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The mathematical incorrectness of the integral isoconversional methods in case of variable activation energy and the consequences

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Abstract Kinetic parameters resulting from the application of isoconversional methods mostly depend on the degree of conversion. This paper shows that the integral isoconversional methods are mathematically incorrect if the activation energy depends on conversion. In this case, the incorrectness resides in improper separation of variables in the general rate equation. As a consequence, nonsensical snake-like shape of the conversion versus time curves is observed when the kinetic results are extrapolated to lower temperatures.

Keywords Integral isoconversional method · Variable activation energy · Incorrectness · Extrapolation

Introduction

Condensed state processes are extensively studied by thermoanalytical methods. Mechanisms of these processes are very often unknown or too complicated to be characterized by a simple kinetic model. They tend to occur in multiple steps that have different rates. To describe their kinetics, isoconversional methods are often used. The number of papers outlining the basic ideas of the isoconversional methods, analyzing the advantages and drawbacks and demonstrating their use, is almost countless, see for example [1–13]. The isoconversional methods can be divided into differential, incremental and integral ones [10]. In this paper, attention is paid to surprising and peculiar results obtained when extrapolating the results of integral isoconversional methods to lower temperatures.

Theoretical

Rate of the processes in condensed state is generally a function of temperature and conversion:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \Phi(T, \alpha). \tag{1}$$

The single-step approximation [14, 15] employs the assumption that the function Φ in Eq. (1) can be expressed as a product of two functions independent of each other, the first one, $k(T)$, depending solely on temperature T and the other one, $f(\alpha)$, depending solely on the degree of conversion of the process, α:

$$\Phi(T, \alpha) = k(T)f(\alpha). \tag{2}$$

Combination of Eqs. (1) and (2) results in:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha). \tag{3}$$

Equation (3) is mostly referred to as the general rate equation. Indeed, it resembles a single-step kinetic equation, even though it is a representation of the kinetics of a complex condensed-phase process. Each elementary step

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of a complex process should be described by its own kinetic equation so that kinetics of a complex process should be described by a set of rate equations. The single-step approximation thus resides in substituting the set of kinetic equations by the sole single-step kinetic equation [14, 15]. Equation (3) is thus a mathematical expression of the single-step approximation.

The isoconversional methods are based on Eq. (3). Their principal idea is that the conversion function $f(\alpha)$ at a fixed value of α holds for any temperature or temperature regime, i.e., the mechanism of the process is solely a function of conversion, and not a function of temperature. The kinetic parameters are obtained from a set of kinetic runs from the dependences of isoconversional time versus temperature (for isothermal measurements), isoconversional temperature versus heating rate (for integral and incremental methods using a linear heating rate), or from the dependence of the reaction rate versus temperature (for differential methods) [10].

The temperature function is almost exclusively expressed by the Arrhenius equation

$$k(T) = A_{\mathrm{k}} \exp\left[-\frac{E}{\mathrm{RT}}\right], \tag{4}$$

where A_{k} is the preexponential factor, E is the activation energy, T is the absolute temperature and R stands for the gas constant. Hence, we limit ourselves to the Arrhenius temperature function and the non-Arrhenian temperature functions will be mentioned at the end of the paper.

Among the isoconversional methods, the integral methods are the most popular. Combining Eqs. (3) and (4), one can get

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A_{\mathrm{k}} \exp\left[-\frac{E}{\mathrm{RT}}\right] f(\alpha). \tag{5}$$

After the separation of variables and setting the integration limits, the latter equation gives the result:

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = A_{\mathrm{k}} \int_0^{t_\alpha} \exp\left[-\frac{E}{\mathrm{RT}}\right] \mathrm{d}t. \tag{6}$$

After integration and some manipulations, one can get

$$1 = \int_0^{t_\alpha} \frac{\mathrm{d}t}{A \exp\left[\frac{E}{\mathrm{RT}}\right]}. \tag{7}$$

