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Kinetic analysis of non-isothermal solid decomposition reactions. An approach to the treatment of experimental data

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Abstract

The kinetics of non-isothermal solid decomposition should be studied with methods which separate the influences of temperature and conversion. Integral and differential methods are used to discriminate between models for both single and two controlling steps. The model and kinetic parameters corresponding to 14 solid decompositions or dehydrations are presented.

The distinct possibilities of non-isothermal techniques are briefly discussed.

LIST OF SYMBOLS

A	pre-exponential factor (min^{-1})
E	activation energy (kJ mol^{-1})
$f(\alpha)$	conversion influence on the decomposition rate
$g(\alpha)$	$= \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)}$
K	rate constant (min^{-1})
K'	constant defined in eqn. (6) (min^{-1})
r	decomposition rate (min^{-1})
R	gas constant (kJ mol^{-1} K^{-1})
t	time (min)
T	temperature (K)

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

Greek letters

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

Subscripts

c	calculated
0	initial
1	first step
2	second step

INTRODUCTION

A knowledge of the kinetic behaviour is necessary for predicting and understanding some important decomposition reactions in chemical processes, e.g. the preparation of catalysts and molecular sieves [1], coal and oil shale pyrolysis [2] and the thermal decomposition of woody material [3].

A solid decomposition occurs as a heterogeneous reaction; a kinetic analysis of this kind of reaction has to take into account several phenomena, such as the chemical reaction, the mass and heat transfer, and the physical changes in the solid [4].

Most of the methods developed to describe the kinetics of the thermal decomposition of solids usually introduce the following simplifying assumptions: the temperature at any point in the solid is the same as in the external fluid at each instant; and the controlling step in the reaction rate does not change throughout the transformation. The validity of these simplifications depends on the type of the reaction and how it has been carried out.

Kinetic studies are normally carried out in isothermal conditions and the influence of the extent of the reaction may be studied separately. In the thermal decomposition of solids, it is very difficult to establish an isothermal condition before a substantial degree of solid reaction has occurred in the solid [1]. This is the main reason why experiments are conducted under conditions of changing temperature (usually in a linear way) [5].

Several procedures have been developed to obtain the kinetic equation of solid decompositions assuming a single-step model. In such cases, the reaction rate is given as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Kf(\alpha) \tag{1}$$

where K is given by the Arrhenius equation

$$K = A\ \exp\left(-\frac{E}{RT}\right) \tag{2}$$

For a linear heating rate

$$T = T_0 + \beta t \tag{3}$$

Combining eqns. (1)–(3) and integrating

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

Integral methods, e.g. Coats and Redfern [6] and Van Krevelen et al. [7], are based on an approximate solution of the right-hand side of eqn. (4). The solution has to be simple enough to yield a linear expression relating temperature and conversion.

Differential methods, e.g. Freeman and Carroll [8] and Sharp and Wentworth [9], are based on the logarithmic form of eqn. (1) which yields straight lines.

Both integral and differential methods have two main disadvantages: the temperature and conversion influences are studied simultaneously although there is clearly interaction between them; sometimes solid decompositions, even in apparently very simple reactions, should be described assuming two controlling steps in the reaction rate, e.g. the calcium oxalate dehydration which is the most studied reaction using classical methods.

A method which we have proposed [10–12] separates the temperature and conversion influences by taking into account the differences between isothermal and dynamic experiments. A way to show these differences is by plotting both kinds of experiments in α–t–T coordinates.

Isothermal data plotted in α–t–T coordinates at infinite distinct temperatures generate a surface. This surface is different from that generated from non-isothermal data obtained at distinct heating rates. Figure 1 shows the intersection of the surface of non-isothermal data with planes of constant heating rate. The plane at constant T intersects the isothermal surface giving the FI curve and intersects the surface of non-isothermal data giving the FTT curve. The latter curve is used to study the conversion influence at constant temperature from dynamic experiments.

INTEGRAL ANALYSIS

Assuming a separable-variables model, the equation corresponding to the FTT curve may be written as [10]

