Thermochimica Acta, 122 (1987) 339–354
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

METHOD OF THE SELECTION OF THE g(α) FUNCTION BASED ON THE REDUCED-TIME PLOT

C. RÓŻYCKI *

Institute of Chemistry, Warsaw University of Technology Branch of Plock,
09-400 Plock (Poland)

M. MACIEJEWSKI

Institute of Basic Chemistry, Warsaw University of Technology, 00-662 Warsaw (Poland)

(Received 10 April 1987)

ABSTRACT

A method for the selection of the g(α) function describing the thermal decomposition of solids based on the reduced-time plot is proposed. This method allows more objective selection of the g(α) function best describing the experimental results from a mathematical point of view, when compared to the graphical method applied up to the present. With the use of variously defined values of reduced time, this method was applied to the investigation of the kinetics of the isothermal decomposition of $CaCO_3$ under nitrogen. The listing of a computer program enabling the carrying out of calculations and the making of plots is given.

INTRODUCTION

The results of kinetic investigations aiming at determining the relationship between the rate of thermal decomposition of solids and temperature are often helpful in drawing conclusions about the mechanism of this process. The above occurs because the f(α) function in the majority of cases is indispensable in determining such kinetic parameters as activation energy E or the pre-exponential factor A in the Arrhenius equation. The mathematical form of this function depends on theoretical assumptions connected with real physico-chemical phenomena that take place during thermal decomposition.

The rate of thermal decomposition is described by the equation

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \tag{1}$$

---

* Author to whom requests for the full listing of the computer program should be addressed.

0040-6031/87/$03.50

where α is the progress of decomposition, varying in the range 0–1, t is the time and $k(T)$ is the rate constant of the reaction for which the dependence on temperature is described by the use of the Arrhenius equation

$$k(T)=A\exp(-E/RT) \tag{2}$$

where A is the pre-exponential factor, E the activation energy, R the gas constant and T the temperature in K.

After the separation of variables and integration, equation (1) becomes

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)}=k(T)\int_0^t \mathrm{d}t \tag{3}$$

The expression $\int_0^\alpha[\mathrm{d}\alpha/\mathrm{f}(\alpha)]$ is denoted as $\mathrm{g}(\alpha)$ in the literature. The $\mathrm{f}(\alpha)$ and $\mathrm{g}(\alpha)$ functions constitute mathematical expressions derived on the basis of theoretical models of the mechanism of thermal decomposition. Under isothermal conditions the equation

$$\mathrm{g}(\alpha)=k(T)\ t=A\exp(-E/RT)\ t \tag{4}$$

shows the relation among the kinetic parameters A, E and $\mathrm{g}(\alpha)$.

The determination of the above equation enables the establishment of the relation between α and time, and thus enables prediction of the progress of the reaction as the function of time at constant temperature T. On the basis of experimental data the solution of this equation requires, however, the knowledge of the $\mathrm{g}(\alpha)$ function.

In the literature considering the kinetics of the thermal decomposition of solids, one of the significant issues not solved up to the present is the discovery of a method that enables the selection of the $\mathrm{g}(\alpha)$ function best describing experimental results. One such method was proposed by the authors of the present paper [1] and checked for the process of the thermal decomposition of calcium carbonate [2]. The method of selection of the $\mathrm{g}(\alpha)$ function presented in this article differs from methods applied up to the present, and is based on the so-called "reduced-time method" [3–8]. This kind of investigation of kinetic relations is based on the comparison of curves plotted in the system α–t_{red} (t_{red} is the "reduced time", generally the ratio $t/t_{0.5}$, where $t_{0.5}$ denotes the time of the progress of the decomposition $\alpha=0.5$ at the given temperature). If the experimental curves are transformed into this coordinate system, they are identical for experiments carried on at various temperatures, thus showing that one form of the $\mathrm{g}(\alpha)$ function describes the decomposition of the compound investigated (so-called iso-kinetics process). The selection of the $\mathrm{g}(\alpha)$ function is based on the comparison of experimental curves plotted in the α–t_{red} system with theoretical curves made for particular forms of the $\mathrm{g}(\alpha)$ function. Theoretical $\mathrm{g}(\alpha)$ models are derived for various assumptions concerning the mechanism of the process dealing with the rate-limiting stage (e.g. nucleation of a new solid phase, the reaction at the phase boundary between the product and reactant, or the diffusion of a gaseous product of reaction). The comparison of experimental and theoretical curves is simple because of the possibility of calculating the values of particular g(α) functions and comparing them to the ratio $t/t_{0.5}$ in relation to the progress of the decomposition α [3,7].

The selection of the g(α) function based on the comparison of the experimental curve with theoretical curves is very subjective. It is additionally made more difficult by the fact that for a number of functions plots are similar and various functions can be selected at various temperatures as best describing experimental data. This deficiency of "the reduced-time method" was often criticised [8–10].

The aim of this paper is to elaborate an objective method for the selection of the g(α) function that enables to select the function describing best the experimental data at all measuring temperatures used. The g(α) function selected in this way from the mathematical point of view enables the determination of kinetic parameters A and E, which makes possible the determination of the relation between α and time in isothermal measurements or between α and temperature for measurements made under rising temperature conditions.

