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ANALOGY OF THERMOGRAVIMETRIC MEASUREMENTS

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Abstract

Dimensionless number has been developed and introduced for quantitative analysis of the effect of thermogravimetric measuring factors like sample quantity, heating rate, etc. The TG, DTG and T data of different thermogravimetric measurements can be used directly for calculation of the three constants of analogy. TG data of $CaCO_3$ measured in very different conditions show the method of transformation and its applicability for calculation of the correlation of measurements.

Introduction

Rapid development began in thermal analysis, in thermogravimetry about four decades ago with an expected promise of hope that our measurements have 'finger print' character in the meaning that they can characterise unanimously the examined materials. It may say with some irony on the basis of far-reaching experience acquired meanwhile, that thermogravimetric (TG) measurements have 'finger print' character only if they were measured in the same laboratory by the same instrument using the same sample inside the same conditions and were evaluated by the same manner. It is a qualitative type of knowledge only that the curve of derivative thermogravimetric measurements, the DTG peaks shift towards the greater temperatures and the shapes of peaks change as well, if e.g. the quantity of the samples or the heating rate is increasing. The measured data, e.g. the temperatures of DTG peaks are not suitable for some direct characterisation of the examined materials or thermal processes respectively.

The same problem showed up, too, on valuation of measured TG data with the so-called formal kinetic analysis as another method for characterisation of

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substances. This had begun by the initiative of Van Krevelen [1] and developed very rapidly [e.g. 2–4]. However, against the expectations, it became known in a short time that the kinetic constants are not constants at all. They depend strongly on the measuring conditions moreover on the method of calculations, too. A further and important experience relating to kinetic calculations is that the kinetic compensation effect (*CE*), namely the strict linear correlation between the activation energy (*E*) and the logarithm of pre-exponential factor ($\ln A$) can be observed in the case when kinetic constants were measured using very different measuring conditions and were calculated with different differential equations and methods [e.g. 5–8]. This phenomenon escapes frequently even the attention of the authors of those published kinetic data [e.g. 9–12].

To the present day, researchers are restricted to qualitative comparison of TG results being measured among different conditions, though it is obvious that decomposition of $CaCO_3$ measured among 'n_i' conditions has to be more or less similar to decomposition of $CaCO_3$ among 'n_k' ones. Actual problem of TG investigation is therefore the quantitative evaluation of the effect of changed measuring factors, the quantitative determination of analogy of TG measurements.

Why is this problem unsolved? The cause is that the purpose of TG investigation has remained up to now determination of data that could characterise the investigated sample, looking for measuring conditions and evaluation methods suitable for this purpose for example looking for some constante like the 'activation energy'. Despite this purpose, it is obvious that the confidence interval of TG measurements fits in with the so-called kinetic compensation effect (*CE*) and this is observable relating with measurements in homogeneous phase, too, referring to the very great complexity of chemical reactions. This complexity makes some postulates questionable; e.g. constancy of activation energy (*E*) during the whole course of thermal processes, and it makes the possibility of separation of material properties from measuring conditions questionable, as well.

Instead of looking for some constant *E*, investigations of how it depends on process parameters can lead to expression of analogy of TG measurements.

Imperfections revealing experience

The contradictions with expectation of original TG conceptions induced very great research activity in connection with

- correction of measuring methods and
- development of kinetic evaluation of measured data and
- criticism of the results obtained in these manners.

As examples of the first group of activities, the decreasing of sample quantity from originally suggested 1 g toward some mg, moreover some tenth mg, the solving of simultaneous measurements, the exact regulation of temperature, the development of isobaric mass-change determinations, the different heating and cooling programs, the coupled simultaneous techniques, e.g. the connection of TG measurements to mass spectrometers, etc. can be mentioned.

Concerning the second group of activities, it is enough to refer to the development of data valuation methods and refer to recommendations of differential equations being introduced on the basis of different physicochemical consideration [e.g. 2, 13], to refer to wide application of 'trial and error' method namely choosing one equation considered it to be suitable [e.g. 11] or to introduction and application of statistical methods and 'moments' [e.g. 14], etc.

