Practical application of isoconversional methods

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Abstract

The new possibilities offered by isoconversional methods as applied to the solution of practical kinetic problems are considered. These problems have been solved by algorithms based on the transformation-degree dependence of the activation energy calculated by the isoconversional method. The distinctive feature of these algorithms is their ability to take into consideration the potential complexity of the process when solving applied problems.

This year we celebrate the seventieth birthday of Dr. J.H. Flynn whose name is closely associated with isoconversional methods [1] of Arrhenius parameters calculation. We are convinced that the potential of these methods will soon be realised — 25 years after they were first described. The reasons for our opinion are discussed below.

Firstly, isoconversional methods are non-discriminatory, i.e. they allow the calculation of both the effective activation energy (E) and the pre-exponent (A) [2] from the equation

$$dw/dT = A \exp(-E/RT)f(w)/q \tag{1}$$

where w is the transformation degree, T the temperature, q the heating rate and R the gas constant, without having to choose the process model, $f(w)$. The results of recent investigations [3–6] show clearly that reliable kinetic information can be extracted from thermoanalytical data by non-discriminatory methods alone.

Secondly, isoconversional methods provide kinetic information about complex processes which are most widespread but least explored. Reference 7 suggests an approach based on the analysis of the transformation-degree dependence of the activation energy calculated by the isoconversional method. This approach can establish if the process under investiga-

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

tion is simple or complex and can suggest its kinetic scheme. Interpretable kinetic schemes of the thermolysis of tetrazole [8] and its polymeric derivatives [9] have been designed with the help of this approach. We realise that the kinetic scheme of the process does not completely describe its mechanism; but it is, perhaps, the most sensitive indicator of the mechanism that can be derived from common thermoanalytical data (TG, DSC, DTA, etc.).

Despite the attraction of obtaining information on the process mechanism, the possible results obtainable from isoconversional methods seem to be more valuable from a practical viewpoint. They are associated with the prediction of the behaviour of the substance under investigation outside the experimental temperature range. Such applied problems cannot be solved by discrimination methods because of the significant errors [10,11] in calculating the Arrhenius parameters caused by the ambiguity in the choice of the process model. In addition, discrimination methods do not take into account the possible complexity of the process under investigation during the calculation. Our paper will review the algorithms of the solutions of applied kinetic problems which do take into consideration the possible complexity of the process, using the transformation-degree dependence of the activation energy calculated by the isoconversional method.

The efficiency of the algorithms considered will be shown by kinetic processing of the model DSC curves for the complex process including two parallel independent first-order reactions with the following activation energy and pre-exponent values: $E_1 = 125.4$ kJ mol^{-1}, $E_2 = 167.2$ kJ mol^{-1} and $A_1 = 10^{14}$ min^{-1}, $A_2 = 10^{18}$ min^{-1}. Figure 1 presents the DSC curves modelled for the three heating rates, 8, 12 and 16°C min^{-1}. Kinetic curves (dependence of w on T) for the calculation were obtained by numerical integration of DSC curves. Figure 2 shows the transformation-degree dependence of the activation energy calculated by the isoconversional method for this complex process.

Prediction of sample behaviour in non-isothermal conditions

Proceeding from the fact that the kinetic equation of the non-isothermal process is representable by $w = w(T, q)$, three types of dependences between the equation parameters can be obtained: w on T with q constant; T on q with w = constant; and w on q, with T = constant. The algorithms presented below for calculating these dependences are based on the assumption that the Arrhenius parameters and the mechanism of a process do not change when the heating rate varies.