$$g(\alpha) = K't \tag{5}$$

The relationship between T and K' is given by

$$K' = \frac{\int_{T_0}^{T} A \exp(-E/RT)\, \mathrm{d}T}{T - T_0} \tag{6}$$

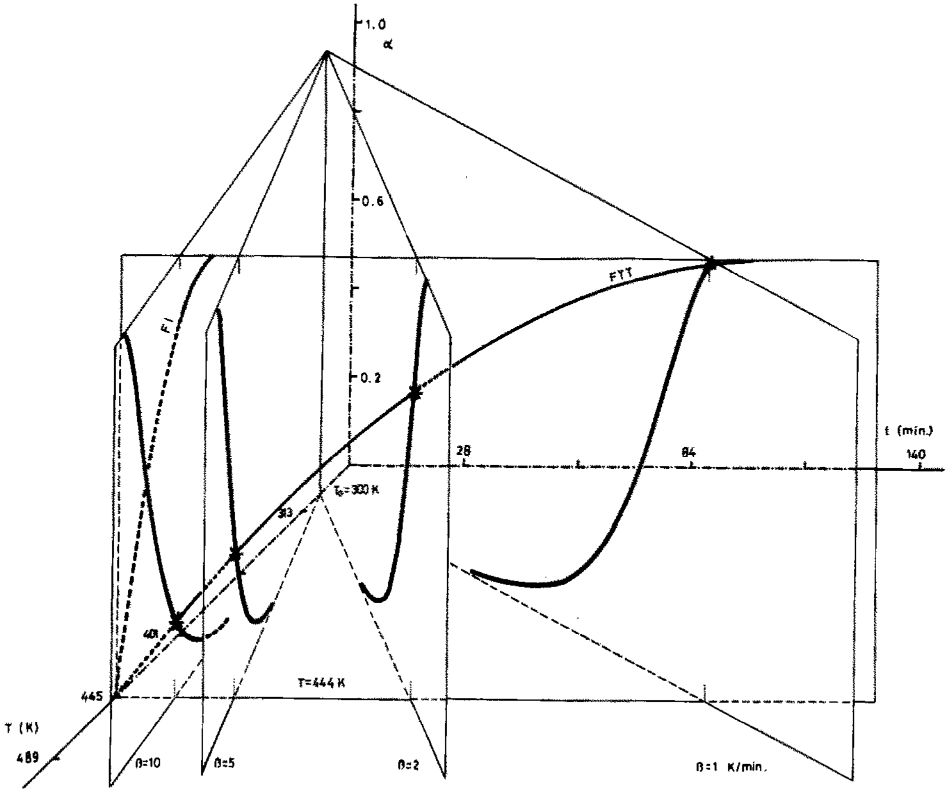

Fig. 1. Three-dimensional plot of isothermal and non-isothermal curves.

Clearly the temperature influence in these kinds of curves is different from that of the Arrhenius equation. The integration of the right-hand side of eqn. (6) has to be approximate. Experimental α–t data at a given T can be obtained from experiments carried out at different heating rates. The model which fits eqn. (5) with the α–t data is selected.

Analysing K' and taking into account the relationship between isothermal and non-isothermal surfaces, it is possible to calculate the kinetic parameters (A and E) and also the temperature at which an isothermal experiment would have the same α–t curve as that corresponding to the FTT curve [13].

An analysis with constant α [10] allows E and A to be calculated over a large range of temperatures or indicates whether the solid decomposition should be studied as a contribution of more than one controlling step.

The approximate integration of eqn. (4) gives

$$\frac{\beta}{RT^2} = \frac{A}{Eg(\alpha)} \exp\left(-\frac{E}{RT}\right) \tag{7}$$

If the reaction is controlled by a single step, plotting eqn. (7) in a logarithmic scale at constant α gives parallel straight lines [10]. However, if the lines are curves and/or they are not parallel, the observed kinetic parameters change with the conversion level and a two-step kinetic model has to be used to analyse experimental data.

The right-hand side of both eqns. (4) and (6) are integrated with simplifying assumptions in order to obtain the kinetic parameters. The main simplification in the approximate solution is to assume that

$$1-2\left(\frac{RT}{E}\right)+6\left(\frac{RT}{E}\right)^2-\ldots=1 \tag{8}$$

The higher the E value, the less the error; for low E and/or A, the differences between calculated and true values may be up to 30%.

Equations (9) and (10) may be used successfully to avoid the integral errors [14]

$$\ln E=0.0368+0.9991\ \ln(E)_c-0.0028\ \ln(A)_c +0.0000085[\ln(A)_c]^2 \tag{9}$$

$$\ln A=0.6269-0.0155\ \ln(E)_c+0.9702\ \ln(A)_c +0.00075[\ln(A)_c]^2 \tag{10}$$

These equations are useful over the whole range of E and A values and for any one-step model; they are also useful for any model.

DIFFERENTIAL ANALYSIS

An alternative method, which avoids the approximative integration, is the differential analysis. It is useful for experiments in which the DTG curves have different sizes at distinct heating rates and where all of them are high enough to obtain experimental data with accuracy.