Criticism has great literature as well. Particularly has had a hard time of Arrhenius equation bringing to light many times that it is unsuitable to kinetic calculations because of its contradiction, it could not be used in the case of more overlapping DTG peaks, it could have been used only in relation to processes in homogeneous phase etc. According to other opinions the formal kinetic calculations can not be successful in consequence of great number of different, during the thermal processes changing factors (diffusion, heat conduction, structure modifications, etc.) [e.g. 15–17]. Moreover, it would have to forbid the calculations with Arrhenius equation, etc.

These listing of efforts, results and disappointments are not complete at all. Much more data are gained by dynamic thermal measurements contrary to isothermal kinetic measurements and this is one important reason of the comprehensive work in thermal analysis. The *CE* is observable, however, in the case of kinetic constants from isothermal measurements as well. According to this the isothermal measurements are not exempt from problems discovered by dynamic measurements which would deserve more attention by evaluative comparison of the two methods.

Starting from the phenomenon of *CE* that is well-known in thermogravimetry and starting from the published data of different authors, it was proved that arbitrary is the choice of one differential equation from a set of equations by using the trial and error method [18, 19] because of

– the calculated kinetic constants, the $\ln A$ *vs.* E are in strict linear correlation in this case also and his correlation enlarges on the calculated reaction order, too [e.g. 11, 18, 21].

– the strictness of correlation is practically the same, independently from the form of differential equations (e.g. all of the calculated '*r*' was greater than 0.97 in the case of 19 different differential equations in [22]).

It follows from the above mentioned phenomena that

– it is a mistake to take out one parameter e.g. the *E* from the system of the together calculated 'kinetic constants'. One of the so-called kinetic constants can not use independently of the others.

– The 'activation energy' like factor is also changing during TG measurements as a consequence of the great number of other changing parameters.

– The characterisation of chemical reactions and that of TG processes can not be reduced to the examined substance by 'correcting' the measuring and calculation methods.

The thermal processes are resultants of the inseparable interactions between the examined materials and the measuring conditions. Consequently, in contrary to the elimination of the effect of these conditions, it can compose – as corresponding in value – the goal of investigation of interactions between the samples and the measuring parameters, to study the effect of the conditions on the thermal processes e.g. investigation of 'how *E* depends' on factors of the measurement instead of looking for some 'constant' activation energy.

I may emphasise as an important methodological fact that the way for the above possibility was opened by far-reaching and great effort of thermal analysts.

Preliminaries of analogy calculations

The very great number of not measurable parameters and their dynamic character make the application of classical methods of dimensional analysis [e.g. 23–25] for evaluation of analogy of TG measurements hopeless.

Damköhler [26] started off principle of the conservation equations studying the problem of size increase relating with analogy of chemical reactions. The conservation of matter, impulse and energy must be fulfilled in all points of the reactors in the case of stationary chemical processes. He deduced four dimensionless numbers for describing the analogy of chemical reactors. According to this, the necessary condition of similarity of two systems is that the numbers of analogy must correspond in all similar positions in concentration fields (Da_I and Da_{II}) and in temperature fields (Da_{III} and Da_{IV}) respectively. The rate of the chemical reactions must show the same concentration and temperature dependency in the case of analogy. The analogies of chemical reactions depend not only on similarity of concentration and temperature fields, but depend on kinetic and substance parameters, too, like density, specific heat, coefficient of diffusion, coefficient of viscosity, coefficient of heat conduction, etc., but according to its dynamic character all these parameters of each component in the sample are changing during TG measurement continually.

Damköhler's last conclusion is that to apply the theory of analogy is theoretically possible beside more or less realization of transport and thermal and kinetically similarity, however the validity of his transport equations is limited only 2–5 scale up factors or efficiency increasing interval and for stationary processes [26].

Despite this the TG measurements have dynamic character and unsolved is the measurement of necessary data for calculations of the Damköhler analogies, thus they can not be used for investigation of analogy in TG.

Investigations of similarity of chemical processes are theoretically possible with the Arrhenius analogy, as well. It is with the usual marks as follows:

$$\Theta = E / RT \tag{1}$$

where:

Θ = value of the dimensionless number,
E = activation energy, kJ·mol^{-1},
R = universal gas constant,
T = temperature, K.

It is obvious as a consequence from the undetermined character of E that the utilisation of Arrhenius analogy can not be successful in this form in industry or for similarity investigation in TG. According to this there is not any reference about such type of initiative.

