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QUANTITATIVE METHOD FOR COMPARING THERMOGRAVIMETRIC DATA UNDER VARIOUS MEASURING CIRCUMSTANCES

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What science does, in fact, is to select the simplest formula that will fit the facts. B. Russell [*1*]

ABSTRACT

The comparability of thermogravimetric data under different circumstances on various balances was studied using calcium carbonate as a model substance. The congruency of different measurements was proved by shifting and turning the co-ordinate axes of ln $(-\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)$ vs. $1/T$ plots.

According to the congruency, the structure of the $-\mathrm{d}\alpha/\mathrm{d}t = A\exp(-E/RT)(1-\alpha)^n$ differential equation, which is very formal but has very great descriptive power, affords the possibility of several methods for comparing quantitatively the data measured under different circumstances. Introducing the idea of the compensation effect of single measurement, $(\mathrm{C.E.})_i$, the change of the straight line determined by two data is applicable to the quantitative analysis of the relation between different measurements. The effect of the measuring circumstances is conveyed more expressively and suggestively by the similarity of the E^* vs. $(1-\alpha)$ functions and can be characterized by two numbers marked expediently as ln A^* and n^*. These are calculated by the $E^* = T[\ln A^* + n^*\ln(1-\alpha) - \ln(-\mathrm{d}\alpha/\mathrm{d}t)]$ equation. The application of the method can be extended to cases with more peaks.

INTRODUCTION

It is a well known fact that thermoanalytical curves can be used as "finger prints" of the substances investigated within one laboratory only, because the measured data are very sensitive to the measuring circumstances, e.g. sample mass, heating rate, shape of the sample holder, etc. The efforts to eliminate these effects were not successful in spite of the far-reaching investigation of measuring circumstances [2–7], errors and accuracy [2,8,9] and the development of very sensitive (or sophisticated?) instruments.

The idea of measuring the data which are characteristic of the examined substance is central to the instrument development and also to a very comprehensive work in another direction: to develop methods and functions

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for the exact description of the different phenomena [2-4,8,10-15], mainly on the basis of the Arrhenius equation. The problem of characterizing the examined materials by kinetic constants is obviously also unsolved. This results from the sharp discussion and the sceptical or even ironical opinions published in the literature [9,16-20].

The cause of the failure is the attempt to characterize by kinetic constants only the examined substance, though its "behaviour" is examined in action and reaction, which cannot be imagined to be independent of the circumstances. It is the general idea to consider the kinetic constants of phenomenological kinetic analysis as characteristic values of the examined substance instead of the substance plus conditions. This is the reason why the elimination of the effects of measuring circumstances seems to be a more important task in the work of instrument and evaluation development than discovering the details of the effects of the circumstances.

The phenomenon that the measured data and calculated constants depend on the measuring circumstances is widely thought to be a problem only of heterogeneous systems. It is obvious, however, that the reactions in the homogeneous phase are not simple either. Only the superimposed complexity of the reaction mechanism can be measured by thermal methods and the internal rates of different part-processes alter together with the circumstances even in the homogeneous phase making the idea of eliminating the effects of circumstances impossible and unnecessary.

Phenomenological kinetics work with macroscopic measurements. Macroscopic measurements are slow in comparison with the atomic time scale (10^{-15} s order of magnitude) and roughly on the atomic length scale (10^{-8} cm). The macroscopical measurements yield some kind of space-time integration of the microscopic processes. The microscopic processes of elementary reactions appear so complicated that it seems impossible to construct a correct generally valid macroscopic model suitable for practical aims within reasonable time; thus the developed systems elaborated up to the present have yet to be described.

The widely used differential equations join through the Arrhenius equation with the Boltzmann equation and though the mathematical status has been discussed recently [21,22], its great descriptive power and manageability account for the practical applicability as long as it cannot be replaced with a better one in the work to develop a method for the quantitative comparison of the data measured under various circumstances.

EXPERIMENTAL

Calcium carbonate was chosen as a model substance because a lot of data have been published about its thermal decomposition, the products of decomposition are definite and it is widely used in industry making it possible to look for the relationship between thermoanalytical and industrial experience.

The sample mass and heating rate ranged from 0.8 to 3460 mg and from 3 to 13 K min^{-1}, respectively. The shape of the sample was varied with the shape of the sample holder and from a pulverised form to a rigid sphere of marble (Fig. 1). The type of thermobalance was also varied (Derivatograph, Heraeus TGA-500, Mettler).

It is a fact that the widely used structure of eqn. (1) can describe the thermoanalytical data (in this case TG and DTG curves) with a very good fit and increasing the number of constants from three (A, E, n) e.g. to five (A, E, n, m, p: eqn. (2)) [10] cannot increase the fit or give some deeper information about the decomposition of calcium carbonate [23,24,25], though the importance of different superimposed part-processes, viz. nucleation, diffusion etc. is obvious. Equations (1) and (2) are as follows

$$-\mathrm{d}\alpha/\mathrm{d}t = A\exp(-E/RT)(1-\alpha)^n \tag{1}$$

$$-\mathrm{d}\alpha/\mathrm{d}t = A\exp(-E/RT)(1-\alpha)^n\alpha^m[-\ln(1-\alpha)]^p \tag{2}$$

where the symbols have their usual meaning.

According to the above results, eqn. (1) was used for evaluation of the measured data.