Taking into account the values of reaction rate for non-isothermal analysis [12] and following the same criteria as the integral method, an analysis at constant T allows the kinetic model to be determined by plotting pairs of r–$f(\alpha)$ values at each temperature. The kinetic model for which $f(\alpha)$ gives straight lines with small or zero intercept at any temperature is chosen.

The slope of these lines is the kinetic constant and the kinetic parameters E and A may be calculated from eqn. (2). However, the narrow range of temperatures used to discriminate among models makes an analysis at constant conversion necessary. This analysis lets us calculate E and A in a large range of temperatures by plotting the equation

$$\ln f(\alpha)=\ln A-E/RT \tag{11}$$

If the reaction is controlled by a single step, eqn. (11) gives parallel straight lines; the E value may be obtained from the slope of the lines and the A values are obtained from the intercept.

If the lines are not straight and/or parallel, the reaction has more than one controlling step within the experimental range.

If the reaction may be described by a two-step in-series model, the reaction rate is [11]

$$\frac{1}{r} = \frac{1}{A_1 \exp(-E_1/RT) f_1(\alpha)} + \frac{1}{A_2 \exp(-E_2/RT) f_2(\alpha)} \tag{12}$$

An analysis at constant temperature gives pairs of r–α values in a small conversion range and a correlation of experimental data using multiple linear regression is difficult.

The discrimination is easier if the approximate values of the kinetic parameters are known. They may be obtained from the analysis (differential or integral) at constant conversion. In fact the observed kinetic parameters in the integral analysis at constant conversion depend on the true values and the relative influence of each step in each conversion level. Assuming a single controlling step at the beginning and the end of the reaction, the E and A values of each step may be obtained from those observed at different conversion levels and by extrapolation to $\alpha = 0$ and $\alpha = 1$.

Using the kinetic parameters obtained in this way and eqn. (12), it is possible to determine the functions $f_1(\alpha)$ and $f_2(\alpha)$, and then the optimal kinetic parameters may be obtained by non-linear regression.

In order to improve the extrapolation method, correlations between the extrapolated and observed values may be used [14].

EXPERIMENTAL

The manufacturers' specifications of the salts used in the decomposition studies are listed in Table 1.

TABLE 1

Sample compositions

Compound	Source	Assay (wt.%, min)
CaC_2O_4	Carlo Erba RPE	99% as $CaCO_3 \cdot H_2O$
$CdCO_3$	Aldrich	99.999%
$CaCO_3$	Carlo Erba RPE-ACS	99.5%
$Ca(OH)_2$	Aldrich ACS	98+%
$Mg(OH)_2$	Fluka	99%
$Cu(CH_3COO)_2 \cdot H_2O$	Fluka	99%

The experiments were carried out at five distinct heating rates (0.5, 1, 2, 5 and 10 K min^{-1}) with solid samples weighing 10 ± 0.1 mg. Other experimental details have been described previously [12].

RESULTS AND DISCUSSION

Figures 2 and 3 show, as examples, experimental and simulated α–T data for each of the five runs carried out at different heating rates for the decompositions of calcium oxalate (single step, integral analysis) and calcium hydroxide (two-step model, differential analysis) respectively.

Table 2 shows the conversion functions used widely in the literature.

A single-step model is valid for the decompositions of cadmium carbonate and calcium carbonate (see Table 3); a two-step model is necessary to describe the decompositions of calcium hydroxide and magnesium hydroxide and the dehydration of cupric acetate monohydrate.

Table 3 also shows the results of the kinetic analysis of reactions previously studied following these methods.

The results of the kinetic analysis of single-controlling-step solid decompositions which appear in Table 3 are obtained from both integral and differential analyses. Some of them were published previously following an integral analysis. The values of E and A are calculated as a mean of the results of both integral and differential analyses. The differences between these results are very small.

A differential kinetic analysis was used when the solid decompositions or dehydrations follow a two-step model. The approximate values of the

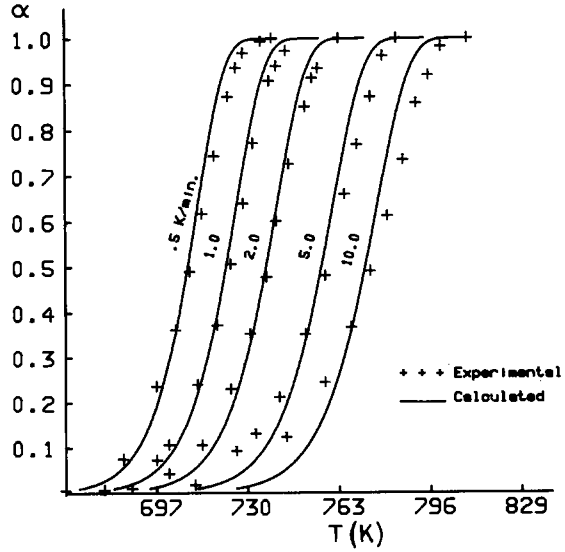

Fig. 2. Experimental and calculated α–T data for CaC_2O_4 decomposition.

