

A comparative study of the resolving power of both conventional thermogravimetry and constant rate thermal analysis

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Abstract

According to literature data, constant rate thermal analysis (CRTA) has a higher resolving power for discriminating overlapping processes than the conventional TG method. However, taking into account that the heating rate and constant reaction rate concepts are quite different, it is of interest to propose a standardization procedure for comparing the results obtained from both methods. The present theoretical kinetic study points out that CRTA and TG have very similar discriminating power, provided that both the heating rate for the TG curve and the constant reaction rate for the CRTA curve are selected in such a way that the total time required for carrying out the reaction in the range $0.05 \leq \alpha \leq 0.95$ is the same in both cases.

INTRODUCTION

Constant rate thermal analysis (CRTA) is a general method of thermal analysis developed independently by Rouquerol [1] and Paulik and co-workers [2]. The basis of this method is that the temperature of the sample is controlled in such a way that the reaction rate is maintained constant throughout the process. It has been shown in previous work [3,4] that this method allows better discrimination between the kinetic models of solid state reactions than conventional thermogravimetry (TG). Moreover, CRTA has been employed with success in the synthesis of materials with controlled texture and structure [5,6].

In contrast, it has been claimed [7,8] that CRTA has a higher resolving power for discriminating mutually independent overlapping reactions than

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

conventional non-isothermal methods. However, it must be pointed out that this conclusion has been drawn by comparing TG experiments carried out at heating rates ranging from 5 to 15 K min⁻¹ with CRTA experiments developed at decomposition rates generally lower than 5 × 10⁻³ min⁻¹. Therefore, taking into account that the heating rate and the constant reaction rate concepts are quite different, it is interesting to propose a standard procedure for comparing the results obtained from both methods.

THEORETICAL

It is known [9] that a process taking place through a series of overlapping mutually independent reactions can be described by the following constitutive equations:

$$\frac{d\alpha}{dt} = \sum_i \lambda_i \left(\frac{d\alpha}{dt} \right)_i \quad (1)$$

$$\left(\frac{d\alpha}{dt} \right)_i = A_i f(\alpha_i) \exp(-E_i/RT) \quad (2)$$

$$\alpha = \sum_i \lambda_i \alpha_i \quad (3)$$

$$\sum_i \lambda_i = 1 \quad (4)$$

where A is the pre-exponential Arrhenius factor, E the activation energy, T the absolute temperature, $f(\alpha)$ a function depending on the reaction mechanism, and the subscript i refers to unit reaction i . The parameter λ_i represents the contribution of the unit reaction i to the overall process expressed by the final weight change of unit reaction i and the final weight change of the overall process.

LINEAR HEATING PROGRAM

If the process is recorded under a linear heating program, the α - T plot can be calculated by integrating eqn. (1) after substituting eqn. (2):

$$\sum_i \lambda_i g(\alpha_i) = \sum_i \frac{\lambda_i A_i}{\beta} \int_0^T \exp\left(-\frac{E_i}{RT}\right) dT \quad (5)$$

where $\beta = dT/dt$ is the heating rate and $g(\alpha)$ is a function depending on the reaction mechanism.

The integral of the right-hand side of eqn. (5) cannot be expressed in a closed form but must be calculated using numerical methods. The integration of the Arrhenius equation has been carried out in this paper with an

accuracy better than $10^{-5}\%$ by means of the fourth-order rational approximation proposed by Senum and Yang [10]:

$$\frac{A_i}{\beta} \int_0^T \exp\left(-\frac{E_i}{RT}\right) dT = \frac{A_i E_i}{\beta R} p(x_i) \quad (6)$$

where $x_i = E/RT$ and $p(x_i)$ is given by the following expression:

$$p(x_i) = \frac{\exp(-x_i)}{x_i} \frac{x_i^3 + 18x_i^2 + 88x_i + 96}{x_i^4 + 20x_i^3 + 120x_i^2 + 240x_i + 120} \quad (7)$$

Equations (1), (2) and (5)–(7) permit the simulation of solid state processes comprising a set of i independent reactions if both the kinetic equation and the kinetic parameters describing every unit reaction are assumed.

CRTA ANALYSIS

In this case the total reaction rate is maintained constant over the whole process at a constant value of $C = d\alpha/dt$. Therefore

$$C = \sum_i \lambda_i \left(\frac{d\alpha}{dt}\right)_i = \sum_i \lambda_i A_i f(\alpha_i) \exp\left(-\frac{E_i}{RT}\right) \quad (8)$$

$$\alpha = \sum_i \lambda_i \alpha_i = Ct \quad (9)$$

The above system of differential equations has been resolved by a numerical method using a modified Runge–Kutta method.

