0$ mg and (b) $m_0 = 1.0$ mg.

nitrogen flow at a heating rate of 20 °C min⁻¹. The difference between 40 and 2300 μm thick samples exceeds 30 °C in the early stages of mass loss. Of course, larger thickness also means larger mass so that the former can be figured out from the latter. A good initial guess for the sample mass can be obtained from a rule of a thumb that the sample mass times heating rate should not exceed 100 mg °C min⁻¹. Obviously, for comparative studies and accurate conclusions, the thickness of the compared materials should always be similar in order to have similar diffusion rates of volatile decomposition products. It should be kept as small as possible in order to improve heat transfer and minimize the thermal gradients within the sample. It is also desirable for the sample to cover uniformly the pan bottom, especially when there is no melting of the sample before the degradation step.

However, these requirements can be very difficult to fulfill for low-density samples such as fibers and foams. Typically one would need to fill the entire crucible volume to get the mass sufficient for reproducible measurements. Fortunately, the mass loss phenomena in polymers and organics are usually quite distinctive; thus, the quantities as small as 1 mg can be sufficient for kinetic studies. If the mass loss is very small which quantitatively means less than three standard deviations of the noise in a blank signal, the sample mass should be increased in order to allow for reliable measurements. Generally, the results are considered reliable when the mass loss is at least 10 times larger than the aforementioned standard deviation. When performing comparative measurements on different samples under the same conditions the sample masses should not deviate for more than 10% from the average mass.

An appropriate use of a carrier gas is another condition for obtaining quality data on the degradation kinetics of polymers and organics. A choice of the gas can affect the rate of degradation as well as the number of the mass loss steps, the temperature of the beginning and end of the process, and the mass of the residue. The use of the inert gases allows one to focus on the kinetics of degradation initiated by heat only i.e., on pyrolysis. Before starting the measurements under inert atmosphere, it is important to get rid of the atmospheric air present inside the instrument. Air can cause undesired oxidation of the sample especially at elevated temperatures. Air is removed by purging with an inert gas prior to actual measurements. Even more efficient air removal can be accomplished by using a vacuum pump. In certain cases, when even the traces of oxygen cause unwanted sample oxidation, one should consider the use of either high vacuum or high pressure of

inert gas. Another approach is removing oxygen by using oxygen getter materials.

An important practical area of studies is thermo-oxidative degradation of organic materials. This type of processes is studied in the flow of air or oxygen. Although polymer degradation is commonly studied in an inert atmosphere, degradation in oxygen environment is equally important. Thermo-oxidative degradation of polymers can provide important practical information on how polymeric materials behave under more realistic atmospheric conditions. When studying thermo-oxidative degradation, one needs to keep in mind that the degradation via reaction with oxygen can occur in competition with pyrolysis. For this reason, it is important to create the conditions under which degradation is dominated by oxidation. These would be the conditions that promote penetration of oxygen inside the sample. For example, the use of thinner films or finer powders, higher content of oxygen (pure $O_2$ vs. air), faster flow rate of these gases, and slower heating rates would allow for better penetration of oxygen. By varying any of these parameters, one can determine the conditions under which thermo-oxidative degradation becomes the dominant process. Typically, switching from an inert gas to oxygen results in faster mass loss that starts at lower temperature while using the same heating rate. If switching from air to oxygen or increasing the flow rate of air or oxygen causes a shift of the mass loss curves to lower temperature, then the concentration of oxygen is not large enough to secure sufficient penetration of a sample. By running consecutive experiments under respectively higher oxygen contents or faster flow rates, one can determine the value of these parameters, above which the mass loss curves do not shift to lower temperature. This means that at these parameters the sample reaches sufficient saturation with oxygen.

In addition, when the TG instrument is capable of measuring DSC/DTA signals, the recorded change in heat can also be useful for selecting the conditions of oxygen saturation. Thermo-oxidative degradation is invariably an exothermic process. If the saturation conditions are reached, the process thermal effect per sample mass reaches some constant value. This property can be used for selecting the maximum heating rate. The use of excessively fast heating rate may not allow sufficient time for saturating the sample with oxygen. Fig. 7 shows TG and DSC signals for a polyolefin nanocomposite [29]. The data demonstrate that increasing the content of oxygen shifts the mass loss curves to lower temperature. It also causes an increase in thermal effect of oxidation. Clearly, the sample is not reaching oxygen saturation in air so that oxygen should be preferred for studying the kinetics of thermo-oxidative degradation.

Some general features of the thermo-oxidative degradation are as follows. It starts with an induction period, during which oxygen saturates the sample. This is followed by an autocatalytic stage accompanied by accelerated rise of the peroxy groups concentration. After reaching the maximum concentration, the process enters a termination stage accompanied by the depletion of peroxy groups. The induction time depends on temperature as well as on the polymer nature, structure, and density. The temperature rise accelerates the rate of the oxygen absorption. The oxygen absorption rate depends on the diffusion coefficient of oxygen as well as on the surface of the polymer sample. The mass of absorbed oxygen in the thermo-oxidative degradation is inversely proportional to the polymer crystallinity. The oxidation process starts within its amorphous phase or inter-fibrillar areas. The stereo regular polymers are less prone to oxidation than the atactic ones. On the other hand, branched polymers are more prone to oxidation than the linear ones.

The mass loss curves measured for the thermal degradation of polymeric and organic materials can demonstrate one or
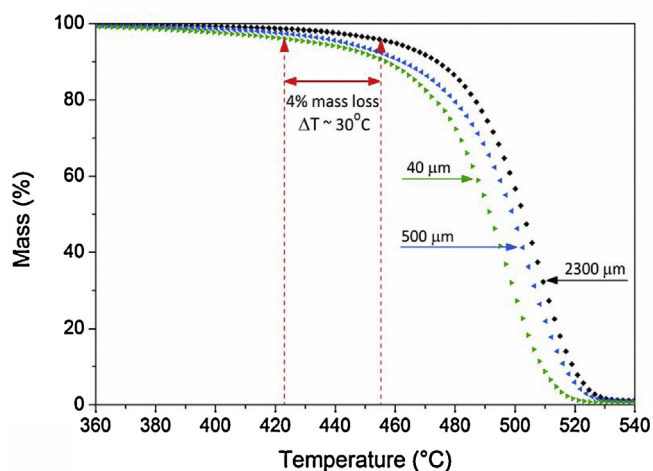


**Fig. 6.** The effect of different sample thickness on the mass loss curves. Crosslinked high density polyethylene samples of 40, 500 and 2300 μm thickness were measured in nitrogen flow at 20 °C min⁻¹.
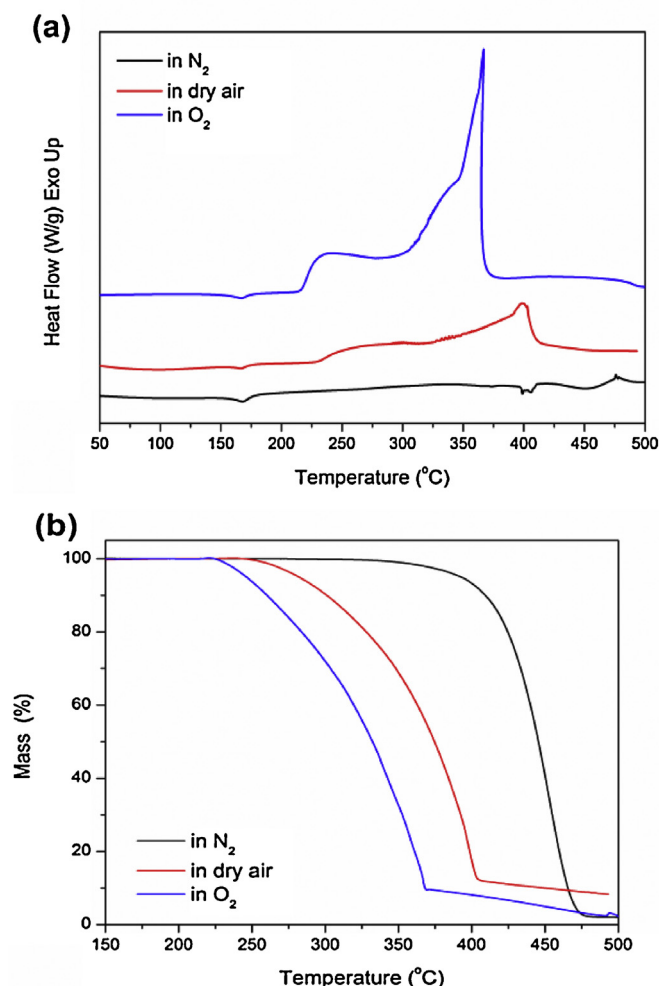
**Fig. 7.** (a) Heat flow signal of isotactic polypropylene/carbon nanotubes 1 wt% nanocomposites under different gas atmospheres. (b) Mass loss of isotactic polypropylene/carbon nanotubes 1 wt% nanocomposites under different gas atmospheres. (Source: data partially adapted from [29] with permission of Elsevier and combined with unpublished results.)



**Fig. 8.** Dependence of the decomposition steps on the heating rate (unpublished data on degradation of poly(propylene pimalate) in 50 mL min$^{-1}$ nitrogen flow).

several distinct steps, or the steps can be strongly overlapped. The occurrence of a single mass loss step should not be understood as the degradation mechanism involves only one step. Usually, the degradation of polymers involves a number of steps such as initiation, propagation, branching and termination. Those mechanisms can be consecutive, parallel and competitive and can have different activation energies. In the case of several overlapping steps, runs performed at different heating rates can provide some useful kinetic insights. For instance, the occurrence of two mass loss steps may suggest the mechanism of consecutive reactions. If this is the only mechanism, the percentage of mass loss in both steps should be independent of the heating rate. In this case, it should be possible to accomplish complete separation of the steps by selecting an appropriate heating rate. However, when the percentage of mass loss in the first (Fig. 8) or any other step varies with the heating rate, this can indicate that the degradation mechanism involves branching. At any rate, the mass loss curves provide very limited mechanistic information. Deeper insights can be obtained by coupling TG with spectroscopic techniques such as mass spectrometry (MS) or Fourier transform infrared (FTIR) spectroscopy for analyzing the evolved gases that can significantly enhance kinetic studies.
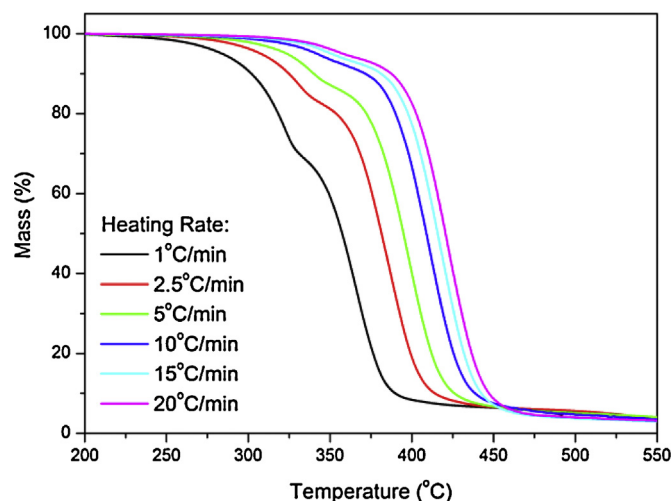
## 4. Reactions of solids with gases

Solid–gas reactions refer to chemical transformations of solids taking place in a reactive atmosphere in accord with the general equation:

$$A + \Sigma v_i G_i = v_B B \qquad (2)$$

where A is the solid reactant, B is the product (typically a solid), $G_i$ represents both reactant and product gases, and $v$ is the stoichiometric coefficient (if the product gases are formed the respective $v_i$ are negative). Solid–gas reactions are usually accompanied by significant changes in the reactant mass that makes TG the most common thermoanalytical technique for measuring their kinetics. The solid A can be in a single piece or dispersed (powder) form. In either case, the nuclei of the new phase B necessarily appear on the surface of the solid reactant A. The phase B grows in size by consuming the phase A until it is gone. The kinetics of solid–gas reactions can be controlled by either nucleation (if nuclei growth is instantaneous) or nuclei growth (if nucleation is instantaneous) as well as by both of them (nucleation and growth controlled reactions). Although each of these processes generally involves a set of elementary steps, one of these steps may be rate-determining.

It should be noted that most of the recommendations given in Section 2 for the thermal decomposition of inorganic solids are also relevant to the solid–gas reactions. Therefore, they will be mentioned briefly without adding many details. Inversely, this section contains a number of recommendations that are also applicable to decomposition reactions, especially the recommendations related to testing the assumptions of Eq. (1).

