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THE APPLICATION OF KINETIC PARAMETERS TO THE INVESTIGATION OF THERMAL STABILITY DETERMINED FROM RISING TEMPERATURE EXPERIMENTS

M. MACIEJEWSKI

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

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ABSTRACT

Correlations between the calculated $\alpha - T$ (temperature) relationships for dynamic heating and $\alpha - t$ (time) for the isothermal run show the necessity of introducing into consideration, not only the two kinetic parameters E and A, but also the form of the $g(\alpha)$ function dependent on the process mechanism.

Isothermal experiments made at the initial temperature of decomposition T_i, determined from rising temperature experiments, can lead to the essential decomposition after 2-3 h, and the progress of the reaction depends, basically, on the form of the $g(\alpha)$ function.

The equation proposed by Piloyan, taking into account for T_i calculations the values of A and E only, leads to correct results only with regard to the "first order" kinetic equation.

Conclusions concerning thermal stability based on dynamic experiments are rather useless for the interpretation of the decomposition mechanism if all the kinetic data are not taken into consideration.

INTRODUCTION

The results of thermal stability obtained in non-isothermal conditions are often used in the literature for the determination of the thermal stability of compounds [1,2]. On the basis of the initial temperature of decomposition, or the temperature of the peak on DTG or DTA curves, it is possible to obtain some information about the energy of the broken bonds [3,4] or the micromechanisms of decomposition. It is assumed that the comparison of the initial temperatures of decomposition achieved in dynamic conditions may enable conclusions about the thermodynamic stability of compounds to be drawn [5]. It is well known that the initial temperature of decomposition —and, of course, the other characteristic temperatures on TA curves—depend not only on the properties of the decomposed reactant, but also on the experimental conditions, such as the heating rate, the weight of the sample, the kind of gaseous atmosphere, etc.

For these reasons, the measurements aiming at drawing conclusions concerning the mechanisms of decomposition are made for a series of

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compounds in strictly defined conditions (described as "standard" conditions by an experimenter). It is generally believed that thanks to the stability of measurement conditions, the data concerning thermal stability obtained from rising temperature experiments may enable conclusions that are identical with those obtained from the measurements carried out in isothermal experiments to be drawn.

There are, however, some reservations about this procedure: it has been emphasized in a number of works [6–10] that, if such a method is used, it is indispensable to consider the parameters of the Arrhenius equation, i.e. activation energy E and the pre-exponential factor A. In the literature there is no work which, in order to compare isothermal and rising temperature data, makes use of another kinetic parameter: the $g(\alpha)$ function, which is dependent on the reaction mechanism. The values of two parameters only, A and E, do not characterize in full the course of the TG curve, which is also, to a large extent, dependent on the mechanism of decomposition, and this, in turn, may depend, for instance, on the crystallographic structure or morphology of a reactant [11,12]. It is therefore probable, that, if a series of compounds of similar composition is analysed thermally, then, although the values of the activation energies and pre-exponential factors of particular compounds may be close, they may have different decomposition mechanisms, which will, in turn, affect the reliability of our conclusions concerning their thermal stability.

The purpose of the present paper is to show how the three kinetic parameters A, E and $g(\alpha)$ affect the mutual relationship of isothermal and dynamic curves and to emphasize that the comparison of the data obtained, even under "standard conditions", may be meaningless.

GENERAL REMARKS

An initial temperature of decomposition T_i for a TG curve is the temperature at which the cumulative weight change reaches a magnitude that can be detected by a thermobalance; for a DTA curve, on the other hand, it is the temperature at which this curve departs from the base line.

The temperature of thermodynamic stability T_{th} is the temperature at which the partial pressure of a gaseous product reaches the value of the equilibrium pressure. It is obvious that T_i in given experimental conditions must be somewhat higher in comparison with T_{th} if a measurable reaction rate is to be achieved. The relationship between these temperatures has been described in the work of Margulis and Chufarov [13]. They have given an equation which indicates that if the thermal effect of the reaction and the sensitivity of the instrument increase, and if the value of T_{th} diminishes, then the difference between T_{th} and T_i becomes smaller. Their conclusion concerning the simple relationship between the initial temperature of decomposition and the temperature at the onset of thermodynamic instability has been verified experimentally for the decomposition of sulphates. The procedure proposed by Margulis and Chufarov cannot be regarded as generally valid because it considers only one of many possible cases of $p-T$ thermodynamic relationships. Nikolaev and Logvinenko [8] have correctly noticed that, in Margulis' work, it has been assumed that $p-T$ relationships are parallel for the compounds under investigation—which is only a specific case of the general relationship (see Fig. 1 in [8]).

The relationship between T_i and T_th becomes complicated if kinetic parameters are taken into consideration. Even in the case when $p-T$ relationships for the compared compounds are parallel (or do not intersect in the decomposition temperature range) a change in the values of the parameters A and E will result in different sequences of thermal stability, as has been shown in the paper of Logvinenko et al. [6].

Piloyan and Kudinov [14], using the kinetic equation of the first-order reaction, have obtained the following formula for T_i:

$$T_\text{i} = \frac{E}{\text{R} \ln(AE/\text{R}\Phi)} \tag{1}$$

where Φ is the heating rate (A, E and R have their usual meanings).

Calculations made by these authors have shown that the progress of decomposition, α, at the temperature T_i has been less than 0.001.

From the above review of the literature it appears that the values of the apparent energy and the pre-exponential factor A exert influence on the value of the initial temperature of decomposition.

The increasing application of non-isothermal measurements to the evaluation of thermal stability of compounds, and, at the same time, the problems with the unequivocal interpretation of the obtained results, make it necessary to elaborate a method enabling the comparison of the results obtained under isothermal and rising temperature conditions. This method should enable the determination of the temperature at which the reaction rate and the progress of decomposition reach some arbitrarily chosen values, and it should also take the kinetic parameters of the examined process into consideration. If these parameters are not taken into account then the term "thermal stability", calculated from the rising temperature experiments, has no real physicochemical meaning, and, according to the point of view expressed by Nikolaev and Logvinenko, it is only "the statement that under the chosen experimental conditions the reaction rates at the starting temperatures of thermal decomposition are equal for the compound under investigation" [8].