It was proved previously [23,24,25] that the kinetic compensation effect (C.E.), namely the linear function of the logarithm of the pre-exponential factor and the activation energy, exists in the case of a single measurement (C.E.)$_i$, too, calculating the kinetic constants with various usual differential

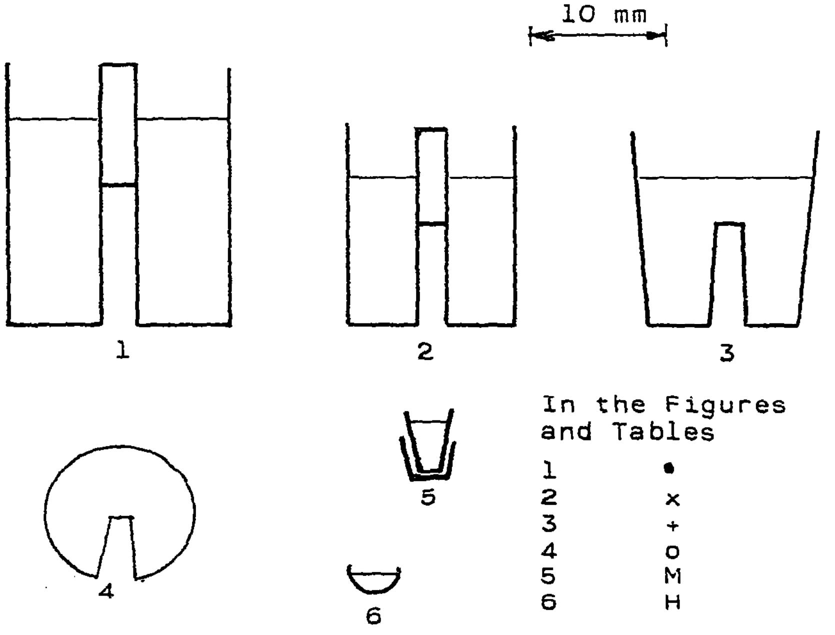

Fig. 1. The shape of the samples.

TABLE I

The kinetic constants and the linear regression coefficients of the (C.E.)$_i$ function

	Observation no.						
	1	2	3	4	5	6	7
"A"							
Shape of sample	1	1	1	1	1	4	4
Type of balance [a]	D	D	D	D	D	D	D
Sample mass; mg	100	200	400	1000	2000	1152	3460
Heating rate; K min^{-1}	9	9	9	9	9	9	9
Temperature range; °C	680–820	670–840	680–850	740–905	830–908	678–908	760–967
ln A	19.69	19.36	17.55	16.25	20.69	9.73	17.12
E; kJ mole^{-1}	229.91	226.85	217.77	213.79	260.22	154.80	230.24
n	0.45	0.38	0.39	0.41	0.52	0.44	0.87
r	0.9986	0.9953	0.9979	0.9980	0.9937	0.9986	0.9961
"B" $\ln A = a_0 E + a_1$							
a_1	−6.3020	−5.7839	−5.4843	−5.6422	−5.9071	−6.0971	−5.7260
a_0	0.1133	0.1112	0.1058	0.1026	0.1022	0.1021	0.0999
r	1.0000	0.9999	1.0000	0.9999	0.9998	1.0000	0.9998

	Observation No.						
	8	9	10	11	12	13	14
"A"							
Shape of sample	5	5	2	2	2	6	6
Type of balance	M	M	D	D	D	H	H
Sample mass; mg	10	20	100	400	800	0,855	10
Heating rate; K min^{-1}	10	4	9	9	9	10	10
Temperature range; °C	610–820	640–840	646–827	676–876	710–899	627–775	638–875
ln A	17.23	16.41	20.21	15.41	14.12	13.21	13.38

r	0.9923	0.9920	0.9792	0.9991	0.9996	0.9752	0.9758
"B" $\ln A = a_0 E + a_1$							
a_1	−5.2726	−6.2832	−5.4572	−5.1198	−5.4647	−5.7217	-6.1565
a_0	0.1108	0.1090	0.1115	0.1020	0.1005	0.1174	0.1099
r	1.0000	1.0000	1.0000	1.0000	0.9998	0.9998	1.0000

	Observation No.					
	15	16	17	18	19	20
"A"						
Shape of sample	3	3	3	3 [b]	3 [c]	3
Type of balance	D	D	D	D	D	D
Sample mass; mg	200	200	200	200	40	1000
Heating rate; K min^{-1}	3.1	7.1	11.7	7.9	11.6	13.5
Temperature range; °C	658–810	699–867	690–880	762–902	680–808	769–986
ln A	19.95	25.77	13.33	13.54	18.87	11.87
E; kJ mole^{-1}	234.98	287.31	180.66	200.63	218.96	182.22
n	1.48	1.72	0.70	−2.52	0.10	0.14
r	0.9979	0.9858	0.9893	0.9995	0.9969	0.9967
"B" $\ln A = a_0 E + a_1$						
a_1	−3.3285	−4.7460	−6.0021	−10.2021	−5.3913	−5.9945
a_0	0.1022	0.1068	0.1074	0.1179	0.1107	0.0980
r	0.9962	0.9999	1.0000	0.9995	0.9999	1.0000

[a] D, Derivatograph; M, Mettler; H, Heraeus.

[b] Covered.

[c] Small.

equations. The inferior letter i indicates the difference between this and the usual idea of the compensation effect (C.E.) [26–33].

Table 1 contains both the kinetic constants of measured data calculated by eqn. (1) and the regression coefficients of $(\text{C.E.})_i$. The ln A and E values were calculated for this by eqns. (1)–(4). Equations (3) and (4) are as follows

$$-\mathrm{d}\alpha/\mathrm{d}t = A\exp(-E/RT)(1-\alpha)^n\alpha^m \tag{3}$$

$$-\mathrm{d}\alpha/\mathrm{d}t = A\exp(-E/RT)(1-\alpha)^n[-\ln(1-\alpha)]^p \tag{4}$$

It is obvious on the basis of Table 1 that the effect of the measuring circumstances cannot be brought into direct connection with either the kinetic constants or the fitness of description.

Experience of comparison in the case of reaction order one

Setting out from the formal character of eqn. (1), namely from the mutual dependence of kinetic constants [23–25], the measured data were examined directly, while the reaction order was chosen expediently as one.