In Eq. (7), A is given as

$$A = \frac{F(\alpha) - F(0)}{A_{\mathrm{k}}}, \tag{8}$$

where $F(\alpha)$ is a primitive function related to $1/f(\alpha)$. Equation (7) gives the isoconversional time for a general time/temperature regime. For an isothermal process, the denominator on the right side of Eq. (7) is constant so that from Eq. (7) it follows

$$t_\alpha = A \exp\left[\frac{E}{\mathrm{RT}}\right]. \tag{9}$$

For the experiments with linear heating, the dependence temperature versus time is expressed as $\mathrm{d}t = \mathrm{d}T/\beta$. Equation (7) can thus be rewritten as [10]

$$\beta = \int_0^{T_\alpha} \frac{\mathrm{d}T}{A \exp\left[\frac{E}{\mathrm{RT}}\right]}. \tag{10}$$

Using the Doyle and Coats-Redfern approximations for the temperature integral in Eq. (10), the Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) methods, respectively, can be derived [10]. The kinetic parameters are usually obtained from a set of isoconversional temperatures for various heating rates from the linearized transformation of Eq. (10):

$$\ln\left(\frac{\beta}{T_\alpha^a}\right) = \mathrm{f}\left(\frac{1}{T_\alpha}\right), \tag{11}$$

where $a = 0$ for the FWO method and $a = 2$ for the KAS method. From Eq. (10), also the Vyazovkin non-linear integral isoconversional method [4, 5] can be derived. In our papers, the kinetic parameters are obtained from the direct minimization of the sum of squares between the experimental and theoretical isoconversional temperatures where the temperature integral is calculated numerically [16].

Mathematical incorrectness of the integral isoconversional methods

In our papers [10, 14, 15], it has been pointed out that, for the integral isoconversional methods, assumption of a constant value of activation energy is implicit and inevitable for the separation of the variables of Eq. (3) in the derivation of Eq. (7). On the other hand, the isoconversional methods are known to provide the activation energies dependent on conversion [17]. This makes the procedure of obtaining the kinetic parameters self-inconsistent. One can easily prove that Eq. (5) cannot be separated if the activation energy depends on conversion. Dependence of the activation energy on the extent of conversion invalidates Eq. (6); the variable α is not separated since it occurs on both sides of the differential equation:

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \int_0^{t_\alpha} A \exp\left[-\frac{E(\alpha)}{\mathrm{RT}}\right] \mathrm{d}t. \tag{12}$$

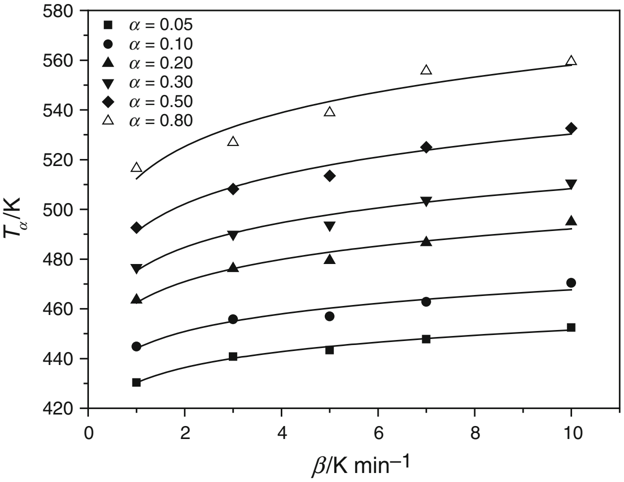

Fig. 1 Dependence of isoconversional temperature on heating rate for the thermal decomposition of the sample HI-6

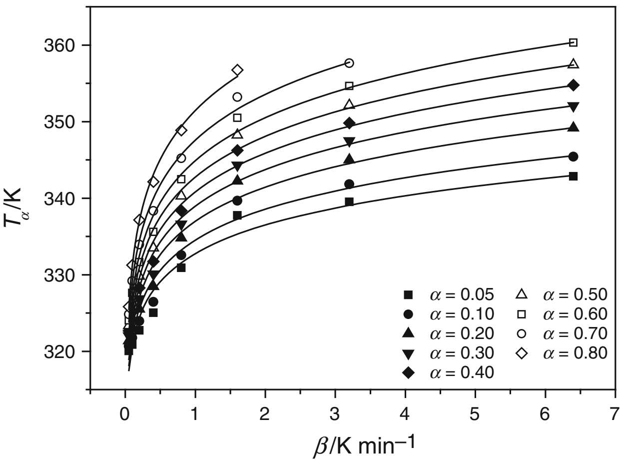

Fig. 2 Dependence of isoconversional temperature on heating rate for the acrylamide polymerization in water solution

