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A differential method for kinetics of non-isothermal solid decomposition

A. Romero

Dto. Ingenieria Quimica, Facultad de Quimica, Universidad Complutense. 28040 Madrid (Spain)

E. Garcia Calvo *, P. Leton and M.A. Arranz

Ingenieria Quimica, Facultad de Ciencias, Universidad de Alcalá, 28871 Alcalá de Henares (Spain)

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Abstract

The kinetics of solid pyrolysis is widely studied for providing kinetic models for engineering purposes. A differential method for model discrimination which separates the influences of temperature and conversion is presented. This simple method is used to analyse, as an example, the kinetics of sodium bicarbonate decomposition. The experimental data of temperature- and conversion-influenced reaction rates are simulated with great accuracy.

INTRODUCTION

The kinetic analysis of thermogravimetric (TG) data is widely used for studying processes such as oil shale pyrolysis [1,2], conversion of heavy petroleum residuum to lighter products [3], preparation of catalysts, molecular sieves [4] or highly reactive solids [5], and pyrolysis of biomass [6].

A TGA apparatus allows use of small sample masses and so the effect of heat and mass transfer processes are usually eliminated. Other advantages of the TGA over tubular reactors are that the weight and the rate of thermal decomposition can be obtained at any instant [5].

In solid thermal decompositions, it is very difficult to establish an isothermal conditions before a substantial degree of the reaction has occurred [4]. That is why experiments with linear temperature change are preferred [7]. Three methods are usually applied to the analysis of nonisothermal data: differential [8], difference-differential [9] and integral [10] methods. The integral methods are the most widely used but they have two significant limitations: the integration of the temperature integral [11] and

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* Author to whom correspondence should be addressed.

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the determination of the kinetic model [12]. The approximation of the temperature integral has been widely treated [11,13,14]; however, it is difficult to correlate experimental TG data using the approximate integral equations because these equations establish a complex relationship between the temperature and the activation energy. The exact solution [15] of the temperature integral also has this disadvantage. Obtaining the kinetic model is an uphill task for all three methods [4,12].

The aim of this paper is to present a differential method which avoids the mentioned limitations. The approximation of the temperature integral is avoided by using reaction rates. The temperature and conversion influences can be separated taking values of reaction rate and conversion at a given temperature from experiments carried out at different heating rates. The method is used to analyse the kinetics of sodium bicarbonate decomposition. The results agree with those published.

EXPERIMENTAL

Sodium bicarbonate (Aldrich) ACS reagent was used. The decomposition behaviour of samples, weighing 10 ± 0.25 mg with a random distribution of solid in the sample pan, was observed in a DuPont model 951 Thermogravimetric Analyser (TGA) connected to a nitrogen flow control system which maintained a flow rate of 2 cm^3 s^{-1}. This gives an approximate linear velocity of 0.71 cm s^{-1} in the reaction chamber. The sample temperature was measured by a chromel–alumel thermocouple placed only a few millimetres from the sample. The weight variation of the sample and the derivative of this curve (TGD) were recorded as a function of the sample temperature.

The decomposition experiments were carried out at five different heating rates (0.6, 1.1, 2.3, 5.7 and 11.0 K min^{-1}). These heating rates were chosen to obtain r–α–T data in a wide temperature range and they are low enough to avoid thermal gradients in the sample.

RESULTS AND DISCUSSION

Figure 1 shows experimental r–T and α–T data for each of the five runs carried out at distinct heating rates. Sets of experimental r–α values at any given constant temperature can be easily obtained from this figure by intersecting both the α–T curve at constant β and its corresponding r–T curve with a vertical line drawn at constant T. The ordinates of the intersections are the α and r values respectively. Temperatures of 410, 415, 420, 425, 430 and 435 K were chosen to obtain at least four pairs of r–α values at each temperature.

