Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 725-739

TRANSFORMATION-GOVERNED HEATING TECHNIQUES IN THERMAL ANALYSIS II.

F. Paulik, E. Bessenyey-Paulik and K. Walther-Paulik

Institute for General and Analytical Chemistry, Technical University Budapest
Budapest, 1521 Hungary

(Received January 30, 1999)

Abstract

The described instrumental method makes it possible that the quasi-static heating technique, well applicable to thermogravimetric measurements, (see Part I of this paper) can be used in the case of DTA and DSC examinations, too. Based on the new type of curves the characteristic transformation temperatures, the whole course of the transformation in dependence of sample temperature, the extent of the enthalpy change caused by the transformation or by its partial processes can accurately be determined. The essentially greater accuracy of the measurements – in comparison to the conventional ones – is due to the quasi-static heating technique which ensures that the transformations should take place under quasi-equilibrium conditions.

Keywords: DDC, DSC, DTA, transformation-governed TA

Introduction

Whereas only part of thermal transformations involves mass changes, all of them result in enthalpy change. The quasi-isothermal, quasi-isobar measuring technique [1] proved to be successful in providing better selectivity and resolution [2, 3], therefore it seemed to be of eminent interest to broaden its measuring principle and include also the fields of differential thermal analysis (DTA), dynamic differential calorimetry (DDC) and differential scanning calorimetry (DSC), as well.

However, control by signal of the enthalpy change rate (DTA curve) could not be applied in the same way, as it was done by the signal of the mass change rate (DTG curve) [1–3], because in contrast to the well-defined, horizontal baseline of the DTG curve, the baseline of the DTA curve shifted as a result of different circumstances (heat asymmetry of the furnace, variation in the heat capacity or heat conduction of the sample due to transformation), as is shown in Fig. 1. As a consequence of this, heating regulation would start to operate before the beginning of transformation, even immediately, when this baseline reached the f or g level.

Paulik, Paulik and Arnold, elaborated in 1985 [3, 4] a measuring technique eliminating the regulation-technical difficulty of the shift of baseline. The inventors have patented this method. The solution of the problem is based on the phenomenon that

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

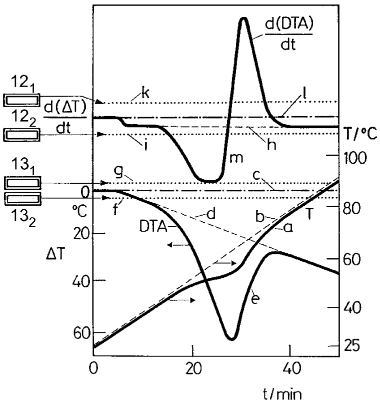

Fig. 1 Conventional DTA curve and its derived d(DTA)/d*T* curve temperature curve, of sample (a) and reference material (b). The original (c) and shifted (d) baseline of the DTA curve (e), Photoelectric detectors (12_1, 12_2, 13_1, 13_2) of the equipment sensing the light beam of the DTA and d(DTA)/d*t* galvanometers and their limit levels (f, g, i, k). Level (h) corresponding to the shifted base line (d) of the DTA curve belonging to the d(DTA)/d*t* curve (m), and the original level of the later one (l)

a derived signal (d(DTA)/d*t*) reacts with a higher sensitivity to the quick direction variation of the basic signal (DTA), but it hardly senses the slow variations in it, in this case the slow shift in the DTA baseline.

Theoretical principle for the operation of a Q-DTA apparatus

Structural parts 1–16 in Fig. 2 are parts of the original apparatus [2–4], whereas elements 17–24 are built into the apparatus only later, during its further development [5].