To obtain the first of the above dependences, eqn. (1) can be expressed in an integral form

$$g(w) = (A/q)\int_0^T \exp(-E/RT)\, \mathrm{d}T = (A/q)\mathrm{I}(T) \tag{2}$$
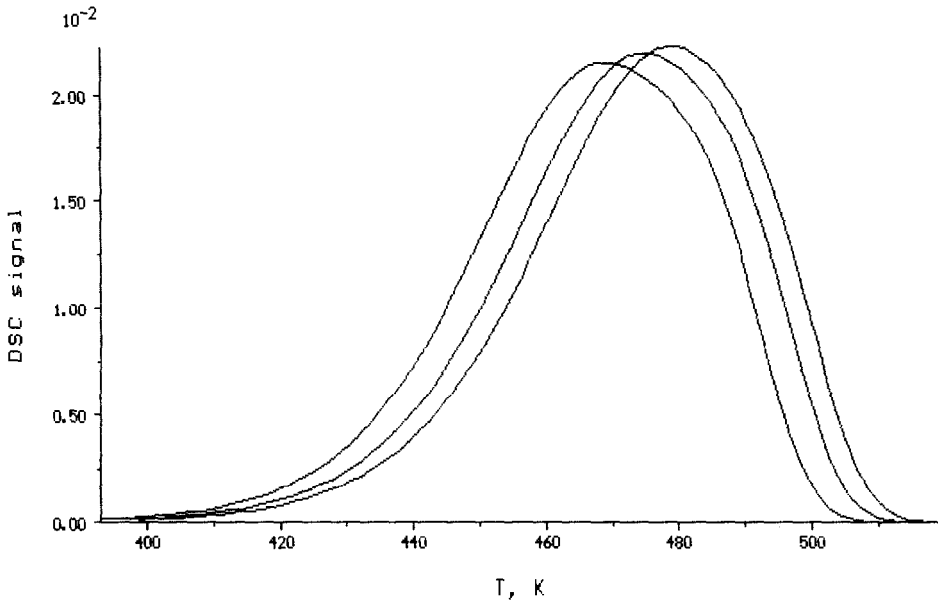
Fig. 1. The model DSC curves for the complex process involving parallel independent reaction at heating rates of 8, 12 and 16°C min^{-1}.

where $g(w)$ is the integral form of the process model and $I(T)$ is the temperature integral. By virtue of the original assumption that the mechanism remains unchanged, the quantity $g(w)$ will be the same for equal
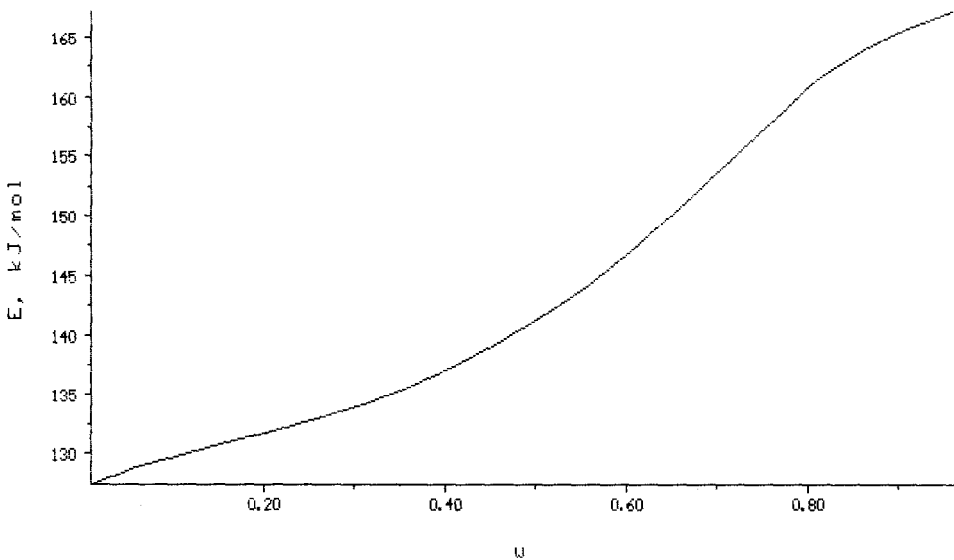