BASIC THEORY

Graphical method of the selection of the g(α) function

Changing the scale of time in eqn. (4) one obtains

$$g(\alpha) = B(t/t_{0.5}) \qquad (5)$$

where $t_{0.5}$ is the time corresponding to $\alpha = 0.5$ and B is a constant depending on the form of the g(α) function.

The value B is calculated by substituting the value $\alpha = 0.5$ in the equation of the g(α) function. For example, for the function derived with the assumption that the rate-limiting stage is the reaction at the phase boundary and of the form

$$g(\alpha) = 1 - (1 - \alpha)^{1/3} \qquad (6)$$

one obtains after substituting $\alpha = 0.5$

$$1 - (1 - 0.5)^{1/3} = 0.2063 = kt_{0.5} \qquad (7)$$

and

$$k = 0.2063/t_{0.5} \qquad (8)$$

and

$$g(\alpha) = 1 - (1 - \alpha)^{1/3} = 0.2063t/t_{0.5} \qquad (9)$$

TABLE 1

Kinetic functions describing the thermal decomposition of solids used in the present paper and constants B calculated from eqn. (5)

Function No.	$g(\alpha)$	B		
		$\alpha = 0.25$	$\alpha = 0.50$	$\alpha = 0.75$
1	$1/(1-\alpha)-1$	0.3333	1.0000	3.0000
2	α^2	0.0625	0.2500	0.5625
3	$\alpha^{1/2}$	0.5000	0.7071	0.8660
4	$\alpha^{1/3}$	0.6300	0.7937	0.9086
5	$\alpha^{1/4}$	0.7071	0.8409	0.9306
6	$1-(1-\alpha)^{1/2}$	0.1340	0.2929	0.5000
7	$1-(1-\alpha)^{1/3}$	0.0914	0.2063	0.3700
8	$-\ln(1-\alpha)$	0.2877	0.6931	1.3863
9	$[-\ln(1-\alpha)]^{2/3}$	0.4358	0.7832	1.2433
10	$[-\ln(1-\alpha)]^{1/2}$	0.5364	0.8326	1.1774
11	$[-\ln(1-\alpha)]^{1/3}$	0.6601	0.8850	1.1150
12	$[-\ln(1-\alpha)]^{1/4}$	0.7324	0.9124	1.0851
13	$(1-\alpha)\ln(1-\alpha)+\alpha$	0.0324	0.1534	0.4034
14	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	0.0079	0.0367	0.1031
15	$[1-(1-\alpha)^{1/3}]^2$	0.0084	0.0426	0.1369

Table 1 shows the $g(\alpha)$ functions most often used in the literature and values of B corresponding to them and calculated from eqn. (5).

Up to the present time the method of selection of the $g(\alpha)$ function used has been based on the calculation for particular $g(\alpha)$ functions of the values of α, and then (with the use of eqn. (5)) the values of $t/t_{0.5}$. Theoretical plots (Fig. 1) are made for the pairs of values of α and $t/t_{0.5}$ thus obtained. Experimental data are plotted on the diagram with the same coordinate system. Time $t_{0.5}$ corresponding to $\alpha = 0.5$ is determined from a diagram of α_{exp} against time. If the thermal decomposition reaction under investigation is isokinetic, experimental data for various temperatures appear on the same curve and the theoretical plot of the selected $g(\alpha)$ function should show the best fit to the plot of the experimental data. This is judged by visual comparison of the two curves, and the method is called "graphical method of the selection of the $g(\alpha)$ function".

Numerical method of the selection of the g(α) function

The graphical selection of the $g(\alpha)$ function requires drawing corresponding plots and is based on a subjective evaluation of the "fit" of the theoretical plot to experimental data. The numerical method described below allows us to make an objective selection of the $g(\alpha)$ function for all temperatures used in the experiment.

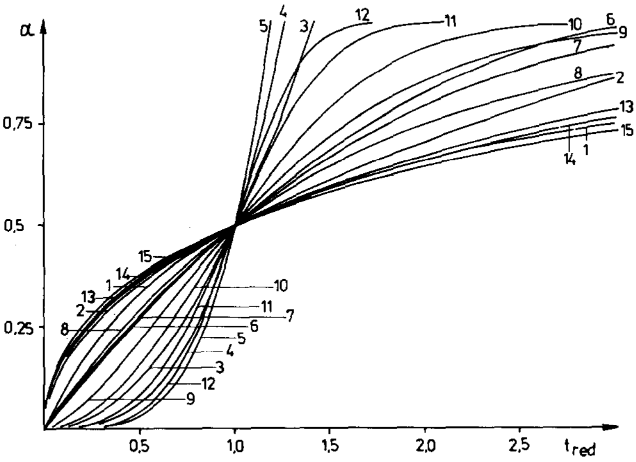

Fig. 1. Theoretical relationships between α and t_{red} for different $g(\alpha)$ functions; t_{red} calculated as the ratio $t/t_{0.5}$, where $t_{0.5}$ is the time at which the progress of the decomposition $\alpha = 0.5$. For designation of the functions see Table 1.

