CRITICAL STUDY OF THE ISOCONVERSIONAL METHODS OF KINETIC ANALYSIS

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A critical study of the use of isoconversional methods for the kinetic analysis of non-isothermal data corresponding to processes with either a real or an apparent variation of the activation energy, E, with the reacted fraction, α, has been carried out using for the first time simulated curves. It has been shown that the activation energies obtained from model-free methods are independent of the heating rate. However, the activation energy shows a very strong dependence of the range of heating rates used for simulating the curves if the apparent change of E with α is caused by overlapping processes with different individual activation energies. This criterion perhaps could be used for determining if a real dependence between E and α is really occurring.

Keywords: *isoconversional methods, kinetics, variable activation energy*

Introduction

The non-isothermal methods are the most commonly used for performing the kinetic analysis of solid state reactions. A number of papers on this topic have been recently published in this Journal [1–9]. These methods were originally developed by assuming a 'n-order' kinetic models. We have carried out a great effort [10–30] in generalizing the non-isothermal methods for being used for all the kinetic models describing solid state reactions. It must be pointed out that all the methods proposed have been developed by assuming that both the activation energy and the kinetic model do not change along the process. However, many authors [31–47] have concluded from model-free kinetic methods of analysis that the activation energy is a function of the reacted fraction. The Friedman [48] and the Ozawa [49] isoconversional methods have been the most generally used for determining the activation energy as a function of the reacted fraction without any previous assumption on the kinetic model fitted by the reaction. The use of the Ozawa method has been strongly criticised because this equation was developed by integrating the Arrhenius equation by assuming that neither the activation energy nor the kinetic model change all over the reaction, suggesting that reliable values of the activation energy would be obtained only if the activation energy remains constant. Vyazovkin [37] has developed an iterative method for overcoming this problem. However, it must be pointed out that a theoretical analysis of the influence of the variation of the

activation energy along the process on the α–T plots and the errors in the determination of the activation energies from isoconversional methods is still missing. This is the scope of the present work.

Theoretical

The rate of a solid-state reaction can be written in the form:

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha) \qquad (1)$$

where A is the preexponential factor of Arrhenius, E is the activation energy, T is the absolute temperature, R is the gas constant and $f(\alpha)$ is a function of the reacted fraction, α, that depends on the reaction model.

If the reaction is studied under non-isothermal conditions at a linear heating rate $\beta = dT/dt$, Eq. (1) becomes:

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

Integration of Eq. (2), after replacing E/RT by x and rearranging, leads to

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{AE}{\beta R} p(x) \qquad (3)$$

where $p(x)$ is a function known as the Arrhenius integral that has not analytical solution, but can be resolved either by numerical methods or by using different approx-

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imations. If we use the Doyle's approximation [50] for $p(x)$ we get from Eq. (3) the popular equation proposed by Ozawa for determining the activation energy by isoconversional methods:

$$\ln \beta = \ln \frac{AE}{g(\alpha)R} - 5.330 - 1.052 \frac{E}{RT} \qquad (4)$$

Equation (4) shows that, provided that $g(\alpha)$ is constant at a given value of α, the slope of the plots of $\ln\beta$ *vs.* the reciprocal of the temperature for particular values of α lead to the activation energy as function of α independently of the kinetic model fitted by the reaction.

The above equations have been derived by assuming that the activation energy is an invariant of the reaction. For the case of varying activation energy, we would consider a logarithmic variation of the activation energy with $(1-\alpha)$ and a compensation effect between A and E as it has been proposed in [31, 32, 42]:

$$E = E_0 + E_1 \ln(1-\alpha) \qquad (5)$$

$$\ln A = aE + b \qquad (6)$$

where E_0, E_1, a and b being constants.

The system constituted by Eqs (2), (5) and (6) can be resolved by the Runge–Kutta method of numerical integration by means of the MathCad software for simulating $d\alpha/dt$–α–T plots of varying activation energy processes.