Analogy for TG measurements

The simplest and generally used differential equation is a suitable and very good tool for quantitative investigation of similarity of TG measurements and looking for the effect of changed measuring parameters. It contains the Arrhenius's equation, too, as follows

$$\mathrm{d}\alpha / \mathrm{d}T\mathrm{d}t = A \exp(-E / RT)(1-\alpha)^n \tag{2}$$

where:

$\mathrm{d}\alpha/\mathrm{d}T\mathrm{d}t$ = velocity of thermal process,
$(1-\alpha)$ = fraction not reacted,
n = order of reaction,
A = pre-exponential factor.

It is known in relation to this equation that it can describe the data of TG measurement with very good closeness if there is only one DTG peak [e.g. 27].

The measured data can be used directly for calculations particularly in the cases of simultaneous TG_i, DTG_i and T_i measurements.

The not reacted fraction can be calculated as a reduced weight decreasing from the measured data after marking out the $m_s - m_f = a$ weight-loss of the investigated TG process;

$$(m_s - m_i) / a = (1-\alpha)_i \tag{3}$$

where:

m_s represents the mass of the sample; m_f represents the final mass;
m_i represents the mass of the sample in a definit time or temperature.

The Eq. (4) below can calculate from the measured values of TG_i, DTG_i and T_i after regrouping the Eq. (2) in logarithm form and substituting the values of $(d\alpha/dTdt)_i$ and $(1-\alpha)_i$ calculated homogeneous manner:

$$I_i = E_i / RT_i = \ln A + n\ln(1-\alpha)_i - \ln(d\alpha / dTdt)_i \tag{4}$$

The dimension of A is $1/s$ with the condition of $n = 1$.

Both sides of Eq. (4) are dimensionless homogeneously and with the conditions that $A = 1$ and $n = 1$ the analogy I_i can be calculated from measured data directly be expressing the values of I_i *vs.* $(1-\alpha)_i$ as function of concentration and I_i *vs.* $1/T_i$ as function of temperature.

Expedient is to multiply both sides of Eq. (4) with the measured T_i values marking the $I_i * T_i$ product as E_i^*. More two functions can calculate in such a way, namely the E_i^* *vs.* $(1-\alpha)_i$ as function of concentration and E_i^* *vs.* $1/T_i$ as function of temperature. The last two functions can have important role at the classification of the analogy level of thermogravimetric measurements.

Determination of analogy of TG measurements

The analogy examination of TG measurements begins by choosing one measurement serving as a base for transformation of another one. Then expedient is to describe the calculated functions of T_i, I_i and E_i^* in polynomial form. The next step is to find the closest connection between the functions of the base and the measurement chose for the similarity examination looking for its best 'A', 'n' and '$\Delta 1/T$' transformation constants by using statistical methods.

Effects of extremely different conditions at decomposition of $CaCO_3$

The TG data are suitable for determination of their analogy by transformation in that case, too, if they were measured among extremely different conditions. Figure 1 shows the E_i^* *vs.* $(1-\alpha)_i$ functions of transformation of two TG measurements. The TG data of 3460 mg spherically shaped marble sample measured in air and without sample holder and with heating rate 9 deg·min^{-1} were transformed onto the TG data as basis of 0.855 mg pulverised $CaCO_3$ sample measured in Ar atmosphere and in corundum sample holder and with heating rate 10 deg·min^{-1}.

