

## COMPARISON OF METHODS CONCERNING THE SELECTION OF A FUNCTION DESCRIBING THE THERMAL DECOMPOSITION OF SOLIDS

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### ABSTRACT

Determination of the kinetic parameters of the thermal decomposition of solids usually requires a knowledge of the function describing the mechanism of decomposition. Research was made to obtain a method that enables the selection of one of the 16 functions used in the literature in such a way that it best describes experimental data in the isothermal measurements. The results obtained indicate that the best fit of experimental and calculated data is gained by using the weighted least-squares method with the equation  $g(\alpha) = kt + b$  and using criteria based on the minimization of the difference between  $\alpha_{\text{exp}}$  and  $\alpha_{\text{calc}}$ .

### INTRODUCTION

The determination of kinetic parameters of the thermal decomposition of solids, such as the apparent activation energy,  $E$ , Arrhenius pre-exponential factor,  $A$ , or the reaction order,  $n$ , requires the knowledge of a function describing the mechanism of the process investigated. The determination of this function, defined in the literature as  $f(\alpha)$  in the differential form, or  $g(\alpha)$  in the integral form, is made by testing which theoretical model of the thermal decomposition mechanism best describes the experimental data. Of the methods most often used for the identification of the equation of a function that gives the best fit to the experimental data are:

- (1) linearity in a system  $g(\alpha) - t$  ( $t = \text{time}$ );
- (2) comparison of plots theoretically obtained with the assumption of particular models of the  $g(\alpha)$  function with experimental data; the plots are applied in systems:  $\alpha - t_r$  ( $t_r = \text{the reduced time, which is the ratio } t/t_{0.5}$ , where  $t_{0.5}$  is the time at which the progress of the decomposition,  $\alpha = 0.5$ ),  $d\alpha/dt - t$ ,  $d\alpha/dt - \alpha$ .

Mathematically, the  $g(\alpha)$  function, determined with the use of one of these methods, best describes the reaction of thermal decomposition. The

knowledge of this function can be a certain premise of the investigation of a mechanism of reaction. Putting aside the question of whether the knowledge of only a mathematical form of the  $g(\alpha)$  function gives any information on real physico-chemical phenomena occurring during the thermal decomposition, one should notice that the exact selection of this function can significantly influence the results of kinetic calculations; e.g., during the calculation of kinetic parameters with the use of the Arrhenius equation, experimental data will determine two different values of rate constants for two different  $g(\alpha)$  functions, and then in the system of  $\ln k-1/T$  ( $T$  = temperature, K) can give two various values of the activation energy,  $E$ . In Criado and Gonzales' work [1] three  $g(\alpha)$  functions based on completely different theoretical assumptions having the same high correlation coefficient (higher than 0.9990) gave various values of the activation energy for the decomposition of cadmium carbonate (31.9, 39.8 and 71.3 kcal mol<sup>-1</sup>). The above example, being one of several to be found in the literature, indicates that attributing a physico-chemical meaning to the  $g(\alpha)$  function can arouse some doubts. For that reason research is necessary on a method enabling the selection of the  $g(\alpha)$  function in order to obtain the best fit of experimental data. Only in this case will the value of the activation energy calculated on its basis most precisely characterise the influence of temperature on the rate of thermal decomposition. In this work the problem of the determination of the  $g(\alpha)$  function giving the best fit of experimental data was restricted to isothermal measurements only since this issue in dynamic measurements with rising temperature arouses many doubts [2,3].

## BASIC THEORY

### *Selection of the straight-line model*

Assuming that the error connected with the determination of time is significantly smaller than the error of the determination of the value of the progress of the decomposition, the least-squares method (LSM) can be used for defining the rate constant as a slope of the straight line in the coordinate system  $g(\alpha)-t$ .

According to the relationship accepted in the literature, the kinetic equation in the integrated form is as follows

$$g(\alpha) = kt \tag{1}$$

This form of representation seems to suggest the application of the LSM to the relationship  $y = ax$  (model 1). The second possibility is the use of the LSM with the relationship  $y = ax + b$  (model 2).

