*Thermochimica Acta*, 236 (1994) 187–197
Elsevier Science B.V., Amsterdam
*SSDI* 0040-6031(93)01610-F

# A simple method of kinetic model discrimination. Part 1. Analysis of differential non-isothermal data

Jiří Málek *,[1] and José M. Criado
*Instituto de Ciencia de Materiales, C.S.I.C., Universidad de Sevilla, 41 071 Seville, Spain*

(Received 25 June 1993; accepted 18 September 1993)

## Abstract

The applicability and relevance of the Freeman and Carroll (FC) method in the kinetic analysis of non-isothermal data are discussed. It was found that the apparent kinetic parameters obtained by the modified FC method allow the kinetic model to be discriminated. A simple, quick method of kinetic model determination is proposed and verified for theoretically calculated thermal analysis data.

## INTRODUCTION

The kinetic treatment of non-isothermal thermoanalytical (TA) data has been a widely discussed topic for many years [1]. The popularity of non-isothermal methods of kinetic analysis of TA data is mainly due to the fact that both analytical and kinetic data can be obtained simultaneously in a relatively short period of time. Unfortunately, the ease with which such data can be obtained has resulted in an increased volume of papers and confusion, rather than in an increase in the quality of TA research. Therefore, it is not surprising that the usefulness and reliability of kinetic parameters, obtained from non-isothermal TA data are questioned. It seems that the problems arise from uncritical application of standard techniques of TA data processing, not taking into account the basic assumptions under which these methods were derived.

Thirty-five years ago, Freeman and Carroll [2] published their method of kinetic analysis of non-isothermal TA data. Ever since, a large number of views have been expressed by various authors, both for and against the technique. Criado et al. [3] have published a critical study concerning the suitability of the Freeman and Carroll (FC) method for the kinetic analysis of reactions including the thermal decomposition of solids. They concluded

---

[1] Permanent address: Joint Laboratory of Solid State Chemistry, Academy of Sciences of the Czech Republic, University of Chemical Technology, 532 10 Pardubice, Czech Republic.
* Corresponding author.

that this method would lead to erroneous interpretation of the reaction mechanism. The authors [3] claimed that the FC method cannot even be used for verification if a solid state reaction follows the *n*th-order kinetic law for which it has been originally derived.

The aim of this paper is a more detailed discussion of the FC method from the point of view of its applicability and relevance in non-isothermal TA kinetics. We would like to show that under certain circumstances this method can be quite useful for a quick, reliable determination of the kinetic model from non-isothermal TA data.

In the first part of the paper, the basic principles of the FC method are briefly reviewed. In the subsequence part, the relationship between true kinetic parameters and those determined by the FC method is discussed. Finally, a simple and reliable method of kinetic model determination procedure is presented. The consistency of the method is verified using theoretically calculated TA curves. A more detailed discussion of the mathematical formulae used throughout the paper is given in the appendix.

## THE FREEMAN AND CARROLL METHOD

A simplified description [1] of kinetic processes in thermal analysis is based on a constitutive system of equations defining the relations between the rate of conversion ($\mathrm{d}\alpha/\mathrm{d}t$) and the state of the system under study represented by the degree of conversion $\alpha$ and temperature $T$. The basic kinetic equation is then expressed in the form

$$(\mathrm{d}\alpha/\mathrm{d}t) = A\mathrm{e}^{-x}f(\alpha) \tag{1}$$

where $A$ is the pre-exponential factor, $x$ is the reduced activation energy ($x = E/RT$) and $f(\alpha)$ represents a function depending on the kinetic model. The $f(\alpha)$ functions corresponding to the kinetic models most commonly used in the literature are listed in Table 1.

TABLE 1

The mathematical expressions of the kinetic models

| Model | Symbol | $f(\alpha)$ |
|---|---|---|
| Johnson–Mehl–Avrami [a] | JMA($m$) | $m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$ |
| Two-dimensional diffusion | D2 | $1/[-\ln(1-\alpha)]$ |
| Jander eqn. | D3 | $(3/2)[(1-\alpha)^{2/3}]/[1-(1-\alpha)^{1/3}]$ |
| Ginstling–Brounhstein eqn. | D4 | $(3/2)/[(1-\alpha)^{-1/3}-1]$ |
| Reaction order | RO($n$) | $(1-\alpha)^{n}$ |

[a] The kinetic exponent of the JMA model is usually quoted as $n$, but is called $m$ here to distinguish it from that of the RO model.

