

ERROR LEVELS OF DIFFERENT METHODS OF EVALUATION OF TG MEASUREMENTS

Z. Adonyi

Department of Chemical Technology, Technical University of Budapest, H-1521 Budapest
Budafoki út 8, Hungary

Abstract

It follows from an analysis of the error levels of TG evaluation methods that it is a conceptual error to disregard the analogies of mass, energy and momentum streams of subordinate partial processes. This error is bypassed by means of the introduced method of dimensionless analysis and by determining the characteristic, constants-like data of thermal processes by using the measured data directly. These methods are very suitable for increasing the consistency of the calculated results by seeking for similarity, even in comparisons of measurements made under very different conditions and for emphasizing the differences too, quantitatively. With this new interpretation of TG processes, the idea of the kinetic compensation effect becomes only a consequence of the discussed conceptual error.

Keywords: compensation effect, dimensionless analysis, DTG, error levels, evaluation, kinetic parameters, TG

Introduction

Although the first thermobalance was developed by Honda in 1915, the initial real evaluation of thermogravimetry (TG) is strictly connected with the work of Duval [1], who drew attention to the application of the thermobalance in the field of inorganic gravimetric analysis in 1947. Besides the increasing importance of TG measurements relating to thermodynamic processes (evaporation, grinding, etc.) and the physicochemical properties of substances (kinetic parameters, etc.), analytical chemistry has remained the chief area of application (e.g. [2]). The purpose of a thermal examination is the chemical characterization of an examined substance.

As with any instrumental technique, a large number of factors (depending on the analytical requirements) affect the precision, accuracy and reproducibility of the experimental results in thermogravimetry. The dynamic temperature change of a sample enhances the number of factors that can influence the mass-change curve. Such factors have been examined since the very beginnings of TG measurements [1-5] and they now number several dozens. In fact, they form the basis

sis for the development of instruments and evaluation methods, as sources of different errors in the measured and calculated data. This is the cause of the very general desire to eliminate the different 'disturbing' factors (diffusion, heat conduction, etc.), which has led to simultaneous measurements [2, 3] and to numerous differential equations [3, 5–8] describing the rate-controlling process and providing the kinetic parameters of the examined sample.

One indisputable result is the extension of gravimetric knowledge relating to the wide-ranging TG research and evaluation efforts, but it is also well-known from the frequent critical, moreover ironical remarks that even formal kinetic evaluations of thermal processes mostly provide 'qualitative'-like results. This was demonstrated persuasively more than 20 years ago [9], in connection with an analysis of 15 TG curves reported on the thermal decomposition of CaCO_3 . The activation energy (E) varied between 109 and 1578 kJ mol^{-1} , and the pre-exponential factor (A) between 10^2 and 10^{69} . On the other hand, it has been emphasized that these parameters correlate with each other strictly linearly [9] according to Eq. (1) as a manifestation of the so-called kinetic compensation effect (CE):

$$\ln A = aE \pm b \quad (1)$$

The CE has been observed, however, in the homogeneous and gas phases, in isothermal measurements and in catalytic reactions since the beginning of the century and independently from the TG processes [10–13]; it exists for one TG measurement too, being evaluated by different differential equations [14, 15]. The interpretation of the CE has been the subject of numerous considerations [12, 16–18].

Because of the great inconsistency in the results, e.g. in the formal kinetic parameters, an exact qualification of substances by means of TG has remained a promising but unsolved problem. Consequently, I have looked into the background of this problem. The recognition and elimination of the conceptual error that generally arises in the evaluation of TG data provide the main features of a practically well-applicable solution. A good tool for the verification of this solution involves determination of the error levels of the different evaluation methods, with a significant increase in the consistency of the calculated data by the dimensionless evaluation and characterization of TG processes and with a new interpretation of the CE . The practical applicability of the solution is also proved by a re-evaluation of literature data.

Analysis and solution of TG evaluation problems

The investigation is based methodologically on the general experience and facts connected with the CE and the inconsistency of TG results, and a break

must be made from some conceptions, e.g. the sometimes unreasonable effectiveness of abstract formalism.