Strictly speaking, the kinetic equation, Eq. (1), applies only to idealized reactions and conditions that are difficult to realize in the solid–gas systems. Even some apparently "simple" reactions tend to reveal a great deal of complexity on closer examination. For example, the purportedly simple carbonation of CaO with $CO_2$ reveals successive changes in the rate controlling steps due to morphological changes in the powder agglomerates [30]. Thus, one should be recommended to test whether Eq. (1) is suitable to the reaction and conditions under study. Eq. (1) is subject to very restrictive assumptions such as:

i) A steady-state is maintained during the major part of the reaction.

ii) The reaction rate is controlled by the rate-determining step over the entire range of $\alpha$; in case of the nuclei growth process, the step can be surface adsorption or, in some cases, desorption, diffusion through the B phase, reaction on the surface of the B phase (external interface step), reaction at B/A interface (internal interface step).

iii) The rate $d\alpha/dt$ can be described by a single function $f(\alpha)$.

iv) The variables $T$ and $P$ (or $P_i$) must be separable.

The first three assumptions are easy to test experimentally. Let us start from the steady state assumption: (i) it is postulated that a reaction mechanism consists of elementary steps involving reactants, products and intermediate species. The kinetic constants of elementary steps are assumed to obey the Arrhenius law. In the case of reactions with solids, one also needs to take into consideration that the elementary steps of nucleation and growth differ from each other even if the reaction balance is the same. It also needs to be considered that the intermediate species can appear in the form of adsorbed species or point defects such as interstitials or vacancies. The steady-state assumption means that all reaction intermediates maintain very small and constant concentration and rate of change. Therefore, there is no accumulation of intermediates in any part of the solid phases. Thus, one is recommended to verify the validity of the steady-state approximation under the experimental conditions used for the kinetic measurements. When a steady-state holds, the reaction rates measured from the mass change (TG signal) and from the heat release (DSC or DTA signal), are practically identical [31]. Fig. 9 shows an example of superimposition of the mass change derivative and the heat flow curves in the case of the oxidation of Mg into MgO by gaseous oxygen at 783 K [31]. In principle, this test can be carried out in a single run on a combined TG–DSC instrument. The test is done preferably under isothermal conditions but is also possible under non-isothermal conditions, which, however, may lead to more complex interpretations in the case of successive reactions. This test also allows for exhibiting intermediate phases that sometimes are difficult to detect from individual kinetic curves [32].

The assumption about the rate-determining step (ii) can be verified by making successive jumps of temperature or partial pressure of a reacting gas and then comparing the ratios of the rates before and after the jumps at various $\alpha$ [31]. If the ratios remain practically equal in a wide range of $\alpha$, the assumption (ii) holds. Fig. 10 illustrates two opposite cases that involve powders of Mg [31] and CaO [30]. The assumption holds for oxidation of Mg but not for carbonation of CaO. In the latter case, three regions can be distinguished, of which only the regions I and III conform to the assumption. However, the fact that the ratio values differ between the regions I and III indicates that the kinetic regimes are respectively different. More examples of changes of the rate controlling regime have been reported elsewhere [33–35].

The assumption (iii) about a single function $f(\alpha)$ may be verified by conducting two runs as reported in [36]. The first run is conducted under constant $T$ and $P_i$ until completion. The second run is started at different $T$ or $P_i$, then a jump of either temperature or partial pressure is performed in such a manner that the conditions are restored to those used in the first run. Fig. 11 illustrates the results of the two runs for oxidation of Mg. It can be seen that the rate curves are superimposed after the jump, which means that the rate follows the same single $f(\alpha)$ function. Such a situation is generally representative of so-called single-step reactions i.e., those controlled by a single process such as nucleation or growth. In other cases, the curves after the jump demonstrate different traces [36]. This test is particularly recommended before applying any kinetic analysis based on Eq. (1). It can provide insights into certain kinetic issues such as a variation of the effective (i.e., experimentally determined) activation energy with $\alpha$, which most commonly arises from the absence of a single rate-determining reaction step. To minimize the buoyancy effect that accompanies the $T$ and $P_i$ jumps one is
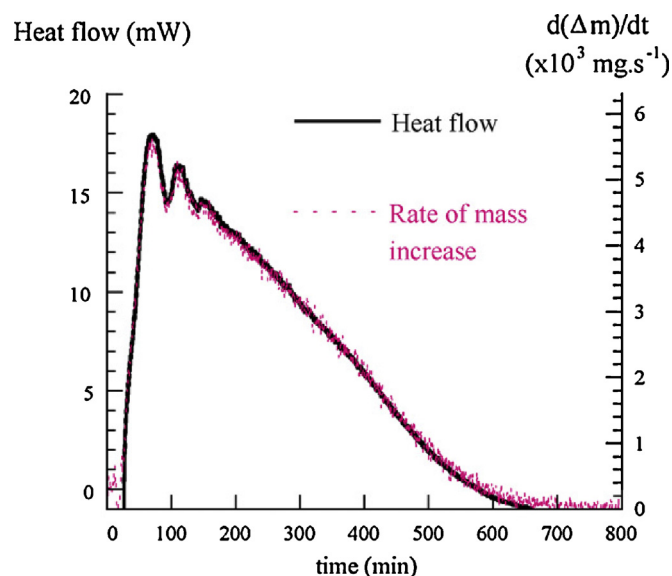


**Fig. 9.** Steady-state test for the oxidation of a Mg powder by oxygen at 783 K (0.2 kPa in $O_2$). (Source: adapted from [31] with permission of Elsevier.)
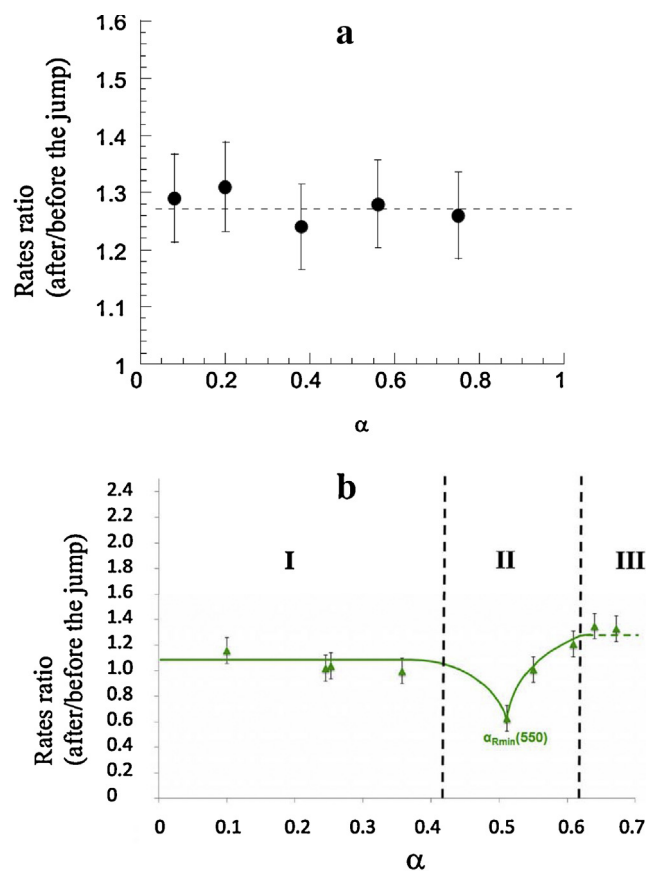


**Fig. 10.** Examples of testing the assumption about the rate-determining step: (a) oxidation of a Mg powder into MgO by $O_2$ (0.2 kPa) with temperature jumps from 773 to 783 K (adapted from [31] with permission of Elsevier); (b) carbonation of a CaO powder by $CO_2$ (5 kPa) with temperature jumps from 823 to 838 K (adapted from [30] with permission of Springer).
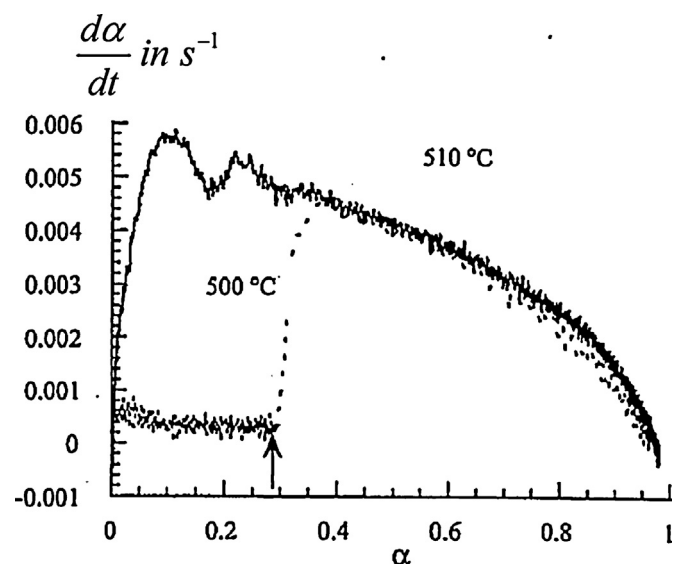
**Fig. 11.** "$f(\alpha)$" Test for the oxidation of Mg powder into MgO by $O_2$ (20 kPa): continuous line at 773 K; dashed line: initial temperature 773 K and jump from 773 to 783 K. (Source: adapted from [36] with permission of Elsevier.)

recommended to use helium as an inert (diluent) gas as well as symmetrical TG instruments.

The last assumption (iv) is obeyed rather infrequently because the intermediate concentrations involved in the rate-determining step tend to vary with $T$ and $P_i$ in a complex manner [33–35,37–39]. In such cases the variables $T$ and $P_i$ are not separable and a more general kinetic equation should be used instead of Eq. (1) [31,40]. No direct experimental test of this assumption has been proposed. When the assumption (ii) or (iii) is confirmed, then it can be deduced that the assumption (i) is confirmed as well. Nevertheless, regardless of the conclusions about the rate-determining step and kinetic model nothing can be concluded about the separation of the variables $T$ and $P_i$.

When it comes to running actual experiments, special attention must be paid to the gas flow rates. As far as possible the reaction gas mixture should contain all the gasses ($G_i$) that enter the reaction balance, Eq. (2). The total flow rate should be kept constant and sufficient to maintain the constancy of the partial pressures of the gaseous reactants and products, if the latter are formed. The amount of gases running through the reaction system (expressed in flow rate) must be no less than 10 times the rate of gaseous reactant consumption and of gaseous product production. Then, the variations of the partial pressures $P_i$ due to the chemical reaction at the surface and/or inside the sample can be neglected. Mass flow-meters can be used to control accurately the partial pressures.

Another closely related issue is that inorganic solids may be very reactive toward water vapor and/or oxygen present as traces in inert gases used for purging. However, more significant amounts (typically 5–10 Pa) of oxygen and water vapor can enter a TG instrument through various micro-leaks in the whole device. The leaks can be checked using inlet or/and outlet devices such as a mass spectrometer as well as humidity and oxygen sensors. By increasing the gas flow-rate e.g., from 1 to 10 L h$^{-1}$ (the upper limit must not exceed the value specified by the manufacturer) the impurities due to the leaks can be greatly reduced (leaks dilution).

As already mentioned, the solid is usually taken in the form of either bulk or powder. In the case of a bulk sample, the most suitable shape is a small disk or a plate cut from metal, alloy, ceramics or other solid of interest. The height of the sample must be significantly smaller than its horizontal dimensions (i.e., diameter or width and length) in order to neglect the mass

changes at the walls of the disk or plate. A typical sample shape and size is a disk of 0.5 mm height and 10 mm diameter. The planar symmetry is recommended because it simplifies the overall kinetics, making it simpler to understand. Another advantage is that the dimensions of such regularly shaped sample can be determined with a great accuracy. This is difficult to accomplish in the case of powders, which also need to be characterized in terms of the specific surface area, particle size distribution, as well as the particle shape. Although it is not obvious from Eq. (1) and rarely discussed in the literature, the measured rate data ($d\alpha/dt$) are strongly affected by the particle shape and size. For example, when a solid reactant has a spherical shape of the radius, $r_0$, and its reaction rate obeys the R3 model (Table 1), the value would increase in proportion to $1/r_0$. However, if the spherical sample is involved in reaction that follows the D4 model (the rate-determining step is diffusion through the layer B), the rate would increase in proportion to $1/r_0^2$ [40]. This is useful to keep in mind when comparing kinetic data obtained for the same reaction performed on the samples of different shapes and sizes.

Complementary characterization of solid samples by means of various structural and textural techniques is always a valuable supplement to kinetic data. In the case of a single piece sample, particular attention should be paid to geometrical dimensions, spatial distributions of phases and interfaces, surfaces, in-depth profiles (major elements, impurities, and segregations), defects such as pores and cracks. For powders, specific surface area, particle size and shape, size distribution, porosity (intra and inter particles), and agglomeration are typical points of interest.

Conditions of kinetic measurements are usually optimized to diminish the effects of mass and heat transfer on the reaction rate. One way to accomplish this is to keep the reaction rate relatively slow. This is done by choosing $T$ and $P_i$ so that the reaction takes a few hours to reach completion ($\alpha = 1$). Another way to diminish the mass and heat transfer effects is to take the sample of smallest possible mass that secures an acceptable signal to noise ratio. Typically with TG instruments offering microgram sensitivity, the sample mass is in the range of 1–20 mg. The effect of the sample mass on the kinetic curves is similar to that depicted in Section 2 for thermal decomposition of inorganic solids. It is, thus, recommended to decrease sequentially the sample mass until obtaining superimposed kinetic curves. The sample pans must be chosen with regard to their thermal stability as well as chemical reactivity towards the gaseous and solid reactants and products. Pans with a porous bottom can be recommended for powdered samples since they enable better gas circulation through the powder bed. Bulk samples of metals and alloys can be hanged by a small hole made in them, whereas ceramic plates can be suspended on microwires placed inside a bottomless pan. Either configuration secures easy access of the reactive gas to all solid surfaces.

