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TRANSFORMATION-GOVERNED HEATING TECHNIQUE IN THERMAL ANALYSIS
Part III. Normalisation of experimental conditions

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Abstract

The thermoanalytical research group at the Technical University Budapest elaborated already in 1962 a measuring technique called by them 'quasi-isothermal, quasi-isobar thermogravimetry' (Q-TG) operating with 'transformation-governed heating control' (TGHC). The course of curves taken by this technique reinterpreted the kinetics and mechanism of transformations and increased the resolution and selectivity of the method.

The authors extended this measuring technique also to the measurement of enthalpy change. They designed a heating control and measuring apparatus which can be used to all types of DTA, DDC, DSC or simultaneous DTA, TG, industrial instruments, even as an alternative solution. By means of these transformed equipments operating alternatively also with the non-isothermal programme, the 'normal' characteristic temperature of reactions or physical transformations could be measured. The 'normalised' course of curves, as well as the enthalpy change at 'normal' temperature could be determined. For this, only a simple transformation of the traditional heating control and the completion of software is necessary. Decomposition reactions of the type $AB^s \leftrightarrow A^s + B^g$ can be investigated only in pure 'self-generated' atmosphere, i.e. in a labyrinth crucible.

The large scatter of the results published in literature – which are justly criticised by physico-chemists – can be totally eliminated by this measuring technique.

Keywords: DDC, DSC, DTA, transformation-governed heating technique

Introduction

The most important task to be solved for the development of thermal analysis today is the accurate measurement of transformation temperatures. In literature, namely, we find a wide variety of data concerning the characteristic temperatures of transformations. The scatter of these temperature values exceeds by orders of magnitude that justified by the precision of temperature measurements by thermocouples.

In the recent half century numerous measuring techniques have been elaborated and/or realised by factories manufacturing instruments by which the accuracy of characteristic temperatures can be increased on the one hand, and on the other hand, the course of curves could be modified, and through this, the resolution and selectiv-

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ity of the measurements can be improved. It should be noted that these objectives are in close connection with each other. The following objectives have been aimed at:

Drastic decrease of the heating rate; A step-wise isothermal heating programme;
Sample holders producing ‘self-generated’ atmosphere;
Sample holders of specific shapes (poly-plates, conical, labyrinth);
Drastic decrease in the amount of samples (semi-micro techniques);
Application of vacuum or controlled high-pressure atmosphere;
DSC, DDC measuring techniques.

These objectives achieved their goal only in part, since the course of the curves could be changed perhaps into the desired direction to the desired extent, and thus the resolution and selectivity of the measurement increased, but at the same time, the scattering of characteristic temperatures increased unavoidably, as well.

In the meantime, the Standardisation Committee of ICTAC made great efforts for prompting professionals dealing with thermal analysis to apply standardised experimental conditions in order to achieve more reliable data in measuring the characteristic temperatures, however, due to the lack of appropriate instruments, they could only achieve the use of standard calibration compounds.

The first thermoanalytical instrument operating on the basis of simultaneous measurements (Derivatograph) was designed by a small group of researchers working in the Department of General and Analytical Chemistry at the Technical University Budapest [1, 2]. This instrument was used first for recording several different thermoanalytical curves (TG, DTA, EGA, TD) so that their characteristic temperatures were fully identical, and their courses could be compared with each other and were interpretable and evaluable together. This was owing to the fact that the Derivatograph measured the numerous variables in one single sample, i.e. under totally identical conditions. However, if only one of the experimental parameters was changed, e.g. the open crucible was covered, the course of the curves changed.

This observation called the attention of this group to the phenomenon that heat and gas transport processes influence directly the course of curves, whereas experimental conditions do indirectly, in some cases even to a great extent. For example, the modification change of $KClO_4$, as studied by the traditional DTA instrument, shows a non-isothermal course, and it resembles the bell curve (normal distribution or Gauss curve). However, physical chemistry knows this process to be an isothermal reaction (Fig. 1, curves 7, 9).