The following differential equation (Eq. (2)) is applied most frequently for the kinetic evaluation of TG measurements because it permits a very good description. A linear temperature program is sometimes achieved with difficulty. According to Eq. (2), this is not an unquestioning, explicit requirement.

$$\frac{d\alpha}{dt} = A \exp(E/RT)(1 - \alpha)^n \quad (2)$$

where $d\alpha/dt$ =velocity of the thermal process, $(1-\alpha)$ =fraction of unreacted substance, A =pre-exponential factor, R =universal gas constant, E =activation energy, T =absolute temperature, and n =order of reaction.

It is known that three principal data are involved in simultaneous measurements on a sample: mass-change (TG), rate of mass-change (DTG) and temperature (T) as functions of time. According to Eq. (2), TG and DTG are equivalent to $(1-\alpha)$ and $d\alpha/dt$, respectively. These measured data include all effects of the factors of a single TG measurement which can influence the results as random and systematic errors. Taking into account the direct, TG-independent precision, accuracy and reproducibility of the measurements (mass, etc.), it is obvious that the scatter in the TG evaluation results [9] can not be explained without the effects of the systematic errors.

Only a few results (and without the method of estimation) have been published on the errors in the TG literature and, in spite of its importance, the systematic error category is not used consistently in this relation. The practice to date has been to eliminate the 'disturbing' factors by changing the conditions of the measurements and the methods of their evaluation [1-8] as a correction task only, instead of carrying out investigations of the effects that depend on the substance examined and on the instrumentation applied and causing systematic errors. ('... the dichotomy between systematic and random errors does not focus on the source of the error; rather, it examines the nature of the error by applying a mathematical criterion.' [19])

Besides the above-mentioned trends of TG development, another and deeper problem is concealed beneath the usual idea of formal kinetic analysis, i.e. to look for kinetic parameters which characterize the examined substance in a constant manner (E , A and n).

It is a conceptual mistake, however, to calculate kinetic parameters in order to characterize a substance on the basis of one of its chemical reactions which depends on the process conditions.

This idea supposes that only the activation energy of the 'pure', i.e. the 'abstract' chemical reaction is exponentially related to the process, and therefore the character of its description differs from those of other partial processes (dif-

ferent forms of diffusion, heat conduction, etc.) which are superimposed, but in an inseparable manner.

In spite of this idea as a principle or conceptual type of error, the analogy between the mass, energy, momentum streams and transport processes, and consequently between their exponential energy relations too, is a known and proved fact in thermodynamics. This problem is solved by introducing Eq. (3), which preserves the structure of Eq. (2), but contains only series of sets of measured discrete values of the TG, DTG and T functions [20, 21]:

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

Both sides of Eq. (3) are homogeneously dimensionless and illustrate the simple connections between the measured data. I_i is reminiscent of the word invariant and Eq. (4) serves as its definition function:

$$I_i = \frac{E_i}{RT_i} \quad (4)$$

The simplifications that $A=1$ and $n=1$ are the basic presumptions for elimination of the usual preconceptions relating to the kinetic parameters and the inseparable partial processes. In this form, the I_i , as function of $(1-\alpha)_i$ and $1/T_i$ can serve as the basis of transformation for the quantitative comparison of data sets measured under very different conditions. ΔA , Δn and $\Delta(1/T)$, as constant-like characteristic results of transformations on the basic measurements, quantitatively show the similarity of the two measurements throughout the thermal process with great accuracy [20, 21].

In strict connection with the dimensionless analysis of TG measurements, Eq. (5) is suitable for the unambiguous and accurate characterization of different TG processes, using the measured data directly [21]:

$$\ln A \cong \overline{(1/RT_i)} \overline{E_i} - n \overline{\ln(1-\alpha)_i} + \overline{\ln(d\alpha/dt)_i} \quad (5)$$

Equation (5) is connected with the CE , but in contrast with Eq. (1), the factors in Eq. (5) have direct and characteristic physical meanings. On comparison with Eq. (1), $a = \overline{(1/RT_i)}$ and shows the average temperature dependence of the thermal process. The sum of the terms $-\overline{n \ln(1-\alpha)_i} + \overline{\ln(d\alpha/dt)_i}$ is equal to b in Eq. (1) and is the intercept on the $\ln A$ axis, pointing in a complex manner to the effect of the concentration, to the structure of the sample and to the mechanism of the thermal process.

