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# Differential thermal analysis under quasi-isothermal, quasi-isobaric conditions (Q-DTA) Examinations using “transformation-governed heating control” and “self-generated atmosphere” (TGHC-SGA)[☆]

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Devoted to the memory of one of the inventors of this measuring technique, Jenő Paulik, to the 75th anniversary of his birth.

## Abstract

The course of conventional DTA or DSC curves is rather characteristic of the experimental conditions then of the transformation itself. The course of Q-TA$_T$ curves taken by the Q-DTA measuring technique is not deteriorated by these factors when using the “transformation-governed heating control” (TGHC). In this technique, namely, the temperature of the sample is governed by the transformation itself based on the feed-back principle so that the relay-switch system of the Q-DTA apparatus sensing the change of the Q-DTA$_t$ signal governs the heating control unit in a way, in which the transformation proceeds with a predetermined, very small and strictly constant rate by providing the suitable difference between the temperatures of the sample and the furnace.

In order to normalise the experimental conditions, for decomposition reactions a particular, so-called “labyrinth crucible” should also be used, which provides a “self-generated atmosphere” already at the beginning of the reaction, and keeps the partial pressure of gaseous decomposition products constant at their maximum value of 100 kPa till the end of the transformation.

This way, the unique normal characteristic temperature of reactions and transformations, together with reaction heat belonging to them can be measured, and the course of transformations free of every foreign influence can also be recorded.

*Keywords:* DTA; DSC; Q-DTA methods; Transformation governed heating control (TGHC); Self-generated atmosphere (SGA)

## 1. Introduction

Thermal methods can be classified as procedures applying static (isothermal) or dynamic (non-isothermal) measuring techniques.

Calorimetry, except of some new methods belongs to the first class of techniques. Most of the calorimetric data of high accuracy in physical chemical tables (molar heats, formation heats, transformation heats, etc.) are determined by calorimetric methods. This means that the scientific and practical significance of calorimetry is unquestionable. However, its possibilities in determining the physical–chemical properties of compounds are restricted. The course of physical transformations and chemical reactions is, namely, impossible to be studied by calorimetry.

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[☆] In memoriam Jenő Paulik.

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Thermal analytical methods applying isothermal or step-wise isothermal heating belong also to the group of static measuring techniques. These experiments are very time-consuming and tiresome, while, at the same time, poor in information, what hindered their spreading all over the practice.

The course of physical transformations and chemical reactions can be studied, if only with some reservation, by traditional dynamic (non-isothermal) methods (DTA, DSC, TG, EGA, TD, etc.). They are applicable, e.g. for studying the modification and state changes of pure compounds, as well as their decomposition reactions. Components in complex systems (e.g. minerals, rocks), can be identified and their amounts can be determined by these methods. Phase transformations in multi-component systems, the course of solid-state reactions, etc. can also be followed this way.

However, these methods have a big fault originating of the basic principle of the measuring techniques. Peaks of curves of isothermal physical transformations or chemical reactions leading to equilibrium taken by traditional DTA or DSC instruments lie in a broad temperature interval making thereby the false impression that the course of the process is not isothermal. This course of DTA and DSC curves not characteristic for the transformation is caused partly by bad heat conductivity of the sample, due to which the sample takes on the transformation heat only very slowly, thus the transformation is delayed, and partly, independently of this condition, because the non-isothermal heating programme increases continuously the temperature of the sample increasing thereby unnecessarily the transformation rate. In case of decomposition reactions this effect is further modified by the equilibrium processes of the decomposition reaction and those of diffusional gas transport.

In order to obtain well interpretable results, it is indispensable to carry out the experiments under appropriate experimental conditions. The changed experimental conditions applied for increasing the resolution and selectivity of measurements, in turn, change the characteristic temperatures of transformations [1,2]. This is the reason why unacceptably scattering characteristic temperature data are published in scientific journals for the same transformations.

Among many other methods, measuring techniques applying e.g. a drastic decrease in the heating rate or in sample weight for increasing the resolution and selectivity of the examinations are already wide-spread. The strict goal might be achieved this way, however, two important objectives are neglected. The accuracy of the measurement of characteristic temperatures has not been improved, moreover, it decreases, the difference between the measured and theoretical temperature values increases, thus a larger scatter is observed. Further on, the deterioration of curves characteristic for non-isothermal measuring techniques remain unchanged.

The method of quasi-isothermal, quasi-isobaric thermogravimetry (Q-TG) [1–10] and differential thermal analysis (Q-DTA) [2,11–13] actually unifies the advantages of the static (isothermal) and dynamic (non-isothermal) measuring techniques without their disadvantages, and it forms a transition between these two measuring principles. This is also reflected in the nomenclature (isothermal → quasi-isothermal → non-isothermal).

The Q-DTA apparatus [11–13] is identical with the apparatuses for DTA, DSC, or simultaneous DTA, TG, DTG, EGA measurements with the exception that it contains a "transformation-governed heating control" (TGHC) instead of the non-isothermal heating control, and a so-called "labyrinth crucible" suitable for producing "self-generated atmosphere" (SGA) instead of the usual open crucible. The operation principle and construction of the Q-DTA apparatus is described earlier [2,11,13]. The present paper is intended for proving the advantages of the Q-DTA measuring technique in scientific works as compared to traditional DTA, DDC, DSC or simultaneous DTA, TG methods.

## 2. Experimental conditions

In order to compare the performance of the DTA and Q-DTA measuring techniques, three compounds were studied in parallel: $KClO_4$, $CaCO_3$, $BaCl_2{\cdot}2H_2O$. Experiments were carried out on the Derivatograph C instrument of the Hungarian Optical Works (MOM), Budapest suitable for performing simultaneous DTA, TG, DTG/Q-DTA, Q-TG measurements.