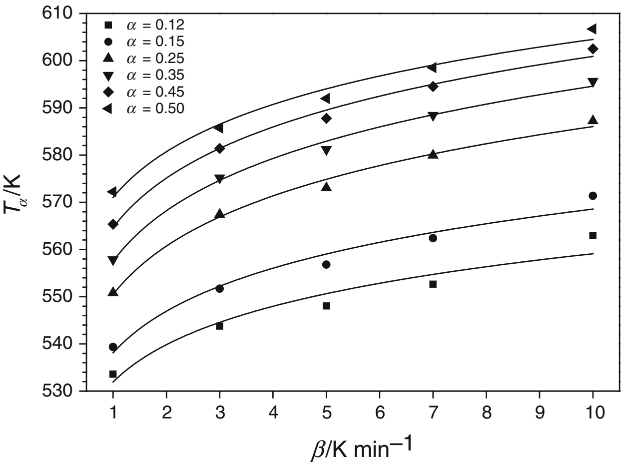

Fig. 3 Dependence of isoconversional temperature on heating rate for the thermooxidative decomposition of the artificially weathered newspaper

Table 1 Kinetic parameters of HI-6 thermal decomposition and their standard deviations obtained by the integral isoconversional method ($B = E/R$)

α	A/min	B .10^{-3}/K
0.05	$(4.2 \pm 14) \times 10^{-20}$	20.1 ± 1.4
0.10	$(1.2 \pm 7.9) \times 10^{-18}$	19.3 ± 3.0
0.20	$(2.8 \pm 12) \times 10^{-15}$	16.6 ± 2.0
0.30	$(4.5 \pm 18) \times 10^{-14}$	15.8 ± 1.9
0.50	$(4.0 \pm 13) \times 10^{-12}$	14.2 ± 1.6
0.80	$(8.4 \pm 40) \times 10^{-11}$	13.4 ± 2.5

Table 2 Kinetic parameters of acrylamide polymerization in water solution and their standard deviations obtained by the integral isoconversional method ($B = E/R$)

α	A/min	B .10^{-3}/K
0.05	$(2.9 \pm 16) \times 10^{-26}$	20.1 ± 1.8
0.10	$(2.0 \pm 9.3) \times 10^{-24}$	18.8 ± 1.5
0.20	$(4.1 \pm 15) \times 10^{-22}$	17.2 ± 1.2
0.30	$(1.1 \pm 3.5) \times 10^{-20}$	16.2 ± 1.0
0.40	$(1.4 \pm 3.8) \times 10^{-19}$	15.5 ± 0.9
0.50	$(1.2 \pm 2.7) \times 10^{-18}$	14.8 ± 0.7
0.60	$(9.4 \pm 17) \times 10^{-18}$	14.2 ± 0.6
0.70	$(10 \pm 16) \times 10^{-17}$	13.6 ± 0.5
0.80	$(3.1 \pm 3.4) \times 10^{-15}$	12.5 ± 0.4

Table 3 Kinetic parameters of newspaper thermooxidative degradation and their standard deviations obtained by the integral isoconversional method ($B = E/R$)

α	A/min	B .10^{-3}/K
0.12	$(2.2 \pm 16) \times 10^{-19}$	24.1 ± 3.8
0.15	$(2.0 \pm 8.6) \times 10^{-17}$	22.0 ± 2.3
0.25	$(3.6 \pm 6.6) \times 10^{-15}$	19.8 ± 1.0
0.35	$(9.9 \pm 16) \times 10^{-15}$	19.5 ± 0.9
0.45	$(2.9 \pm 5.7) \times 10^{-15}$	20.4 ± 1.1
0.50	$(9.0 \pm 28) \times 10^{-17}$	22.6 ± 1.8

As seen from Eq. (12), in the case of variable activation energy, Eq. (10) is not a solution of Eq. (6) for linear heating. Equation (10) is thus incorrect so that all the subsequent formulas are mathematically incorrect. The values of kinetic parameters obtained from the treatment of experimental data are, obviously, unpredictably skewed by the mathematical incorrectness of the procedure applied.