Comparing the plots of $1/T$ vs. logarithm of measured data of reaction rate proved to be very fruitful among the different possible combinations. It was established graphically that such curves for the thermogravimetric data of calcium carbonate are congruent. If only the quantity of the sample was changed while the same sample holder or sample shape is used, the parallel

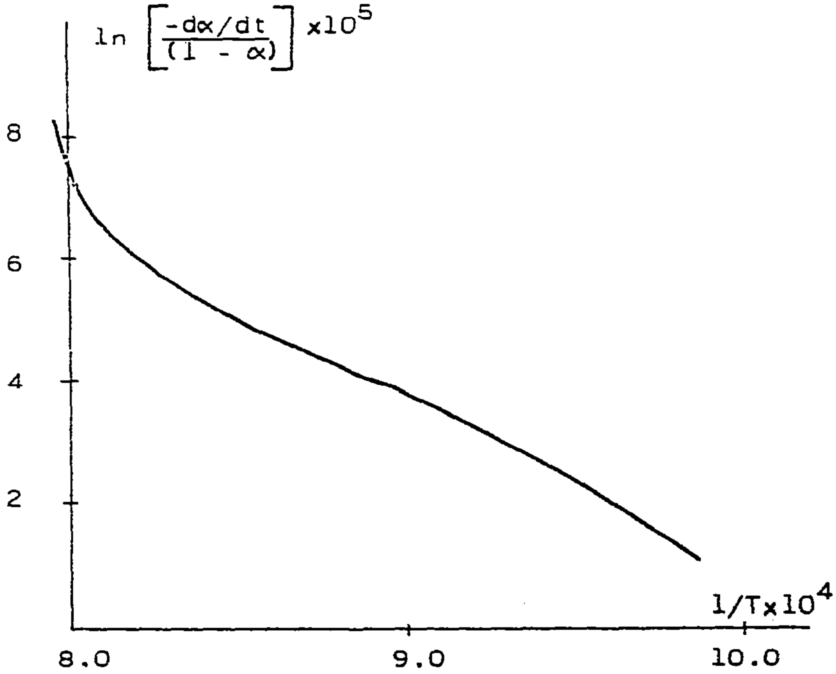

Fig. 2. The ln $[(-\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)] \times 10^5$ vs. $1/T$ plot of 3460 mg spherical form sample received by Derivatograph (No. 7 in Table 1).

shift of the coordinate axes is enough for a complete covering of the different curves. In the case of comparison of various measuring systems, including vacuum and isotherm measurements as well, the coordinate axes must be both shifted and turned. There is no need to alter the scale of the coordinates to reach congruency. This results indicates the similarity of the measurements using different circumstances.

The results of the following measurements are presented as examples.

(1) 3460 mg sample mass of spherical form recorded by Derivatograph (Fig. 2; observation no. 7 in Table 1).

(2) 10 mg sample mass of powder form recorded by Mettler apparatus with sample holder PID-203 (Fig. 3; observation no. 8 in Table 1).

(3) 400 mg sample mass of powder form recorded by Derivatograph (Fig. 4; observation no. 3 in Table 1).

Figure 5 shows how these curves cover each other by shifting and turning the coordinate axes.

Figure 6 shows the coordinates of similar points for several different measurements as a function of sample mass using one point of the measurement (100 mg initial sample mass in the sample holder type 1) as a reference point chosen at random. The data indicate a characteristic function-like change in connection with both the sample quantity and the shape of

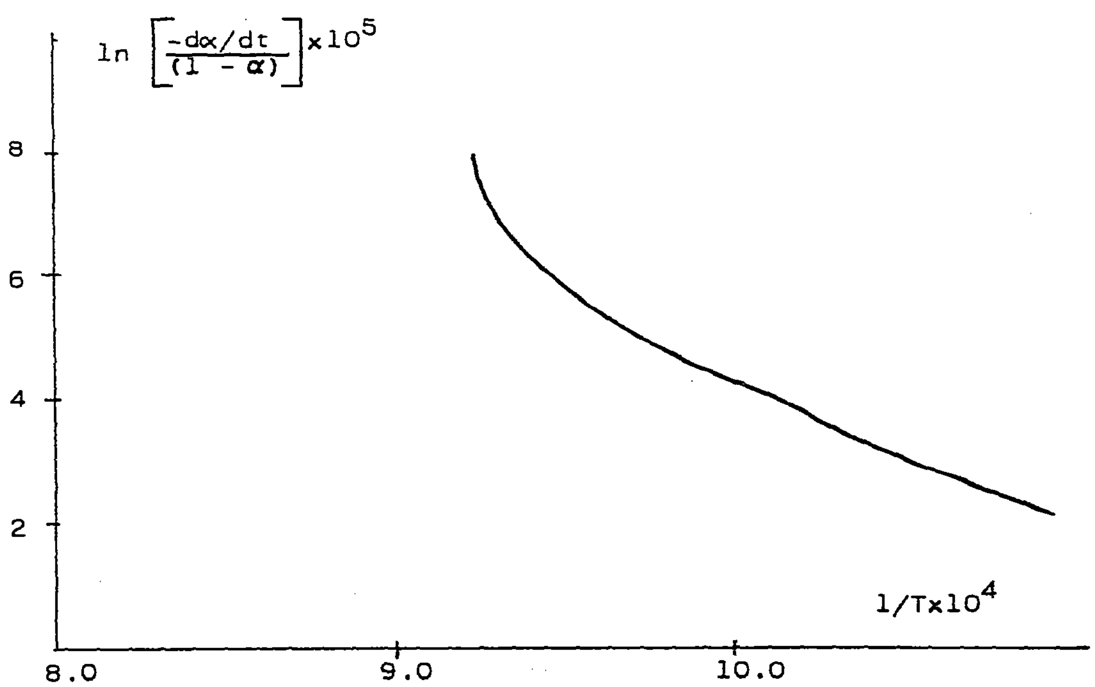

Fig. 3. The ln $[(-d\alpha/dt)/(1-\alpha)]\times 10^5$ vs. $1/T$ plot of 10 mg sample recorded by Mettler balance using sample holder 5 (No. 8 in Table 1).