On the modification change of $KClO_4$ serving as an example, it is shown how the kinetics of physical transformations is modified by a slow heat transport if it is studied by the traditional DTA instrument (Fig. 1a), and how if it is investigated by the Q-DTA instrument

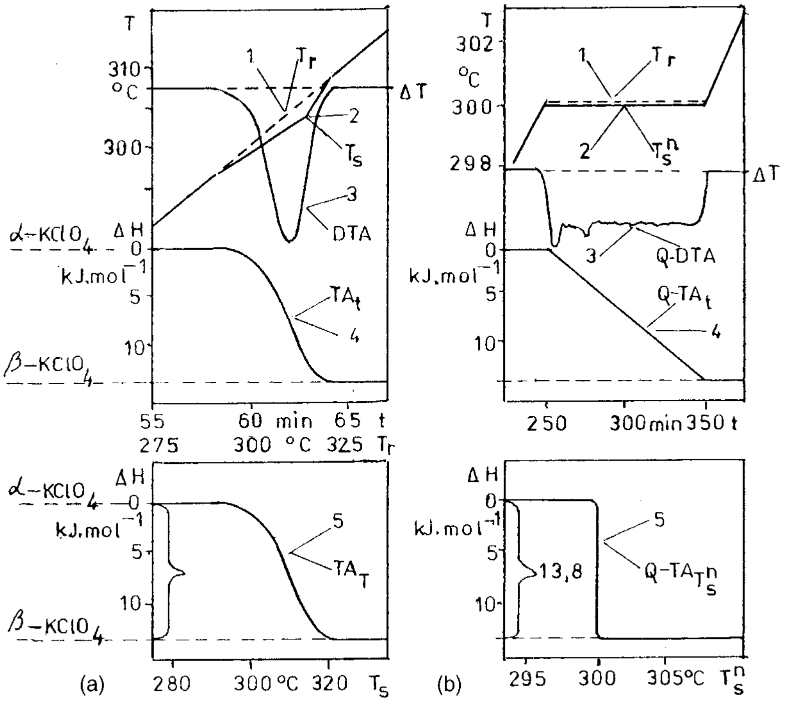

Fig. 1. Modification change of $KClO_4$. (a) Measurement by the conventional DTA method. Curve 1: $T_r$, the temperature change in the furnace and reference point. Curve 2: $T_s$, temperature change in the sample. Curve 3: DTA curve. Curve 4: $TA_t$, the integrated curve of the DTA curve in function of time. Curve 5: $TA_T$, the integrated curve of the DTA curve in funcion of sample temperature. (b) Measurement by the Q-DTA method. Curves 1–5 correspond to curves 1–5 in part a.

(Figs. 1b and 2), that is by the TGHC heating technique. Curves illustrating the changes in the temperature of the reference point (empty crucible) ($T_r$) and that of the sample ($T_s$), as well as the enthalpy changes (DTA) are well-known. However, less known is the interpretation of curves $TA_t$, $TA_T$ and Q-$TA_t$, Q-$TA_T$. These (curves 4 and 5) are derived by integration from curves DTA and Q-DTA, with the purpose to compare them with the corresponding curves 4 and 5 in Fig. 1a and b in order to detect the differences in the course of transformations (e.g. isothermal–non-isothermal) obtained by the two different measuring techniques. No answer can be obtained, namely, to this question by the comparison of curves DTA and Q-DTA. The same concerns also Figs. 4–6.

In the two kinds of experiments (Fig. 1a and b) only heating control was different. In the case of the DTA experiment (Fig. 1a), the heating rate was 5 °C min$^{-1}$. In the case of TGHC (Figs. 1b and 2), no heating rate can be defined, only the rate of transformation

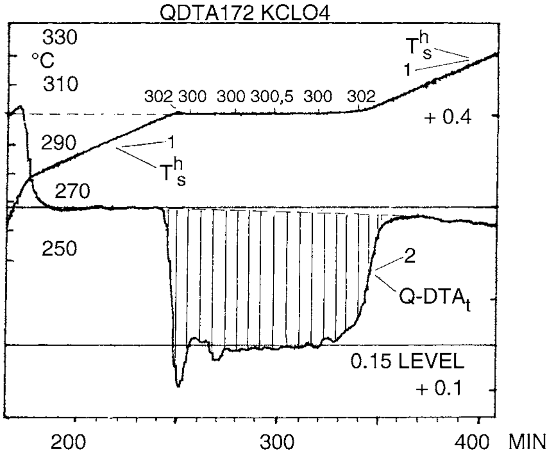

Fig. 2. Modification change of $KClO_4$. Original record as examined by the Q-DTA method under "normal" conditions (TGHC). Curve 1: $T_s^n$, temperature change in the sample. Curve 2: Q-$DTA_t$, enthalpy change transformation rate: 154 J mol$^{-1}$ min$^{-1}$ (open sample holder).

has a definite meaning, which was 140 J mol$^{-1}$ min$^{-1}$. The weight of the sample was uniformly 250 mg. The kinetics of the modification change of $KClO_4$ can be studied on the original record in Fig. 2.

Fig. 3 illustrates how the course of the DTA curves for transformation $AB^s \rightarrow A^s + B^g - Q$ is shifted towards higher temperatures at changing the open crucible for more closed ones (curve 1: multi-plates, curve 2: open, curve 3: covered, curve 4: labyrinth sample holder) which means, at the same time, that the partial pressure of the gas decomposition product ($CO_2$) being in contact with the sample ($CaCO_3$) is increased. In other words, this figure illustrates the effect of gas transport on the course of DTA curves.