Paulik, Paulik and Arnold [4] built into the DTA circuit of the derivatograph [2, 3] a deriving unit (10), thus the heating control (4) of the furnace (3) was regulated by the derived signal (Q-DDTA) and the basic signal (Q-DTA) together, in the following way:

The derived signal was led into a mirror galvanometer (11), and in the way of the light signal of the galvanometer, photoelectric detectors were placed on both sides (12_1, 12_2). When transformation started (time β) and the sample started to absorb (γ–δ interval), or produce (φ–κ interval) heat, the light signal of Q-DDTA galvanometer (11) was deflected to the direction of the one or the other photoelectric cell.

In this example, from the time on the light signal reached the photoelectric detector (12_2) (time β), the heating mode changed basically. The signal induced in the photoelectric detector, set the multifunction relay system 14 into operation, which, in turn, made the following operations:

a. It sensed that transformation started (β) or ended (γ), or that the signals changed sign (δ→ε) in other words, that the sample absorbed or produced heat.

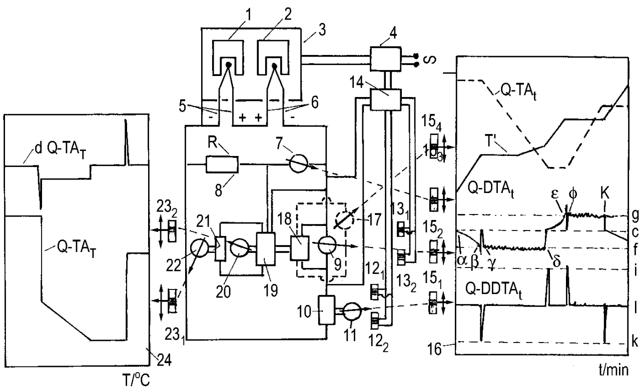

Fig. 2 DTA apparatus for studies under quasi-isothermal and quasi-isobaric conditions; Sample (1), reference material (2), furnace (3), heating programmer (4), counter connected thermocouples (5, 6), galvanometers (7, 9, 11, 17, 20, 22) compensating resistance (8), deriving units (10, 21) photoelectric detectors (12_1, 12_2, 13_1, 13_2), multifunction relay and controller system (14), recorder (15_1–15_4, 23_1, 23_2) chart (16, 24), integrating unit (18), converter (19);
Limit levels: f, g, i, k, base levels: c, l. Non-isothermal heating starts (α), endothermic transformation starts (β), quasi-isothermal heating control starts (γ), and ends and non-isothermal heating starts resp. (δ), exothermal transformation starts (ε), quasi-isothermal heating starts (φ) and ends (κ) etc.

b. It set the baseline of Q-DTA curve (time β), i.e. it gave to the poles of the galvanometer a countervoltage sufficient to direct the signal of the Q-DTA galvanometer back to the base level (Fig. 1, d→c level) independently how big was the shift in the baseline (Fig. 1, straight line d) of the Q-DTA curve.

c. After that, the control of the heating programmer (4) was taken over by the DTA signal. In other words, it allowed the transformation to progress correspondingly to the predetermined and programmed constant rate of transformation (levels g or f). After starting the heating (time γ), namely, when the light signal of galvanometer 9 fell on photoelectric detector 13_2, this latter, by means of the relay system (14), commanded the heating programmer system (4) to decrease the temperature of the furnace. Temperature decreased, rate of transformation decreased, thus the light signal of galvanometer 9 drafted from the photoelectric detector, the heating programmer started to increase the temperature again. This regulation period lasting only for few second is repeated till the end of transformation (time δ) over and over again.

d. In the case of exothermic or endothermic transformations, the only difference in the principle of heating control was that the regulating system (4, 14) kept the temperature of the furnace automatically somewhat higher than the temperature of the sample when the sample absorbed heat, and somewhat lower, if it produced heat.

e. When transformation ended (time δ or κ), the light signal of the Q-DTA galvanometer (9) returned quickly to the baseline, as a consequence of which the light signal of Q-DDTA galvanometer (11) swang out into the opposite direction than at the beginning of transformation. The light signal reached photoelectric detector cell 12_1, which, in turn, effected the ceasing of the intervention of the multifunctional relay system (14). From this time on (δ), the heating programmer system (4) raised the temperature of the furnace again in the traditional way, with a steady rate, up to the next transformation (φ).