For the reaction order kinetic model, eqn. (1) can be rewritten in the form

$$(\mathrm{d}\alpha/\mathrm{d}t) = A\mathrm{e}^{-E/RT}(1-\alpha)^n \tag{2}$$

By differentiating the logarithmic form of eqn. (2) with respect to $\mathrm{d}\ln(1-\alpha)$, Freeman and Carroll [2] obtained

$$\frac{\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)}{\mathrm{d}\ln(1-\alpha)} = -\frac{E}{R}\frac{\mathrm{d}(1/T)}{\mathrm{d}\ln(1-\alpha)} + n \tag{3}$$

The plots of the left-hand-side of eqn. (3) against $\mathrm{d}(1/T)\ \mathrm{d}\ln(1-\alpha)$ should be a straight line with a slope $-E/RT$ and an intercept equal to the kinetic exponent $n$. Therefore this method allows one to determine simultaneously both the activation energy and the kinetic exponent. It should be born in mind that this is valid only if the kinetic data correspond to the reaction order model RO($n$). However, due to the mutual correlation of kinetic parameters it can be shown that if eqn. (3) is applied to any kinetic data, then the reaction would be seen apparently to obey the RO($n$) model, in spite of really following a quite different mechanism. In this case, an apparent reaction order $n_a$ and an apparent activation energy $E_a$ would be obtained instead the true kinetic parameters.

## RESULTS AND DISCUSSION

It seems reasonable to assume that the FC method always gives apparent kinetic parameters and that only for a special case of the RO($n$) model are these parameters equal to the true ones, i.e. $E_a = E$ and $n_a = n$. Criado et al. [3] have found the average values of the $(E_a/E)$ ratio as well as the apparent exponents $n_a$ for the basic kinetic models used in the literature. Recently, it was found [4, 5] that the ratio $(E_a/E)$ can be expressed by the equation

$$(E_a/E) = -\left[\frac{f(\alpha_p)}{f'(\alpha_p)}\right]\frac{n_a}{1-\alpha_p} \tag{4}$$

where $\alpha_p$ is the degree of conversion at the maximum of the TA peak and $f'(\alpha)$ is the derivative of the $f(\alpha)$ function with respect to $\alpha$ (see also the Appendix).

For practical reasons, it is suitable to rewrite eqn. (4) in a somewhat different form

$$(E_a/n_aE) = -f(\alpha_p)[f'(\alpha_p)(1-\alpha_p)]^{-1} \tag{5}$$

The right-hand-side of eqn. (5) depends only on the value of $\alpha_p$. Thus it is possible to express the $(E_a/n_aE)$ ratio as a function of $\alpha_p$ for all the kinetic models listed in Table 1. These expressions are summarized in Table 2. Figure 1 presents the $(E_a/n_aE)$ vs. $\alpha_p$ dependences in graphical form. It is seen that the value of $(E_a/n_aE)$ increases with $\alpha_p$ for the D2, D3, D4 and

TABLE 2

The expressions and limiting values for $(E_a/n_aE)$

| Model | $(E_a/n_aE)$ | $\alpha_p^\infty$ | $(E_a/n_aE)^\infty$ |
|---|---|---|---|
| JMA($m$) | $\dfrac{-\ln(1-\alpha_p)}{1+\ln(1-\alpha_p)-1/m}$ | 0.632 | $m$ |
| D2 | $-\ln(1-\alpha_p)$ | 0.834 | 1.796 |
| D3 | $\dfrac{3[1-(1-\alpha_p)^{-1/3}]}{1-2(1-\alpha_p)^{-1/3}}$ | 0.704 | 0.750 |
| D4 | $3[1-(1-\alpha_p)^{1/3}]$ | 0.776 | 1.178 |

JMA ($n < 1$) models (Fig. 1a). The limiting values corresponding to the infinite value of the reduced activation energy (see the appendix) are shown by open squares, and the numerical values are listed in Table 2. A different behavior is observed for the JMA ($n > 1$) model (Fig. 1b) where the value of $(E_a/n_aE)$ decreases with increasing $\alpha_p$. Figure 1 can easily be used for the kinetic model determination provided that the activation energy is known, because the parameter $\alpha_p$ can be obtained from experimental data, and both $E_a$ and $n_a$ are results of the FC analysis.

