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AN INCREMENTAL INTEGRAL ISOCONVERSIONAL METHOD
Determination of activation parameters

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Abstract

An incremental integral isoconversional method for the determination of activation energy as a function of the extent of conversion is presented. The method is based on the treatment of experimental data without their transformation so that the resulting values of activation parameters should not be biased. The method was tested for recovering the activation energies from simulated data and employed for the treatment of experimental data of the NiS recrystallisation.

Keywords: activation parameters, integral isoconversional method, NiS recrystallisation

Introduction

Integral isoconversional methods for the treatment of kinetic data are widely used in the determination of activation energies. The basic idea of these methods is that the kinetics of the process occurring in the system can be described by the general rate equation.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kf(\alpha) \tag{1}$$

where α is the extent of conversion and $f(\alpha)$ is the conversion function reflecting the mechanism of the process. The temperature dependence of the rate constant k is usually taken to follow an Arrhenius-type dependence:

$$k=A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where A is the preexponential factor, E is the activation energy, T is the absolute temperature and R stands for the gas constant.

For the linear increase of temperature in DSC measurements, the furnace temperature can be expressed as

$$T_\mathrm{f}=T_0+\beta t \tag{3}$$

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where T_f is the furnace temperature, T_0 is the starting temperature of the measurement and β stands for the heating rate. If it is assumed that the temperature of the sample equals that of the furnace ($T=T_f$), combination of Eqs (1)–(3) gives:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{4}$$

Since the reaction rate at the starting temperature is negligible, the starting temperature can be set as T=0 K. The variables can then be separated and Eq. (4) can be integrated:

$$\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^{\mathrm{T}}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{5}$$

Integration of Eq. (4) makes the implicit assumption that the function $f(\alpha)$ holds throughout the reaction process and is independent of temperature and heating rate. Integration of the left side of Eq. (5) results in:

$$F(\alpha)-F(0)=\frac{A}{\beta}\int_0^{\mathrm{T}}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{6}$$

where $F(\alpha)$ is the primitive function of $1/f(\alpha)$. Rearrangement of Eq. (6) yields:

$$\beta=\frac{A}{F(\alpha)-F(0)}\int_0^{\mathrm{T}}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{7}$$

Equation (7) represents the general equation for the development of the conventional integral isoconversional methods of kinetic analysis. Using the Doyle [1] and Coats–Redfern [2] approximations for the temperature integral in Eq. (7), the Flynn–Wall–Ozawa (FWO) [3, 4] and Kissinger–Akahira–Sunose (KAS) [5] methods, respectively, can be derived. Equation (7) is also the basis for the non-linear isoconversional method [6].

The limitations of conventional integral isoconversional methods lie in the assumption that a single set of activation parameters and a unique function of α describe the whole conversion range of the process. This assumption results in averaged activation energies from the kinetic analysis. This paper attempts to address this issue by the development of an incremental integral isoconversional method of kinetic analysis that will yield actual values of the activation energies at discreet extents of conversion.

Theoretical part

Assumption of a constant value of activation energy is implicit and inevitable for the separation of the variables of Eq. (4) in the derivation of Eq. (5). On the other hand, the application of isoconversional methods naturally leads to effective activation parameters dependent on the extent of conversion [7, 8]. One can easily see that, even for the case of the simplest linear dependence of activation energy on α, the variables in Eq. (4) cannot be separated. Any dependence of the activation energy on the extent of conversion invalidates Eq. (5) 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 distorted by the mathematical incorrectness of the procedure applied.