It was thus obvious to propose some normalisation of experimental conditions, in other words, to bring them into harmony with the laws of physical chemistry. In this case, the results of the measurement would also harmonise with these laws. The characteristic temperatures of curves thus obtained would not scatter any more, and their courses can be brought to overlapping each other without any further restrictions.

The first step to this normalisation was made by Paulik, Paulik, Erdey [1–4] in 1962, when the authors elaborated the so-called ‘transformation-governed heating technique’ (in what follows, the TGHC control), and designed a heating-regulating system controlling the heating of the furnace on the basis of feed-back by the rate of change in sample mass, i.e. by the DTG signal. The course of the Q-TG$_T$ curve thus obtained was quasi-isothermal, as opposed to the non-isothermal course of TG curves taken in traditional way. At the same time, the partial pressure of gaseous products in the environment of the sample remained constant till the end of the reaction (quasi-isobar). If, however, in a next experiment the partial pressure of the gaseous product contacting with the sample was changed (Fig. 2), the transformation temperature changed, too [4].

By experiencing this, in 1971 Paulik, Paulik [1, 2, 5, 6] designed a sample holder set consisting of more crucibles, fitted into each other, through the narrow channel of which, limited by their walls, the gaseous decomposition product could leave unhindered, while the air could not intrude into the crucible against the counter-current of the gaseous product. Inside the crucible, a pure, so-called ‘self-generated’ atmosphere developed. This ensured that the heat decomposition reactions leading to equilibrium take always place at a temperature corresponding to a theoretical partial pressure of gaseous decomposition products of 100 kPa. Paulik, Paulik [4] proved experimentally, what was later proved also by the practice of three decades [1, 2, 7–9], that the joint application of TGHC heating control and the labyrinth crucible in thermogravimetric studies makes the investigation of reactions and physical transformations according to a basically new aspect possible.

After 1973, the Hungarian Optical Works, Hungary traded a new type of instrument, suitable for the simultaneous study of TG, DTG, DTA, EGA and the so-called quasi-isothermal, quasi-isobar processes, the Derivatograph-Q.

As a result of favourable experience, Paulik, Paulik, Arnold extended the joint application of TGHC heat regulation and labyrinth crucible (this crucible is needed only in case of decomposition reactions) to the field of enthalpy change in 1985, and by solving several difficult regulation problems [2, 10, 12], elaborated a method in which the heating control of the DTA, DDC, DSC or that of simultaneous DTA and TG instruments are governed, instead of the DTG signal, by the DTA signal, i.e. by the rate of enthalpy change. Though this instrument was suitable only for measuring normal transformation temperatures, it proved to be very useful. The majority of physical transformations and chemical reactions, namely, does not involve mass changes, thus they could not be investigated by the Q-TG method. The Hungarian Optical Works, Budapest, provided its Derivatograph-C type also with this alternative measuring possibility.

In 1995, Paulik, Bessenyey-Paulik and Walther-Paulik developed further this measuring technique [11, 12], and designed a combined regulating and, at the same time, measuring apparatus, in which signal Q-DTA, proportional to the enthalpy change was divided into two parts. One part of the signal regulated further the heating, whereas the other, known part of this signal was integrated and recorded as a function of sample temperature, T_s^n. The Q-TA$_T$ curve thus obtained provided also the accurate value of the enthalpy change.

Experimental

Curves in Original records 1, 2 and Figs 1–3 were taken by the simultaneous DTA, TG, DTG – Q-DTG, Q-TG – Q-DTA, Q-TA$_T$, Q-TG apparatus (Derivatograph-C) of the Hungarian Optical Works, Hungary. Original record 1 shows the modification change of $KClO_4$ investigated by the Q-DTA method.

The authors show on the example of the modification change of $KClO_4$ in Fig. 1, how the characteristic temperature of physical transformations, and in general, the course of transformations look, if they are recorded by the traditional DTA (non-isothermal heating programme) apparatus (curves 1–4), and how if they are investigated by the Q-DTA measuring technique (TGHC heating control), (curves 5–9). Curve TA$_T$ is actually the integrated DTA curve produced by its graphical integration. On the basis of the course of curve pair Q-TA$_T$ and TA$_T$, namely, the favourable and/or unfavourable effect of experimental conditions on the course of the reaction can be interpreted much better than by comparing curves Q-DTA$_t$ and DTA$_t$. Original record 2 shows the course of decomposition of $CaCO_3$ investigated by Q-DTA method.

