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Review

ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data

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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 reliable evaluation of kinetic parameters (the activation energy, the pre-exponential factor, and the reaction model) from the data obtained by means of thermal analysis methods such as thermogravimetry (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). The recommendations cover the most common kinetic methods, model-free (isoconversional) as well as model-fitting. The focus is on the problems faced by various kinetic methods and on the ways how these problems can be resolved. Recommendations on making reliable kinetic predictions are also provided. The objective of these recommendations is to help a non-expert with efficiently performing analysis and interpreting its results.

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Foreword

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 14th ICTAC Congress (São Pedro, Brazil, 2008) and further publicized during the kinetics symposium at the 37th NATAS Conference (Lubbock, USA, 2009). Consistent kinetic recommendations had long been overdue and the idea gained a strong support of the participants of both meetings as well as of the thermal analysis community in general. 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. Data requirements (Burnham); 3. Isoconversional methods (Vyazovkin and Sbirrazzuoli); 4. The method of Kissinger (Pérez-Maqueda and Criado); 5. The method of Invariant kinetic parameters (Sbirrazzuoli); 6. Determining reaction models and preexponetial factors (Pérez-Maqueda, Criado, and Vyazovkin); 7. Model-fitting methods (Burnham, Pérez-Maqueda, and José Criado). 8. Kinetic predictions (Popescu). The first draft of the document was finished in July, 2010 and was a result of extensive discussion and reconciliation of the opinions of all authors. The draft was presented at the 10th ESTAC Conference (Rotterdam, the Netherlands, 2010) at the kinetics workshop organized by Vyazovkin and Popescu (the chairman of the ICTAC Committee on life-time prediction of materials). The presentation was followed by a two hours discussion during which numerous suggestions were made by some 20 attendees. The workshop was finished by encouraging the audience to provide further written comments on the draft of recommendations. Separately, a number of experts were approached individually with a similar request. The written comments were received from thirteen individuals.

The collected comments were very supportive, instructive, and important that, however, did not make the task of properly accommodating them an easy one. After careful discussion it was decided to make a good faith effort to accommodate the suggestions as much as possible while keeping the final document concise and consistent with its major objective. This objective was to provide a newcomer to the field of kinetics with pragmatic guidance in efficiently applying the most common computational kinetic methods to a widest variety of processes such as the thermal decomposition of solids, thermal and thermo-oxidative degradation of polymers, crystallization of melts and glasses, polymerization and crosslinking, and so on. In keeping with this objective, it was not possible to include detailed recommendations on specific types of processes as well as on the methods that were either less common or too new to gain sufficient usage in the community.

1. Introduction

The previous project by the ICTAC Kinetics Committee was focused on extensive comparison of various methods for computation of kinetic parameters [1]. It was a conclusion of the project that the methods that use multiple heating rate programs (or, more generally, multiple temperature programs) are recommended for computation of reliable kinetic parameters, while methods that use a single heating rate program (or, single temperature program) should be avoided. The present recommendations result from a new project by the ICTAC Kinetics Committee. It is still maintained that only multiple temperature programs methods should be used for kinetic computations, and expert advice on the efficient use of these methods is provided.

Kinetics deals with measurement and parameterization of the process rates. Thermal analysis is concerned with thermally stimulated processes, i.e., the processes that can be initiated by a change in temperature. The rate can be parameterized in terms of three major variables: the temperature, T; the extent of conversion, α; the pressure, P as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \tag{1.1}$$

The pressure dependence, $h(P)$ is ignored in most of kinetic computational methods used in the area of thermal analysis. It should, however, be remembered that the pressure may have a profound effect on the kinetics of processes, whose reactants and/or products are gases. Unfortunately, monographic literature on thermal analysis rarely mentions the effect of pressure on the reaction kinetics, which can be represented in different mathematical forms [2–4]. The kinetics of oxidation and reduction of solids depends on the partial pressure of the gaseous oxidant or reductant. The gaseous products of decomposition can be reactive toward the decomposing substance causing autocatalysis as frequently seen in decomposition of nitro energetic materials. In this case, the local concentration of the reactive product depends strongly on the total pressure in the system and can be expressed in the form of the power law [5]:

$$h(P) = P^n \tag{1.2}$$

Similar formalism can be suitable for the reactions of oxidation and/or reduction, where P would be the partial pressure of the gaseous reactant. The rate of reversible decompositions can demonstrate a strong dependence on the partial pressure of the gaseous products. If the latter are not removed efficiently from the reaction zone, the reaction proceeds to equilibrium. Many of reversible solid-state decompositions follow the simple stoichiometry: $A_{\text{solid}} \Leftrightarrow B_{\text{solid}} + C_{\text{gas}}$ so that the pressure dependence of their rate can be presented as

$$h(P) = 1 - \frac{P}{P_{eq}} \tag{1.3}$$

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

	Reaction model	Code	$f(\alpha)$	$g(\alpha)$
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	One-dimensional diffusion	D1	$1/2\alpha^{-1}$	α^{2}
6	Mampel (first order)	F1	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami–Erofeev	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
8	Avrami–Erofeev	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion	D3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^{2}$
11	Contracting sphere	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	Contracting cylinder	R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	Two-dimensional diffusion	D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$

where P and P_{eq} are respectively the partial and equilibrium pressures of the gaseous product C. Although $h(P)$ can take other more complex forms, a detailed discussion of the pressure dependence is beyond the scope of the present recommendations. The latter concern exclusively the most commonly used methods that do not explicitly involve the pressure dependence in kinetic computations. This is equivalent to the condition $h(P) = \text{const}$ throughout an experiment. For pressure dependent reactions, this condition can be accomplished by supplying a large excess of a gaseous reactant in gas–solid reactions and/or by effectively removing reactive gaseous products in reversible and autocatalytic reactions. If the aforementioned condition is not satisfied, an 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 [4].

As already stated, the majority of kinetic methods used in the area of thermal analysis consider the rate to be a function of only two variables, T and α:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1.4}$$

The dependence of the process rate on temperature is represented by the rate constant, $k(T)$, and the dependence on the extent of conversion by the reaction model, $f(\alpha)$. Eq. (1.4) describes the rate of a single-step process. The extent of conversion, α, is determined experimentally as a fraction of the overall change in a physical property that accompanies a process. If a process is accompanied by mass loss, the extent of conversion is evaluated as a fraction of the total mass loss in the process. If a process is accompanied by release or absorption of heat, the extent of conversion is evaluated as a fraction of the total heat released or absorbed in the process. In either case, α increases from 0 to 1 as the process progresses from initiation to completion. It must be kept in mind that the physical properties measured by the thermal analysis methods are not species-specific and, thus, usually cannot be linked directly to specific reactions of molecules. For this reason, the value of α typically reflects the progress of the overall transformation of a reactant to products. The overall transformation can generally involve more than a single reaction or, in other words, multiple steps each of which has it specific extent of conversion. For example, the rate of the overall transformation process that involves two parallel reactions can be described by the following equation:

$$\frac{d\alpha}{dt} = k_1(T)f_1(\alpha_1) + k_2(T)f_2(\alpha_2) \tag{1.5}$$

In Eq. (1.5), α_1 and α_2 are the specific extents of conversion respectively associated with the two individual reactions (steps), and their sum yields the overall extent of conversion: $\alpha = \alpha_1 + \alpha_2$. More complex multi-step models are discussed in Section 7.

One of the present recommendations is that it is crucial for reliable kinetic methods to be capable of detecting and treating the multi-step kinetics. Note that if a process is found to obey a single-step equation (Eq. (1.4)), one should not conclude that the process mechanism involves one single step. More likely, the mechanism involves several steps but one of them determines the overall kinetics. For instance, this would be the case of a mechanism of two consecutive reactions when the first reaction is significantly slower than the second. Then, the first process would determine the overall kinetics that would obey a single-step Eq. (1.4), whereas the mechanism involves two steps.

The temperature dependence of the process rate is typically parameterized through the Arrhenius equation

$$k(T) = A\exp\left(\frac{-E}{RT}\right) \tag{1.6}$$

where A and E are kinetic parameters, the preexponential factor and the activation energy, respectively, and R is the universal gas constant. It must be kept in mind that some processes have a non-Arrhenius temperature dependence, an important example being the temperature dependence of the rate of the melt crystallization (nucleation) [4]. The experimentally determined kinetic parameters are appropriate to call "effective", "apparent", "empirical", or "global" to stress the fact that they can deviate from the intrinsic parameters of a certain individual step. Because of both non-species specific nature of the thermal analysis measurements and complexity of the processes studied by the thermal analysis techniques, it proves extremely difficult to obtain intrinsic kinetic parameters of a step that are not affected by kinetic contributions from other steps and diffusion. Generally, effective kinetic parameters are functions of the intrinsic kinetic parameters of the individual steps. For example, the effective activation energy is most likely to be a composite value determined by the activation energy barriers of the individual steps. As such, it can demonstrate the behavior not typically expected from the activation energy barrier. For instance, the effective activation energy can vary strongly with the temperature and the extent of conversion [6,7] or take on negative values [8].

The temperature is controlled by thermal analysis instruments in accord with a program set up by an operator. The temperature program can be isothermal, $T = \text{const}$, or nonisothermal, $T = T(t)$. The most common nonisothermal program is the one in which the temperature changes linearly with time so that

$$\beta = \frac{dT}{dt} = \text{const} \tag{1.7}$$

where β is the heating rate.

The conversion dependence of the process rate can be expressed by using a wide variety [9] of reaction models, $f(\alpha)$, some of which are presented in Table 1. It should be remembered that most of these models are specific to the solid-state reactions. That is, they may have a very limited (if any) applicability when interpreting the reaction kinetics that do not involve any solid phase. It is always useful to make sure whether a solid substance would react in the

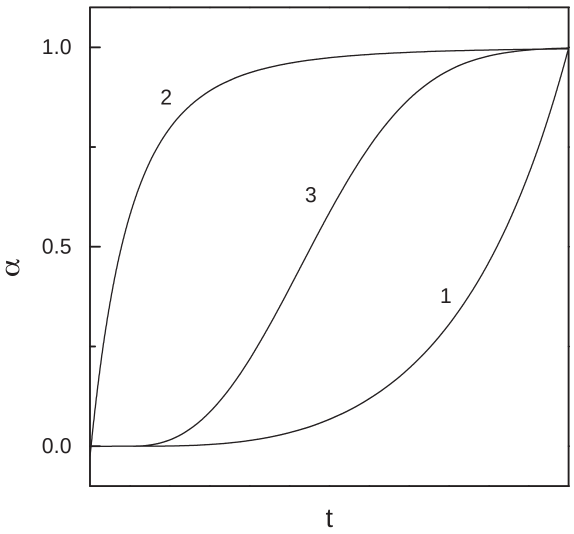

Fig. 1. Characteristic α vs. t "reaction profiles" for (1) accelerating, (2) decelerating, and (3) sigmoidal models.

solid state when heated. On heating, before a reaction starts a solid crystalline substance can melt or a solid amorphous substance can undergo the glass transition so that in either case the reaction would take place in the liquid phase. At any rate, one should be advised to use the reaction models appropriate to the process being studied.

Although there is a significant number of reaction models, they all can be reduced to three major types: accelerating, decelerating, and sigmoidal (sometimes also called autocatalytic). Each of these types has a characteristic "reaction profile" or "kinetic curve", the terms frequently used to describe a dependence of α or $d\alpha/dt$ on t or T. Such profiles are readily recognized for isothermal data because in this case $k(T)$ = const in Eq. (1.4) so that the kinetic curve shape is determined by the reaction model alone. However, under non-isothermal conditions both $k(T)$ and $f(\alpha)$ vary simultaneously giving rise to sigmoidal α vs. T curves that makes it rather difficult to recognize the reaction model type. The respective isothermal α vs. t reaction profiles are shown in Fig. 1. Accelerating models represent processes whose rate increases continuously with increasing the extent of conversion and reaches its maximum at the end of the process. Models of this type can be exemplified by a power–law model:

$$f(\alpha) = n\alpha^{(n-1)/n} \tag{1.8}$$

where n is a constant. Models of the decelerating type represent processes whose rate has maximum at the beginning of the process and decreases continuously as the extent of conversion increases. The most common example here is a reaction-order model:

$$f(\alpha) = (1-\alpha)^n \tag{1.9}$$

where n is the reaction order. Diffusion models (Table 1) are another class of decelerating models. Sigmoidal models represent processes whose initial and final stages demonstrate respectively the accelerating and decelerating behavior so that the process rate reaches its maximum at some intermediate values of the extent of conversion. The Avrami–Erofeev models

$$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n} \tag{1.10}$$

provide a typical example of the sigmoidal kinetics. Only those kinetic methods that are capable of treating all three types of the conversion dependencies can be recommended as reliable methods. Sestak and Berggren [10] have introduced an empirical model:

$$f(\alpha) = \alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p \tag{1.11}$$

that depending on the combination of m, n, and p can represent a number of different reaction models. It is normally used in truncated form (p = 0 in Eq. (1.11)) that is sometimes also called extended Prout–Tompkins model (the regular Prout–Tompkins model is $f(\alpha) = \alpha(1-\alpha)$). The truncated Sestak–Berggren model is an example of an autocatalytic model.

Combining Eqs. (1.4) and (1.6) yields:

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{1.12}$$

The resulting equation provides a basis for differential kinetic methods. In this form, the equation is applicable to any temperature program, be it isothermal or nonisothermal. It also allows for substitution of the actual sample temperature variation, $T(t)$, for T that can be useful when the sample temperature deviates significantly from the reference temperature (i.e., temperature of the furnace). For constant heating rate nonisothermal conditions, Eq. (1.12) is frequently rearranged as:

$$\beta\frac{d\alpha}{dT} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{1.13}$$

Introduction of the explicit value of the heating rate reduces the applicability of Eq. (1.13) to processes in which the sample temperature does not deviate significantly from the reference temperature.