The data for calculation constitute the set of m pairs of values of the progress of the decomposition α and corresponding values of time t (for a particular temperature). If among experimental data the value $\alpha = 0.5$ occurs the determination of reduced times $t/t_{0.5}$ is simple. Otherwise the value $t_{0.5}$ can be calculated with the use of the least squares method of the following polynomial equation [11]

$$g(\alpha) = a_0 + a_1 t + a_2 t^2 + \ldots + a_n t^n \tag{10}$$

and the value $t_{0.5}$ can be calculated on this basis. The following equation is to be solved

$$0.5 = a_0 + a_1 t + \ldots + a_n t^n \tag{11}$$

The degree of a polynomial n is determined beginning with degree 1 (a straight line) up to the $(n+1)$th degree. Since the residual variance decreases for the polynomial from 1 to n degree and then increases, the degree of the polynomial n is determined for the minimum of the residual variance. After the calculation of $t_{0.5}$, the experimental reduced time $(t/t_{0.5})_{exp}$ for the experimentally determined values of the progress of the decomposition α_{exp} can be calculated. Theoretical reduced time $(t/t_{0.5})_i$, where i denotes the number of the $g(\alpha)$ function, can be calculated for the value α_{exp} from eqn. (5).

In order to select the $g(\alpha)$ function best describing the experimental data the following sum should be calculated

$$D_i = \sum_{j=1}^{m} \left[(t/t_{0.5})_{exp,j} - (t/t_{0.5})_{i,j} \right]^2 \tag{12}$$

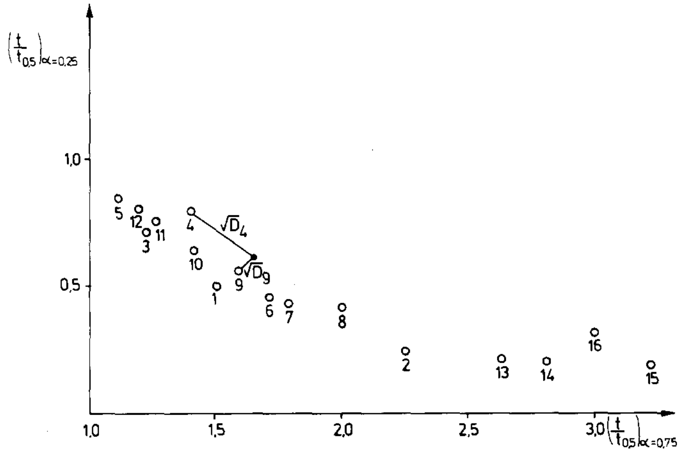

Fig. 2. The interpretation of the D_i criteria (see eqn. 12) for the case when two values of α are being considered. Theoretical points for different g(α) functions, ○; experimental points, ●.

The value D_i is calculated for particular temperatures and various functions denoted $i = 1, 2, \ldots, 15$, and simultaneously the value D_{sum} can be denoted being the sum of values D_i for particular temperatures. Thus the value of D_i constitutes the sum of squares of differences between experimental and theoretical values. D_i can be also interpreted as a square of the Euclidean distance between the point representing the experimental curve and the point representing the theoretical curve (center of gravity of the class) in a multidimensional space created by the axis of coordinates $(t/t_{0.5})$ for various values of α. In this case one should make use of notions connected with the pattern recognition method [12–14]. In the case when only two values of α (e.g. $\alpha = 0.25$ and $\alpha = 0.75$) are being considered the interpretation of D_i can be shown on the plane (Fig. 2). Each g(α) function corresponds to the theoretical point determined by two coordinates $(t/t_{0.5})_{i,\alpha=0.25}$ and $(t/t_{0.5})_{i,\alpha=0.75}$. The experimental point will have the following coordinates $(t/t_{0.5})_{\exp,\alpha=0.25}$ and $(t/t_{0.5})_{\exp,\alpha=0.75}$. The square of a distance between points corresponding to theoretical and experimental curves constitutes the measure of their fit and in this case is calculated with the use of the eqn. (12) for $m = 2$.

Regardless of the method of determination of the value of D_i, the selection of the most appropriate g(α) function resolves itself into the selection of the function with the minimum value of D_i, which equals zero in the case of an ideal conformity of the experimental and theoretical curves.

EXPERIMENTAL

The investigation of the process of the thermal decomposition of $CaCO_3$ (calcite) was carried out under nitrogen atmosphere. Experiments were made

TABLE 2

Experimental results of the isothermal decomposition of calcium carbonate under nitrogen atmosphere (temperature in K, time in min)

