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ISOCONVERSIONAL METHODS
Fundamentals, meaning and application

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Abstract

In this paper, fundamentals of the isoconversional methods are summarized and the methods are analyzed from the point of view of their correctness, their applications and the physical meaning of the activation parameters obtained. It is concluded that the activation parameters represent apparent quantities without a mechanistic interpretation. The parameters cannot be used for any theoretical considerations; however, they enable modelling the processes for other temperature regimes than those applied in the measurements. The differential and incremental isoconversional methods give the actual values of activation parameters whereas the isothermal and integral isoconversional methods provide the averaged values. For the modelling, the activation parameters obtained from the treatment of non-transformed kinetic data should be used.

Keywords: isoconversional methods, kinetics, modelling, solid-state processes

Introduction

Solid-state processes are extensively studied by thermal analysis methods. Mechanisms of these processes are very often unknown or too complicated to be characterised 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 and textbooks outlining the basic ideas of the isoconversional methods, analysing the advantages and drawbacks and demonstrating their use, is almost countless, see for example [1, 2]. Despite their wide use, the physical meaning of the activation parameters obtained is not fully clear and it is still a matter of heated debates [3–5].

In this paper, fundamentals of the isoconversional methods are summarised and the methods are analysed from the point of view of their correctness, their applications and the physical meaning of the activation parameters obtained.

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Theoretical

The principal idea of the isoconversional methods is very simple, there are only two basic assumptions:

(*i*) 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 isoconversional methods employ the assumption that the function 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, $f(\ )$, depending solely on the conversion of the process, :

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

Combining Eqs (1) and (2), the rate of the process can then be formally described by a single-step general rate equation [1–3]

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

The function $k(T)$ is usually considered to be the rate constant and $f(\ )$ is considered the conversion function reflecting the mechanism of the process. The main implication of Eq. (3) is that the conversion function $f(\ )$ at a fixed value of holds for any temperature or temperature regime, i.e., the mechanism of the process is solely a function of conversion, it is not a function of temperature.

(*ii*) The activation parameters are obtained from a set of kinetic runs from the dependences of time *vs*. temperature (for isothermal measurements), temperature *vs*. heating rate (for integral and incremental methods with linear heating rate) or from reaction rate *vs*. temperature (for the differential Friedman method). The evaluation is carried out at the fixed conversion .

Isothermal isoconversional method

For isothermal conditions, the rate constant is a constant. After separation of variables, Eq. (3) can be rearranged into the form:

$$\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=k\int_0^{t_\alpha}\mathrm{d}t \tag{4}$$

where t is the time at which the conversion is reached. If we denote the primitive function of the integral at the left side of Eq. (4) as F, one can get:

$$F(\alpha)-F(0)=kt_\alpha\rightarrow t_\alpha=\frac{F(\alpha)-F(0)}{k} \tag{5}$$

The temperature dependence of the rate constant k is usually expressed by the Arrhenius equation

$$k(T)=A\exp\left[-\frac{E}{RT}\right] \tag{6}$$

where A is the preexponential factor, E is the activation energy, T is the absolute temperature and R stands for the gas constant. Combination of Eqs (5) and (6) gives the expression for the time t :

$$t_\alpha=\frac{1}{A_\alpha\exp[-B_\alpha/T]} \tag{7}$$

where the activation parameters A and B are given as:

$$\begin{aligned} A_\alpha&=\frac{A}{F(\alpha)-F(0)} \\ B_\alpha&=E/R \end{aligned} \tag{8}$$

The subscript at A_α, B_α and t_α designates the values related to the fixed value of conversion. Hence, the parameters A and B_α can be obtained from a series of isothermal measurements, even by direct treatment using Eq. (7) or from its logarithmic transformation leading to the linear dependence $\ln t_\alpha=f(1/T)$.