It should be emphasized that all further considerations given in the present paper dealing with the correlation between isothermal and dynamic measurements are valid only when these measurements are carried out under the same pressure of the gaseous product of the reaction.

The change of pressure in the case of a reversible reaction may bring about a change in the reaction rate: it may affect the change of the process mechanism, and, consequently, the form of the $g(\alpha)$ function may be changed. Only if the pressure of the gaseous product is constant [15–17] can the reaction rate equation

$$\frac{d\alpha}{dt} = k(T)f(\alpha)\phi(p, T) \tag{2}$$

$$k(T) = A\ \exp(-E/RT)$$

be transformed into the form which is commonly used in the literature:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{3}$$

For non-isothermal conditions and linear time–temperature dependence, the relationship between t and T can be expressed as:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t A\ \exp(-E/RT)dt \tag{4}$$

$$T = T_0 + \Phi t \tag{5}$$

The integral $\int_0^\alpha \frac{d\alpha}{f(\alpha)}$ is designated as $g(\alpha)$.

The comparison of the reaction rates under iso- and non-isothermal conditions has been made recently by Romero Salvador et al. [18,19], who have tried to solve the controversy existing in the literature with regard to the equation expressing the rate of decomposition under rising temperature conditions.

Romero Salvador has expressed the variation of α as a function of the variables t, T and the heating rate Φ in three ways:

(a) $\alpha = \mathrm{NIF}(t, \Phi)$,

$$g(\alpha) = \int_0^t A\ \exp\left[-\frac{E}{R(T_0 + \Phi t)}\right]dt \tag{6}$$

(b) $\alpha = \mathrm{NIF}\ (T, \Phi)$,

$$g(\alpha) = \int_{T_0}^T A\ \exp\left(-\frac{E}{RT}\right)\frac{dT}{\Phi} \tag{7}$$

(c) $\alpha = \mathrm{NIF}(t, T)$,

$$g(\alpha) = \int_0^t A\ \exp\left(-\frac{E}{RT}\right)dt \tag{8}$$

where $T = T_0 + \Phi t$ and NIF is the non-isothermal function.

EXPERIMENTAL

In order to determine the relationships between iso- and non-isothermal results, calculations for three different $g(\alpha)$ functions were made. The following functions based on three different decomposition mechanisms were chosen:

(a) the rate-limiting process is nucleation (the so called KEKAM equation, where $n = 2$),

$$g(\alpha) = -\ln(1-\alpha)^{1/2} \tag{9}$$

(b) the rate-limiting process is diffusion (the Jander equation),

$$g(\alpha) = \left[1-(1-\alpha)^{1/3}\right]^2 \tag{10}$$

(c) the reaction on the phase boundary is rate limiting (the contracting area model designated as R2),

$$g(\alpha) = 1-(1-\alpha)^{1/2} \tag{11}$$

In order to obtain the α–T relationships under non-isothermal conditions, equation (7) was used. Calculations were carried out according to the following conditions and assumptions:

(a) The temperature of 373 K (or 423 K in other calculations) was chosen as the initial temperature of decomposition. It was assumed that at this temperature the progress of the reaction reaches the value of 0.01. This is an arbitrarily chosen value, but all the relationships will be similar at different α values.

(b) The heating rate was 10 K min^{-1}.

(c) The E values ranged from 14000 to 34000 cal mol^{-1} (with steps of 4000 cal mol^{-1}) and the A values were chosen by means of Newton's method, which satisfies the following equation ($E = 14000$ cal mol^{-1}, for example):

$$\int_{300}^{373} A \exp\left(-\frac{14000}{\mathrm{R}373}\right)\frac{\mathrm{d}T}{10} = g(\alpha_{0\,01}) \tag{12}$$

(d) The integration of equation (7) was made by means of Simpson's method with the value of $T_0 = 300$ K and a temperature step of 0.5 K. For the above example and for, let us say, the Jander equation, it was necessary to find the solution of the equation:

$$\frac{A}{10}\int_{300}^{373} \exp\left(-\frac{14000}{\mathrm{R}373}\right)\mathrm{d}T - \left[1-(1-0.01)^{1/3}\right]^2 = 0 \tag{13}$$

This procedure was repeated for all the three forms of the $g(\alpha)$ function and for the temperatures of 373 and 423 K. As a result of this, a set of kinetic parameters (A, E and $g(\alpha)$) was obtained. For these parameters, at the heating rate of 10 K min^{-1}, the progress of decomposition $\alpha = 0.01$ was achieved at 373 and 423 K, respectively. Using the values of E and A, determined according to the procedure described above, and also, by applying Simpson's method, the right-hand member of equation (7) (RH 7) was determined using $T_0 = 300$ K and $\Delta T = 0.5$ K, which, in turn, enabled the determination of the α–T relationship for the respective g(α) equations:

$$\alpha = 1 - \left[1 - (\mathrm{RH7})^{1/2}\right]^3 \quad \text{(Jander)} \tag{14}$$

$$\alpha = 1 - \left[\exp - (\mathrm{RH7})^2\right] \quad \text{(KEKAM)} \tag{15}$$

$$\alpha = 1 - (1 - \mathrm{RH7})^2 \quad \text{(R2)} \tag{16}$$

The values of A and E and the α–T relationships for particular g(α) functions are listed in Tables 1–6. Tables 1–3 contain the data obtained at $\alpha = 0.01$ at the temperature of 373 K; in Tables 4–6 $\alpha = 0.01$ at the temperature of 423 K.