It is advisable to start data collection by running experiments under non-isothermal conditions. The runs can readily reveal the presence of consecutive reactions. In this case, each reaction can be studied separately under isothermal conditions by selecting proper temperatures from the lower temperature portion of the corresponding derivative TG (i.e., DTG) peak. Although isothermal runs allow for better resolution, and thus, for acquiring kinetic data specific to a single reaction, they are much more time consuming than non-isothermal runs.

In solid–gas reactions, the initial warm-up period plays relatively unimportant role in the overall kinetic experiment. This is because the sample heated to desired isothermal temperature does not react until introduction of the reactive gas. Instead, the early reaction stages are affected by initial instability of the gas pressure $P_i$ that depending on the TG instrument may take 3–5 min.

## 5. Polymerization and crosslinking

Reactions of polymerization are accompanied by significant release of heat that makes DSC one of the most common methods for studying the kinetics of polymerization and, especially, crosslinking (curing) [41]. As mentioned in introduction, the temperature and heat calibrations of DSC should be performed by measuring the physical transitions of some reference materials. It is recommended that the conditions of calibration should be similar to those of the actual measurements. That is, the mass, thermal conductivity, and temperature range of the transition of the reference material should be as close as possible to those of the actual sample. The application of other thermal methods to polymerization and crosslinking processes is much rarer and thus is beyond the present recommendations.

A polymerization kinetics study starts with a careful preparation of the reaction mixture. It usually contains at least two components: monomer and initiator (e.g., styrene and azobisisobutyronitrile), or monomer and comonomer (e.g., diepoxy and diamine) that have to be carefully mixed. Sometimes before mixing, the components need to be dried in a vacuum oven to remove moisture [42]. Since both drying and mixing become more efficient with increasing temperature, the temperature should be raised carefully to avoid homopolymerization of monomers during drying as well as a reaction of the components during mixing. Mixing should always be performed at a temperature that is at least 30 °C lower than the temperature at which the reaction becomes detectable by DSC. To avoid the occurrence of the reaction during mixing, the latter should be limited to a few minutes. If one of the components is solid, it may be possible to melt it and then cool down to supercooled liquid that can be mixed with another liquid component while being below the melting point. It is also important to avoid the formation of bubbles [43]. Generally, coreactive monomers (or pre-polymers) are mixed in a stoichiometric ratio, but studying off-stoichiometric mixtures may also provide important mechanistic insights [44,45]. The mixtures prepared can be stored. However, the storage temperature should be below the glass transition temperature of at least one of the component (typically monomer), and the storage time should be limited to no more than 2–3 days. After this period, a fresh batch should be prepared. It is highly recommended to perform all kinetic runs on the samples from the same batch and conduct all runs consecutively in one day.

When the reactive components are solids, they can be grinded into a uniform mixture. The uniformity of mixing improves with decreasing the size of solid particles. Alternatively, the mixture can be prepared by melting one component that has a lower melting point and then dissolving another component in the melt. This approach is not viable when the melting point is too close to the reaction temperature.

Once prepared, the mixtures should be accurately weighed in a certain amount and placed in a pan (crucible). The choice of both mass and crucible type is very important. Polymerization typically involves liquid monomers that are volatile especially when heated. To prevent vaporization, the samples are analyzed in hermetically closed pans. Because the sample is in a closed pan, the choice of the purge gas type and gas flow rate is relatively unimportant. However, whatever the gas type and flow rate are chosen they must be kept the same within a single series of kinetic measurements.

Most commonly used are aluminium pans that are inexpensive and have good thermal conductivity. Sometimes, pierced pans are used to avoid closed pan rupture due to the pressure build-up. Note that the use of pierced pans is not the best practical solution as it can lead to a significant loss of volatile reactants that can entirely invalidate kinetic measurements. When pierced pans have to be used, it is absolutely necessary to weigh the sample before and after completion of the run to determine what percentage of the initial mass is lost. Acceptable loss should not exceed a few percent. When closed, aluminium pans can withstand only about 0.15–0.20 MPa pressure. To hold significantly larger pressures, one should use high pressure pans that are made of stainless steel and can withstand up to 10–15 MPa. Gold plated steel pans are available to study the reactants reactive toward aluminium [46–48]. Unlike aluminium pans, stainless steel pans have significantly lower thermal conductivity, and thus, their application should be limited to lower heating rates and temperatures to decrease the maximum heat flow, and therefore, the thermal lags and gradients. Regardless of whether the pans are pierced or closed, it is imperative to check for possible mass losses by weighing the sample before and after a run.

The sample mass should be large enough to produce reliable DSC signal, but small enough to minimize the temperature lags and gradients. The resulting temperature deviations are proportional to the total thermal effect of the reaction as well as to the maximum heat flow. This is especially important when the measurements are done with a heat-flux DSC, while in the case of a power-compensated DSC, the deviation of the sample temperature from the reference one is much smaller. Fig. 12 shows the heat release data for non-isothermal polymerization of furfuryl alcohol (FA) and of bisphenol A diglycidyl ether epoxy resin (DGEBA) at the same heating rate [45,48]. Although the total thermal effect of these reactions is comparable, the temperature lags, and gradients will be higher for FA polymerization because the reaction has markedly larger maximum heat flow. At any rate, both thermal effect and maximum heat flow can be controlled by controlling the sample mass. An appropriate mass can be determined by running several experiments at the same heating rate while varying the masses between 2 and 30 mg. The resulting DSC curves should then be either normalized per sample mass (i.e., presented in $W g^{-1}$ units) or converted to the $\alpha$–$T$ curves. In either case, if below a certain mass the curves can be superimposed, it can be considered that the temperature lags and gradients are practically negligible and that the respective sample mass is appropriate for kinetic analysis. It should be noted that the mass appropriate at a given heating rate may still be excessive for a higher heating rate. That is why one can either determine the appropriate mass for the highest heating rate and maintain it at lower heating rates or to
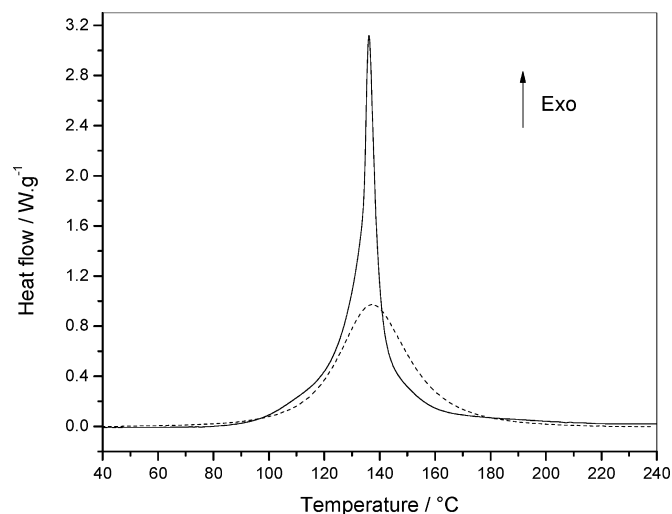


**Fig. 12.** DSC data of the heat release during nonisothermal polymerization of FA (solid line, hermetically sealed crucibles, reaction heat ~620 J g$^{-1}$) and of DGEBA (dash line, crucibles with a pin hole in the lid, reaction heat ~560 J g$^{-1}$) at 4 °C min$^{-1}$. (Source: adapted from [45] with permission of Elsevier.)

determine the appropriate mass for the lowest heating rate and then decrease it in inverse proportion to increasing the heating rate. That is, if at $2\,^\circ C\,min^{-1}$ an appropriate mass is determined to be 10 mg, then for $10\,^\circ C\,min^{-1}$ the sample mass should be about 2 mg.

Sample shape as well as its thickness may affect the reproducibility of the measurements. It has been reported that thick samples of a droplet-like shape can give rise to poorly reproducible measurements [49]. Since the droplet-like shape is naturally assumed by a viscous liquid monomer, it is recommended to spread it even along the pan bottom to form a thin layer. Best reproducibility is accomplished in the samples of controlled shape and thickness.

Polymerization studies are usually conducted under either nonisothermal (constant heating rate) or isothermal conditions. From the experimental standpoint, nonisothermal runs are easier to perform. On the other hand, isothermal runs allow for much simpler kinetic analysis, although the runs are more challenging to perform. Due to the sensitivity and time constant of a DSC instrument, the temperature range of isothermal experiments is unavoidably narrower than that of the non-isothermal ones that is a disadvantage for kinetic computations [50,51], There are two ways to heat a sample from an ambient to an isothermal temperature of interest. The first way is to heat the sample to the isothermal temperature at a high heating rate [52]. The second way consists of directly inserting the sample into the DSC furnace preheated to the desired isothermal temperature. This is easily done in a reproducible manner when DSC is equipped with a robotic device. The isothermal temperature is selected so that the instrument stabilization time is negligible relative to total duration time of the reaction. The stabilization time is readily estimated in a blank run (isothermal run conducted with an empty pan) as the period of the initial signal deviation from the flat baseline. If the stabilization time cannot be neglected, the data can be corrected for the initial period of instability by subtracting a blank DSC run. To do that one first needs to perform a DSC run on an empty pan, then fill this pan with a sample and run again under the same temperature program as the first run. A better alternative can be to use as a blank a DSC run on the fully polymerized (crosslinked) sample. That is, first a regular isothermal run is performed. Then, the resulting sample is cooled down and reheated nonisothermally to 30–50 °C above the isothermal temperature used. Under isothermal conditions, polymerization can practically stop before completion because the reaction system vitrifies when the glass transition temperature of the growing polymer rises above the experimental temperature (Fig. 13). Then, successive nonisothermal heating raises temperature above the glass transition temperature of partially reacted system ($T_v$) so that the reaction mixture devitrifies and continues to react releasing so-called residual reaction heat [44]. The latter appears in DSC as a relatively small exothermic effect, evaluation of which provides a quantitative estimate for the unreacted fraction of the reactive components. The nonisothermal runs should yield a completely cured sample. The sample can then be cooled down and subjected to the same isothermal program as the initial reaction mixture to produce a blank DSC curve.

The highest isothermal temperature is selected as the one that leads to a reaction time much larger than the instrument stabilization time. The lowest temperature is chosen as the one that gives rise to the lowest acceptably detectable DSC signal. This is usually taken as the signal whose amplitude exceeds the limit of quantification i.e., 10 times the standard deviation of the blank signal under the same conditions as the measurement. Since the reaction rate and heat flow at lower temperatures are small, the resulting temperature gradients are negligible. This means that the lower temperature limit can be lowered further by using larger

sample mass. However, the mass chosen should be maintained reasonably constant within a series of kinetic measurements. Expanding the temperature range of measurements as much as possible allows one to improve the quality and reliability of kinetic computations.

Performing nonisothermal runs provides a simpler alternative, especially for a beginner. The slowest heating rate is chosen so that the DSC signal reaches acceptable intensity i.e., its value is markedly above the sensitivity limit. Because the slower heating rates lead to smaller temperature gradients, the heating rate can further be decreased by using a larger sample mass. When selecting the fastest heating rate, one should keep in mind that the heat flow increases proportionally to the heating rate so that the temperature lags and gradients may become quite large. For this reason, an appropriate sample mass should be chosen as described earlier i.e., by performing a series of runs with decreasing sample masses.

Since nonisothermal runs cover a wide temperature range, and thus, can stretch to rather high temperatures especially at the faster heating rates, one needs to be careful to avoid the thermal degradation of the reactants and products. The respective limits of the thermal stability can always be checked by carrying out TG runs.