The analysis by means of isoconversional methods of solid–state processes taking place through competitive or parallel reactions is of interest because it would lead to an apparent dependence of E with α. If two competitive reactions were involved the reaction rate would be expressed in the following form:

$$\frac{d\alpha}{dT} = \frac{A_1}{\beta} e^{-E_1/RT} + \frac{A_2}{\beta} e^{-E_2/RT} \qquad (7)$$

where the subscripts 1 and 2 refer to the particular kinetic parameters of the competitive reactions (1) and (2), respectively.

Equation (7) can be resolved by the numerical integration method of Runge–Kutta in order to simulate a series of $d\alpha/dt$–α–T curves at different heating rates.

Results and discussion

Figure 1 shows the sets of $d\alpha/dt$–T curves simulated by assuming a first order kinetic model [i.e. $f(\alpha)=(1-\alpha)$] and the following relationships between E and α and $\ln A$ and E, respectively:

$$E = 250 + 65\ln(1-\alpha) \text{ [kJ mol}^{-1}] \qquad (8)$$

$$\ln A = 0.25E-5 \qquad (9)$$

where A is expressed in min^{-1}.

Equation (8) has been chosen in such a way that the activation energy undergoes changes as large as 150% as a function of the reacted fraction that are considerably larger than those generally reported in literature as obtained from model-free methods.

The values of E obtained as a function of α from the Friedman's and the Ozawa's methods, respectively, are included in Table 1. The values of the acti-
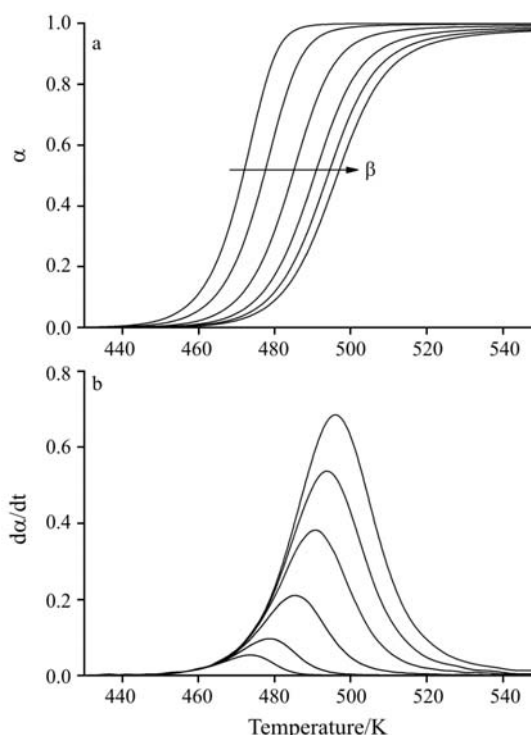

Fig. 1 Simulated curves obtained by assuming the following kinetic parameters: $E=E_0+65\ln(1-\alpha)$ ($E_0=250$ kJ mol^{-1}) $\ln A=0.25E-5$ (A is in min^{-1}), F_1 kinetic model. β=1, 2, 5, 10, 15, 20°C min^{-1}

Table 1 Activation energies obtained from the Ozawa's and Friedman's isoconversional methods for simulated curves obtained by assuming the following kinetic parameters: $E=E_0+65\ln(1-\alpha)$ ($E_0=250$ kJ mol^{-1}) $\ln A=0.25E-5$ (A is in min^{-1}), F_1 kinetic model. β=1, 2, 5, 10, 15, 20°C min^{-1}

α	Friedman	Ozawa		
	E/kJ mol^{-1}	E_a/kJ mol^{-1}	ε/%	r
0.10	242.9	241.5	–0.6	1.00
0.20	235.4	238.2	1.2	1.00
0.30	226.8	234.2	3.3	1.00
0.40	216.8	229.6	5.9	1.00
0.50	204.9	224.1	9.3	1.00
0.60	190.7	217.4	13.9	1.00
0.70	171.8	207.9	21.0	1.00
0.80	144.6	193.3	33.7	1.00
0.90	100.8	168.5	67.2	1.00

vation energies obtained from the Friedman method are in excellent agreement with those expected from Eq. (8). However, the error in the activation energies obtained from the Ozawa isoconversional method is significant and largely increases as far as the conversion increases. This behaviour is due to the fact that the Ozawa's equation was derived integrating the Arrhenius equation by assuming that the activation energy remains constant all over the reaction, what in the case of variable activation energy is far to be true. Finally, it is noteworthy to remark that although the Ozawa's method would not lead to reliable values of the activation energy, the perfect linear relationship obtained in the Ozawa plot for the whole set of heating rates considered ($r=1.0000$, Table 1) indicates that the activation energy obtained is independent of the range of heating rates selected.