The latter possibility seems to be more correct since:

(1) in the initial stage of measurement, errors connected with unstabilized experimental conditions can occur;

(2) the deviation of experimental points ( $g(\alpha)$  values) in relation to equations of the type  $y = ax + b$  can be smaller than for those of the type  $y = ax$ .

### *Selection of weights*

One of the assumptions of usual LSM is the assumption of the constant variation of the dependent variable (in our case  $g(\alpha)$ ). In the case when this assumption is not fulfilled, the weighted method of least squares should be applied.

The weights used most often are the inverse of the deviation of the dependent variable [4].

The deviation of  $\alpha$  can be estimated in the following way: the fraction reacted is calculated from the relation

$$\alpha = \frac{\Delta m}{\Delta m_f} \quad (2)$$

where  $\Delta m_f$  = final mass loss (means complete decomposition of the sample),  $\Delta m$  = mass loss at time  $t$ . The deviation can be calculated on the basis of  $\Delta m$  and  $\Delta m_f$  using the propagation of error [5]

$$s_\alpha^2 = s_{\Delta m}^2 \left( \frac{\partial \alpha}{\partial \Delta m} \right)^2 + s_{\Delta m_f}^2 \left( \frac{\partial \alpha}{\partial \Delta m_f} \right)^2 \quad (3)$$

One can assume that the deviation  $s_{\Delta m}^2 = s_{\Delta m_f}^2 = s^2 = \text{const}$ . From eqn. (3), after calculating corresponding partial derivatives, one obtains

$$s_\alpha^2 = s^2 \frac{1}{\Delta m_f^2} (1 + \alpha^2) \quad (4)$$

Multiplication of the deviation by a constant value does not influence the results of calculations [6], thus, since  $s^2$  and  $\Delta m_f^2$  are constant values, for weights calculation, one can use

$$s_\alpha^2 = 1 + \alpha^2 \quad (5)$$

The second reason of the use of weighted LSM is connected with the fact that rate constants,  $k$ , are determined from the linear relationship of the  $g(\alpha)$  value with time,  $t$ . Transforming  $\alpha$  into  $g(\alpha)$ , one should also correspondingly transform  $s_\alpha^2$  into  $s_{g(\alpha)}^2$ . The deviation of  $g(\alpha)$  is calculated from the formula

$$s_{g(\alpha)}^2 = s_\alpha^2 \left( \frac{g(\alpha)}{\alpha} \right)^2 \quad (6)$$

TABLE 1

Kinetic functions for description of the thermal decomposition of solids used in the present paper

Function No.	$g(\alpha)$	Deviation of $g(\alpha)$
1	$\alpha^2$	$4\alpha^2 s_\alpha^2$
2	$\alpha^{1/2}$	$s_\alpha^2/(4\alpha)$
3	$\alpha^{1/3}$	$s_\alpha^2/(9\alpha^{4/3})$
4	$\alpha^{1/4}$	$s_\alpha^2/(16\alpha^{3/2})$
5	$1-(1-\alpha)^{1/2}$	$s_\alpha^2/(4-4\alpha)$
6	$1-(1-\alpha)^{1/3}$	$s_\alpha^2/[9(1-\alpha)^{4/3}]$
7	$-\ln(1-\alpha)$	$s_\alpha^2/(1-\alpha^2)$
8	$[-\ln(1-\alpha)]^{2/3}$	$4s_\alpha^2/\{3(1-\alpha)[-\ln(1-\alpha)]^{1/3}\}^2$
9	$[-\ln(1-\alpha)]^{1/2}$	$s_\alpha^2/\{4[-\ln(1-\alpha)](1-\alpha)^2\}$
10	$[-\ln(1-\alpha)]^{1/3}$	$s_\alpha^2/\{3[-\ln(1-\alpha)]^{2/3}(1-\alpha)\}^2$
11	$[-\ln(1-\alpha)]^{1/4}$	$s_\alpha^2/\{4[-\ln(1-\alpha)]^{4/3}(1-\alpha)\}^2$
12	$(1-\alpha)\ln(1-\alpha)+\alpha$	$s_\alpha^2[-\ln(1-\alpha)]^2$
13	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$4s_\alpha^2/\{3[(1-\alpha)^{-1/3}-1]\}^2$
14	$[1-(1-\alpha)^{1/3}]^2$	$4s_\alpha^2[1-(1-\alpha)^{1/3}]^2/[3(1-\alpha)^{2/3}]^2$
15	$\ln \alpha/(1-\alpha)$	$s_\alpha^2/[\alpha(1-\alpha)]^2$
16	$1/(1-\alpha)-1$	$s_\alpha^2/(1-\alpha)^4$

