

# **DEVELOPMENT OF MASTER CURVES FOR DISCRIMINATING THE MECHANISM OF SOLID STATE REACTIONS FROM EXPERIMENTAL DATA OBTAINED BY USING THE CYCLIC AND CONTROLLED RATE THERMAL ANALYSIS**

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## **Abstract**

The cyclic and Controlled Rate Thermal Analysis method (CRTA) has been used. The two rates automatically selected in the cyclic curve are small enough to allow the two states of the sample to be compared have nearly the same reacted fraction. Thus, the activation energy can be calculated without previous knowledge of the actual reaction mechanism.

Provided that the activation energy,  $E$ , is known, a procedure has been developed for determining the kinetic law obeyed by the reaction by means of master curves that represent the values of the reacted fraction,  $\alpha$ , as a function of  $-E/R(1/T-1/T_{0.5})$ ,  $T_{0.5}$  being the temperature at which  $\alpha = 0.5$ . This procedure has been tested by studying the thermal decomposition reaction of  $\text{BaCO}_3$ .

**Keywords:** CRTA, kinetics, solid state reactions

## **Introduction**

It has been proved in a previous reference [1] that the shape analysis of a single thermoanalytical curve obtained using the Constant Rate Thermal Analysis (CRTA) method allows to discriminate without ambiguities among Avrami-Erofeev, ' $n$  order' and diffusion controlled reactions. This does not occur if the conventional TG technique is employed [2-3]. Therefore, CRTA holds a number of advantages with regards to TG in order to perform the kinetic analysis of solid state reactions. However, it has been shown in the literature [4] that when ' $n$  order' reactions are involved, one standard CRTA curve does not supply enough information for calculating  $n$ , what is a limitation of this method of kinetic analysis. Master curves that allow the accurate discernment of the kinetic law obeyed by solid state reactions are developed in the present paper in order to overcome the above limitation.

## Experimental

BaCO<sub>3</sub> from DHemio (a.r. grade) was used.

It was employed the CRTA system developed by Rouquerol *et al.* that was described elsewhere [5–6]. This apparatus permits to maintain constant at values previously selected both the rate of decomposition and the residual pressure in the close vicinity of the sample. On the other hand, an automatic device (including a timer and an air-operated butterfly valve joined to the equipment) allows an alternative control of the reaction at two different rates in order to carry out cyclic CRTA experiments.

## Theoretical

Bearing in mind that CRTA diagrams are obtained at a constant decomposition rate,  $C$ , and taking into account the general expression of the reaction rate of thermal decomposition of solids, we can write

$$\frac{d\alpha}{dt} = C = A \cdot \exp(-E/RT) \cdot f(\alpha) \quad (1)$$

that can be rearranged in the form:

$$\ln \frac{1}{f(\alpha)} = \ln \frac{A}{C} - \frac{E}{RT} \quad (2)$$

where  $\alpha$  is the reacted fraction at the time  $t$ ;  $f(\alpha)$  is a function depending on the reaction mechanism and the other symbols have their usual meaning.

According to Eq. (2), it is accomplished the following expression at the temperature  $T_{0.5}$  at which the reacted fraction is  $\alpha = 0.5$ .

$$\ln \frac{1}{f(0.5)} = \ln \frac{A}{C} - \frac{1}{RT_{0.5}} \quad (3)$$

From Eqs (2) and (4) we get:

$$\ln \frac{f(\alpha)}{f(0.5)} = -\frac{E}{R} \left[ \frac{1}{T} - \frac{1}{T_{0.5}} \right] \quad (4)$$

In the case of a cyclic CRTA experiment we can easily derive from Eq. (2):

$$\ln \frac{C_1}{C_2} = -\frac{E}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad (5)$$

where  $C_1$  and  $C_2$  are the two rates in the cycle to which correspond the temperatures  $T_1$  and  $T_2$ , respectively.

