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EXTENDING THE APPLICABILITY OF TG MEASUREMENTS TO INDUSTRY AND TO QUALITY ENSURING BY DIMENSIONLESS ANALYSIS

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Abstract

The $I_i=E_i/RT_i$ dimensionless evaluation is very suitable for describing the TG measurements according to the $E_i/RT_i=\ln A+n[\ln(1-\alpha)_i]-\ln(d\alpha/dt)_i$ equation. The I_i and E_i functions make the comparison of the different TG measurements possible quantitatively in the case of more DTG peaks as well.

The I_i and E_i values as function of $(1-\alpha)_i$ and $1/T_i$ open new way for further theoretical and practical studies by TG measurements. Such types of results are the quantitative determination of the effect of the measuring conditions, the measuring of the mechanochemical effect of grinding and among others the explanation of the self-hardening process of fly ashes of power stations.

Strict connections exist between the I_i functions and the constants of the compensation effect (*CE*). These constants (tanα, axis intersect) can be calculated directly from the average of the measured data of the I_i function making the introduction and theoretical and practical application of the idea of 'general activation energy' ($\bar{E}$) possible. The quantitative characterisation of the examined materials of the fine structure of *CE* and of the thermal processes together proves the extending importance of TG measurements from industrial and material qualification aspects as well.

Keywords: calcium carbonate, compensation effect, dimensionless analysis, fly ash, grinding, kinetic constants, lime burning, quantitative evaluation, thermogravimetry

Introduction

It is a general experience in thermal analysis that the calculated formal kinetic data depend on the measuring conditions strongly, moreover on the methods of the calculation, too. This unpleasant experience induced great research effort. It is a fact, that numerous sophisticated measuring (e.g. [1–4]) and evaluation methods (e.g. [5–15]) had been developed for the elimination of the 'disturbing' side-effects (e.g. the different types of diffusions and heat conduction partial processes) from beside the 'chemical reaction'. The resulting experience led to the international work organised by Kambe and Garn to standardise the measuring conditions and to introduce standardised materials already in 1974 [16]. The limited efficiency of this initiative is a known fact.

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The direct characterisation of the examined materials was the original purpose of thermoanalysis (TA), among others of thermogravimetric (TG) measurements, but the qualitative consideration remained an important tool at the evaluation of the measured data. These qualitative considerations, however, lead to arbitrary conclusions in many cases and the quantitative characterisation of the examined materials e.g. by TG measurements remained unsolved.

For example, in spite of the accurate measurements and exact calculation, it is not verifiable that the second order 'mechanism' (described by the Eq. (18) [12]) is the characteristic 'mechanism' for the examined nineteen other reaction rate controlling possibilities of four similar compounds, if all the calculated kinetic constants and each examined compound show the kinetic compensation effect (*CE*), and the correlation coefficient (*r*) of the *CE* is equal with 1.0000 in each case. Similar arbitrary conclusions can be observed frequently in the literature (e.g. [13, 17, 18, 19]).

A further important known fact is that the different differential equations describe the thermal processes with similar accuracy. So it is arbitrary from this aspect, too, to choose one from the equations on the base of some preconceptions.

The *CE*, the strict linear connection between the logarithm of the pre-exponential factor ($\ln A$) and the activation energy (*E*) exists not only among the very different kinetic constants of one TG measurement calculated by very different differential equations but also among the different kinetic constants, measured under different conditions (laboratories).

The physicochemical meaning of the *CE* is also a subject of research for long ago (e.g. [20]), but the direct, measurable cause of the strict connection among the kinetic constants has not been found till now. The conception and the results of dimensionless analysis make way for the interpretation of the origin of *CE*, too, direct by measured data besides the quantitative characterisation and comparison of industrial products and processes.

The dimensionless analogy of TG measurements

It is theoretically and practically more useful to set out directly from the discrete data of the measured thermogravimetric (TG), differential thermogravimetric (DTG) functions of temperature (*T*) and time (*t*) for characterisation of the thermal processes instead of trying to separate the partial processes with measuring and calculation methods and using preconceptions like the so-called kinetic constants.

The simplest and generally used differential equation Eq. (1) is suitable for this purpose and represents a very good tool for quantitative investigation of the similarity of TG measurements and for looking for the effect of the measuring factors quantitatively [21].

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

where: $d\alpha/dt$=velocity of thermal process, n=order of reaction, $(1-\alpha)$=fraction not reacted, A=pre-exponential factor, R=universal gas constant, E=activation energy, T=absolute temperature.