TABLE 1

α–T relationships for the function $g(\alpha) = -\ln(1-\alpha)^{1/2}$ (KEKAM equation with $n = 2$). For each E value A is calculated such that, for a heating rate $\Phi = 10$ K min^{-1}, progress of the decomposition $\alpha = 0.01$ at 373 K

E (cal mol^{-1})	14000	18000	22000	26000	30000	34000
A (min^{-1})	8.995×10^{6}	2.490×10^{9}	6.622×10^{11}	1.711×10^{14}	4.328×10^{16}	1.077×10^{19}
T(K)	Progress of the decomposition ($\times100$)					
333	0.006	0.002	0.000	0.000	0.000	0.000
338	0.012	0.004	0.001	0.000	0.000	0.000
343	0.025	0.010	0.004	0.001	0.000	0.000
348	0.049	0.023	0.011	0.005	0.002	0.001
353	0.093	0.051	0.028	0.015	0.008	0.004
358	0.173	0.111	0.071	0.045	0.028	0.018
363	0.316	0.236	0.176	0.131	0.097	0.072
368	0.567	0.491	0.424	0.366	0.316	0.273
373	1.000	1.000	1.000	1.000	1.000	1.000
378	1.733	1.993	2.295	2.642	3.042	3.501
383	2.954	3.885	5.114	6.722	8.815	11.516
388	4.945	7.381	10.979	16.185	23.519	33.444
393	8.116	13.581	22.327	35.451	53.173	73.147
398	13.022	23.931	41.642	65.406	87.666	98.384
403	20.324	39.646	67.611	91.950	99.642	99.999
408	30.632	60.096	90.160	99.714	99.999	
413	44.136	80.762	99.080	99.999		
418	60.032	94.594	99.991			
423	76.062	99.839	99.999			
428	88.995	99.999				
433	96.574					
438	99.396					
443	99.999					

TABLE 2

α–T relationships for the function $g(\alpha)=[1-(1-\alpha)^{1/3}]^2$ (Jander equation). For each E value A is calculated such that, for a heating rate $\Phi=10$ K min^{-1}, progress of the decomposition $\alpha=0.01$ at 373 K

E (cal mol^{-1})	14000	18000	22000	26000	30000	34000
A (min^{-1})	1.004×10^3	2.778×10^5	7.391×10^7	1.910×10^{10}	4.829×10^{12}	1.202×10^{15}
T(K)	Progress of the decomposition ($\times100$)					
333	0.278	0.204	0.149	0.108	0.078	0.057
343	0.397	0.317	0.251	0.199	0.157	0.124
353	0.552	0.475	0.409	0.351	0.301	0.259
363	0.749	0.697	0.647	0.601	0.558	0.518
373	1.000	1.000	1.000	1.000	1.000	1.000
383	1.407	1.509	1.619	1.736	1.862	1.997
393	1.699	1.945	2.230	2.556	2.928	3.355
403	2.172	2.647	3.230	3.940	4.802	5.851
413	2.743	3.547	4.591	5.937	7.664	9.879
423	3.425	4.686	6.410	8.750	11.903	16.125
433	4.234	6.107	8.796	12.615	17.971	25.367
443	5.182	7.856	11.868	17.788	26.331	38.247
453	6.285	9.982	15.748	24.515	37.316	54.763
463	7.556	12.532	20.553	32.975	50.896	73.403
473	9.010	15.553	26.378	43.202	66.316	90.177
483	10.659	19.085	33.274	54.968	81.676	99.192
493	12.515	23.159	41.227	67.647	93.841	99.999
503	14.588	27.974	50.117	80.098	99.563	
513	16.887	32.991	59.696	90.676	99.999	
523	19.418	38.727	69.549	97.576		
533	22.184	44.954	79.088	99.938		
543	25.185	51.587	87.573	99.999		
553	28.418	58.505	94.205			
563	31.875	65.548	98.341			
573	35.544	72.516	99.898			
583	39.408	79.175	99.999			
603	47.631	90.523				
623	65.138	99.999				

The results from the tables are presented in Figs. 1–7. Figure 7 shows the curves of five equations, three of which are discussed above, and two additional equations: R3, describing the contracting sphere mechanism and the F1 equation, i.e. the kinetic equation of the first order,

$$g(\alpha)=-\ln(1-\alpha) \tag{17}$$

Having calculated the set of the kinetic parameters (A and E for the particular forms of the $g(\alpha)$ function) for the rising temperature conditions, it was possible to calculate the α–t relationships for an arbitrarily chosen temperature for isothermal decomposition. This dependence was calculated after the integration of equation (4). Calculations were made using a

TABLE 3

$\alpha - T$ relationships for the function $g(\alpha) = 1-(1-\alpha)^{1/2}$ (R2, contracting area equation). For each E value A is calculated such that, for a heating rate $\Phi = 10$ K min^{-1}, progress of the decomposition $\alpha = 0.01$ at 373 K

E (cal mol^{-1})	14000	18000	22000	26000	30000	34000
A (min^{-1})	4.497×10^{5}	1.245×10^{8}	3.311×10^{10}	8.556×10^{12}	2.164×10^{15}	5.385×10^{17}
T(K)	Progress of the decomposition (×100)					
333	0.077	0.042	0.022	0.011	0.006	0.003
338		0.065	0.037	0.022	0.012	0.007
343	0.158	0.100	0.063	0.039	0.024	0.015
348		0.151	0.103	0.070	0.047	0.032
353	0.304	0.226	0.167	0.123	0.091	0.068
358		0.333	0.266	0.212	0.169	0.135
363	0.562	0.486	0.419	0.361	0.311	0.268
368		0.700	0.651	0.605	0.562	0.522
373	1.000	1.000	1.000	1.000	1.000	1.000
378		1.414	1.518	1.630	1.750	1.879
383	1.724	1.981	2.278	2.621	3.014	3.467
388		2.750	3.381	4.158	5.111	6.279
393	2.888	3.784	4.963	6.507	8.520	11.137
398		5.162	7.204	10.038	13.942	19.279
403	4.709	6.980	10.335	15.244	22.325	32.334
408		9.355	14.647	22.741	33.943	51.807
413	7.484	12.426	20.482	33.207	52.163	76.992
418		16.352	28.212	47.183	73.780	98.423
423	11.598	21.304	38.178	64.579	94.559	
428		27.460	50.557	83.556		
433	17.522	34.976	65.103	98.191		
438		43.951	80.665			
443	25.778	54.358	94.326			
448		65.947				
453	36.838	78.077				
458		89.475				
463	50.909	97.869				
473	67.513					

temperature of 333 K, at which value, under dynamic conditions, the progress of decomposition α is very small, i.e. for $E = 18000$ cal mol^{-1} and $T = 333$ K, it is less than 0.00002 for the KEKAM equation, and less than 0.002 and 0.0005 for the Jander and R2 equations, respectively.