Isoconversional methods at linear heating

Integral methods

For non-isothermal conditions, combination of Eqs (3) and (6) gives:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kf(\alpha)=A\exp\left[-\frac{E}{RT}\right]f(\alpha) \tag{9}$$

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

$$\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}=A\int_0^{t_\alpha}\exp\left[-\frac{E}{RT}\right]\mathrm{d}t \tag{10}$$

Taking into account Eqs (8) and (10) can be rewritten as:

$$1=A_\alpha\int_0^{t_\alpha}\exp\left[-\frac{B_\alpha}{T}\right]\mathrm{d}t \tag{11}$$

Equation (11) should hold for any temperature regime and enables to calculate the time at which the fixed conversion is reached. For the linear heating program, the furnace temperature can be expressed as

$$T_f=T_0+\ t \tag{12}$$

where T_f is the furnace temperature, T_0 is the starting temperature of the measurement and stands for the heating rate. It is mostly assumed that the temperature of the sample, T, equals that of the furnace ($T=T_f$). From Eqs (11) and (12) can thus be obtained [6]:

$$\beta = A_\alpha \int_0^{T_\alpha} \exp\left[-\frac{B_\alpha}{T}\right] \mathrm{d}T \qquad (13)$$

where T is the temperature at which the fixed conversion is reached. The lower integration limit in Eq. (13) is usually set T_0=0 K since there is no process observed to occur in the sample at the starting temperature of the experiment.

The temperature integral at the right side of Eq. (13) cannot be expressed in a closed form. Using the Doyle [7] and Coats–Redfern [8] approximations for the temperature integral in Eq. (13), the Flynn–Wall–Ozawa (FWO) [9, 10] and Kissinger–Akahira–Sunose (KAS) [11] methods, respectively, can be derived. The kinetic parameters are usually obtained from a set of isoconversional temperatures for various heating rates, from the linearized transformation of Eq. (13):

$$\ln\left(\frac{\beta}{T_\alpha^{a}}\right) = f\left(\frac{1}{T_\alpha}\right) \qquad (14)$$

where $a=0$ for FWO method and $a=2$ for KAS method. From Eq. (13) the non-linear isoconversional method [12] can be derived.

Differential method

For the linear temperature program, from Eq. (9) one can obtain

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\alpha = \left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_\alpha = [A_k f(\alpha)]\exp\left[-\frac{E}{RT_\alpha}\right] = A_\alpha \exp\left[-\frac{B_\alpha}{T_\alpha}\right] \qquad (15)$$

The subscript at the reaction rate indicates the rate at the fixed conversion . In Eq. (15), the parameter A is defined as the product $Af($ $)$. Equation (15) is generally used after a logarithmic transformation:

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_\alpha = \ln A_\alpha - \frac{B_\alpha}{T} \qquad (16)$$

From Eq. (16) it follows that the dependence of ln(d /dT)=f(1/T) should be linear. The method represented by Eq. (16) is named after Friedman [13].

Incremental method

Since the Friedman method employs instantaneous rate values, it is very sensitive to experimental noise and tends to be numerically unstable [11, 14]. Using incremental methods can obviate this trouble. An incremental integral isoconversional method has been suggested recently [6]. For the linear heating program, if Eq. (10) is integrated within the conversion increment ${}_1-{}_2$, one can arrive at:

$$\beta=\frac{A}{F(\alpha_2)-F(\alpha_1)}\int_{T_1}^{T_2}\exp\left[-\frac{B_\alpha}{T}\right]\mathrm{d}T=A_\alpha\int_{T_1}^{T_2}\exp\left[-\frac{B_\alpha}{T}\right]\mathrm{d}T \qquad (17)$$

In this case, the definition of the parameter A is obvious from Eq. (17). Due to the integration, the influence of experimental noise is eliminated to a great extent. For an infinitely small increment, Eq. (17) degenerates into Eq. (15) [6]. If it is set $_1$=0 at T_1=0, Eq. (17) degenerates into Eq. (13). From Eq. (17), the incremental isoconversional method to account for variation in the activation energy [14] can be derived.

Discussion

Activation parameters from various isoconversional methods

It is generally understood that the application of isoconversional methods naturally leads to effective activation parameters dependent on the extent of conversion [3, 14, 15].