The Eq. (2) from Eq. (1) contains only the measured discrete values of TG_i, DTG_i, T_i directly.

$$E_i/RT_i = n\ln(1-\alpha)_i - \ln[1/A(d\alpha/dt)_i] \tag{2}$$

Both sides of Eq. (2) are homogeneously dimensionless.

Using the simplification that $A=1$ and $n=1$ and saving the dimensionless character of the Eq. (2), the Eq. (3) shows the simple connections among the measured data and Eq. (4) serve as definition function.

$$E_i/RT_i = \ln\left[A\frac{(1-\alpha)_i^n}{(d\alpha/dt)_i}\right] \tag{3}$$

$$I_i = E_i/RT_i \tag{4}$$

The values of I_i *vs.* $(1-\alpha)_i$ and I_i *vs.* $1/T_i$ as dimensionless functions of the concentration and temperature characterise the thermal processes. Expedient is to multiply both sides of Eqs (2 and 3) with the measured T_i or advantageously with T_iR values marking the I_iT_iR results as E_i. Further two functions can be calculated in such a way, namely the E_i *vs.* $(1-\alpha)_i$ as function of the concentration and E_i *vs.* $1/T_i$ as function of the temperature.

These four functions characterise the examined material and the measuring conditions together. They make comparison of the measurements possible, looking for and expressing the effect of the different conditions of reactions quantitatively [21].

The calculation and the sensitivity of the dimensionless transformation

The examination of the similarity of TG measurements begins by choosing one measurements as a base ($A=1$; $n=1$) for the transformation of another one. Then expedient is to describe the calculated function of I_i and E_i in polynomial form. The next step is to look for the best '$\Delta(1/T)$', 'A' and 'n' transformation constants between the functions of the base and the measurement were chosen for the similarity examination.

The surprisingly great sensitivity of the suggested transformation method can be proved by the following results of transformation of TG data measured among extremely different conditions.

The TG data of a 3460 mg sphere shaped marble sample were transformed onto the TG data of 0.855 mg pulverised $CaCO_3$ sample as the basis. The sample weighing 3460 mg was measured without sample holder, in air with 9°C min^{-1} heating rate. On the other hand the 0.855 mg pulverised sample was measured in Ar atmosphere, in corundum sample holder and with 10°C min^{-1} heating rate.

The constants of the similarity of the two measurements are between $(1-\alpha)_i=0.946-0.0196$ range with a correlation coefficient $r=0.9986$ as follows [21]:

$$\Delta(1/T)=1.50\cdot 10^{-4} \qquad A=0.653 \qquad n=1.33$$

The E_i *vs.* $(1-\alpha)_i$ results of the two measurements and the effects of the transformation constants are shown in the Fig. 1.

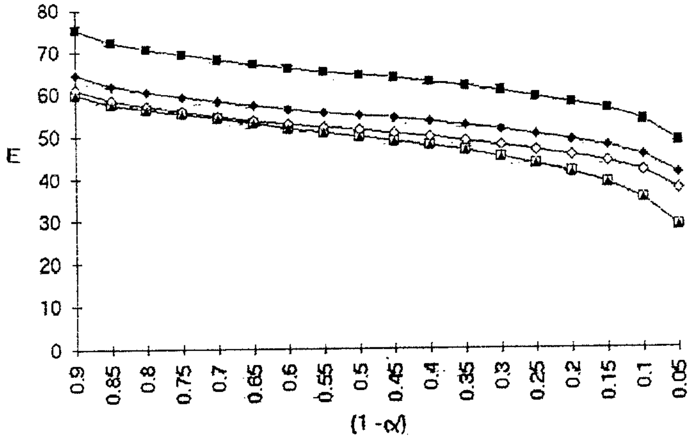

Fig. 1 E_i *vs.* $(1-\alpha)_i$ functions of 3460 mg (■) sample transformed by the following constants; $\Delta(1/T)$ (♦), $\Delta(1/T)$ and A (◊), $\Delta(1/T)$, A and n (▲) into values of 0.855 mg sample (□)

According to Fig. 1, the transformation can be completed with very good result in spite of the extremely different experimental conditions in a very wide range of the decomposition processes. The meanings of the constants of the similarity are:

1. $\Delta(1/T)=1.50\cdot 10^{-4}$. There is a constant $\Delta(1/T)$ difference between the temperature of the two decomposition processes. (The temperature of the sample weighing 3460 mg is greater with 166°C comparing the values at $(1-\alpha)_i=0.50$ decomposition.)

2. $A=0.633$. It means that referring to the base sample, the decomposition velocity of the sample weighing 3460 mg is only 65.3% during the whole process.