When analyzing the thermal effect of polymerizations, it is important to remember that it can be dependent on the temperature program [45,48,53]. For example, when the studies are conducted under isothermal conditions below the so-called limiting glass transition temperature ($T_{g,\infty}$), the reaction mixture vitrifies and reaction practically stops before completion (Fig. 13). That is why the thermal effect of the process may demonstrate an increase with increasing the temperature of an isothermal run [53–55]. However, the runs conducted above the limiting glass transition temperature are likely to demonstrate similar thermal effects. An exception is when the process involves competing steps having different enthalpies. In this case, the relative contribution of the steps in the overall process, and thus, its total thermal effect may depend on temperature as well as on heating rate. For this reason, quite different values of the thermal effect can be obtained for isothermal and non-isothermal measurements [56].
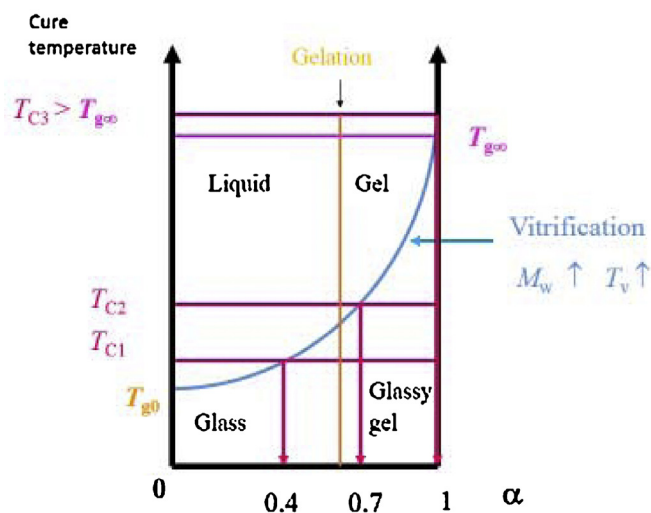


**Fig. 13.** The vitrification temperature, $T_v$ (i.e., the glass transition temperature of reacting system) increases with the progress of polymerization, $\alpha$, because of the increase in the molecular weight, $M_w$, of the forming polymer. $T_v$ reaches its maximum at $T_{g,\infty}$ that represents the limiting glass transition temperature for fully reacted system. At any temperature below $T_{g,\infty}$ (e.g., $T_{c1}$, $T_{c2}$) the system will vitrify yielding partially reacted system ($\alpha < 1$). The process will be complete at $T > T_{g,\infty}$ (e.g., at $T_{c3}$).

## 6. Crystallization of polymers

DSC is a well established method for measuring the polymer crystallization kinetics. Typically, a polymer sample needs to be heated above its equilibrium melting temperature or at least 20 °C above the melting peak temperature measured by DSC, and then held there for 5–10 min to secure complete melting i.e., destruction of any traces of crystallinity. After that, crystallization kinetics of the melt can be measured either under isothermal or non-isothermal conditions. For isothermal measurements, the sample needs to be rapidly cooled to the desired crystallization temperature and maintained at it until completion of crystallization that is detected as heat release in DSC. When the measurements are conducted under nonisothermal conditions, the polymer sample is cooled at a constant rate until crystallization is completed. Alternatively, one can measure the crystallization kinetics in glassy samples. Such samples are produced by quenching the polymer melt to a temperature below the glass transition ($T_g$). On heating the glassy samples crystallize giving rise to the so-called cold crystallization. The latter can be studied under isothermal as well as nonisothermal conditions. In all cases, the heat released during crystallization is recorded as a function of time or temperature. The fractional area of a DSC peak provides an estimate for the fraction of crystallized polymer or relative extent of crystallinity. The experimentally measured evolution of crystallinity with time or temperature provides important information on the process of polymer crystallization.

The important difference between melt and glass crystallization is that homogeneous nuclei are activated during cooling to below $T_g$ and/or subsequent heating to the selected crystallization temperature. This usually results in a faster crystallization rate, although exceptions have been reported [57]. Moreover, the glass is a metastable state that depends strongly on the conditions of preparation and, in particular, on the cooling rate of the glass forming melt, time and temperature of storage, and so on. For this reason, the kinetics of cold crystallization must be studied on a set of samples prepared under the same conditions. Generally, it should be kept in mind that the data gathered for a given polymer sample both on melt or cold crystallization may not be transferable to other samples of the same polymer, since small variations in molecular microstructure, molecular mass distribution, presence of additives, etc., can significantly affect the crystallization kinetics. Therefore, each polymer batch requires respective measurements of the crystallization rate.

Polymer samples are usually studied in 20–40 μL aluminium pans, which are inexpensive and possess good thermal conductivity. A choice between open, pierced, or closed pan is not critical as well as a choice of the purge gas and its flow rate. However, the gas needs to be inert (e.g., nitrogen or argon) to prevent oxidation of the sample especially at elevated temperatures. Nevertheless, a particular chosen combination should be maintained within a series of kinetic measurements. It is also important to stay within the parameters recommended by the instrument manufacturer and to perform kinetic measurements under the same parameters that were used for calibration. Additionally, it is recommended to use a fresh sample for each analysis, to minimize the problems due to thermal degradation.

One of the major issues in studies of polymer crystallization kinetics is proper erasing of prior thermo-mechanical history, which may affect both onset and rate of the process. Memory of the previous crystalline order is erased by bringing the polymer sample to a temperature sufficiently higher than the melting temperature measured by DSC. If the temperature is not sufficiently high, some crystals or crystal-like aggregates may remain in the melt and can, therefore, induce accelerated crystallization due to self-seeding nucleation [58]. This issue is especially critical in polymers with a low nucleation density. Unfortunately, the use of excessively high temperatures may lead to degradation of the polymer, which can change its structure and crystallization kinetics. Polyesters and polyamides can undergo ester and amide interchange, even at temperatures below the melting point, which can lead to a molecular mass change or crosslinking. For instance, it was shown for poly(ethylene terephthalate) (PET) that prolonged annealing at 250 °C (i.e., below the melting point) leads to chemical rearrangement of the molecular chains in the amorphous regions, which results in the formation of tie molecules and in the loss of chain mobility, as well as in the increase of the overall molecular mass [59–61]. Another example is poly[(R)-3-hydroxybutyrate] (PHB) and related copolymers that include 3-hydroxyvalerate, 4-hydroxybutyrate, or other hydroxyalcanoate units. These polymers are thermally unstable at temperatures above 170 °C i.e., at temperatures where PHB is incompletely melted, or immediately above the melting point of the copolymers. Thermal degradation of these polymers is due to random chain scission at ester groups, which causes a significant decrease in the molecular mass [62]. Unless a polymer is known to be thermally stable in the melt, it is a good practice to check its thermal stability by conducting a TG run for checking whether there is any sizeable mass loss in the melting region.

Melting conditions are selected by melting a polymer at different temperatures and times, before cooling it at a chosen rate for non-isothermal crystallization measurements, or to a predetermined crystallization temperature for isothermal measurements. Analysis of the heat evolved during crystallization, of the onset point, and of the curve shape permits to determine the minimum melting temperature and time needed to destroy the traces of crystallinity, which can accelerate the crystal growth during analysis [63,64]. Another option is to use polarized light optical microscopy for determining the nucleation density after melting at different temperatures and/or times. The procedure is exampled in [58], where the nucleation density of PHB crystallized at 5 °C min$^{-1}$ from the melt is quantified as a function of the preceding thermal treatment.

Preliminary experiments must also be conducted to optimize sample preparation. Precise control of the sample mass and thickness is a key in controlling the thermal gradients within the samples, as mentioned in Section 1. This issue is especially important for non-isothermal crystallization analysis, as explained below. In order to produce samples that have well defined thickness and uniformly cover the bottom of a DSC pan, one can use powder or compression-molded sheets. If the sample thickness is not uniform, the crystals may grow only in a limited part of the sample giving rise to irreproducibility of the crystallization kinetics [65]. It should, however, be kept in mind that grinding of the polymer to obtain a thin powder, as well as compression molding, solution casting, or other procedures that allow to obtain a polymer sample with controlled and uniform thickness, may also result in polluting the sample with small particles that may be present in the mill or on the mold surface, as well in the glassware used for the solvent casting. These particles may act as nucleation sites for the growth of polymer crystals, and accelerate the onset of crystallization as well as to give rise to a much higher enthalpy of crystallization due to an increase in the crystallinity [64]. An example is seen in Fig. 14, which compares the DSC traces of poly (lactic acid) in the form of a compression-molded film and an untreated sliced chip of the same polymer. The DSC plots display significant differences, with an earlier onset and higher enthalpy of crystallization determined for the compression-molded film, which reveals undesired alteration of the crystallization kinetics caused by polymer processing. Since the inclusion of unwanted nucleants as well as possible thermal degradation occurring during compression molding is difficult to control, the use of non-
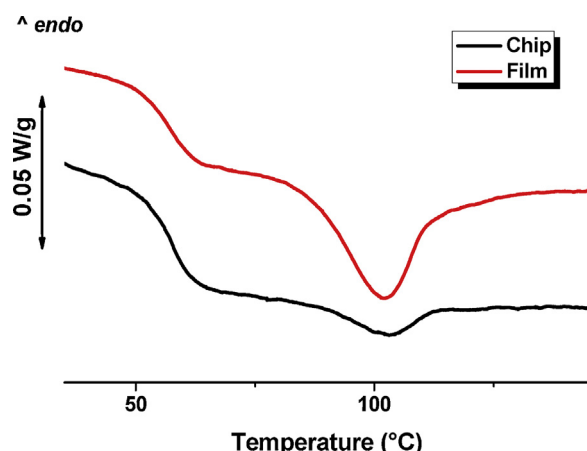
**Fig. 14.** DSC plots of poly(lactic acid), chip, and 150 μm thick film, during cooling from the melt at 4°C min⁻¹. (Source: adapted from [64] with permission of Springer.)



**Fig. 15.** Heat-flow rate plots of poly(butylene terephthalate) PBT: experimental raw data during isothermal crystallization at 196 °C (red solid line), blank run recorded above the melting temperature (blue line), subtracted line (black solid line). The extrapolated onset time for crystallization ($t_0$) is also indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (Source: adapted from [68] with permission of Elsevier.)

processed samples may be advisable for the analysis of crystallization kinetics of polymers with a very low nucleation rate and density, even though this may mean a non-uniform sample thickness. Considering that the error introduced by imprecise control of sample thickness may be less relevant than the unwanted addition of nucleating particles [64], the use of non-processed samples should allow one to avoid measuring abnormally fast crystallization rate.

As mentioned above, polymer crystallization kinetics can be analyzed under isothermal and nonisothermal conditions. When temperature is constant the theoretical analysis is relatively easy and the problem of the temperature gradients within the sample is less critical. The major problem of the isothermal runs is to determine accurately the time when crystallization begins. For fast crystallizing polymers, high cooling rates from the melt are needed to avoid crystallization before reaching the desired temperature. Due to the finite response time of DSC, a switch from cooling to an isothermal step always produces a transient overshoot in the heat flow signal followed by its gradual return to the steady state. In some cases, crystallization may start during this stabilization period so that the initial stages of the process are masked by the transient overshoot. The latter needs to be separated from the crystallization exotherm to determine exactly the onset of the process and properly follow its kinetics.

A special procedure was developed to reconstruct the initial period of the isothermal crystallization [66,67]. The procedure involves performing a blank experiment with the same sample at a temperature above the melting point, where no crystallization takes place, as illustrated in Fig. 15 [68]. The blank run is then subtracted from the actual crystallization exotherm, and the intersection of the extrapolated baseline with the resulting exothermal curve is taken as the crystallization onset. The use of this procedure can expand the temperature range for isothermal crystallization to lower temperatures, where crystallization is faster.

Accurate determination of the parameters of the crystallization kinetics is limited by the temperature dependence of the nucleation rate and by the choice of the crystallization temperature ($T_c$) for the melt and/or glass crystallization. The heating/cooling rates to reach $T_c$ should be sufficiently fast (typically at least tens of degrees per minute) to prevent crystallization before $T_c$ is reached. The maximum rates of heating and cooling depend on the model of DSC as well as on the cooling device used. For example, liquid nitrogen cooling devices allow for much faster cooling than the devices that use water as a coolant.
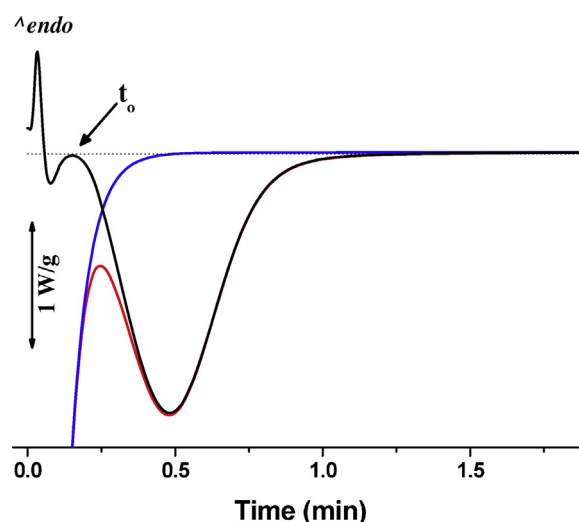
The crystallization rate measurements are limited by the sensitivity of DSC and by the crystallization enthalpy of a polymer. The time-dependent evolution of crystallization heat depends on $T_c$. At too high (melt crystallization) or too low (glass crystallization) temperature, the heat evolution may be too slow and lead to a poor signal to noise ratio. This complicates evaluation of the crystallization kinetics, due to a significant errors in integration of the crystallization exotherm. An acceptable experimental uncertainty in crystallization heat amounts to a few percent, for both isothermal and non-isothermal experiments [69,70]. A proper choice of $T_c$ can be made from a nonisothermal run. For the melt crystallization, $T_c$ should be selected somewhat below the DSC onset temperature on cooling, whereas for the glass crystallization, it should be somewhat above the onset temperature measured on heating.