It is well known, however, that $\alpha_p$ depends on the reduced activation energy at the maximum of the TA peak, i.e. $x_p$. Therefore any possible application of the FC method requires a discussion of this problem. Analytical expressions can be found (see the appendix) for the JMA($m$) model [5]

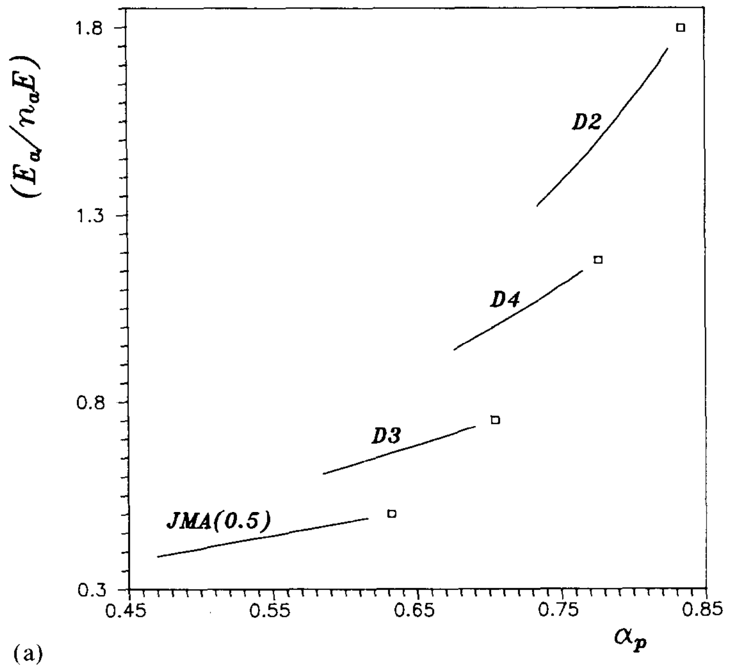
$$(E_a/n_aE) = \frac{m-1}{x_p\pi(x_p)} + 1 \tag{6}$$

and for the D3 model

$$(E_a/n_aE) = \frac{3}{2}\left[1 - \frac{1}{2x_p\pi(x_p)}\right] \tag{7}$$

Unfortunately, such equations cannot be derived for the D2 and D4 models. In these cases, the $(E_a/n_aE)$ versus $x_p$ dependence has to be determined numerically. Calculated data (full lines) are shown in Fig. 2 for all the kinetic models discussed. It is clear that the $(E_a/n_aE)$ versus $x_p$ dependence increaes for the D2, D3, D4 and JMA($n < 1$) models (Fig. 2a) and decreases for the JMA($n > 1$) models (Fig. 2b). The limiting values corresponding to $x_p \rightarrow \infty$ are marked by arrows at the right-hand-side of the figure.

It should be stressed that the value of $(E_a/n_aE)$ is practically constant for $x > 20$ for all kinetic models and varies only within a few percent. The average values are summarized, together with corresponding error limits, in Table 3.