Integration of Eq. (1.12) leads to:

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A\int_0^t \exp\left(\frac{-E}{RT}\right)dt \tag{1.14}$$

where $g(\alpha)$ is the integral form of the reaction model (Table 1). Eq. (1.14) lays a foundation for a large variety of integral methods. In this form, Eq. (1.14) is applicable to any temperature program that can be introduced by replacing T with $T(t)$. This also means that one can use this equation to introduce in kinetic calculations the actual sample temperature variation, $T(t)$, which is helpful in the situations when the sample temperature demonstrates significant deviation from the reference temperature. For constant heating rate conditions, the integral with respect to time is usually replaced with the integral with respect to temperature:

$$g(\alpha) = \frac{A}{\beta}\int_0^T \exp\left(\frac{-E}{RT}\right)dT \tag{1.15}$$

This rearrangement introduces the explicit value of the heating rate in Eq. (1.15) that means that the application area of the equation is limited to the processes, in which the sample temperature does not deviate significantly from the reference temperature. Because the integral in Eq. (1.15) does not have an analytical solution, a number of approximate solutions were offered in the past. These approximations gave rise to a variety of approximate integral methods. The approximate methods were developed in the early years when neither computers nor software for numerical integration were widely available. Modern integral methods make use of numerical integration that allows one to solve the integrals with very high accuracy.

From the computational standpoint, the purpose of kinetic analysis of thermally stimulated processes is to establish mathematical relationships between the process rate, the extent of conversion, and the temperature. This can be accomplished in several ways. The most straightforward way is determining a kinetic triplet, which is a term frequently used to describe a single set of A, E, and $f(\alpha)$ or

$g(\alpha)$. For a single-step process, evaluating a single kinetic triplet and substituting it into Eq. (1.12) or (1.14) should be sufficient to predict the process kinetics for any desired temperature program, $T(t)$. Multi-step kinetics are predicted by determining several kinetic triplets (one per each reaction step) and substituting them into a respective rate equation, such as Eq. (1.5).

Kinetic analysis can have either a practical or theoretical purpose. A major practical purpose is the prediction of process rates and material lifetimes. The predictions are reliable only when sound kinetic analysis methods are used. The theoretical purpose of kinetic analysis is interpretation of experimentally determined kinetic triplets. Each of the components of a kinetic triplet is associated with some fundamental theoretical concept. E is associated with the energy barrier, A with the frequency of vibrations of the activated complex [8], and $f(\alpha)$ or $g(\alpha)$ with the reaction mechanism [9]. It is recommended that such interpretations of experimentally determined kinetic triplets be made with extreme care. It should be remembered that the kinetic triplets are determined by first selecting a rate equation and then fitting it to experimental data. As a result, meaningful interpretability of the determined triplets depends on whether the selected rate equation captures adequately the essential features of the process mechanism. Note that the issue of the adequateness of a rate equation to a process mechanism goes far beyond the issue of the goodness of statistical fit, because an excellent data fit can be accomplished by using a physically meaningless equation such as that of a polynomial function. The adequacy of a rate equation to represent a process mechanism is primarily the issue of knowing and understanding the process mechanism. For example, a single-step rate equation cannot generally be adequate for a multi-step mechanism. However, it can provide an adequate kinetic representation of a multi-step process that has a single rate-limiting step.

The following sections provide recommendations on the application of the most common model-fitting and model-free methods as well as on their use for the purpose of kinetic predictions.

2. Data requirements

The first requirement for kinetic analysis is to have high quality data. Although measurement methods are not covered by these recommendations, a few of the important required attributes of the resulting data are highlighted. Preprocessing methods are also discussed briefly.

2.1. Effect of temperature errors

The temperature used in the kinetic analysis must be that of the sample. Thermal analysis instruments control precisely the so-called reference (i.e., furnace) temperature, whereas the sample temperature can deviate from it due to the limited thermal conductivity of the sample or due to the thermal effect of the process that may lead to self-heating/cooling. This problem is more severe with larger sample masses and faster heating rates (or higher temperatures), so tests are advisable to demonstrate that there is no sample mass dependence. This is easily tested by performing runs on samples of two markedly different masses (e.g., 10 and 5 mg) and making sure that the obtained data give rise to the kinetic curves that can be superposed or, in other words, are identical within the experimental error. Otherwise, the sample mass needs to be decreased until the superposition is accomplished.

Some computational methods rely on the reference temperature. For example, if a kinetic method uses the value of β in computations, it assumes that a sample obeys the temperature variation predetermined by the value of the heating rate, i.e., the sample temperature does not practically deviate from the reference temperature. In such situation, one should verify this assumption by comparing the sample and reference temperatures. Both values are normally measured by modern thermal analysis instruments. Typical approaches to diminishing the deviation of the sample temperature from the reference temperature are decreasing the sample mass as well as the heating rate (constant heating rate nonisothermal runs) or temperature (isothermal runs). Alternatively, one can use kinetic methods that can account for the actual variation in the sample temperature.

Temperature errors have two types of effects on kinetic parameters and the resulting kinetic predictions [11]. A constant systematic error in the temperature will have a minor effect on the values of A and E, and the predictions will be off by roughly the same amount as the original temperature error, even if the predictions are far outside the temperature range of measurement. A systematic error that depends upon heating rate is far more important, and only a few degrees difference in error between the high and low heating rates can cause an error of 10–20% in E and $\ln A$. Such an error might occur, for example, because the difference in sample and reference temperature becomes larger at faster heating rates. Consequently, it is important that the temperature be calibrated or checked at every heating rate used. When kinetic predictions are made within the temperature range of measurement, their error is only as large as the average temperature error. However, if the prediction is made outside the temperature range of calibration, the error in prediction can be enormous. Understanding the purpose of the kinetic parameters helps define the required accuracy of temperature measurement.

Although kinetic parameters can be determined from data obtained from only two different temperature programs, the use of at least 3–5 programs is recommended. Three different temperatures or heating rates can detect a non-Arrhenius temperature dependence, but the accuracy of the Arrhenius parameters is dominated by the extreme temperatures or heating rates, so replication of the runs at least at those extremes is imperative. The actual range of temperatures and/or heating rates needed in each situation depends on the measurement precision available and on the required accuracy of the kinetic parameters. For example, a $\pm 1\,^\circ\mathrm{C}$ error in temperature measurement leads to a 5% error in E and $\ln A$ if the temperature range related to a given conversion is $\sim 40\,^\circ\mathrm{C}$. Since a doubling of heating rate typically causes the kinetic curve to shift by about $15\,^\circ\mathrm{C}$, a sixfold variation in heating rate would be required for this level of precision.

2.2. Differential vs. integral data

All experimental data have noise. The amount of noise can affect the choice of kinetic analysis method. For example, integral and differential methods are best suitable for respectively analyzing integral (e.g., TGA) and differential (e.g., DSC) data, especially if the data points are sparse. However, good numerical integration and differentiation methods are available to convert integral data to differential data and vice versa as long as the data do not contain too much noise and are closely spaced (e.g., hundreds to thousands of points per kinetic curve). This condition is usually satisfied for modern thermal analysis equipment. Differentiating integral data tends to magnify noise. Data smoothing is a possibility, but the procedure must not be used uncritically. Smoothing may introduce a systematic error (shift) in the smoothed data that would ultimately convert into a systematic error in the values of kinetic parameters. As an extreme smoothing procedure, the noisy data can be fitted to some mathematical function so that the resulting fitted curve can then be used for determining kinetic parameters. A good example of such a function is the Weibull distribution function that is capable of fitting various kinetic curves. However, such an approach should be used with caution. While flexible, the Weibull distribution function can distort the kinetic parameters by inexact kinetic curve matching and by smoothing out real reaction features.

Although differential data are more sensitive to revealing reaction details, their kinetic analysis involves an additional problem of establishing a proper baseline. For nonisothermal conditions, this is rather non-trivial problem because the baseline DSC signal is determined by the temperature dependence of the heat capacities of all individual reactants, intermediates, and products as well as by their amounts that change continuously throughout a process. Thermal analysis instrument software typically offers several types of the baseline corrections (e.g., straight line, integral tangential, and spline). The choice of a baseline may have a significant impact on the kinetic parameters, especially those associated with the initial and final stages of a process. It is, therefore, recommended that one repeats kinetic computations by using different baselines to reveal the effect of the baseline choice on the kinetic parameters. Since the present recommendations are concerned with computational methods that use multiple temperature programs, it is recommended to synchronize the baseline corrections of individual runs with each other by using the same type of a baseline for each temperature program. Also, by assuming that the thermal effect of a process is independent of the temperature program, the individual baselines should be adjusted so that the thermal effects obtained for different temperature programs demonstrate minimal deviations from each other [12]. However, care must be exercised not to force the data into this assumption because some multi-step processes can demonstrate a systematic change in the value of the thermal effect with a change in the temperature program (see [13] and references therein).

Integral TGA data obtained under the conditions of continuous heating also require a baseline correction for the buoyancy effect that reveals itself as an apparent mass gain. However, this correction is quite straightforward. It is accomplished by first performing a blank TGA run with an empty sample pan and then subtracting the resulting blank TGA curve from the TGA curve measured by having placed a sample in this pan. The blank and sample run must obviously be measured under identical conditions.

2.3. *Isothermal vs. constant heating rate runs*

It is frequently asked whether isothermal or constant heating rate experiments are better. The answer is that both have advantages and disadvantages. In fact, strictly isothermal experiments are not possible, because there is always a finite nonisothermal heat-up time (usually a few minutes). The biggest disadvantage of isothermal experiments is a limited temperature range. At lower temperatures, it may be very difficult to reach complete conversion over a reasonable time period. At higher temperatures, the heat-up time becomes comparable to the characteristic time of the process, which means a significant extent of conversion is reached before the isothermal regime sets in. This situation may be practically impossible to avoid, especially when a process demonstrates the decelerating kinetics (Eq. (1.9)), i.e., its rate is the fastest at $\alpha = 0$. Then, the non-zero extent of conversion reached during the nonisothermal heat-up period should be taken into account. It can be readily accounted for in differential kinetic methods (Eq. (1.12)) as well as in the integral methods that perform integration over the actual heating program (i.e., when $T = T(t)$ in Eq. (1.14)). However, this situation cannot be accounted for in the integral methods that integrate Eq. (1.14) assuming strictly isothermal program (i.e., T = const) giving rise to Eq. (3.5). Such methods would unavoidably suffer from computational errors due to the non-zero extent of conversion reached during the nonisothermal heat-up period.

The problem of non-zero conversion is easy to avoid in constant heating rate experiments by starting heating from the temperature that is well below the temperature at which a process becomes detectable. It can generally be recommended to start heating no less than 50–70 °C below that temperature [14]. The biggest disadvantage of constant heating rate experiments is that it is more difficult to identify acceleratory and sigmoidal models and, in particular, the induction periods associated with this type of models. In contrast, the induction periods in an isothermal experiment are hard to miss as long as the sample heat-up time is much shorter than the characteristic reaction time. At any rate, best practice would be to perform at least one isothermal run in addition to a series of constant heating rates runs. The isothermal run would be of assistance in selecting a proper reaction model. As mentioned in Section 1, each of the three model types can be easily recognized from isothermal kinetic curves (Fig. 1). It would also help to verify the validity of kinetic triplets derived from the constant heating rate runs by checking if they can be used to satisfactorily predict the isothermal run. Note that experimental data do not have to be restricted to isothermal or constant heating rate conditions. Numerical methods are available to use any combination of arbitrary temperature programs. In fact, a combination of nonisothermal and isothermal experiments is the best way to properly establish kinetic models. A truly good model should simultaneously fit both types of runs with the same kinetic parameters. It should be stressed that the necessary requirement for assessing the validity of a kinetic model fit is a comparison of the measured and calculated reaction profiles, either rates, or extents of conversion, or both. Only by showing good correspondence using the same kinetic parameters over a range of temperatures and/or heating rates can the parameters have any credence whatsoever.

3. Isoconversional methods

3.1. *General idea*

All isoconversional methods take their origin in the isoconversional principle that states that the reaction rate at constant extent of conversion is only a function of temperature. This can be easily demonstrated by taking the logarithmic derivative of the reaction rate (Eq. (1.4)) at α = const:

$$\left[\frac{\partial \ln(\mathrm{d}\alpha/\mathrm{d}t)}{\partial T^{-1}}\right]_\alpha = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_\alpha + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}}\right]_\alpha \tag{3.1}$$

where the subscript α indicates isoconversional values, i.e., the values related to a given extent of conversion. Because at α = const, $f(\alpha)$ is also constant, and the second term in the right hand side of Eq. (3.1) is zero. Thus:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha = -\frac{E_\alpha}{R} \tag{3.2}$$

It follows from Eq. (3.2) that the temperature dependence of the isoconversional rate can be used to evaluate isoconversional values of the activation energy, E_α without assuming or determining any particular form of the reaction model. For this reason, isoconversional methods are frequently called “model-free” methods. However, one should not take this term literally. Although the methods do not need to identify the reaction model, they do assume that the conversion dependence of the rate obeys some $f(\alpha)$ model.