3. $n=1.33$. It means that, if the $(1-\alpha)_i$ concentration or mass data of the sample weighing 3460 mg are raised to 1.33 power, they are equivalent to the convenient data of the base measurement.

The difference between the sample quantity of the two measurements is more than 4000 times. It means that if the smaller DTG surface is 10 cm^2, the larger is more than 4 m^2, proving the accomplishment and the sensitivity of the dimensionless transformation. In spite of the extremely different sample quantities and the fundamentally different measuring conditions the differences of constants of transformation are only 3–5% by changing the base function of the two measurements.

It has to emphasise that this dimensionless analysis makes the quantitative comparison of the dynamic thermal processes possible and in a very wide range, while the known – and in the praxis of industry indispensable – dimensionless analogies are applicable for comparing of stationary processes only [21].

Some industrial and qualification application of the dimensionless analysis

The sample quantity problem induced also an extended research work in TA. About this subject, the following series of measurements [22] were revaluated by the dimensionless analysis [21]. The weights of powdered $CaCO_3$ samples were 100, 200, 400, 1000, 2000 mg, the heating rate in air 9°C min^{-1}. This series was completed with TG measurement of the 3460 mg sphere shaped marble sample. The measurement of the 200 mg sample served as base for the transformation.

The $\Delta(1/T)$ data as logarithmic function of sample quantity can be described well with Eq. (5).

$$\Delta(1/T) = 2.98\cdot10^{-5}(\ln \text{mg}) - 1.775\cdot10^{-4} \qquad r = 0.9990 \tag{5}$$

Consequently, a linear relation exists between the logarithm of the sample quantity and the $\Delta(1/T)$ in a very wide (100–3460 mg) range. The $\Delta(1/T)$ is the most important constant of the similarity of thermal decomposition.

These TG results show direct quantitative information about the industrial burning of powdered and coarse limestone (e.g. in cement and caustic lime manufacturing).

As another application example, it was examined, whether the dimensionless analysis of the TG measurements can give further quantitative knowledge relating to the cement and caustic lime manufacture [23]. Only empirical experience is at present, that the quality of the product and the energy requirement of the production depend on the place of origin of the limestone as raw material.

The sources of limestone samples were two Triassic mines (Keszeg, Naszály) in Hungary and the different places of the cement kiln according to the Table 1 [23].

Table 1 The $CaCO_3$ content (%) and the sources of the examined materials

No.	Sources	%	No.	Sources	%	°C
1	Keszeg	99.0	5	Raw mixture	80.2	
2	Keszeg	95.2	6	II. grade	73.3	600–700
3	Naszály	96.2	7	Eddy chamber	68.8	650–750
4	Naszály	86.7	8	III. grade	46.7	750–850
			9	Dopol (inflow)	46.5	800–850

The sample 1 (Keszeg, 99.0%) served as base for the dimensionless comparison of the sample 2 and 3, for the two Triassic samples with fairly similar $CaCO_3$ content. The results are in Table 2.

Table 2 Difference of Triassic limestone samples depending on the place of origin

Sample sign	1 (Keszeg, 99.0%)	2 (Keszeg, 95.2%)	3 (Naszály, 96.2%)
Signs of constants	Constants of base	Transformation	
		Difference from base	Difference from base
$\Delta(1/T)$	0	$-2.45\cdot10^{-5}$	$-8.56\cdot10^{-6}$
A	1	–5.8%	–12%
n	1	–6.0%	–1.8%
Δt°C$(1-\alpha)=0.5$	0	–32°C	–11°C

According to the Table 2, the mean temperature ($\Delta(1/T)$, the velocity of the thermal decomposition (A) and the reaction order (n) was decreased by the contamination beside the $CaCO_3$, but this decreasing value depends on the place of the origin of the samples in a very well distinguishable manner showing the difference between two Triassic limestone samples.

As it can be seen on the Table 3, the temperature of the thermal decomposition increased by the increasing quantity of contamination of the $CaCO_3$. Beside this the velocity of the decomposition (A) increased also significantly and the modifying effect of the changed chemical composition (n) is significant, too, on the decomposition.

Table 4 compares sample 4 (Naszály, 86.7%), the most important raw material in the examined cement factory, as the base of transformation, with the sample 5 (Raw mixture, 80.2%). This is the prepared material for cement production by mixing and grinding with additives.