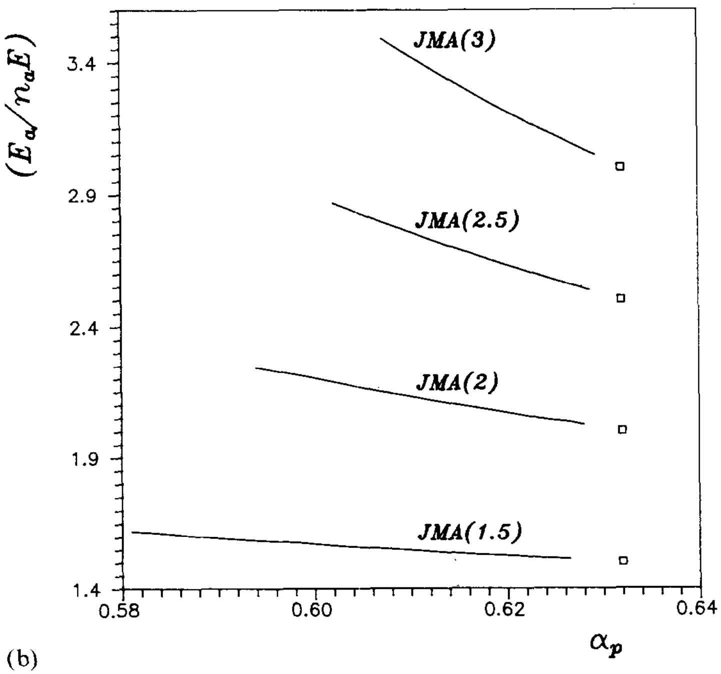


Fig. 1. The $(E_a/n_aE)$ ratio as a function of $\alpha_p$ for the JMA($m$), D3, D2 and D4 kinetic models calculated using the formulae listed in Table 2. The limiting values corresponding to infinite $x_p$ are marked as open squares.

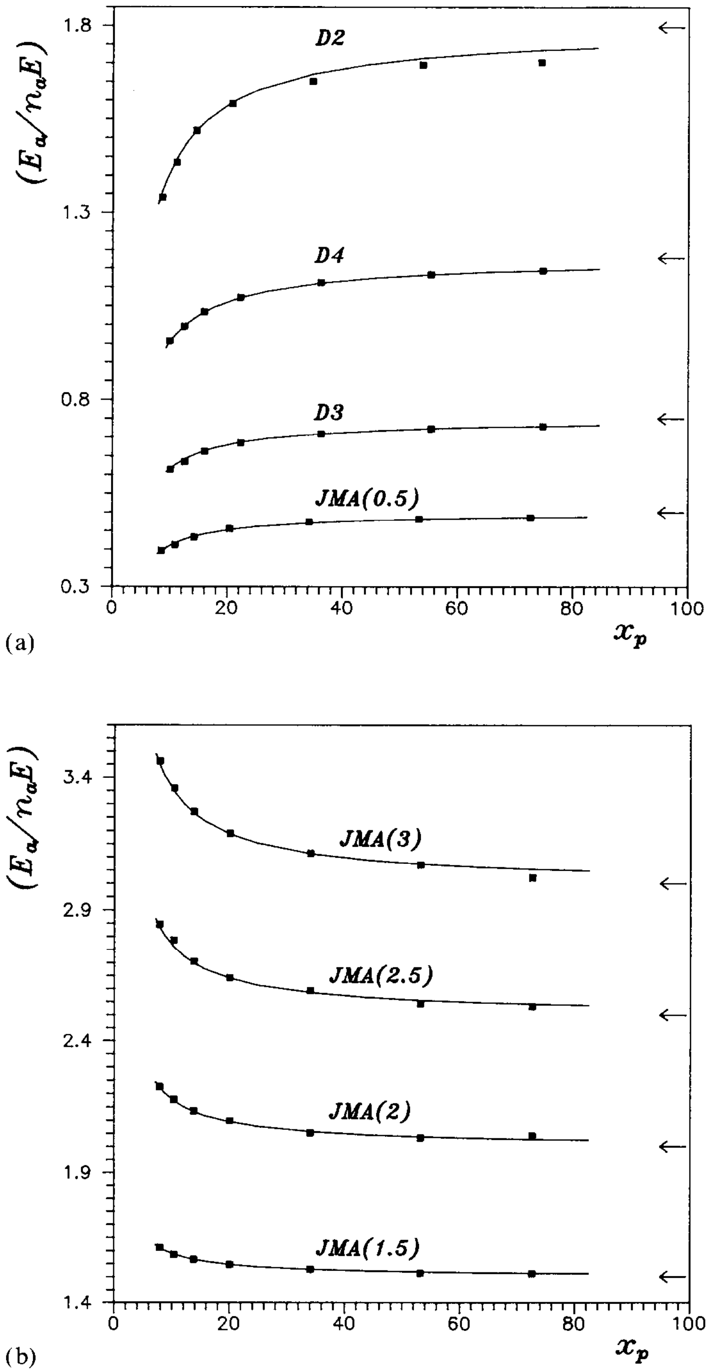


Fig. 2. The dependence of the $(E_a/n_aE)$ ratio as a function of reduced activation energy corresponding to the maximum of the TA peak (full lines). The data calculated by FC analyses of the theoretical TA peaks are plotted as filled squares. The limiting values corresponding to infinite $x_p$ are marked by arrows.