Similar comparison can be carried out in Figs 2a and 2b for the decomposition of $CaCO_3$. A further curve is shown in these figures, namely the p_{CO_2} curve, which visualises approximately how the partial pressure of gaseous product CO_2 changes during the decomposition of $CaCO_3$ in the immediate neighbourhood of the sample.

The course of curves in Figs 2a and 2b can be generalised, and it can be established that this is characteristic for each decomposition reactions leading to equilibrium. To the contrary, Fig. 2c shows the course of a heat decomposition reaction for some reason not leading to equilibrium. In case of reactions, the course of curves is similar to that in Fig. 2c, if their course does not remain isothermal for some reason (e.g. formation of intermediates in the second stage of decomposition of $BaCl_2{\cdot}H_2O$: Part II., Fig. 11 [12]).

Curves Q-TA$_T$ and TA$_T$ in Fig. 3 show the course of the decomposition of $CaCO_3$ for cases when it was studied by the Q-DTA (curves 1–3), and by the traditional DTA (curves 4–6) apparatus respectively, in open (curves 1, 4), in closed (curves 2, 5) and in labyrinth (curves 3, 6) crucibles. It should be noticed that in thermoanalytical practice, curves of the TA$_T$ type cannot be found [12]. Curve 7 shows the decomposition pressure *vs*. temperature curve for the decomposition of $CaCO_3$.

Discussion

As already mentioned, highly differing values can be found in literature for the characteristic temperature of the same physical transformation or chemical reaction. This scatter in the temperatures can be completely and easily eliminated by using the Q-DTA measuring technique.

Basic principles of the Q-DTA technique

The instrument applied for the Q-DTA technique differs from the traditional DTA instrument only in using the so-called 'transformation-governed heating' (TGHC) control system [12] for heating the furnace instead of traditional non-isothermal heating programme. The essence of the TGHC regulation is that the heating regulation of the DTA, DDC, DSC or the simultaneous DTA, TG, DTG (Derivatograph) governed in Q-DTA instruments by the DTA signal, generates automatically and continuously a temperature difference between the sample and the furnace, which keeps the reaction to go on with a strictly constant rate being by orders of magnitude lower than the traditional rate [1, 2, 7–9].

Another essential feature of this new measuring technique is a particular crucible, the so-called 'labyrinth crucible' [1, 2, 6–9], which, in cases of reactions of the type $AB^s \leftrightarrow A^s + B^g$ leading to equilibrium generates in the inside of the sample holder a pure, 'self-generated' atmosphere already at the very beginning of the reaction. By this, a further important requirement of physical chemistry is fulfilled. Thus, namely, reactions take place under normal (isobar, at a partial pressure of 100 kPa conditions, i.e. in a pure, self-generated atmosphere) conditions [1, 2].

Physical transformations leading to equilibrium

The phenomenon why and how for physical transformations (modification change, melting-crystallisation) the non-isothermal course of traditional DTA and T_s curves is modified to an isothermal course by using the Q-DTA measuring technique, can be studied on the example of the modification change of $KClO_4$ taken at a heating rate of 5°C min^{-1}, shown in Fig. 1. For example, the courses of T_s and DTA curves (curves 2, 3) prove that this sample of poor heat conductivity was unable to take up the transformation heat immediately, thus the modification change took place in about 5 min, in a non-isothermal way, while the temperature increased by about 10°C.

To the contrary, when using the Q-DTA instrument, after the temperature curve T_s^n (curve 7) reached the transformation temperature, its course remained strictly unchanged for about 50 min (quasi-isothermal), till the end of the transformation (Original record 1). The various temperature values between the limit values 302–302°C on the T_s^n curve were determined by means of computer. In this way authors found the 'normal' characteristic temperature of the modification change to be 300.2±0.2°C.