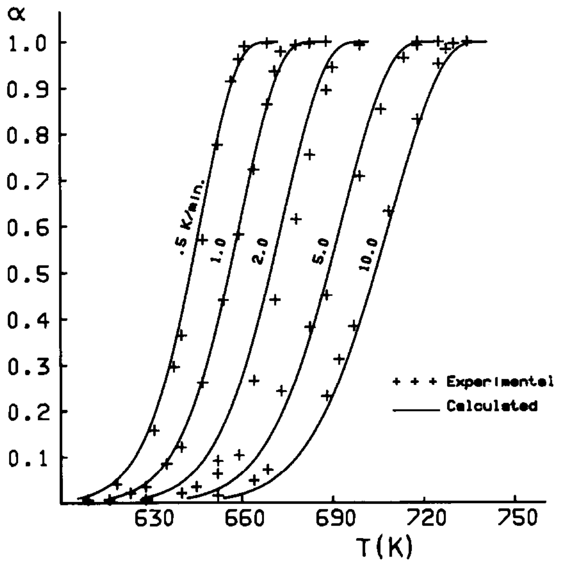

Fig. 3. Experimental and calculated $\alpha - T$ data for $Ca(OH)_2$ decomposition.

kinetic parameters were obtained from both differential and integral analyses. The latter was used previously for some of the reactions; the former is a new alternative method which yields similar results.

TABLE 2

Conversion functions of different kinetic models

Rate mechanism	Symbol	$f(\alpha)$	$g(\alpha)$
Nucleation and nuclei growth			
(a) Random nucleation	F1	$1\text{-}\alpha$	$-\ln(1-\alpha)$
(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	α^{-1}	$\alpha^2/2$
(b) Two-dimensional transport (cylindrical geometry)	D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
(c) Three-disional 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	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$

TABLE 3

Kinetic parameters and models for description of some solid decompositions

Decomposition or dehydration of	A_1 (min^{-1})	E_1 (kJ mol^{-1})	A_2 (min^{-1})	E_2 (kJ mol^{-1})	Model	Reference
CaC_2O_4	3.0×10^{12}	192.6	–	–	F3	This work
$CdCO_3$	1.0×10^{10}	129.6	–	–	R1	This work
$CaCO_3$	2.0×10^{9}	197.0	–	–	R2	This work
Calcite (99.5% $CaCO_3$)	1.9×10^{9}	193.8	–	–	R2	16
Aragonite (98.7% $CaCO_3$)	4.5×10^{4}	87.2	–	–	R2	17
$Zn(CH_3COO)\cdot2H_2O$	1.8×10^{11}	85.0	–	–	R3	18
$CaCO_3H$	2.2×10^{11}	98.8	–	–	F1	12
$Ca(OH)_2$	1.6×10^{15}	208.0	2.0×10^{9}	135.5	F2R3	This work
$Mg(OH)_2$	1.6×10^{12}	79.6	5.1×10^{6}	44.0	F1R2	This work
$Cu(CH_3COOH)_2\cdot H_2O$	3.0×10^{16}	61.5	8.7×10^{10}	244.6	F2R2	This work
$FeC_2O_4\cdot2H_2O$	5.5×10^{13}	121.0	6.0×10^{7}	78.9	F3R2	19
$Ni(CH_3COO)_2\cdot4H_2O$	1.0×10^{20}	137.0	2.1×10^{7}	60.0	F2R2	15
$CO(CH_3COO)_2\cdot4H_2O$	2.0×10^{15}	105.5	6.9×10^{3}	34.9	F2R2	15
$Mg(CH_3COO)_2\cdot4H_2O$	1.6×10^{18}	118.8	8.9×10^{6}	56.0	F2R2	15

The literature references cited in Table 3 indicate whether the kinetic analysis of the solid is new (this work) or has been previously published following one of the described methods, in which case the results of the kinetic analysis are confirmed following the alternative method.

CONCLUSIONS

Thermogravimetric data are easily analysed if the temperature and conversion influences are separated and if the reaction follows a simple or two-step model.

Some of the thermal decomposition reactions in chemical processes are accompanied by physical phenomena, namely, changes in the solid structure, influence of internal and/or external diffusion, etc. In such cases, the discrimination methods have to be improved. The discrimination method proposed in this work may be used in fluid-solid catalytic and non-catalytic reactions in order to determine the kinetic parameters of the chemical steps.

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