TABLE 3

Characteristic values of apparent kinetic parameters as determined by the FC method

| Model | $n_a$ | $(E_a/n_aE)$ |
|---|---|---|
| JMA($m$) | 1 | $m \pm 0.05m$ |
| D2 | 0.27 | $1.7 \pm 0.1$ |
| D3 | 0.67 | $0.72 \pm 0.03$ |
| D4 | 0.42 | $1.12 \pm 0.06$ |
| RO($n$) | $n$ | $1/n$ |

It is also very important to note that the apparent kinetic exponent $n_a$, as determined from the FC plot, is a characteristic constant for the true kinetic model (see Table 3) and does not depend on $x_p$. Therefore, its value can be used as a first approach for the kinetic model determination from the FC plot. Of course, this is not sufficient to resolve the problem completely because there is still some uncertainty as to whether $n_a$ corresponds to the true kinetic exponent of the RO($n$) model or if it is an apparent value of the D2, D3, D4 or JMA($m$) model, respectively. Nevertheless, if the true activation energy is known, the $(E_a/n_aE)$ value can be calculated and the kinetic model can be definitely determined. The activation energy value can easily be determined from a series of non-isothermal measurements carried out at different heating rates. The Friedman [6] and Ozawa–Flynn–Wall [7–9] analyses are recommended.

The discrimination procedure is outlined schematically in Fig. 3. It can be seen that the difference in the $(E_a/n_aE)$ values for the RO($n$) and diffusion models (D2, D3, D4) is large; thus there is no possibility of confusion even for low values of reduced activation energy. The method proposed also allows the kinetic exponent for the JMA($m$) model to be determined with an error not exceeding 5%.

To verify the proposed concept of kinetic model determination using the FC analysis, theoretical TA curves were simulated (see the appendix). Typical curves calculated for $\alpha \in (0.03, 0.99)$ are shown in Fig. 4. These curves were subsequently analyzed by the FC method (in the range: $0.4 < \alpha < 0.9$) as illustrated in Fig. 5. The results of the analysis are plotted as filled squares in Fig. 2. There is no doubt that the results obtained agree well with theoretically predicted dependences. Therefore, the proposed discrimination procedure seems to be consistent.

## CONCLUSIONS

The method developed by Freeman and Carroll [2] to analyze data following $n$th-order kinetics has been extended for the different kinetic models describing solid state reactions. It is found that the results obtained

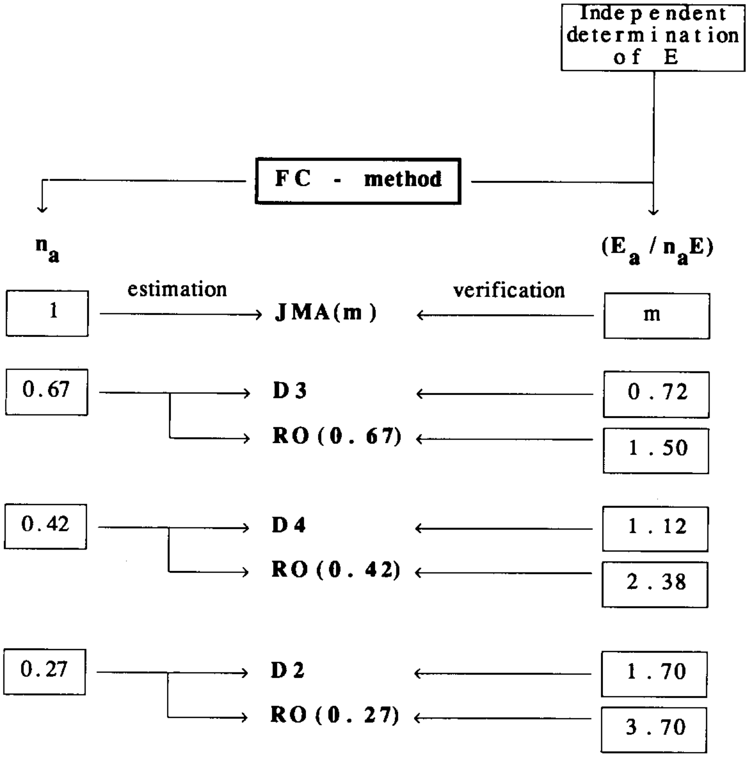


Fig. 3. The schematic outline of the proposed method for kinetic model determination.