The change of the temperature of thermal decomposition is smaller than the measuring error (0.9°C) and not very significant is the effect of the additives as well, because 'n' changed from 1 only to 1.05. The velocity of the decomposition process increased, however, significantly with 27%. In this case the change

Table 3 The effect of the quantity of the compounds accompanying the $CaCO_3$

Sample sign	3 (Naszály, 96.2%)	4 (Naszály, 86.7%)
Signs of constants	Constants of base	Transformation Difference from base
$\Delta(1/T)$	0	$1.04\cdot10^{-5}$
A	1	+39%
n	1	+32%
$\Delta t°C(1-\alpha)=0.5$	0	+13°C

of 'A' is the quantitative measure of the mechanochemical effect of the grinding. There is no other known method to measure the mechanochemical effect quantitatively today.

The other transformation data of Table 4 show the effect of manufacturing temperature on the decomposition of $CaCO_3$ in the cement kiln.

A remark is to the Table 1, that the *CE* observable in this case as well using the Eq. (1) for formal kinetic analysis of the thermal decomposition of these samples. The Eq. (6) shows the close connection between ln*A* and *E*

$$\ln A = 0.1085E - 6.46 \qquad r = 0.9995 \tag{6}$$

A known fact is, that there are industrial, environmental, and qualification problems related to the fly ash deposits of power stations. A further industrial example about the applicability of the 'I_i' functions is that TG measurements of the fly ash and cold water mixtures proved a self-hardening activity of the fly ashes, beyond the known pozzolanic activity, but without any basic additives. The industrial and environmental protection costs can decrease by using this self-hardening activity, that could be recognised only by the help of dimensionless analysis of TG measurements [24].

The DTG curves have more peaks in this case. The dimensionless analysis could be applied and proved to be very sensitive independently from the number of the DTG peaks.

A general explanation of the compensation effect

Not only the chemical composition, but more physical, among others structural factors are changing during the thermal decomposition continuously (e.g. [2]). It is impossible today to measure all the data for the exact describing and calculation of the superimposed partial processes of the decomposition, particularly in the case of solid materials. Attempting to solve this problem, the calculation of the so-called kinetic constants for characterisation of the material

Table 4 The change of decomposition of $CaCO_3$ during the cement manufacturing process

Sample sign	4 (Naszály, 86.7%)	5 (Raw mixture, 80.2%)	6 (II grade, 73.3%)	7 (Eddy chamber, 68.8%)	8 (III grade, 46.7%)	9 (Dopol (inflow) 46.5%)
Sign of constants	Constants of base	Transformation Differences from base				
$\Delta(1/T)$	0	$-3.95 \cdot 10^{-7}$	$-1.23 \cdot 10^{-5}$	$-1.11 \cdot 10^{-5}$	$-1.51 \cdot 10^{-5}$	$-1.76 \cdot 10^{-5}$
A	1	+27.0%	–11.5%	–0.7%	+5.5%	+29.0%
n	1	+5%	–0.7%	–10%	–4%	+7%
Δt°C$(1-\alpha) = 0.5$	0	–0.9	–16	–15	–19	–23
$\Delta(1-\alpha)$	0.97–0.12	0.96–0.03	0.94–0.03	0.96–0.02	0.92–0.09	0.95–0.09

has a hidden supposition. This supposition is that only the ‘chemical’ partial process depends on the temperature and disregards the temperature dependence of the diffusion, heat conduction, etc. This simplification leads to the apparent contradiction, expressed itself in the *CE* of the formal kinetic constants of one measurement calculated with very different equations and with similar describing accuracy, so the criticism of this simplification is very rightful (e.g. [25]).

For solving the problem, it has to be taken into consideration that analogy exist among the component, the heat and the momentum streams in thermodynamics (e.g. [26]). It follows from this, that there is analogy and inseparable manner among the exponential temperature dependence of the chemical processes and the different forms of the diffusion (e.g. [27]) and the heat conduction, too, during the TG measurements. This exponential temperature dependence of the different chemical and physical partial processes is validated practically by the dimensionless analysis [21]. This is the basis of the great sensitivity and transformability of the I_i functions and makes the realisation of the connection between the measured data and the *CE* possible as follows.

The usual form of the *CE* is Eq. (7).

$$\ln A = aE \pm b \tag{7}$$

The Eq. (8) shows the properly regrouped Eq. (2) with the average values of the measurements for comparison to Eq.(7) with the original conditions, that $A=1$ and $n=1$.

$$\ln A \cong \overline{(1/RT_i)}\,\overline{E_i} - \overline{n\ln(1-\alpha)_i} + \overline{\ln(\mathrm{d}\alpha/\mathrm{d}t)_i} \tag{8}$$

Consequently the ‘*a*’ as the $\tan\alpha$ of the *CE* is

$$a \cong \overline{1/RT_i} \tag{9}$$

and ‘*b*’ as the axis intersect of the *CE* is

$$b \cong \overline{-n\ln(1-\alpha)_i} + \overline{\ln(\mathrm{d}\alpha/\mathrm{d}t)_i} \tag{10}$$

One part of Table 5 shows the constants of the *CE* calculated with the average data of the I_i function, it means that with the measured data directly and without any preconception.