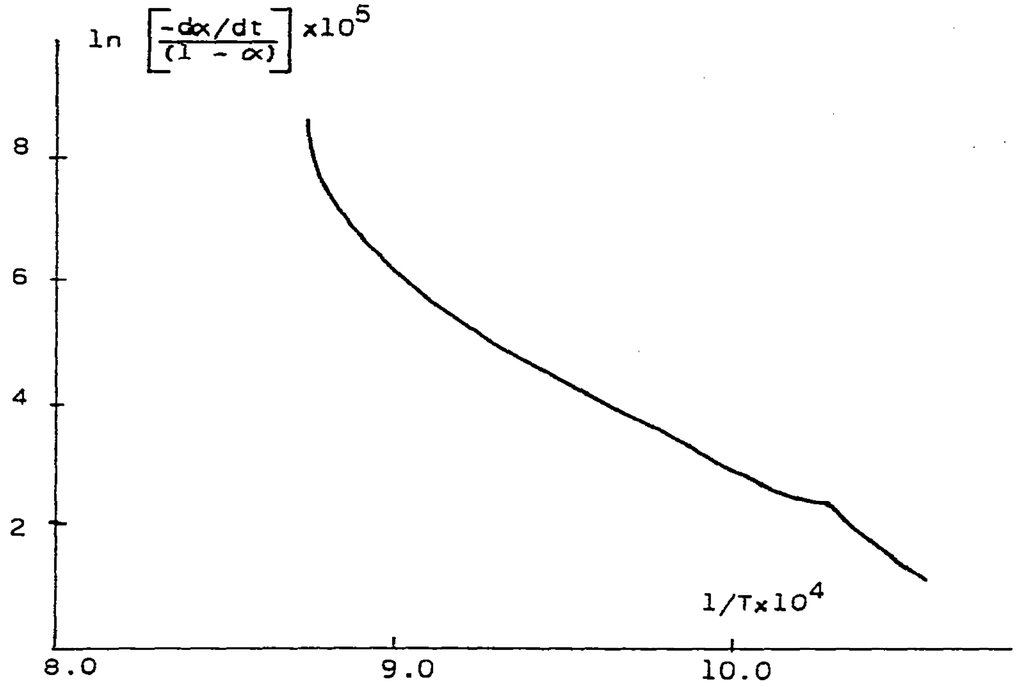

Fig. 4. The ln $[(-\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)]\times10^5$ vs. $1/T$ plot of 400 mg sample recorded by Derivatograph using sample holder 1 (No. 3 in Table 1).

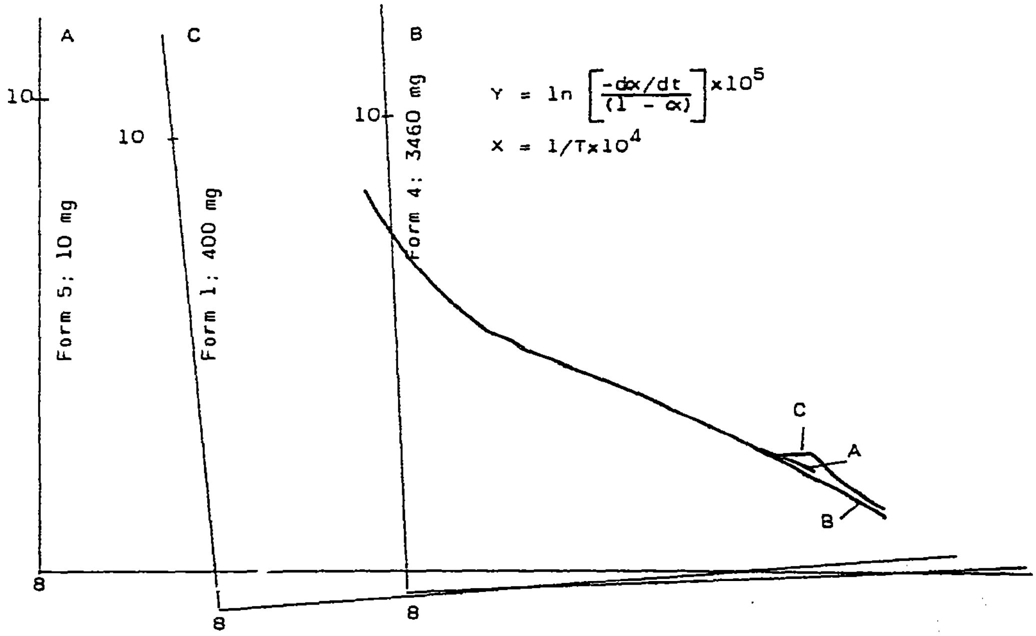

Fig. 5. The congruency of data of various measurements by shifting and turning the coordinate axes (Figs 2–4 together).