To obtain experimentally the temperature dependence of the isoconversional rate, one has to perform a series of runs with different temperature programs. This would typically be a series of 3–5 runs at different heating rates or a series of runs at different constant temperatures. It is recommended to determine the E_α values in a wide range of α = 0.05–0.95 with a step of not larger than 0.05 and to report the resulting dependencies of E_α vs. α. The E_α dependence is important for detecting and treating the multi-step kinetics. A significant variation of E_α with α indicates that a process is kinetically complex, i.e., one cannot apply a single-step

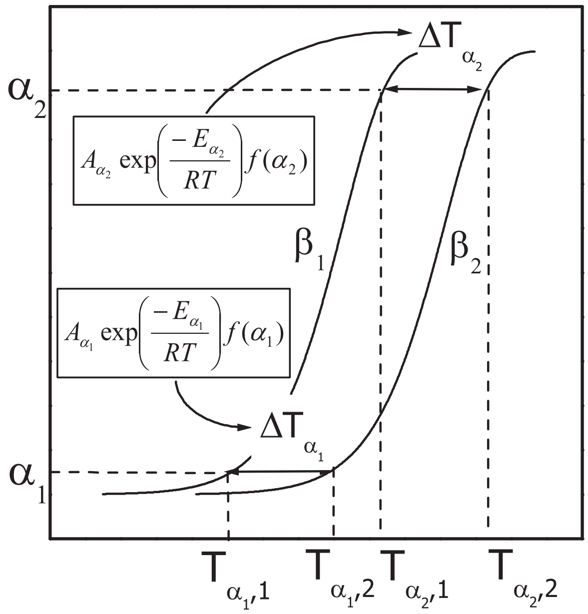

Fig. 2. Each single-step rate equation is associated with a single value of α and a narrow temperature region ΔT related to it.

rate equation (Eq. (1.4) and/or (1.12)) to describe the kinetics of such a process throughout the whole range of experimental conversions and temperatures. Note that the occurrence of a multi-step process does not immediately invalidate the application of the isoconversional principle, although the latter holds strictly for a single-step process. The principle continues to work as a reasonable approximation because isoconversional methods describe the process kinetics by using multiple single step kinetic equations, each of which is associated with a certain extent of conversion and a narrow temperature range (ΔT) related to this conversion (Fig. 2). As a matter of fact, the E_α dependencies evaluated by an isoconversional method allow for meaningful mechanistic and kinetic analyses as well as for reliable kinetic predictions [4,15].

The isoconversional principle lays a foundation for a large number of isoconversional computational methods. They can generally be split in two categories: differential and integral. Several of the most popular methods of these two categories are discussed in the following two sections.

3.2. *Differential isoconversional methods*

The most common differential isoconversional method is that of Friedman [16]. The method is based on the following equation

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \qquad (3.3)$$

Eq. (3.3) can be easily derived by applying the isoconversional principle to Eq. (1.12). As with Eq. (1.12), Eq. (3.3) is applicable to any temperature program. At each given α, the value of E_α is determined from the slope of a plot of $\ln(d\alpha/dt)_{\alpha,i}$ against $1/T_{\alpha,i}$. The index i is introduced to denote various temperature programs. $T_{\alpha,i}$ is the temperature at which the extent of conversion α is reached under ith temperature program. For isothermal temperature programs, i identifies an individual temperature. For linear nonisothermal programs (Eq. (1.7)), i identifies an individual heating rate. In the latter case, Eq. (3.3) is frequently used in the following form:

$$\ln\left[\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \qquad (3.4)$$

The resulting Eq. (3.4) assumes that $T_{\alpha,i}$ changes linearly with the time in accord with the heating rate β_i. That is, one cannot substitute the actual sample temperature for $T\alpha_{,i}$ in Eq. (3.4) to account for effect of self-heating/cooling. However, Eq. (3.3) can be used for this purpose. It should be noted that both equations are applicable to the processes that occur on cooling ($\beta < 0$) such as crystallization of melts.

Since the differential isoconversional methods do not make use of any approximations, they are potentially more accurate than the integral methods considered in the following section. However, the practical use of the differential methods is unavoidably associated with certain inaccuracy as well as with imprecision. Firstly, when the methods are applied to the differential data such (e.g., DSC and DTA), significant inaccuracy in the rate values can be introduced due to the difficulty of determining the baseline [17]. Inaccuracies also arise when the reaction heat shows a noticeable dependence on heating rate [13]. As mentioned earlier, the application of the differential methods to the integral data (e.g., TGA) requires using numerical differentiation that introduces imprecision (noise) into the rate data and may also introduce inaccuracy when the noisy data are smoothed. With these problems in mind, the differential methods should not be considered as being necessarily more accurate and precise than the integral methods.

3.3. *Integral isoconversional methods*

Integral isoconversional methods originate from the application of the isoconversional principle to the integral equation (1.14). The integral in Eq. (1.14) does not have an analytical solution for an arbitrary temperature program. However, an analytical solution can be obtained for an isothermal temperature program:

$$g(\alpha) = A\exp\left(\frac{-E}{RT}\right)t \qquad (3.5)$$

Some simple rearrangement followed by the application of the isoconversional principle gives rise to Eq. (3.6)

$$\ln t_{\alpha,i} = \ln\left[\frac{g(\alpha)}{A_\alpha}\right] + \frac{E_\alpha}{RT_i} \qquad (3.6)$$

where $t_{\alpha,i}$ is the time to reach a given extent of conversion at different temperatures T_i. This is an equation for an integral isoconversional method for isothermal conditions. The value of E_α is determined from the slope of the plot $\ln t_{\alpha,i}$ vs. $1/T_i$.

For the commonly used constant heating rate program, Eq. (1.14) transforms into Eq. (1.15) that does not have an analytical solution. For this reason, there is a number of integral isoconversional methods that differ in approximations of the temperature integral in Eq. (1.15). Many of these approximations give rise to linear equations of the general form [17]:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^B}\right) = Const - C\left(\frac{E_\alpha}{RT_\alpha}\right) \qquad (3.7)$$

where B and C are the parameters determined by the type of the temperature integral approximation. For example, a very crude approximation by Doyle [18] yields $B = 0$ and $C = 1.052$ so that Eq. (3.7) takes the form also known as the Ozawa [19], and/or Flynn and Wall [20] equation:

$$\ln(\beta_i) = \mathrm{Const} - 1.052\left(\frac{E_\alpha}{RT_\alpha}\right) \qquad (3.8)$$

The crude temperature integral approximation results in inaccurate values of E_α. A more accurate approximation by Murray and White gives rise to $B = 2$ and $C = 1$ and leads to another popular equation that is frequently called the Kissinger–Akahira–Sunose equation [21]:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{Const} - \frac{E_\alpha}{RT_\alpha} \tag{3.9}$$

Compared to the Ozawa–Flynn–Wall method, the Kissinger–Akahira–Sunose method offers a significant improvement in the accuracy of the E_α values. As shown by Starink [17], somewhat more accurate estimates of E_α are accomplished when setting $B = 1.92$ and $C = 1.0008$ so that Eq. (3.7) turns into:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = \text{Const} - 1.0008\left(\frac{E_\alpha}{RT_\alpha}\right) \tag{3.10}$$

Since the aforementioned Eqs. (3.7)–(3.10) are equally easy to solve by applying linear regression analysis, it is recommended to use the more accurate equations such as (3.9) and (3.10). Eq. (3.8) is very inaccurate and should not be used without performing an iterative correction procedure for the value of E_α. Examples of such procedures can be found in the literature [22,23]. Here, one should be strongly advised against the frequently encountered practice of performing and reporting kinetic analyses based on the concurrent use of more than one form of Eq. (3.7). The concurrent use of two or more such equations only reveals the trivial difference in the E_α values computed by the methods of different accuracy. Since no kinetic information is produced from such comparison, the practice of the concurrent use of Eqs. (3.7)–(3.10) should be eliminated in favor of using of only one more accurate equation.

Further increase in the accuracy can be accomplished by using numerical integration. An example of such approach is integral isoconversional methods developed by Vyazovkin [24–26]. For a series of runs performed at different heating rates, the E_α value can be determined by minimizing the following function [24]:

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} \tag{3.11}$$

where the temperature integral:

$$I(E_\alpha, T_\alpha) = \int_0^{T_a}\exp\left(\frac{-E_\alpha}{RT}\right)dT \tag{3.12}$$

is solved numerically. Minimization is repeated for each value of α to obtain a dependence of E_α on α.

All the integral methods considered so far (Eqs. (3.6)–(3.12)) have been derived for a particular temperature program, e.g., Eq. (3.6) holds when the program is strictly isothermal, Eqs. (3.7)–(3.12), when the temperature changes linearly with the time in accord with the heating rate β. Integral isoconversional methods can be made as applicable to any temperature program as the differential method of Friedman (Eq. (3.3)) is. This is accomplished by performing numerical integration over the actual temperature programs. Eqs. (3.11) and (3.12) are readily adjusted for this purpose. Indeed, for a series of runs conducted under different temperature programs, $T_i(t)$, the E_α value is determined by minimizing the following function [25]:

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{J\left[E_\alpha, T_i(t_\alpha)\right]}{J\left[E_\alpha, T_j(t_\alpha)\right]} \tag{3.13}$$

where the integral with respect to the time:

$$J[E_\alpha, T(t_\alpha)] = \int_0^{t_a}\exp\left[\frac{-E_\alpha}{RT(t)}\right]dt \tag{3.14}$$

is solved numerically. Minimization is repeated for each value of α to obtain a dependence of E_α on α.

Performing integration with respect to the time expands significantly the application area of integral isoconversional methods. Firstly, it allows one to account for the effect of self-heating/cooling by substituting the sample temperature variation for $T_i(t)$. Secondly, it gives rise to the integral methods that are applicable to the processes that occur on cooling ($\beta < 0$) such as melt crystallization. Note that Eqs. (3.7)–(3.11) cannot be used for a negative value of β. These equations are based on the integration from 0 to T_α that always yields a nonnegative value of the temperature integral (Eq. (3.12)) which if divided over negative β would yield nonsensical negative values of $g(\alpha)$ (Eq. (1.15)). On the other hand, Eq. (3.11) can be easily adjusted to the conditions of cooling by carrying out integration not from 0 to T_α but from T_0 to T_α where T_0 is the upper temperature from which the cooling starts. Because $T_0 > T_\alpha$, the respective temperature integral will be negative and being divided over negative β will yield physically meaningful positive values of $g(\alpha)$.

All integral isoconversional equations considered so far (Eqs. (3.6)–(3.14)) are based on solving the temperature integral under the assumption that the value of E_α remains constant over the whole interval of integration, i.e., E_α is independent of α. In practice, E_α quite commonly varies with α [4,15]. A violation of the assumption of the E_α constancy introduces a systematic error in the value of E_α. The error can be as large as 20–30% in the case of strong variations of E_α with α [26]. This error does not appear in the differential method of Friedman and can be eliminated in integral methods by performing integration over small segments of either temperature or time. This type of integration is readily introduced into Eq. (3.11) by computing the temperature integral as

$$I(E_\alpha, T_\alpha) = \int_{T_{a-\Delta\alpha}}^{T_a}\exp\left(\frac{-E_\alpha}{RT}\right)dT \tag{3.15}$$

or into Eq. (3.13) by computing the time integral as:

$$J[E_\alpha, T(t_\alpha)] = \int_{t_{a-\Delta\alpha}}^{t_a}\exp\left[\frac{-E_\alpha}{RT(t)}\right]dt \tag{3.16}$$

In both cases, the constancy of E_α is assumed only for small intervals of conversion, $\Delta\alpha$. The use of integration by segments yields E_α values that are practically identical with those obtained when using the differential method of Friedman [13,26,27].

It should be stressed that the present overview of isoconversional methods is not meant to cover all existing isoconversional methods, but to present the major problems and typical approaches to solving these problems. Among computationally simple methods, the differential method of Friedman is the most universal one because it is applicable to a wide variety of temperature programs. Unfortunately, this method is used rather rarely in actual kinetic analyses, whereas the most commonly used is the integral method of Ozawa–Flynn–Wall that has a very low accuracy and limited to linear heating rate conditions. Integral isoconversional methods can accomplish the same degree universality as the differential method, but at expense of relatively complicated computations (e.g., Eqs. (3.11)–(3.16)). However, for most practical purposes computationally simple integral methods (e.g., Eqs. (3.9) and (3.10)) are entirely adequate. There are some typical situations when one should consider using either more computationally complex integral methods or differential methods. First, when the E_α values vary significantly with α, e.g., when the difference between the maximum and minimum values of E_α is more than 20–30% of the average E_α. To eliminate the resulting systematic error in E_α, one would have to employ a method that involves integration over small segments. Second, when the sample temperature deviates significantly from the reference temperature or, generally, when the experiment is conducted under an arbitrary temperature program. To account for this difference in integral methods, one would have to employ a method that makes use of integration over the actual temperature program. Third, when experiments are conducted under linear cooling rate conditions ($\beta < 0$). Negative heating rates can be accounted for by the methods that allow integration to be carried out from larger to smaller temperature. As mentioned earlier, all these situations are resolved by using advanced integral methods (Eqs. (3.11)–(3.16)). However, in the recent literature several simplified versions of this approach have been proposed that can provide adequate solutions in the aforementioned situations.

3.4. *Interpreting E_α vs. α dependencies*

Although the isoconversional activation energies can be used in applications without interpretation, the latter is often desirable for obtaining mechanistic clues or for providing initial guesses for model fitting methods. If E is roughly constant over the entire conversion range and if no shoulders are observed in the reaction rate curve, it is likely that a process is dominated by a single reaction step and can be adequately described by a single-step model. However, it is more common that the reaction parameters vary significantly with conversion. If the reaction rate curve has multiple peaks and/or shoulders, the E and $\ln A$ (for determination of pre-exponential factors see Section 6) values at appropriate levels of conversion can be used for input to multi-step model fitting computations (Section 7).

As far as the mechanistic clues, one should keep in mind that many thermally initiated processes have characteristic E_α vs. α dependencies as follows [4,15]. Crosslinking reactions can demonstrate a change in E_α associated with vitrification that triggers a switch from chemical to diffusion control. Processes having a reversible step, such as dehydration, tend to yield a decreasing E_α vs. α dependence that reflects a departure from the initial equilibrium. Crystallization of melts on cooling commonly yields negative values of E_α that increase with α. In the glass transitions, E_α can demonstrate a significant decrease with α as a material converts from glass to liquid. Fossil fuels, polymers and other complex organic materials tend to have $\ln A$ and E increase as conversion increases. This is consistent with the residual material becoming increasingly refractory. Characteristic E_α vs. α dependencies can also be observed for the processes of protein denaturation [28], gelation [29], gel melting [30], and physical aging or structural relaxation [31].