Fig. 2. The transformation-degree dependence of the activation energy calculated by the isoconversional method for the model process.
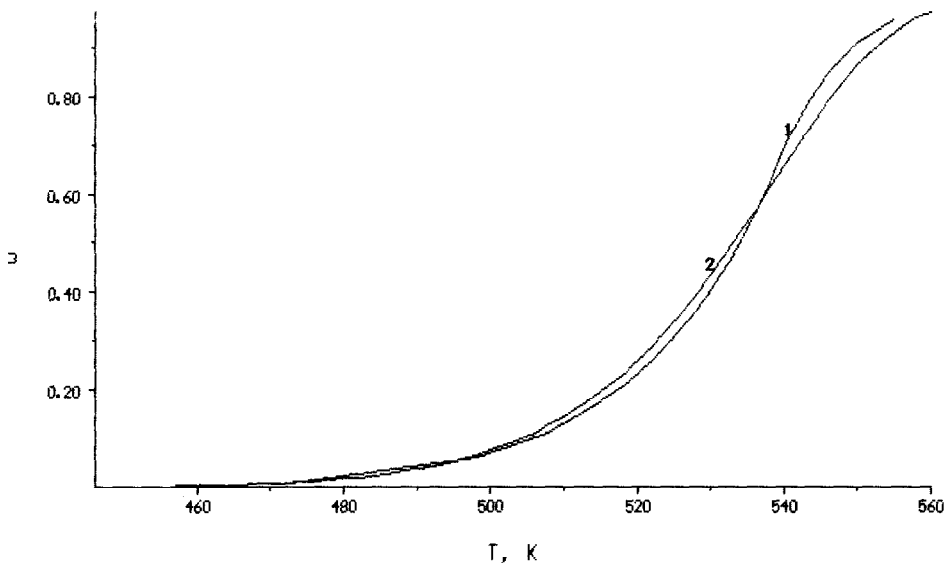
Fig. 3. The non-isothermal kinetic curve plotted by our algorithm (1) and the model curve (2) for the complex process at a heating rate of 1000°C min⁻¹.

transformation degrees (w) reached at different heating rates. We can therefore equate the right-hand parts of eqn. (2) which correspond to different heating rates, thus eliminating the A values

$$I(Tx)/q_x - I(T_0)/q_0 = 0 \qquad (3)$$

A numerical solution of eqn. (3) makes it possible, at a given heating rate q_x, to find the temperature T_x corresponding to the transformation degree that was reached in the non-isothermal experiment (at the heating rate q_0) at temperature T_0. The entire kinetic curve for the desired heating rate q_x can be obtained by solving eqn. (3) for different transformation degrees. Figure 3 shows the kinetic curve plotted by the above algorithm in comparison with the model curve for the process under consideration at the heating rate of 1000°C min⁻¹.

To calculate the second dependence, the dependence of the temperature at which the given transformation degree is reached on the heating rate, one can vary the quantity q_x in eqn. (3). The second term of the difference in eqn. (3) will therefore be constant because the transformation degree and, consequently, the activation energy remain unaltered; the dependence calculated for the complex process considered here is given in Fig. 4. Attention is drawn to the fact that the dependence of T on q_x reveals saturation with increasing heating rate, which can probably be used to estimate the limiting temperatures of the decomposition of materials [12]. Furthermore, using such a dependence, one can solve applied problems
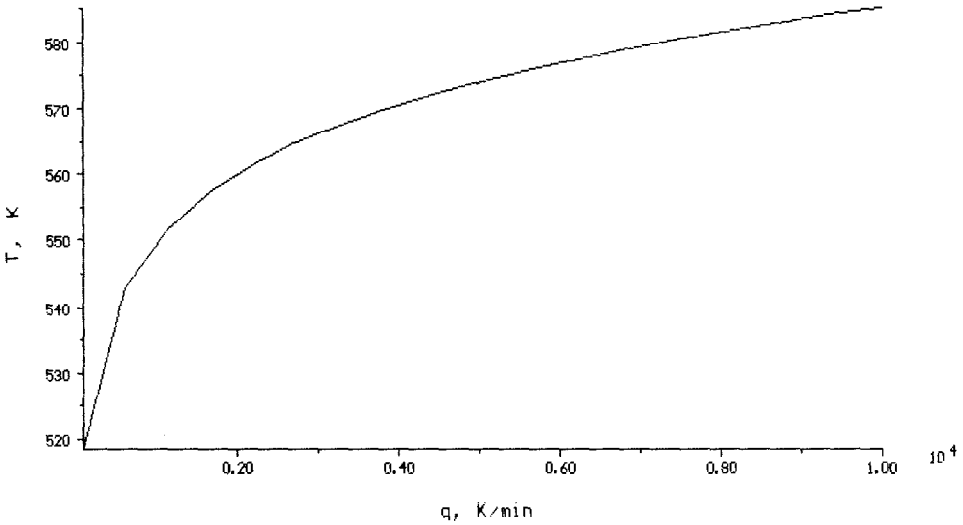
Fig. 4. The dependence of the temperature at which 90% transformation degree is reached on the heating rate for the model process.