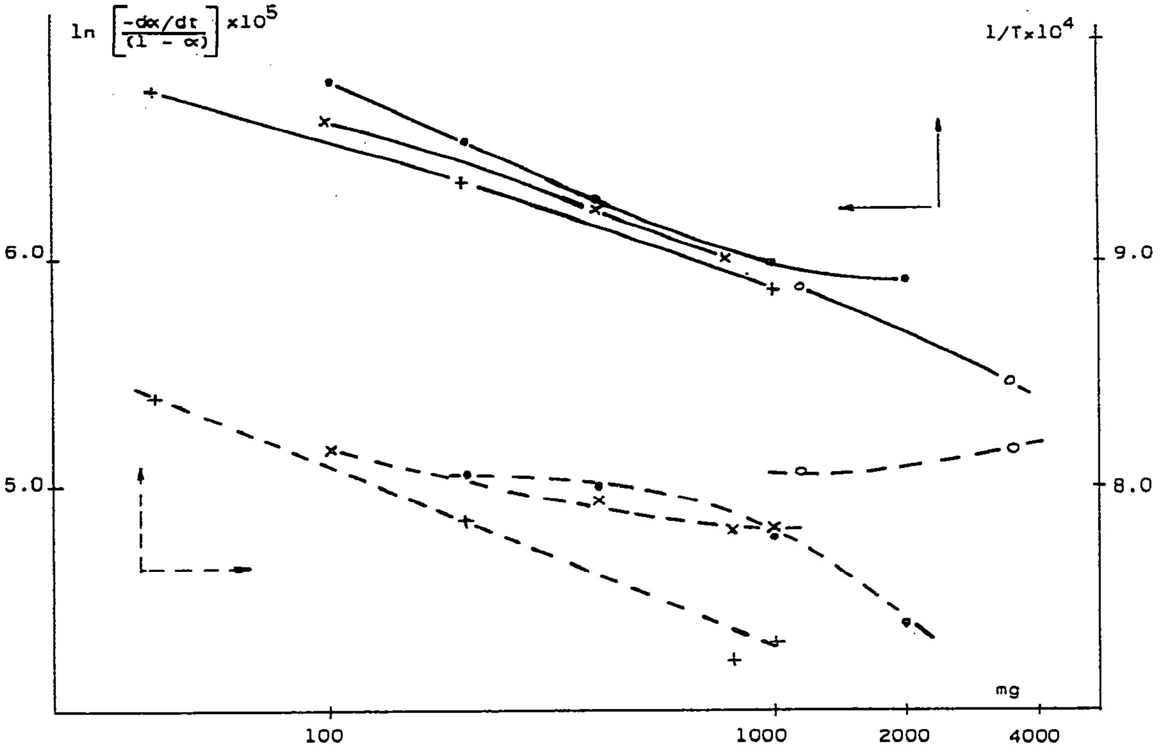

Fig. 6. The dependence of the coordinates of one similar points series of various measurements on sample mass (marks according to Fig. 1).

sample. The results show the measurements to be convertible among each other and beside the similarity the differences are also remarkable.

The comparison of functions (C.E.)$_i$

The moving of coordinates is connected with the alteration of the logarithm of the pre-exponential factor and the activation energy, so it is in close connection with the compensation effect. The (C.E.) is related to the similarity of thermal decomposition data measured under various circumstances, the differences are expressed in the small deviation of the data of single measurements from the function (C.E.). The attachment of a "compensation effect" to the single measurements made possible the examination of this difference.

The calculation of the data ln A and E by various differential equations was chosen from the possible methods for the determination of the function (C.E.)$_i$ based on the mutual dependence of the kinetic constants [25]. The evaluation of the various measurements was performed by four different equations [eqns. (1)–(4)]. Table 1 contains the linear regression coefficients of the (C.E.)$_i$ functions. The (C.E.)$_i$ plots of one series of measurements are

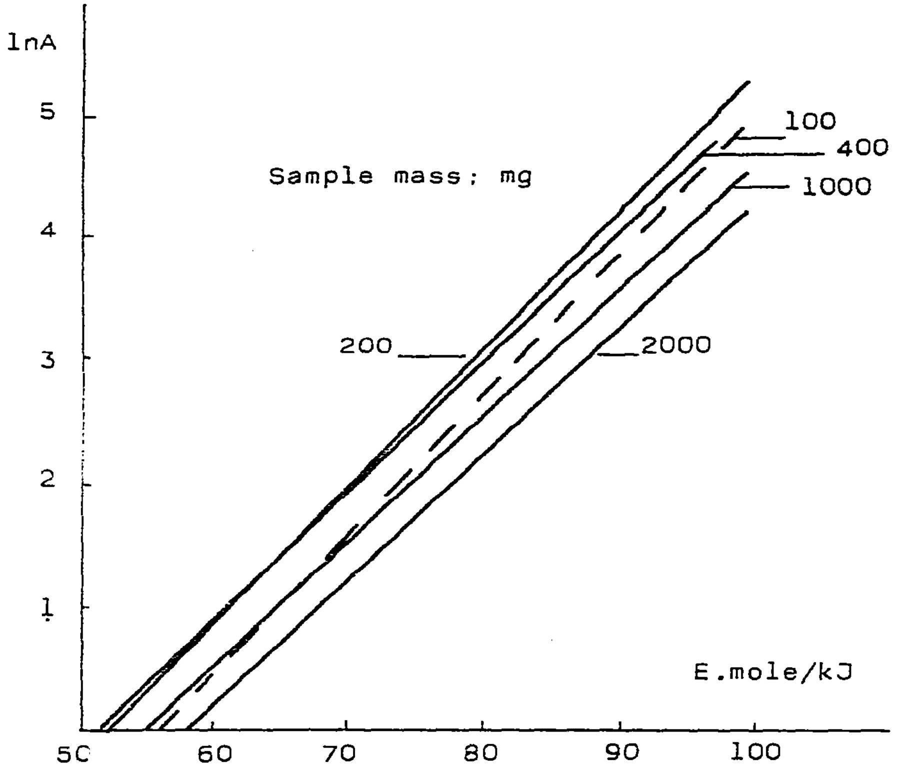

Fig. 7. The (C.E.)$_t$ plots of the measurements 1–5 in Table 1.

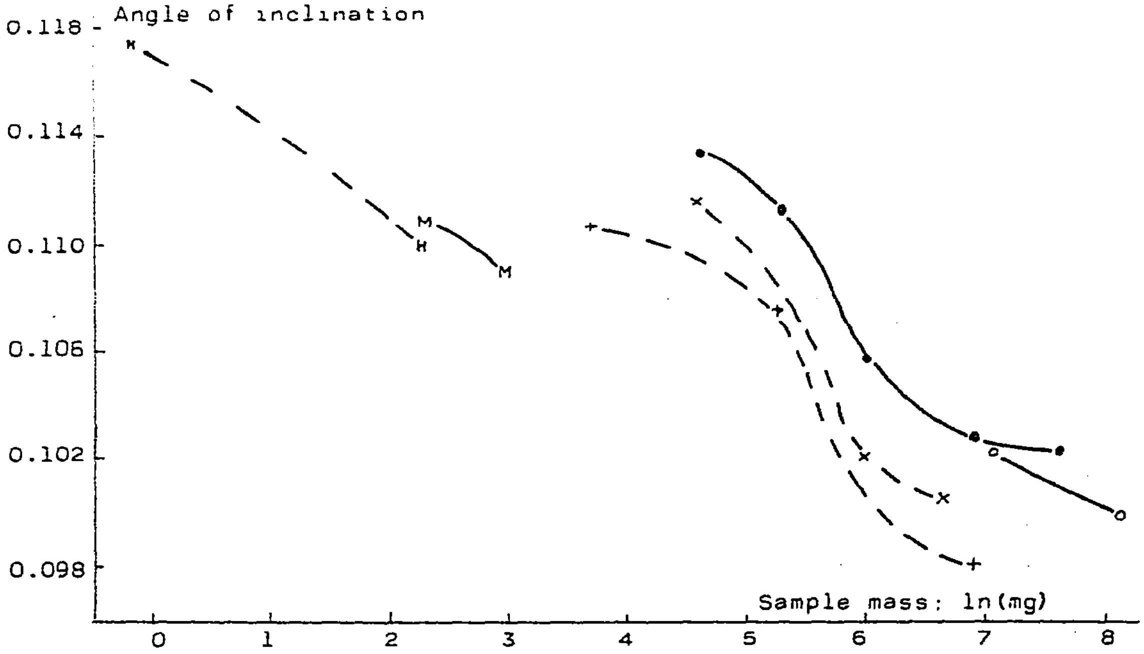

Fig. 8. The dependence of the angle of inclination of (C.E.)$_t$ plots on the sample mass and on the shape of the sample (marks according to Fig. 1).