It should be noted that the deterioration of the course of DTA curves is due not only to the heat transport, but to the joint effect of heat and gas transport. An

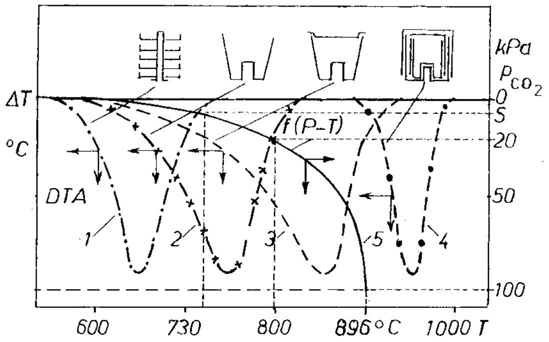

Fig. 3. Decomposition of $CaCO_3$. Measurements by the conventional DTA using multi-plate (curve 1), open (curve 2), covered (curve 3) and labyrinth (curve 4) sample holders. Curve 5: f(P, T), correlation between the decomposition pressure and temperature.

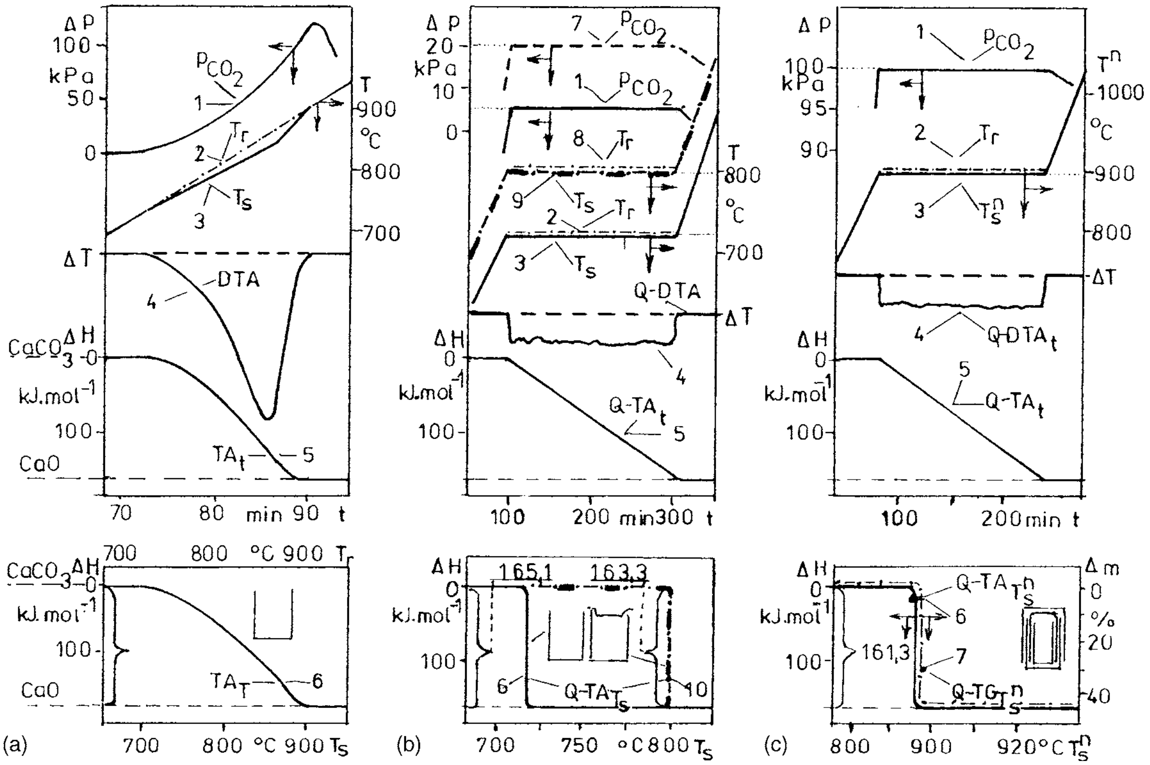

Fig. 4. Decomposition of $CaCO_3$. (a) Measurement by the conventional DTA method: Curve 1: $p_{CO_2}$, change in the partial pressure of $CO_2$. Curve 2: $T_r$, temperature change of the furnace and the reference point. Curve 3: $T_s$, temperature change in the sample. Curve 4: DTA curve. Curve 5: $TA_t$, the integrated curve of the DTA curve in function of time. Curve 6: $TA_T$, the integrated curve of the DTA curve in function of sample temperature. (b) Measurement by the Q-DTA method. Curves 1–6 and curves 7–10 correspond to curves 1–6 in part a, respectively. (c) Measurement by the Q-DTA method under "normal" conditions (TGHC + SGA). Curves 1–6 correspond to curves 1–6 in part a. Curve 7: $Q - TG_{T_s^n}$ weight change.

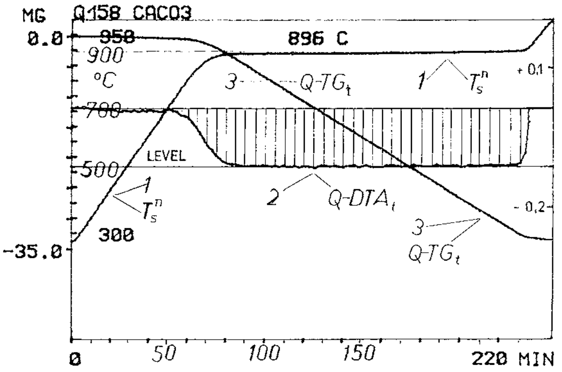

Fig. 5. Decomposition of $CaCO_3$. Original record as taken by the Q-DTA method under "normal" conditions (TGHC + SGA), in function of time. Curve 1: $T_s^n$, temperature change. Curve 2: Q-DTA$_t$, enthalpy change. Curve 3: Q-TG$_t$, weight change of the sample. Transformation rate: $1\,kJ\,mol^{-1}\,min^{-1}$, labyrinth sample holder.

exception is curve 4, where only the effect of heat transport is manifested. This curve is, namely, taken by using the so-called labyrinth crucible. This means that the partial pressure of $CO_2$ reached initially the maximum value of 100 kPa which did not change till the end of transformation, thus, if the reaction was in its steady state, its equilibrium could not change either. Curve 5 shows the equilibrium decomposition pressure versus temperature correlation.