The mathematical incorrectness can be overcome, at least partly, by assuming that the activation energy does not vary significantly within a short conversion interval. Using this approximation, Eq. (4) leads to the result

$$\beta=\frac{A}{F(\alpha_2)-F(\alpha_1)}\int\limits_{T_1}^{T_2}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{8}$$

where T_1 and T_2 are the temperatures at which the extents of conversion α_1 and α_2 are reached. Equation (8) enables an averaged value of activation energy, in the conversion increment α_1–α_2 from the treatment of a series of runs with linear heating rates, to be obtained. For the sake of simplicity, Eq. (8) can be rewritten as:

$$\beta=A_\alpha\int\limits_{T_1}^{T_2}\exp\left(-\frac{B_\alpha}{T}\right)\mathrm{d}T \tag{9}$$

where the parameters A_α and B_α are functions of the extent of conversion and may be defined as:

$$\begin{aligned} A_\alpha&=\frac{A}{F(\alpha_2)-F(\alpha_1)}\\ B_\alpha&=\frac{E}{R}\end{aligned} \tag{10}$$

In this paper Eq. (9) was applied to a simulated data set with two sets of activation parameters, and the experimental data acquired for the recrystallisation of nickel sulphide. The method developed was also compared to the conventional non-incremental isoconversional method in the determination of the activation energy.

Experimental

The material used was high purity nickel(II) sulphide powder (99.95%, 100 μm particle size) supplied by Johnson Matthey GmbH. The sample of NiS was conditioned in the sample holder of the DSC calorimeter by a procedure similar to that described in [9].

For the study of NiS recrystallisation, the differential scanning calorimeter Perkin Elmer DSC-7 with the Pyris software was employed. The temperature scale was calibrated using the standards In, Sn and Zn. The enthalpic scale was calibrated to the enthalpy of In fusion. The sample of NiS was placed in a crimped standard aluminum pan. The purge gas was nitrogen.

Results and discussion

For the determination of the parameters A_α and B_α in Eq. (8), a FORTRAN-77 program was written. The parameters were obtained by minimizing the sum of squares between experimental and theoretical values of isoconversional temperatures for various heating rates by the simplex method [10]. In order to avoid inaccuracies associated with analytical approximations of the temperature integral, the integration indicated in Eq. (9) is carried out using the Simpson rule. The program was used for the treatment of kinetic curves using the conditions described by both Eqs (7) and (8) as Eq. (7) is only a special case of Eq. (8) where $T_1=0$.

The clearest test of a method for kinetic analysis is its ability to recover the activation parameters from a simulated data set for which the input parameters are known exactly. The conversion-temperature data of a hypothetical first-order reaction with two activation energies and two preexponential factors were, therefore, initially treated using the dependence of the activation energy and preexponential factor on α given by:

$$\begin{gathered} E=E_1(1-\alpha)+E_2\alpha \\ \mathrm{A}=\mathrm{A}_1^{1-\alpha}A_2^{\alpha} \end{gathered} \tag{11}$$

The values of activation energies were taken to be $E_1=80$ kJ mol^{-1} and $E_2=120$ kJ mol^{-1}, the values of preexponential factors were $A_1=10^8$ min^{-1} and $A_2=10^{13}$ min^{-1}. The conversion-temperature curves for individual heating rates were obtained by integrating Eq. (4) using the fourth-order Runge–Kutta method, where $f(\alpha)=1-\alpha$. The recovery of activation energy from the simulated kinetic curves is illustrated in Fig. 1. It can be seen that the conventional non-incremental integral isoconversional method, represented by Eq. (7), gives the dependence much different from that defined by the conditions of Eq. (11). For the method represented by Eq. (8), the width of the conversion increment was chosen as $\alpha_2-\alpha_1=0.1$. Figure 1 shows that the calculated dependence is much more similar to the input data. In this case, the extent of conversion is taken as the higher limit, α_2. If the extent of conver-