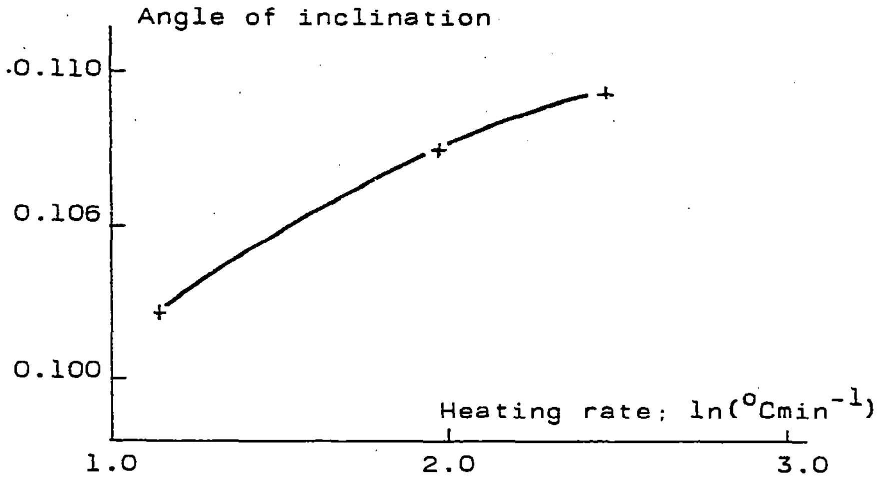

Fig. 9. The dependence of the angle of inclination of (C.E.)$_i$ plots on the heating rate (mark according to Fig. 1).

shown in Fig. 7. The angle of inclination of the various (C.E.)$_i$ functions are plotted in Figs. 8 and 9.

It can be ascertained that the change in the slope of (C.E.)$_i$ lines is unambiguously related to the change in the measuring circumstances so the effect of measuring circumstances can be characterized unambiguously with the difference in the segments of axes and slopes.

Figures 8 and 9 draw attention to the ineffectiveness of the measuring methodology in aiming to eliminate the "disturbing" circumstances. At the same time, these figures indicate the importance of a definite examination of the measuring circumstances and the possibility of extrapolation of thermoanalytical data serving their industrial utilization.

Quantification of similarity of thermogravimetric measurements

The comparison of (C.E.)$_i$ functions proves the possibility of the quantitative evaluation of their similarity. For this purpose the differences of the regression coefficients can be used. However, the determination of the differences of the regression coefficeints are connected with the measuring data through the compensation effect and this presumes that the calculation of the so-called kinetic constants limits the application of this method to processes showing only one thermal peak, which can be described well by eqn. (1).

For the simple quantitative determination of the similarity, it is necessary to start from eqn. (1). The very formal, polynom-like character of eqn. (1) makes it obvious that its great descriptive power is the result of its construction. This structure is overloaded, however, in practice by the postulates of the linearity of the Arrhenius plot and the constancy of the pre-exponential factor, the activation energy and the reaction order.

An examination is made here as to how this structure (which is very useful for describing other processes, too, from vapour–liquid equilibrium to the specific electric conductivity of semiconductors, etc.) can exist without the above postulates expressing $E^* = E/R$ and using only the measured TG, DTG and T data as a funtion of the reaction coordinate $(1-\alpha)$.

Considering A (pre-exponential factor) and n (reaction order) equal to one and expressing E^* the result is eqn. (5) containing only the measured data.

$$E^*_i = T_i[\ln(1-\alpha)_i - ln(-\mathrm{d}\alpha/\mathrm{d}t)_i] \tag{5}$$

Figure 10 shows the TG and DTG curves of the 0.855 mg (Observation no. 13 in Table 1) and the 3460 mg (observation no. 7 in Table 1) samples. The ratio of DTG_7 to DTG_{13} is 990,17.

Figure 11 shows some E^* vs. $(1-\alpha)$ plots using extremely diverse measuring circumstances. It is quite easy to make each E^* vs. $(1-\alpha)$ plot congruent with the other as a basis. One has to multiply the logarithm of the reaction coordinate of the compared substance suitably, using n^* as a "reaction order like" factor and increasing the right hand side of eqn. (5) with a suitable number which is indicated as ln A^* for the sake of similarity. The form of similarity (E^*_s) is eqn. (6).

$$E^*_s = T[\ln A^* + n^* \ln(1-\alpha) - \ln(-\mathrm{d}\alpha/\mathrm{d}t)] \tag{6}$$

Some results of this comparison are demonstrated in Fig. 12 referring to the data of the measurements for the 3460 mg spherical form sample (by Derivatograph) and 10 mg powdered sample (by Mettler) to 0.855 mg sample mass (by Heraeus).