Fig. 4 shows the conventional DTA curve (Fig. 4a) and curves taken by the Q-DTA instrument (Fig. 4b and c) for the decomposition of $CaCO_3$. Curves $p_{CO_2}$ (curve 1) require some interpretation. These illustrate the approximate change in the partial pressure of $CO_2$ being in contact with the solid phase during decomposition. The course of these curves was calculated by the correlation between the actual transformation

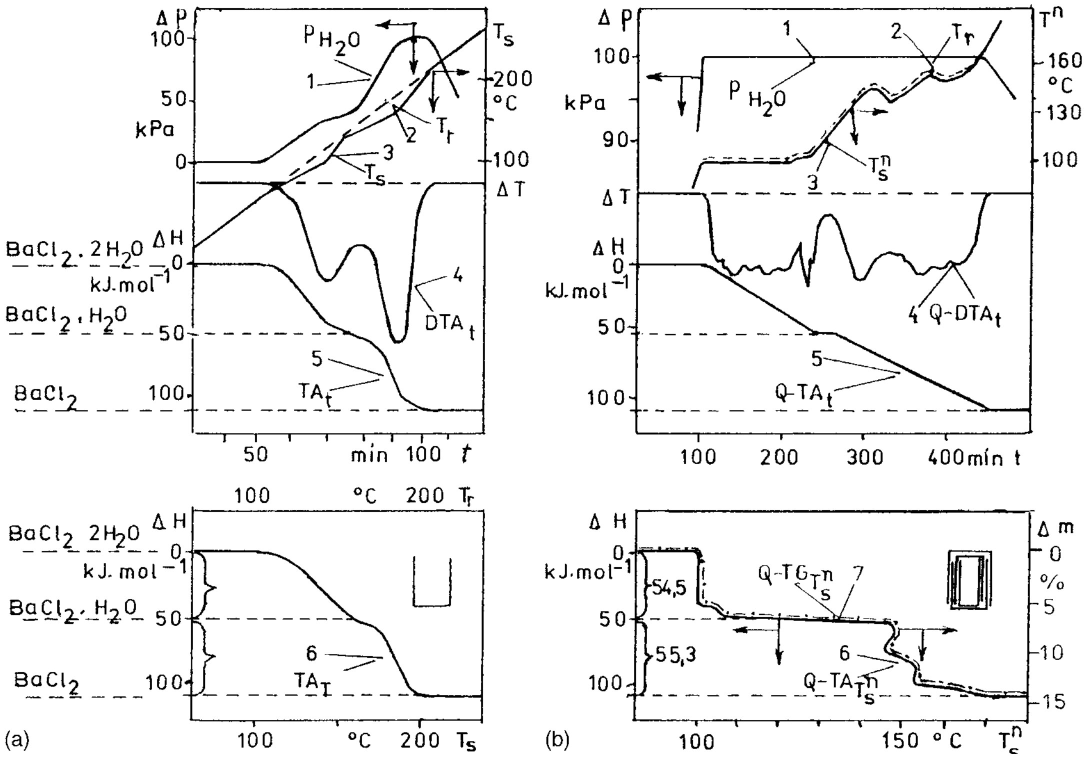

Fig. 6. Dehydration of $BaCl_2{\cdot}2H_2O$. (a) Measurement by the conventional DTA method. Curve 1: $p_{H_2O}$, change in the partial pressure of $H_2O$. Curve 2: $T_r$, temperature change of the furnace and the reference point. Curve 3: $T_s$, temperature change in the sample. Curve 4: DTA$_T$ curve. Curve 5: $TA_t$, integrated curve of the DTA$_T$ curve in function of time. Curve 6: $TA_T$, integrated curve of the DTA curve in function of temperature. (b) Measurement by the Q-DTA method under "normal" conditions (TGHC + SGA) (Fig. 7). Curves 1–6 correspond to the curves 1–6 in part a. Curve 7: Q − TG$_{T_s^n}$ weight change.

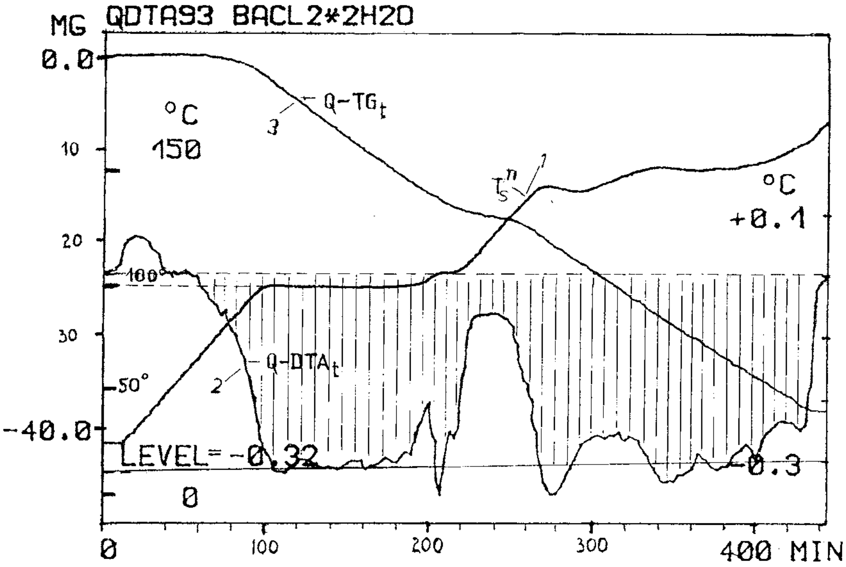

Fig. 7. Dehydration of $BaCl_2{\cdot}2H_2O$. Original record as examined by the Q-DTA method under "normal" conditions (TGHC + SGA), in function of time. Curve 1: $T_s^n$, temperature change. Curve 2: Q-DTA$_T$, enthalpy change. Curve 3: Q-TG$_T$, weight change in the sample. Transformation rate: 300 J mol$^{-1}$ min$^{-1}$, labyrinth sample holder.

temperatures (720, 800 and 896 °C) or the actual temperature range (700–900 °C) and the equilibrium decomposition pressure–temperature relationship of $CaCO_3$ [1,2].