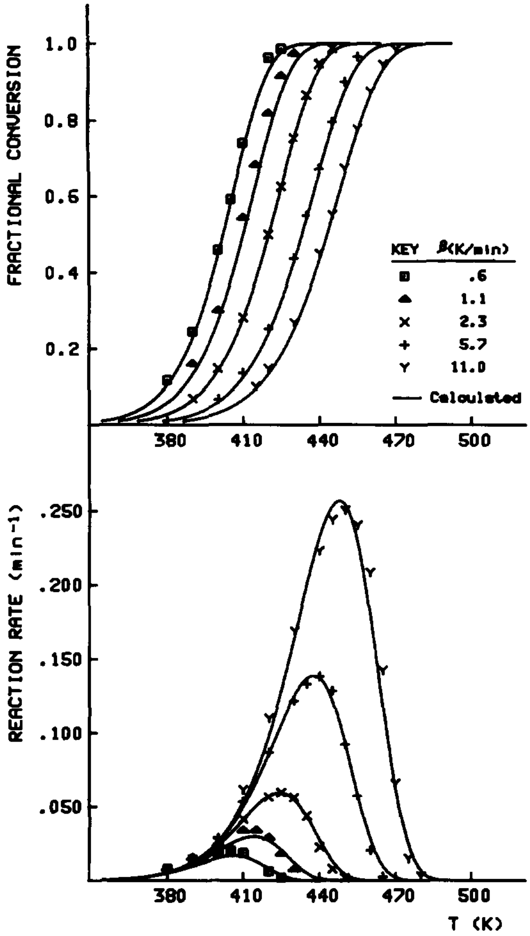

Fig. 1. Experimental and calculated data.

The general rate equation in solid decomposition is

$$r = \frac{d\alpha}{dt} = Kf(\alpha) \tag{1}$$

where K is the rate constant given by the Arrhenius equation

$$K = K_0 \exp(-E/RT) \tag{2}$$

The $f(\alpha)$ function depends on the kinetic model. Table 1 shows a list of typical models reported in the TGA literature and their corresponding $f(\alpha)$ functions. The R1 model is clearly discarded in the present case because at constant temperature it predicts constant decomposition rates and Fig. 1 shows that decomposition rates depend on conversion. Table 2 shows the parameters of the regression lines obtained by fitting r vs. $f(\alpha)$ for different decomposition models at each chosen temperature. We used the F test in order to discriminate between decomposition models. F_{cal} is obtained by

TABLE 1

Conversion functions of different kinetic models

Rate mechanism	Symbol	$f(\alpha)$	$g(\alpha)$
Nucleation and nuclei growth			
(a) Random nucleation	F1	$1-\alpha$	$-\ln(1-\alpha)$
(b) Two-dimensional nuclei growth	F2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$-[\ln(1-\alpha)]^{1/2}$
(c) Three-dimensional nuclei growth	F3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$-[\ln(1-\alpha)]^{1/3}$
Diffusion			
(a) One-dimensional transport	D1	$\alpha-1$	$\alpha^2/2$
(b) Two-dimensional transport (cylindrical geometry)	D2	$[-\ln(1-\alpha)]^{-2}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
(c) Three-dimensional diffusion (spherical geometry)	D3	$[(1-\alpha)^{-1/3}-1]$	$(3/2)[1-2\alpha/3-(1-\alpha)^{2/3}]$
Phase boundary reaction			
(a) One-dimensional (zero order)	R1	Constant	α
(b) Two-dimensional (cylindrical geometry)	R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
(c) Three-dimensional (spherical geometry)	R3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$

dividing the variance of the estimated decomposition rates about the mean of experimental values by the variance of experimental reaction rates about the regression lines. F_{tab} are the tabulated values at a probability level of 99%.

Only the F1 model allows the data to fit a straight line at any temperature (F_{cal} is larger than F_{tab} in any case). Using the R2 or R3 models the data fit straight lines at four or five temperatures respectively. Other models can clearly be discarded. The F1 model generates the intercepts nearest to zero in accordance with eqn. (1). The choice of the F1 model is clear by considering both the F test and the intercept values. In a recent paper, Hu et al. [5] also chose the F1 model to describe the kinetic behaviour of such a reaction.

The slopes obtained in the regression analysis are the rate constants K which are related to temperature in eqn. (2). We obtained $K_0 = 2.16 \times 10^{11}$ min^{-1} and $E = 98.81$ kJ mol^{-1}. The E value is very close to that obtained by Hu et al. [5] with the difference being less than 3%. The values of K_0 are not compared since the sample masses were different. Figure 1 shows the calculated r–T and α–T data using the obtained values of the kinetic parameters. To obtain the α–T curves, eqns. (1), (2) and (3) are taken into account

