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INFLUENCE OF MASS-TRANSFER PHENOMENA ON THE SHAPE OF EGA TRACES OF SOLID-STATE REACTIONS

J. M. Criado, C. Real, A. Ortega and *M. D. Alcala*

INSTITUTO DE CIENCIAS DE MATERIALES (C. S. I. C.), UNIVERSIDAD DE SEVILLA,
41071 SEVILLA, SPAIN

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A theoretical analysis of the influence of mass-transfer phenomena on the shape of EGA traces of the thermal decompositions of solids has been carried out by assuming that the partial pressures of the gases generated in the reactions are proportional to the reaction rate. It has been shown that the EGA curves move to higher temperatures and the apparent reaction order *n* approaches zero as the efficiency of the system for removing the gas product decreases, while the activation energy remains nearly constant. These statements have been checked experimentally.

Thermal analysis methods (i.e. TG, DTG, DTA, EGA, DTP, etc.) have been widely used in studies of the kinetics of thermal decomposition of solids [1-3]. A serious drawback of these techniques is the lack of reproducibility because of the influence of heat and mass-transfer phenomena, which are strongly dependent on the experimental conditions [4]. It is of interest to carry out a theoretical analysis of the influence of the above phenomena on the thermoanalytical curves in order to make a comparison with the experimental behavior.

Theoretical

It is well known that the rate of the reversible solid-state reaction

$$A(s) \rightarrow B(s) + C(g) \tag{1}$$

can be expressed in the form

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$$\frac{d\alpha}{dt} = A f(\alpha) \left[1 - \frac{P_C}{P_{eq}}\right] \exp(-E/RT) \tag{2}$$

where α is the reacted fraction at time t; E is the activation energy; A is the pre-exponential Arrhenius factor; T is the absolute temperature; $f(\alpha)$ is a function depending on the reaction kinetic model; P_C is the actual pressure of the gas self-generated in the reaction [1] at temperature T; and $P_{eq.}$ is the equilibrium pressure at the same temperature given by the Clausius-Clapeyron law

$$P_{eq} = Z \exp(-\Delta H/RT) \tag{3}$$

Z being a constant and ΔH being the reaction enthalpy.

On the other hand, the theoretical basis of both evolved gas analysis (EGA) and temperature-programmed desorption (TPD) techniques [5] indicates that the partial pressure of the gas C in the close vicinity of the sample at the reaction temperature is proportional to the reaction rate, i.e.

$$P_C = a\frac{d\alpha}{dt} \tag{4}$$

a being a constant. Therefore, from Eqs (1), (2) and (3) we get

$$\frac{d\alpha}{dt} = \frac{A \exp(-E/RT) f(\alpha)}{1 + \frac{a \cdot A}{Z} \exp\left[(\Delta H - E)/RT\right] f(\alpha)} \tag{5}$$

If the solid-state reaction is carried out at a linear heating rate, i.e. $\beta = dT/dt$, Eq. (5) can be numerically integrated. Therefore, theoretical $d\alpha/dt$ *vs.* T plots can be calculated in order to determine the influence of mass-transfer phenomena on the kinetics of solid-state reactions.

Analysis of the influence of the mass transfer phenomenon from simulated EGA curves of thermal decomposition reactions

The reaction

$$CaCO_3 \rightarrow CaO + CO_2$$

has been chosen for this analysis because values of the CO_2 equilibrium pressure, P_{eq}, at different temperatures have been reported in the literature

[6]. Therefore, it can be easily deduced from the data in [6] that between 500° and 1000° Eq. (3) is very closely fitted with $Z = 4.10^7$ atm and $\Delta H = 169$ kJ/mole.

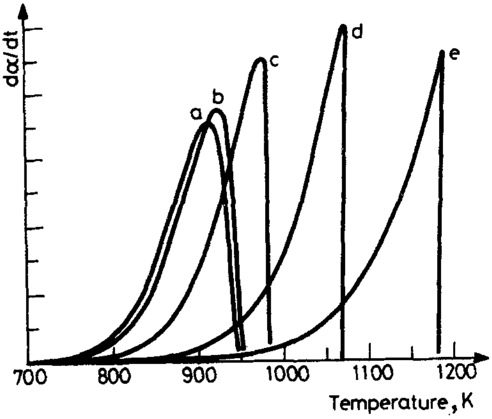

Fig. 1 Theoretical EGA curves constructed by assuming a contracting sphere kinetic model ($E = 167$ kJmole^{-1}, $A = 2\cdot10^8$min^{-1}) and different values of the parameters -*a*-

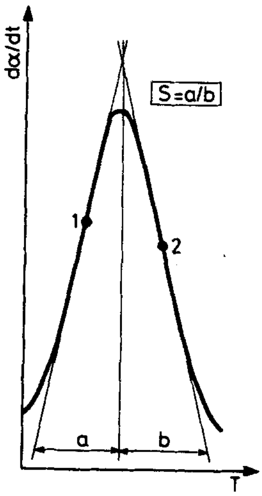

Fig. 2 Graphical method of the determination of the "Shape Index" *S* from a differential curve

Table 1 Theoretical values of the Kissinger's shape index, reaction order and activation energies as a function of the parameter -*a*-

a	*E*, KJ/mol	S	*n*	pressure at the peak mbar
0.0	167	0.35	0.70	0.09
0.1	168	0.30	0.60	1.20
1.0	169	0.01	0.33	11.40
10.0	168	0.00	0.06	126.20
80.0	168	0.00	0.00	760.00

On the other hand, it has been concluded previously [7] that the thermal decomposition of $CaCO_3$ under a high vacuum (i.e. $P_C/P_{eq} \cong 0$) obeys the "contracting sphere" kinetic model $f(\alpha)=(1\text{-}\alpha)^{2/3}$, yielding the following kinetic parameters: E = 167 kJ/mole and A = 2.10^8 min^{-1}.