In addition, the E_α vs. α dependencies or derived from them E_α vs. T_α dependencies can be used for model fitting purposes [32,33]. This is done by fitting an experimentally evaluated E_α vs. α or vs. T_α dependence to the theoretical one. The latter is derived by applying Eq. (3.2) to the rate equation specific to a process being studied [32,33].

4. The method of Kissinger

Because of its easy use the Kissinger method [34] has been applied for determining the activation energies more extensively than any other multiple-heating rate method. However, the method has a number of important limitations that should be understood. The limitations arise from the underlying assumptions of the method. The basic equation of the method has been derived from Eq. (1.12) under the condition of the maximum reaction rate. At this point $d^2\alpha/dt^2$ is zero:

$$\frac{d^2\alpha}{dt^2} = \left[\frac{E\beta}{RT_m{}^2} + Af'(\alpha_m)\exp\left(\frac{-E}{RT_m}\right)\right]\left(\frac{d\alpha}{dt}\right)_m = 0 \qquad (4.1)$$

where $f'(\alpha) = df(\alpha)/d\alpha$ and the subscript m denotes the values related to the rate maximum. It follows from Eq. (4.1) that:

$$\frac{E\beta}{RT_m^2} = -Af'(\alpha_m)\exp\left(\frac{-E}{RT_m}\right) \qquad (4.2)$$

After simple rearrangements Eq. (4.2) is transformed into the Kissinger equation:

$$\ln\left(\frac{\beta}{T_{m,i}^2}\right) = \ln\left(-\frac{AR}{E}f'(\alpha_m)\right) - \frac{E}{RT_{m,i}} \qquad (4.3)$$

In the Kissinger method, the left hand side of equation (4.3) is plotted against $1/T_m$ giving rise to a straight line whose slope yields the activation energy.

One limitation of the method is associated with the fact that determination of an accurate E value requires $f'(\alpha_m)$ to be independent of the heating rate. Otherwise, the first term in the right hand side of Eq. (4.3) would not be constant and the plot of $\ln(\beta/T_{m,i}{}^2)$ vs. $1/T_{m,i}$ would deviate systematically from a straight line, producing a systematic error in E. Strict independence of $f'(\alpha_m)$ on β is accomplished for a first order kinetic model (F1) because $f'(\alpha) = -1$ (see Table 1). Since for other models $f'(\alpha)$ depends on α, a variation of α_m with β would result in violating the independence of $f'(\alpha_m)$ from β. A variation of α_m with β is negligible for nth-order and Avrami–Erofeev models (i.e., A1, A2, A3 in Table 1) [35] and minor for distributed reactivity models [36]. However, α_m may vary significantly with β [37–39]. That is the reason why the Kissinger method should not be generally called “isoconversional” and confused with the isoconversional Kissinger–Akahira–Sunose method (Eq. (3.9)). Since the Kissinger method yields a reliable estimate of E only when α_m does not practically vary with β, the latter condition must be checked by evaluating the α_m values. A significant variation of α_m with β can be detected on visual inspection as a change in the peak shape with the heating rate [23]. It should be noted that the magnitude of the systematic error in E decreases with increasing the E/RT value so that for E/RT values larger than 10 the error in E does not exceed 5% for many reaction models [37–39].

Another important limitation is that the Kissinger method produces a single value of the activation energy for any process regardless of its actual kinetic complexity. As a result, the activation energy determined can adequately represent only single-step kinetics (Eq. (1.4)). An adequate representation of the commonly encountered multi-step kinetics would normally require more than a single value of the activation energy. Therefore, it is necessary to use an isoconversional method to back up the veracity of the Kissinger estimates. Note that a quick check for the validity of the single-step assumption can be performed by comparing the Kissinger estimate against the E value derived from the slope of the $\ln(\Delta t_{1/2})$ vs. $1/T_m$ plot, where $\Delta t_{1/2}$ is the $d\alpha/dt$ peak width at its half-height [40]. As long as the single-step assumption is valid, the two values must be practically identical.

In addition to the aforementioned limitations, the Kissinger method is applicable only to the processes that occur under linear heating rate conditions. Sometimes the method has been used in the case of nonlinear heating programs such as those observed in so called Hi-Res TGA experiments. It has been shown [41] that such use could only be justified when α_m does not change between different heating programs. However, typically α_m varies significantly with the heating program so that the application of the Kissinger method results in large errors in the activation energy. Another commonly encountered incorrect application of the Kissinger method is kinetic analysis of data obtained under linear cooling conditions such as in the case of the melt crystallization. It has been demonstrated [42] that β in the Kissinger method cannot be replaced with a positive value of the "cooling rate" and that such practice results in incorrect values of the kinetic parameters. It is, therefore, recommended that the application of the Kissinger method be generally limited to the data obtained under linear heating rate conditions.

The Kissinger method can be extended to a simple form of model fitting. The *A* and *E* values derived from the application of Eq. (4.3) imply a specific peak width and asymmetry if the reaction is first order. Deviations of the measured width and asymmetry from that predicted from the first-order model can be used to estimate reaction parameters for both nucleation-growth [43] and Gaussian distributed reactivity [44] models. These parameters are particularly useful to choose an appropriate model and provide initial guesses for model fitting by nonlinear regression described in Section 7.

A note of caution must be made about using the following equation:

$$\ln\beta = \text{Const} - \frac{E}{RT_m} \tag{4.4}$$

This equation is frequently referred to as the method of Takhor [45] or of Mahadevan [46]. As the Kissinger method, this method also relies on the shift in the peak maximum with the heating rate. However, the equation was introduced as an approximation [46] to the Kissinger equation and thus is less accurate. For this reason it should not be used especially concurrently with the Kissinger method [47]. The Kissinger method particularly when backed up by isoconversional analysis provides a better option.

5. The method of invariant kinetic parameters

The method of invariant kinetic parameters [48] makes use of the so-called "compensation effect" that is observed when a model-fitting method is applied to a single-heating rate run. Substitution of different models $f_i(\alpha)$ (Table 1) into a rate equation (e.g., Eq. (1.13)) and fitting it to experimental data yields different pairs of the Arrhenius parameters, $\ln A_i$ and E_i. Although the parameters vary widely with $f_i(\alpha)$, they all demonstrate a strong correlation known as a compensation effect:

$$\ln A_i = aE_i + b \tag{5.1}$$

The parameters *a* and *b* depend on the heating rate. The invariant kinetic parameters, $\ln A_{inv}$ and E_{inv}, are evaluated from several sets of b_j and a_j obtained at different heating rates β_j as follows:

$$b_j = \ln A_{inv} + E_{inv}a_j \tag{5.2}$$

The method is used rather rarely because it requires more computations than the Kissinger method or most of the isoconversional methods. The only seeming advantage that the method offers is simultaneous evaluation of both ln*A* and *E*, but not the reaction model. However, as shown in Section 6, there are several quite simple techniques for evaluating the preexponential factor and the reaction model once the activation energy has been determined. In addition, the aforementioned advantage is outweighed entirely by the daunting problem of estimating the errors in $\ln A_{inv}$ and E_{inv}. Because of the indirect way of evaluating these parameters, the experimental error propagates in several steps (first into $\ln A_i$ and E_i, then into a_j and b_j, and then into $\ln A_{inv}$ and E_{inv}) that makes it extremely difficult to properly evaluate the error in the invariant kinetic parameters.

Overall, when considering this method one should be aware that simpler and more reliable alternatives might be available. There are several recommendations for obtaining better values of $\ln A_{inv}$ and E_{inv}. First, before applying the method one needs to test whether the process under study can be adequately described as single-step step kinetics, because only in this case a single pair of $\ln A_{inv}$ and E_{inv} produced by this method can be deemed adequate. The test can be done by applying an isoconversional method and making sure that E_α does not vary significantly with α. Second, one needs to use the most accurate model fitting methods to obtain better values of $\ln A_i$ and E_i. This is especially important when choosing between numerous integral model-fitting methods whose accuracy in evaluating $\ln A_i$ and E_i depends largely on the accuracy of the approximation of the temperature integral [17,49,50]. Third, when choosing the reaction models for calculation of $\ln A_i$ and E_i, it is advisable to pick a set of models that yields a wide range of the $\ln A_i$ and E_i values. The wider the range the smaller the error in determining the parameters of the compensation effect, *a* and *b*. The choice of specific models also affects the errors in *a* and *b* and the quality of the correlation [51] that can be improved by eliminating the diffusion models [52]. Fourth, it is important to use a wider range of the heating rates to secure smaller errors in estimating $\ln A_{inv}$ and E_{inv}.

6. Determining reaction models and preexponential factors for model-free methods

6.1. General idea

The aforementioned model-free methods (e.g., isoconversional, Kissinger, invariant kinetic parameters) allow one to evaluate the activation energy without determining the reaction model. However, this should not be understood to imply that the model-free methods cannot be used for determining the reaction models. Both reaction model and preexponential factor can be readily determined when using model-free methods subject to one important condition. This condition is that the process can be reasonably approximated as single-step kinetics or, in other words, can be adequately described by Eq. (1.4). It is recommended that the validity of this condition is checked by performing isoconversional analysis of the data and making sure that the isoconversional activation energy does not vary significantly with the extent of conversion. If this condition cannot be satisfied, then the process cannot be described adequately by a single reaction model and a single pair of Arrhenius parameters. Under these circumstances, one is advised to resort to a multi-step kinetic analysis that would yield an individual reaction model and a pair of Arrhenius parameters for each of the reaction steps. Such an analysis can be accomplished by using the model-fitting methods described in Section 7. The following sections present some simple and efficient techniques that permit determination of the reaction model and preexponential factor in the case when a process has been demonstrated to obey single-step kinetics.

6.2. Making use of compensation effect

The reaction model and preexponential factor are sometimes determined by combining the results of a model-free method and some method that involves model fitting of single heating rate data. The model-fitting method (e.g., Eq. (1.13) or its integral analog) yields as many kinetic triplets (E_i, A_i, and $f_i(\alpha)$ or $g_i(\alpha)$) as the number of the reaction models used. Then, out of these kinetic triplets one selects a triplet, whose E_i value matches most closely the activation energy value, E_0, obtained by a model-free method. However, such approach to determining the reaction models and preexponential factors cannot be recommended due to its methodological flaws. First, the single heating rate model-fitting value E_i rarely matches the model-free value E_0 with good accuracy. Second, it is not uncommon when two or more different $f_i(\alpha)$ or $g_i(\alpha)$ yield E_i that fit within the confidence limits for E_0. Third, for the same reaction model, the E_i and A_i values tend to change with the heating rate. All these factors result in inaccurate determination of the reaction models and preexponential factors.

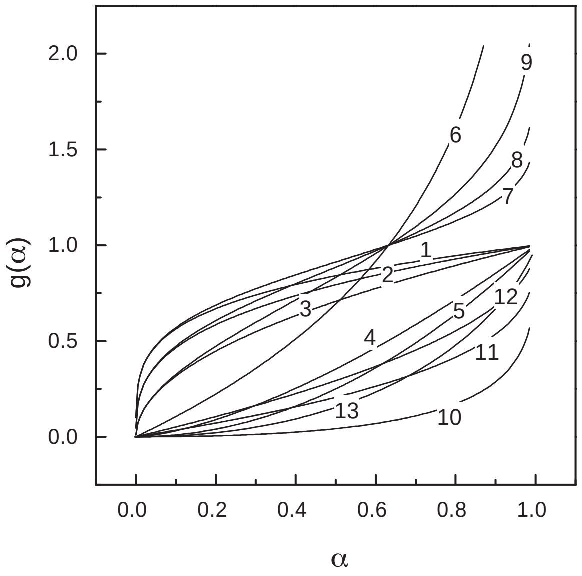

Fig. 3. Theoretical $g(\alpha)$ plots for the reaction models listed in Table 1.

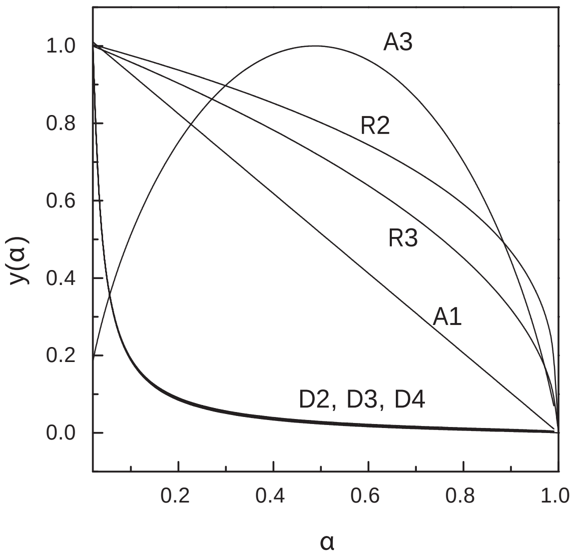

Fig. 4. Theoretical $y(\alpha)$ master plots for the reaction models collected in Table 2.

Instead, accurate determination of the reaction model and preexponential factor can be accomplished [4,53] by using the aforementioned compensation effect (Eq. (5.1)). For this purpose, the E_i and A_i values are used to determine the a and b parameters of the compensation effect. Then, substitution of the model-free activation energy into Eq. (5.1) gives a model-free estimate for the pre-exponential factor, A_0:

$$\ln A_0 = aE_0 + b \tag{6.1}$$

It should be noted that the same principle can be used to determine a dependence of $\ln A_\alpha$ on α by substituting isoconversional values of E_α into Eq. (6.1). However, as mentioned earlier, determination of the reaction model requires that a variation of E_α with α to be negligible so that the E_α dependence can be replaced with a single average value, E_0. Once both E_0 and A_0 have been determined, one can numerically reconstruct the reaction model in either integral or differential form. The integral form can be reconstructed by substituting the values E_0 and A_0 into Eq. (1.15) that takes the following form:

$$g(\alpha) = \frac{A_0}{\beta}\int_0^{T_\alpha} \exp\left(\frac{-E_0}{RT}\right) dT \tag{6.2}$$

Eq. (6.2) allows one to obtain a set of numerical values of $g(\alpha)$ corresponding to different values of α. This is accomplished by using a dependence of α vs. T measured experimentally at a given heating rate, β. By substituting a certain experimental value of T_α (i.e., T corresponding to a certain α) as the upper limit of the integral one obtains a numerical value of $g(\alpha)$ for the respective value of α. The use of a particular β in Eq. (6.2) obviously requires the use of the respective experimental α vs. T dependence. Nevertheless, the resulting numerical values of $g(\alpha)$ should not demonstrate any significant variation with β giving rise to a single dependence of $g(\alpha)$ on α. The analytical form of the reaction model (i.e., equation) can then be established by plotting the numerical $g(\alpha)$ values against the theoretical dependencies (Fig. 3) obtained from the $g(\alpha)$ equations representing the reaction models (e.g., Table 1) and finding the best matching theoretical dependence.