In order to further expand the temperature range of crystallization analysis, one can use nonisothermal conditions. Non-isothermal studies require more care as they may be complicated by the occurrence of temperature gradients within the sample and between the furnace and the sample. The latter gradient is relatively unimportant as long as the sample is sufficiently small and thin and the heating or cooling rate is not very fast. For example, it can be disregarded when the heating or cooling rates do not exceed 1 and 100 °C min⁻¹ for samples of 1 g and 1 mg, respectively [71], or do not exceed 80 °C min⁻¹, for samples of 300 μm thickness [72]. However, the heat evolved during crystallization may cause additional temperature gradients within the sample. As a consequence, the process may occur at temperatures that deviate from those maintained by the instrumentation. The thicker the sample, the more critical this problem is. In order to minimize the temperature gradients inside the sample during nonisothermal crystallization, it is suggested to limit the scanning rate to 8 °C min⁻¹, and to use samples of 150–200 μm thickness, with a mass not exceeding 3–4 mg [73]. For isothermal crystallization, a somewhat larger sample mass of 5–10 mg can be used.

Note that nonisothermal crystallizations studied on cooling may require some additional calibration performed on cooling [74,75]. Standard calibration of DSC is conducted on heating by using high purity metal standards such as In and Zn. However, DSC instruments are not necessarily symmetrical, which means that a

calibration performed on heating may not hold on cooling. To check whether a calorimeter is symmetrical with respect to heating and cooling, one can measure the temperature of a phase transition that occurs without supercooling. The melting standards when cooled undergo crystallization at temperatures that are significantly lower than the melting point [76]. Supercooling is practically absent in the solid–solid lambda transitions and in transition of liquid crystalline phase in liquid crystals [77]. A number of high purity, thermally stable liquid crystals have been proposed as possible calibrants on cooling for DSC e.g., 4-(4-pentyl-cyclohexyl)-benzoic acid-4-propylphenyl ester (HP-53), 4′-ethyl-4-(4-propyl-cyclohexyl)-biphenyl (BCH-52), or 4-cyano-4′-octylbiphenyl (8OCB). The smectic to nematic transition in 8OCB fulfils the requirements for these purposes best, since it shows no detectable discontinuity in the rate dependence of the transition temperature at zero rates and the compound is sufficiently stable to allow multiple measurements [78]. If the instrument is symmetrical, the phase transition temperature measured on cooling should not deviate from that measured on heating by more than twice the standard deviation in the phase transition temperature determined from repetitive measurement performed on heating. Otherwise, a correction factor needs to be determined and accounted for [75,76].

## 7. Crystallization of inorganics

The procedure for collecting experimental data on crystallization kinetics of inorganic materials such as individual elements or alloys is well established. Most commonly studied is the so-called cold crystallization i.e., crystallization that takes place on heating of a glass (amorphous) material. The process generally involves crystalline nucleation and growth. If the sample structure is entirely amorphous, the crystallization kinetics, especially, in the early stages is likely to be determined by nucleation. If the initial structure is partially crystalline (nanocrystalline), crystallization is mainly due to the growth of pre-existing nuclei. Crystallization is typically accompanied by significant heat release that makes DSC the most popular tool for measuring the process kinetics. The heat flow of crystallizing material can be traced as a function of time (isothermal scan) or temperature (nonisothermal, constant heating rate scan). DSC is also useful for studying "hot" crystallization i.e., crystallization that occurs on cooling of the melt. Since the melt is obviously amorphous, its crystallization kinetics is predominately determined by nucleation. The following recommendations focus primarily on two aspects of obtaining crystallization kinetics data, namely: sample preparation and experimental conditions.

When studying cold crystallization, special care should be taken to control accurately the thermal history of the sample. It is absolutely necessary because the glassy samples are metastable and their properties change with time, temperature, and other conditions. For example if preparation of material starts by melting inside an ampoule, an inert atmosphere should be used to prevent oxidation, and the ampoule should be rocked frequently to ensure homogenization of the melt [79]. Furthermore, temperature, time as well as cooling program should be also controlled. A sample prepared by quenching into ice cooled water would not be generally identical to that quenched into liquid nitrogen. Nevertheless, the differences are not nearly as dramatic as in the case of polymers whose molecular mobility and crystallization rates are typically much slower than in the case of inorganics.

One issue to keep in mind is that when the glassy state is apparently confirmed by X-ray diffraction (XRD) data, the sample may still have small nanocrystalls embedded in the amorphous matrix that would affect the crystallization kinetics. A typical assumption is that the crystalline fraction in the glass does not exceed $10^{-9}$ at the glass transition. Note that in magnetic glassy materials the disordered glassy phase has a magnetic order that may affect crystallization kinetics [80].

The structure and properties of glassy material are largely affected by the cooling conditions of the melt as well as by the heating conditions of glass during cold crystallization. To avoid any significant crystallization while cooling the melt, one should use sufficiently fast cooling rate to reach the glass transition temperature. An important characteristic of a crystallizable material is the critical cooling rate, $R_c$, needed to prevent crystallization. The smaller the $R_c$ the higher the glass forming ability of the material and the latter is said to be a good glass former [81]. The crystallization temperature observed on subsequent reheating of the glassy material would generally depend on the melt cooling rate because of the possible formation of the crystalline nuclei during cooling. The more nuclei are formed on cooling the easier (i.e., at lower temperature) glass crystallizes on heating. An increase in kinetic resistance toward crystallization can be characterized by an increase in: (a) activation energy of crystallization; (b) crystallization temperature; (c) the Hruby parameter defined as the difference between onset of crystallization and glass transition temperatures divided by the difference between melting and onset of crystallization temperatures; or (d) the Weinberg parameter defined as the difference between onset of crystallization and glass transition temperatures divided by melting temperature. Care must be exercised when comparing these parameters between different research groups and samples. It is necessary to establish whether the materials were prepared under similar cooling conditions and then measured under similar heating conditions.

Once the samples have been made under well controlled conditions they should be prepared in the form that secures a proper thermal contact with the sample pan. If a sample is a single piece, the proper form is the flat one i.e., when the sample height is much smaller that its width (diameter) and the bottom part is polished by using, for example, 1200 grit SiC abrasive. Thin powder sample needs to be spread as a thin layer across the pan bottom. The samples can also be available in the form of amorphous microwires, thin films, and ribbons [82,83]. In this case, the samples need to be pressed against the pan bottom to improve thermal contact by reducing their bending. Last but not least, many inorganic materials are hydrophilic so that they should be stored in a desiccator or subjected to drying before studying the crystallization kinetics.

Before collecting kinetic data, the DSC equipment must be properly calibrated with respect to both temperature and heat. When selecting calibration standards, one should choose substances, for which (a) the thermal conductivity reasonably close to that of the sample; (b) the mass similar to the sample mass (typical sample mass used for crystallization of inorganics is 5–15 mg); (c) the phase transition temperature is close to the temperature interval of the sample crystallization. For instance, typical standards for crystallization of metallic glasses are In, Pb, and Zn, whose heats of melting are well established and melting temperatures cover a sufficiently wide temperature range. Calibration should be performed under the same conditions as the actual crystallization runs. That is, one should use the same: (a) pan material and size; (b) gas (recommended to be dry and inert); (c) gas flow rate; and (d) heating or cooling rate. If the DSC instrument software performs calibration at a single heating rate and introduces some sort of correction for other heating rates, it is wise to check whether the correct value of the melting temperature is obtained by performing a run at a different heating rate.

One of specific problems related to the pans selection is an interaction between the sample and the pan material. It is advisable to check the phase diagrams. A possible result is the formation of eutectic systems that can be recognized by lowering

the melting temperature. If this problem is found in aluminum (typical pan material), the pan material alternatives are platinum or gold, both of which are better materials than low conductivity alumina. The sample should be placed in either open or pierced pan. Sometimes one of the alloy elements such as phosphorus may not react completely and can readily oxidize and even ignite on heating. Similarly, metallic glasses can undergo significant oxidation during DSC measurements especially when high surface area powdered samples are used. In such cases good practice is (a) to use open pans under inert gas atmosphere (argon or nitrogen as second choice); (b) check the mass before and after the experiment or, if available, run a TG or TG–DTA, TG–DSC experiments to make sure that mass remains unchanged during crystallization. The gas flow rates are typically maintained in the range 30–50 mL min$^{-1}$. If closed pans have to be used, they should be closed in a glove bag under inert gas.

DSC measurements are conducted in either isothermal or nonisothermal mode. Isothermal measurements are typically preceded by a nonisothermal scan, whose aim is to select a proper temperature range for subsequent isothermal runs. For glass crystallization, the proper range is usually somewhat above the onset temperature but markedly below the peak temperature on the DSC signal. A similar approach can be used for melt crystallization but selected temperature should be somewhat below the onset temperature measured by DSC on cooling. Then a series of isothermal measurements is performed within the selected range of temperatures. The heating or cooling rate to reach the isothermal crystallization temperature should be sufficiently fast (typically $\geq$50 K min$^{-1}$). This would minimize the formation of new nuclei, thereby ensuring that the crystallization event is fully detected during the isothermal scan. When collecting a set of data in a series of isothermal or nonisothermal runs, it is important to make sure that the heat of crystallization is consistent within the series. The respective variation within the series should not exceed a few percent.

One of the most important problems of nonisothermal measurements is associated with collecting data at excessively fast heating rates. Due to the limited thermal conductivity, the temperature inside the sample can deviate markedly from that of the reference or, in other words, of the furnace. The temperature difference can cause an error of 10–20% in values of the activation energy and the logarithm of preexponential factor [1]. Keeping in mind that the thermal conductivity of inorganic materials is significantly larger than that of polymers, crystallization of the former can be studied by using larger masses and faster heating/ cooling rates (see Section 6). It is recommended that the heating and cooling rates are kept under 40 K min$^{-1}$ and the sample mass under 15 mg to prevent the appearance of significant temperature gradients due to the heat of crystallization. Fig. 16 shows how the heat released during crystallization may cause a noticeable increase in the sample temperature relative to the programmed (reference) temperature [84]. The upward peaks between 375 and 600 °C appear during the crystallization process. For kinetic purposes, this difference should be as small as possible. Unfortunately, some older DSC models do not allow for evaluating the sample temperature. However, if they do, one should certainly be advised to check the deviation between the sample and reference temperatures (for details see Section 8).

The baseline selection is important for accurate determination of the transformed fraction at any temperature/time, and thus, for correct conversion of DSC data into kinetic curves ($\alpha$ vs. $t$ or $T$). Baseline selection affects the DSC peak onset temperature, the peak area, and ultimately the kinetic curve shape. For nonisothermal crystallization, an accurate baseline can be obtained in two steps. First is heating the sample to the temperature, at which the process is complete (no further heat release). Second is cooling
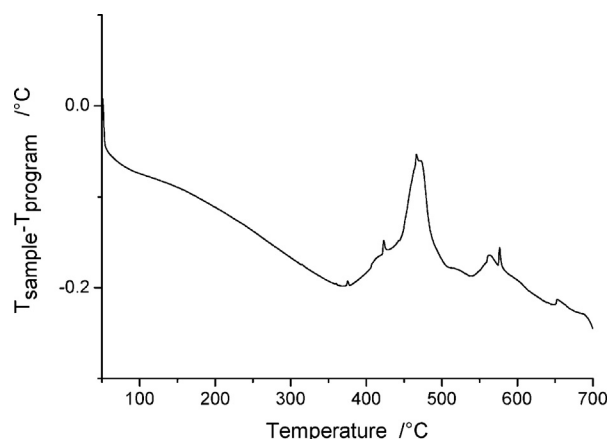


**Fig. 16.** Difference between the sample and program temperature versus the programmed temperature collected during the DSC scan of a Fe rich metallic glass at a heating rate of 20 K min$^{-1}$.

it back to the initial temperature and heating again at the same heating rate to the completion temperature [85]. Then, the DSC signal produced in the second scan can be used as the baseline that should be subtracted from the first scan so that the resulting peak can be used for accurate evaluation of characteristic temperatures (onset, peak, etc) and of kinetic curves. To obtain a good baseline, it is recommended to start and finish heating respectively at ~50 °C below and above the crystallization event i.e., the respective on-set and off-set temperatures. Before applying this two-step procedure, one needs to check that no reverse processes take place on cooling. A similar two-step procedure can be applied to isothermal data to account properly for the warm-up period during which the sample temperature rises to the preset isothermal temperature. Care should be taken to avoid crystallization during this nonisothermal period. This process is especially undesired considering that the initial heating to the present temperature is done at very fast heating rate. That is, if crystallization does take place during the warm-up period, the fast heat release from the crystallizing sample can significantly raise the sample temperature [86]. To avoid this kind of problems, one is recommended to select lower isothermal temperature and repeat the experiment.