On the other hand, it has been considered of interest to analyse the behaviour of a process constituted by two competitive reactions that would lead to an apparent dependence between E and α when analysed by isoconversional methods, in spite that such a dependence is not real. Figure 2 shows a set of $d\alpha/dt$–T curves simulated for two competitive reactions from Eq. (7) by assuming the same F_1 kinetic model for both reactions
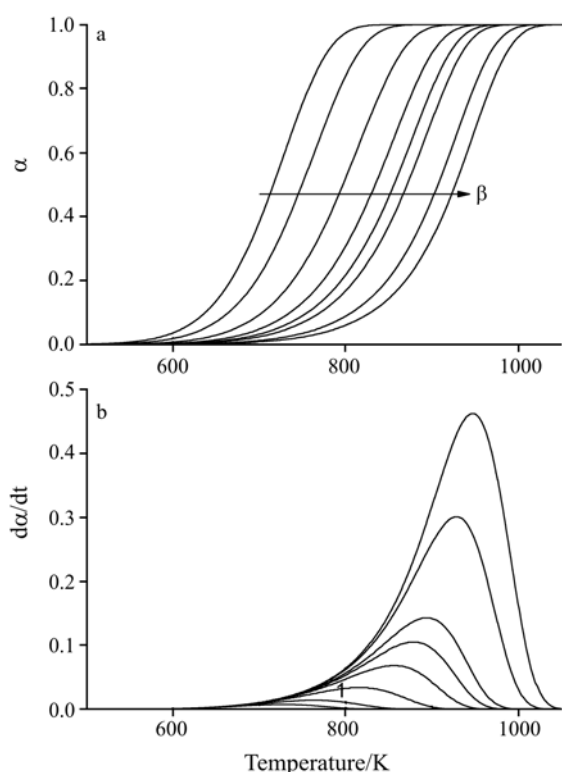
and the following kinetic parameters: $A_1=10^4$ min^{-1}, $E_1=80$ kJ mol^{-1}, $A_2=10^{11}$ min^{-1} and $E_2=200$ kJ mol^{-1}.

The plots of the activation energies determined as a function of α from the Friedman's and the Ozawa's methods for different ranges of heating rates are compared in Fig. 3. These results demonstrate that the apparent activation energy obtained for competitive reactions from isoconversional methods depend on the heating rate; in other words, the activation energies determined from 'model-free' methods seem to be dependent of the experimental conditions that it is apparent rather than real. This is because the relative contribution of the two competitive reactions to the overall process strongly depends on the heating rate as Fig. 4 shows. Thus, considering the apparent activation energy obtained from the Friedman method as the real value of this parameter has no physical meaning if overlapping processes are concerned. In such a case, the Friedman's activation energies cannot be taken as reference values for checking new integral methods that take into account the variation of the activation energy with α as some authors [37] have done. A rigorous kinetic analysis for discriminating the overlapping reactions rather than merely assuming that the activation energy is a function of α would be required for understanding the reaction mechanism. Galwey [51, 52] suggests that a real dependence between E and α has not physical meaning and he reports a detailed analysis of the different causes that would lead to an apparent dependence of the activation energy with the reacted fraction. Thus, the varying activation energy processes reported in literature should be reanalysed carefully controlling the experimental conditions in order to identify the real factors that would cause the variation of the activation energy in order to determine if this variation is apparent or real.
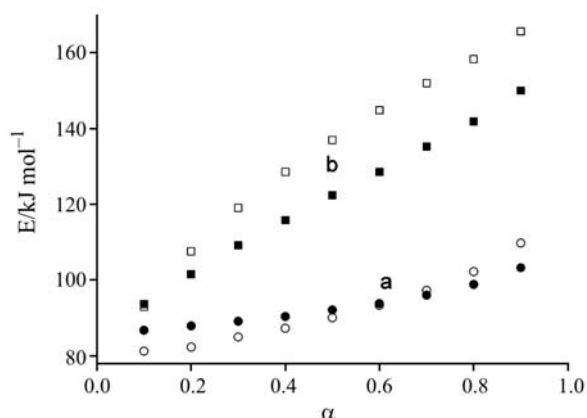