The approach used for determining the integral form of the reaction model is equally suitable for determining the differential form. The values E_0 and A_0 should then be substituted into rearranged Eq. (1.13):

$$f(\alpha) = \beta\left(\frac{d\alpha}{dT}\right)_a \left[A_0 \exp\left(\frac{-E_0}{RT_\alpha}\right)\right]^{-1} \tag{6.3}$$

The resulting numerical values of $f(\alpha)$ can then be compared against the theoretical dependencies obtained from the $f(\alpha)$ equations (e.g., Table 1) in order to identify the best matching model.

6.3. The $y(\alpha)$ and $z(\alpha)$ master plots

In order to make sure that the $y(\alpha)$ or $z(\alpha)$ master plots can be used, one must use an isoconversional method to determine E_α and make sure that it does not vary significantly with α. Then the approximately constant value of E_α can be replaced with an average value of E_0 that is inserted in Eqs. (6.4) or (6.7). The $y(\alpha)$ function [54] has the following form:

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)_\alpha \exp\left(\frac{E_0}{RT_\alpha}\right) = Af(\alpha) \tag{6.4}$$

Eq. (6.4) is easily arrived at by rearranging Eq. (1.12). The values of $y(\alpha)$ are determined directly from experimental data by substituting E_0 into Eq. (6.4). Then, for each value of α, one needs to determine experimental values of $(d\alpha/dt)_\alpha$ and T_α related to this α and insert them into Eq. (6.4). The resulting experimental values of $y(\alpha)$ are plotted as a function of α and compared against theoretical $y(\alpha)$ master plots. A suitable model is identified as the best match between the experimental and theoretical $y(\alpha)$ master plots. From a series of experimental kinetic curves $(d\alpha/dt)$ vs T obtained at different β one can obtain a series of the experimental $y(\alpha)$ plots.

The resulting numerical values of $y(\alpha)$ should not demonstrate any significant variation with β giving rise to a single dependence of $y(\alpha)$ on α. As seen from Eq. (6.4), the shape of the theoretical $y(\alpha)$ master plots is entirely determined by the shape of the $f(\alpha)$ functions because A is a constant. However, because the preexponential factor is yet unknown, the experimental and theoretical $y(\alpha)$ plots have to be normalized in a similar manner. For practical reasons, the $y(\alpha)$ plots are normalized to vary from 0 to 1. Fig. 4 displays some examples of the normalized theoretical $y(\alpha)$ plots for the models from Table 2. The type of a reaction model can be recognized by the shape of the experimental $y(\alpha)$ plot. The contracting geometry models (coded R) yield convex decreasing dependencies. The diffusion models (coded D) demonstrate characteristic concave decreasing plots. The Avrami–Erofeev models (coded A)

Table 2
Values of α_m and α_p corresponding respectively to the maximum of the $y(x)$ and $z(x)$ functions for different kinetic models.

Kinetic model	α_m	α_p
R2	0	0.750
R3	0	0.704
F1	0	0.632
A2	0.393	0.632
A3	0.283	0.632
SB[a]	$m/(n+m)$	?[b]
D2	0	0.834
D3	0	0.704
D4	0	0.776

[a] SB stands for the truncated Sestak–Berggren's equation (Eq. (6.5)).
[b] There is no general analytical solution for α_p.

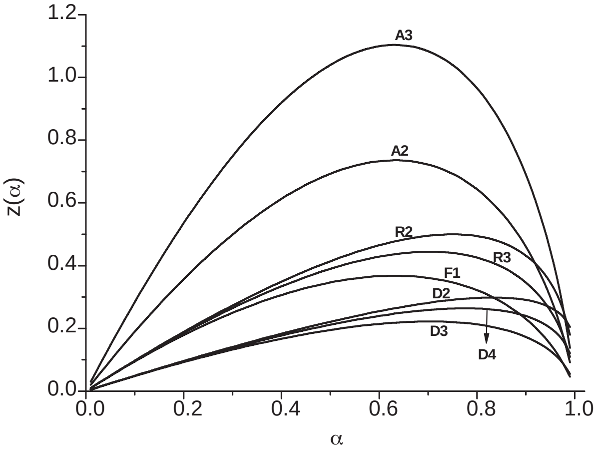

Fig. 5. Theoretical $z(\alpha)$ master plots for the reaction models from Table 2.

with $n > 1$ exhibit a maximum, whose position (α_m) depends on the value of n. The same property is demonstrated by the truncated Sestak–Berggren ($p = 0$ in Eq. (1.11)) or extended Prout–Tompkins model:

$$f(\alpha) = \alpha^m (1-\alpha)^n \tag{6.5}$$

The $z(\alpha)$ master plots are derived by combining the differential and integral forms of the reaction models. The temperature integral in Eq. (1.15) can be replaced with various approximations [9], $\pi(x)$ as follows:

$$g(\alpha) = \frac{AE}{\beta R}\exp(-x)\left[\frac{\pi(x)}{x}\right] \tag{6.6}$$

where $x = E/RT$. Combining Eqs. (1.12) and (6.6) followed by some rearrangement allows one to introduce the $z(\alpha)$ function as:

$$z(\alpha) = f(\alpha)g(\alpha) = \left(\frac{d\alpha}{dt}\right)_\alpha T_\alpha^2 \left[\frac{\pi(x)}{\beta T_\alpha}\right] \tag{6.7}$$

It has been established [55] that the term in the brackets of Eq. (6.7) has a negligible effect on the shape of the $z(\alpha)$ function. Thus, the values of $z(\alpha)$ can be determined for each value of α by multiplying the experimental values of $(d\alpha/dt)_\alpha$ and T_α^2. The resulting experimental values of $z(\alpha)$ are plotted as a function of α and compared against theoretical $z(\alpha)$ master plots. A suitable model is identified as the best match between the experimental and theoretical $z(\alpha)$ master plots. From a series of experimental kinetic curves measured at different β one can obtain a series of the experimental $z(\alpha)$ plots that should, however, yield a single dependence of $z(\alpha)$ on α which is practically independent of β. The theoretical $z(\alpha)$ plots are obtained by plotting the product $f(\alpha)g(\alpha)$ against α for different reaction models. Fig. 5 shows the theoretical $z(\alpha)$ master plots for the models from Table 2.

It should be noted that $z(\alpha)$ plots demonstrate a maximum at a specific value of conversion, α_p, that can be found from the condition [54]

$$g(\alpha)f'(\alpha) = -1 \tag{6.8}$$

The α_p values have been calculated [56] for a number of the reaction models (Table 2). The values can provide some extra help in identifying appropriate reaction models for experimental data. Once the reaction model has been identified, the pre-exponential factor is determined from the following equation [54]:

$$A = \frac{-\beta E_0}{RT_{\max}^2 f'(\alpha_{\max})}\exp\left(\frac{E_0}{RT_{\max}}\right) \tag{6.9}$$

In Eq. (6.9), the subscript max denotes the values related to the maximum of the differential kinetic curve obtained at a given heating rate.

7. Model fitting methods

7.1. General idea

Model fitting is the derivation of kinetic parameters associated with a particular reaction model that is assumed to represent the conversion dependence of the reaction rate. The integral and differential forms of the reaction model are used in Eqs. (1.4) and (1.14) for rate and extent of conversion data, respectively. Some common kinetic models are listed in Table 1. There are many ways model fitting can be accomplished. They all involve minimizing the difference between the experimentally measured and calculated data on the reaction rate. The data can be isothermal, constant heating rate data, or a mixture of the two. Minimization can be accomplished by using linear or non-linear regression methods. One key difference between linear and nonlinear methods is that linear methods do not need an initial estimate of A and E, while non-linear methods do. Consequently, even though non-linear methods are superior in many ways, they greatly benefit from initial estimates provided by linear methods.

It is very important to understand that the model-fitting methods differ significantly in their reliability. In particular, model-fitting based on a single heating rate is known to be notoriously unreliable [57]. On the other hand, the ICTAC kinetic study [1] showed that the model fitting methods can be as reliable as the model-free isoconversional methods as long as the models are fitted simultaneously to multiple data sets obtained under different temperature programs. Unlike isoconversional methods, the model-fitting methods are capable of identifying multi-step reaction models suitable for the description of complex kinetics. However, this process is associated with a number of nontrivial problems that are not encountered when using the model-free methods. Some of these problems are briefly addressed below.

7.2. Picking an appropriate reaction model

The first and most important step in model fitting is to identify an appropriate model. If this is not done correctly, the kinetic parameters will be meaningless. It is always wise to start by taking into consideration the type of a reaction being studied and the morphology of the reactant (e.g., liquid vs. solid, amorphous vs. crystalline, shape of crystals and distribution of their sizes, etc.). This information is helpful in identifying suitable models because they have typically been derived for specific reaction types and/or morphologies In addition, a correct model, or limited set of suitable models, can usually be identified by inspecting the data and answering specific questions as follows.

1. Is there evidence for multiple reactions based on inflection points and shoulders in the data? Differential data are more sensitive than integral data for this purpose.
2. How does the isoconversional activation energy vary with conversion?
3. Is the reaction of acceleratory, deceleratory, or sigmoidal (autocatalytic) type? This is easily decided by visually inspecting isothermal reaction profiles as each of the reaction types has a profile of distinctive shape (Fig. 1). As mentioned in Section 1, a link between the shape of nonisothermal reaction profile and the reaction model type is not nearly as straightforward, but there are methods of identification based on width of the reaction profile obtained at multiple heating rates.
4. How does the reaction profile shape compare to those for various possible models? There are several normalized plots that can be used in this comparison.

If there is evidence for multiple overlapping reactions, a non-linear regression method is essential. Overlapping parallel reactions are relatively straightforward to fit by these methods, but consecutive reactions are far more difficult. If multiple observables are available, e.g., weight loss and heat flow, then simultaneous analysis of both signals is more likely to result in a unique model. Isoconversional kinetic analysis can guide multi-step model optimization. Model-free E and $\ln A$ values for α in the vicinity of the mid-conversion of those reaction segments can be used as initial estimates for the non-linear regression optimization. One should always ask, of course, whether development of a multistep model is beneficial relative to isoconversional kinetics, but it is often the case when developing complex chemical process models.

If there is no evidence of multiple reactions from the reaction profile at constant heating rates, or if the reactions are sufficiently separated such that they can be considered independent reactions, the likelihood of finding an adequate single-step model is far greater if the isoconversional analysis indicates that E and $\ln A$ are approximately constant with conversion. Variation of E and $\ln A$ for $\alpha < 0.1$ and $\alpha > 0.9$ is not automatically a major concern, because those parameters can be affected greatly by possible minor errors in baseline determination. On the other hand, they should not be dismissed lightly, as they could indicate, for example, a distinct initiation process or a heating rate dependence for the ultimate amount of reacted material, as in additional carbonaceous residue from organic material heated slowly. Note that in the case when the reaction profile demonstrates well separated steps under constant heating rate conditions, it is a good idea to separate the steps entirely (e.g., by using peak separation methods) and analyze their kinetics individually.

The best single-step model or best few candidate models can be selected by a variety of numerical and graphical methods. Selection of the method depends upon whether the reaction data is integral (e.g., TGA) or differential (e.g., DSC) and whether the reaction conditions are isothermal, constant heating rate, or other. Isothermal data suffer from an inherent limitation that there is always an initial nonisothermal heatup time and that complete conversion may not always be determined for methods that measure reaction rates.

For isothermal data, the simplest test is to determine whether the reaction rate is at its maximum value as soon as the sample reaches the isothermal temperature. If so, the reaction is deceleratory, and a deceleratory model must be used. An appropriate method to narrow the possibilities is to plot the $\ln(d\alpha/dt)$ or $\ln(1-\alpha)$ vs time. If the plot is linear for times after the sample is truly isothermal, the reaction is first-order or nearly so. If the plot is concave downward, the reaction is likely to be a contracting volume (e.g., models 11 and 12 in Table 1). If the plot is concave upward, the reaction probably has an increasing diffusion resistance (e.g., model 10 or 13 in Table 1) or a reactivity distribution (Table 4).

Table 3
Parameters of Eq. (7.1) fitted to different reaction models $f(\alpha)$.