Curves in Fig. 4a were taken in the traditional way, by using a conventional crucible and with a heating rate of 10 °C min$^{-1}$. The rate of transformation controlled by the TGHC unit in cases shown in Figs. 4b,c and 5 was 1 kJ mol$^{-1}$ min$^{-1}$. Later on, the experiments were performed by using open (Fig. 4b, curves 1–6), covered (Fig. 4b, curves 7–10) and labyrinth (Figs. 4c and 5, curves 1–7) crucibles. Sample weights were 75 mg in each case.

As is clear from Fig. 5 (original graph), in addition to temperature curve $T_s^n$ (curve 1) and enthalpy change curve Q-DTA$_t$ (curve 2), the weight change curve Q-TG$_t$ (curve 3) could also be recorded. It should be noted that the course of curve Q-TG$_t$ recorded as a function of time (Fig. 5, curve 3) and that of curve Q-TG$_T$ constructed as a function of temperature (Fig. 4c, curve 7) is identical with the course of curves Q-TA$_t$ and Q-TA$_T$ (Fig. 4c, curves 5 and 6), only their scale became different. The course of enthalpy- and weight changes is not always parallel, thus the difference observable in the course of curves Q-TA$_T$ and Q-TG$_T$ may be an important source of information.

Fig. 6a shows the traditional DTA curve of the dehydration of $BaCl_2{\cdot}2H_2O$, whereas Figs. 6b and 7 illustrate curves taken by the Q-DTA instrument. Curve $p_{H_2O}$ (curve 1) shows the change in the partial pressure of $H_2O$ being in contact with the solid phase. In the case of the DTA study (Fig. 6a), the crucible is open, and the heating rate is 2 °C min$^{-1}$. The Q-DTA study shown in Figs. 6b and 7 (original record) was performed with a sample weight of 250 mg placed into the labyrinth crucible and using a transformation rate of 0.4 kJ mol$^{-1}$ min$^{-1}$.

## 3. Measuring techniques based on "transformation-governed heating control" and "self-generated atmosphere"

The first step for the instrumental realization of "transformation-governed heating control" (TGHC) was made in 1962 by Paulik, Paulik and Erdey, when studying reactions of the type $AB^s \rightleftharpoons A^s + B^g - Q$, they elaborated the so-called "quasi-isothermal, quasi-isobaric" thermogravimetric (Q-TG) method [1–8] and constructed a heating control system [9] in which the heating programmer of the thermobalance, and through it, that of the furnace was controlled by the rate of weight change, i.e. by the DTG signal, based on the feed-back principle.

The essence of TGHC is that the heating control unit governed by the DTG signal provides continuously and automatically a difference between the temperature of the sample and the furnace so that the weight change, i.e. the formation of the gaseous decomposition product, should proceed by a strictly constant rate by orders of magnitude smaller than in the traditional method. Thus, the partial pressure of the gaseous decomposition product remains constant (quasi-isobar, quasi equilibrium) [5] in the environment of the sample, even at using open crucibles, while the temperature of the sample remains constant (quasi-isothermal) at a value corresponding to the ventilation conditions of the sample holder.

This method was further developed by Paulik and Paulik in 1972 [1,2,4,10], when they constructed a sample-holder set consisting of several crucibles fitted into each other, through the narrow channel system of which between the walls of the crucibles the gaseous decomposition products could leave unhindered, but no air could penetrate in counter-current. Thus in the inside of the crucible, a pure “self-generated atmosphere” (SGA) was formed. This ensured that the decomposition reactions of the $AB^s \rightleftharpoons A^s + B^g - Q$ type proceeded through the whole process at the theoretical partial pressure of 100 kPa, i.e. in the pure atmosphere of the decomposition product. The decomposition of, e.g. $CaCO_3$ takes place under the so-called “normal” temperature corresponding to the equilibrium decomposition pressure–temperature of $CO_2$ at 896 °C (Fig. 4c, curve 3; Fig. 5, curve 1).

Based on favourable experience, Paulik, Paulik and Arnold [12] tried to apply TGHC and SGA also to measuring enthalpy changes (DTA, DDC, DSC, simultaneous DTA, TG, etc.). However, for this, some difficult regulation problems had to be solved. For example, for governing the heating control unit of the DTA instrument, in spite of their mathematical similarity and similar course, instead of the DTG signal, the DTA signal could not be used without any modification, as the base line of the DTA curve is not constant, thus the relay may start to operate the heating control unit before the reaction starts. By indicating the actual start of the reaction by the derived DTA signal, the DDTA signal, [2,11,12], the problem could be solved.

This measuring technique was developed further by Paulik et al. in 1995 [11,13] by constructing a complex regulating and measuring instrument dividing the Q-DTA signal proportional to the enthalpy change. One part of the signal was used further on to regulate heating, whereas the other, known part was integrated and then recorded as a function of sample temperature. The Q-$TA_T$ curve obtained by this double transformation is actually analogous to the Q-$TG_T$ curve. From the course of this curve not only the “normal” characteristic temperature of the transformation can be determined, but also the process of enthalpy change free of every foreign effect (heat and gas transport) can be observed on the basis of the information-rich course of this curve. By calibrating the instrument, the direct determination of reaction heat became also possible.

## 4. Kinetics of physical transformations leading to equilibrium mechanism of heat transport

The form of traditional DTA curves for physical transformations leading to equilibrium (modification and state changes) are basically defined by the sum of the effects of two physical processes. One of them is the slow heat transfer due to the bad heat conductivity of the sample, and the other one is the continuous increase in the sample temperature governed by the non-isothermal heating control program. The resultant of these two processes is called heat transport.