Temp. 928		Temp. 933		Temp. 943		Temp. 953		Temp. 963		Temp. 973		Temp. 993	
Time	α	Time	α	Time	α	Time	α	Time	α	Time	α	Time	α
1.95	0.058	1.80	0.057	1.50	0.057	0.83	0.057	0.75	0.057	0.68	0.057	0.60	0.059
3.98	0.116	3.75	0.114	3.00	0.114	1.88	0.114	1.73	0.113	1.20	0.114	0.90	0.118
5.85	0.174	5.40	0.170	4.35	0.170	2.85	0.170	2.40	0.170	1.88	0.171	1.35	0.176
7.65	0.231	7.13	0.227	5.55	0.227	3.75	0.227	2.85	0.226	2.48	0.228	1.88	0.235
9.45	0.289	8.70	0.284	6.75	0.284	4.65	0.284	3.90	0.283	3.08	0.285	2.33	0.294
11.25	0.347	10.35	0.341	7.95	0.341	5.63	0.341	4.65	0.339	3.75	0.342	2.85	0.353
13.05	0.405	11.93	0.398	9.23	0.398	6.68	0.398	5.48	0.396	4.34	0.400	3.30	0.412
15.00	0.463	13.58	0.455	10.50	0.455	7.65	0.455	6.23	0.452	5.10	0.457	3.75	0.471
16.88	0.521	15.30	0.511	11.78	0.511	8.70	0.511	7.05	0.509	5.70	0.514	4.28	0.529
18.90	0.579	17.10	0.568	13.20	0.568	9.90	0.568	7.80	0.566	6.45	0.571	4.80	0.588
20.85	0.637	18.75	0.625	14.55	0.625	10.95	0.625	8.70	0.622	7.13	0.628	5.40	0.647
22.88	0.694	20.55	0.682	15.83	0.682	12.15	0.682	9.60	0.679	7.88	0.685	5.93	0.706
24.90	0.752	22.50	0.739	17.25	0.739	13.35	0.739	10.43	0.735	8.55	0.742	6.60	0.765
27.00	0.810	24.45	0.795	18.67	0.795	14.48	0.795	11.40	0.792	9.30	0.799	7.35	0.824
29.25	0.868	26.55	0.852	20.17	0.852	15.83	0.852	12.75	0.848	10.05	0.856	8.18	0.882
31.65	0.926	28.80	0.909	21.68	0.909	17.25	0.909	13.35	0.905	10.95	0.913	9.15	0.941
34.35	0.984	31.43	0.966	23.63	0.966	18.75	0.966	14.85	0.962	11.85	0.970	9.75	0.965

TABLE 3

The value of D_i for respective temperatures and functions of g(α) calculated for the reduced time defined as $t_{\text{red}} = t/t_{0.5}$

Temp. 928		Temp. 933		Temp. 943		Temp. 953		Temp. 963		Temp. 973		Temp. 993	
No.	*D*	No.	*D*	No.	*D*	No.	*D*	No.	*D*	No.	*D*	No.	*D*
10	0.29	10	0.19	10	0.18	10	0.34	10	0.26	10	0.28	9	0.30
11	1.08	9	0.81	9	0.95	9	0.59	9	0.57	6	0.87	6	0.32
6	1.30	6	0.92	11	0.96	6	0.59	6	0.67	9	0.89	10	0.48
9	1.68	11	1.10	6	1.09	11	1.56	11	1.36	11	1.29	7	1.54
3	1.69	3	1.57	3	1.38	7	1.92	3	1.86	3	1.82	11	2.25
12	1.97	12	1.94	12	1.75	3	2.14	7	1.97	12	2.21	3	3.26
4	2.76	7	2.47	4	2.34	12	2.55	12	2.27	7	2.50	12	3.52
5	3.41	4	2.58	7	2.74	4	3.28	4	2.93	4	2.91	4	4.64
7	3.63	5	3.21	5	2.94	5	3.98	5	3.59	5	3.57	5	5.44
2	8.91	2	7.85	2	8.31	2	6.75	2	6.99	2	7.68	2	6.43
8	20.12	8	11.85	8	12.42	8	10.66	8	10.03	8	12.85	8	10.97
13	32.27	13	26.59	13	27.44	13	24.60	13	24.29	13	27.15	13	26.49
14	57.38	14	44.72	14	45.83	14	42.19	14	40.86	14	46.52	14	47.05
15	183.00	15	123.20	15	125.02	15	119.19	15	111.28	15	133.05	15	138.81
1	3577.97	1	777.50	1	781.60	1	769.47	1	600.59	1	1032.96	1	850.72

under isothermal conditions (temperature range 928–993 K) on a Mettler 2000 C thermoanalyser. The mass of samples was ~ 10 mg. Table 2 shows the times (in min) required at a given temperature, to attain corresponding values of the progress of decomposition α.

RESULTS AND DISCUSSION

Table 3 shows for particular temperatures the values of D_i determined on the basis of eqn. (12), thus for the reduced time calculated for $\alpha = 0.5$. This way of calculating reduced time with the use of $t_{0.5}$ is most often used in the literature without theoretical justification. It seems reasonable to check whether the application of reduced time defined differently will enable confirmation of the isokinetics of the process and influence the results of the selection of the g(α) function. Calculations were made with the use of the reduced time defined as $t_{\text{red}} = t/t_{0.25}$ and $t_{\text{red}} = t/t_{0.75}$, where $t_{0.25}$ and $t_{0.75}$ denote time during which the progress of the decomposition α, at a given temperature, attains the values 0.25 and 0.75 respectively. Theoretical plots of particular g(α) functions with the values of the reduced time defined this way are shown in Fig. 3 ($t_{\text{red}} = t/t_{0.25}$) and Fig. 4 ($t_{\text{red}} = t/t_{0.75}$).

The global comparison of the criterion D_{sum} for the reduced times defined differently are shown in Table 4. The values of $t_{0.25}$ and $t_{0.75}$ were calculated by the solution of the polynomial (eqns. 10, 11).