One of the main problems of analysis of experimental data on crystallization is the process complexity due to an overlap between surface and bulk nucleation-growth mechanisms [87]. Note that the respective contribution of the surface process would increase with decreasing the particle size i.e., increasing the surface-to-volume ratio. The relative contributions may also change due to the temperature gradient e.g., if crystallization heat cannot dissipate quickly enough to the surroundings, the temperature inside the sample can be markedly higher than on the surface that would accelerate bulk crystallization to a larger extent than the surface one. Other factors to consider are the creation of surface crystallization centers arising from the sample preparation/ treatment (e.g., polishing, grinding) and changing the amount of volume nuclei due to changing the time lengths of pre-nucleation and glass preparation. Changing the relative contribution of the surface and bulk crystallization may result in obtaining different kinetic parameters (e.g., the activation energy). For example, different activation energies can be observed when changing the heating rates because the latter can affect the magnitude of the temperature gradients, and thus, the relative contributions of the surface and bulk processes. Furthermore, the enthalpies of crystallization of bulk (low surface area) and powder (high surface area) samples can differ [88].

## 8. Hazardous processes

Hazardous materials include so-called "reactive or self-reactive chemicals" which may decompose exothermically without reacting with oxygen in air. Sometimes, self-reactive substances are referred to as unstable because many of them may undergo thermal decomposition at a relatively low temperature. It is commonly assumed that in thermal analysis experiments the heat released (or absorbed) by a reaction is exchanged with the surroundings so fast that the rate of heat transfers can be ignored. However, hazardous materials tend to generate heat at very fast rates that can easily exceed the rate of heat transfer. The resulting heat accumulation leads to self-heating of the sample and creation of a temperature gradient inside it. When the local sample temperature rises above the preset and controlled temperature of surroundings, the local reaction rate exceeds the rate expected at the temperature of surroundings that may become a source of significant errors in kinetic analysis. The influence of self-heating and temperature gradients within the sample on reaction kinetics was reported in numerous studies [89–98].

The magnitude of temperature gradients inside the sample depends on the physical parameters of the material (heat capacity, thermal conductivity, and density), the thermodynamic and kinetic parameters of the reaction (reaction heat, activation energy, pre-exponential factor, and reaction kinetic model), and the user-controlled parameters of experiment (sample size, heating rate or temperature, type of sample crucible, gas atmosphere). The present recommendations are focused primarily on selecting appropriate sample masses as well as heating rates (nonisothermal measurements) and temperatures (isothermal measurements) that are the user-controlled parameters that affect most strongly the quality of kinetic data.

Detection of self-heating is not always straightforward because its magnitude and appearance may depend on various technical parameters and, in particular, on the type and position of the temperature sensor. For example in TG instruments, which measure suspended samples, the temperature sensor is necessarily located at a distance from the sample that creates a difficulty of detecting self-heating even when the sample and reaction heat are relatively large.

The effect of self-heating on the course of $d\alpha/dt$ and $\alpha$ vs. $T$ curves is presented in Fig. 17. The curves have been simulated using a reaction model of the sigmoidal type (truncated Šesták–Berggren model [1]), $f(\alpha) = \alpha(1 - \alpha)$, and the following values of the reaction heat and kinetic parameters: $\Delta H_r = -500\,J\,g^{-1}$, $A = 10^{10}\,s^{-1}$, $E = 100$ $kJ\,mol^{-1}$. The sample size was taken to be 8 mg for heating rates ($\beta$) 0.5; 1; 2; 4 and 8 K min$^{-1}$. In addition, for 8 K min$^{-1}$ the simulation was also performed for a smaller mass of 4 mg. As seen in Fig. 17, the temperature gradient inside the sample can be revealed by comparing the kinetic curves plotted against the sample temperature ($T_s$) with those plotted against the reference temperature ($T_{Ref.}$). The gradient is obviously increasing with increasing the heating rate, and at $\beta = 8$ K min$^{-1}$ the shift of the peak maxima is as large as 47 °C. Undoubtedly, such deviations from the expected temperature ($T_s$) would give rise to inadequate kinetic data that must be discarded from any kinetic analysis. Note that lowering the mass to 4 mg reduces the temperature shift at 8 K min$^{-1}$ to less than 6 °C.

Fig. 18 provides an example of estimating the activation energy by applying a differential isoconversional method [1] to the $\alpha$ vs. $T$ dependences presented in Fig. 17. The computations were carried out using the data $\alpha$ vs. $T_{Ref.}$ and $\alpha$ vs. $T_s$ for the samples masses 1, 2, 4 and 8 mg. Also, the same computations were performed by replacing the $\alpha$ vs. $T$ data obtained for 8 mg sample at $\beta = 8$ K min$^{-1}$ with the data obtained at the same heating rate for 4 mg sample (curves labeled as "8/4"). Analysis of the estimated values of the activation energy clearly illustrates the significant impact of the sample mass and self-heating on the kinetic evaluations. The deviation between the accurate value $E = 100\,kJ\,mol^{-1}$ and estimated values is the largest when the temperature used in kinetic computations does not represent adequately the actual temperature distribution within the sample. This happens when one conducts the computation by using $T_{Ref.}$ (plots on the right of Fig. 18) instead of $T_s$. Reducing self-heating improves the results of kinetic computations. Replacing the curve in which self-heating is the largest (8 mg at $\beta = 8$ K min$^{-1}$) with the one obtained at the same heating rate by lower mass (4 mg) results in significantly more accurate value of the activation energy.

It should be noted that above simulations are done for the extreme case i.e., for autocatalytic reactions. If a reaction of the same reaction heat follows decelerating ($n$-th order) kinetics, the
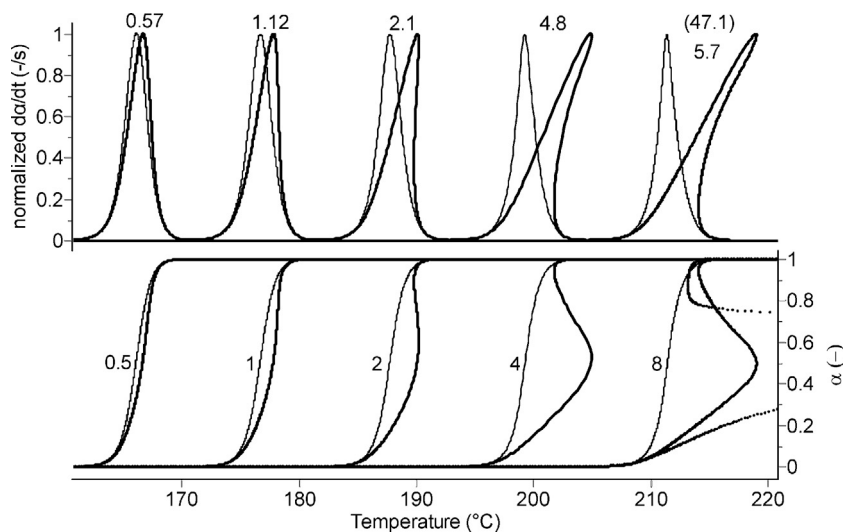


**Fig. 17.** Dependence of normalized reaction rate (top) and extent of conversion (bottom) on the sample (bold line) and reference (thin line) temperatures simulated for nominal heating rates of 0.5, 1, 2, 4 and 8 K min$^{-1}$ (marked on curves). The simulations were done for sample mass of 8 mg, for $\beta = 8$ K min$^{-1}$ an additional simulation for 4 mg is presented in the graph. The shift of peak maxima (displayed in °C) indicates self-heating of the samples, its maximum value for $\beta = 8$ K min$^{-1}$ and $m = 8$ mg is 47.1 °C, the $\alpha$–$T_s$ dependence for this case is displayed as dashed line (bottom graph).
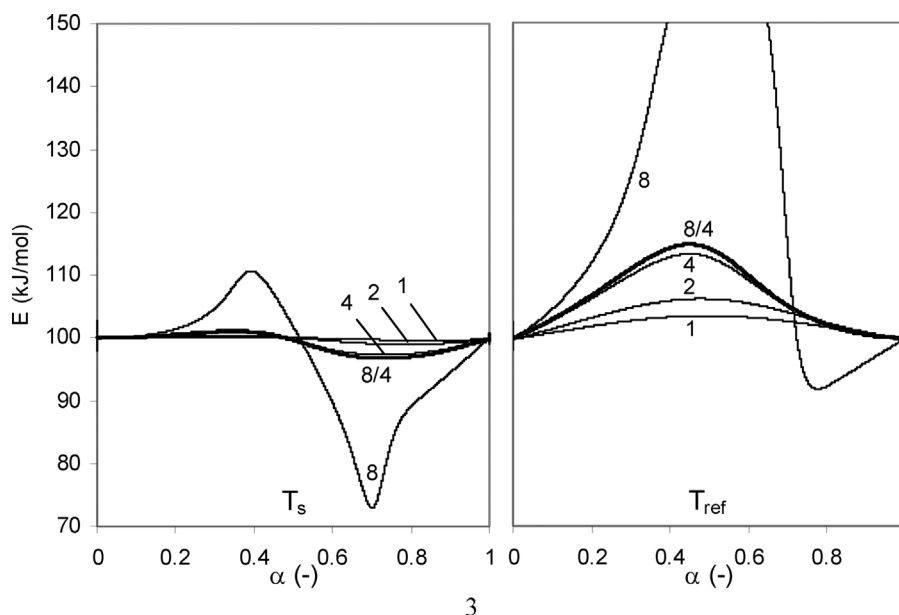
**Fig. 18.** Dependences $E$–$\alpha$ computed from the data simulated as a function of $T_s$ and $T_{Ref.}$ for sample masses 1, 2, 4 and 8 mg (marked on curves). The case when mass 8 mg applied at all heating rates was replaced by 4 mg at $\beta = 8\,K\,min^{-1}$ is marked in bold and labelled by "8/4".

temperature gradients inside the sample are significantly smaller. However, because the reaction mechanism and kinetics are usually unknown it is safer to make the extreme case assumptions.

The simulated example just considered gives rise to the following set of recommendations on collecting adequate kinetic data for processes that occur with large reaction heat. First off, in case of large self-heating, the measurements in which only the reference (or oven) temperature is measured may not be suitable for kinetic computations. It is always recommended to use the sample temperature which represents more adequately the actual reaction temperature. The accuracy of such computations (Fig. 18, left) is significantly better than that of the computations based on the reference temperature (Fig. 18, right), which cannot account in principle for any self-heating.

The heating rates of non-isothermal experiments and the temperatures of isothermal ones should be selected as low as possible. When selecting the ranges of $\beta$ it is necessary to take into account that at least 4–5 runs with the ratio of the highest to lowest $\beta$ of about 10 is recommended. The doubling of heating rates in the consecutive experiments is a rational approach. The sample mass should be as small as possible while being representative of the material under study. The optimal sample mass is typically in the range 1–10 mg and it should be maintained reasonably similar at all heating rates.

To reveal possible self-heating, the collection of data should start from the maximum heating rate (typically around $10\,K\,min^{-1}$, in Fig. 17 it is $8\,K\,min^{-1}$) and using the mass deemed suitable for all heating rates (in Fig. 17 it is 8 mg). The choice of the starting heating rate and sample (mass, size) generally depends on the sample properties as well as on the previous experiences with the materials of similar kind. To check the presence of self-heating the measured heat flow (DSC) or mass loss (TG) data should be converted to the form $d\alpha/dt$ or $\alpha$ and plotted as a function of $T_s$ and $T_{Ref.}$ as illustrated in Fig. 17. The difference between respective dependences vs. $T_s$ and $T_{Ref.}$ indicates the presence of temperature gradients (i.e., self-heating or self-cooling) and gives an idea about their sizes. If the gradient is large (as in the case of 8 mg at $8\,K\,min^{-1}$ in Fig. 17), the sample size should be decreased by half at the highest heating rate (in our example 8/2 = 4 mg at $8\,K\,min^{-1}$), and the experiment should

be repeated. This procedure is also recommended for measurements containing only the reference temperature. Then the effect of self-heating can be detected as the effect of the sample mass on the values of the kinetic parameters (see below).

After preliminary runs with largest mass and heating rate, the data collection should be completed by carrying out at least four additional runs with lower heating rates e.g., 0.5, 1, 2 and $4\,K\,min^{-1}$ as shown in Fig. 17. It is recommended to use similar sample mass for these heating rates. As a rule of a thumb (see results displayed in Fig. 17), the value of the heating rate times the sample mass should be constant for two highest heating rates. For example, in Fig. 17, the selected sample mass is 8 mg; therefore, for the two fastest heating rates of 4 and $8\,K\,min^{-1}$ the sample masses are 8 and 4 mg, respectively. The effectiveness of this rule is clear from the kinetic computations shown in Fig. 18.

To check the effect of the temperature gradients on kinetic parameters, one can use two sets of data obtained for the samples of different masses. The first should include the higher mass at the fastest heating rate (as 8 mg at $8\,K\,min^{-1}$ in our example), the second a lower mass (4 mg) at the same heating rate. A change in the $E$ value with the sample mass (see Fig. 18) indicates the presence of the temperature gradients. If evaluated $E$ values depend strongly (a change in $E$ is larger than the average error in $E$) on the sample mass it is recommended to collect a new dataset with smaller sample mass at the highest $\beta$. This test is most useful when measurements contain only the reference temperature. If both $T_s$ and $T_{Ref.}$ are available, comparison of kinetic evaluations obtained from $d\alpha/dt$ (or $\alpha$) vs. $T_s$ and from $d\alpha/dt$ (or $\alpha$) vs. $T_{Ref.}$ can provide information about the effect of the temperature gradients. For example, if the $E$ values calculated from the two respective datasets are similar within the average error in $E$, then the temperature gradients are practically negligible and the reference (or oven) temperature can be used for kinetic computations.