Examples of $\alpha - t$ relationships for isothermal conditions ($T = 333$ K) are presented in Fig. 8, where the curves for different forms of $g(\alpha)$ and $E = 18000$ cal mol^{-1} are given. For all the sets of kinetic parameters (A, E and $g(\alpha)$) the progress of the reaction, α, was 0.01 at 373 K under rising temperature conditions with a heating rate of 10 K min^{-1}.

Of course, at constant temperature, the $\alpha - t$ relationship will vary, if A

TABLE 4

$\alpha - T$ relationships for the function $g(\alpha) = -\ln(1-\alpha)^{1/2}$ (KEKAM equation with $n = 2$). For each E value A is calculated such that, for a heating rate $\Phi = 10$ K min^{-1}, progress of the decomposition $\alpha = 0.01$ at 423 K

E (cal mol^{-1})	14000	18000	22000	26000	30000	34000
A (min^{-1})	7.542×10^5	1.105×10^8	1.553×10^{10}	2.119×10^{12}	2.829×10^{14}	3.718×10^{16}
T(K)	Progress of the decomposition ($\times100$)					
373	0.007	0.002	0.000	0.000	0.000	0.000
383	0.021	0.008	0.001	0.000	0.000	0.000
393	0.059	0.029	0.014	0.006	0.003	0.001
403	0.159	0.099	0.062	0.038	0.024	0.015
413	0.408	0.324	0.257	0.204	0.162	0.128
423	1.000	1.000	1.000	1.000	1.000	1.000
428	1.539	1.749	1.919	2.144	2.392	2.671
433	2.344	2.919	3.618	4.490	5.562	6.885
438	3.529	4.854	6.673	9.133	12.424	16.800
443	5.521	7.956	11.985	17.835	26.060	37.149
448	7.714	12.769	20.778	32.748	49.081	68.309
453	11.175	19.969	34.263	54.580	77.303	93.848
458	15.928	30.199	52.586	78.718	95.941	99.869
463	22.280	43.704	73.064	94.977	99.889	99.999
468	30.470	59.723	89.761	99.666	99.999	
473	40.556	75.974	98.006	99.999		
478	52.249	89.098	99.871			
483	64.769	96.710	99.999			
488	76.837	99.456				
493	86.961	99.999				
498	94.039					
503	97.934					
508	99.503					
513	99.926					
518	99.999					

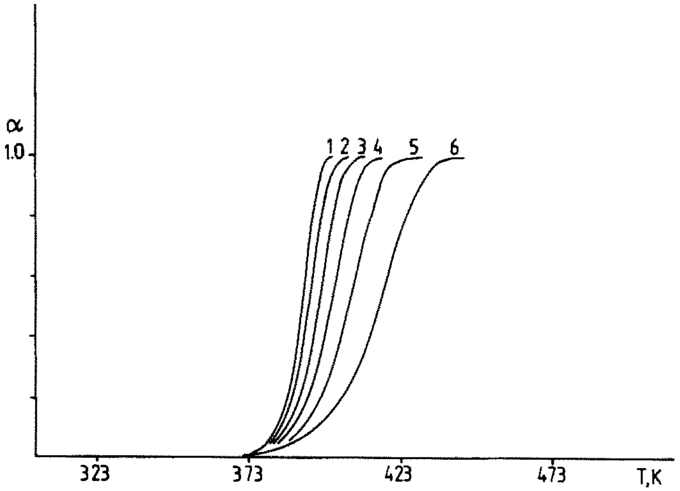

Fig. 1. $\alpha - T$ relationship for the function $g(\alpha) = -\ln(1-\alpha)^{1/2}$. For the selected E values, A is calculated such that, for $\Phi = 10$ K min^{-1}, $\alpha = 0.01$ at 373 K. The values of E, in kcal mol^{-1}, are: curve 1, 34; curve 2, 30; curve 3, 26; curve 4, 22; curve 5, 18; curve 6, 14.

TABLE 5

α–T relationships for the function $g(\alpha)=[1-(1-\alpha)^{1/3}]^2$ (Jander equation). For each E value A is calculated such that, for a heating rate $\Phi = 10$ K min^{-1}, progress of the decomposition $\alpha = 0.001$ at 423 K

E (cal mol^{-1})	14000	18000	22000	26000	30000	34000
A (min^{-1})	0.841×10^{2}	1.233×10^{4}	1.732×10^{6}	2.363×10^{8}	3.157×10^{10}	4.148×10^{12}
T(K)	Progress of the decomposition (×100)					
373	0.290	0.211	0.153	0.111	0.081	0.058
383	0.381	0.297	0.232	0.181	0.141	0.110
393	0.494	0.412	0.343	0.286	0.238	0.199
403	0.632	0.561	0.499	0.443	0.394	0.350
413	0.799	0.754	0.712	0.672	0.635	0.599
423	1.000	1.000	1.000	1.000	1.000	1.000
433	1.238	1.308	1.381	1.459	1.542	1.628
443	1.518	1.691	1.881	2.094	2.331	2.593
453	1.847	2.161	2.528	2.956	3.456	4.039
463	2.227	2.733	3.352	4.108	5.033	6.158
473	2.666	3.423	4.390	5.625	7.198	9.195
483	3.167	4.246	5.682	7.591	10.117	13.436
493	3.737	5.219	7.272	10.100	13.971	19.205
503	4.380	6.361	9.205	13.253	18.950	26.808
513	5.102	7.689	11.528	17.151	25.231	36.463
523	5.908	9.222	14.287	21.887	32.940	48.157
533	6.804	10.977	17.528	27.534	42.099	61.463
543	7.793	12.970	21.287	34.131	52.558	75.305
553	8.800	15.217	25.593	41.659	63.908	87.820
563	10.069	17.730	30.459	50.018	75.406	96.581
573	11.364	20.521	35.881	59.003	85.942	99.886
593	14.284	26.954	48.240	77.367	98.843	
613	17.657	34.512	62.030	92.482	99.999	
633	21.489	43.095	75.980	99.591		
653	25.774	52.483	88.197			
673	30.492	62.321	96.552			