Figure 5 shows the three theoretical curves for the case when the selection of the g(α) function best describing experimental results is simple. In the case given experimental results are best described by function (10) (for the meaning of numbers see Table 1). The selection of the g(α) function is much

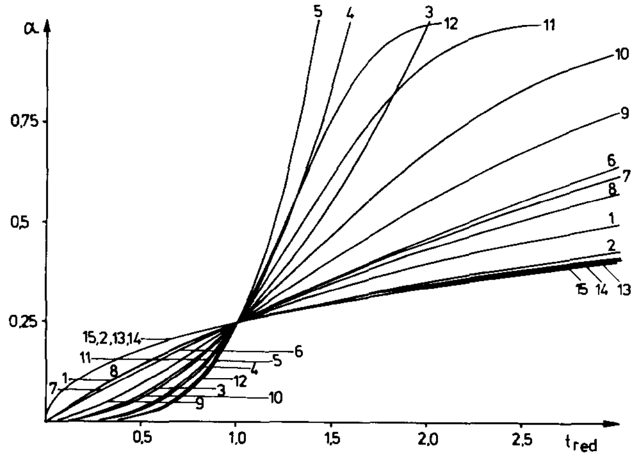

Fig. 3. Theoretical relationships between α and t_{red} for different g(α) functions; $t_{\text{red}} = t/t_{0.25}$.

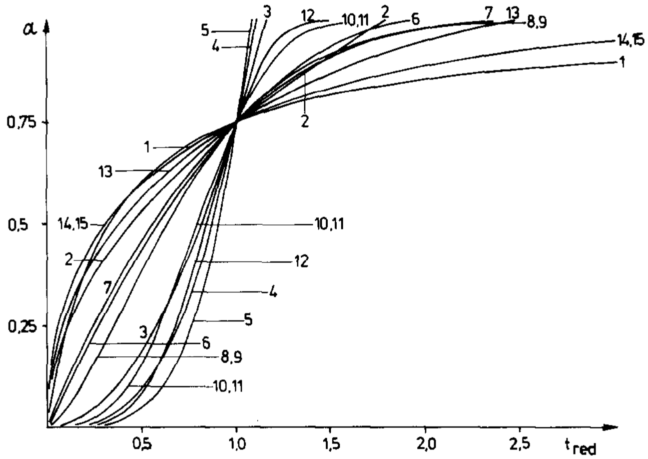

Fig. 4. Theoretical relationships between α and t_{red} for different g(α) functions; $t_{red} = t/t_{0.75}$.

more difficult when the curves in the system α–t_{red} differ slightly. This is presented in Fig. 6 where experimental points are described by the curves corresponding to g(α) functions of eqns. (6), (9) and (10) (see Table 1). In this case the graphical method of the selection of the function used up to the present does not allow objective results.

The issue of graphical selection of the g(α) function is more complicated when results obtained at various temperatures are being considered. Figures

TABLE 4

The values of D_{sum} calculated for variously defined reduced time t_{red}

$t_{red} = t/t_{0.25}$		$t_{red} = t/t_{0.50}$		$t_{red} = t/t_{0.75}$	
No.	D_{sum}	No.	D_{sum}	No.	D_{sum}
9	12.212	10	2.024	6	0.874
10	50.994	6	5.765	10	1.218
6	53.448	9	5.797	9	1.912
7	144.537	11	9.594	7	2.474
11	145.105	3	13.707	2	3.639
3	153.645	12	16.201	11	3.963
12	196.624	7	16.774	3	4.245
4	218.286	4	21.429	12	7.119
5	250.036	5	26.142	4	8.520
8	727.192	2	52.916	13	9.959
2	2825.367	8	88.901	5	11.791
13	8209.693	13	188.827	8	12.456
14	13197.180	14	324.552	14	16.543
15	35769.720	15	933.540	15	45.195
1	79883.630	1	8390.799	1	803.800

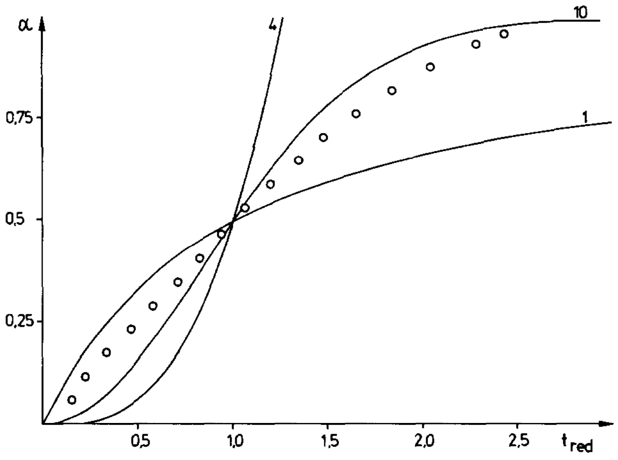

Fig. 5. Experimental results for decomposition of $CaCO_3$ at 993 K (○) described by three $g(\alpha)$ functions: (1), (4) and (10) (see Table 1); t_{red} calculated for $\alpha = 0.5$.