connected with the evaluation of thermostability of materials in non-isothermal conditions, for example, on burning.

Of no less practical interest is the third dependence: the calculation of the dependence of the transformation degree reached at a given temperature on the heating rate. If for the material being investigated the critical temperature (the temperature of phase transition, ignition, explosion, etc.) is known, then using the dependence of w on q_x, the intervals of heating rates at which complete or partial transformation of the material will occur, before or after the critical temperature, can be estimated. Calculation of this dependence is carried out by the equation

$$q_x = q_0 I(T_x)/I(T_0) \tag{4}$$

by substituting into it the critical temperature value, T_x, and subsequently changing the values of T_0 and activation energy in accordance with the change in the transformation degree. The dependence of w on q_x calculated by the above algorithm for the complex model process under consideration, is given in Fig. 5.

Prediction of sample behaviour in isothermal conditions

In accordance with the form of the kinetic equation for the isothermal process, $w = w(t, T)$, one can obtain three types of kinetic dependence between its parameters: w on t with T constant; t on T with w constant; and w on T with t constant. The algorithms considered below to plot these
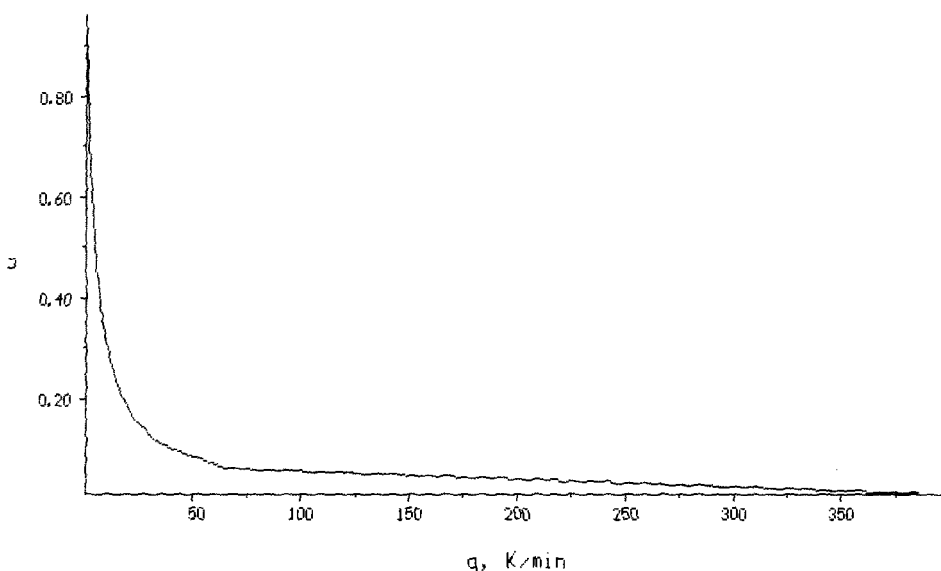
Fig. 5. The dependence of the transformation degree reached at $T = 460$ K on the heating rate for the model process.

dependences are based on the assumption that the Arrhenius parameters and mechanism of a process do not change with varying temperature.