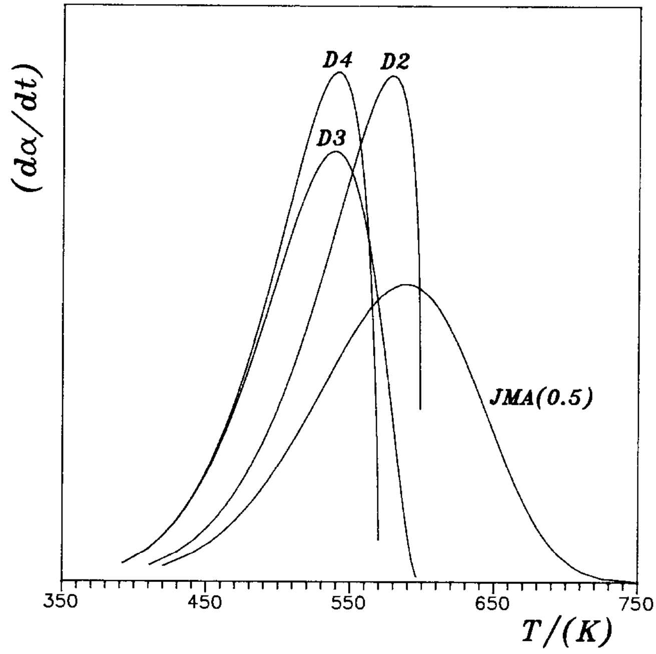


Fig. 4. The theoretical TA curves calculated for the defined range of degree of conversion: $0.03 < \alpha < 0.99$.

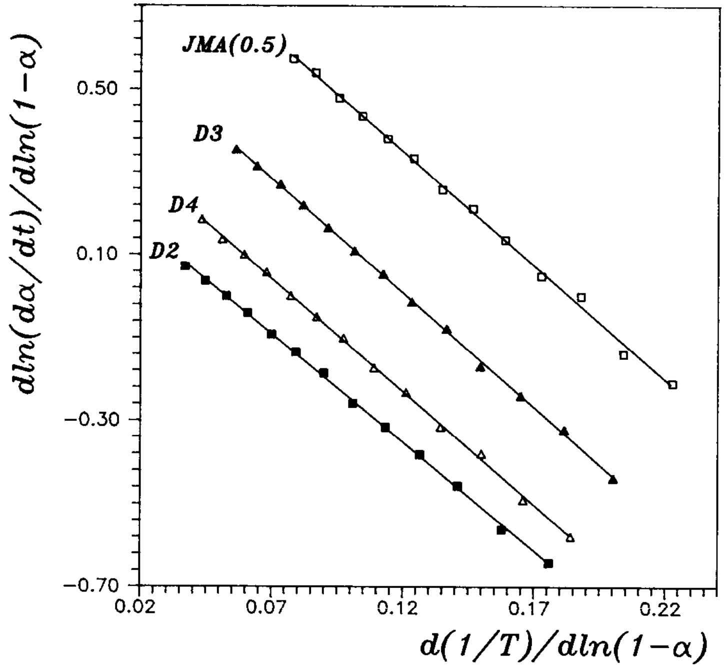


Fig. 5. The FC analysis of the theoretical TA curves shown in Fig. 3.

by this analysis permit an unambiguous determination of the kinetic model provided that the true activation energy is known. A simple and quick method for the kinetic model determination is proposed and verified using theoretically calculated TA curves.

## ACKNOWLEDGEMENTS

One of the authors (J.M.) is indebted to the Junta de Andalucía for financial support which has permitted his temporary stay in the Instituto de Ciencia de Materiales de Sevilla. The financial support of DGICYT through the project No. PB 90-0130 is acknowledged.

## REFERENCES

1 J. Šesták, Thermophysical Properties of Solids, Their Measurements and Theoretical Analysis, Elsevier, Amsterdam 1984.
2 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
3 J.M. Criado, D. Dollimore and G.R. Heal, Thermochim. Acta, 54 (1982) 159.
4 N. Koga, J. Šesták and J. Málek, Thermochim. Acta, 188 (1991) 333.
5 J. Málek and J.M. Criado, Thermochim. Acta, 203 (1992) 25.
6 J. Friedman, J. Polym. Sci., Part C, 6 (1965) 175.
7 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
8 J.H. Flynn and L.A. Wall, Polym. Lett., 4 (1966) 232.