and for weights used for the calculation of rate constants,  $k$ , for particular  $g(\alpha)$  functions, the following is used

$$w = \frac{1}{s_{g(\alpha)}^2} \quad (7)$$

Formulae on the basis of which  $s_{g(\alpha)}^2$  were calculated are shown in Table 1.

### *Selection of the function $g(\alpha)$*

Values most often used for the selection of  $g(\alpha)$  which best describe experimental results are: the correlation coefficient (for values of  $g(\alpha)$  and  $t$ ); the deviation of the regression coefficient of the straight line or the deviation of experimental  $g(\alpha)$  values in relation to the straight line determined [7-12]; the ratio of the standard deviations of the regression coefficient to its actual value [9]. One finds from the literature that the correlation coefficient is not a good index for selecting the proper  $g(\alpha)$  equation [9,13].

The application of statistical criteria is possible with the assumption that data have a normal distribution. However, in the case of transforming  $\alpha$  into  $g(\alpha)$  values, the above condition is not satisfied. In this case, the application of tests connected with a normal distribution is unjustified.

Since the aim of the calculations is to determine parameters that describe experimental data relatively well, the conformity of  $\alpha_{\text{exp}}$  and  $\alpha_{\text{calc}}$  (on the

basis of the equations  $g(\alpha) = kt$  or  $g(\alpha) = kt + b$ ) is often used as a criterion of selecting the  $g(\alpha)$  function [14–16].

In this paper the following value (at constant temperature) was calculated

$$R = \frac{1}{n} \sum_{i=1}^n (\alpha_{\text{calc},i} - \alpha_{\text{exp},i})^2 \quad (8)$$

where  $n$  = the number of experimental  $\alpha$  values,  $\alpha_{\text{exp},i}$  = the progress of decomposition (formula 2) for a given time,  $t$ ,  $\alpha_{\text{calc},i}$  = the  $\alpha$  value calculated for a given time and on the basis of the corresponding  $g(\alpha)$  function that equals  $kt$  or  $kt + b$ . From the  $g(\alpha)$  functions used, the function with the minimum  $R$  value is selected as the one that best describes the experimental data.

During the study of series obtained at various temperatures, an additional difficulty, connected with the determination of the form of the  $g(\alpha)$  function, arises. It occurs when different  $g(\alpha)$  functions are selected for various temperatures. In this case the function which best describes the data for the maximum number of temperatures is selected. Another method is by increasing the number of experimental data on the basis of which the selection of  $g(\alpha)$  is made (it is possible to increase the number of measurements at a given temperature, or to conduct measurements for further temperatures). This can simplify the selection of the  $g(\alpha)$  function describing the thermal decomposition over the whole range of temperatures investigated by the increase in the number of series of isothermal measurements best described by the same  $g(\alpha)$  function.