The mathematical incorrectness of the integral isoconversional methods in the case of variable activation energy has been recognized also by Budrugeac et al. [9]. The constancy of activation energy is a prerequisite in the concept of the generalized time introduced by Ozawa [1].

Experimental

The integral isoconversional method was applied to three systems in this paper to demonstrate the inconsistency of Eq. (7) for the case of variable activation energy. All the experiments were carried out at linear heating for several heating rates:

1. Thermal degradation of the pharmaceutic HI-6 by thermogravimetric measurements applying the simultaneous DTA/TG thermoanalyzer Shimadzu DTG-60 under the nitrogen atmosphere. HI-6 is 1-[((4-(aminocarbonyl)pyridinio)methoxy)-methyl)-2-((hydroxyimino)methyl) pyridinium dichloride monohydrate] and appears to be an enzyme-reactivating oxime [18]. Injection of oximes in combination with atropine is regarded to be the most efficient procedure in poisonings with organophosphorus compounds, particularly with nerve agents. The measurements were carried out in nitrogen by TG applying Shimadzu DTG-60. The dependences of isoconversional temperatures on heating rate are given in Fig. 1.
2. Polymerization of acrylamide in water solution. The experimental details are described in [19]. This polymerization reaction is intended to be applied in sandstone consolidation. The experimental results are shown in Fig. 2.
3. Thermooxidative degradation of newspaper with a surface density 45 g m^{-2}, surface pH 5.4. The paper was subjected to artificial weathering in an oven at 98 °C, in a self-generated atmosphere, relative humidity (50 ± 2) % for 5 days. After the artificial weathering, the paper was subjected to the study of thermooxidative stability. The measurements were carried out in air by DTA applying Shimadzu DTG-60. The experimental results are shown in Fig. 3.

Results and discussion

The kinetic parameters *A* and *E* were obtained from the experimental data applying Eq. (10) by the minimization of the sum of squares between the experimental and