In summary, in the quasi-isothermal period of transformation (γ–δ and φ–κ), the heating regulation system (4 and 14) produces a temperature difference between the furnace and the sample sufficient to ensure a predetermined, very small and constant transformation rate (Fig. 2, limit levels f and g). Thus temperature is regulated again by the transformation, fully automatically, on the feed-back principle.

In sake of better understanding, in Fig. 2 a simplified structure for the principal operation of the quasi-isothermal heating programmer system is shown. In reality, the complex operation described above, as well as data acquisition, data recording and processing were performed by the personal computer of the Derivatograph.

Interpretation and evaluation of the curves

In Part I of this publication [1] we have dealt with the question, which elementary processes govern the course of reactions taking place with mass changes, and illustrated it also with examples.

By the present measuring technique another big group of transformations can be studied as well, namely those not suffering mass, only enthalpy changes, such as e.g. modification and state changes, reactions occurring only in melts or in solid phase, and the big family of phase transformations in multicomponent systems. A lot of the latter ones are composed of many elementary processes, such as e.g. the precipitation and melting of eutectics, as well as compound formation, congruent or incongruent decompositions in multicomponent systems.

Interpretation and evaluation of the results of these transformations occur similarly to the principles and regularities already described [1]. The close relationship between the two methods can be proved by the fact that reactions including mass change can also be studied by the measuring technique presented here (Figs 6 and 10). Mass change curves (Q-TG'_T) can simultaneously be detected together with the enthalpy change curves (Q-TA_T). The difference in taking such Q-TG'_T curves and original Q-TG_T curves is that in the first case heating regulation is not performed by the Q-DTG_t signal, but by the Q-DTA_t signal.

In this broadened circle of transformations there are not only individual reactions leading or not leading to equilibrium, but complex or multiple complex transformations, as well.

Transformations leading to equilibrium

The DTA and *T* curves in Fig. 3 illustrate the modification change of potassium perchlorate. These curves were first taken with the traditional DTA apparatus (curves 1 and 2), by applying non-isothermal heating (heating rate: $2^{o}C\ min^{-1}$), then

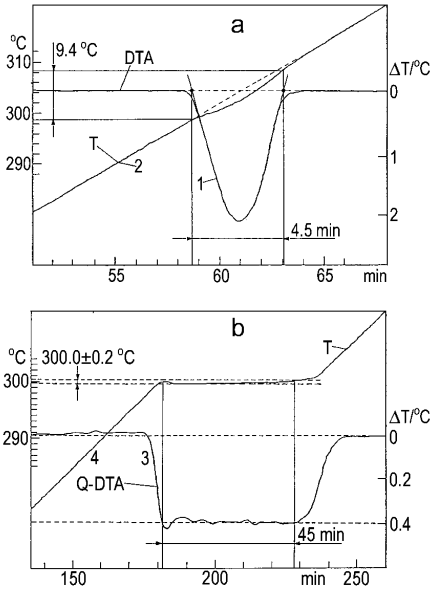

Fig. 3 Modification change of potassium perchlorate under non-isothermal (a-curves 1 and 2) and quasi-isothermal (b-curves 3 and 4) condition

with the above described Q-DTA apparatus (curves 3 and 4), by quasi-isothermal heating technique (rate of transformation=limit level ΔT=0.4°C).

From curves 1 and 2 it is obvious that by the conventional technique, the originally isothermal modification change took place in a non-isothermal way, in a broad, nearly 10°C temperature interval. Though, based on different theoretical considerations, such as e.g. the "on set" design mode, it can be deduced that the modification variation took place at around 300°C, but this is only an estimated, and not a measured value.

