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ISOTHERMAL AND NON-ISOTHERMAL KINETICS WHEN MECHANISTIC INFORMATION AVAILABLE

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Abstract

In the case of a complex mechanism of two parallel independent reactions, peak maximum evolution methods and model-fitting methods give only a mean value of the kinetic parameters, while isoconversional methods are useful to describe the complexity of the mechanism. Isothermal and non-isothermal isoconversional methods can be used to elucidate the kinetics of the process. Nevertheless, isothermal isoconversional methods can be limited by restrictions on the temperature regions experimentally available because of duration times or detection limits.

Keywords: complex process, DSC, isoconversional methods, kinetics, model-free kinetics, peak maximum evolution methods, simulations

Introduction

Various multiple-scan methods can be used for extracting kinetic data from thermogravimetric or differential calorimetric measurements. Among these methods, we can distinguish peak maximum evolution methods and isoconversional methods. These methods allow for model-independent estimates of the activation energy, so that one can speak of model-free kinetics. In addition to this possibility, it has been shown that the sole dependence of the activation energy on conversion, obtained with isoconversional methods, is sufficient to reliably predict the kinetics of a process over a wide range of temperature. Analysis of this dependence often permits the identification of the kinetic scheme of the process, and allows for identification of the complexity of the transformation [1]. In a previous study, the influence of acquisition time and of simulated random error was reported, for peak maximum evolution methods and isoconversional methods. The sensitivity of isoconversional methods to the number of points was pointed out. Nevertheless, we have shown that if acquisition times were correctly chosen, these methods gave smaller errors than peak maximum evolution methods, and that isoconversional methods should be preferred [2]. Systematic evaluation of these errors using Student's estimates have been reviewed and a method was given for estimating valid confidence intervals for the activation energy computed by the isoconversional method. Valid 95% confidence intervals can be constructed by using corrected Student's percentiles for 3, 4, and 5 heating rates experiments, respectively [3].

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The Málek method will be discussed separately. This method generally uses the Kissinger method for the determination of the activation energy, but an isoconversional method can be used. This evaluation implies that a series of experiments has to be conducted at different heating rates, and that one activation energy will be obtained for this series. This activation energy is computed at the peak maximum or for a given conversion degree (generally α=50%) [2]. Then, calculation of the kinetic exponents m and n and of the logarithm of the pre-exponential factor (ln$A$), is possible by treating each curve, so that one set of parameter is obtained for each heating rate. This method combines some aspects of model-free kinetics (for the evaluation of the activation energy) and some of model-fitting methods (for the evaluation of the logarithm of the pre-exponential factor and of the kinetic exponents). However, this method allows to select the function $f(\alpha)$ that is supposed to describe the kinetic model. This function can be chosen from the shape of the plot of the standardized curve $y(\alpha)$. Three possible models can be studied with this method: the reaction order model (RO), the Johnson-Mehl-Avrami model, and the Šesták-Berggren model (SB) with two kinetic exponents (also called the autocatalytic model for homogeneous kinetics) [2, 4]. Nevertheless, computation of the standardized curve requires the activation energy. If the value computed at the peak maximum, or for a given conversion degree, is solely considered, the information on the complexity of the process is lost.

Theoretical

Isoconversional methods were extensively described in previous papers [2, 3]. The general equation for the reaction rate may be written as [5, 6]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \tag{1}$$

where $k(T)$ is the Arrhenius rate constant, α the extent of reaction (conversion degree), t the time, T the temperature and $f(\alpha)$ the reaction model (or conversion function).

For non-isothermal conditions, at a constant heating rate $\beta=\mathrm{d}T/\mathrm{d}t$, Eq. (1) may be rewritten as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}e^{-E/RT}f(\alpha) \tag{2}$$

where A is the pre-exponential factor, E is the activation energy, and R is the gas constant.

Let us call $g(\alpha)=\int_0^\alpha \mathrm{d}\alpha/f(\alpha)$ then the integral form of Eq. (2) is obtained [7]:

$$g(\alpha)=\frac{AE}{R\beta}\left[\frac{e^{-x}}{x}-\int_x^\infty\left(\frac{e^{-x}}{x}\right)\mathrm{d}x\right] \tag{3}$$

where $x=E/RT$ is the reduced activation energy at the temperature T. As no exact solution exists for Eq. (3), this equation is generally written as:

$$g(\alpha)=\frac{AE}{R\beta}p(x) \tag{4}$$

where $p(x)$ is the temperature integral.

Non-isothermal integral isoconversional methods

Using Doyle's approximation [8], the linear equation of Ozawa-Flynn-Wall can be obtained [9, 10]:

$$\ln\beta_i=\text{const.}-1.052\left(\frac{E_\alpha}{RT_{\alpha,i}}\right) \tag{5}$$

where the subscript α designates values related to a given conversion degree, and i is an ordinal number of the experiment conducted at the heating rate β_i.