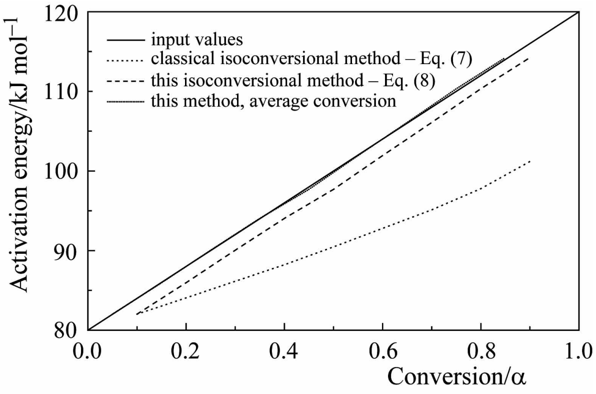

Fig. 1 Dependence of the activation energy on the extent of conversion for the simulated data

sion is taken as the arithmetic mean of α_1 and α_2, the recovered dependence is identical to the input data.

The method was also applied to experimental data measured for the recrystallisation of NiS. NiS behaves quite strangely and the number of recrystallisation peaks depends also on the heating rate [11]. In the range of heating rates 2.5–15 K $\min^{-1}$, the curves show one recrystallisation peak. The kinetic curves for the recrystallisation step are shown in Fig. 2. The curves were treated by both the integral isoconversional methods represented by Eqs (7) and (8). In the case of Eq. (8), the width of the conversion increment was again chosen to be $\alpha_2-\alpha_1=0.1$. As it can be seen in Fig. 3, the dependence of the activation energy on α resulting from the method of Eq. (8), exhibits a maximum at about $\alpha=0.4$. At about $\alpha=0.8$ a steep decrease in activation energy is observed. The conventional non-incremental integral isoconversional method (Eq. (7)) gives a flattened dependence with a maximum at $\alpha=0.7$. The relatively smooth shift in the calculated activation energy is consistent with the averaging of processes as the extent of conversion is increased. The activation energy calculated using Eq. (8), showed a much stronger dependence of the activation energy on the extent of conversion. The sharp decline in the activa-

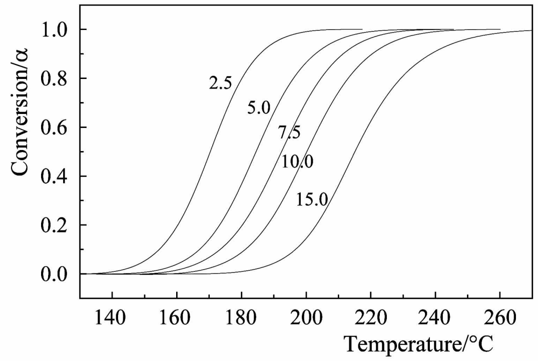

Fig. 2 Experimental kinetic curves of the recrystallisation of NiS. The numbers at the curves indicate the heating rates

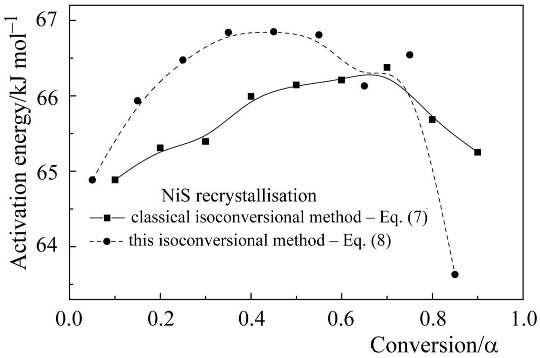

Fig. 3 Dependence of the activation energy on the extent of conversion for the recrystallisation of NiS

tion energy above α=0.8 is averaged out in the non-incremental method of Eq. (7). Given that Eq. (8) produced a more accurate description of the simulated data, it is likely that the values of the activation energy determined for the recrystallisation data are more robust than those using the averaging method of Eq. (7). Equation (7) represents a similar procedure than described earlier for the integral isoconversional method applied to the study of processes exhibiting the induction period [9, 12–14].