Apart from the determination of the  $g(\alpha)$  function with the minimum  $R$  value (eqn. 8), still another method exists for the selection of the  $g(\alpha)$  function: for particular  $g(\alpha)$  functions at different temperatures, rate constants,  $k_{\text{exp},i}$ , are determined then with the non-linear least-squares method [6], coefficients  $A$  and  $E$  of the Arrhenius equation are determined from the relationship

$$\sum_{i=1}^n (k_{\text{exp},i} - Ae^{-E/RT_i})^2 = \min \quad (9)$$

Next, using the Arrhenius equation, rate constants,  $k_{\text{calc},i}$ , for particular temperatures are determined

$$k_{\text{calc},i} = Ae^{-E/RT_i} \quad (10)$$

and on their basis  $\alpha_{\text{calc}}$  is calculated after solution of the equation

$$g(\alpha_{\text{calc}}) = k_{\text{calc},i}t \quad (11)$$

or

$$g(\alpha_{\text{calc}}) = k_{\text{calc},i}t + b_i \quad (12)$$

The value of  $b_i$  was calculated during the calculation of  $k_{\text{exp},i}$  by applying the LSM.

For all pairs ( $\alpha_{\text{exp}}$ ,  $\alpha_{\text{calc}}$ ), the following can be obtained

$$S = \frac{1}{N} \sum_{i=1}^l \sum_{j=1}^{n_i} (\alpha_{\text{exp},ij} - \alpha_{\text{calc},ij})^2 \quad (13)$$

where  $l$  = the number of temperatures,  $n_i$  = the number of the stage of decomposition at temperature  $i$ ,  $N$  = the sum of  $n_i$ ,  $N = \sum_{i=1}^l n_i$ ,  $\alpha_{\text{exp},ij}$  = the progress of the decomposition determined experimentally,  $\alpha_{\text{calc},ij}$  = the progress of the decomposition determined from the Arrhenius equation for a given  $g(\alpha)$ .

The value of  $S$  was calculated for these  $\alpha_{\text{exp},ij}$ ,  $\alpha_{\text{calc},ij}$  pairs for which  $\alpha_{\text{calc},ij}$  belongs to the range 0–1.

The selection of the  $g(\alpha)$  function on the basis of the  $S$  consists of establishing the  $g(\alpha)$  function with the minimum  $S$  value. In this case the mean square of the difference between calculated (on the basis of the Arrhenius equation) and experimental  $\alpha$  values is a minimum for the  $g(\alpha)$  selected.

## EXPERIMENTAL

The present work compared several criteria for selection of the  $g(\alpha)$  function connected with the application of the LSM for determining rate constants of the isothermal decomposition of calcium carbonate. Table 1 shows the  $g(\alpha)$  functions most often used in investigations of the kinetics of thermal decomposition of solids.

The decomposition of polycrystalline calcium carbonate (manufactured by Merck, p.a.) was carried out on a Mettler 2000-C thermoanalyser. Measurements were made in a nitrogen atmosphere in the temperature range 973–1043 K. The mass of decomposing calcium carbonate was  $\sim 20$  mg.

The range of temperatures (and particularly the value of maximum temperature) was chosen so that the mass loss was a minimum under unstabilized measuring conditions. Isothermal conditions, on average, were achieved with a progress of decomposition  $\alpha = 0.02$  only at the highest temperatures with  $\alpha = 0.05$ .

## RESULTS AND DISCUSSION

Table 2 shows the experimental results. The algorithm of the determination of straight-line parameters was evaluated in accordance with refs. 17 and 18. The calculations were realized using a program written in BASIC for a microcomputer with a 48k RAM.

For each temperature and particular  $g(\alpha)$  function the straight-line parameters and their deviations were calculated (correspondingly for models

TABLE 2

Isothermal decomposition of  $\text{CaCO}_3$  under nitrogen ( $\Delta m_f$  = final mass loss (mg),  $t$  = time (min))