The modification change of $KClO_4$ is considered in thermodynamics also as an isothermal process leading to equilibrium. Namely, according to statistical mechanism the modification change always occurs at a given temperature provided that the external pressure is constant.

The equilibrium curves in the P–T diagrams can also prove the stability of the temperature of the modification change. These curves show the equilibrium series of the two phases in question. By deriving these curves one get to the Clapeyron equation:

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

where Δ means the difference of molar value of the quantity in question. In the case of condensed phases a high change of external pressure (dP/dT) results small change in the sample volume (ΔV), but the small change of the atmospheric pressure causes practically no change any more in it. That is why the temperature of the modification remains constant.

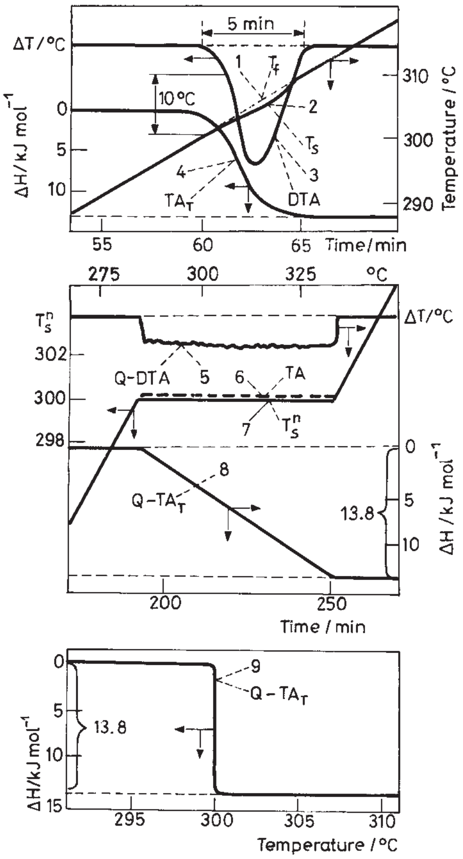
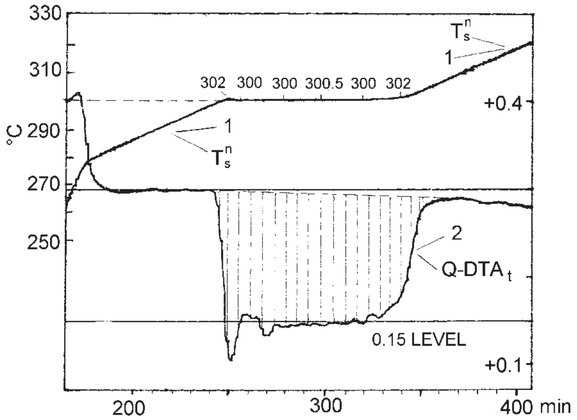


Fig. 1 Modification change of $KClO_4$ examined by conventional DTA method. T_f (curve 1) temperature change of the furnace, T_s (curve 2) temperature change of sample, DTA (curve 3) conventional DTA curve, TA (curve 4) integrated curve of the DTA. Curves are shown in function of time and temperature. Q-DTA (curve 5) T_f (curve 6) temperature change of the furnace. T_s^n (curve 7) temperature change of the sample, Q-TA$_t$ (curve 8) integrated curve of Q-DTA in function time, Q-TA$_t$ (curve 9) integrated curve of Q-DTA in function of sample temperature



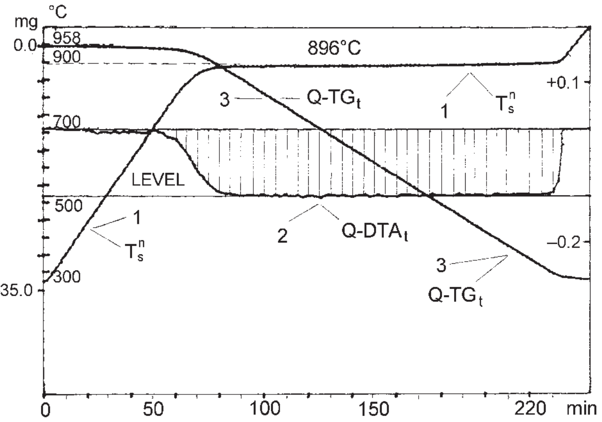
Original record 1 Modification change of $KClO_4$ curve 1: normal temperature change (T_s^n), curve 2: enthalpy change (Q-DTA_t) investigated by simultaneous DTA-TG-DTG apparatus, using 'transformation-governed heating control'