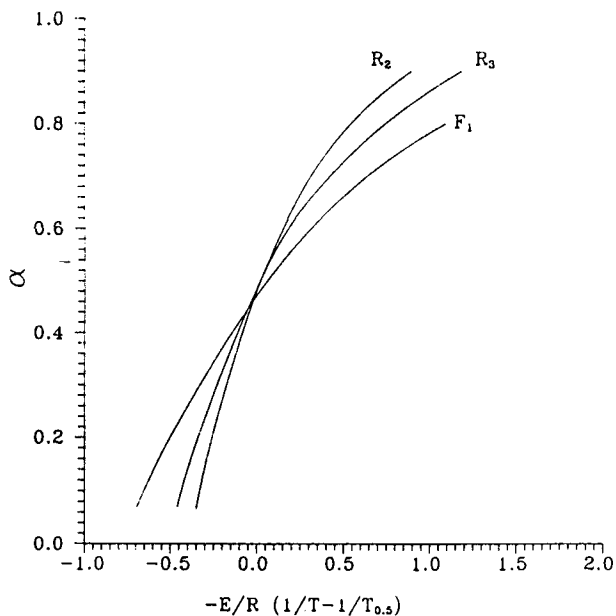


Fig. 1 Master curves for 'n order reactions'

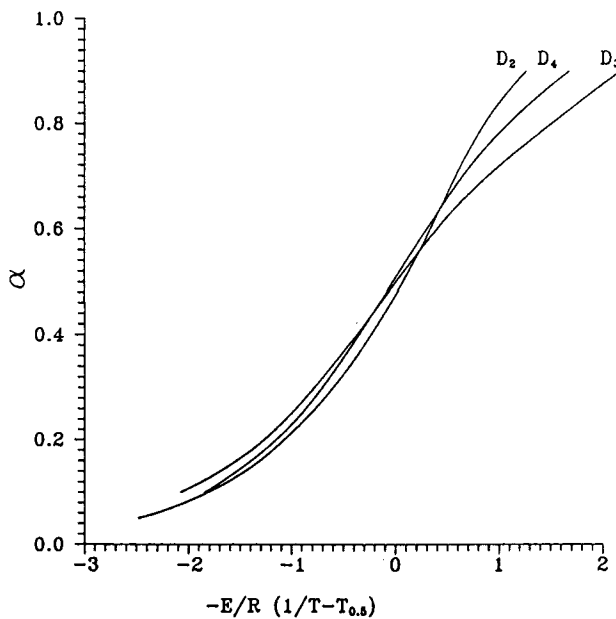


Fig. 2 Master curves for diffusion controlled reactions

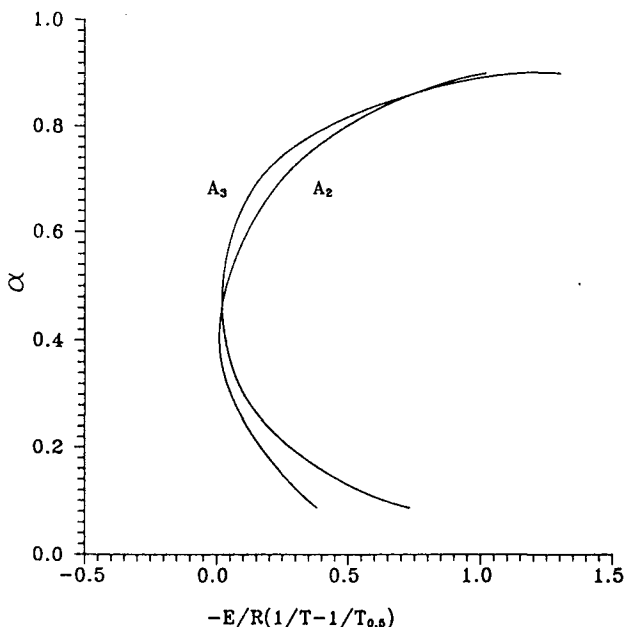


Fig. 3 Master curves for reactions obeying the Avrami-Erofeev kinetic law

On the other hand, as  $\ln[f(\alpha)/f(0.5)]$  is a function of  $\alpha$  which is equal to  $(-E/R)(1/T - 1/T_{0.5})$ ,  $\alpha$  can be calculated as a function of the right hand side of Eq. (4). Figures 1 to 3 show the theoretical master curves calculated by this way from the  $f(\alpha)$  functions more commonly used for describing solid state reactions. Therefore, the plot of the experimental values of  $\alpha$  against the right hand side of Eq. (4), once the activation energy has been obtained from the cyclic CRTA curve, allows to discriminate the kinetic law fitted by the reaction.