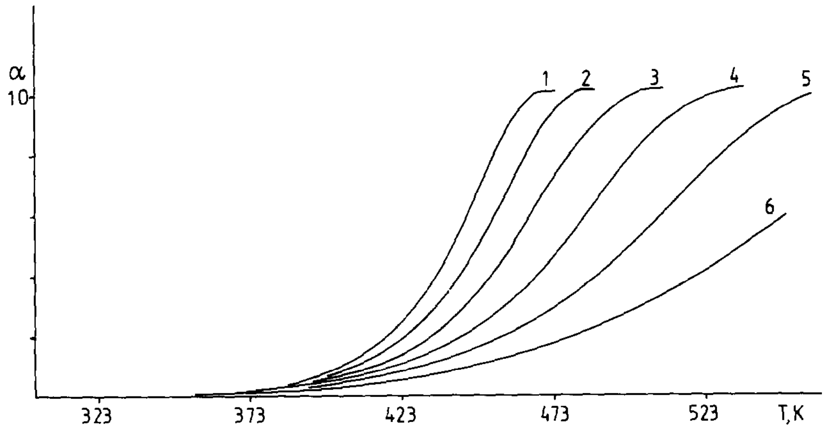

Fig. 2. α–T relationship for the function $g(\alpha)=[1-(1-\alpha)^{1/3}]^2$. For the selected E values, A is calculated such that, for $\Phi = 10$ K min^{-1}, $\alpha = 0.01$ at 373 K. The values of E, in kcal mol^{-1}, are: curve 1, 34; curve 2, 30; curve 3, 26; curve 4, 22; curve 5, 18; curve 6, 14.

TABLE 6

$\alpha - T$ relationships for the function $g(\alpha) = 1 - (1-\alpha)^{1/2}$ (R2, contracting area equation). For each E value A is calculated such that, for a heating rate $\Phi = 10$ K min^{-1}, progress of the decomposition $\alpha = 0.001$ at 423 K

E (cal mol^{-1})	14000	18000	22000	26000	30000	34000
A (min^{-1})	3.771×10^4	5.528×10^6	7.766×10^8	1.059×10^{11}	1.415×10^{13}	1.859×10^{15}
T(K)	Progress of the decomposition ($\times 100$)					
373	0.084	0.044	0.023	0.012	0.006	0.003
383	0.145	0.088	0.053	0.032	0.020	0.012
393	0.244	0.169	0.117	0.082	0.057	0.039
403	0.399	0.315	0.249	0.196	0.155	0.122
413	0.639	0.569	0.507	0.452	0.403	0.359
423	1.000	1.000	1.000	1.000	1.000	1.000
433	1.534	1.712	1.910	2.132	2.379	2.653
443	2.309	2.860	3.541	4.383	5.421	6.699
453	3.412	4.666	6.372	8.686	11.811	16.001
463	4.957	7.440	11.126	16.547	24.405	35.520
473	7.082	11.591	18.810	30.079	46.878	69.601
478	8.413	14.240	24.133	39.672	62.356	89.015
483	9.953	17.633	30.653	51.346	79.468	99.986
488	11.728	21.544	38.497	64.868	94.963	
493	13.764	26.148	47.772	79.316	99.999	
498	16.087	31.510	58.246	92.477		
503	18.726	37.678	69.738	99.845		
508	21.707	44.674	81.463			
513	25.056	52.467	92.025			
518	28.794	60.956	99.008			
523	32.940	69.927	99.999			
528	37.505	79.009				
533	42.490	87.608				
543	53.654	94.822				
553	66.095	99.328				

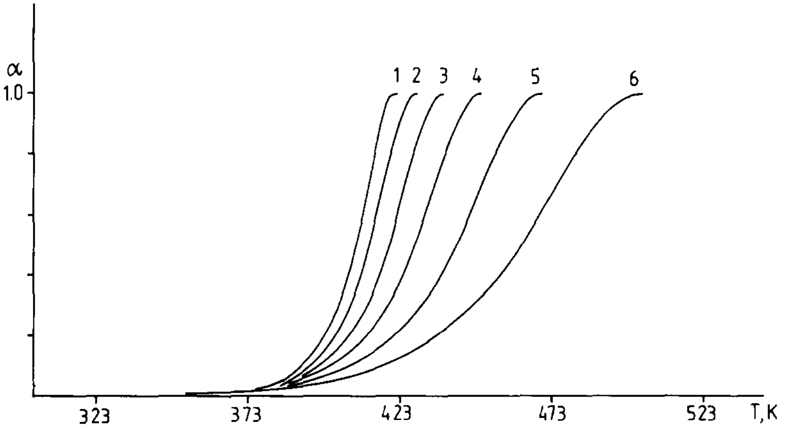

Fig. 3. $\alpha - T$ relationship for the function $g(\alpha) = 1 - (1-\alpha)^{1/2}$. For the selected E values, A is calculated such that, for $\Phi = 10$ K min^{-1}, $\alpha = 0.01$ at 373 K. The values of E, in kcal mol^{-1}, are: curve 1, 34; curve 2, 30; curve 3, 26; curve 4, 22; curve 5, 18; curve 6, 14.