In taking the temperature curves T_s and T_s^n (curves 2, 7) and enthalpy change functions TA_T and Q-TA_T (curves 4, 9) which are the integrated form of the DTA curve, the only difference was the difference in heating control. Thus it is justified to suppose that the characteristic, non-isothermal course of the DTA curve (curve 3) is not characteristic for the transformation itself, since it is originally an isothermal process leading to equilibrium. The process is deteriorated by the slow heat take-up of the sample, and on the other hand, due to a constant increase in the furnace temperature. At the beginning, the temperature difference between the furnace and the sample (curves 1, 2) increases faster, then, in the decay period of the transformation, it quickly decreases. However, at taking the DTA curve, just this difference is measured by the oppositely coupled thermocouples.

Decomposition reactions leading to equilibrium

Figures 2b and 3 and the original record 2 prove unanimously that the decomposition of $CaCO_3$ is originally a reaction leading to equilibrium, and its isothermal course is deteriorated partly by heat transport, partly by gas transport processes.

According to Fig. 2a slow heat transport resulted obviously in the decomposition time of 15 min, despite the fact that the temperature of the sample increased from 800 to 950°C. There is no reason in supposing that heat transport does not affect the decomposition of $CaCO_3$ similarly to that we observed for the modification change of $KClO_4$. Moreover, we found a convincing proof for this in the differing course of curves Q-TA_T, TA_T (curves 3, 6) in Fig. 3. Both curves were taken under identical conditions the only difference being that for taking curve 3 TGHC heating control, whereas for curve 6 traditional non-isothermal heating programme was used. A further important feature is that the sample was studied in both cases in the labyrinth cru-



Original record 2 Decomposition of $CaCO_3$. Curve 1: normal temperature change (T_s^n), curve 2: enthalpy change (Q-DTA), curve 3: mass change (Q-TG), investigated by simultaneous DTA-TG-DTG apparatus, using‘transformation-governed heating control’ and ‘self generated atmosphere’ (labyrint sample holder)

cible. This ensured that the pressure of CO_2 could not increase above the top limit of 100 kPa. Thus, by choosing sufficiently large transformation rate, it had only be ensured that it did not fall below this value. In this way, no deteriorating effect originating from gas transport could be observed.

The result of the measurement depended in both DTA and Q-DTA studies on the form of the sample holder. It could be proven, namely, that the course of gas transport is determined by a double equilibrium.

In the gas layer in contact with the sample the partial pressure of CO_2, p_{CO_2} (Fig. 2a, curve 1) increases gradually during the DTA study, as the temperature of the sample, T_s (curve 3) also increases. The transformation consists of a long chain of micro-equilibria, and in the meantime, equilibrium is gradually shifted towards higher temperatures because of the increased temperature. In the present case e.g. the partial pressure of CO_2 was only 0 kPa at 700°C, whereas it reached 100 kPa already at 900°C.

As it is proven by the course of curves 4–6 in Fig. 3, another diffusion equilibrium was also achieved between the gas layer contacting with the sample and the gas atmosphere in the sample holder. This equilibrium depends on the ever changing concentration of CO_2 in the gas layer, and on the ventilation conditions in the sample holder.

The Q-DTA measuring technique provides very favourable conditions from the viewpoint of gas transport, as well. This is also in accordance with both relation of decomposition pressure – temperature and of the Gibbs phase rule.