For the isothermal isoconversional method given by Eq. (7), at the fixed conversion , the system has undergone all the changes in its state over the conversion region <0; >. Thus, if the evaluation of the activation parameters is carried out at the conversion , the resulting values of A and B implicitly involve all the changes occurred in the region. For example, for the simplest case of a linear dependence of activation energy on conversion, the kinetic equation resulting from the combination of Eqs (3) and (6) is:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\exp\left[-\frac{E_0+\Delta E\alpha}{RT}\right]f(\alpha) \qquad (18)$$

where E_0 is the activation energy at the zero conversion and E is the slope of the linear increase of activation energy. For an isothermal process, the kinetic equation Eq. (18) is separable. If the activation energy is obtained from the dependence ln$t$ =f(1/T), it can be simply derived:

$$E=E_0+\frac{\Delta E\alpha\exp[\Delta E\alpha/RT]}{f(\alpha)[F(\alpha)-F(0)]} \qquad (19)$$

As a consequence, the activation energy and, hence, the parameter B , is averaged over the region <0; > in the way given by Eq. (19).

The integral isoconversional methods with linear heating program represented by Eq. (13) also give averaged values of activation energy over the region <0; >. Even for the simplest case of a linear dependence of activation energy on conversion, the kinetic Eq. (18) is not separable [6]. The treatment of experimental data using integral isoconversional methods gives values of activation energy which, obviously, are again averaged over the whole conversion range. However, the way of averaging entirely differs for the isothermal and non-isothermal methods. This is obviously the reason of inconsistency between the activation parameters derived from isothermal and non-isothermal experiments. Besides this, also other reasons can contribute to the inconsistency, such as different temperature regions for conducting isothermal and non-isothermal experiments or the time needed to reach the experimental temperature in isothermal measurements [15]. Since the activation parameters are averaged in both methods, their values cannot reproduce the actual rate of the process at the fixed conversion .

The Friedman method represented by Eqs (15) and (16) should provide actual values of activation parameters, not averaged over a temperature interval. In the case of variable activation energy, their values have to be different from those obtained by isothermal or integral methods. It is a matter of course that the greater variations in actual values of activation parameters, the greater differences should appear.

For a well-balanced length of the conversion increment, the incremental integral isothermal method represented by Eq. (17) should also provide the actual values. An advantage in comparison with the Friedman method is that the values should be free of the effects of experimental noise and baseline. The method represented by Eq. (17) is a reasonable compromise between the stability of calculations and obtaining good estimates of actual activation energies, particularly if the arithmetic mean of the conversion interval is taken as the value at the conversion axis [6].

Mathematical incorrectness of integral isoconversional methods

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. (10) in the derivation of Eq. (13), as it has been mentioned in the previous section. One can easily prove that, even for the case of the simplest linear dependence of activation energy on , the variables in Eq. (18) cannot be separated. Any dependence of the activation energy on the extent of conversion invalidates Eq. (10) which means that all the subsequent formulas are mathematically incorrect. Nonetheless, procedures for the treatment of experimental data using integral isoconversional methods give values of activation energy. The values determined are, obviously, averaged over the whole conversion range and unpredictably skewed by the mathematical incorrectness of the procedure applied.

Another serious source of errors in the integral isoconversional methods resides in the approximations of the temperature integral in Eq. (13). The approximations themselves may lead to an error of the order of percent. Attempts to increase the accuracy of the approximation are noted up to now [16]. However, one should take into consideration that all the approximations are based on the assumption of constant activation energy. Since this is not generally valid for the isoconversional methods, the application of approximations introduces an additional systematic error in the values of activation parameters. The methods expressed by Eq. (14) represented undoubtedly a great progress at the time of their introduction, i.e., in 1960's. Nowadays, I think it would be advisable to decline them since the powerful personal computers make possible to calculate the temperature integral very precisely in no time.

The mathematical incorrectness mentioned above can be overcome, at least partly, by assuming that the activation energy does not vary significantly within a short conversion interval. The incremental integral isoconversional method based on Eq. (17) assume that the function $f(\alpha)$ holds in the conversion interval $<\alpha_1; \alpha_2>$. This is much less severe restriction than that introduced in derivation of Eq. (13) where it is assumed that the function $f(\alpha)$ holds in the whole conversion interval.

Errors in the treatment of experimental data

The treatment of experimental kinetic data should depend on the intention of further employment of the activation parameters obtained. First of all, it is necessary to keep in mind that the experimental data carry random errors. Any transformation of experimental data leads to the deformation of the distribution of errors, heteroskedasticity and a shift in the position of minima of the sum of squares between experimental and calculated values [17]. Thus, the methods using the objective functions with transformed experimental data have to lead principally to biased estimates of activation parameters comparing to the values using directly the source experimental data.