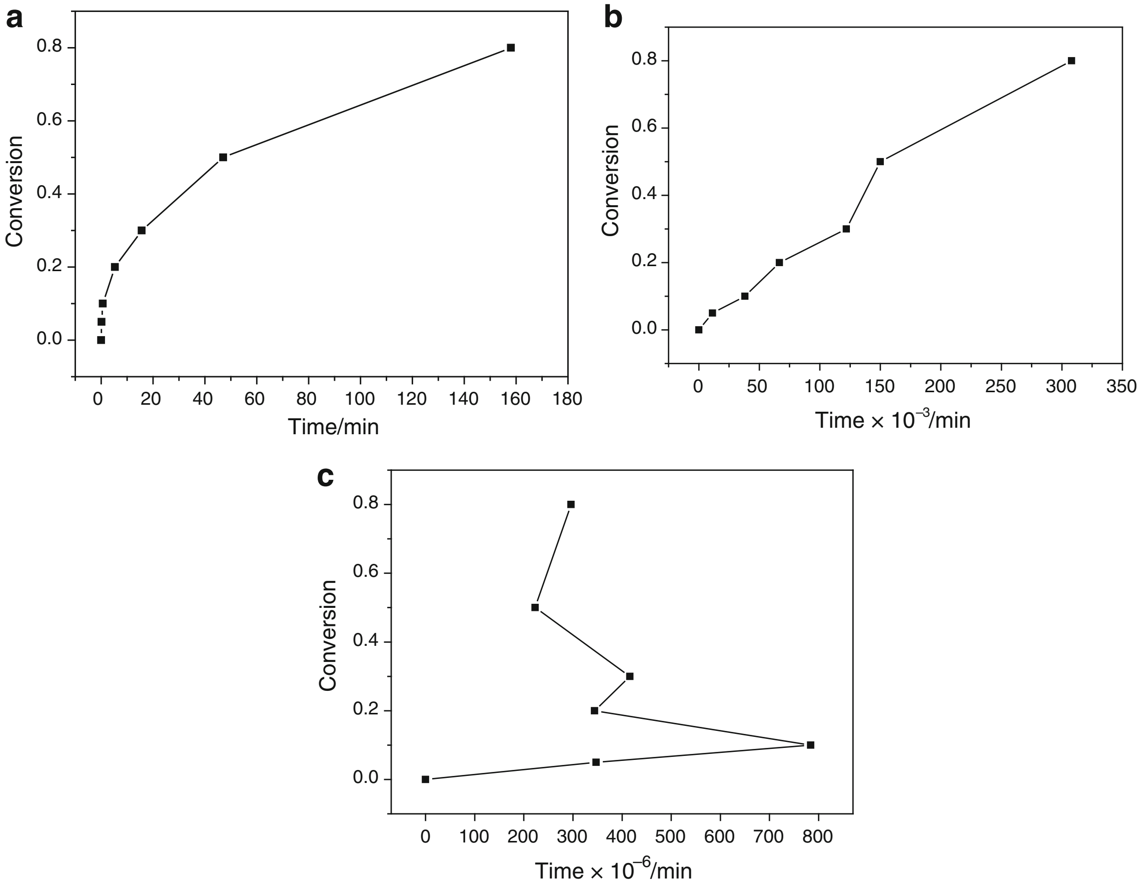

Fig. 4 Dependence of the degree of conversion of HI-6 thermal decomposition on time calculated from the kinetic parameters listed in Table 1 for temperature: **a** 200 °C; **b** 100 °C; **c** 40 °C

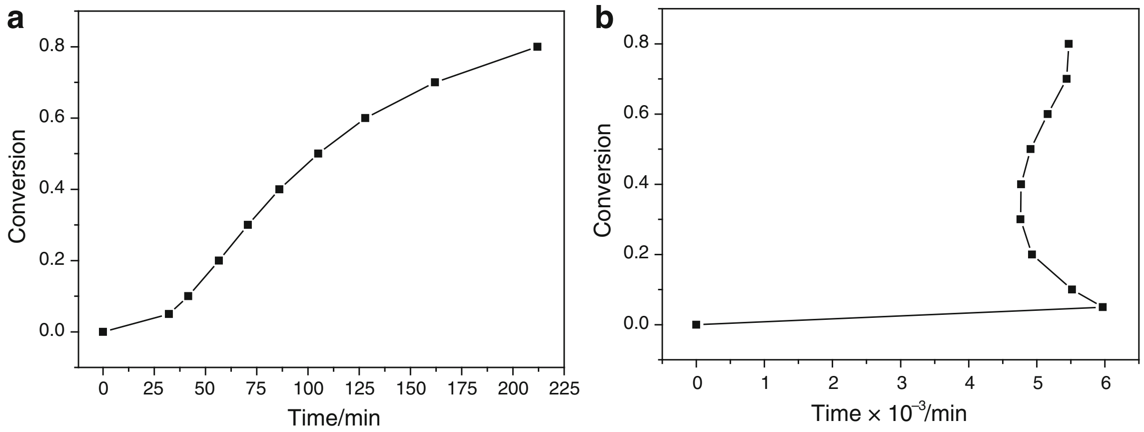

Fig. 5 Dependence of the degree of conversion of the acrylamide polymerization in water solution on time calculated from the kinetic parameters listed in Table 2 for temperature: **a** 50 °C; **b** 25 °C