In spite of the identical dimensions, the meaning of $\overline{E_i}$, differs fundamentally from the idea of the activation energy in the Arrhenius equation [22]. $\overline{E_i}$ characterizes the energy level of the chemical reaction and the partial processes to-

gether. The three parameters of Eq. (5) are the significant data of the thermal process and the system of the measurement.

It is an important conceptual result that Eqs (3), (4) and (5) allow a quantitative examination of the effects of disturbing factors instead of the customary striving to eliminate them.

Since there is an irreconcilable distance between the random, the systematic and the theoretical or conceptual errors of TG evaluations, it is expedient to consider the results determined in different manners as measured data in order to qualify the different evaluation methods by their error levels. This permits application of the statistical methods of analysis of random errors.

Comparison of groups of TG evaluations

The analysis of TG evaluation problems (section 2) helps one to avoid a systematic listing and grouping of the great number and very different types of TG evaluation methods originating from the very extensive research and methodological development. In a search for the types of errors, the investigation provides a fairly simple framework for grouping of the TG evaluation methods and for comparing their error levels without disturbing arbitrariness. The Tables present the \pm percentages of the reduced scatter as measures of error $\{(\text{scatter}/2)*100/\text{average}\}$, because these are more vividly descriptive than, for example, the confidence interval data.

Evaluation with several differential equations

The 'trial and error' method is frequently suggested as a means of establishing which differential equation, i.e. which mechanism, furnishes the best correlation coefficient (r), best describing the thermal process. The selection is always difficult because $r \geq 0.95$ in most cases, and the CE exists in each case, with its r value generally >0.99 . As examples of connected results, data were

Table 1 TG evaluation with several differential equations; \pm percentage reduced scatter of formal kinetic parameters

	Compounds of				Mg(OH) ₂			
	La	Ce	Pr	Nd				
E	34.9	35.5	35.0	36.3	28.3	30.7	28.6	31.1
$\ln A$	39.8	43.4	41.1	51.0	33.8	37.6	33.9	37.6
n (used)		2				1.6		
No. of equations		17				19		
Methods*		Integral method			1/a	1/b	2/a	2/b

* 1. Coats and Redfern; 2. Satava; a and b relate to parallel measurements

published on the thermal decomposition of $\text{Mg}(\text{OH})_2$ [14] and on the analysis of the first DTG peaks of four lanthanide isothiocyanate *dl*-(α)-alanine complexes [15] with 17 and 19 different differential equations, respectively. Table 1 shows the percentages of the reduced scatter and their sources.

Error levels with a single differential equation

The purpose of this group of methods is to calculate kinetic parameters which characterize the chemical reaction of the examined substance without any disturbing effects of other partial processes. This is the largest group of evaluation methods and only some typical ones may be referred to for comparison of the levels of errors.

a) For calculation of the formal kinetic parameters of lanthanide compounds, the mechanism of differential equation 18 was chosen from the 19 considered [15]. The published data were suitable for this examination. Results are presented in Table 2.

b) Another possibility for qualification of the error level in this group involves the evaluation of parallel measurements with the same differential equation or method.

A two-stroke engine lubricating oil (commercial code: MDC-60) was applied as the sample for these TG measurements. It gave only one DTG peak. Twelve parallel measurements were evaluated with the Freeman-Carroll method [23] to get a well-defined reaction order in the $(1-\alpha)$ interval 0.70–0.05. Table 2 gives the results.

c) The dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ was studied with regard to the effects of dry and wet N_2 as purge gas and the structure of the sample (powdered, pressed, plate and cubic crystals) [24]. The Ozawa method was used for kinetic evaluation [25, 26]. Accordingly, the basis of calculation was the same reaction co-ordinate intervals of TG measurements with different heating rates. The *CE* exists in this case too, covering the effect of the change of heating rate and, among others, conflicting with the published quality conclusions, e.g. those relating to the change in mechanism as a function of the reaction co-ordinates. The series of calculated kinetic parameters permit determination of the reduced scatter in them. These results are also given in Table 2.