The sample with heat conductivity can take on the heat ($Q$) needed for the transformation (e.g. for modification change $\alpha - A^s \rightarrow \beta - A^s - Q$) only slowly from the furnace, thus the transformation gets delayed. The transformation in the sample starts at the wall of the crucible and proceeds towards the centre, for which process the necessary heat is mediated by the wall of the crucible and the sample already transformed.

The program control unit of the DTA instrument increases steadily the furnace temperature. A temperature drop appears inside the material already transformed. At the border of the original and transformed material, in the reaction zone, the rate of transformation increases correspondingly to the descending branch of the DTA peaks. When the starting material is consumed, the whole system takes up the furnace temperature, as is shown by the ascending branch of DTA peaks (Fig. 1a, curve 3).

The results of our experiment concerning the $\alpha$–$\beta$ modification change of $KClO_4$ shown in Fig. 1a is in accordance with the above. The $T_s$ temperature curve of the figure proves, e.g. that under traditional conditions, the modification change could proceed only in about 5 min, and in the meantime, the temperature of the sample was raised by about 15 °C (curves 1 and 2). The DTA curve (curve 3) gives the false impression that the modification change of $KClO_4$ takes place in a non-isothermal way.

Based on thermodynamic considerations (Eq. (1)), however, it can be supposed that the temperature of the original material cannot exceed the theoretical transformation temperature. The transformation takes place along the reaction zone by shifting towards the centre at the theoretical transformation temperature in an isothermal way under equilibrium conditions.

When studying the sample by the Q-DTA instrument (Figs. 1b and 2), the course of all curves was changed, because the TGHC unit, corresponding to the feed-back principle, governed the heating by sensing the transformation rate so that the difference between the temperatures of the sample and the furnace (Fig. 1b, curves 1 and 2) should be, such that the transformation proceeded by a predetermined, strictly steady rate by more than one order of magnitude smaller than under traditional conditions (curves 3 and 4). This means that the TGHC unit provided directly not a constant temperature, but a steady rate of transformation. Thus, the constancy of temperature is a result only of the modification change, and indicates that the transformation takes place under ideal conditions, free of every foreign effect, at the temperature characteristic for this transformation, correspondingly to the reqirements of physical chemistry.

Transformation, considered from the viewpoint of the cross section of the crucible, occurred similarly to the traditional DTA investigation. Inside the material already transformed, a temperature drop develops, however, by orders of magnitudes smaller than in traditional DTA measurements. Also in this case, the reaction zone is shifted gradually towards the middle of the material, but extraordinarily slowly.

According to the original graph (Fig. 2), the average transformation temperature of $KClO_4$, when taking away the very start and very end of the isothermal section of temperature curve $T_s^n$ (curve 1), is 300.1 ± 0.2 °C. It should be noted that temperature values of such accuracy could be read only from the computer display, and not from the Q-DTA$_T$ curve.

The constancy of the equilibrium temperature for modification changes can be proved by the Clapeyron equation. The equilibrium curve of $P$–$T$ diagrams shows a possible series of parameters ($P$, $T$) for the two modifications ($\alpha$, $\beta$) being in equilibrium. The differential equation of this curve is the so-called Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{1}$$

in which $\Delta$ means the difference in the molar quantity of the amount in question. In condensed phases, large pressure differences ($dP/dT$) result only in a negligibly small change in the volume ($\Delta V$), whereas the change in the atmospheric pressure practically does not cause any volume change. Thus, according to the Clapeyron equation, the equilibrium temperature of modification changes under laboratory conditions is well-defined and constant.

## 5. Kinetics of decomposition reactions leading to equilibrium mechanism of heat and gas transport

In case of decomposition reactions of the type $AB^s \rightleftharpoons A^s + B^g - Q$, the course of traditional DTA curves is influenced by three elementary processes being in a narrow correlation with each other. From among them, the effect of heat transport is already known (Fig. 1a). Decomposition is a chemical process taking place in frame of the equilibrium decomposition pressure–temperature correlation (Fig. 3, curve 5). Gaseous decomposition products are removed from the surface of sample particles and/or from the crucible by gas transport based on the physical process of gas diffusion.

Fig. 3 shows DTA curves of $CaCO_3$ taken under otherwise fully identical conditions, but by using four different types of sample holders. Curve 4 provides the rare opportunity to study the joint effect of heat transport and non-isothermal heating mode on the shape of DTA curves, free of other effects. This curve, namely, was taken by using the labyrinth crucible. This ensured that the decomposition of $CaCO_3$ took place in a "self-generated atmosphere", i.e. without the deteriorating effect of gas transport, at the constant 100 kPa pressure of $CO_2$ which is the maximum value for equilibrium. According to curve 5 showing the correlation of equilibrium decomposition pressure versus temperature, the atmospheric decomposition pressure of $CaCO_3$, 100 kPa is reached at 895 °C. Above this temperature, $CaCO_3$ decomposes with a very high rate. In spite of this fact, according to the DTA curve (curve 4), the sample decomposed between 895 and 950 °C, what is impossible. This often observed contradiction can be resolved only by supposing that also in this case, a significant temperature drop was present inside the sample and that only the temperature of the wall of the crucible containing the sample (Fig. 4a, curve 3) could be raised to 950 °C, whereas the temperature of the $CaCO_3$ phase not yet transformed could not be higher than 895 °C (Eq. (2)).

The gradual shifting of the course of curves 1–3 to lower temperatures can be brought into connection with the ventilation conditions in sample holders, and it proves, at the same time, the undisputable role of gas transport on the course of DTA curves.