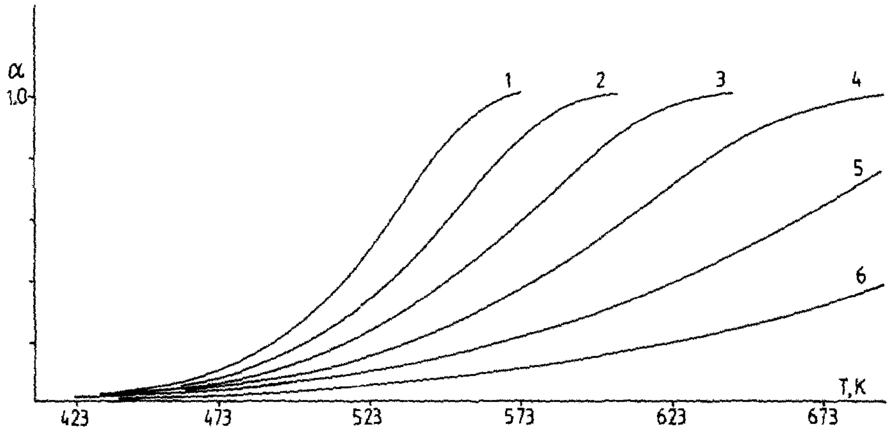

Fig. 4. α–T relationship for the function $g(\alpha) = -\ln(1-\alpha)^{1/2}$. For the selected E values, A is calculated such that, for $\Phi = 10$ K min^{-1}, $\alpha = 0.01$ at 423 K. The values of E, in kcal mol^{-1}, are: curve 1, 34; curve 2, 30; curve 3, 26; curve 4, 22; curve 5, 18; curve 6, 14.

and E values vary, although the basic assumptions that, at the heating rate $\Phi = 10$ K min^{-1}, the value of $\alpha = 0.01$ is reached (at the temperature of 373 K), is maintained and, apart from the fact that the form of $g(\alpha)$ function is constant. This relationship is shown in Fig. 9, where, for a particular $g(\alpha)$ function, the value of α, after a 100 min reaction at a temperature of 333 K, is presented as the function of the value of the activation energy E.

Figures 8 and 9 show clearly how unreliable the conclusions are concerning the "thermal stability", based on the results of the rising temperature experiments, if the values of all the kinetic parameters are not taken into

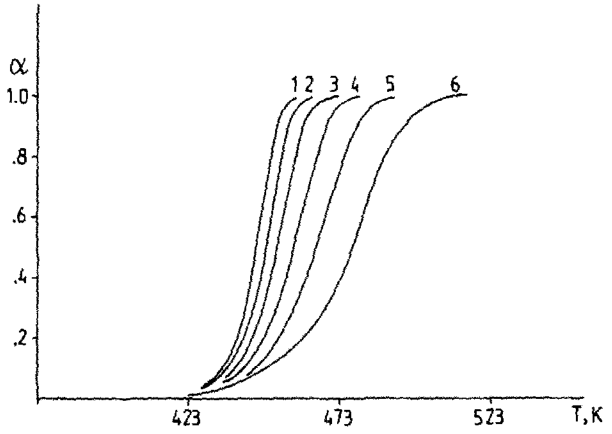

Fig. 5. α–T relationship for the function $g(\alpha) = [1-(1-\alpha)^{1/3}]^2$. For the selected E values, A is calculated such that, for $\Phi = 10$ K min^{-1}, $\alpha = 0.01$ at 423 K. The values of E, in kcal mol^{-1}, are: curve 1, 34; curve 2, 30; curve 3, 26; curve 4, 22; curve 5, 18; curve 6, 14.

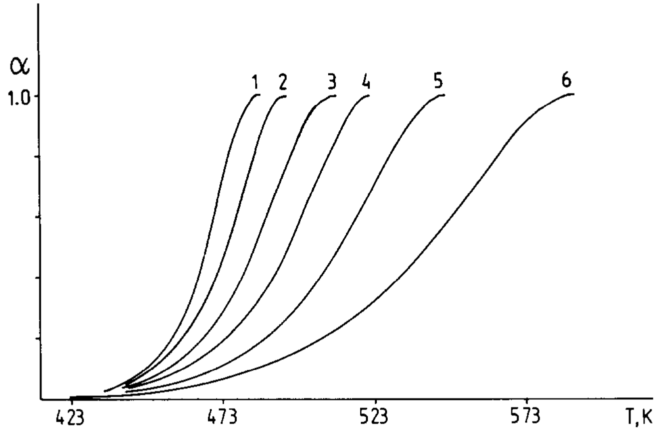

Fig. 6. α–T relationship for the function $g(\alpha) = 1-(1-\alpha)^{1/2}$. For the selected E values, A is calculated such that, for $\Phi = 10$ K min^{-1}, $\alpha = 0.01$ at 423 K. The values of E, in kcal mol^{-1}, are: curve 1, 34; curve 2, 30; curve 3, 26; curve 4, 22; curve 5, 18; curve 6, 14.

consideration. For all the cases, the progress of decomposition under a dynamic heating rate of 10 K min^{-1} is the same ($\alpha = 0.01$ at 373 K) but, depending on the form of $g(\alpha)$ and the value of the activation energy, at constant temperature there are considerable differences between isothermal α–t relationships. The initial temperature of decomposition is obtained from non-isothermal experiments as 373 K, but, at a distinctly lower temperature