To the contrary, by applying quasi-isothermal heating regulation, the temperature of the sample became stabilised at 300±0.2°C, and practically did not change for 45 min, i.e. the modification change occurred in an isothermal way, correspondingly to its character. This value agrees well with the mean value of 299.8°C determined by other physico-chemical methods [6, 7].

These two kinds of figures prove convincingly that the characteristic temperatures for transformations can be determined more accurately by the quasi-isothermal measuring technique than by the conventional method.

Transformations not leading to equilibrium. Transformations leading and not leading to equilibrium together

Good examples for the complex processes are the phase transformations in multicomponent systems (Fig. 4).

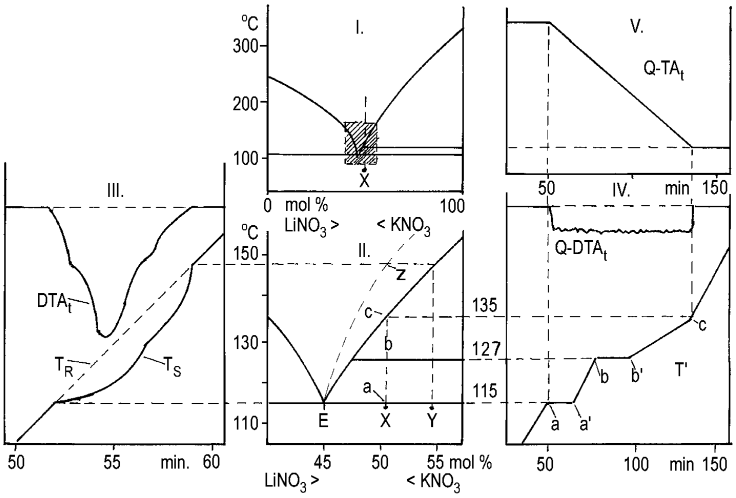

Fig. 4 Phase diagram of $LiNO_3$–KNO_3 system (I), and framed and enlarged part of it (II), and the results of DTA examinations of the heated system containing $LiNO_3$–KNO_3 (51 mol.%) under conventional (III) and quasi-isothermal (IV, V) condition; Curves DTA_t, $Q\text{-}DTA_t$, $Q\text{-}TA_t$ (integrated curve of the later one), T_S, T_S', T_R (temperature curves of the sample (S) and reference material (R)); E: eutectic point a–a': melting of the eutectic mixture, a'–b: melting of α-KNO_3, b–b': transition of α–β-KNO_3, b'–c: melting of the β-KNO_3, *x*: end and *y* and *z*: virtual end of the transformation

DTA, DDC or DSC measurements are used for a long time to the construction or revision of phase diagrams. From the beginning, a possible error in temperature measurement have been taken into consideration, and results have always been accepted only with restrictions. The failure is, in fact, caused by non-isothermal heating control, and can be ascribed to the phenomenon that the sample is not capable of taking up the big amount of heat needed for the progress of transformation from its environment instantaneously, thus a temperature drop happens in the interval part of the sample. A further cause of fault can be the slow set-in of equilibrium, for this phenomenon, the slow and strongly temperature-dependent diffusion is responsible. Even isothermal transformations take place delayed, in a broad temperature interval, as a consequence of which only false, virtual temperature values can be read from the DTA and *T* curves, thus subsequent processes following each other very quickly overlap.

Figure 4. I. is the phase diagram of the $LiNO_3$–KNO_3 system, Fig. 4. II. shows an enlarged version of the framed part of the former. Figure 4. III. illustrates the conventional DTA study of a mixture containing 51 mol% KNO_3 (heating rate: $2^oC\ min^{-1}$), whereas Fig. 4. IV. shows the curves for the same mixture but taken by the quasi-isothermal heating technique (limit level rate of transformation: 0.2^oC).