Code	$f(\alpha)$	Parameters of equation: $c(1-\alpha)^n\alpha^m$
R2	$(1-\alpha)^{1/2}$	$(1-\alpha)^{1/2}$
R3	$(1-\alpha)^{2/3}$	$(1-\alpha)^{2/3}$
F1	$(1-\alpha)$	$(1-\alpha)$
A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$2.079(1-\alpha)^{0.806}\alpha^{0.515}$
A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$3.192(1-\alpha)^{0.748}\alpha^{0.693}$
D2	$[-\ln(1-\alpha)]^{-1}$	$0.973(1-\alpha)^{0.425}\alpha^{-1.008}$
D3	$(3(1-\alpha)^{2/3})/(2[1-(1-\alpha)^{1/3}])$	$4.431(1-\alpha)^{0.951}\alpha^{-1.004}$

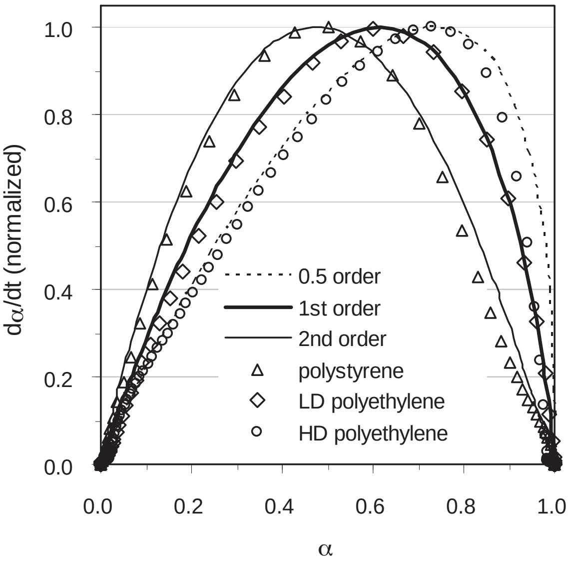

Fig. 6. Normalized reaction rate versus extent of conversion at a constant heating rate for three reaction orders, n, as defined in Eq. (6.5). The conversion at maximum rate increases as reaction order decreases. This plot is insensitive to the value of m in the truncated Sestak–Berggren's model, which is ∼0.5 for these polymer samples.

If the reaction rate is not at its maximum value when the sample reaches isothermal conditions, the reaction is sigmoidal or acceleratory. If the reaction rate does eventually peak, an Avrami–Erofeev (models 7–9 in Table 1) or truncated Sestak–Berggren (extended Prout–Tompkins) (Eq. (6.5)) are appropriate. If the reaction rate continues to accelerate to the end of the reaction, a power–law model (models 1–4 in Table 1) should be considered.

For a constant heating rate, a plot of reaction rate versus conversion can be instructive. Fig. 6 shows how reaction profile shape changes with reaction order n in Eq. (6.5). The profile shape is relatively insensitive to the value of m in Eq. (6.5). Instead, it can be estimated from the width of the reaction profile relative to that of a first-order reaction having A and E derived from Kissinger's equation, as discussed by Burnham [43]. In the examples shown in Fig. 6, both polystyrene and polyethylene have narrow reaction profiles characteristic of linear polymers ($m > 0.5$ in Eq. (6.5)), but the normalized shape is substantially different, leading to different values of n. The concept of using reaction profile shapes has been efficiently implemented in the $y(\alpha)$ and $z(\alpha)$ plots described in Section 6. The use of these plots can be recommended for picking appropriate reaction models for model-fitting.

7.3. Linear model-fitting methods

Linear model-fitting methods make use of linear regression techniques. In order to employ such techniques the rate equation should be converted to a linear form. This is readily accomplished for a single-step rate Eq. (1.12) by rearranging and taking the

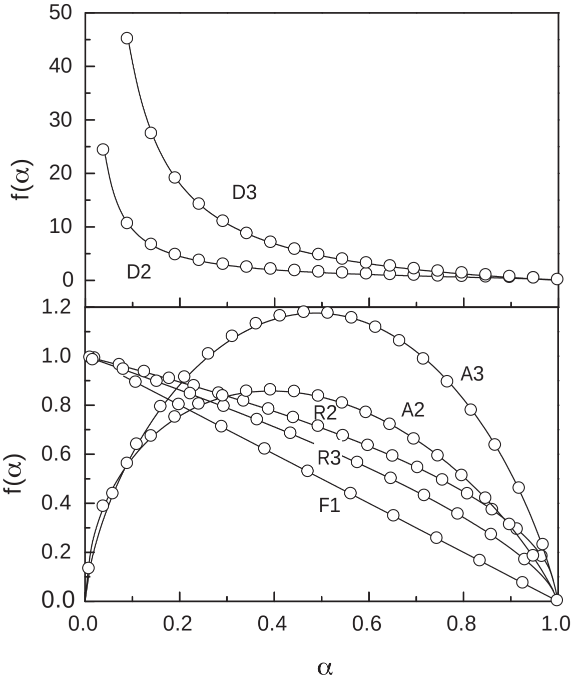

Fig. 7. Fits of Eq. (7.1) (solid lines) to the $f(\alpha)$ reaction models (dots) listed in Table 3.

Table 4
Four distributed reactivity models used to model the thermal behavior complex heterogeneous materials.

Name	Distribution in	Function
Gaussian	E	$D(E) = (2\pi)^{-1/2}\sigma^{-1}\exp[-(E-E_0)^2/2\sigma^2]$
nth-order	k	$D(k) = a^{\nu}k^{\nu-1}e^{-ak}/\Gamma(\nu)$
Weibull	E	$D(E) = (\beta/\eta)[(E-\gamma)/\eta]^{\beta-1}\exp\{-[(E-\gamma)/\eta]^{\beta}\}$
Discrete	E	$D(E)$ is any set of weights adding to unity
Extended discrete	A and E	Same, except $\ln(A) = a + bE$

logarithm that makes a plot linear with respect to the reciprocal temperature. However, linearization of multi-step rate equations is generally problematic as many of these cannot be linearized.

Linear model-fitting can be performed in a number ways. A good example of such method is the combined kinetic analysis [58,59]. It has been proposed for determining the whole kinetic triplet (E, A, and $f(\alpha)$) from the simultaneous treatment of several kinetic curves measured under different arbitrary temperature programs. An advantage of this method is that the determination of the reaction model is not limited to some list of kinetic models such as that shown in Table 1 or similar. Instead, the kinetic model is determined in the following general form:

$$f(\alpha) = c\alpha^m(1-\alpha)^n \tag{7.1}$$

This can be considered as a modified form of the truncated equation by Sestak and Berggren (Eq. (6.5)). It has been shown [59] that by adjusting the parameters c, n and m Eq. (7.1) can fit very accurately various ideal kinetic models derived under certain mechanistic assumptions. Table 3 provides examples of the values of the c, n, and m values for some of the ideal models, whereas Fig. 7 shows the examples of the respective fits.

The combined kinetic analysis is based on the following equation [59]:

$$\ln\left[\frac{d\alpha}{dt}\frac{1}{\alpha^m(1-\alpha)^n}\right] = \ln(cA) - \frac{E}{RT} \tag{7.2}$$

that is derived by rearranging the basic Eq. (1.12) and replacing $f(\alpha)$ with the right hand side of Eq. (7.1). Evaluating the parameters of Eq. (7.2) requires one to simultaneously substitute kinetic data α and $d\alpha/dt$ vs. T obtained at several different temperature programs, $T(t)$. The best fit values of the parameters are considered to be those that yield the best linearity of a plot of the left hand side of Eq. (7.2) against the reciprocal temperature. The linearity is evaluated as the coefficient of linear correlation, r, whose maximum is found through numerical optimization of the parameters n and m. Taking into consideration that the relative experimental errors in the kinetic data are larger at lowest and highest conversions, it might be advisable to limit analysis to the α range such as 0.10–0.90 or 0.05–0.95. Once the values of n and m that maximize r are found, the values of E and $\ln(cA)$ are estimated respectively from the slope and intercept of the linear plot.

The found values of n and m should then be checked against the values specific to the ideal kinetic models (Table 3) to see if the experimentally evaluated $f(\alpha)$ matches any of them. For instance, finding the values of n and m to be respectively around 0.8 and 0.5 means that the experimentally evaluated $f(\alpha)$ is similar to the Avrami–Erofeev model, A2. In such a case, the value of c is known from the previous fits of Eq. (7.1) to specific $f(\alpha)$ models (Table 3). This allows one to extract the value of c from $\ln(cA)$ and, thus, to accurately determine the pre-exponential factor. If the values of n and m do not match the values specific to any of the kinetic models, the separation of c and A cannot be accomplished. However, since the value of c is relatively small (Table 3), it does not affect significantly the value of the preexponential factor which is typically reported as $\log A$. It should be noted that even if the experimentally evaluated $f(\alpha)$ does not match any ideal kinetic models, it would still be entirely suitable for describing the effect of the extent of conversion on the reaction rate.

7.4. Nonlinear model-fitting methods

Fitting of either single or multi-step models is commonly accomplished by means of nonlinear regression that works by minimizing the difference between the measured and calculated data. The method of least squares evaluates the difference in the form of the residual sum of squares (RSS):

$$RSS = \sum(y_{\exp} - y_{\text{calc}})^2 = \min \tag{7.3}$$

The values of $y_{\exp}$ can, for example, be the values of the experimentally measured rate ($d\alpha/dt$) at different temperature programs. Then, y_{calc} would be the rate values calculated by substituting the variables (e.g., t, T, and α) and kinetic parameters (e.g., A and E) in the right hand side of a rate equation such as Eq. (1.4) or (1.5). A minimum of RSS is found numerically by varying the values of the kinetic parameters for the individual reaction steps. Estimates of the kinetic parameters are obtained as the values that secure a minimum of RSS.

While some rate equations can be linearized and analyzed by linear regression, this is generally not as good as using nonlinear methods. This is because linearization will magnify the sensitivity of the kinetic parameters to small-value points and distort the parameters away from doing the best match to the most important part of the reaction. In addition, nonlinear regression methods can easily optimize relative to reaction rates, extents of conversion, or both simultaneously. Furthermore, nonlinear methods can accommodate any set of differential rate equations by numerical integration.

Generally the use of the model-fitting methods unavoidably gives rise to the problems of:

N1. Establishing the uniqueness of the kinetic parameters obtained for the individual steps.

N2. Selecting a proper multi-step mechanism.
N3. Determining the proper number of individual steps in the multi-step mechanism.
N4. Selecting proper reaction models for the individual steps.

In order to address the problem N1, one is advised to always check whether the kinetic parameters determined by minimization of RSS are unique. Nonlinear multi-parametric minimization is a computationally involved iterative process that may result in convergence to local minima rather than a unique global minimum. All iterative procedures have to start from some initial "guessed" values of the kinetic parameters. Good starting values are obtained by using isoconversional methods. For example, if the isoconversional E_α values range from 50 to 150 kJ mol^{-1}, it is reasonable to use a two-step mechanism and use 50 and 150 kJ mol^{-1} as the initial "guess" values for E_1 and E_2 along with their corresponding A_1 and A_2. As the minimization process converges to a minimum, the values of the kinetic parameters may change markedly with respect to the initial values. To verify that the evaluated kinetic parameters are not associated with some local minimum, one needs to repeat the process of minimization several times using significantly different initial values of the kinetic parameters. It is particularly important to test whether the initial values chosen on different sides of a minimum converge to the same value. For example, if the initial value of E was chosen as 50 kJ mol^{-1} and a minimum was found at 100 kJ mol^{-1}, one would be advised to repeat computations by using the initial value of, say, 200 kJ mol^{-1} (along with a correspondingly appropriate value of A) and make sure that iterations would converge to the same minimum at 100 kJ mol^{-1}. Failure to accomplish this would mean that the minimization procedure does not converge to a global minimum and that the kinetic parameters evaluated as a result of minimization are not unique or simply are incorrect. This situation can be resolved by decreasing the number of individual steps in the multi-step mechanism used as well as by obtaining additional experimental data, perhaps, trying to cover a wider temperature range, and by improving the computational algorithms of minimization.

Addressing the problem N2 requires one to decide which formal mechanism (parallel, consecutive, reversible reactions as well as combinations of thereof) should be used in the model-fitting method. A decision is best reached when one has some information about the actual mechanism of the process. When such information is unavailable, a proper multi-step mechanism is chosen by exploring several alternative mechanisms and finding the one that yields the lowest value of RSS. In doing so one should not forget about the statistical nature of RSS. That is, the lowest value of RSS may not differ significantly from the second smallest. One is advised to use the *F*-test [60] to check whether the difference in the values of RSS is significant. Note that RSS can be readily converted to the variance, S^2 as:

$$S^2 = \frac{RSS}{n-p} \tag{7.4}$$

where n is the total number of experimental points used in the calculation and p is the total number of kinetic parameters determined as a result of the calculation. The significance of the difference in two variances is readily checked by using the regular *F*-test. It is not uncommon that a statistical test suggests that there is no significant difference between two entirely different mechanisms (e.g., two parallel vs. two consecutive reactions), which simply means that both mechanisms provide similar goodness of fit.

In addressing the problem N3 one needs to decide on the number of individual steps to be included in the multi-step mechanism, i.e., to decide, for example, between using three and four parallel reactions. Some clues can be obtained from inspection of the data. Does the $d\alpha/dt$ reaction profile look like a smooth, single peak, or are there shoulders or even multiple peaks? Each shoulder or peak represents at least one reaction step. Again, having some mechanistic information can aid greatly in making a decision. However, one should keep in mind that the maximum number of steps is restricted by computational difficulties as well as by limited precision of the experimental data. Each additional step requires determination of at least two additional kinetic parameters (A and E). As the number of parameters increases so does interaction between them (mutual correlation) that may create significant difficulties in finding the global minimum in RSS and, thus, in determining a unique set of the kinetic parameters. One is recommended to introduce a new step only when this is justified statistically, i.e., only when this results in a significant decrease in RSS [61]. The significance is readily verified by applying the *F*-test to the variances (7.4) obtained before and after introduction of a new step. It should be stressed that a decrease in RSS and, thus, the maximum number of the steps are limited by the intrinsic precision of the data y_{exp} or, in other words, by the variance due to the experimental noise.