The Kissinger-Akahira-Sunose method [11] is valid at any given conversion and is derived using the approximation $p(x)\cong e^{-x}/x^2$ $(20\leq x\leq 50)$. Under this assumption, Eq. (6) is obtained. This equation, can also be derived by using the more precise approximation of Coats and Redfern [12]:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)=\text{const.}-\frac{E_\alpha}{RT_{\alpha,i}} \tag{6}$$

Isothermal integral isoconversional method

For isothermal conditions, Eq. (1) may be rewritten as :

$$g(\alpha)=k(T)t \tag{7}$$

and leads to the isothermal integral isoconversional method:

$$\ln t_\alpha=\ln g(\alpha)-\ln A_\alpha+\frac{E_\alpha}{RT_{\text{iso}}} \tag{8}$$

where t_α and A_α are the time and the pre-exponential factor at given conversion degree, and where T_{iso} is the isothermal temperature.

Isothermal model-fitting methods

The usual isothermal method for a single step mechanism governed by a reaction order rate equation is expressed by Eq. (9):

$$\ln\left(\frac{d\alpha}{dt}\right)=\ln k(T)+n\ln(1-\alpha) \tag{9}$$

where n is the reaction order. The values of $\ln k(T)$ and n can be obtained from Eq. (9) for each temperature. Then, the values of E and $\ln A$ can be estimated by plotting $\ln k(T)$ *vs.* $1/T$.

An alternative to this is to plot Eq. (10) for a given conversion degree (generally α=50%):

$$\ln\left(\frac{d\alpha}{dt}\right) - \ln f(\alpha) = \ln A - \frac{E}{RT_{iso}} \tag{10}$$

Those methods (Eqs (9) and (10)) imply that the reaction is governed by the same mechanism for the whole process.

Numerical simulations

The generation of simulated data was previously presented [2]. Evaluation of kinetic parameters was performed on the artificially created data using a computer program described elsewhere [13].

A complex mechanism of two parallel independent reactions governed by a reaction order model was simulated. If only the rate of product formation is measured, the mechanism may correspond to the following kinetic scheme:

$$A \xrightarrow{k_1} C \xleftarrow{k_2} B \tag{11}$$

Non-isothermal synthetic data

The kinetic parameters were: kinetic orders n_1=1.2, n_2=1; activation energies E_1=143 and E_2=74 kJ mol^{-1}, logarithms of the pre-exponential factor $\ln(A_1/s^{-1})$=29.4, $\ln(A_2/s^{-1})$=11.7; acquisition time sr=2 s; scanning rates β=0.1–10 K min^{-1}; initial temperature T_0=313.15 K. The heat of each exothermic effect was chosen in order that reaction 1 contribute 70% and reaction 2 contribute 30% to the overall reaction. This case is referred as $Q_1>Q_2$, where Q_1 and Q_2 represent the heat effects of reaction 1 and 2, respectively.

Isothermal synthetic data

The same parameters were used in isothermal mode. Several thermoanalytical curves were simulated at seven temperatures, every 20 K from 373 to 493 K.

Results

Non-isothermal model fitting-methods

Results already presented in our previous work, have shown that in the case of a complex process, a single-scan method will give different kinetic parameters when the heating rate is increased and different kinetic parameters for the beginning and for the end of the thermoanalytical curve. The Arrhenius plots of the Achar-Brindley-Sharp method for various values of the kinetic exponent (n), can show the existence of several mechanisms depending on the choice of the kinetic interval [2]. Nevertheless, if only one value of the activation energy is computed (i.e. if only one heating rate is used), as it is usually done, information on the complexity of the mechanism is lost.

Isothermal model fitting-methods

The values of ln$k(T)$ and n computed from Eq. (9) are reported in Table 1. A plot of ln$k(T)$ *vs.* $1/T$ gave E=138.70 kJ mol^{-1} and ln(A/s^{-1})=28.19. Figure 1 gives the Arrhenius plot for the isothermal method according to Eq. (9), in the case of the complex process studied. This plot does allow for identification of the complexity of the transformation. Similar conclusions were drawn for experimental data [14].