$T$ (K) = 973		983		993		1003		1013		1023		1033		1043	
$\Delta m_f = 8.82$		8.86		8.90		8.89		8.91		8.98		8.92		8.93	
$t$	$\Delta m$	$t$	$\Delta m$	$t$	$\Delta m$	$t$	$\Delta m$	$t$	$\Delta m$	$t$	$\Delta m$	$t$	$\Delta m$	$t$	$\Delta m$
3	0.48	1.8	0.40	1.5	0.35	22	0.64	0.6	0.19	0.45	0.30	1	0.42	1.35	0.67
6	1.04	4.8	1.08	4.5	1.18	3	0.69	2.1	0.74	1.95	0.97	2	1.00	2.00	1.17
9	1.60	7.8	1.77	7.5	1.98	4	1.37	3.6	1.39	3.45	1.72	3	1.60	2.50	1.67
12	2.12	10.8	2.40	10.5	2.80	5	1.76	5.1	2.02	4.95	2.53	4	2.21	3.10	2.17
15	2.26	13.8	3.10	13.5	3.60	6	2.12	6.6	2.64	6.45	3.22	5	2.81	3.65	2.67
18	3.20	16.8	3.75	16.5	4.38	8	2.84	8.1	3.26	7.95	3.99	6	3.43	4.80	3.67
21	3.73	19.8	4.38	19.5	5.15	10	3.58	9.6	3.89	9.45	4.75	7	4.03	6.00	4.67
24	4.28	22.8	5.02	22.5	5.92	12	4.29	11.1	4.53	10.95	5.48	8	4.60	7.21	5.67
27	4.79	25.8	5.63	25.5	6.60	14	5.06	12.6	5.14	12.45	6.18	9	5.20	8.45	6.67
30	5.31	28.8	6.27	28.5	7.33	16	5.69	14.1	5.76	13.95	6.86	10	5.57	9.10	7.17
33	5.80	31.8	6.84	31.5	8.03	18	6.32	15.6	6.34	15.45	7.55	11	6.31	9.75	7.67
36	6.28	34.8	7.42	34.5	8.65	20	6.99	17.1	6.89	16.95	8.18	12	6.89	10.50	8.17
39	6.73	37.8	7.97			22	7.61	18.6	7.47	18.45	8.78	13	7.41	11.30	8.67
42	7.21	40.8	8.47			24	8.19	20.1	7.99			14	7.94		
45	7.66					25	8.49	21.6	8.47			15	8.34		
48	8.08					26	8.72					16	8.82		
51	8.50														

TABLE 3

Weights calculated according to eqns. (5), (6) and (7) at 1043 K

Function No.	$\alpha = 0.075$	0.187	0.859	0.971
1	14.1627	6.9069	0.1950	0.1365
2	0.2984	0.7228	1.9771	1.9991
3	0.2832	0.9300	4.2285	4.4540
4	0.3270	1.2502	7.3292	7.8792
5	3.6792	3.1421	0.3248	0.0600
6	8.0657	6.5982	0.3804	0.0415
7	0.8508	0.6386	0.0115	0.0004
8	0.3494	0.5029	0.0403	0.0023
9	0.2654	0.5287	0.0897	0.0062
10	0.2551	0.7040	0.2526	0.0212
11	0.2965	0.9626	0.5023	0.0464
12	163.4798	22.5412	0.1501	0.0412
13	3225.3308	425.8514	1.5270	0.2287
14	3061.9163	370.9495	0.4138	0.0216
15	0.0048	0.0223	0.0085	0.0004
16	0.7279	0.4221	0.0002	$3.699 \times 10^{-7}$

TABLE 4  
Results of calculations of the criterion for selection of  $g(\alpha)$  ( $T = 1043$  K)