The decomposition reaction, similarly to the modification change of $KClO_4$, takes place in the reaction zone at the border of the original and the new compound. Decomposition is a long chain of infinitesimal chemical equilibrium processes taking place between the surface of particles of the compound and the very thin gas layer being in a direct contact with their surface. The equilibrium of this elementary micro decomposition processes can be modified from moment to moment according to the decomposition pressure–temperature relationship (Fig. 3, curve 5). The proceeding of the process is basically determined by the intensity of the heat flux between the furnace and the material not yet transformed.

Gas transport based on gas diffusion is also an organic part of the decomposition mechanism. From the very thin gas layer being in direct contact with the solid phase, $CO_2$ more or less accumulated diffuses into the empty parts of the sample holder, then from there, it leaves towards the furnace. This process of gas diffusion is influenced, in addition to the shape of the sample holder (Fig. 3, curves 1–4; Fig. 4b and c), also by the mass of the sample, the rate of heating, etc. in other words, by experimental conditions.

When studying the decomposition of $CaCO_3$ by the traditional DTA instrument (Fig. 4a) it was found that the reaction proceeds delayed, in about 15 min, during which time the temperature of the sample increased by about 150 °C (curve 3), the partial pressure of $CO_2$ (curve 1) increased to 100 kPa despite the study being carried out in an open crucible. According to the DTA curve (curve 4), decomposition took place in the temperature interval of about 750–900 °C, making the false impression that the decomposition of $CaCO_3$ is a non-isothermal, non-equilibrium process.

The TGHC heating technique provides very clear conditions not only from the viewpoint of heat transport, but concerning the gas liberation as well, by keeping the rate of decomposition and $CO_2$ formation (Fig. 4b, curves 1 and 7) constant. Due to this fact, the partial pressure of $CO_2$ adjusts itself to a value determined by the chemical micro-equilibriums between the solid $CaCO_3$ particles and the thin gas layer being in contact with them together with the gas diffusion equilibrium defined by the ventilation conditions of the sample. This partial pressure value and the corresponding decomposition temperature (Fig. 3, curve 5; Fig. 4b, curves 1 and 7) remain constant till the end of the reaction.

This is in accordance not only with the equilibrium decomposition pressure–temperature relationship (Fig. 3, curve 5), but also with Gibbs' rule. In case of $CaCO_3$ decomposition, according to this rule, the system consisting of two components ($C$) and three phases (Ph) has one degree of freedom ($F$):

$$F = C + 2 - \mathrm{Ph} = +2 + 2 - 3 = 1 \tag{2}$$

It means that the change of one state determining parameter from the two ($P$, $T$) results obligatorily in the change of the other.

From the Gibb's rule another important conclusion can also be drawn. As both DTA and Q-DTA investigations are carried out usually at atmospheric pressure, the partial pressure of $CO_2$ in case of $CaCO_3$ decomposition cannot exceed the value of atmospheric pressure, i.e. 100 kPa even in pure "self-generated" atmosphere, and according to Gibb's rule, cannot exceed 896 °C, the equilibrium decomposition temperature. From this it follows that in both DTA and Q-DTA examinations, the decomposition of $CaCO_3$ can proceed only in the reaction zone shifting gradually to the middle, and only at the equilibrium decomposition temperature corresponding to the partial pressure of $CO_2$ in this zone, and the temperature of the core of the sample not yet decomposed could not increase above this decomposition temperature.

The labyrinth crucible ensures automatically the constancy of the maximum value (100 kPa) of the partial pressure of gaseous decomposition products (Fig. 4c, curve 1). Thus, in case of reactions of the type $AB^s \to A^s + B^g - Q$, the labyrinth crucible (SGA) together with the TGHC heating technique, produce "normal" (isobaric, self-generated atmosphere of 100% purity, quasi-isothermal, quasi equilibrium) experimental conditions. This is the only state in which, from among the practicable experimental conditions, the only characteristic "normal" temperature of the reaction ($T_s^n$) (Fig. 4c, curve 3; Fig. 5, curve 1) can be measured. On the other hand, instead of different reaction heats measurable at different reaction conditions ($\Delta H_{T_1}, \Delta H_{T_2}, \ldots$), (Fig. 4b, curves 6 and 10) the only one ($\Delta H_{T_s^n}$) (Fig. 4c, curve 6), belonging to normal reaction temperature, $T_s^n$, can be determined by a good approximation, and further on, in which the course of the reaction ($Q - TA_{T_s^n}$) (Fig. 4c, curve 6) can be recorded free of every foreign effect.

According to curve 1 in Fig. 5 (original graph), decomposition of $CaCO_3$ takes place at 896 °C (by reading the characteristic temperature value from the display of the computer), and it did not scatter more than ±1 °C till the end of the reaction. The average of the most probable 20 values found in the literature [14] is 895 ± 1 °C.

According to the $Q - TA_{T_s^n}$ curve (Fig. 4, curve 6), the normal decomposition heat of $CaCO_3$ measured at the normal temperature $T_s^n = 896\,°C$ by the Q-DTA measuring technique is: $\Delta H_{896}^n = -161.3\,\text{kJ mol}^{-1}$.

## 6. Change of reaction heat with the temperature

Reaction heat can be determined in two ways. The normal reaction heat valid for 25 °C ($\Delta H_{25}^o$) can be calculated by Hess' theorem, from the formation heats of the reaction partners determined by calorimetric measurements of high accuracy (e.g. in the case of $CaCO_3$: $\Delta H_{25} = -178.1\,\text{kJ mol}^{-1}$). By DTA, DDC, DSC methods, reaction heats can be determined directly (e.g. for $CaCO_3$: $\Delta H_{896}^n = -161.3\,\text{kJ mol}^{-1}$). This big difference is owing to the fact that the former reaction heat value is calculated from formation heats at ambient temperature, whereas the latter is measured at the reaction temperature. According to Kirchhoff's law, the reaction heat changes with temperature. The extent of this change, however, can be determined only by very complicated calculations, and only in exceptional cases. Thus the possibility for determining normal reaction heat ($\Delta H_{T_s^n}$) by the Q-DTA measuring technique fills up a gap.