7.5. *Distributed reactivity and regular models*

This section provides some recommendations for addressing the problem N4 which is related to selecting the reaction models of the individual steps. Because of the obvious differences in the reaction profiles associated with the major types of the common reaction models (Fig. 1), determining an appropriate type is relatively simple. However, it is important to emphasize that some complex processes do not obey any of the regular models in Table 1. For example, the thermal degradation of biomass and fossil fuels follow distributed reactivity models, which partition the overall process into a set of independent, parallel reactions whose contributions are controlled by the mathematical distribution function. The respective rate equation takes the following general form:

$$\frac{d\alpha}{dt} = \sum w_i k_i(T) f_i(\alpha_i) \tag{7.5}$$

where w_i is the relative weight of an individual parallel reaction ($\Sigma w_i = 1$ and $\Sigma \alpha_i = \alpha$). Commonly used reactivity models are given in Table 4. Distributed reactivity is often introduced as a distribution in the activation energies. For the commonly used Gaussian distribution of activation energies, initial guess for the mean activation energy E_0 and the standard deviation σ can be estimated from the width of the reaction profile relative to that of a first-order reaction using A and E estimated from the Kissinger method [36,44]. A computationally efficient method for the nonlinear regression is to partition the continuous E into discrete E values that are spaced at 2–5 kJ mol^{-1}. A disadvantage of the Gaussian distribution is that it is symmetric whereas the actual reactivity distributions tend to be asymmetric. This can be rectified by several methods. One is changing the reaction order of the individual reactions from 1 to n. Then, the values of n and σ can be used to control the reactivity distribution asymmetry and the distribution width [62]. It should be noted that introduction of the nth-order reactions is mathematically equivalent to introduction of a gamma distribution in the preexponential factors for a set of parallel first-order reactions [63]. The asymmetry can also be accounted for by replacing the Gaussian distribution in E with the Weibull distribution [63]. Finally, distributed reactivity can also be introduced by using discrete distributions [63], which are optimized by a nested nonlinear-constrained linear regression method.

8. Kinetic predictions

8.1. General idea

Kinetic predictions are the most important practical application of kinetic analysis. As mentioned in the introduction, the purpose of kinetic analysis is to parameterize the process rate in terms of such variables as the temperature, the extent of conversion, and, sometimes, pressure. Parameterization is accomplished by evaluating parameters of the equations that describe the effect of the variables on the process rate. For example, parameterization in terms of the temperature and conversion can be accomplished by evaluating the kinetic triplet that should be sufficient to quantify the process kinetics at any desired temperature and/or extent of conversion. Of special interest and importance are kinetic predictions that deal with quantifying the process kinetics outside the temperature range in which the kinetics was measured experimentally. The need for kinetic predictions typically arises when experiments in the temperature range of interest are deemed impractical due to technical difficulties, costs and/or time constrain.

One of the most common ways of quantifying the process kinetics is estimating a parameter called the lifetime. The lifetime of a material is the time after which the material loses its properties to such extent that it cannot fulfill efficiently the function for which it was created. All materials change their properties to some extent when exposed to heat. Even while stored at ambient temperatures polymeric materials may outgas plasticizer, losing their mechanical properties; drugs may degrade losing their therapeutic properties; and energetic materials may decompose, losing their performance properties. The process of time-dependent decay of material properties is frequently called aging. Thermal analysis is widely applied to study thermal aging, i.e., aging caused by exposure of materials to heat. It should be stressed that aging may also be caused by other factors such as pressure, mechanical stress, moisture, etc. This section addresses only the issue of predicting the life time of materials that exclusively undergo thermal aging. It is, therefore, assumed that the kinetics of aging can be described in terms of the equations introduced in Section 1.

Before making lifetime predictions, one needs to link the property of interest to a property measured by thermal analysis, e.g., mass loss or heat release. It should be kept in mind that in many cases the link can be rather indirect. For example, TGA is widely used to monitor the thermal degradation of polymeric materials. However, mass loss measurements would provide limited information on the decay of mechanical properties during degradation. This is because these properties start to decay as soon as the polymer chains start breaking, but well before the formation of low molecular mass volatile products can cause a detectable mass loss in TGA. Once the decay in the property of interest is linked to mass loss or heat release, it can be expressed in terms of the extent of conversion, α so that $\alpha = 0$ represents the initial non-decayed property and $\alpha = 1$ is ultimately decayed property. Then one needs to define some limiting extent of decay beyond which the material becomes unusable, e.g., 5% decay relative to the initial value that would be equivalent to reaching $\alpha = 0.05$. Consequently, the problem of the lifetime prediction reduces to the kinetic problem of computing the time to reach the limiting extent of conversion.

8.2. Typical approaches to the problem

In the case of a single-step process taking place under isothermal conditions (constant temperature, T_0), the time to reach a given extent of conversion can be readily determined by rearranging Eq. (3.5):

$$t_\alpha = \frac{g(\alpha)}{A\exp(-E/RT_0)} \tag{8.1}$$

Eq. (8.1) can be used to predict the lifetime of material under isothermal conditions at the temperature T_0. The prediction requires knowledge of the kinetic triplet for the process that causes decay in the property of interest. The triplet can be determined from either isothermal or nonisothermal experiments. It is, however, critical that the triplet be determined by a kinetic method that makes simultaneous use of multiple temperature programs. The use of single heating rate methods for the purpose of kinetic predictions is unacceptable practice that is generally not capable of producing meaningful results [57].

Eq. (8.1) is exploited by two popular ASTM methods respectively designed for evaluating the thermal stability from TGA and DSC data: E1641 [64] and E698 [65]. The E1641 method is based on the following predictive equation:

$$t_\alpha = \frac{-\ln(1-\alpha)}{A\exp(-E/RT_0)} \tag{8.2}$$

where the value of E is determined by the Flynn and Wall method (Eq. (3.8)). Eq. (8.2) assumes that the process obeys first-order kinetics, i.e., $g(\alpha)$ in Eq. (8.1) is replaced with $-\ln(1-\alpha)$. The same assumption is made to evaluate the pre-exponential factor in Eq. (8.3):

$$A = \frac{-\bar{\beta}R}{E_r}\ln(1-\alpha)10^a \tag{8.3}$$

where $\bar{\beta}$ is the mean of the experimental heating rates used to determine E by the Flynn and Wall method (Eq. (3.8)). The E_r value is the corrected value of the activation energy that is obtained by dividing the experimental value of E by the correction factor. Values for both the correction factor and the parameter a in Eq. (8.3) are tabulated in the ASTM method.

The E698 method uses the same predictive equation as E1641 (Eq. (8.2)). The value of E is determined either by the Kissinger method (Eq. (4.3)) or by the Ozawa and Flynn and Wall methods (Eq. (3.8)). In the latter case, the method suggests replacing T_α in Eq. (3.8) with the peak temperature, T_p. The lifetime prediction by the E698 method is again based on the assumption of the first-order kinetics. The same assumption is used to determine the pre-exponential factor as

$$A = \frac{\beta E}{RT_p^2}\exp\left(\frac{E}{RT_p}\right) \tag{8.4}$$

The major limitation of both E1641 and E698 methods is that the lifetime predictions can only be made with the first order kinetic model and assuming constant activation energy, regardless of the actual reaction path. This can lead to erroneous predictions when the process obeys a different reaction model and/or when the process demonstrates a significant variation of E_α with α. That is, before using these methods one should make sure that E_α does not vary significantly with α and that the reaction model of the process is consistent with 1st order kinetics.

The limitations of the ASTM E1641 and E698 methods are avoided in the model-free predictions that make use of the dependence of E_α on α determined by an isoconversional method. The predictive equation was originally proposed [53] in the following form:

$$t_\alpha = \frac{\int_0^{T_\alpha} \exp(-E_\alpha/RT)dT}{\beta\exp(-E_\alpha/RT_0)} \tag{8.5}$$

and was later modified to employ data from arbitrary heating programs, as follows:

$$t_\alpha = \frac{J[E_\alpha, T(t_\alpha)]}{\exp(-E_\alpha/RT_0)} \tag{8.6}$$

Eqs. (8.5) and (8.6) are obtained by equating the right hand side of Eq. (3.5) to the right hand side of either Eq. (1.15) or Eq. (1.14) and cancelling the parameter A. The respective predictions are called "model-free predictions", because they eliminate the reaction model $g(\alpha)$ in the numerator of Eq. (8.1). Because the model-free predictions are not limited to a given form of $g(\alpha)$ and because they are applicable to the processes for which E_α varies with α, they generally produce more reliable estimates for the lifetime, t_α then the aforementioned ASTM methods.

Although predictions of the lifetime at a given isothermal temperature, T_0, are most common, they can also be made for any desired temperature program, $T'(t)$. Applying the same principle as in deriving Eqs. (8.5) and (8.6), one obtains a model-free equation:

$$J[E_\alpha, T'(t'_\alpha)] = J[E_\alpha, T(t_\alpha)] \tag{8.7}$$

The right hand side of Eq. (8.7) represents the integral (Eq. (3.14) or (3.16)) over the actual experimental temperature program. Then the lifetime $t_\alpha{}'$ at any desired temperature program $T'(t)$ can be found as a numerical solution of Eq. (8.7).

Note that the model-free equations ((8.5)–(8.7)) are not the only way to make predictions when dealing with multi-step processes (i.e., processes for which E_α varies with α). In this circumstance, the lifetime predictions can be just as readily made by using multi-step model-fitting methods. Since these methods produce an explicit form of the rate equation (e.g., Eq. (1.5) or (7.5)), the time to reach a given extent of conversion (i.e., the lifetime, t_α) is determined by numerical integration of the rate equation that yields the α vs. t dependence. The predictions can be accomplished for any desired temperature program $T'(t)$ by integrating the rate equation over this program. For example, integration of the rate equation over a constant temperature T_0 would yield an isothermal prediction for t_α.

8.3. *Understanding kinetic predictions*

When making kinetic predictions, one should clearly understand that no matter how sophisticated predictive algorithms are, the resulting predictions are always limited in both precision and accuracy. An inherent limit in precision arises from the limited precision of experimental data (i.e., T, α, $d\alpha/dt$) that gives rise to random errors in the kinetic triplet. It can be easily illustrated by using Eq. (8.1) and introducing an error in the activation energy, $E \pm \Delta E$. Then the respective error in the lifetime can be expressed through the lower and upper limits of E as:

$$\Delta t_\alpha = \frac{g(\alpha)}{A}\left[\exp\left(\frac{E+\Delta E}{RT_0}\right) - \exp\left(\frac{E-\Delta E}{RT_0}\right)\right] \tag{8.8}$$

From Eq. (8.8), the relative error in the lifetime is:

$$\frac{\Delta t_\alpha}{t_\alpha} = \exp\left(\frac{\Delta E}{RT_0}\right) - \exp\left(\frac{-\Delta E}{RT_0}\right) \tag{8.9}$$

It follows from Eq. (8.9) that the relative error in the lifetime depends on the temperature to which prediction is made. At a certain value of T_0 the relative error would rise above 1 (i.e., above 100%) making the absolute error Δt_α larger than the t_α value itself that makes the prediction meaningless. While simplified, this example clearly shows that the predictive power is inherently limited by the precision of experimental data.

The lifetime predictions are also limited in their accuracy. The predictions are based on a simple assumption that the rate equation and respective kinetic triplet(s) determined within a certain experimental temperature range would remain unchanged in the temperature range to which the predictions are made. Obviously, the resulting predictions are only as accurate as the underlying assumption. Normally, the latter is reasonably accurate as long as the temperature range of the predictions does not stretch too far beyond the experimental range. However, even a small change in the temperature can invalidate the underlying assumption when crossing the temperature of a phase transition. For example, the kinetic triplet determined for the liquid state decomposition of a material can be inapplicable to predict the lifetime of this material below its melting point, i.e., when it decomposes in the solid state.

Another implicit assumption used in kinetic predictions is that a change in α from 0 to 1 represents the same change in a physical property measured (e.g., mass loss in TGA or heat release in DSC) regardless of the heating rate and/or temperature. However, for some processes a change in the measured property may depend on the heating rate and/or temperature, a common example being epoxy curing reactions. When cured at relatively high temperatures and/or heating rates, epoxy materials reach the extent of cure of ~100% that is characterized by the limiting glass transition temperature. Isothermal curing below the limiting glass transition temperature results in vitrification that effectively stops curing at some ultimate extent of cure, which is less than 100% and decreases as one uses progressively smaller temperatures for curing. In this situation, the use of the higher temperature complete cure kinetics data would lead to inaccurate predictions of the incomplete cure kinetics at the lower temperatures, and vice versa. This is simply because $\alpha = 1$ corresponds to respectively different absolute extents of cure under the conditions of complete and incomplete curing.

Also, some inaccuracy of kinetic predictions is associated with the uncertainty of determining $\alpha = 0$. Note that Eq. (8.1) derives from the integral Eq. (1.14) in which the lower limits of integration are 0. This is equivalent to assuming that the reaction starts when t and α are zero. However, in practical terms the reaction starts when it becomes detectable experimentally, i.e., when α reaches the detection limit, α_0. At this point t reaches a nonzero value of t_0. The assumption that α_0 and t_0 are negligibly different from zero gives rise to a systematic error in the predicted life time, t_α making its value shorter by the actual value of t_0:

$$t_0 = \frac{g(\alpha_0)}{k(T)} \tag{8.10}$$

The size of this error depends on the type of the actual kinetics or simply on the type of $g(\alpha)$. Fig. 3 suggests that at $\alpha_0 \to 0$ the value of $g(\alpha_0)$ is negligibly small for decelerating kinetics but relatively large for the kinetics of sigmoidal and accelerating type. For the kinetics of the latter type, the assumption that α_0 and t_0 are negligibly small may cause significant errors in life-time predictions. Experimentally, these kinetics can be recognized as isothermal kinetic profiles with a distinct induction period (curves 1 and 3 in Fig. 1). The value of t_0 provides an estimate for the length of the induction period, which is a period of time during which the reaction proceeds without a detectable change in the measured physical property (e.g., mass in TGA or heat flow in DSC). It should be stressed that the error (i.e., the value of t_0) increases quickly with decreasing temperature (i.e., decreasing $k(T)$ in Eq. (8.10)), which is important to remember when using accelerated higher temperature tests for predicting long term lower temperature behavior of materials.