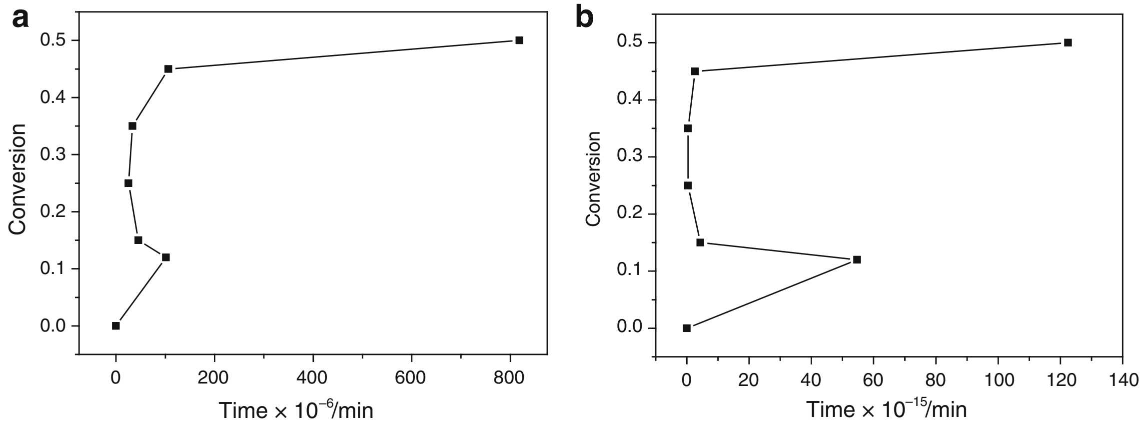

Fig. 6 Dependence of the degree of conversion of the thermooxidative decomposition of the artificially weathered newspaper on time calculated from the kinetic parameters listed in Table 3 for temperature: **a** 120 °C; **b** 23 °C

theoretical values of isoconversional temperatures for various heating rates. The temperature integral in Eq. (10) was calculated by the continued fractions [20]. The resulting kinetic parameters are listed in Tables 1, 2 and 3 for the thermal decomposition of HI-6, acrylamide polymerization and thermooxidative degradation of paper, respectively.

As discussed in [14, 17], the concept of activation energy generally identifies the energy connected with the barrier to the bond redistribution process for the rate-determining step in an elementary reaction. When employing the isoconversional methods, a complex multistep process is treated as a single-step one. In [15] it has been demonstrated that kinetics of the simplest processes, such as reversible, parallel and consecutive processes comprising two elementary first-order reactions, cannot be in general expressed in the factorized form of Eq. (3). Equation (3) is just a mathematical tool so that the kinetic parameters obtained, i.e., the activation energy and pre-exponential factor, are thus apparent and do not have any mechanistic significance. There is no reason to interpret the apparent activation energy in terms of a free energy barrier. The value of activation energy cannot be used for the far-reaching conclusions frequently encountered in literature, such as systematization of the information available, developing theories on the mechanisms of the processes, etc. The values of these apparent kinetic parameters, however, do enable the modelling of the kinetics of complex processes without a deeper insight into their mechanism [14, 15]. The kinetic parameters therefore should only be applied to the estimation of the isoconversional temperature, isoconversional time, reaction rate, etc., for other time/temperature regimes than applied during measurements. For example, once the kinetic parameters A and E have been determined by application of Eq. (10), the isoconversional time for a constant temperature T can be calculated by applying Eq. (9).

The principal goal of degradation/stability studies is to extrapolate the kinetic data, obtained from accelerated stability tests, to the application conditions. In the case of

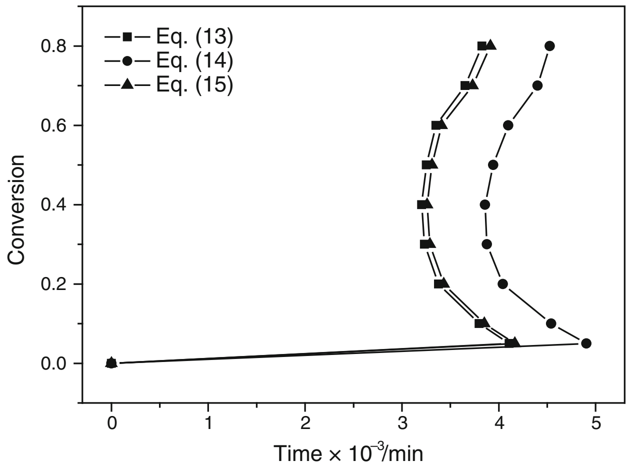

Fig. 7 Dependence of the degree of conversion of the acrylamide polymerization in water solution on time for temperature 25 °C. The kinetic parameters are obtained by the isoconversional integral methods based on the non-Arrhenian temperature functions (Eqs. 11–13)

the drug HI-6, the aim of the kinetic analysis is to assess the stability in a relatively warm environment where the temperature of interest is 40 °C. Figure 4a–c shows the dependence of the degree of conversion of HI-6 thermal decomposition on time calculated from the kinetic parameters listed in Table 1 for the temperatures 200, 100 and 40 °C using Eq. (9). The first temperature is from the temperature range of measurement and the dependence of conversion on time looks quite reasonable. At 100 °C, the conversion versus time curve begins to have a zig-zag shape. Extrapolation of the kinetic data to 40 °C leads to the non-sensical results shown in Fig. 4c. The conversion versus time curve becomes snake-like and higher conversions are achieved for shorter times. Several values (maximum 4) of conversion are predicted from extrapolation for certain values of time.