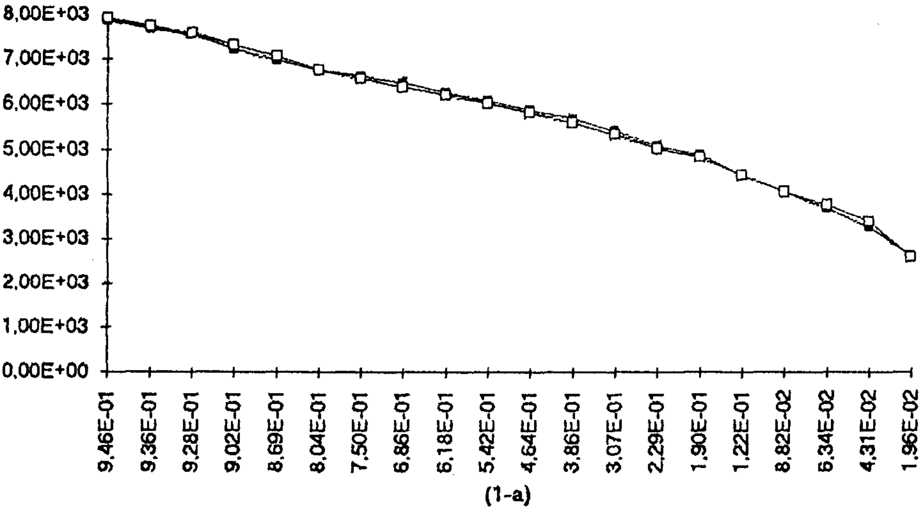

Fig. 1 Analogy of thermal decomposition of 3460 mg (□) and of 0.855 mg (■) $CaCO_3$ samples. The TG data of the 0.855 mg sample was the base of transformation (E^* *vs.* $(1-\alpha)$ functions) (Corr. coeff. = 0.9986)

Figure 1 shows the calculated constants of transformation for the E_i^* concentration and temperature function as well.

It can be stated that

– transformation can complete with good result despite the extremely different measuring conditions;

– the grade of analogy is high as it is shown by the constants;

– the analogy interval can be characterised with the $(1-\alpha)_i$ as not reacted factor. It is between 0.9460–0.0196 in this case.

– It is enough to refer only to the masses of the samples by characterisation of transformation accomplishment of the analogy. The difference between the sample quantities of the two measurements is more than 4000 times. It means that if the smaller DTG surface is 10 cm^2, the greater is 4 m^2. Despite this, the application of the Damköhler's analogies for describing similarity of reactions in chemical reactors was suggested only in the case of 2–5 times scale change.

– The differences of constants of transformation are only 3–5% by changing the base function of the two measurements despite the extremely different sample quantities and the fundamentally different measuring conditions.

The meanings of constants of analogy on Fig. 1 are:

1. $\Delta 1 / T = 1.50 \cdot 10^{-4}$. According to this, the difference of decomposition temperature of the two samples is 166°C at $(1-\alpha)_i = 0.5$, that is at 50% decomposition. The temperature of 50% decomposition of the 3460 mg sample is with 166°C greater than at the 50% decomposition of the 0.855 mg sample.

2. $A = 0.653$. It means that the decomposition rate of the 3460 mg sample is 65.3% smaller than the decomposition rate of the base sample.

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

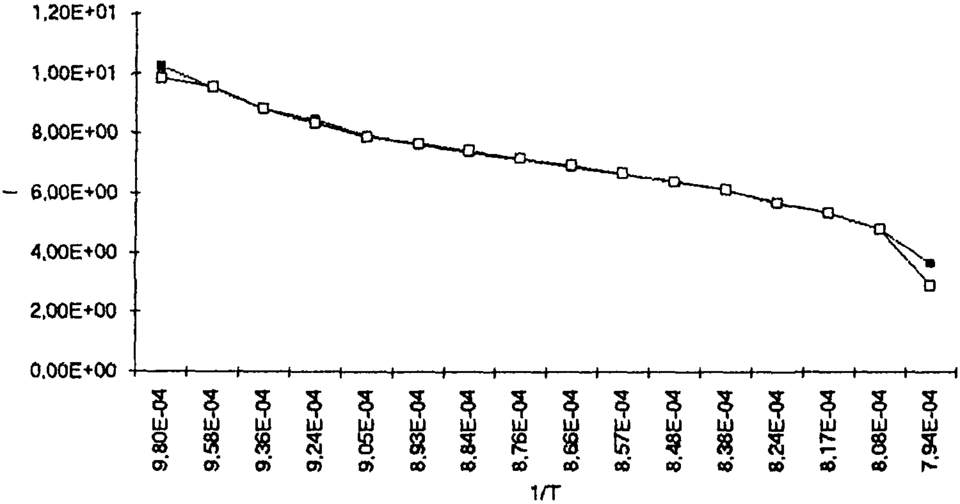

Fig. 2 Analogy of thermal decomposition of 0.855 mg (□)) and of 3460 mg (■) CaCO$_3$ samples. The TG data of 3460 mg sample was the base of transformation (I vs. $\Delta 1/T$ functions)(Corr. coeff. = 0.9968)

Figure 2 shows the result as I_i vs. $1/T_i$ functions using the TG data measured with the 3460 mg sample as base for transformation of data measured with 0.855 mg sample in this case.