According to the congruency, the expressed similarity or analogy can be

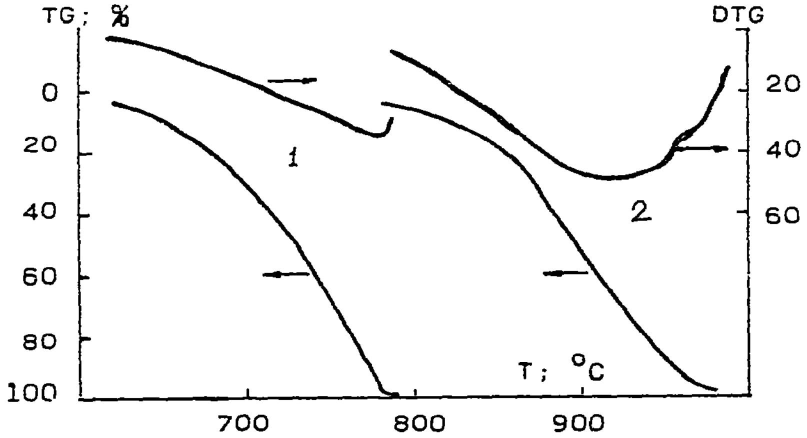

Fig. 10. The TG and DTG curves of calcium carbonate decomposition. 1, 0.855 mg sample (No. 13 in Table 1); 2, 3460 mg sample (No. 7 in Table 1). The ratio of DTG_2 to DTG_1 is 990.17.

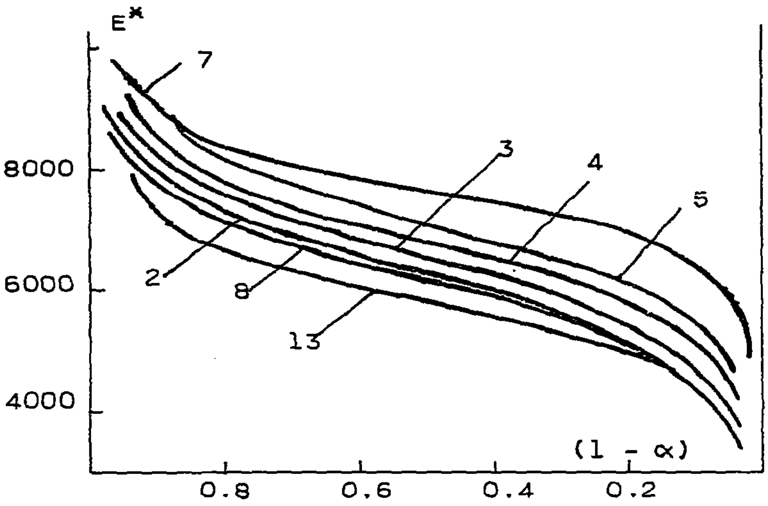

Fig. 11. The reduced temperature (E^*) as the function of the conversion ($1-\alpha$) (observation numbers 2–5, 7, 8, 13 in Table 1).

considered as very good, reducing the effect of measuring circumstances to two factors. These express how many times the reaction rate of the examined substance differs from the reaction rate of the basis measuring (A^*) over the

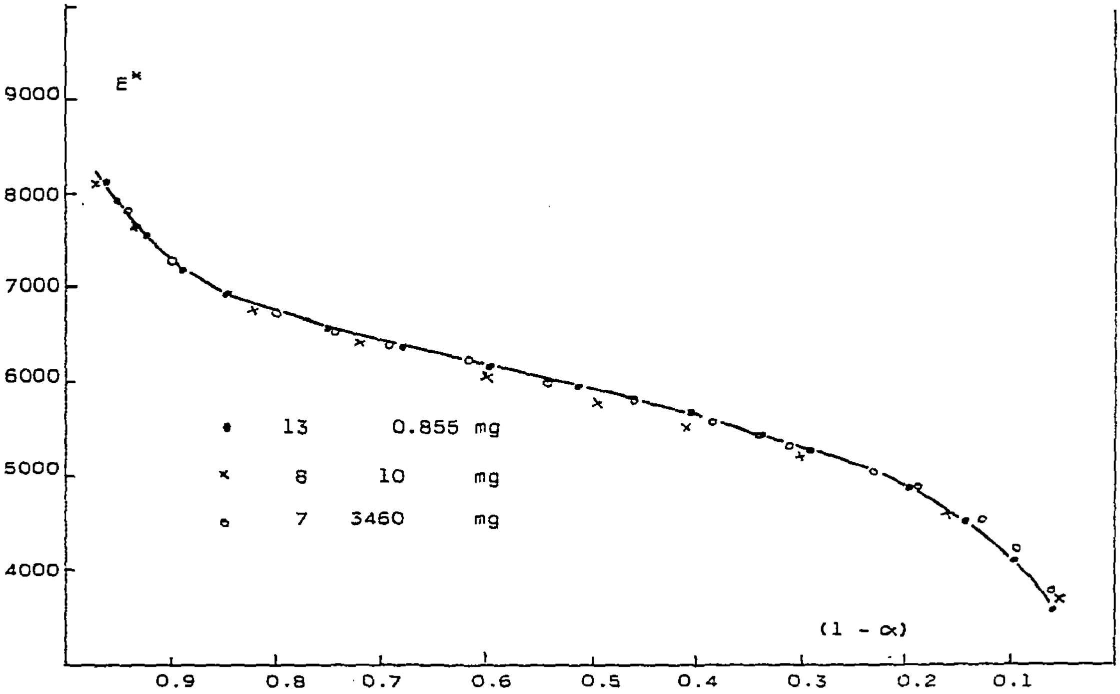

Fig. 12. The transformated reduced temperature as a function of the conversion. The data of measurement with 0.855 mg sample are the bases of transformation (observation numbers 7, 8, 13 in Table 1).

TABLE 2

Comparison of data of different thermogravimatric measurements

Observation no.	Type of balance	Sample mass (mg)	n^*	$-\ln A^*$
"A"				
13	H	0.855	1.00	0.00
14	H	10.0	1.03	0.66
8	M	10.0	0.735	0.145
6	D	1152	1.00	1.19
7	D	3460	1.05	1.96
"B"				
2	D	200	1.00	0.00
3	D	400	1.00	0.23
4	D	1000	1.00	0.60
5	D	2000	1.00	0.86
1	D	100	1.082	0.89
6	D	1152	1.23	2.15
7	D	3460	1.33	3.45