## Results

Figure 4 shows the CRTA curve corresponding to the thermal decomposition of  $\text{BaCO}_3$  obtained at a constant decomposition rate  $C = 1.1 \cdot 10^{-3} \text{ min}^{-1}$  using a sample weight of about 30 mg under a constant residual pressure of  $1 \cdot 10^{-5}$  mbar.

Cyclic CRTA curves of  $\text{BaCO}_3$  were recorded by using a weight sample of about 150 mg and a residual pressure of  $5 \cdot 10^{-5}$  mbar. The two states of the sample to be compared have almost the same reacted fraction. Thus, the activation energy can be calculated without prior knowledge of the actual reaction mechanism. These conditions allowed to perform about 15 cycles (i.e., 15 successive measurements of  $E$  during the decomposition of  $\text{BaCO}_3$ ). By way of example,

Fig. 5 shows one of this cycles. The mean value of the activation energy calculated from the cyclic CRTA experimental has been  $E = 268 \pm 9 \text{ kJ}\cdot\text{mol}^{-1}$  and it is independent of the reacted fraction  $\alpha$ . By using this activation energy, the  $\alpha$  values taken from the CRTA curve included in Fig. 4 have been drawn against  $-(E/R)(1/T-1/T_{0.5})$  and matched with the master curves included in Figs 1 to 3. This analysis allows to conclude that the thermal decomposition of  $\text{BaCO}_3$  fol-

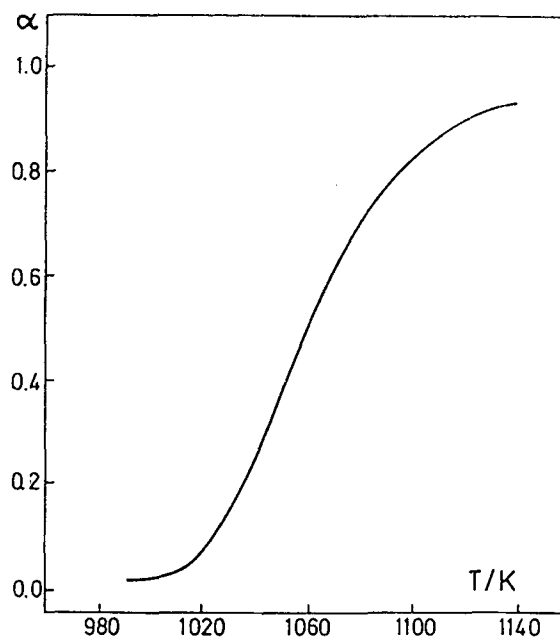


Fig. 4 CRTA curve for the thermal decomposition of  $\text{BaCO}_3$  recorded at a residual pressure of  $5 \cdot 10^{-5}$  mbar and a constant rate  $C = 1.1 \cdot 10^{-3} \text{ min}^{-1}$

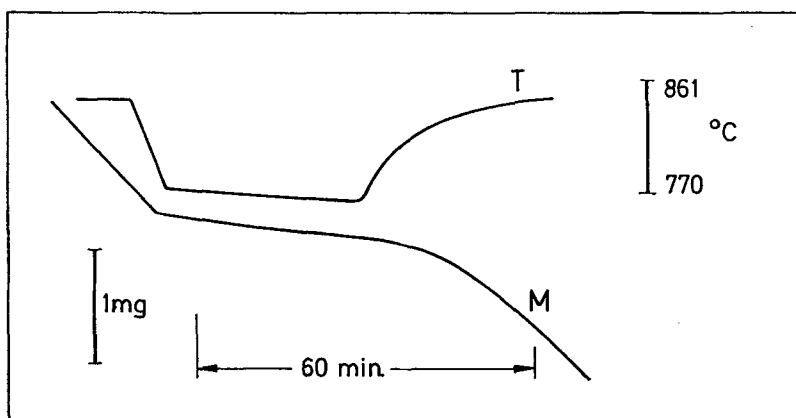


Fig. 5 A cycle in a CRTA curve of  $\text{BaCO}_3$

lows a first order kinetic laws ( $F_1$ ) as shown in Fig. 6. The kinetic parameters and the kinetic law here reported are in very good agreement with those previously determined [7] from a comparison of standard TG and CRTA data obtained by using the same sample.