To obtain the first of the above dependences, a method that we have proposed will be used [13]. By virtue of the assumption made, one can easily obtain the following expression

$$t = I(T_0) / [q_0 \exp(-E/RT_{iso})] \qquad (5)$$

Equation (5) makes it possible, for a given temperature T_{iso} of the isothermal experiment, to calculate the value of the time t corresponding to the transformation degree w, which is reached in the non-isothermal experiment at temperature T_0 and heating rate q_0. The isothermal kinetic curve, in accordance with eqn. (5), is obtained by varying the quantity T_0. To transform non-isothermal data by this algorithm, one should substitute into eqn. (5) the activation energy values that correspond to the transformation degree for which the calculation of t is carried out. Figure 6 shows the isothermal kinetic curve plotted by the above algorithm in comparison with the model curve for the above-mentioned process at $T_{iso} = 400$ K.

The second dependence, the dependence of the time at which a given transformation degree is reached on the temperature of the isothermal experiment, is obtained by substituting into eqn. (5) the values of T_0 and activation energy corresponding to the given transformation degree, and subsequently varying the value of T_{iso}. This dependence for the complex
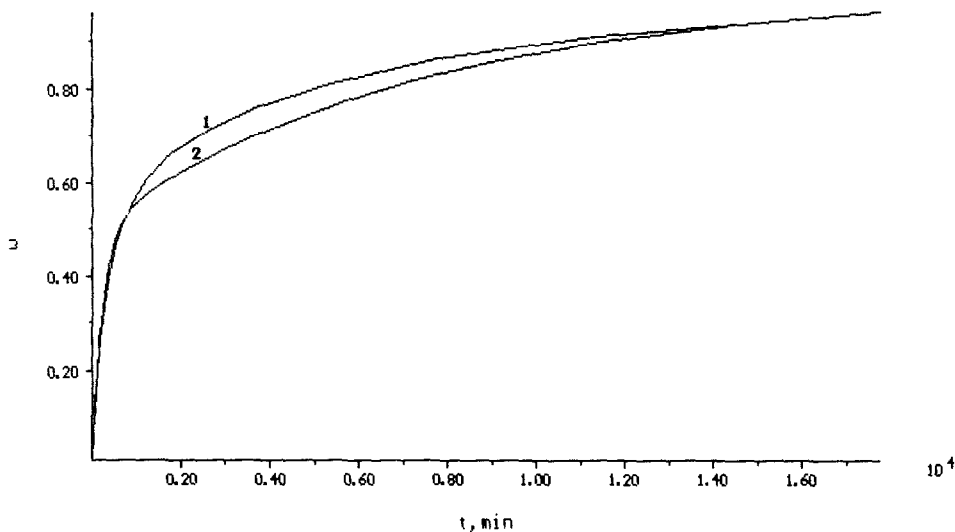
Fig. 6. The isothermal kinetic curve plotted by our algorithm (1) and the model curve (2) for the model process at $T_{iso} = 400$ K.

process under consideration is given in Fig. 7. Using such a dependence, it is easy to estimate the time required for full or partial completion of the process or the life-time of a substance.
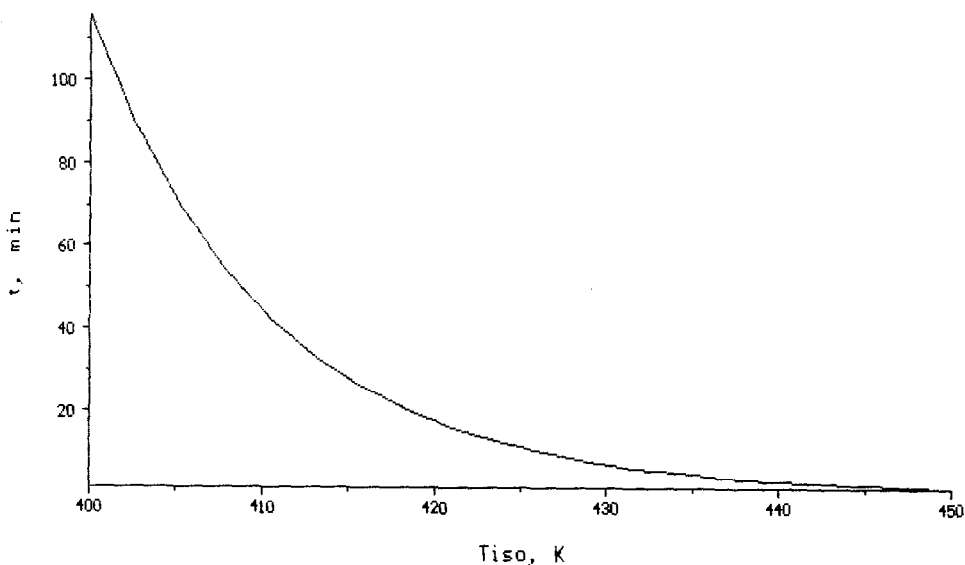