Similar non-sensical results are obtained for the dependence of the degree of conversion of the acrylamide polymerization in water solution on time calculated from the kinetic parameters listed in Table 2. As seen from Fig. 5a, at 50 °C, the dependence of conversion on time looks reasonable. However, at the temperature of interest, 25 °C, since this is a typical temperature at which the consolidants would be applied to the stone, a snake-like curve is once again obtained for the dependence of conversion on time (Fig. 5b).

The results of the extrapolation for the dependence of the degree of conversion of the thermooxidative decomposition of the artificially weathered newspaper on time were calculated from the kinetic parameters listed in Table 3 and are shown in Fig. 6a, b. It can be seen that a snake-like curve is again obtained for temperature as high as 120 °C. The temperature of interest is the “museum temperature” 23 °C. Again, as seen from Fig. 6b, the conversion versus time curve is far from reasonable.

It is generally understood that the application of isoconversional methods naturally leads to effective activation parameters dependent on the extent of conversion [17]. Quite frequently, conclusions about the mechanism of the process are drawn from the dependence of the activation energy on the conversion, whilst neglecting the role of the preexponential factor. Our opinion is that such a procedure is incorrect. Both the activation energy and preexponential factor are just fitting parameters. Only the quantities accessible from the measurement, calculated from the combination of both the kinetic parameters, should be used for making conclusions and predictions. Such quantities are mainly the isoconversional temperature, the isoconversional time and the rate of the process.

In this paper, we dealt with the study of processes at linear heating. However, as can be seen from Eq. (12), the integral isoconversional methods are mathematically incorrect also for isothermal studies if the activation energy depends on the degree of conversion.

In [21] the kinetic parameters are reasoned to be solely apparent quantities without a mechanistic interpretation. As the temperature function is just a mathematical tool enabling description of the kinetic hypersurface, there is no need to be limited to the Arrhenius relationship; alternative temperature functions may be equally applied [21–23]:

$$k(T) = Ae^{\mathrm{DT}} \tag{13}$$

$$k(T) = AT^{\mathrm{m}} \tag{14}$$

$$\frac{k(T)}{F(\alpha) - F(0)} = \frac{\left(\ln\frac{T_\infty}{T_\infty - T}\right)^{\frac{1-a}{a}}}{(T_\infty - T)a}, \tag{15}$$

where A, D, m, a and T_∞ are adjustable parameters. When applying these temperature functions in the integral isoconversional method, the isoconversional times are shorter than those calculated by applying the Arrhenius temperature function. However, as seen in Fig. 7, the snake-like shape of the extrapolated conversion versus time curves is retained. This implies that the strange snake-like shape of the extrapolated curves is not a consequence of the temperature function applied. It has to be a consequence of the mathematical incorrectness hidden in Eq. (12).

Conclusions

The model-free isoconversional methods represent a facile way to treat the experimental condensed-phase kinetic data. The kinetic parameters obtained enable the modelling of processes for other temperature regimes than were applied in the measurements. The greatest advantage of the model-free analysis is its simplicity and the avoidance of the errors connected with the selection of a kinetic model.

Since the kinetic parameters do not have any clear physical meaning in general, no conclusions could be drawn from the value of a single kinetic parameter, in particular, from the value of activation energy. The conclusions that can be drawn using these methods are limited to the estimations of modelled physical quantities, i.e., the isoconversional temperature, the isoconversional time and the rate of the process.

In case the activation energy resulting from the integral isoconversional methods depends on conversion, the application of integral isoconversional methods is mathematically incorrect and the strange snake-like shape of the extrapolated conversion versus time curves is obviously the consequence of that incorrectness. The only conclusion that can be drawn from the dependence of the activation energy on the conversion is that the process is not elementary but complex. Therefore, in case of variable activation energy, the integral isoconversional methods, such as FWO, KAS, integral Vyazovkin, Li-Tang and Capela-Ribeiro methods, are advisable to be avoided. In this sense, the recommendations of the ICTAC kinetic committee [6] should be modified.

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