The phenomenon observed by Kirchhoff causes other problems in DTA, DSC or DDC investigations, as well. It is well known that the characteristic temperature of reactions ($T_1 = 730\,°C$, $T_2 = 800\,°C$, ...) changes with the method and the experimental conditions. However, according to Kirchhoff, reaction heats ($\Delta H_{730} = -165.1$, $\Delta H_{800} = -163.3\,\text{kJ mol}^{-1}$) (Fig. 4b, curves 6, 10, ...) change necessarily with the characteristic temperature, too.

## 7. Kinetics and mechanism of non-isothermal reactions not leading to equilibrium

In the Q-DTA study of $KClO_4$ and $CaCO_3$ meant as typical examples (Figs. 1b, 4b and c) only one transformation leading to equilibrium takes place, thus it is simple to interpret these processes. However, in the majority of cases, the processes are much more eventful, isothermal and non-isothermal transformations alternate often with each other, and by using this Q-DTA technique, until now unknown processes become clarified, which do not show themselves in traditional DTA, DDC or DSC curves remaining thus hidden for the observer (Fig. 6b).

In case of non-isothermal reactions not leading to equilibrium ($AB^s \to A^s + B^g - Q$), the temperature of the sample should be increased continuously, since otherwise the reaction slowes down, and sooner or later it even stops. This is no problem in case of traditional DTA, DDC or DSC instruments, as they increase continuously the temperature of the furnace (non-isothermal heating programme).

The need for increasing the temperature continuously does not cause any problem in the Q-DTA method either; the TGHC unit keeps the temperature of the sample automatically and continuously at the value at which the reaction can proceed with uniform rate. When the Q-DTA$_T$ signal indicates that the reaction does not proceed with the predetermined rate, the TGHC unit interferes immediately and adjusts the temperature to the desired value. This possibility has a further advantage, e.g. in multi-component phase transformations in which the slow heat transport is accompanied by slow diffusion.

The fact that the operation of the TGHC system is governed by the transformation studied is best proved when during the transformation an exothermic process follows an endothermic one. In this case, the heating control unit automatically lets the temperature of the furnace fall below the sample temperature, and provides a temperature difference of opposite sign between the sample and the furnace, which lets the exothermic transformation proceed further on with the predetermined small and uniform rate.

As it turns out from the course of temperature (Fig. 6a, curves 2 and 3) and DTA (curve 4) curves in Fig. 6, dehydration of $BaCl_2 \cdot 2H_2O$ occurred under the conditions of traditional DTA investigation in a delayed period of about 50 min, while the sample temperature increased by 100 °C. From this it follows that the course of the DTA curves is determined, similarly to that for $CaCO_3$, by the joint effect of heat transport and chemical dissociation and physical diffusion, i.e. gas transport processes leading to equilibrium.

From the course of the DTA curve, and from that of its integrated TA$_t$, TA$_T$ curves it can only be justified that the reaction occurred in two steps (Fig. 6a).To the contrary, from Q-TA$_T$ curves taken by the TGHC and SGA measuring techniques, information can be read which cannot be found in the traditional DTA, DSC or DDC curves (Fig. 6b). For example, the course of the $Q - TA_{T_s^n}$ curve of $BaCl_2 \cdot 2H_2O$ shows unambiguously that the first section of dehydration is an isothermal process, whereas the second section shows a non-isothermal course.

Under the given conditions, the selectivity of the measurement is significantly higher, thus the two dehydration processes can be totally separated (curve 6) on the Q-TA$_T$ curve, in contrast to the DTA curve (Fig. 6a, curve 4).

The resolution of the Q-DTA investigation is also much better than that of the DTA method. Thus it can be supposed, e.g. that the second step of dehydration is non-isothermal, because in the temperature interval in question two intermediate salt-hydrates were formed and decomposed subsequently. This assumption is supported by Garn [14] who, by high pressure TG studies, made the formation of such intermediate salt-hydrates probable. Their formation and decompositions were supposedly also reactions leading to equilibrium, and only the strong overlapping of these processes made the resultant process seeming non-isothermal.

In order to support the assumption that in the second part of the decomposition reaction, the course of the Q-TA$_T$ curve indicates only the removal of crystal water, the Q-TG$_T$ curve (Fig. 7, curve 3) was recorded simultaneously as well. This was then reconstructed to a function of sample temperature, and fitting the ordinates of the $Q - TA_{T_s^n}$ and $Q - TG_{T_s^n}$ curves (Fig. 6b, curves 6 and 7), the two curves were drawn side by side.

The "normal" enthalpy change of reactions leading to equilibrium ($\Delta H_{T_s^n}$) can be determined only by using the labyrinth sample holder, but in case of reactions not leading to equilibrium open crucibles can also be applied.

The normal enthalpy changes for the two steps ($\Delta H_{100}^n = 54.5$, $\Delta H_{150}^n = 55.3\,kJ\,mol^{-1}$) in the $Q - TA_{T_s^n}$ curve of $BaCl_2 \cdot 2H_2O$ decomposition reaction (Fig. 6b, curve 6) can be read individually, which is not possible, e.g. with static calorimetric measurements.

When analysing the course of curves in Fig. 6b, one can arrive at surprising conclusions. It turns out, namely, that the information carrying curve as to the course of reaction is the temperature curve of the sample, $T_s^n$ (curve 3). Curves Q-DTA$_t$ (curve 4) and its integrated form, curve Q-TA$_t$ (curve 5) provide information only on the extent of enthalpy change. Reconstructing the latter as the function of sample temperature, curve $Q - TA_{T_s^n}$ is obtained (Fig. 6b, curve 6), and by complementing it eventually with curve $Q - TG_{T_s^n}$ (curve 7), one obtains the usually published curves, the reason for which is that they carry every information measured.

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