$$\beta = \frac{\mathrm{d}T}{\mathrm{d}t} \qquad (3)$$

TABLE 2

Discrimination between models

T(K)		Probed model							
(F_{tab})		F1	F2	F3	R2	R3	D1	D2	D3
410.0	Slope	0.590×10^{-1}	-0.417×10^{-1}	-0.485×10^{-1}	0.870×10^{-1}	0.725×10^{-1}	0.293×10^{-2}	0.292×10^{-2}	-0.717×10^{-1}
(34.1)	Intercept	0.379×10^{-2}	0.702×10^{-1}	0.840×10^{-1}	-0.264×10^{-1}	-0.112×10^{-1}	0.254×10^{-1}	0.270×10^{-1}	0.570×10^{-1}
	F_{cal}	72.5	0.4	4.1	55.6	61.7	12.5	12.8	29.7
415.0	Slope	0.834×10^{-1}	0.658×10^{-1}	-0.144×10^{-1}	0.109	0.949×10^{-1}	0.698×10^{-2}	0.692×10^{-2}	-0.644×10^{-1}
(34.1)	Intercept	0.395×10^{-2}	0.789×10^{-2}	0.625×10^{-1}	-0.270×10^{-1}	-0.114×10^{-1}	0.215×10^{-1}	0.256×10^{-1}	0.727×10^{-1}
	F_{cal}	90.8	0.7	0.0	50.3	62.7	17.2	18.3	17.2
420.0	Slope	0.118	0.111	0.631×10^{-1}	0.132	0.123	0.156×10^{-1}	0.153×10^{-1}	-0.445×10^{-1}
(34.1)	Intercept	0.307×10^{-2}	-0.657×10^{-2}	0.852×10^{-2}	-0.244×10^{-1}	-0.106×10^{-1}	0.997×10^{-1}	0.200×10^{-1}	0.864×0^{-1}
	F_{cal}	161.6	4.1	1.1	53.5	81.3	20.7	23.9	9.5
425.0	Slope	0.164	0.142	0.987×10^{-1}	0.166	0.160	0.324×10^{-1}	0.311×10^{-1}	-0.368×10^{-1}
(34.1)	Intercept	0.115×10^{-2}	-0.112×10^{-1}	-0.790×10^{-2}	-0.260×10^{-1}	-0.123×10^{-1}	-0.110×10^{-1}	0.113×10^{-1}	0.102
	F_{cal}	368.4	9.9	4.1	61.0	111.2	28.5	37.3	7.0
340.0	Slope	0.223	0.184	0.130	0.223	0.217	0.557×10^{-1}	0.527×10^{-1}	-0.582×10^{-1}
(98.5)	Intercept	0.117×10^{-2}	-0.197×10^{-1}	-0.185×10^{-1}	-0.379×10^{-1}	-0.184×10^{-1}	-0.282×10^{-1}	0.103×10^{-1}	0.136
	F_{cal}	502.5	8.9	3.6	42.3	83.5	24.1	34.5	6.2
435.0	Slope	0.297	0.213	0.152	0.260	0.267	0.998×10^{-1}	0.901×10^{-1}	-0.314×10^{-1}
(98.5)	Intercept	0.188×10^{-2}	-0.160×10^{-1}	-0.188×10^{-1}	-0.305×10^{-1}	-0.150×10^{-1}	-0.769×10^{-1}	-0.222×10^{-2}	0.143
	F_{cal}	3528.3	20.1	9.0	41.3	109.7	29.7	56.2	3.5

Combining these equation and integrating results in

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = g(\alpha) = \frac{K_0}{\beta} \int_{T_0}^{T} \exp\left(- \frac{E}{RT} \right) \mathrm{d}T \tag{4}$$

Simpson's rule ($\Delta T = 0.25$ K) was used to calculate the righthand side of eqn. (4). Once the α–T data are obtained for a given β, eqn. (3) is used to calculate the r–α curves.

This very simple method also satisfactorily analyses kinetic data from calcium carbonate decomposition, the model being R2 and $E = 209$ kJ mol^{-1}. This value is very similar to that proposed by Borgwardt [16]. Other kinetics such as cadmium carbonate decomposition (model F3, $E = 132$ kJ mol^{-1}) were also analysed with this method. In any case, discrimination between models is easy and the calculated data are very close to those of the experiment.

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APPENDIX: NOMENCLATURE

E	activation energy (kJ mol^{-1})
$f(\alpha)$	conversion influence in the decomposition rate
$g(\alpha)$	$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)}$
K	rate constant (min^{-1})
K_0	pre-exponential factor (min^{-1})
r	decomposition rate (min^{-1})
R	gas constant (kJ mol^{-1} K^{-1})
t	time (min)
T	temperature (K)
T_0	initial temperature (K)

Greek letters

α	fractional conversion
β	heating rate (K min^{-1})