7 and 8 present global results for the thermal decomposition of $CaCO_3$ under nitrogen atmosphere at temperatures 928, 933, 943, 953, 963, 973 and 993 K. In Fig. 7 experimental points are described by the theoretical curve for function (10) i.e. $g(\alpha) = [-\ln(1-\alpha)]^{1/2}$ and in Fig. 8 by the theoretical curve for function (6) i.e. $g(\alpha) = 1 - (1-\alpha)^{1/2}$. The "numerical" method presented in this paper enables an objective selection of the function that mathematically best describes experimental results—the value D_{sum} is minimal for function (10) with reduced time defined $t_{red} = t/t_{0.5}$ (Table 4). The above could indicate that the mechanism of isothermal decomposition

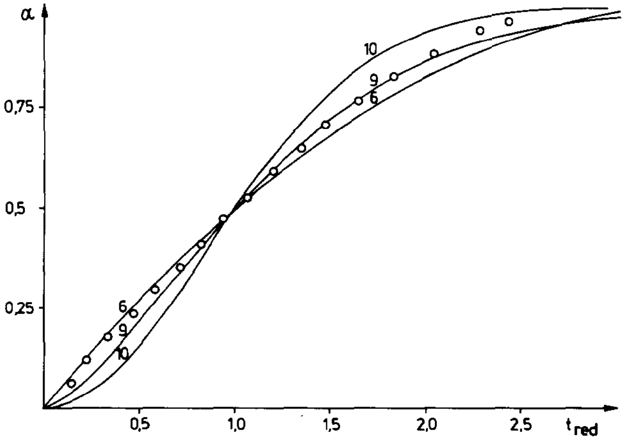

Fig. 6. Experimental results for decomposition of $CaCO_3$ at 993 K (○) described by $g(\alpha)$ functions (6), (9) and (10) (see Table 1); t_{red} calculated for $\alpha = 0.5$.

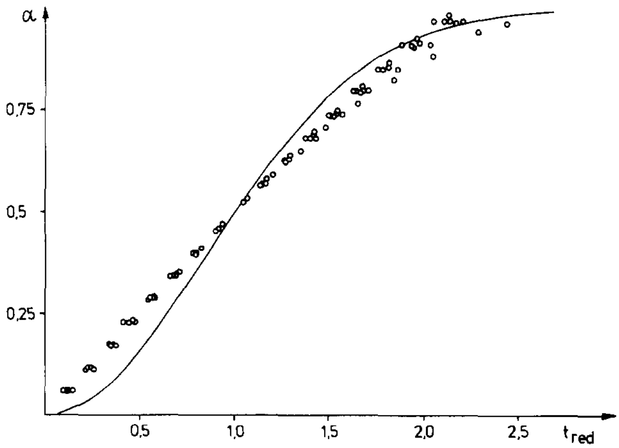

Fig. 7. Experimental results for decomposition of $CaCO_3$ in the temperature range 928–993 K described by the function $g(\alpha)=[-\ln(1-\alpha)]^{1/2}$; t_{red} calculated for $\alpha=0.5$.

of calcite under nitrogen is best described by the Avrami–Erofeev equation with the value of $n=2$.

The results included in this paper indicate, however, that conclusions about the mechanism of decomposition, based on the fact a given $g(\alpha)$ function describes the thermal decomposition better than others, should be drawn very carefully. Data included in Table 4 indicate for example, that the arbitrary selection of the way of defining the reduced time significantly changes the values of D_{sum} for particular functions and, what is even more significant, changes also their sequence.

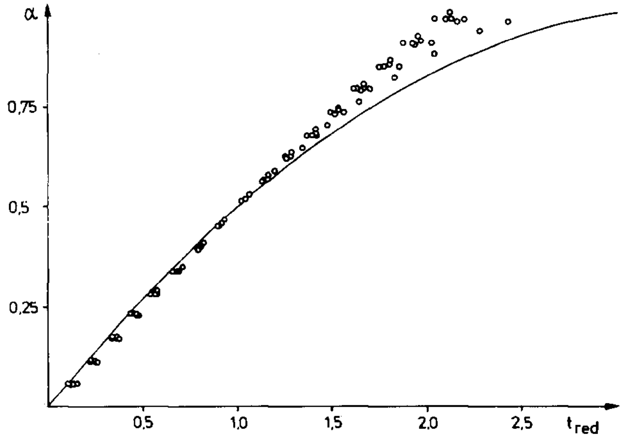

Fig. 8. Experimental results for decomposition of $CaCO_3$ in the temperature range 928–993 K described by the function $g(\alpha)=1-(1-\alpha)^{1/2}$; t_{red} calculated for $\alpha=0.5$.

According to the way of defining the reduced time other g(α) functions best describe experimental data. If $t_{red} = t/t_{0.25}$ results are best described by function (9) derived on the basis of the assumption of two-dimensional growth of nuclei under constant nucleation rate, or three-dimensional growth of a constant number of nuclei if the rate of nucleation is zero [15].

If the definition of t_{red} used is $t_{red} = t/t_{0.5}$ results are best described by function (10) (one- or two-dimensional growth of nuclei under conditions cited above). If $t_{red} = t/t_{0.75}$ the best fit is function (6) based on advance of the reaction interface (contracting area model). Thus, depending on the accepted way of calculating t_{red} the results based on various models of the real physico-chemical phenomena occurring during thermal decomposition appear to be "best".

Selecting the g(α) function by the method described in this paper, or by methods discussed previously [1,2], one of these functions (the best form for mathematical description of the experimental results) is chosen from their set. Any modification, from the mathematical point of view, of the method of calculation (in this case the change of t_{red} definition) does not influence significantly the fit of experimental data. It can, however, significantly change conclusions referring to the mechanism of reaction of thermal decomposition, making them less reliable.