Figure 4. IV. provides the following pieces of information: Upon heating the solid sample, first the eutectic fraction of the mixture melts (straight line a–a'), in an isothermal way, at 115^oC. Subsequently (curve a'–b), the melt solves part of the

solid α-KNO_3 fraction in a non-isothermal manner, during which the temperature gradually increases to 127°C. By reaching this temperature, the crystal structure of the remaining α-KNO_3 changes isothermally, and the β-modification appears (straight line b–b'). Finally, between 127 and 135°C, β-KNO_3 also melts (curve b'–c).

Characteristic temperatures of the isothermal sections at 115 and 127°C, similarly to $KClO_4$ (Fig. 3), can be determined by a high accuracy. The initial and end temperatures of transformation is unambiguously determined by the Q-DTA curve. By projecting the latter (point c) to the liquidus curve, the composition of the mixture studied (point x) can also be read accurately.

To the contrary, due to the temperature delay discussed, we could have made a serious mistake, if we tried to determine the composition of the mixture by means of curves DTA_t and *T* (Fig. 4. III) (point y), or oppositely, when knowing the composition, we tried to construct the liquidus curve (point z). By the way, the isothermal and non-isothermal processes closely following each other, did not leave any interpretable trace on these conventional curves, either.

Further development of the Q-DTA measuring technique

It turned out that the resolution and selectivity of the Q-DTA studies carried out under quasi-isothermal conditions could be increased further, and there is even a chance for determining the enthalpy changes of transformations by a high accuracy.

Paulik, Bessenyey-Paulik and Walther-Paulik [5] recognized and realized these hidden possibilities, according to the train of thoughts shown in Fig. 5.

Let us consider the functions of the well-known quasi-isothermal thermal gravimetric curves. Curve Q-DTG_t (curve 1) governs the heating control. Curve Q-TG_t

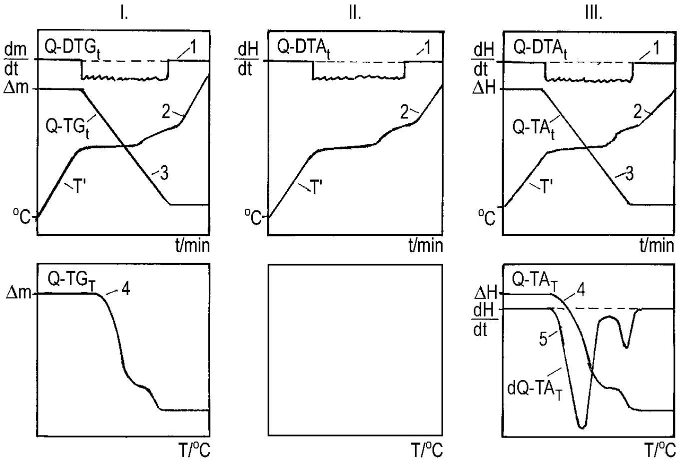

Fig. 5 Curves of a complex transformation in function of time and in function of temperature, examined with a thermobalance (I), with a DTA apparatus (II) and with a new version of the later one under quasi-isothermal condition

(curve 3) contains information on the mass change. Curve T' (curve 2) is characteristic for the temperature course of the transformation, but only in a hidden, not apparent manner. In order to get a true picture about the course of transformations, in practice we let a computer to reconstruct the Q-TG$_t$ curve as a function of temperature T', and the result of the study is interpreted and evaluated on the basis of this Q-TG$_T$ curve (curve 4).

However, there is no chance for this reconstruction in the case of the Q-DTA measuring technique, as it is seen from Fig. 5.II. The reason for this is that the DTA apparatus does not record the function of enthalpy change (Q-TA$_t$ curve), only its differential quotient (Q-DTA$_t$ curve). The patent of Paulik, Bessenyey-Paulik and Walther-Paulik patented in 1996 makes up for this deficiency [5].