Table 1 Isothermal model-fitting method of Eq. (9)

T/K	Arrhenius rate constant ln[$k(T)$/s^{-1}]	Reaction order n
373	–16.68851	1.007
393	–14.26151	1.038
413	–12.07351	1.063
433	–10.10656	1.074
453	–8.44165	1.027
473	–7.11367	0.925
493	–5.87340	0.995

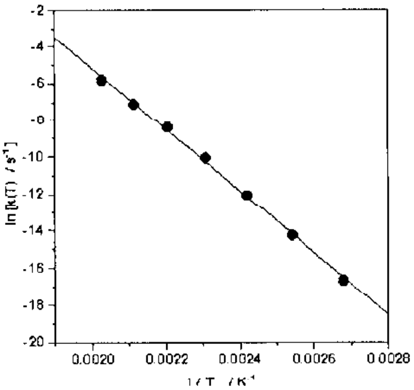

Fig. 1 Arrhenius plot for a complex process according to the isothermal model-fitting method (r=–0.99902)

Table 2 Isothermal model-fitting method of Eq. (10)

Conversion degree α	Activation energy E/kJ mol^{-1}	Pre-exponential factor $\ln(A/s^{-1})$	r
0.10	98.75352	18.08409	–0.99586
0.50	128.86202	25.82115	–0.99925
0.90	137.96771	27.99523	–0.99944

The use of Eq. (10) leads to the results presented in Table 2. Usually, a single value is reported for the activation energy, and is computed for α=50%. It is not allowed for the identification of the complexity of the mechanism. Nevertheless, this complexity can be shown considering the variation of the Arrhenius parameters for several conversion degrees (Table 2).

Málek method

Application of the Málek method indicated that the reaction follows a simple n^{th}-order model, deduced from a strictly decreasing $y(\alpha)$ function obtained, whatever the heating rate (Fig. 2). Nevertheless, the complexity of the mechanism can be deduced from the changes in the reaction order [2].

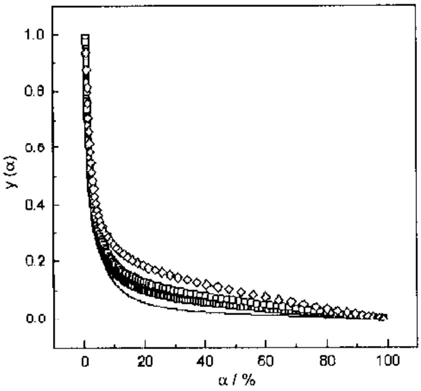

Fig. 2 Plot of the standardized curve $y(\alpha)$ *vs.* α for a complex process: — – β=0.1 K min^{-1}; □– β=0.3 K min^{-1}; o – β=0.5 K min^{-1}; ◊ – β=1 K min^{-1}

Isothermal and non-isothermal isoconversional methods

Isoconversional methods allow a possible change of rate-limiting step (and associated Arrhenius parameters) of the process. The dependences of the activation energy computed for isothermal and non-isothermal isoconversional methods, according to Eqs (6) and (8), are shown in Fig. 3. The activation energies of each reaction

(Eq. (11)), are well separated in non-isothermal conditions, while the activation energy of the low temperature reaction (reaction 2) is about 20 kJ mol^{-1} higher with the isothermal method. This is due to the lower total thermal effect attributed to this reaction that can be identified at low temperature, i.e. when its thermal flow is low. Fortunately, this total thermal effect can be experimentally amplified or lowered by modifying the concentrations (or the proportions) of the species. For example, if the values of Q_1 and Q_2 are inverted, the activation energies of each reaction can be better separated in isothermal conditions (Fig. 3).

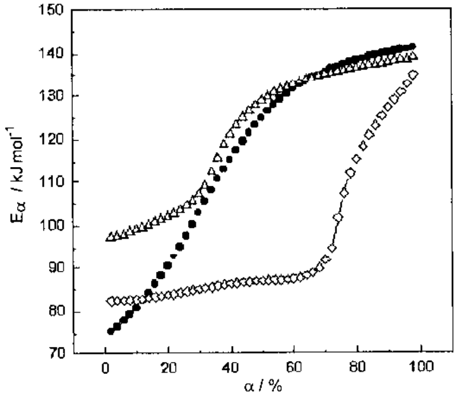

Fig. 3 Dependences of the activation energy (E) *vs.* conversion (α): • – non-isothermal isoconversional method; Δ – isothermal isoconversional method for $Q_1>Q_2$; ◊ – isothermal isoconversional method for $Q_1<Q_2$

Hence, this temperature region (373 to 493 K) was only possible for simulated data. In the isothermal mode the reactions are very slow at the lowest temperatures ($T<443$ K), so that the experiments will be limited by long times to completion and low detection limits, while, for high temperatures, the reaction will be too fast. A practical temperature region would be 443 to 493 K, with times to completion of 26 h and 30 min, respectively, for $\alpha=0.99$. These restrictions imply that the experimental isothermal domain of temperature available is limited, hence the possible separation of several reactions with isothermal isoconversional methods will depend on this. The temperature region covered for non-isothermal simulations at 0.1 to 5 K min^{-1} is 323 to 573 K. Isothermal and non-isothermal experiments are thus necessarily conducted in different temperature regions. Non-isothermal runs cover a wider temperature range than that of isothermal experiments, but compress the α-range reducing resolution.