Fig. 7. The dependence of the time at which 20% transformation degree is reached on the temperature of isothermal experiment for the model process.
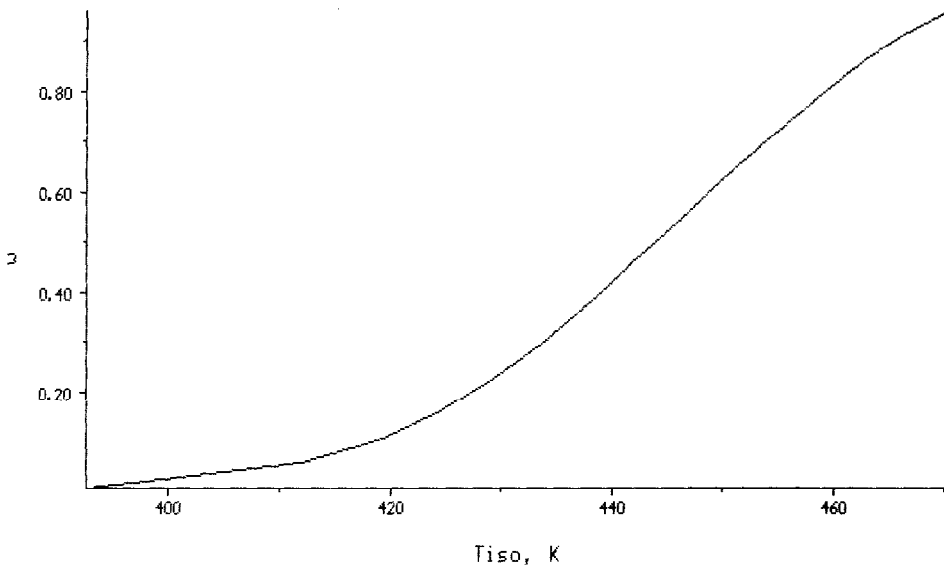
Fig. 8. The dependence of the transformation degree which is reached at $t = 10$ min on the temperature of isothermal experiment for the model process.

Transforming eqn. (5) to the form

$$T_{iso} = E / \{ R \ln[tq_0 / I(T_0)] \} \tag{6}$$

and varying in it the values of T_0 and activation energy in accordance with the value of the transformation degree, we can calculate the third dependence, that of the transformation degree reached at a given value of time t on the temperature of the isothermal experiment. The dependence of w on T_{iso} calculated for the model process is given in Fig. 8. Such dependences allow the solution of applied kinetic problems connected with selecting the temperature regime of storing or of using materials for which some critical time values are known.

All the algorithms described in this paper form the basis of the KINTOOL software developed by S. Vyazovkin and V. Goryachko.

CONCLUSION

At the beginning of this paper, we mentioned two reasons for our confidence in the future of isoconversional methods, i.e. the possibility of calculating reliable Arrhenius parameters values and the possibility of obtaining kinetic information about complex processes. The above algorithms offer a further possibility from isoconversional methods, that of considering the potential complexity of the process when solving applied kinetic problems. It is appropriate that the potential offered by isoconver-

sional methods be recognised on the occasion of the anniversary of Dr. J.H. Flynn, who is rightly considered one of the authors of these methods.

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