The transformation-governed heating control (TGHC) limits the rate of the decomposition (Fig. 2b curve 4) to a preselected value and along with it also the rate of evolving of CO_2 (Fig. 2b curve 1) keeping these values constant up to the end of the reaction. According to relation of decomposition pressure – temperature the sample

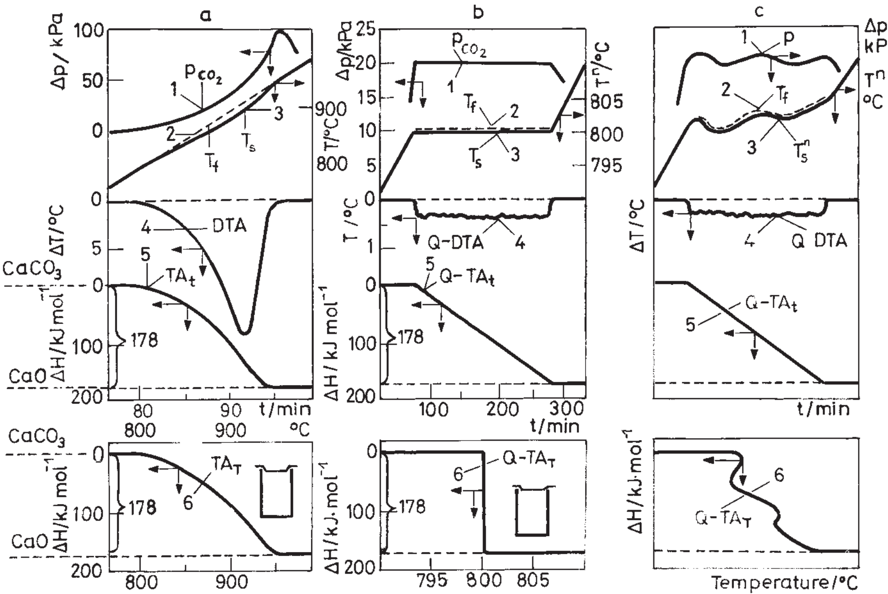


Fig. 2 Decomposition of CaCO$_3$ examined by conventional DTA. This example is characteristic of isothermal reactions leading to equilibrium, in general. p_{CO_2}(curve 1) change in partial pressure of gaseous product (CO$_2$), T_f (curve 2) temperature change of the furnace, T_s (curve 3) temperature change of the sample, DTA (curve 4) conventional DTA, TA$_t$ (curve 5) integrated curve of DTA in function of time and TA$_T$ (curve 6) in function of sample temperature, sample holder: covered crucible, heating rate: 10°C min $^{-1}$ (a)
Decomposition of CaCO$_3$ examined by Q-DTA. This example is characteristic of isothermal reactions leading to equilibrium, in general. Curves 1–6 are in correspondence with curve 1–6 in Fig 2a. Sample holder: covered crucible, transformation rate: 1 kJ mol^{-1} min^{-1} (b)
Fictive non-isothermal reaction, not leading to equilibrium, examined by Q-DTA. Curves 1–6 in this figure are in correspondence to the curves 1–6 in Fig. 2a and Fig. 2b (c)

temperatute must also must remain constant, and the course of the raction quasi-isothermal.

According the Gibbs phase rule the state parameters (*p, T*) of the system consisting of one component (*C*), and three phases (*Ph*) have no freedom (*F*):

$$F= C+2-Ph=1+2-3=0 \tag{2}$$

Consequently the constant state of one of the parameter prescribes the constancy of the other one.

At taking curves 1–3 of Fig. 3 it was experienced that though the concentration of CO$_2$ and the decomposition temperature remained constant till the end of the reaction, it took a certain value at the very beginning of the reaction depending on the shape and ventilation of the sample holder. As is seen in Fig. 3, the partial pressure of

CO_2 was 5 kPa when using the open sample holder (curve 1), 20 kPa with the covered (curve 2), and 100 kPa with the labyrinth (curve 3) crucible. These pressures were calculated [2] from the decomposition pressure – temperature functions (Fig. 3, curve 7) on the one hand, and from sample temperatures (720, 800, 895°C) on the other hand. This circumstance should be taken into account when we want to determine the normal temperature or normal course of a decomposition. In case of decomposition reactions, the use of labyrinth crucible is indispensable, in addition to TGHC heating control.