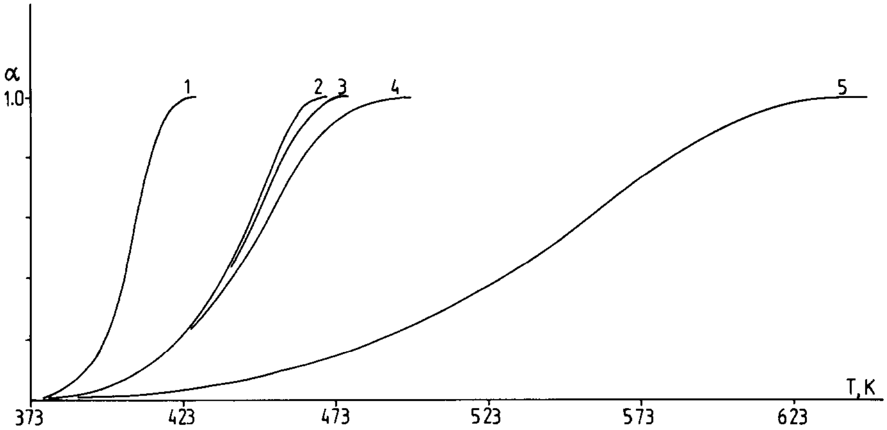

Fig. 7. α–T relationships for the heating rate $\Phi = 10$ K min^{-1} and activation energy $E = 18000$ cal mol^{-1} for five different $g(\alpha)$ functions. The values of pre-exponential factor A are calculated such that $\alpha = 0.01$ at 373 K: curve 1, $g(\alpha) = -\ln(1-\alpha)^{1/2}$; curve 2, $g(\alpha) = 1-(1-\alpha)^{1/2}$; curve 3, $g(\alpha) = 1-(1-\alpha)^{1/3}$; curve 4, $g(\alpha) = -\ln(1-\alpha)$; curve 5, $g(\alpha) = [1-(1-\alpha)^{1/3}]^2$.

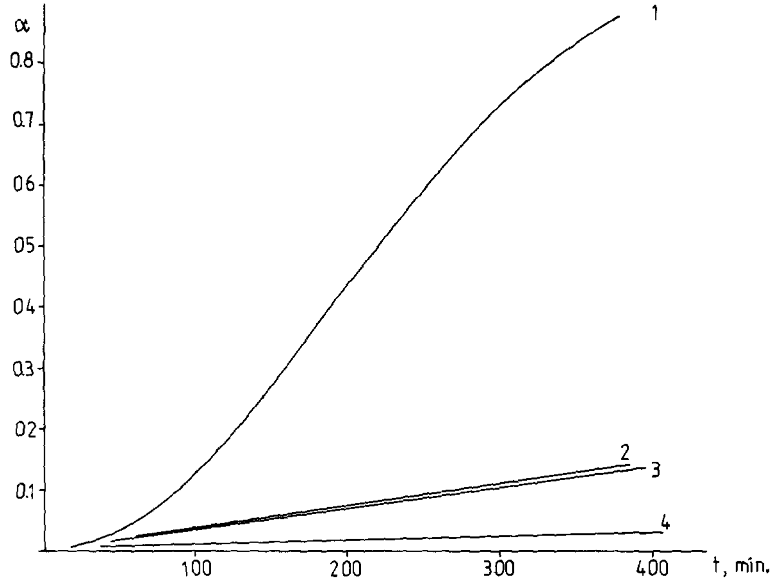

Fig. 8. Isothermal $\alpha - t$ relationships at 333 K for four forms of the $g(\alpha)$ function. For each $g(\alpha)$ function the progress of the reaction α is 0.01 at 373 K during dynamic heating with $\Phi = 10$ K $\min^{-1}$: curve 1, $g(\alpha) = -\ln(1-\alpha)^{1/2}$; curve 2, $g(\alpha) = 1-(1-\alpha)^{1/2}$; curve 3, $g(\alpha) = -\ln(1-\alpha)$; curve 4, $g(\alpha) = [1-(1-\alpha)^{1/3}]^2$.

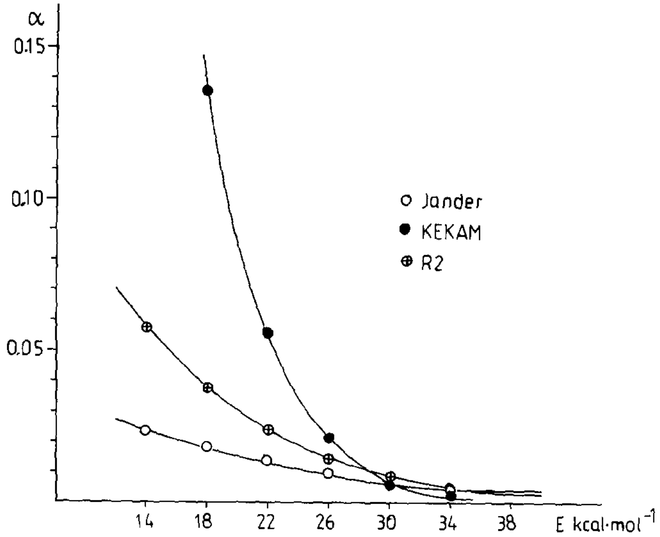

Fig. 9. $\alpha - E$ relationships for different forms of the $g(\alpha)$ function at constant temperature $T = 333$ K. For each $g(\alpha)$ function the progress of the reaction $\alpha = 0.01$ at 373 K during dynamic heating with $\Phi = 10$ K $\min^{-1}$.

of 333 K, in isothermal investigations, after, for instance, 200 min, the progress of the reaction varies, depending on which equation is used, from 0.025 (Jander), through 0.075 (R2) to 0.441 (KEKAM).

The last example demonstrates how important it is, if, apart from the values of the activation energy and the pre-exponential factor, the form of $g(\alpha)$ is introduced into "thermal stability" considerations. Without the knowledge of the form of the $g(\alpha)$ equation, the conclusions about the "initial temperature of decomposition" might be, in certain cases, incorrect. This can be clearly shown by the calculations based on the Piloyan formula for T_i determinations. Table 7 contains calculations made for four different equations using the conditions mentioned above (heating rate of 10 K min^{-1}, E ranging from 14000 to 34000 cal mol^{-1} and A calculated in such a way that $\alpha = 0.01$ at 373 K). It should be noted that Piloyan's formula gives the correct values only for the kinetic equations $f(\alpha) = 1 - \alpha$ or $g(\alpha) = -\ln(1 - \alpha)$.