It has to emphasise that by the use of the here introduced dimensionless number, comparison is made possible surprisingly wide interval of dynamic chemical processes despite the fact that the known – and in the praxis of industry indispensable – dimensionless analogies are applicable for comparing of stationary processes only.

Sample quantity effect at decomposition of $CaCO_3$

The weights of powdered $CaCO_3$ samples were 100, 200, 400, 1000, 2000 mg for the determination of the effects of sample quantity on analogy. The conditions of the measurements were: heating rate 9 deg·min^{-1}, weight of the cylindrical Pt sample holder 9.3 g in air. This series was completed with TG measurement of the 3460 mg spherically shaped marble sample. The measurement of the 200 mg sample served as base for transformation.

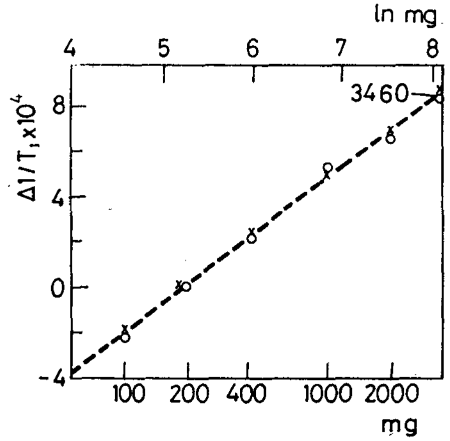

Fig. 3 The effect of sample quantity on decomposition temperature ($\Delta 1/T$) of $CaCO_3$. The TG data of the 200 mg sample was the base of transformations. (o measured, x calculated)

The most important constant is $\Delta 1/T$ among the constants of transformation. Figure 3 shows the calculated $\Delta 1/T$ data as function of sample quantity.

These results can be described well with logarithmic function as follows.

$$\Delta 1\ /\ T = -1.775 \cdot 10^{-4} + 2.98 \cdot 10^{-5} \cdot \ln\,(\text{mg}); \qquad r^2 = 0.998 \tag{5}$$

It is obvious that correlation exist between the sample quantity and $\Delta 1/T$ as analogy constant of decomposition temperatures in a very wide (100–3460 mg) interval and this functional correlation can be described with great accuracy.

Figure 4 shows the value of *A* constants of transformation for the data measured with 3460 mg sample as base. The figure marks the values for *I* and E^* analogy separately.

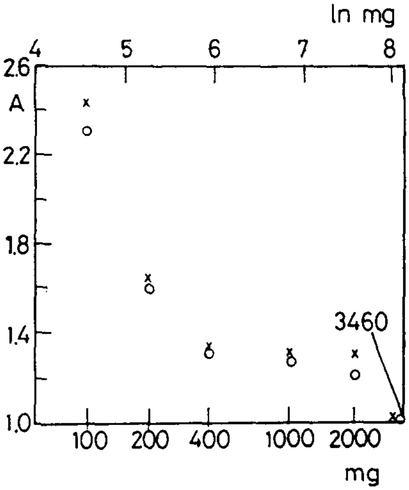

Fig. 4 The effect of sample quantity on the rate (*A*) of thermal decomposition of $CaCO_3$ samples. The TG data of the 3460 mg sample was the base of transformation. (*x* with *I*, o with E^* analogy)

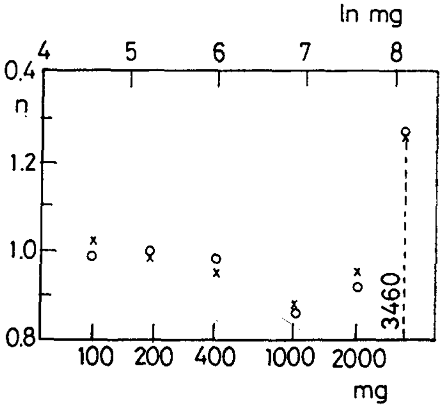

Fig. 5 The effect of sample quantity on order (*n*) of thermal decomposition of $CaCO_3$ samples. The TG data of 200 mg sample was the base of transformation. (*x* with *I*, o with E^* analogy)

It can be stated that *A* as process constant sensitively indicates the change of sample quantity and measuring conditions. The values of *A* decrease remarkably with sample quantity in the range of 100–400 mg, but do not change greatly in 400–2000 mg interval. The additional decrease of the value at 3460 mg is probably due to the very great difference in measuring conditions.