In conclusion, there are a few more important miscellaneous recommendations which are as follows. For materials in which melting occurs before or during the chemical reaction (not uncommon for energetic materials), the kinetic parameters determined for the reaction in the liquid state can be inapplicable to predict the reaction kinetics in the solid phase. In such situation,

the experiments should be performed either isothermally or at very slow heating rates to keep the reaction temperature below the melting temperature as reported elsewhere [99,100].

Many hazardous materials are designed for service in hermetically closed cartridges. Also, many safety tests require the use of closed containers. Therefore, rate measurements performed by using hermetically sealed and oftentimes high pressure crucibles in DSC are most relevant [101] for kinetic computations as well as for scaling-up the results from milligram to kilogram scale [102]. If for some reason the open crucibles have to be used, it is important to remember that results obtained in sealed and open crucibles may be significantly different [103]. An interesting solution for diminishing large temperature gradients inside the sample consists in placing heat exchange elements of high thermal conductivity inside the sample crucibles [104]. Due to the fact that DSC on sealed crucibles is usually recommended for data collection, the flow rate and a kind of the purge gas play secondary role. When working with open crucibles, one has to carry the experiments in an inert atmosphere ($N_2$, Ar). On the other hand, the use of helium can be problematic because due to its high thermal conductivity it can decrease the sensitivity of the heat flow signals in DSC.

Last but not least, a comment should be made about the use of sparse kinetic data that are used sometimes for predicting the lifetime of energetic materials as well as pharmaceutical, polymeric and other materials. Such data are collected in a discontinuous mode, sometimes taking one point per day or week. Recommendations on checking reliability of such data and their suitability for making predictions are discussed in detail elsewhere [105].

## 9. Conclusions

The present recommendations offer plenty of practical advice as to how to deal with typical problems that can make experimental data inadequate to the processes of interest. All these recommendations boil down to several general guiding principles, which are as follows. Kinetic measurements should never be conducted under a set of arbitrarily chosen conditions as well as on a set of samples of randomly chosen shape and size. Before embarking on performing actual kinetic measurements, one must invest time and effort in exploratory runs. Such runs should reveal the effects of the sample and conditions on the kinetic data as well as repeatability of the measurements. The purpose is to select the sample and conditions so that their effects on the kinetic data are minimized. Since it is rarely possible to obtain kinetic data that are conditions and sample independent, care must be taken to ensure that throughout the whole series of measurements the conditions and sample are well defined and controlled, and that their effects on the kinetics are known. Also, the measurements should always be performed on the instrument that is calibrated under the conditions similar to those of the actual measurements and by using a calibrant whose physical parameters are reasonably close to those of the actual sample. Only when these principles are followed, one can obtain kinetic data that are adequate to the process kinetics.

## Acknowledgements

## References

[1] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, Thermochim. Acta 520 (2011) 1–19.

[2] S. Vyazovkin, The handbook of thermal analysis and calorimetry, in: M.E. Brown, P.K. Gallagher (Eds.), Recent Advances, Techniques and Applications, vol. 5, Elsevier, 2008, pp. 503–538.

[3] P.K. Gallagher, The handbook of thermal analysis and calorimetry, in: M.E. Brown (Ed.), Principles and Practice, vol. 1, Elsevier, Amsterdam, 1998, pp. 225–278.

[4] P.K. Gallagher, R. Blaine, E.L. Charsley, N. Koga, R. Ozao, H. Sato, S. Sauerbrunn, D. Schultze, H. Yoshida, Magnetic temperature standards for TG, J. Therm. Anal. Calorim. 72 (2003) 1109–1116.

[5] A.R. McGhie, J. Chiu, P.G. Fair, R.L. Blaine, Thermogravimetric apparatus temperature calibration using melting point standards, Thermochim. Acta 67 (1983) 241–250.

[6] S. Vyazovkin, I. Dranca, A DSC study of $\alpha$- and $\beta$-relaxations in a PS-clay system, J. Phys. Chem. B 108 (2004) 11981–11987.

[7] K. Chen, S. Vyazovkin, Isoconversional kinetics of glass aging, J. Phys. Chem. B 113 (2009) 4631–4635.

[8] K. Chen, S. Vyazovkin, Temperature dependence of sol–gel conversion kinetics in gelatin-water system, Macromol. Biosci. 9 (2009) 383–392.

[9] S. Vyazovkin, B. Yancey, K. Walker, Nucleation driven kinetics of poly(ethylene terephthalate) melting, Macromol. Chem. Phys. 214 (2013) 2562–2566.

[10] S. Vyazovkin, B. Yancey, K. Walker, Polymer melting kinetics appears to be driven by heterogeneous nucleation, Macromol. Chem. Phys. 215 (2014) 205–209.

[11] C.E.H. Bawn, in: W.E. Garner (Ed.), Chemistry of the Solid State, Butterworth, London, 1955, pp. 254–267.

[12] S. Vyazovkin, J.S. Clawson, C.A. Wight, Thermal dissociation kinetics of solid and liquid ammonium nitrate, Chem. Mater. 13 (2001) 960–966.

[13] J.A. Hedvall, Changes in crystal structure and their influence on the reactivity and catalytic effect of solids, Chem. Rev. 15 (1934) 139–168.

[14] P.K. Gallagher, The handbook of thermal analysis and calorimetry, in: M.E. Brown, P.K. Gallagher (Eds.), Applications to Inorganic and Miscellaneous Materials, vol. 2, Elsevier, Amsterdam, 2003, pp. 191–260.

[15] A.K. Galwey, Structure and order in thermal dehydrations of crystalline solids, Thermochim. Acta 355 (2000) 181–238.

[16] N. Koga, H. Tanaka, A physico-geometric approach to the kinetics of solid-state reactions as exemplified by the thermal dehydration and decomposition of inorganic solids, Thermochim. Acta 388 (2002) 41–61.

[17] A. Khawam, D.R. Flanagan, Solid-state kinetic models: basics and mathematical fundamentals, J. Phys. Chem. B 110 (2006) 17315–17328.

[18] N. Koga, J. Málek, J. Šesták, H. Tanaka, Data treatment in non-isothermal kinetics and diagonostic limits of phenomenological models, Netsu Sokutei 20 (1993) 210–223.

[19] N. Koga, J.M. Criado, Kinetic analyses of solid-state reactions with a particle-size distribution, J. Am. Ceram. Soc. 81 (1998) 2901–2909.

[20] H. Tanaka, N. Koga, Self-cooling effect on the kinetics of nonisothermal dehydration of lithium sulfate monohydrate, J. Therm. Anal. 36 (1990) 2601–2610.

[21] N. Koga, J.M. Criado, The influence of mass transfer phenomena on the kinetic analysis for the thermal decomposition of calcium carbonate by constant rate thermal analysis (CRTA) under vacuum, Int. J. Chem. Kinet. 30 (1998) 737–744.

[22] N. Koga, Y. Goshi, S. Yamada, L.A. Pérez-Maqueda, Kinetic approach to partially overlapped thermal decomposition processes, J. Therm. Anal. Calorim. 111 (2013) 1463–1474.

[23] H. Tanaka, N. Koga, A.K. Galwey, Thermal dehydration of crystalline hydrates: microscopic studies and introductory experiments to the kinetics of solid-state reactions, J. Chem. Educ. 72 (1995) 251–256.

[24] N. Koga, Y. Goshi, M. Yoshikawa, T. Tatsuoka, Physico-geometrical kinetics of solid-state reactions in an undergraduate thermal analysis laboratory, J. Chem. Educ. 91 (2014) 239–245.

[25] N. Koga, H. Tanaka, Effect of sample mass on the kinetics of thermal decomposition of a solid. 2. Isothermal dehydration of Li2SO4·H2O, J. Therm. Anal. 40 (1993) 1173–1179.

[26] N. Koga, J.M. Criado, H. Tanaka, Apparent kinetic behavior of the thermal decomposition of synthetic malachite, Thermochim. Acta 341 (1999) 387–394.

[27] J.M. Criado, L.A. Pérez-Maqueda, in: O.T. Sörensen, J. Rouquerol (Eds.), Sample Controlled Thermal Analysis: Origin, Goals, Multiple Forms and Future, Kluwer, Dordrecht, 2003, pp. 62–101.

[28] http://www.noble.matthey.com/pdfs-uploaded/16%20Platinum%20Labware.pdf.

[29] D. Bikiaris, A. Vassiliou, K. Chrissafis, K.M. Paraskevopoulos, A. Jannakoudakis, A. Docoslis, Effect of acid treated multi-walled carbon nanotubes on the mechanical, permeability, thermal properties and thermo-oxidative stability of isotactic polypropylene, Polym. Deg. Stab. 93 (2008) 952–967.

[30] L. Rouchon, L. Favergeon, M. Pijolat, Analysis of the kinetic slowing down during carbonation of CaO by CO2, J. Therm. Anal. Calorim. 113 (2013) 1145–1155.

[31] M. Pijolat, M. Soustelle, Experimental tests to validate the rate-limiting step assumption used in the kinetic analysis of solid-state reactions, Thermochim. Acta 478 (2008) 34–40.

[32] S. Perrin, Modélisation de la cinétique de transformations non isothermes et (ou) non isobares. Application à la déshydroxylation de la kaolinite et à la réduction de l'octooxyde de triuranium par l'hydrogène, Thèse Saint-Etienne (2002) 158.

[33] K. Surla, F. Valdivieso, M. Pijolat, M. Soustelle, M. Prin, Kinetic study of the oxidation by oxygen of liquid Al–Mg 5% alloys, Solid State Ionics 143 (2001) 355–365.

[34] M. Tupin, M. Pijolat, F. Valdivieso, M. Soustelle, A. Frichet, P. Barberis, Differences in reactivity of oxide growth during the oxidation of zircaloy-4 in water vapor before and after the kinetic transition, J. Nucl. Mater. 317 (2003) 130–144.

[35] M. Tupin, M. Pijolat, F. Valdivieso, M. Soustelle, Oxidation kinetics of ZrNbO in steam: differences between the pre- and post-transition stages, J. Nucl. Mater. 342 (2005) 108–118.

[36] M. Pijolat, F. Valdivieso, M. Soustelle, Experimental test to validate the rate equation "dα/dt=kf(α)" used in the kinetic analysis of solid state reactions, Thermochim. Acta 439 (2005) 86–93.

[37] C. Brun, F. Valdivieso, M. Pijolat, M. Soustelle, Reduction by hydrogen of U₃O₈ into UO₂ : nucleation and growth, influence of hydration, Phys. Chem. Chem. Phys. 1 (1999) 471–477.

[38] H. Galai, M. Pijolat, M. Soustelle, Mechanism of growth of MgO and CaCO₃ during a dolomite partial decomposition, Solid State Ionics 178 (2007) 1039–1047.

[39] K. Nahdi, S. Perrin, M. Pijolat, F. Rouquerol, N. Ariguib, M. Ayadi, Nucleation and anisotropic growth model for isothermal kaolinite dehydration under controlled water vapor pressure, Phys. Chem. Chem. Phys. 4 (2002) 1972–1977.

[40] M. Pijolat, Favergeon Loic, M. Soustelle, From the drawbacks of the Arrhenius-f(α) rate equation towards a more general formalism and new models for the kinetic analysis of solid–gas reactions, Thermochim. Acta 525 (2011) 93–102.

[41] R.B. Prime, in: E.A. Turi (Ed.), Thermal Characterization of Polymeric Materials, Academic Press, New York, 1981, pp. 435 (Chapter V).

[42] F. Dimier, N. Sbirrazzuoli, B. Vergnes, M. Vincent, Curing kinetics and chemorheological analysis of polyurethane formation, Polym. Eng. Sci. 44 (2004) 518–527.

[43] V.L. Zvetkov, Comparative DSC kinetics of the reaction of DGEBA with aromatic amines. I. Non-isothermal kinetic study of the reaction of DGEBA with m-phenylene diamine, Polymer 42 (2001) 6687–6697.

[44] N. Sbirrazzuoli, S. Vyazovkin, A. Mititelu, C. Sladic, L. Vincent, A study of epoxy-amine cure kinetics by combining isoconversional analysis with temperature modulated DSC and dynamic rheometry, Macromol. Chem. Phy. 204 (2003) 1815–1821.

[45] N. Sbirrazzuoli, A. Mititelu-Mija, L. Vincent, C. Alzina, Isoconversional kinetic analysis of stoichiometric and off-stoichiometric epoxy-amine cures, Thermochim. Acta 447 (2006) 167–177.

[46] J. Wang, M.P.G. Laborie, M.P. Wolcott, Comparison of model-free kinetic methods for modeling the cure kinetics of commercial phenol–formaldehyde resins, Thermochim. Acta 439 (2005) 68–73.