The method of selection of the g(α) function proposed by the authors, based on the application of reduced time, enables the selection to be more objective in comparison with the graphical method currently used. The method, however, much the same as other kinetic investigations not based on morphological investigation or structural considerations [16], does not enable us to draw conclusions about the real mechanism of the thermal decomposition of solids.

DESCRIPTION OF THE PROGRAM

The results in Tables 2–4 and Figs. 5–8 were obtained using a program written in BASIC (for IBM PC or compatible; operating system MS DOS). The listing of the main part of program is presented in Fig. 9. The full listing of the program can be obtained from the first-named author.

The execution of the program begins with defining reduced time by giving the appropriate value of α (line 130). Next, experimental data (from the keyboard or as block data): number of sets (temperatures), and for a particular set: the value of temperature, global mass loss and pairs of time and mass loss (no more than 20 pairs, the set ending with the pair 0,0) are loaded (lines 140–160). If necessary values loaded incorrectly can be corrected (lines 270–340). On the basis of these data the values of α_{exp} (lines 240 and 320) are calculated. After printing experimental data (if necessary) and after declaring the arrays (lines 350–400) the program calculates the value of time corresponding to the value of α (line 450) previously selected, the value of D_i for particular temperatures and the global criterion D_{sum} (the program allows print-out of ordered values of the criterion). The program will plot the relation between α and t_{red} within the range of t_{red} calculated from experimental data or assumed (0–3.0) (α range: 0–1.0) for arbitrarily selected g(α) functions and temperature (lines 480–640). Charts can also be plotted for the range of the values of α arbitrary chosen (lines 650–680). It is also possible to redraw charts for some other temperatures and g(α) functions (lines 690–710). Next the program establishes the sequence of the global criteria and enables drawing plots of the relation between α and t_{red} (lines 720–950). After finishing the calculations one can change the way of defining reduced time (lines 950–980) or can check and modify experimental data if necessary.

```
100 REM Thermal analysis. Time reduced method.
110 CLS: ' Data input
114 PRINT "ATTENTION": PRINT " For each temperature (set) ";
115 PRINT "max.20 pair of measurments: time, mass loss.": PRINT
120 OPTION BASE 1: KEY OFF: NUMTAB=0: NUMFIG=0
130 PRINT "What " ;:PRINT CHR$(224);
131 INPUT " is used for reduced time calculation";ALFAS
140 READ L  ' numbers of temperatures (sets)
150 DIM TEMP(L), NUMEXP(L) ' NUMEXP(I) - numbers of data in i-th set
160 DIM ALEXP(L,20),TIEXP(L,20) ' experimental values of alpha and time
170 FOR I=1 TO L
180 CLS: PRINT "Set";I;: READ TEMP(I): PRINT " temperature";TEMP(I)
190 READ FML: PRINT  "Final mass loss:";FML
200 FOR J=1 TO 20
210 READ TIEXP(I,J), ML   ' ML - exp. mass loss at time TIEXP(I,J)
220 IF ML=0 AND TIEXP(I,J)=0 THEN GOTO 270
230 ALEXP(I,J)=ML/FML
240 PRINT J,:PRINT USING "time ##.##,  mass loss ##.###,  ";TIEXP(I,J),ML;
241 PRINT USING "alpha ##.####";ALEXP(I,J)
250 NUMEXP(I)=NUMEXP(I)+1
260 NEXT J
270 PRINT "Data correct? y/n"
280 A$=INKEY$:IF A$=""THEN 280
290 IF A$="y" THEN GOTO 340 ELSE IF A$<>"n" THEN GOTO 280
310 INPUT "Input correct data: nr, time and mass loss";A,TIEXP(I,A),ML
320 ALEXP(I,A)=ML/FML: GOTO 270
340 NEXT I
350 PRINT "Printing ";:PRINT CHR$(224):
351 INPUT " experimental data (no more then 7 sets)?  y/n";PR$
360 IF PR$="y" THEN GOSUB 4120 ELSE IF PR$="n" THEN GOTO 380 ELSE GOTO 350
370 REM Declaration of tables
380 DIM B(7), A(7,7), P(7,7), COEF(7), TIALS(L), TIRED(L,20), K(15)
390 DIM DIS(15,L), ORD(15,L), SUM(15), ORDSUM(15), GRAPH(15)
400 FOR I=1 TO L:TIALS(I)=0: FOR J=1 TO 20: TIRED(I,J)=0: NEXT J:NEXT I
405 FOR I=1 TO 15: SUM(I)=0 : NEXT I
410 REM Time (TIALS(I)) calculations corresponding to ALFAS
420 GOSUB 1130   ' Polynomial and TIALS(I) calculations
460 REM Calculations of criteria
470 GOSUB 2320   ' Calc. of K(I), DIS(I,J), SUM(I) and screening
480 PRINT "Make a plot for selected temperature? y/n"
490 PRINT "When the plot is complete: PrtSC or hit any key."
500 A$=INKEY$: IF A$=""THEN GOTO 500   'Printing screen
510 IF A$="y" THEN GOTO 520 ELSE  IF A$<>"n" THEN GOTO 500 ELSE GOTO 720
```