Only for this "first order" equation are the values of T_i independent of A and E, and they are in a narrow temperature range ($\approx$ 3 K). For other $g(\alpha)$ functions, the initial temperatures of decomposition, which, it should be remembered, was 373 K in the dynamic experiments, are, depending on the values of E and A, in the following ranges: 354–360 K (R2 equation), 405–523 K (Jander equation) and 312–333 K (KEKAM equation).

Piloyan's equation has been slightly modified by Gorbachev [10], who has introduced into consideration a very well-known relationship, the so-called "compensation effect":

$$\ln A = aE + b \tag{18}$$

where a and b are constants. Gorbachev's equation has the following form:

$$T_i = \frac{E}{R(aE + b) + R \ln E/R\Phi} \tag{19}$$

TABLE 7

Initial temperatures of the decomposition T_i, in K, calculated from the Piloyan equation (1) for the rising temperature experiments for the different forms of the $g(\alpha)$ function: E in cal mol^{-1}, A in min^{-1}

E	$-\ln(1-\alpha)^{1/2}$		$[1-(1-\alpha)^{1/3}]^2$		$1-(1-\alpha)^{1/2}$		$-\ln(1-\alpha)$	
	A	T_i	A	T_i	A	T_i	A	T_i
14000	8.995×10^{6}	312.1	1.004×10^{3}	523.1	4.497×10^{5}	359.9	9.017×10^{5}	347.6
18000	2.490×10^{9}	318.5	2.778×10^{5}	468.3	1.245×10^{8}	355.9	2.496×10^{8}	346.5
22000	6.622×10^{11}	323.5	7.391×10^{7}	441.6	3.311×10^{10}	354.5	6.639×10^{10}	346.8
26000	1.711×10^{14}	327.5	1.910×10^{10}	424.1	8.556×10^{12}	354.1	1.715×10^{13}	347.5
30000	4.328×10^{16}	330.9	4.829×10^{12}	413.4	2.164×10^{15}	354.2	4.339×10^{15}	348.5
34000	1.077×10^{19}	333.8	1.202×10^{15}	405.8	5.385×10^{17}	354.5	1.079×10^{18}	349.4

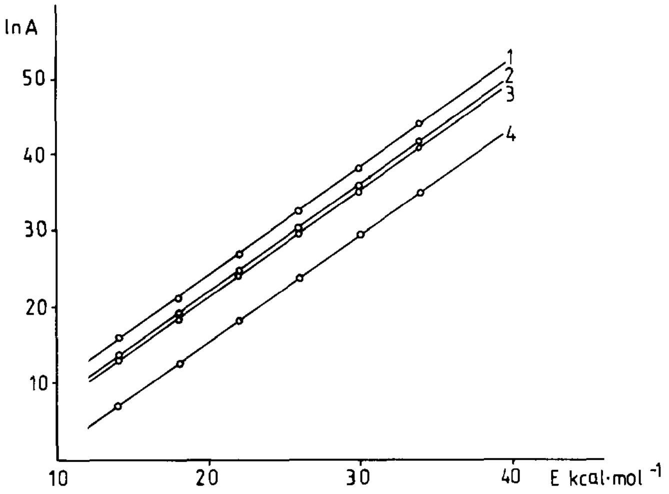

Fig. 10. ln $A-E$ relationships (the "compensation effect") for four forms of the g(α) function. The values of the constants a and b (equation 18) are: $a = 0.00139$ for all g(α) functions, $b = -3.402$ for the KEKAM equation (curve 1), $b = -5.702$ for the F1 equation (curve 2), $b = -6.673$ for the R2 equation (curve 3) and $b = -12.502$ for the Jander equation (curve 4).

For all the four equations of the g(α) function, the constants of the "compensation effect" were calculated and ln $A-E$ relationships are presented in Fig. 10 (for all the straight lines the correlation coefficient is higher than 0.99999). Calculations based on equation (19) gave, and this is, of course, obvious, the same results as those in Table 7. So, even if the so-called "compensation effect" relationship is exhibited by A and E, the disregard for the g(α) form in our considerations may result in wrong conclusions with respect to the thermal stability of the investigated compound.

The conclusions presented in this paper were verified experimentally [20].

CONCLUSIONS

The values of the initial temperature of decomposition, T_i, are often determined on the basis of the results of rising temperature experiments. Calculations presented above show clearly the unreliability of a method into which the kinetic parameters A, E and g(α) are not introduced. The temperature, determined in dynamic conditions, at which a compound may be kept isothermally without change in its stoichiometry (that is to say, a temperature which is lower by 20–30 K than T_i) may turn out to be a temperature at which, after a short time, significant decomposition of the compound will occur. If the temperature of decomposition (e.g. the temperature at which α reaches the value of 0.01), determined on the basis of a dynamic run at the often-used heating rate of 10 K $\min^{-1}$, is 423 K (150°C) then, depending on the values of the kinetic parameters, the progress of the reaction in isothermal experiments may exhibit substantial differences.

At a constant temperature of 333 K (60°C), which is 90 K lower than the temperature of "dynamic thermal stability", after only 100 min, the total percentage weight loss may vary from 3.31 ($E = 18\,000$ cal mol^{-1}, KEKAM equation) to 0.05% ($E = 30\,000$ cal mol^{-1}, R2 equation).

It is evident that thermodynamic data were not included in the above calculations and that the values of the equilibrium pressure may affect the real values of the progress of the reaction. Apart from this reservation, the calculations presented in this paper demonstrate that there is a possibility of making significant errors in, for instance, attempts aimed at the interpretation of the thermal decomposition mechanism on the basis of dynamic experiments. A complete disregard for the kinetics of decomposition, and omitting the mathematical form of the equation describing the reaction rate, make it impossible for the data obtained in these experiments to provide relevant information about the thermodynamic stability of compounds. Furthermore, drawing conclusions about the decomposition mechanism, the strength of the broken bonds, etc., should be done with due caution.

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