Depending on the temperature regime during measurement, the experimental data are most often treated by using a logarithmic transformation of Eq. (7), using Eq. (14) or using Eq. (16), which is the logarithmic transformation of Eq. (15). If the parameters are to be used just for subsequent qualitative considerations, this approach is justifiable and can be considered correct. Since the activation parameters obtained are biased, their absolute values should not be taken into account, just the tendency towards improvement or deterioration is important. As there is no reason to expect that the bias of different methods has the same sign and magnitude, only the results of the same method should be mutually compared. For example, I do not consider correct to compare the activation parameters obtained from isothermal and non-isothermal isoconversional methods, or from various non-isothermal methods. As an example, the parameters obtained can be used for a qualitative investigation of the influence of an additive on the polymer stability, etc.

An essentially different situation arises if one has an ambition to make quantitative predictions. It is a matter of course that the output results of modelling depend on the quality of input parameters. The input parameters should be correct, free of bias and systematic errors. No inaccuracies associated with analytical approximations of the temperature integral should be introduced. The methods represented by Eqs (7), (13), (15) and (17) do not use any transformation of the experimental data nor the mathematical simplification. The activation parameters are determined directly from the comparison of experimental and calculated values of isoconversional times or temperatures for a set of isothermal kinetic curves or for a set of heating rates by the non-linear least squares method. The activation parameters are determined from the quantities measured directly by thermoanalytical techniques, such as temperature, time, heating rate, reaction rate (DSC) or extent of conversion (TG).

Physical meaning and use of the activation parameters

The most plausible interpretation of activation parameters has emerged from the discussion between Galwey and Vyazovkin [3–5]. It is to emphasise that the term ‘activation energy’ in isoconversional methods differs significantly from its meaning as originally defined and generally accepted in chemical kinetics. The concept of activation energy generally identifies the energy connected with the barrier to the bond redistribution process for the rate-determining step in a single reaction [5].

When employing the isoconversional methods, a complex multi-step process is treated as a single-step one. The activation energy obtained is thus apparent and does not have any mechanistic significance. There is no reason to interpret the effective activation energy in terms of a free energy barrier [4]. Kinetic studies frequently appear to be motivated in reporting magnitudes of the activation parameters. In some articles, the magnitude of activation energy reported appears to be the principal result, perhaps even the dominant motivation for the investigation. However, compelling reasons for such a preoccupation with the measurements of activation parameters are not usually provided [3]. The value of activation energy cannot be used for far-reaching conclusions frequently encountered in academic environment, such as systematisation of the information available, developing theories on the mechanisms of the processes, etc.

For practitioners, the values of the apparent activation parameters enable to model the process without a deeper insight into its mechanism. In my opinion, this is the principal merit of the isoconversional methods. As it follows from the discussion above, the differential method represented by Eq. (15) and the incremental integral method represented by Eq. (17) provide the actual values of the parameters. In both methods, the parameter A is equal to the product $Af($ $)$. From the combination of Eqs (3) and (6) it then follows:

$$\alpha=\int_0^t A_\alpha \exp\left[-\frac{B_\alpha}{T}\right]\mathrm{d}t \qquad (20)$$

In order to integrate Eq. (20), both parameters A and B are needed. Temperature can be an arbitrary function of time. Equation (20) can be used to evaluate either the conversion reached at a given time t, or the time at which a given conversion is reached. Using Eq. (15), the actual reaction rate at the conversion   can be evaluated.

The isothermal method represented by Eq. (7) can be used to calculate the temperature, at which the time t is reached or vice-versa. The integral isoconversional method represented by Eq. (11) enables to evaluate the time at which the conversion   is reached. In both cases, the value of conversion is fixed. The parameters A and B are averaged over the region <0; >. The way of averaging is different in both cases so that the parameters obtained by the isothermal and integral methods may be different. Hence, for modelling the isothermal processes, the parameters obtained from isothermal experiments should be used. For modelling the non-isothermal processes, one should employ the parameters obtained from non-isothermal experiments, i.e., the experiments with linear heating program. The activation parameters should depend not only on , but also on temperature. Thus, the results obtained by modelling the processes for the temperature region far from the region explored experimentally, may not be trustworthy.