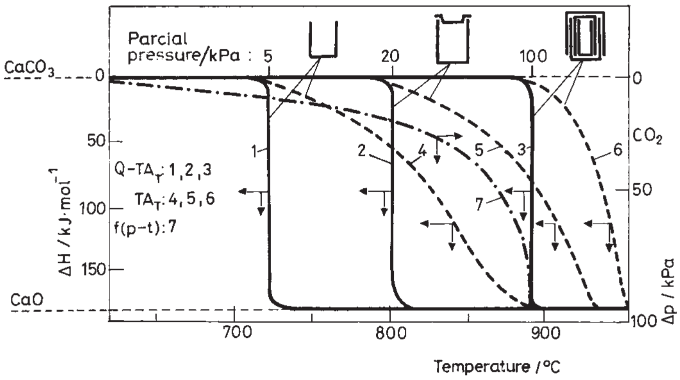


Fig. 3 Decomposition of $CaCO_3$ examined by conventional DTA (curves 4–6) and Q-DTA (curves 1–3). Examined in open (curves 1, 4), in covered (curves 2, 5) and in labyrinth crucible (curves 3, 6). Curve (p, T) (curve 7) correlation of decompoasition pressure (p) and temperature (T). Heating rate in the case of curves 4–6: 10°C min^{-1}, and the transformation rate in the case of curves 1–3: 0.5 mg min^{-1}. Curves 2 and 5 are in correspondence to the curves 6 in Fig. 2a and Fig. 2b, resp.

The authors determined the normal decomposition temperature of $CaCO_3$ as being 896.0±1.0°C, (Original record 2, cuve 1), and found the reaction isothermal and leading to equilibrium. The temperature inquestion was determined by means of computer.

Physical transformations and reactions leading not to equilibrium

Experience shows that part of the T_s^n and Q-TA$_T$ curves has an isothermal course (Figs 1, 2b), whereas the other part is of non-isothermal course (Fig. 2c). Moreover, in many cases, isothermal and non-isothermal sections follow each other on these curves. Such are, e.g. the phase transformations of multicomponent systems (Part II., Fig. 8 [12]).

The course of traditional DTA, DDC or DSC curves is always non-isothermal. The reason for this is the use of non-isothermal heating programme. From this it follows that these curves contain much less information concerning the kinetics or mechanism of reactions or physical transformations than those taken by using the Q-DTA method.

In cases of non-isothermal reactions, i.e. for those not leading to equilibrium, the gaseous decomposition products do not play any role in the course of DTA, DDC or DSC curves, however, heat transport can significantly modify it. This deteriorating effect can be eliminated totally by applying TGHC heating control, similarly to the case of reactions or physical transformations leading to equilibrium. The TGHC heating control unit operates in the same way in both cases, only the result of regulation differs.

The TGHC control unit also in this case provides automatically a temperature difference between the furnace and the sample, which lets the reaction to take place with a preselected, very small and constant rate till the end of the reaction. If for some reason the rate of the reaction starts to decrease, the regulating system increases the temperature to a sufficient degree, and if the reaction starts to accelerate, it decreases the temperature.

Moreover, if the reaction would start to generate heat, the heating control operates further without any intervention, it changes sign, and modifies the heating intensity in such a sense that the temperature of the furnace decreases below that of the sample. After this, a temperature difference between the furnace and the sample is generated automatically so that the reaction should proceed further with the same very small, preselected and strictly constant rate.

Measurement of the characteristic temperature of reactions and physical transformations under 'normal' experimental conditions

As it has been proven, by using the Q-DTA measuring technique, reactions and physical transformations can be investigated under conditions quasi corresponding to the so-called 'normal' conditions prescribed by physical chemistry, thus the so-called 'normal' temperatures (T_s^n) of transformations close to the 'theoretical' value can be measured.

The use of TGHC heating control and the labyrinth crucible determines strictly the experimental conditions. As a consequence, by applying the Q-DTA measuring technique only one single characteristic temperature, the singular 'normal' characteristic temperature can be measured (Original record 2 curve 1 and Fig. 3 curve 3).

Consequently, thermoanalysts could perform their Q-DTA measurements by using quite different types of industrial instruments, if their apparatus were suitable for carrying out TGHC heating control, at least as an alternative solution, – this is only a question of software – , and at the same time, a labyrinth crucible were used as sample holder. Under this condition, different laboratories could determine the very same 'normal' temperature, as well.