Figure 5 shows the dependence of *n* as the third constant of analogy relating with sample quantity. The measurement with 200 mg sample served as base in this case.

Change can be observed in the character of the process above 400 mg sample quantity.

It can be seen from the data that the calculation of *A* and *n* constants of analogy as functions of measuring parameters needs a lot of further work, but they open the way for experimental determination and realization of the causes of changes, because one of them is connected to the rate of the processes and the other to the actual mass of the sample.

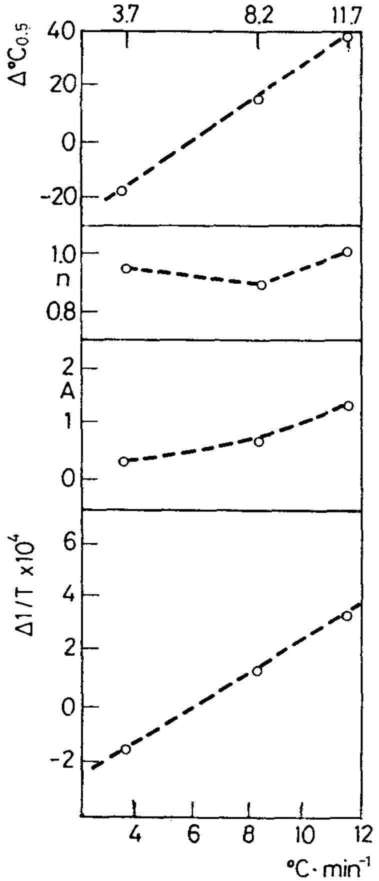

Fig. 6 The effect of heating rate on the $\Delta 1/T$, *A* and *n* constants of analogy

The effect of heating rate

The heating rates were 3.8, 8.2 and 11.7 deg·min^{-1} at TG measurements of 200 mg powdered $CaCO_3$ samples in 5 g slightly conic Pt sample holder. The measurement from the previous series (powdered 200 mg $CaCO_3$, 9.3 g cylindrical sample holder, heating rate 9 deg·min^{-1}) served as base for similarity evaluation. Figure 6 summarises the similarity constants as the functions of heating rate.

It follows from the data of Fig. 6 that analogy examination leads to quantitatively manageable connections related with the heating rate as important TG measuring condition as well.

Conclusions

The described results prove that the introduced '*Γ*' concentration and temperature analogies are suitable for the theoretical dimensionless postulates. The introduced functions are suitable for quantitative comparison of results from very different TG measuring conditions, namely they are suitable for determination of the temperature ($\Delta 1/T$), the process rate (A; 1/s) and the concentration or mass (n) difference between the examined measurements and the base for transformation. The concentration $[(1-\alpha)_i]$ and temperature $(1/T_i)$ functions of '*Γ*' as analogy, as dimensionless number, is applicable to determine the similarity of the dynamic TG processes in a very wide interval of their measuring conditions. Despite this the Damköhler's analogies can be used only in stationary processes and are not suitable for similarity evaluation of TG measurements. It becomes possible to get deeper knowledge relating to the effects of changed TG measuring conditions despite the usual qualitative characterisation.

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Zusammenfassung — Zur quantitativen Analyse des Effektes verschiedener Faktoren bei thermogravimetrischen Messungen wie z. B. Probenmenge, Aufheizgeschwindigkeit usw. wurde eine dimensionslose Zahl entwickelt und eingeführt. Die TG-, DTG- und T-Angaben verschiedener gravimetrischer Messungen können direct zur Berechnung der drei Vergleichskonstanten verwendet werden. Die unter verschiedenen Bedingungen gemessenen TG-Daten für $CaCO_3$ zeigen die Transformationsmethode und ihre Anwendbarkeit für die Berechnung der Korrelation der Messungen.