For the same process, the activation parameters obtained by various thermoanalytical methods may be different. In DSC, the conversion is calculated from the heat released/absorbed by the sample. In TG, the conversion is obtained from the sample mass loss. One can imagine that processes exist where the conversion curves determined by the both methods are not identical and, subsequently, the activation parameters obtained differ as well. Thus, for modelling the heat released/absorbed by the sample, the activation parameters obtained from DSC measurements should be used. Analogically, the TG activation parameters should be used for modelling the sample mass loss.

Conclusions

The isoconversional methods are often used to describe the kinetics of the solid-state processes. The activation parameters, i.e. the activation energy and preexponential factors, are the apparent quantities without a mechanistic interpretation. In fact, they are only adjustable parameters in the fitting temperature function $k(T)$ of Eq. (3). The temperature function generally employed is the Arrhenius equation given by Eq. (6). It would be perhaps advisable to test the use of other fitting functions for the temperature function $k(T)$. The two of the functions summarised in [18] seem to be highly suitable:

$$k(T)=AT^{\mathrm{m}} \tag{21}$$

$$k(T)=A\mathrm{e}^{\mathrm{Dt}} \tag{22}$$

where A, m and D are adjustable parameters. When using the functions given by Eqs (21) and (22), the problems with calculating the temperature integral in Eqs (13) and (17) would be eliminated since the corresponding integrals could be expressed in a closed form.

The model-free isoconversional methods represent a feasible way to treat the experimental condensed-phase kinetic data. The activation parameters obtained enable modelling the processes for other temperature regimes than those applied in the measurements. The large advantage of the model-free analysis is founded in its simplicity and the avoidance of the errors connected with the selection of a kinetic model. The differential and incremental isoconversional methods give the actual values of activation parameters. The isothermal and integral isoconversional methods provide the averaged values and this should be taken in mind when modelling the processes. For the modelling, the parameters obtained from the treatment of non-transformed kinetic data should be used. The parameters obtained from the transformed logarithmic relationships can be used as starting parameters for the non-linear least squares method, similarly as in our previous papers [19–22].

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References

1 J. Šesták, Measurement of thermophysical properties of solids. Theoretical thermal analysis. Academia, Prague 1982 (in Czech).
2 M. E. Brown, D. Dollimore and A. K. Galwey, Comprehensive chemical kinetics, Vol. 22. Elsevier, Amsterdam 1980.
3 S. Vyazovkin, Int. Revs. Phys. Chem., 19 (2000) 45.
4 A. K. Galwey, Thermochim. Acta, 397 (2003) 249.
5 S. Vyazovkin, Thermochim. Acta, 397 (2003) 269.
6 P. Šimon, P. S. Thomas, J. Okuliar and A. Ray, J. Therm. Anal. Cal., 72 (2003) 867.
7 C. D. Doyle, J. Appl. Polym. Sci., 6 (1962) 639.
8 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
9 J. H. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 323.
10 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
11 N. Sbirazzuoli, Y. Girault and L. Elégant, Thermochim. Acta, 293 (1997) 25.
12 S. Vyazovkin and D. Dollimore, J. Chem. Inf. Comp. Sci., 36 (1996) 42.
13 H. L. Friedman, J. Polym. Sci., 6C (1965) 183.
14 S. Vyazovkin, J. Comput. Chem., 22 (2001) 178.
15 S. Vyazovkin and C. A. Wight, Ann. Rev. Phys. Chem., 48 (1997) 125.
16 T. Wanjun, L. Yuwen, Z. Hen, W. Zhiyong and W. Cunxin, J. Therm. Anal. Cal., 74 (2003) 309.
17 M. Meloun and J. Militký, Statistical treatment of experimental data, Edition Plus, Prague 1994 (in Czech).
18 K. J. Laidler, J. Chem. Educ., 61 (1984) 494.
19 P. Šimon and A. Kučma, J. Therm. Anal. Cal., 56 (1999) 1107.
20 P. Šimon, L. Kolman, I. Niklová and Š. Schmidt, J. Amer. Oil Chem. Soc., 77 (2000) 639.
21 P. Šimon and L. Kolman, J. Therm. Anal. Cal., 64 (2001) 813.
22 P. S. Thomas, P. Šimon and A. Ray, J. Therm. Anal. Cal., 72 (2003) 801.