9 J.H. Flynn and L.A. Wall, J. Res. Natl. Bur. Stand., Sect. A, 70 (1966) 487.
10 G.I. Senum and R.T. Yang, J. Therm. Anal., 11 (1977) 445.
11 J. Málek and J.M. Criado, Thermochim. Acta, 164 (1990) 199.
12 J.M. Criado and A. Ortega, Thermochim. Acta, 103 (1986) 317.

## APPENDIX

If the temperature rises at a constant rate $\beta$, then, after integration of eqn. (1) we obtain

$$g(\alpha) = \frac{AE}{\beta R} e^{-x} \left[ \frac{\pi(x)}{x} \right] \tag{A1}$$

where $\pi(x)$ is an approximation of the temperature integral [1]. There are many approximate expressions of $\pi(x)$ in the literature. For all calculations presented in this paper, we have used the approximation [10]

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{A2}$$

which gives sufficiently accurate results. The $g(\alpha)$ function is an integral form of the kinetic model defined as

$$g(\alpha) = \int \frac{d\alpha}{f(\alpha)} + C \tag{A3}$$

where $C$ is a constant which can be determined from the condition

$$\lim_{\alpha \to 0} g(\alpha) = 0 \tag{A4}$$

Using eqn. (A3) and applying the condition (A4), we can determine the integral forms of all the kinetic models, as summarized in Table A1.

Equation (A1) was used for calculation of theoretical TA curves in the integral form, for the degree of conversion range $0.03 < \alpha < 0.99$. The TA

TABLE A1

Integral forms of the kinetic models

| Model | $g(\alpha)$ |
|---|---|
| JMA($m$) | $[-\ln(1-\alpha)]^{-1/m}$ |
| D2 | $(1-\alpha)\ln(1-\alpha)+\alpha$ |
| D3 | $[1-(1-\alpha)^{1/3}]^2$ |
| D4 | $\left(1-\frac{2}{3}\alpha\right)-(1-\alpha)^{2/3}$ |
| RO($n$) | $\frac{1-(1-\alpha)^{1-n}}{1-n}$ |

TABLE A2

| Model | $\alpha_p$ |
|---|---|
| JMA($m$) | $1-\exp\left[\frac{1-x_p\pi(x_p)}{m}-1\right]$ |
| D3 | $1-\left[\frac{1}{2}+x_p\pi(x_p)\right]^{-3}$ |
| RO($n$) | $1-\left[1+\frac{1-n}{n}x_p\pi(x_p)\right]^{1/(1-n)}$ |

curves shown in Fig. 4 were then calculated by means of eqn. (1) using these integral data.

Differentiating eqn. (1) with respect to time yields the equation [11]

$$(\mathrm{d}^2\alpha/\mathrm{d}t^2)=\left[\frac{\beta}{T\pi(x)}\right]^2 f(\alpha)g(\alpha)[f'(\alpha)g(\alpha)+x\pi(x)] \tag{A5}$$

where $f'(\alpha)=\mathrm{d}f(\alpha)/\mathrm{d}t$. The condition for the maximum of the TA peak is obtained by setting eqn. (A5) equal to zero

$$-f'(\alpha_p)g(\alpha_p)=x_p\pi(x_p) \tag{A6}$$

This is the basic equation expressing the dependence of the parameter $\alpha_p$ on the reduced activation energy. When $x_p$ is infinite, then

$$\lim_{x\to\infty}[x\pi(x)]=1 \tag{A7}$$

and eqn. (A6) can be written as

$$-f'(\alpha_p^\infty)g(\alpha_p^\infty)=1 \tag{A8}$$

Hence the value of the degree of conversion at the peak reaches its maximum value $\alpha_p^\infty$ for infinite $x_p$. An identical result is also obtained for hyperbolic or logarithmic heating programs [12] where the $\alpha_p$ does not depend on the reduced activation energy.

From eqn. (A6) we can obtain the dependence of $\alpha_p$ versus $x_p$ in explicit form, as shown in Table A2 for some kinetic models. Combining these relationships with the expressions for $(E_a/n_aE)$ listed in Table 2, we can obtain eqns. (6) and (7).