Information content of temperature: T_s^n and enthalpy change: Q-TA_T curves

It is remarkable that curve Q-DTA$_t$ (Fig. 1, curve 5; Fig. 2b, curve 4) and its integrated form, curve Q-TA$_t$ (Fig. 1, curve 8; Fig. 2b, curve 5) do not provide any information on the course of transformations, and they are suitable only for determining the value of enthalpy change. The course of the transformation temperature curve T_s^n (Fig. 1, curve 7; Fig. 2b, 2c curve 3; and curve Q-TA$_T$ recorded as a function of the former temperature (Fig. 1, curve 9 and Fig 2b, 2c curves 6) carry information.

In identifying the given transformation it is already a support, if we know whether the transformation is isothermal or non-isothermal. Only some examples for this: If the course of curves T_s^n and Q-TA$_T$ is isothermal, we can be sure that the transformation lead to equilibrium, such are e.g. modification changes (Fig. 1), state modifications (Part II.), eutectic and peritectic melting of salt hydrates [2], melting of eutectic salt mixtures (Part II.), precipitation of solids from saturated solutions (Part I., Fig. 7 [2]) or decomposition reactions of the type $AB^s \leftrightarrow A^s + B^g$ (Fig. 2b). If the curve or curve section is non-isothermal, an increase of the temperature was required e.g. in the following cases: nucleus formation (Part II.), increase in the thickness of the new phase at the interface decreasing the rate of gas diffusion through (Part I., [2]), precipitation of a solid from unsaturated solutions (Part I., Fig. 7, [2]), or decomposition reactions of the type $Ab^s \rightarrow A^s + B^g$ (Part II.). The temperature of sample can be lower at the end of the transformation (e.g. nucleus formation) (Part I., Figs 5, 6).

Measurement of enthalpy changes by the Q-DTA method

Enthalpy changes accompanying reactions and physical transformations can be determined by this technique simpler and more accurately than by using DTA, DDC or DSC instruments. This measurement is carried out as follows (Part II.): Instrument Q-DTA halves the measured Q-DTA$_t$ signal (Fig. 1, curve 5; Fig. 2b, curve 4). The one part of the signal governs further the heating control as earlier, whereas the other known part is integrated, then the signal Q-TA$_t$ thus obtained (Fig. 1, curve 8, Fig. 2b, curve 5) is recorded as a function of temperature, T_s^n of the sample (Fig. 1, curve 7; Fig. 2b, curve 3). Curve Q-TA$_T$ obtained by double transformation (Fig. 1, curve 9; Fig. 2b, curve 6) is actually analogous with curve Q-TG$_T$ (Part II., Fig. 5). By calibrating the instrument (Part II.), the value of enthalpy change can be read directly from this curve, either for the elementary steps, or for the whole of the transformation. The advantage of this method over the static methods measuring the whole enthalpy change, e.g. calorimetric methods, is that if the transformation takes place in more steps, the enthalpy change values can be determined individually also for the steps (Part II., Fig. 8).

Accuracy and reproducibility of this quantitative Q-DTA method have been studied on practical examples. The results of these studies will be provided in Parts IV and V [14, 15].

Conclusions

The Q-DTA measuring technique is suitable for answering the same questions for which the DTA, DDC and DSC methods were used till now, moreover, it is more suitable, as:

a) All the elementary processes remained hidden due to heat and gas transport processes in DTA, DCC or DSC investigations can be seen in the Q-TA_T curves.

b) The normal characteristic temperature (T_s^n) of transformations can be determined by the Q-DTA method, together with the normal course of the enthalpy change (Q-TA_T).

c) The value of enthalpy change can be read directly from curve Q-TA_T, for part of the transformation or for the whole of it.

d) According to thermodynamics (Kirchoff law), the heat of reaction changes with the temperature. By using the Q-DTA measuring technique, the heat of reactions (ΔH^n) belonging to the 'normal' characteristic temperature (T_s^n) can be determined (Part V., [15]).

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