There are several recommendations that should be followed to improve the precision and accuracy of kinetic predictions. First, the best possible quality experimental data should be obtained. It should be remembered that the precision and reproducibility of raw data ultimately determine the precision of predictions. Second, the experimental temperature range should be brought as close as possible to the temperature range of predictions. Minimizing the gap between these temperature ranges secures the accuracy of predictions. Third, one should follow the present recommendations (Sections 3–7) in selecting appropriate computational methods. Only the methods that avoid unnecessary approximations and account properly for specifics of a process can produce kinetic parameters whose quality is adequate to secure the accuracy and precision of predictions. Fourth, before making predictions one should check whether experimentally evaluated kinetic parameters can be used to reconstruct accurately the experimental data that were used to evaluate these parameters. If the reconstructed kinetic curves deviate systematically from the experimental ones, this deviation is likely to increase significantly when predictions are made for temperatures that lie outside the experimental range. Fifth, when predictions are based on nonisothermal data, at least one isothermal run should be performed to validate the life-time predictions. The isothermal run is also helpful for identifying the type of kinetics (Fig. 1) and, in particular, for alerting one to the sigmoidal and accelerating kinetics with an induction period.

9. Conclusions

In conclusion, one can be recommended to follow certain steps in performing kinetic computations. The first step obviously is obtaining quality kinetic data at no less than three different temperature programs. The second step is to apply an isoconversional method. Obtaining the E_α vs. α dependence is by itself sufficient for making kinetic predictions. If the latter is the sole goal of kinetic analysis then further computations may not be necessary. Note, that the E_α vs. α dependence can also be used in model-fitting to evaluate the parameters of a rate equation. Accomplishing other goals may require evaluating the whole kinetic triplets, which is the third step in kinetic computations. Here, the E_α vs. α dependence can offer important clues. If E_α does not vary significantly with α, the process can be adequately described as single-step kinetics, i.e., by a single kinetic triplet. This can be accomplished through linear model-fitting as well as by employing afore-described methods for determining reaction models and preexponential factors. If E_α varies with α, the process has to be described as multiple-step kinetics, i.e., by a multiple kinetic triplets. They should be evaluated by the techniques of nonlinear model-fitting, and the E_α vs. α dependence may provide useful ancillary information in selecting a particular mechanistic scheme. As the fourth step, one is recommended to validate the computed kinetic parameters by demonstrating that they can be used to satisfactorily predict (reproduce) the experimental kinetic curves from which these parameters have been computed. Even more rigorous validation is to test whether the computed kinetic parameters can be used to predict an experimental kinetic curve not included in kinetic computations.

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References

[1] M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyn, C.-R. Li, T.B. Tang, B. Roduit, J. Malek, T. Mitsuhashi, Computational aspects of kinetic analysis. Part A: The ICTAC kinetics project: data, methods, and results, Thermochim. Acta 355 (2000) 125–143.
[2] J. Sestak, Thermal Analysis. Part D: Thermophysical Properties of Solids: their Measurements and Theoretical Thermal Analysis, Elsevier, New York, 1984.
[3] J. Sestak, Science of Heat and Thermophysical Studies. A Generalized Approach to Thermal Analysis, Elsevier, Amsterdam, 2005.
[4] S. Vyazovkin, The Handbook of Thermal Analysis & Calorimetry, in: M.E. Brown, P.K. Gallagher (Eds.), Recent Advances, Techniques and Applications, vol. 5, Elsevier, 2008, p. 503.
[5] A.K. Burnham, R.K. Weese, A.P. Wemhoff, J.L. Maienschein, A historical and current perspective on predicting thermal cookoff behavior, J. Therm. Anal. Calorim. 89 (2007) 407–415.
[6] S. Vyazovkin, Kinetic concepts of thermally stimulated reactions in solids: a view from a historical perspective, Int. Rev. Phys. Chem. 19 (2000) 45–60.
[7] S. Vyazovkin, On the phenomenon of variable activation energy for condensed phase reactions, New J. Chem. 24 (2000) 913–917.
[8] P. Atkins, J. de Paula, Physical Chemistry, 9th ed., W.H. Freeman, New York, 2010 (discussion of negative activation energies is also found in earlier editions, see subject index under "activation energy, negative").
[9] M.E. Brown, Introduction to Thermal Analysis, 2nd ed., Kluwer, Dodrecht, 2001.
[10] J. Sestak, G. Berggren, Study of the kinetics of the mechanism of solid-state reactions at increased temperature, Thermochim. Acta 3 (1971) 1–12.
[11] A.K. Burnham, R.L. Braun, H.R. Gregg, A.M. Samoun, Comparison of methods for measuring kerogen pyrolysis rates and fitting kinetic equations, Energy Fuels 1 (1987) 452.
[12] 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.
[13] N. Sbirrazzuoli, Is the Friedman method applicable to transformations with temperature dependent reaction heat? Macromol. Chem. Phys. 208 (2007) 1592–1597.
[14] M.J. Starink, Activation energy determination for linear heating experiments: deviations due to neglecting the low temperature end of the temperature integral, J. Mater. Sci. 42 (2007) 483–489.
[15] S. Vyazovkin, N. Sbirrazzuoli, Isoconversional kinetic analysis of thermally stimulated processes in polymers, Macromol. Rapid Commun. 27 (2006) 1515–1532.
[16] H.L. Friedman, Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic, J. Polym. Sci., Part C 6 (1964) 183–195.
[17] M.J. Starink, The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods, Thermochim. Acta 404 (2003) 163–176.
[18] C.D. Doyle, Estimating isothermal life from thermogravimetric data, J. Appl. Polym. Sci. 6 (1962) 639.
[19] T. Ozawa, A new method of analyzing thermogravimetric data, Bull. Chem. Soc. Japan 38 (1965) 1881.
[20] J.H. Flynn, L.A. Wall, General treatment of the thermogravimetry of polymers, J. Res. Nat. Bur. Standards, Part A 70 (1966) 487.
[21] T. Akahira, T. Sunose, Method of determining activation deterioration constant of electrical insulating materials, Res. Report Chiba Inst. Technol. (Sci. Technol.) 16 (1971) 22–31.
[22] J.H. Flynn, The isoconversional method for determination of energy of activation at constant heating rates, J. Therm. Anal. 27 (1983) 95–102.
[23] N. Sbirrazzuoli, Y. Girault, L. Elégant, Simulations for evaluation of kinetic methods in differential scanning calorimetry. Part 3—Peak maximum evolution methods and isoconversional methods, Thermochim. Acta 293 (1997) 25–37.
[24] S. Vyazovkin, D. Dollimore, Linear and nonlinear procedures in isoconversional computations of the activation energy of thermally induced reactions in solids, J. Chem. Inf. Comp. Sci. 36 (1996) 42–45.
[25] S. Vyazovkin, Evaluation of the activation energy of thermally stimulated solid-state reactions under an arbitrary variation of the temperature, J. Comput. Chem. 18 (1997) 393–402.
[26] S. Vyazovkin, Modification of the integral isoconversional method to account for variation in the activation energy, J. Comput. Chem. 22 (2001) 178–183.
[27] P. Budrugeac, Differential non-linear isoconversional procedure for evaluating the activation energy of non-isothermal reactions, J. Therm. Anal. Calorim. 68 (2002) 131–139.
[28] S. Vyazovkin, L. Vincent, N. Sbirrazzuoli, Thermal denaturation of collagen analyzed by isoconversional method, Macromol. Biosci. 7 (2007) 1181–1186.
[29] K. Chen, S. Vyazovkin, Temperature dependence of sol–gel conversion kinetics in gelatin–water system, Macromol. Biosci. 9 (2009) 383–392.
[30] I. Dranca, S. Vyazovkin, Thermal stability of gelatin gels: effect of preparation conditions on the activation energy barrier to melting, Polymer 50 (2009) 4859–4867.
[31] K. Chen, S. Vyazovkin, Isoconversional kinetics of glass aging, J. Phys. Chem. B 113 (2009) 4631–4635.
[32] S. Vyazovkin, I. Dranca, Isoconversional analysis of combined melt and glass crystallization data, Macromol. Chem. Phys. 207 (2006) 20–25.
[33] C. Alzina, N. Sbirrazzuoli, A. Mija, Hybrid nanocomposites: advanced nonlinear method for calculating key kinetic parameters of complex cure kinetics, J. Phys. Chem. B 114 (2010) 12480–12487.
[34] H.E. Kissinger, Reaction kinetics in differential thermal analysis, Anal. Chem. 29 (1957) 1702–1706.
[35] D. Chen, X. Gao, D. Dollimore, A generalized form of the Kissinger equation, Thermochim. Acta 215 (1993) 109–117.
[36] R.L. Braun, A.K. Burnham, Analysis of chemical reaction kinetics using a distribution of activation energies and simpler models, Energy Fuels 1 (1987) 153–161.
[37] J.M. Criado, A. Ortega, Non-isothermal transformation kinetics: remarks on the Kissinger method, J. Non-Cryst. Solids 87 (1986) 302–311.

[38] J.M. Criado, A. Ortega, Non-isothermal crystallization kinetics of metal glasses: simultaneous determination of both the activation energy and the exponent n of the JMA kinetic law, Acta Metall. 35 (1987) 1715–1721.

[39] P. Budrugeac, E. Segal, Applicability of the Kissinger equation in thermal analysis: revisited, J. Therm. Anal. Calorim. 88 (2007) 703–707.

[40] J. Farjas, N. Butchosa, P. Roura, A simple kinetic method for the determination of the reaction model from non-isothermal experiments, J. Therm. Anal. Calorim. 102 (2010) 615–625.

[41] P.E. Sanchez-Jimenez, J.M. Criado, L.A. Perez-Maqueda, Kissinger kinetic analysis of data obtained under different heating schedules, J. Therm. Anal. Calorim. 94 (2008) 427–432.

[42] S. Vyazovkin, Is the Kissinger equation applicable to the processes that occur on cooling? Macromol. Rapid Commun. 23 (2002) 771–775.

[43] A.K. Burnham, Application of the Sestak–Berggren equation to organic and inorganic materials of practical interest, J. Therm. Anal. Calorim. 60 (2000) 895–908.

[44] R.L. Braun, A.K. Burnham, Pyrolysis kinetics for lacustrine and marine source rocks by programmed micropyrolysis, Energy Fuel 5 (1991) 192–204.

[45] R.L. Takhor, in: L.L. Hench, S.W. Freiman (Eds.), Advances in Nucleation and Crystallization of Glasses, Amer. Ceram. Soc., Columbus, OH, 1971, pp. 166–172.

[46] S. Mahadevan, A. Giridhar, A.K. Singh, Calorimetric measurements on As–Sb–Se glasses, J. Non-Cryst. Solids 88 (1986) 11–34.

[47] M.J. Starink, Comments on “Precipitation kinetics of Al–1.12Mg_2Si–0.35Si and Al–1.07Mg_2Si–0.33Cu alloys”, J. Alloys Compd. 433 (2007) L4–L6.

[48] A.I. Lesnikovich, S.V. Levchik, A method of finding invariant values of kinetic parameters, J. Therm. Anal. 27 (1983) 89–93.

[49] P.M. Madhysudanan, K. Krishnan, K.N. Ninan, New equations for kinetic analysis of non-isothermal reactions, Thermochim. Acta 221 (1993) 13–21.

[50] W. Tang, Y. Liu, H. Zhang, C. Wang, New approximate formula for Arrhenius temperature integral, Thermochim. Acta 408 (2003) 39–43.

[51] P. Budrugeac, J.M. Criado, F.J. Gotor, J. Malek, L.A. Perez-Maqueda, E. Segal, On the evaluation of the nonisothermal kinetic parameters of $(GeS_2)(0.3)(Sb_2S_3)(0.7)$ crystallization using the IKP method, Int. J. Chem. Kinet. 36 (2004) 309–315.

[52] P. Budrugeac, The Kissinger law and the IKP method for evaluating the non-isothermal kinetic parameters, J. Therm. Anal. Calorim. 89 (2007) 143–151.

[53] S. Vyazovkin, A unified approach to kinetic processing of nonisothermal data, Int. J. Chem. Kinet. 28 (1996) 95–101.

[54] J. Malek, The kinetic-analysis of nonisothermal data, Thermochim. Acta 200 (1992) 257–269.

[55] J. Malek, The applicability of Johnson–Mehl–Avrami model in the thermal analysis of the crystallization kinetics of glasses, Thermochim. Acta 267 (1995) 61–73.

[56] J.M. Criado, J. Malek, A. Ortega, Applicability of the master plots in kinetic-analysis of non-isothermal data, Thermochim. Acta 147 (1989) 377–385.

[57] S. Vyazovkin, C.A. Wight, Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data, Thermochim. Acta 340–341 (1999) 53–68.

[58] L.A. Perez-Maqueda, J.M. Criado, F.J. Gotor, J. Malek, Advantages of combined kinetic analysis of experimental data obtained under any heating profile, J. Phys. Chem. A 106 (2002) 2862–2868.

[59] L.A. Perez-Maqueda, J.M. Criado, P.E. Sanchez-Jimenez, Combined kinetic analysis of solid-state reactions: a powerful tool for the simultaneous determination of kinetic parameters and the kinetic model without previous assumptions on the reaction mechanism, J. Phys. Chem. A 110 (2006) 12456–12462.

[60] J.E. Freund, B.M. Perles, Modern Elementary Statistics, 12th ed., Prentice Hall, Upper Saddle River, NJ, 2006 (as well as any other textbook on statistics).

[61] J. Opfermann, Kinetic analysis using multivariate non-linear regression I. Basic concepts, J. Therm. Anal. Calorim. 60 (2000) 641–658.

[62] A.K. Burnham, An *n*th-order Gaussian energy distribution model for sintering, Chem. Eng. J. 108 (2005) 47–50.

[63] A.K. Burnham, R.L. Braun, Global kinetic analysis of complex materials, Energy Fuels 13 (1999) 1–22.

[64] ASTM E1641-07 Standard Test Method for Decomposition Kinetics by Thermogravimetry, Annual Book of ASTM Standards, vol. 14.02, ASTM International, West Conshohocken, PA, 2007.

[65] ASTM E698-05 Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials, Annual Book of ASTM Standards, vol. 14.02, ASTM International, West Conshohocken, PA, 2005, p. 226.