As has been mentioned above, from Eq. (7) other methods (KAS, FWO, non-linear, etc.) can be derived. Since these methods are based on the mathematical treatment of the same idea, the resulting activation energies should be of the same quality; for simulated kinetic curves free of random errors, they should even provide identical results. However, it is generally known that the application of a variety of methods to the analysis of a single set of experimental data provides different dependences of activation energy, as it has been very clearly demonstrated in [15]. Apart from the inaccuracies associated with analytical approximations of the temperature integral, to our meaning, this could be elucidated by the use of different objective functions in the treatment of experimental data. The method represented by Eq. (7) does 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 temperatures 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). The other methods use transformations such as $\ln\beta=f(1/T)$, $\ln(\beta/T^2)=f(1/T)$, or find a minimum of the function specifically constructed for eliminating the preexponential factor. Any transformation of experimental data leads to the deformation of the distribution of errors and a shift in the position of minima of the sum of squares between the experimental and calculated values [16]. Thus, the methods using the objective functions with transformed experimental data have to lead to biased values of activation parameters comparing to the values using directly the experimental data.

We are not the first ones introducing the idea of incremental isoconversional method. An incremental integral isoconversional method to account for variation in the activation energy has been recently published by Vyazovkin [7]. He obtains the activation energy by the minimization of the function Φ, which is in fact the sum of ratios of temperature integrals. The main differences between the method presented here and that published in [7] is that we use directly Eq. (9) without any transformation of experimental data and that we use the least-square method for obtaining the values of activation parameters. The minimization of the function Φ used in [7] corresponds to a different objective function in the treatment of experimental data than employed in this paper. Thus, the method [7] supposedly should give the values of activation energy different from ours.

The methods based on Eq. (8) assume that the function $f(\alpha)$ holds within the conversion increment $<\alpha_1;\alpha_2>$. This is much less severe restriction that introduced in derivation of Eq. (7) where it is assumed that the function $f(\alpha)$ holds in the whole conversion interval. For an infinitely short interval α_1 and α_2, Eq. (8) degenerates back to

Eq. (4). Equation (4) should provide true values of activation energies, not averaged over a temperature interval. However, the differential isoconversional methods represented by Eq. (4) are very sensitive to noise and tend to be unstable [5, 7] and also may yield the effective activation energy which deviates largely from that of the individual reactions [17]. The method represented by Eq. (8) is a reasonable compromise between the stability of calculations and obtaining good values of activation energies, particularly if the arithmetic mean of the conversion interval is taken as the value at the conversion axis (Fig. 1). Optimization of the width of the conversion interval used in the determination of the activation energy has not been attempted here, but is important and will have to be tested in future. It should also be tested how the method indicates a sudden jump in activation energy.

The parameters A_α and B_α, occurring in Eq. (9), can be used either for subsequent theoretical considerations or for modeling the kinetics of the process under study. As for the modeling, for a sufficiently short conversion increment, the parameter A_α is approximately equal to the product $Af(\alpha)$. From the combinations of Eqs (1) and (2) it then follows:

$$\alpha = \int_0^t A_\alpha \exp\left(-\frac{B_\alpha}{T}\right)\mathrm{d}t \qquad (12)$$

In order to integrate Eq. (12), both parameters A_α and E_α are needed. Temperature can be an arbitrary function of time. It is a matter of course that the reliability of the results of modeling depends on the reliability of the parameters A_α and B_α. As it is stated above, the incremental integral isoconversional method proposed here should provide reliable parameters. The reliable parameters free of systematic errors are particularly important when extrapolation of the results outside the measured temperature range is carried out.

A DOS version of the program KINPAR for the calculation of the parameters A_α and B_α in Eq. (8) is available on request.

Conclusions

This paper has presented an incremental integral isoconversional method for the determination of the activation energy as a function of the extent of conversion. The method is based on the treatment of experimental data without their transformation so that the resulting values of activation parameters should not be biased. As the method calculates the activation energy from the incremental differences in the extent of conversion, the resulting values of the activation energy are more representative for the processes that are occurring in the system under study.

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