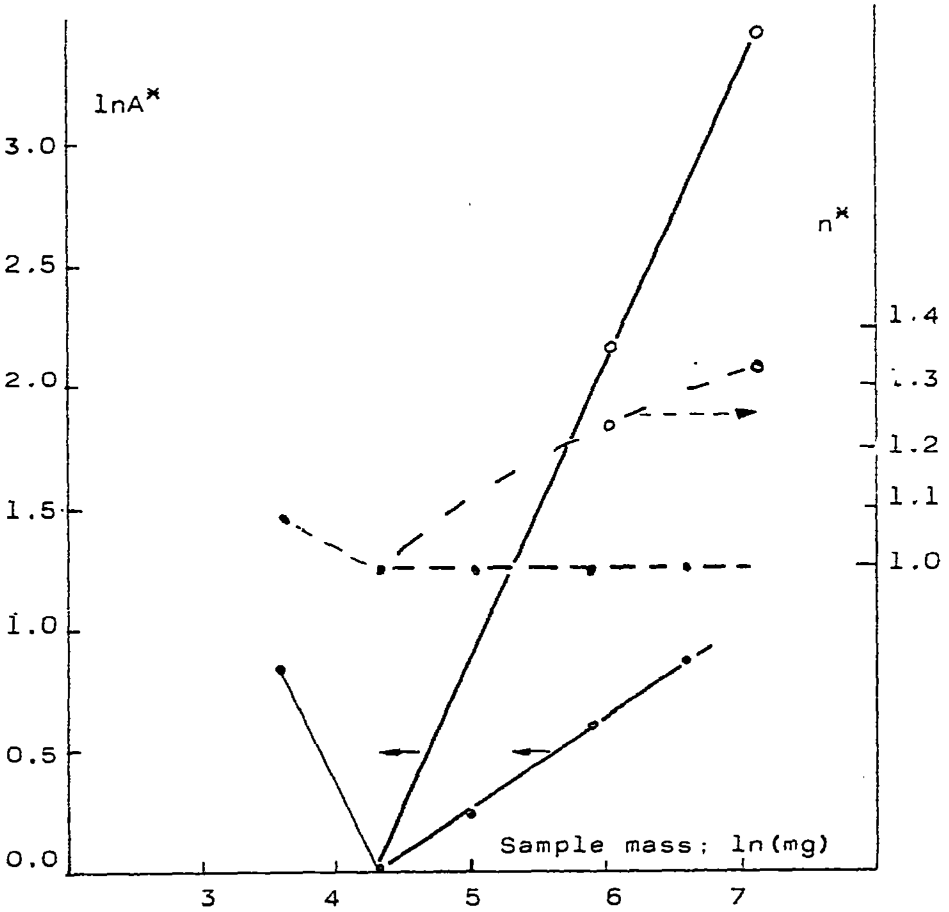

Fig. 13. The dependence of the characteristic numbers of similarity (ln A^* and n^*) on the measuring circumstances.

whole range of the decomposition process and some parts of the effect of various circumstances transformed to a sample mass effect (n^*).

Table 2 shows some more results using the data of 0.855 mg (Heraeus; part "A") and 200 mg sample mass (Derivatograph; part "B") as the basis, respectively.

The values of the "B" part of Table 2 are plotted in Fig. 13. The ln A^* values seem to be a linear function of the sample mass and together with n^* are very sensitive to the change in the measuring circumstances.

CONCLUSIONS

This quantification of simlilarity has some very important advantages both from the practical and theoretical aspects.

It makes possible the comparison of results obtained in different laboratories. The different approaches, methods and instruments seem equivalent to each other (but not from all aspects, of course).

The numerical values of the similarity make possible the definite examination of the effect of circumstances and thence to judge the homogeneity of such series, making questionable their validity in numerous cases. For example, among these measurements the results with the 100 mg sample seem not to be homogeneous with the other members of the series (observation nos. 1–5 in Table 1) indicating a fundamental change in the decomposition mechanism because of the characteristic change in physical circumstances (Table 2; Figs. 7, 13).

The definite similarity will probably be a good basis for extrapolation. This is very important from the technological aspect (scale-up effect).

The experience gained from the presented method of comparing the measured data shows that in the course of the usual kinetic analysis the proceedings happen essentially in a similar way when an activation energy as a fixed constant datum is approached by choosing the pre-exponential factor and the reaction order. In this process the measured data are transformed to $E^* = \mathrm{f}(1-\alpha) = \text{constant}$.

The numerical values of such a curve transformation called kinetic analysis depend considerably on the interval of the measured data used by calculation. Extending the examined conversion or the temperature range results in different kinetic constants. It is to be noted that the whole range of the thermal decomposition process is never used in these calulations. This is one cause also of the kinetic compensation effect. In such a situation the (C.E.) is not the result of some mistake and the different series of kinetic constants are obviously equivalent.

Arnold et al. [20] come to the conclusion from an examination of eqn. (1) that "it is senseless to speak about the interpretation of the reaction kinetic parameters, since these parameters can be characteristic only of the physical conditions of the process... when processes examined by the quasi-isothermal –quasi-isobaric measuring technique are taking place at varying temperatures, the Arrhenius' equation must not be applied at all not even as a formal model and consequently no reaction kinetic calculation may be performed with this equation."

In comparing measured curves, the above opinion is imperfect because of the false consequence drawn from the correct calculation. Namely, the great condition number means exclusively that if we prescribe difficult conditions (linear plot of ln k, constant and independent E, A, n) this is hard to accomplish. The presumption of diffucult conditions is not a law of nature, and the processes have their kinetics if the ln k vs. $1/T$ function is not linear and if the activation energy is not constant at all. It is senseless to imagine the chemical process without the physical circumstances intruding and to give up the evaluation of data because a better method has not been developed is not logical.

A measuring method which does not give any information about the kinetics of the process is not suitable for analytical examination either. It could be useful as a standard method as are the Engler viscosity or the Conradson coke number, but for this case the cheapest thermobalance would be too expensive. The quantitative characterization of the examined processes is more than a qualitative description, even if the parameters A, E, n reflect a combination of physical and chemical factors concerning the examined process.

The curves with more peaks were not a successful domain of kinetic analysis at all until now. It was "declined to derive or even try to write an equation describing such type of process" [19]. It is considered that the method outlined here can be used for the examination of curves with more peaks, for more complex processes than the decomposition of calcium carbonate [34].

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