Function No.	Correlation coefficient	$s_k/k$		$R$					
		Unweighted LSM		Weighted LSM		Unweighted LSM		Weighted LSM	
		Model 1	Model 2	Model 1	Model 2	Model 1	Model 2	Model 1	Model 2
1	0.9853	0.0734	0.0521	0.2452	0.1094	0.0236	0.0022	0.0420	0.0070
2	0.9859	0.0531	0.0512	0.0421	0.0504	0.0139	0.0018	0.0149	0.0016
3	0.9760	0.0809	0.0672	0.0550	0.0645	0.0329	0.0028	0.0371	0.0025
4	0.9700	0.0972	0.0757	0.0610	0.0717	0.0481	0.0032	0.0577	0.0031
5	0.9907	0.0404	0.0414	0.0512	0.0345	0.0058	0.0011	0.0052	0.0010
6	0.9786	0.0562	0.0633	0.0647	0.0486	0.0101	0.0024	0.0082	0.0020
7	0.9336	0.0966	0.1157	0.0887	0.0752	0.0248	0.0064	0.0159	0.0051
8	0.9738	0.0424	0.0704	0.0190	0.0352	0.0036	0.0023	0.0017	0.0012
9	0.9872	0.0227	0.0488	0.0241	0.0242	0.0015	0.0009	0.0015	0.0005
10	0.9942	0.0427	0.0326	0.0530	0.0244	0.0108	0.0005	0.0104	0.0003
11	0.9949	0.0694	0.0304	0.0676	0.0284	0.0214	0.0051	0.0200	0.0004
12	0.9597	0.0999	0.0883	0.3398	0.1780	0.0383	0.0049	0.0740	0.0178
13	0.9401	0.1154	0.1093	0.3636	0.2004	0.0467	0.0066	0.0855	0.0237
14	0.8883	0.1518	0.1559	0.3968	0.2350	0.0665	0.0124	0.1031	0.0349
15	0.9876	0.4160	0.0480	0.4113	0.0347	0.0735	0.0010	0.0774	0.0006
16	0.6767	0.2916	0.3281	0.1377	0.1380	0.1310	0.0030	0.0444	0.0205



TABLE 5  
Parameters of Arrhenius equation and criterion  $S$  ( $E$  in cal mol<sup>-1</sup>,  $A$  in s<sup>-1</sup>)

Function No.	Unweighted LSM						Weighted LSM					
	Model 1			Model 2			Model 1			Model 2		
	$A \times 10^7$	$E$	$S$	$A \times 10^7$	$E$	$S$	$A \times 10^7$	$E$	$S$	$A \times 10^7$	$E$	$S$
1	3.1204	41470	0.0188	9.2645	43057	0.0034	0.1328	36244	0.0259	3.0899	41773	0.0117
2	3.9058	41107	0.0181	6.7764	43063	0.0028	3.9176	41163	0.0200	6.1293	43107	0.0032
3	3.9184	40994	0.0395	5.4504	43111	0.0045	3.8218	41052	0.0471	4.4067	43121	0.0045
4	3.9890	40966	0.0568	4.4895	43127	0.0057	3.7919	41009	0.0703	3.3858	43110	0.0053
5	2.9893	41558	0.0036	9.0422	43490	0.0020	1.2112	40009	0.0031	5.2686	42719	0.0020
6	2.7328	41898	0.0068	7.7307	43602	0.0035	0.7308	39705	0.0051	3.2235	42397	0.0032
7	16.9639	42672	0.0182	44.6615	44042	0.0077	1.7277	39062	0.0103	8.0695	41792	0.0069
8	10.5375	42145	0.0031	26.9529	43867	0.0032	3.9194	40404	0.0017	11.839	42690	0.0020
9	9.3199	42063	0.0030	20.5789	43857	0.0015	6.0054	41201	0.0029	12.458	43127	0.0012
10	5.8474	41296	0.0134	14.6008	43871	0.0011	5.2723	40945	0.0122	9.8463	43293	0.0010
11	5.2619	41155	0.0255	10.0675	43635	0.0012	5.1458	40916	0.0219	7.4612	43252	0.0012
12	3.3344	42059	0.0285	8.6099	43235	0.0069	0.0118	33111	0.0507	0.5192	39590	0.0025
13	1.0850	42404	0.0355	2.6711	43427	0.0088	0.0016	32277	0.0608	0.0742	39761	0.0032
14	2.4947	43176	0.0523	5.6699	43934	0.0134	0.0008	31213	0.0778	0.0403	37615	0.0043
15	11.0479	42398	0.0672	79.5366	43928	0.0017	0.1604	36558	0.0707	46.890	43263	0.0014
16	371.516	45893	0.0952	676.550	46078	0.0271	0.7943	37200	0.0306	5.5250	40557	0.0023