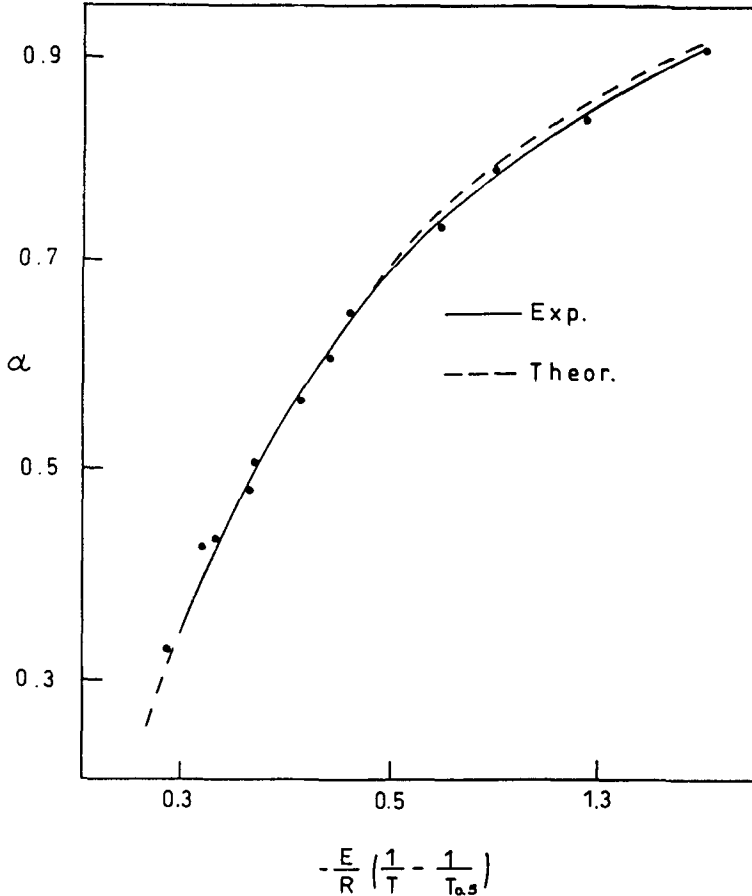


Fig. 6 Kinetic analysis of the CRTA curve included in Fig. 4. A comparison with the master curve corresponding to a first order law ( $F_1$ )

In summary, we can conclude that the method of kinetic analysis of thermal decomposition of solids developed in the present paper supplies an easy and quick way for discriminating the actual reaction mechanism and calculating the values of the kinetic parameters.

## References

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**Zusammenfassung** — Cyclische und Controlled Rate Thermal Analysis (CRTA) wurde verwendet. Die in der cyclischen Kurve automatisch gesetzten zwei Geschwindigkeiten sind klein genug, um zuzulassen, daß die beiden zu vergleichenden Proben annähernd die gleiche umgesetzte Fraktion zu beinhalten. Somit kann die Aktivierungsenergie ohne vorheriges Wissen des jeweiligen Reaktionsmechanismus berechnet werden.

Für den Fall, daß die Aktivierungsenergie  $E$  bekannt ist, wurde mit Hilfe von Master-Kurven, welche die Werte für die bereits reagierte Fraktion als Funktion von  $-E/R(1/T-1/T_{0.5})$  darstellen, ein Verfahren zur Bestimmung des Geschwindigkeitsgesetzes entwickelt, dem die Reaktion unterliegt (bei der Temperatur  $T_{0.5}$  ist  $\alpha = 0.5$ ). Dieses Verfahren wurde an der Untersuchung der thermischen Zersetzungsreaktion von  $\text{BaCO}_3$  getestet.