Fig. 9. The listing of the main part of the program.

```
520 FOR I=1 TO 15: GRAPH(I)=0: NEXT I
530 NUMFIG=NUMFIG+1
540 PRINT "Input numbers of selected functions." :NUMFUN=0
550 INPUT "Function no or 0";NR
560 IF NR<0 OR NR>15 THEN GOTO 550
570 IF NR<>0 THEN GRAPH(NR)=1: NUMFUN=NUMFUN+1: GOTO 550
580 INPUT "Set nr ";D
600 GOSUB 2820   ' Selecting of extreme value of x and y
610 GOSUB 2940   ' Drawing of axis
620 GOSUB 3150   ' Drawing of given functions
630 GOSUB 3300   ' Drawing of experimental data
640 A$=INKEY$: IF A$="" THEN GOTO 640    ' Printing screen
650 LOCATE 24,1: PRINT "Another scale of the plot? y/n"
660 A2$=INKEY$: IF A2$="" THEN GOTO 660
670 IF A2$="y" THEN GOSUB 3410 ELSE IF A2$<>"n" THEN GOTO 660
680 IF A2$="y" THEN NUMFIG=NUMFIG+1: GOTO 610
690 CLS: SCREEN 0: PRINT "Print another plot? y/n"
700 A$=INKEY$: IF A$="" THEN GOTO 700
710 IF A$="y" THEN GOTO 480 ELSE IF A$<>"n" THEN GOTO 700
720 REM Ordering and display of global criteria
730 GOSUB 3560
740 PRINT "Make a plot for global criterion? y/n"
750 PRINT "When the graph is complete: PrtSc or hit any key."
760 A$=INKEY$: IF A$=""THEN GOTO 760
770 IF A$="y" THEN GOTO 780 ELSE  IF A$<>"n" THEN GOTO 760 ELSE GOTO 960
780 NUMFUN=0: FOR I=1 TO 15: GRAPH(I)=0: NEXT I
790 NUMFIG=NUMFIG+1
800 PRINT "Input numbers of functions."
810 INPUT "Function no or 0";NR
820 IF NR<0 OR NR>15 THEN GOTO 800
830 IF NR<>0 THEN GRAPH(NR)=1: NUMFUN=NUMFUN+1: GOTO 810
840 GOSUB 3740  ' Selection of extreme value of x and y
850 GOSUB 2940  ' Drawing axis
860 GOSUB 3150  ' Drawing of selected functions
870 GOSUB 3880  ' Drawing experimental points
880 A$=INKEY$: IF A$="" THEN GOTO 880    ' Printing screen
890 LOCATE 24,1: PRINT "Another scale of the plot? y/n"
900 A2$=INKEY$: IF A2$="" THEN GOTO 900
910 IF ALFAS=0 THEN GOTO 990 ELSE GOTO 400
920 IF A2$="y" THEN NUMFIG=NUMFIG+1: GOTO 850
930 CLS: SCREEN 0: PRINT "Print another plot? y/n"
940 A$=INKEY$: IF A$="" THEN GOTO 940
950 IF A$="y" THEN GOTO 740 ELSE IF A$<>"n" THEN GOTO 940
960 CLS: PRINT "The calculations were done for ";CHR$(224);"=";ALFAS;"."
970 PRINT :PRINT "Input another value of ";CHR$(224);" or 0";:INPUT ALFAS
980 IF ALFAS<0 OR ALFAS>1 THEN GOTO 970
981 IF ALFAS=0 THEN GOTO 990 ELSE GOTO 400
990 PRINT "May be you wish to verify the data? y/n"
1000 A$=INKEY$: IF A$="" THEN GOTO 1000
1010 IF A$="t" THEN GOTO 4000 ELSE IF A$<>"n" THEN GOTO 1000
1020 CLS: PRINT "HAPPY END.":END
```

Fig. 9 (continued).

REFERENCES

1 C. Różycki and M. Maciejewski, Thermochim. Acta, 96 (1985) 91.

2 C. Różycki and M. Maciejewski, Proceedings of the Fourth Polish Symposium on Thermal Analysis, Płock, Poland, 1986, p. 21.

3 J.H. Sharp, G.W. Brindley and B.N.N. Achar, J. Am. Ceram. Soc., 49 (1966) 379.

4 J.D. Hancock and J.H. Sharp, J. Am. Chem. Soc., 52 (1969) 591.

5 K. Kishore, Thermochim. Acta, 19 (1977) 226.

6 K. Kishore, Indian J. Chem., 16A (1978) 553.

7 C.J. Keattch and D. Dollimore, An Introduction to Thermogravimetry, Heyden, 2nd edn., 1975, p. 66.
8 B. Delmon, Introduction à la cinétique hétérogène, Technip, Paris, 1964.
9 P. Barret, Cinétique hétérogène, Gauthier-Villars, Paris, 1973.
10 E. Giess, J. Am. Chem. Soc., 46 (1963) 374.
11 K.J. Johnson, Numerical Methods in Chemistry, Marcel Dekker, New York, 1980.
12 K. Varmuza, Anal. Chim. Acta, 122 (1980) 227.
13 B.R. Kowalski and C.F. Bender, J. Am. Chem. Soc., 94 (1972) 6532.
14 G. Boulle and J. Peisach, J. Radioanal. Chem., 50 (1979) 205.
15 T.J.W. de Bruijn, W.A. de Jong and P.J. van den Berg, Thermochim. Acta, 45 (1981) 315.
16 A. Reller and H.R. Oswald, J. Therm. Anal., 29 (1984) 1013.