[47] G. He, B. Riedl, Phenol-urea-formaldehyde cocondensed resol resins: their synthesis, curing kinetics, and network properties, J. Polym. Sci.: Part B 41 (2003) 1929–1938.

[48] N. Guigo, A. Mija, L. Vincent, N. Sbirrazzuoli, Chemorheological analysis and model-free kinetics of acid catalysed furfuryl alcohol polymerization, Phys. Chem. Chem. Phys. 9 (2007) 5359–5366.

[49] X.F. Fnandez-Francos, J.M. Salla, A. Cadenato, J.M. Morancho, A. Mantecon, A. Serra, X. Ramis, Novel thermosets obtained by UV-induced cationic copolymerization of DGEBA with an spirobislactone, J. Polym. Sci. A: Polym. Chem. 45 (2007) 5446–5458.

[50] N. Sbirrazzuoli, L. Vincent, J. Bouillard, L. Élégant, Isothermal and non-isothermal kinetics: when mechanistic information available, J. Therm. Anal. Calorim. 56 (1999) 783–792.

[51] H. Cai, P. Li, G. Sui, Y. Yu, G. Li, X. Yang, S. Ryu, Curing kinetics study of epoxy resin/flexible amine toughness systems by dynamic and isothermal DSC, Thermochim. Acta 473 (2008) 101–105.

[52] L. Zhao, X. Hu, A variable reaction order model for prediction of curing kinetics of thermosetting polymers, Polymer 48 (2007) 6125–6133.

[53] S. Vyazovkin, N. Sbirrazzuoli, Effect of viscosity on the kinetics of initial cure stages, Macromol. Chem. Phys. 201 (2000) 199–203.

[54] G. Van Assche, A. Van Hemelrijck, H. Rahier, B. Van Mele, Modulated differential scanning calorimetry: non-isothermal cure, vitrification, and devitrification of thermosetting systems, Thermochim. Acta 286 (1996) 209–224.

[55] S. Montserrat, F. Roman, P. Colomer, Vitrification and dielectric relaxation during the isothermal curing of an epoxy–amine resin, Polymer 44 (2003) 101–114.

[56] S. Vyazovkin, N. Sbirrazzuoli, Kinetic methods to study isothermal and nonisothermal epoxy-anhydride cure, Macromol. Chem. Phys. 200 (1999) 2294–2303.

[57] R. Androsch, M.L. Di Lorenzo, Crystal nucleation in glassy poly(ʟ-lactic acid), Macromolecules 46 (2013) 6048–6056.

[58] M.L. Di Lorenzo, P. Sajkiewicz, A. Gradys, P. La Pietra, Optimization of melting conditions for the analysis of crystallization kinetics of poly(3-hydroxybutyrate), e-Polymers 9 (2009) 313–324.

[59] A. Miyagi, B. Wunderlich, Superheating and reorganization on melting of poly(ethylene terephthalate), J. Polym. Sci. Part A-2: Polym. Phys. 10 (1972) 1401–1405.

[60] A. Miyagi, B. Wunderlich, Etching of crystalline poly(ethylene terephthalate) by hydrolysis, J. Polym. Sci.: Polym. Phys. Ed. 10 (1972) 2073–2083.

[61] A. Miyagi, B. Wunderlich, Annealing during polymerization of crystalline poly(ethylene terephthalate), J. Polym. Sci.: Polym. Phys. Ed. 10 (1972) 2085–2092.

[62] M. Kunioka, Y. Doi, Thermal degradation of microbial copolyesters: poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and poly(3-hydroxybutyrate-co-4-hydroxybutyrate), Macromolecules 23 (1990) 1933–1936.

[63] M.L. Di Lorenzo, P. Sajkiewicz, P. La Pietra, A. Gradys, Irregularly shaped DSC exotherms in the analysis of polymer crystallization, Polym. Bull. 57 (2006) 713–721.

[64] M.L. Di Lorenzo, P. Rubino, R. Luijkx, M. Hélou, Influence of chain structure on crystal polymorphism of poly(lactic acid). Part 1: effect of optical purity of the monomer, Colloid Polym. Sci. 292 (2014) 399–409.

[65] M.C. Righetti, M.L. Di Lorenzo, Nonlinear determination of the equilibrium melting temperature from initial nonreorganized crystals of poly(3-hydroxybutyrate), Polym. Eng. Sci. 52 (2012) 2383–2390.

[66] J.N. Hay, P.J. Mills, The use of differential scanning calorimetry to study polymer crystallization kinetics, Polymer 23 (1982) 1380–1384.

[67] J.J. Cruz-Pinto, J.A. Martius, M.J. Oliveira, The isothermal crystallization of engineering polymers – POM and PEEK, Colloid Polym. Sci. 272 (1994) 1–16.

[68] M.C. Righetti, M.L. Di Lorenzo, M. Angiuli, E. Tombari, P. La Pietra, Poly (butylene terephthalate)/poly(ε-caprolactone) blends: influence of PCL molecular mass on PBT melting and crystallization behaviour, Eur. Polym. J. 43 (2007) 4726–4738.

[69] J.N. Hay, P.A. Fitzgerald, M. Wiles, Use of differential scanning calorimetry to study polymer crystallization kinetics, Polymer 17 (1976) 1015–1018.

[70] A. Mehmet-Alkan, J.N. Hay, The crystallinity of poly(ether ether ketone), Polymer 33 (1992) 3527–3530.

[71] B. Wunderlich, The basis of thermal analysis, in: E. Turi (Ed.), Thermal Characterization of Polymeric Materials, Revised second ed., Academic Press, New York, 1997, pp. 205–482 (Chapter 2).

[72] B. Monasse, J.M. Haudin, Thermal dependence of nucleation and growth rate in polypropylene by non isothermal calorimetry, Colloid Polym. Sci. 264 (1986) 117–122.

[73] M.L. Di Lorenzo, S. Cimmino, C. Silvestre, Nonisothermal crystallization of isotactic polypropylene blended with poly(α-pinene). I. Bulk crystallization, J.Appl. Polym. Sci. 82 (2001) 358–367.

[74] S.M. Sarge, W. Hemminger, E. Gmelin, G.W.H. Höhne, H.K. Cammenga, W. Eysel, Metrologically based procedures for the temperature, heat and heat flow rate calibration of DSC, J. Therm. Anal. 49 (1997) 1125–1134.

[75] G.W.H. Höhne, H.K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, The temperature calibration of scanning calorimeters, Thermochim. Acta 160 (1990) 1–12.

[76] E. Gmelin, S.M. Sarge, Temperature, heat and heat flow rate calibration of differential scanning calorimeters, Thermochim. Acta 347 (2000) 9–13.

[77] J.D. Menczel, Temperature calibration of heat flux DSC's on cooling, J. Therm. Anal. 49 (1997) 193–199.

[78] S. Neuenfeld, C. Schick, Verifying the symmetry of differential scanning calorimeters concerning heating and cooling using liquid crystal secondary temperature standards, Thermochim. Acta 446 (2006) 55–65.

[79] M.A. Abdel-Rahim, A.Y. Abdel-Latief, M.N. Abd-el Salam, Kinetic analysis of crystallization process of Se-In-Pb glasses-isoconversion method, Thermochim. Acta 573 (2013) 57–64.

[80] T. Sánchez, J. Bonastre, J.D. Santos, M.L. Sánchez, A. Chizhik, J. González, J.J. Suñol, B. Hernando, The effect of field-quenching fabrication on the magnetoimpedance response in Co66Fe4Ni1Si15B14 amorphous ribbons, J. Appl. Phys. 111 (2012) 053913.

[81] P.K. Singh, K.S. Dubey, Thermodynamical analysis of the glass-forming ability of bulk metallic glasses, J. Therm. Anal. Calorim. 110 (2012) 1443–1450.

[82] V. Zhukova, S. Kaloshkin, A. Zhukov, J. González, DSC studies of Finemet-type glass-coated microwires, J. Magn. Magn. Mater. 249 (2002) 539–542.

[83] J. Bonastre, L. Escoda, J. Saurina, J.J. Suñol, J.D. Santos, M.L. Sánchez, B. Hernando, Non-isothermal approach to crystallization process of a Co-rich alloy, J. Non-Cryst. Solids 354 (2008) S126–S128.

[84] S. Vyazovkin, Evaluation of the activation energy of thermally stimulated solid-state reactions under arbitrary variation of temperature, J. Comput. Chem. 18 (1997) 402–593.

[85] S. Zuzjakova, P. Zeman, S. Kos, Non isothermal kinetics of phase transformations in magnetron sputtered alumina films with metastable structure, Thermochim. Acta 572 (2013) 85–93.

[86] R.F. Speyer, S.H. Risbud, Kinetics of phase transformations in amorphous materials by DSC. Part II, Thermochim. Acta 131 (1988) 225–240.

[87] R. Svoboda, J. Málek, Crystallization kinetics of amorphous Se: part 1. Interpretation of kinetic functions, J. Therm. Anal. Calorim. 114 (2013) 473–482.

[88] J. Málek, Kinetic analysis of crystallization processes in amorphous materials, Thermochim. Acta 395 (2000) 239–253.

[89] P.K. Gallagher, D.W. Johnson Jr, The effects of sample size and heating rate on the kinetics of the thermal decomposition of CaCO₃, Thermochim. Acta 6 (1973) 67–83.

[90] S.S. Alves, Simple estimation of the temperature error in thermogravimetric experiments, Thermochim. Acta 157 (1990) 249–257.

[91] H. Bockhorn, A. Hornung, U. Hornung, P. Jakobströer, Modelling of isothermal and dynamic pyrolysis of plastics considering non-homogeneous temperature distribution and detailed degradation mechanism, J. Anal. Appl. Pyrolysis 49 (1999) 53–74.

[92] G. Várhegyi, The effects of imperfect temperature programming on the kinetic evaluation of thermoanalytical curves. Part 3. Error bounds for the activation energy and the formal reaction order, Thermochim. Acta 65 (1983) 333–350.

[93] U. Biader Ceipidor, R. Bucci, A.D. Magri, Using thermoanalytical data. Part 2. The dependence of kinetic data available from thermogravimetry on sample and instrument parameters: a method for calculating "true" kinetic parameters, Thermochim. Acta 161 (1990) 37–49.

[94] R.E. Lyon, N. Safronova, J. Senese, S. Stoliarov, Thermokinetic model of sample response in nonisothermal analysis, Thermochim. Acta 545 (2012) 82–89.

[95] J.Y. Armand, J.M. Vergnaud, Effects of the value of heating rate in DSC on the kinetic parameters, when there is high enthalpy of reaction, Thermochim. Acta 131 (1988) 15–27.

[96] X. Gao, D. Chen, D. Dollimore, The effect of the reaction heat on kinetic analysis by TG under a rising temperature program, part 3, Thermochim. Acta 221 (1993) 1–12.

[97] K.N. Ninan, Thermal decomposition kinetics. XIII. Effect of sample mass on the thermal decomposition kinetics of $CaC_2O_4 \cdot H_2O$ from isothermal mass-loss data, Thermochim. Acta 74 (1984) 143–150.

[98] N. Koga, H. Tanaka, Effect of sample mass on the kinetics of thermal decomposition of a solid. Part 3. Non-isothermal mass-loss process of molten $NH_4NO_3$, Thermochim. Acta 240 (1994) 141–151.

[99] A.K. Burnham, R.K. Weese, Thermal Decomposition Kinetics of HMX, LLNL Report UCRL-TR-204262-Rev-1, (2004). https://e-reports-ext.llnl.gov/pdf/314135.pdf.

[100] B. Roduit, M. Hartmann, P. Folly, A. Sarbach, P. Brodard, R. Baltensperger, Determination of thermal hazard from DSC measurements. Investigation of Self Accelerating Decomposition Temperature (SADT) of AIBN, J. Therm. Anal. Calorim. (2014). . (in press) http://dx.doi.org/10.1007/s10973-014-3903-3.

[101] T. Yoshida, Y. Wada, N. Foster, Safety of reactive chemicals and pyrotechnics, industrial safety series, Experimental Evaluation of Fire and Explosion Hazard of Reactive Substances, vol. 5, Elsevier, 1995 (Chapter 3), p. 73–86.

[102] B. Roduit, P. Folly, B. Berger, J. Mathieu, A. Sarbach, H. Andres, M. Ramin, B. Vogelsanger, Evaluating SADT by advanced kinetics-based simulation approach, J. Therm. Anal. Calorim. 93 (2008) 153–161.

[103] U. Ticmanis, G. Pantel, S. Wilker, G. Holl, New setup for microcalorimetry of dangerous reactions- estimation of critical data of propellants, Proceedings of 37th International Annual Conference of ICT, Karlsruhe, Germany, 2006, pp. 31.

[104] G.W. Suter, V. Stocks, C. Gwereder, M. Eiche, Heat exchange elements in sample cells for thermal analysis, Chem. Eng. Trans. 31 (2013) 895–900.

[105] B. Roduit, M. Hartmann, P. Folly, A. Sarbach, R. Baltensperger, Prediction of thermal stability of materials by modified kinetic and model selection approaches based on limited amount of experimental points, Thermochim. Acta 579 (2014) 31–39.