Figure 1 shows the $d\alpha/dt$ *vs.* T plots calculated by integrating Eq. (5) by means of the Runge-Kutta algorithm after taking into account the above kinetic and thermodynamic parameters. The range of values of the constant a defined by Eq. (3) was chosen by considering that the pressure of CO_2 generated in the reaction cannot exceed 1 atm in EGA experiments carried out with a conventional open system under a controlled flow of the sweep gas.

The results in Fig. 1 show that, by increasing the constant a (i.e. by decreasing the efficiency of the experimental system for removing the gases yielded in the reaction), the EGA traces are shifted to higher temperatures.

On the other hand, Table 1 shows the values of the Kissinger shape index S [8] defined in Fig. 2. These results demonstrate that S decreases from S = 0.35 in the curve calculated with a = 0 to S = 0, if the EGA traces are simulated by assuming $a > 10$.

This behavior means [8] that, on increase of the value of the constant a the apparent reaction order changes from n = 2/3 to n = 0.

In order to prove the above conclusion, it would be interesting to analyze the data included in Fig. 1 according to the Freeman and Carroll kinetic equation [9]:

$$\frac{d\ln(d\alpha/dt)}{d\ln(1-\alpha)} = -\frac{E}{R}\,\frac{d(1/T)}{d\ln(1-\alpha)} + n \tag{6}$$

The left-hand side of Eq. (6), obtained from the different $d\alpha/dt$ *vs.* T traces in Fig. 1, is plotted as a function of the corresponding values of $d(1/T)/d\ln(1-\alpha)$. The calculated values of the apparent activation energy and the reaction order are shown in Table 1.

To summarize, the previous calculations show that the EGA curves move to higher temperatures and the apparent reaction order approaches zero as the efficiency of the system for avoiding mass-transfer phenomena decreases. However, the apparent activation energy seems to be independent of the parameter a.

Results

The EGA curves obtained for the thermal decomposition of $CaCO_3$ at a heating rate $\beta = 10$ deg/min and different flow rates of helium are shown in Fig. 3. The values of the apparent reaction order and activation energies obtained from these data are included in Table 2, together with the corresponding Kissinger shape indices calculated from the EGA traces.

Table 2 Values of activation energies, Shape index and reaction order as a function of helium flow rate, for the thermal decomposition of $CaCO_3$

Flow rates cc/min	E, kJ/mol	S	n
150	238	0.243	0.66
95	230	0.225	0.44
70	218	0.254	0.39
50	218	0.119	0.39
25	218	0.096	0.30

It would be expected that the efficiency of the experimental system to remove the gases self-generated in the reaction would increase on increase of the carrier gas flow; in other words, the constant a in Eq. (5) would decrease on increase of the helium flow rate. The fact that the peak temperature in Fig. 3 becomes lower on increase of the flow rate is in agreement with this statement. Moreover, the results in Table 2 demonstrate that the apparent reaction order of the thermal decomposition of $CaCO_3$ calculated from EGA experiments decreases on decrease of the helium flow rate while the activation energy remains nearly constant. This behaviour is in good agreement with that forecast from the theoretical calculations. The fact that the activation energies in Table 2 are about 20% higher than those

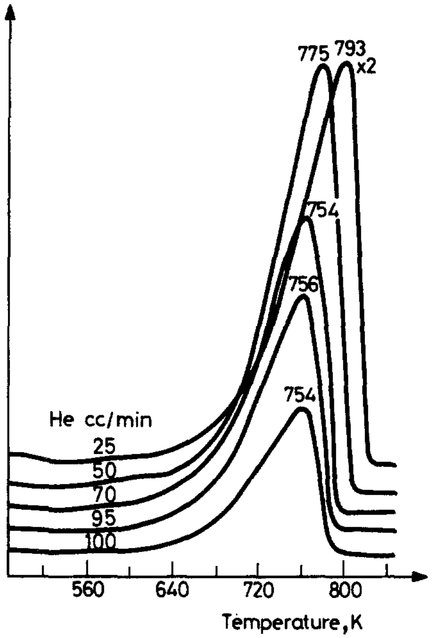

Fig. 3 EGA curves for the thermal decomposition of CaCO3, at different flow rates of He

calculated in the previous section can perhaps be explained in terms of the influence of the heat-transfer phenomenon on the reaction. This will be discussed in a subsequent paper.

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Zusammenfassung — Unter der Annahme der Proportionalität der partiellen Drücke der während der Reaktion entstehenden Gase zur Reaktionsgeschwindigkeit wurde eine theoretische Analyse des Einflusses von Stoffübergangserscheinungen auf die Gestalt von EGA-Kurven bei der thermischen Zersetzung von Feststoffen durchgeführt. Werden gasförmige Produkte vom System weniger wirksam abgegeben, verschieben sich die EGA-Kurven zu höheren Temperaturen und die scheinbare Reaktionsordnung n nähert sich Null, während die Aktivierungsenergie annähernd konstant bleibt. Die Feststellungen wurden experimentell überprüft.