It is ascertainable, that the angle of inclination $\overline{(1/RT_i)}$ shows the general temperature dependence and the axis intersect $(\overline{-n\ln(1-\alpha)_i} + \overline{\ln(\mathrm{d}\alpha/\mathrm{d}t)_i})$ shows the general structure dependence of the thermal process. It is obvious, that the value of average $\overline{E}$, calculated by the Eq. (8) has a very different meaning than that of the usual idea of activation energy in the literature. According to this it

Table 5 The constants of the *CE* of some thermal decomposition processes

		$\ln A = aE \pm b$						
		Functions calculated by Eq. (8)				Other origin		
Sample name	quantity/mg	$\overline{a}$	$\overline{E}_i$/kJ mol^{-1}	$\overline{b}$	$\overline{\tan\alpha}$	$\tan\alpha$	b	
$CaCO_3$	0.855	0.1254	51.37	–6.4442	7°09'12''	6°41'45''	–5.7217	(1)
	100	0.11976	52.32	–6.2657	6°49'45''	6°27'51''	–6.3020	(1)
	200	0.11536	54.26	–6.2596	6°34'50''	6°20'43''	–5.7839	(1)
	400	0.11265	57.69	–6.4994	6°25'39''	6°02'22''	–5.4843	(1)
	1000	0.10924	59.51	–6.5009	6°14'03''	5°51'29''	–5.6422	(1)
	3460	0.10466	63.34	–6.6297	5°58'28''	5°42'18''	–5.7260	(1)
Kaolin (loose sample)						8°15'22''	–	(2)
$CaC_2O_4{\cdot}H_2O$ (loose sample)						13°23'34''	–	(2)
	(pressed sample)					12°59'07''	–	(2)
Gypsum;	first peak	0.29020	20.91	–6.0693	16°10'58''	16°10'54''	–6.6738	(4)
200 mg	second peak	0.27240	17.78	–4.8425	15°14'16''	15°14'17''	–5.9489	(4)
	total dehydr.	0.28540	19.98	–5.7012	15°08'39''	15°55'50''	–6.9138	(4)
	usual kinetic evaluation					15°47'08''	–4.7672	(5)
$(NH_4)_2SO_3{\cdot}H_2O$ (dehydration)						19°06'40''	–	(3)

(1) *CE* calculated by four equations [22]
(2) *CE* calculated by ten equations [28]
(3) *CE* from [29]
(4) *CE* calculated by different '*n*' values
(5) *CE* calculated by eight equations, data from [30]

is justified to introduce the idea of the 'general activation energy' for this average $\overline{E}$ because it characterises the total process and not only the 'chemical' part.

The measuring conditions influence the thermal process through the different partial processes, but the character of the system does not change fundamentally during the decomposition. Consequently, the I_i functions show the details of the partial processes of the different measurements and the *CE* characterises the status of the examined system generally.

The data of Table 5 prove these conclusions as examples comparing the constants of the *CE* by I_i to data of other origin, completed from the literature [22, 28–30]. In addition Table 5 shows the trend of the dependence of $\tan\alpha\ \overline{(1/RT_i)}$ on the examined materials, morover the fine structure of the *CE*.

These experience and results about the *CE* together with the I_i functions make possible the further study of the analogies in thermodynamics and the industrial qualification of raw materials and products as new fields for the practical application of TG measurements.

Conclusions

The application of the I_i functions, the dimensionless description and evaluation of the TG measurements are a good tool for solving the contradictions of formal kinetic constants. The I_i functions can be used for quantitative characterisation and comparison of the thermal processes with more DTG peaks as well and it makes the searching of the effect of the different measuring conditions possible also quantitatively; giving useful, new information from industrial and material qualification aspect as well.

Strict connections exist between the I_i functions making the explanation of the *CE* possible by measured data directly. The I_i functions characterise the details of the TG processes, and the constants of the *CE* characterize the examined system generally. Among these constants, the content of the $\overline{E}$ as the 'general activation energy' differs from the usual idea of the activation energy. The I_i functions and the constants of the *CE* together are very suitable for quantitative characterisation of the TG processes of industrial raw materials and products.

These experience and results about the *CE* together with the I_i functions can open up new way for the industrial qualification of raw materials and products. The introduced results do not close, but make way for further study of the discussed problems, like the application of TG measurements studying the analogies in thermodynamics.

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