TABLE 6  
Selected  $g(\alpha)$  functions

Temp. (K)	Correlation coefficient	$s_k/k$		$R$					
		Unweighted LSM		Weighted LSM		Unweighted LSM		Weighted LSM	
		Model 1	Model 2	Model 1	Model 2	Model 1	Model 2	Model 1	Model 2
973	11,10,5,1	9,5,8,10	11,10,5,1	8,5,9,6	9,10,11,5	9,5,8,6	11,10,5,9	8,5,9,6	10,11,9,15
983	10,11,5,9	9,5,8,6	10,11,9,5	8,5,9,6	9,10,11,5	8,5,9,6	10,11,9,5	8,5,9,6	10,9,11,15
993	10,12,5,9	9,5,8,6	10,11,5,9	8,5,9,6	9,10,8,5	8,5,9,6	10,11,5,9	8,5,9,6	10,11,9,15
1003	11,10,5,15	9,5,8,6	11,10,5,15	8,5,9,6	9,10,11,5	9,8,5,6	11,10,15,9	8,5,9,6	10,11,9,15
1013	10,9,5,11	9,8,5,6	10,9,5,11	8,9,5,6	9,10,11,8	8,9,5,6	10,9,11,5	8,5,9,6	10,9,11,15
1023	10,11,5,9	9,5,8,6	10,11,5,9	8,5,9,6	9,10,11,8	9,5,8,6	10,11,9,5	8,5,9,6	10,11,9,15
1033	11,10,5,2	9,5,10,8	11,10,5,2	8,9,5,2	9,10,11,8	9,8,6,10	11,10,5,9	8,5,9,6	11,10,9,15
1043 <sup>a</sup>	11,10,5,15	9,5,8,10	11,10,5,15	8,9,2,5	9,10,11,5	9,8,5,6	10,11,9,5	9,8,5,6	10,11,9,15
On the basis of criterion S		9,8,5,6	10,11,9,15	8,9,5,6	10,11,9,15				

<sup>a</sup> See Table 4.

1 and 2) using the simple and weighted LSMs. The weights were calculated according to formulae (5), (6) and (7). Table 3 shows exemplary weights for functions 1–16 (listed in Table 1). From these data it is evident that weights change significantly depending on  $\alpha$ . This fact justifies the application of the weighted LSM.

In order to compare various criteria of the selection of the  $g(\alpha)$  function for which the dependence on time is approximated as much as possible to a straight line, or as that best describing the dependence of  $\alpha$  on time at a given temperature, the following data were calculated:

- (1) correlation coefficient,  $g(\alpha)$  and  $t$ ;
- (2) ratio of standard deviation of regression coefficient to its actual value ( $s_k/k$ );
- (3) values of  $R$  (formula 8) ( $R_1$  for model 1,  $R_2$  for model 2);
- (4) values of  $S$  (formula 12) ( $S_1$  for model 1,  $S_2$  for model 2).

Criteria 2–4 were calculated for the simple and weighted LSMs and selected results are shown in Table 4. Table 5 presents the values of the Arrhenius equation coefficients and of the criterion  $S$ .

Table 6 shows the  $g(\alpha)$  functions which best satisfy particular criteria.

The above data indicate that selection of the  $g(\alpha)$  function depends on the method of calculation used—the simple or weighted LSMs (models 1 or 2)—and on the criterion selected. The data shown in Tables 4 and 5, as well as other results not included in this paper, indicate that the best fit of the experimental data and the calculated values is achieved with the use of the weighted LSM and model 2.

## CONCLUSIONS

Depending on the criteria applied, selection of various forms of the  $g(\alpha)$  function describing the process of thermal decomposition is possible. This can lead to various values of the kinetic parameters  $A$  and  $E$  which change according to the form of the  $g(\alpha)$  function applied to calculations.

The results presented indicate that the best fit of experimental and calculated data was obtained using the weighted least-squares method with the equation  $g(\alpha) = kt + b$ . The selection of the  $g(\alpha)$  function best describing the experimental data should be made on the basis of criteria considering the difference between  $\alpha_{\text{exp}}$  and  $\alpha_{\text{calc}}$ .

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