RESULTS AND DISCUSSION

Figures 1 and 2 include a series of TG and DTG curves simulated by considering heating rates ranging from 0.1 to 1 K min⁻¹ and assuming two independent first-order reactions with the following kinetic parameters: $E_1 = 167$ kJ mol⁻¹; $A_1 = 6 \times 10^{14}$ min⁻¹ and $E_2 = 334$ kJ mol⁻¹; $A_2 = 1.8 \times 10^{29}$ min⁻¹. An identical contribution of the two units reactions to the overall process is assumed (i.e. $\lambda_1 = \lambda_2 = 0.5$).

Figure 3 shows the CRTA traces calculated by assuming the same kinetic parameters and selecting the constant reaction rate C in such a way that the time required for developing the overall process in the range $0.05 \leq \alpha \leq 0.95$ is equal to the time required for recording this conversion range in the corresponding TG curve.

The results included in Figs. 1–3 allow us to conclude that CRTA and TG have almost the same discriminating power provided that both the heating rate β for the TG trace and the constant reaction rate C for the CRTA corresponding CRTA curve are selected in such a way that the total time required for completing the reaction is the same in both experiments.

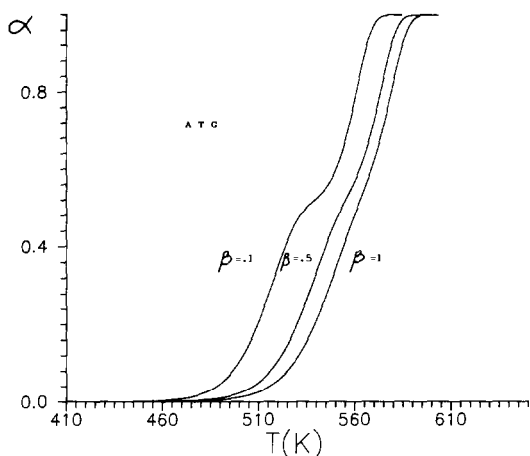


Fig. 1. Influence of the heating rate on the resolving power of TG. Two overlapping first-order reactions with the following kinetic parameters have been assumed: $E_1 = 167 \text{ kJ mol}^{-1}$; $A_1 = 6 \times 10^{14} \text{ min}^{-1}$; $E_2 = 334 \text{ kJ mol}^{-1}$, $A_2 = 1.8 \times 10^{29} \text{ min}^{-1}$.

However, it must be remarked that under the above standard conditions the real time for recording the whole TG trace is much longer than the time used in the CRTA experiment. This is because the starting reaction temperature is almost instantaneously reached when the CRTA method is employed.

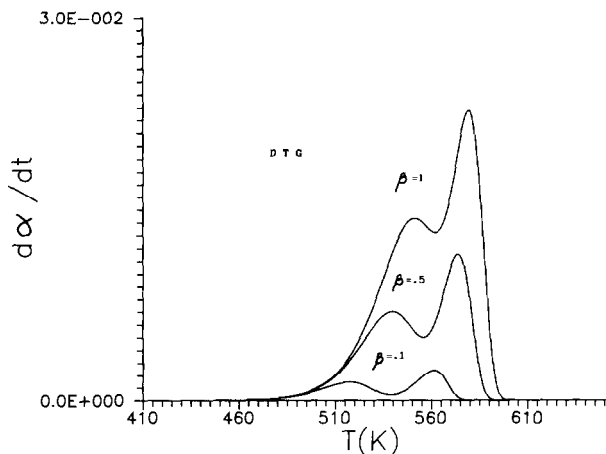


Fig. 2. Influence of the heating rate on the resolving power of DTG traces simulated by assuming the same kinetic model and kinetic parameters used in Fig. 1.

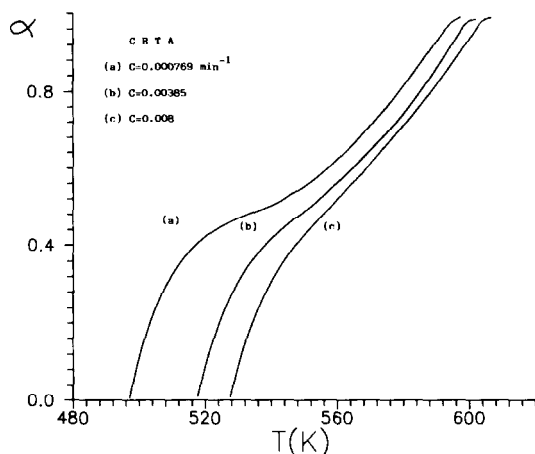


Fig. 3. Influence of the constant reaction rate on the resolving power of CRTA. The same unit reactions indicated in Fig. 1 have been assumed.

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