An obvious consequence of these data is that the Ozawa and similar methods (e.g. model-free kinetics) do not decrease the level of errors or the inconsistency of the kinetic parameters significantly.

Error levels of similarity evaluations with dimensionless analysis

The twelve parallel TG measurements on the two-stroke engine lubricating oil (MDC-60) served for this examination with Eq. (3). An arbitrarily chosen one

Table 2 TG evaluation with one differential equations; \pm percentage reduced scatter of formal kinetic parameters

Methods	Compounds of La, Ce, Pr and Nd		Li ₂ SC ₄ H ₂ O Ozawa				Lubricating oil Freeman-Carroll								
	Differential	Integral													
<i>E</i>	13.1	13.7	20.3	8.0	6.8	4.1	6.8	6.0	7.2	7.0	2.7	5.7	4.5	2.2	6.3
lnA	14.4	15.8	21.7	8.6	8.2	5.2	7.8	6.8	8.3	8.1	3.6	6.4	5.9	3.4	13.9
<i>n</i>	2.0	2.0													12.7
Character of sample*	0	0	1	2	3	4	1	2	3	4	1	2	3	4	MDC-60
Characteristic condition	TG, N ₂	TG, N ₂	TG, dry N ₂	TG, dry N ₂	TG, dry N ₂	TG, dry N ₂	TG, wet N ₂	TG, wet N ₂	TG, wet N ₂	TG, wet N ₂	DSC, dry N ₂	DSC, dry N ₂	DSC, dry N ₂	DSC, dry N ₂	TG, dry air

* 0 specialized in [15]; 1 powder; 2 pellet; 3 plate crystal; 4 cubic crystal; MDC-60 commercial code

of the parallel measurements was used as the basis of similarity transformations, as the results were independent of the chosen basis. Table 3 lists the calculated results.

Multiplication of Eq. (3) by RT_i doubles the numbers of transformation functions and the characteristic, constant-like results of the calculations.

The transformation of the twelve parallel measurements on the lubricating oil MDC-60 was repeated by using the TG data of on a four-stroke engine lubricating oil (commercial code: AGIP SAD SAE 15W-40) as the basic of the transformation. These results are likewise reported in Table 3. Figure 1 depicts the TG and DTG data on the two lubricating oils as functions of temperature. Attention should be drawn to the scatter in the $\Delta(1/T)$ results as an important side-result. The results are practically the same, independently of the change of the basis of transformation. Consequently, the oil fractions of these two lubricating oil prod-

Table 3 TG evaluation with dimensionless analysis and transformation of parallel TG measurements of two-stroke engine lubricating oil (MDC-60); \pm percentage reduced scatter of constants of transformations

Method	Basic of transformation			
	MDC-60		AGIP SAD SAE 15W-40	
	I_i	E_i	I_i	E_i
ΔE	0.046	0.048	0.047	0.048
ΔA	5.2	3.6	3.3	3.1
Δn	2.1	1.3	2.6	2.9
Scatter in $\Delta(1/T)^*$	$1.56 \cdot 10^{-5}$		$1.54 \cdot 10^{-5}$	
Average $\Delta(1/T)$	$1.16 \cdot 10^{-5}$		$5.13 \cdot 10^{-5}$	

* The reduced scatter in $\Delta(1/T)$ is ± 2.8 K for the 260 measured T data used in the calculations