Fig. 2 Simulated overlapping competitive reactions simulated by assuming the following kinetic parameters: $A_1=10^4$ min^{-1}, $E_1=80$ kJ mol^{-1}, $A_2=10^{11}$ min^{-1} and $E_2=200$ kJ mol^{-1}. For both reactions F_1 kinetic model was assumed. $\beta=1, 2, 5, 10, 15, 20, 40$ and 60 K min^{-1}

Fig. 3 Values of activation energies determined as a function of α from $\square, \circ$ – Friedman and $\blacksquare, \bullet$ – Ozawa methods at different ranges of heating rates: a – 1, 2, 5, 10 K min^{-1} and b – 15, 20, 40, 60 K min^{-1}
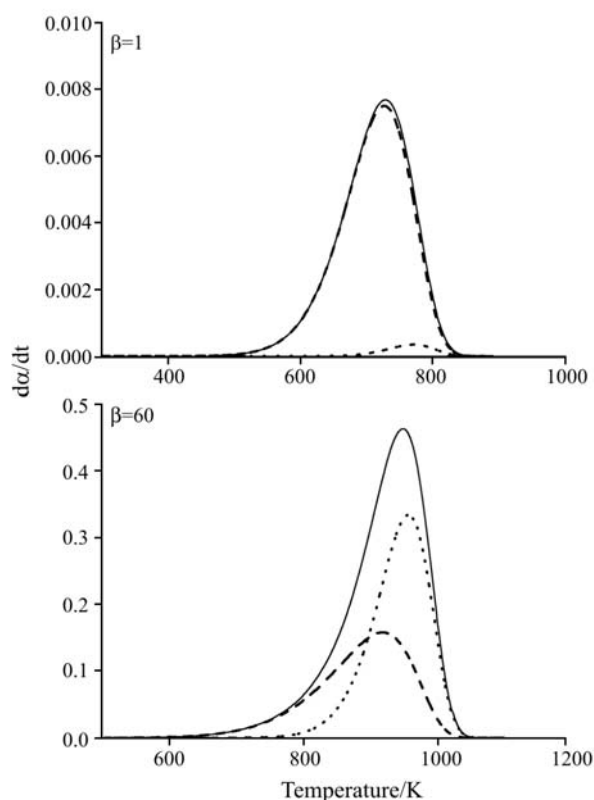
Fig. 4 - - - – Contribution of the competitive reaction 1 with
E_1=80 kJ mol^{-1} and A_1=10^4 min^{-1} and
$\cdots$ – the competitive reaction 2 with E_2= 200 kJ mol^{-1}
and A_2=10^{11} min^{-1} to the overall process (—) at
β=1 K min^{-1} and β=60 K min^{-1}, respectively

Conclusions

It has been shown by first time from theoretical simulated curves that if the activation energy is a real function of the reacted fraction, the differential model-free method, i.e. Friedman's, provides accurate values of activation energies, while the conventional integral model-free methods, i.e. Ozawa, would lead to important errors in the determination of the activation energy. Additionally, the activation energy values obtained from both methods as a function of α are independent of the range of heating rates selected. On the other hand, when the change of the activation energy with α occurs because of competitive reactions instead of a real dependence between E and the reacted fraction, the resulting activation energy values calculated by either model-free methods would seem to be dependent on the heating rate. Thus, this criterion could be used for discriminating if a real dependence between E and α is really occurring.

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