As shown in Fig. 3, these dependences could have different shapes. This happens because for the same multi-step mechanism and at the same values of α and T, the contributions of the individual reactions are different for different heating programs. However, this does not signify that the general kinetic equation (Eq. (1)) is not valid for non-isothermal conditions, but that the global extent of conversion cannot

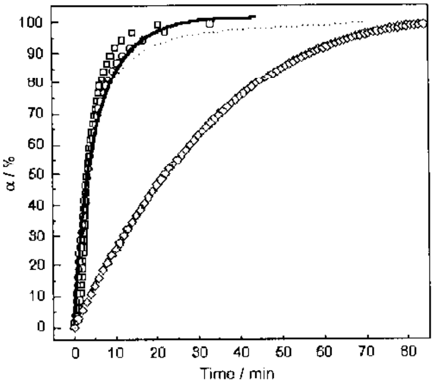

Fig. 4 Isothermal simulated curve and isothermal predictions made using non-isothermally estimated kinetic parameters: — – isothermal simulated curve for T=493 K; □ – non-isothermal isoconversional method at β=0.1, 0.3, 0.5 K min^{-1}; o – non-isothermal isoconversional method at β=1, 2, 3, 4, 5 K min^{-1}; ◊ – model-fitting method at β=0.1 K min^{-1}; - - - – model-fitting method at β=5 K min^{-1}

uniquely determine the composition of a multi-step reaction system. Figure 4 gives a comparison of the isothermal simulated curve for T=220°C with isothermal predictions made using non-isothermally estimated kinetic parameters. A good agreement is obtained whatever the set of scanning rates used for estimating the kinetic parameters when using the non-isothermal isoconversional method. According to Eq. (6) this method implies that Eq. (2) is valid. Poor agreement is obtained when a low heating rate is used with a model-fitting method (multiple linear regression method) based on a reaction order model [15], because these methods do not take into account the complexity of the reaction.

Surface plots

According to our idea that the experimental isothermal domain of temperature is limited by experimental durations, Fig. 5 gives the surface plot of activation energy as a function of extent of conversion and temperature under isothermal conditions for several isothermal simulated data. The temperature was varied from 443 to 493 K, and this corresponds to the practical temperature region. These surfaces plot can directly be obtained by solving Eq. (12), which illustrates the basic idea of isoconversional analysis, i.e. that the reaction rate at a constant conversion depends only on temperature:

$$\frac{\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)_\alpha}{\mathrm{d}T^{-1}}=-\frac{E_\alpha}{R} \qquad (12)$$

These dependences clearly show that in such a case, the activation energy of the low temperature reaction (E_2) is not accessible in the isothermal temperature domain

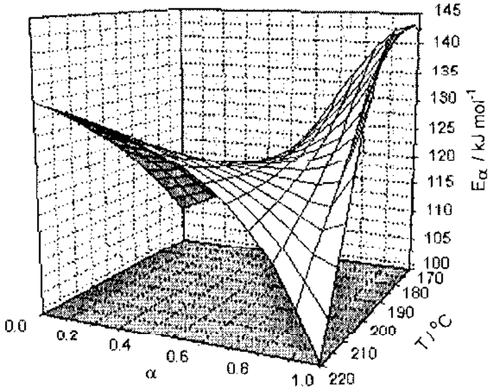

Fig. 5 Surface plot of activation energy as a function of extent of conversion and temperature under isothermal conditions in the case of $Q_1 > Q_2$

experimentally available. If the experimental temperature region cannot be extended to lower or higher temperatures for practical reasons, it is possible, for a mechanism of two parallel independent reactions, to modify the proportions of each reactant.

Conclusions

In the case of the complex process studied, peak maximum evolution methods and model-fitting methods give only a mean value of the kinetic parameters. The variation of the kinetic parameters obtained using the model-fitting methods can be used to show a complex behaviour. Nevertheless, this was not possible using the usual isothermal model-fitting method based on a reaction order rate equation.

Isoconversional methods are useful to describe the complexity of a process. Isothermal and non-isothermal isoconversional methods can be used to elucidate the kinetics of the process. Nevertheless, isothermal and non-isothermal experiments are necessary conducted in different temperature regions, and non-isothermal runs cover a wider temperature range but compress the α range reducing resolution. Hence, isothermal isoconversional methods can be limited by restrictions inherent to isothermal experiments. If the experimental temperature region cannot be extended to lower or higher temperatures for practical reasons, it is possible, for a mechanism of two parallel independent reactions, to modify the proportions of each reactant.

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