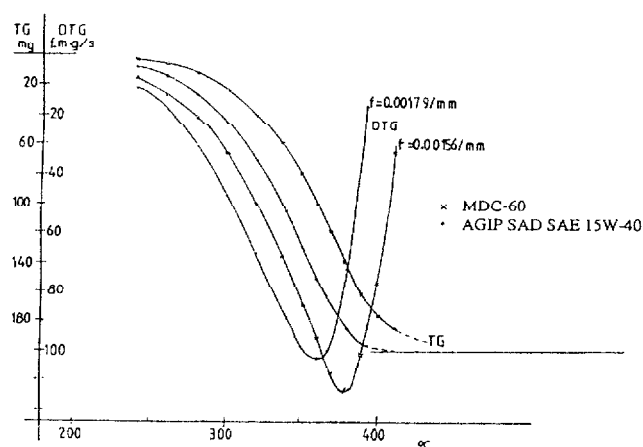


Fig. 1 TG diagrams of MDC-60 and AGIP SAD SAE 15W-40 commercial lubricating oils

ucts are the same, although the requirements are very different. Accordingly, they differ only in their additives. This conclusion was verified by the producer firm. These findings demonstrate the sensitivity of TG measurements and the possibilities of their sensitive evaluation and of a significant decrease in the inconsistency of the calculated results.

General evaluation and comparison of thermal processes

Equation (5) was used to evaluate the error levels of the parallel TG measurements on the lubricating oil (commercial code: MDC-60) and it was also possible to apply the method to the lanthanide compounds referred to above [15]. Table 4 shows the reduced scatter data.

The method for the evaluation of TG processes with Eq. (5) is very suitable for the comparison of kinetic parameters originating from very different TG conditions, laboratories and methods of calculations. It can serve for the deeper, and even quantitative investigation of various factors now included in the systematic

Table 4 Evaluation of thermal processes with Eq. (5); \pm percentage reduced scatter of results

	Lubricating oil	Compounds of			
		La	Ce	Pr	Nd
E	0.7	3.8	4.9	4.2	3.2
$1/RT$	0.5	0.7	1.0	0.8	1.6
$\ln A$	0.7	0.0	0.0	0.0	0.0
$(1-\alpha)$ interval	$\approx 0.95-0.06$	$\approx 0.91-0.40$			

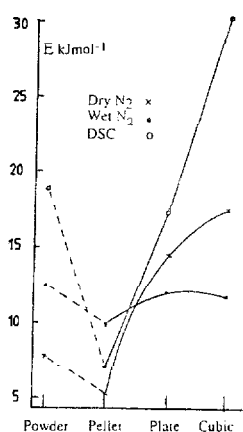


Fig. 2 Results of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration [23], recalculated with Eq. (5)

error category. Table 5 presents some data on the decomposition of CaCO_3 , the published data being subjected to recalculation with Eq. (5).

Table 5 Comparison of published data on the decomposition of CaCO_3 with those evaluated with Eq. (5)

Sample mass/mg	a	$\bar{E}_p/\text{kJ mol}^{-1}$	b	\bar{K}	References
0.855	0.12540	51.37	-6.4442	958	[27]
200	0.11536	54.26	-6.2596	1043	[27]
1000	0.10924	59.51	-6.5009	1101	[27]
3460	0.10466	63.34	-6.6297	1149	[27]
$\approx 6^*$	0.12333	45.76	-5.6440	975	[28]
Varying**	0.11135	52.70	-5.9814	787	[9]

$$a=(1/RT)_i; b=-n \ln(1-\alpha)_i; \ln(d\alpha/dt)_i$$

* Two parallel measurements; heating rate: 20 K min^{-1}

** From E and $\ln A$ results from 11 different measurements with the Coats-Redfern method

The published activation energies of dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ range between 219.74 and 61.31 kJ mol^{-1} [24]. Figure 2 shows the decrease in the inconsistency when the published data are recalculated with Eq. (5).

Conclusions

Consideration of calculated results as measured data for estimation of the error levels of different methods of evaluation of TG data appears to be a useful tool. It follows from an analysis of the evaluation methods that it is a conceptual error to disregard the analogies of mass, energy, momentum streams and transport processes in the evaluation (e.g. by the usual formal kinetic analysis) of TG measurements. This error may be bypassed by means of the introduced method of dimensionless analysis and by determining the characteristic, constants-like data of thermal processes [20, 21] by using the measured data directly. These methods are very suitable for increasing the consistency of the calculated results by seeking for similarity, even in comparisons of measurements made under very different conditions and for emphasizing the differences too, quantitatively. With this new interpretation of TG processes, the idea of the kinetic compensation effect becomes only a consequence of the discussed conceptual error.

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