The basic principle of this invention can be studied in Fig. 5. III. To the analogy of Fig. 5. I, curve Q-DTA$_t$ (curve 1) is left in its original function, i.e. it further governs on the heating programmer system, but at the same time, it is also integrated. Thus, we obtain curve 3, which, though does not provide information about the course of enthalpy change, but it shows its measure. By redrawing curve Q-TA$_t$ as a function of T', we obtain curve Q-TA$_T$ (curve 4), which is practically the analogue of the Q-TG$_T$ curve. If it seems to be necessary to increase further the resolution of curve Q-TA$_T$, then we derive it (dQ-TA$_T$ curve). The difference existing in the shapes of curve Q-DTA$_t$ (curve 1) and dQ-TA$_T$ (curve 5) is very remarkable, since both illustrate the rate of the enthalpy change in the sample, but former one as a function of time, the latter one as a function of temperature.

Construction and operation of the developed Q-DTA apparatus

For lucidity's sake, the multiple function transformation is illustrated by the elements 17–24 of the connection system shown in Fig. 2 and by their operation. In practice, this is performed also, of course, by the computer.

Into the DTA circuit of the apparatus, parallel to galvanometer 9, an integrating unit (18) is connected, the output of which is measured by galvanometer 17, and/or recorded by recorder 15$_4$. As the integrated curve Q-TA$_t$ provides information only about the quantity of enthalpy change, its recording is unnecessary. The output signal of integrating unit 18 is led into a converter (19), which converts the Q-TA$_t$ signal into another one, which is a function of sample temperature (T'). The converted signal is then recorded by galvanometer 20 and recorder 23$_1$ (curve Q-TA$_T$). If it is necessary, the derived signal of Q-TA$_T$, i.e. curve dQ-TA$_T$ can also be recorded by utilising deriving unit 21, galvanometer 22 and recorder 23$_2$.

Determination of transformation heat

Based on the course of the Q-TA$_T$ curve obtained by integration and redrawn in function of temperature, quantitative conclusions can be drawn for the enthalpy change in the sample, as well. For this purpose, however, the apparatus should be calibrated in the conventional mode, by some standard material the transformation heat of which is accurately known. Thus, to the ordinate of the Q-TA_T curves absolute values expressed in Joule can be ascribed.

For justifying the measuring principle, before manufacturing the prototype of the new apparatus, the Q-DTA circuit of the original Derivatograph Q to be modified was subsequently calibrated, and the earlier routinishly taken curves (Figs 6 and 10) were subsequently graphically integrated and evaluated. The following practical examples were evaluated this way.

Determination of the evaporation heat for water, ethanol, methanol and acetone

For calibration, curves for the modification change of $KClO_4$ (Fig. 3. II), and for determining the error in the quantitative measurement, curves taken for the determination of the latent heat for water boiling (Fig. 6, original curve) were used.

Calibration

By the graphic integration of curve Q-DTA_t of $KClO_4$ (Fig. 3 II), and by the careful consideration of experimental conditions (time and rate of transformation, mass of sample, etc.), we calculated how large an area under the Q-DTA_t peak was generated by the modification of the known amount of the sample. Knowing the mass of the sample and the transformation heat of potassium perchlorate [6], we calculated how large an enthalpy change (in Joule) corresponded to a unit of integrated area.

We established in a similar way also the area under the peak on the Q-DTA_t curve generated by the latent heat of boiling water (Fig. 6), and from this, in the knowledge of the calibrated value for a unit area, the latent heat for the boiling of water. Results of these calculations, compared with literary [7] data are summarized in Table 1.

In the course of graphic integration of the peak on the Q-DTA_t curve of water (Fig. 6), values calculated were progressively summarized. This series of numbers was recalculated in Joule and plotted as a function of temperature. Thus, we obtained curve Q-TA_T for water shown in Fig. 7 (curve 1) together with the corresponding curves for ethanol, methanol and acetone (curves 2, 3, 4). These latter have been chosen for our study, since their latent heat is also well-known, just like that of water [7]. The final results of these studies, together with literary data for latent heat values of these solvents are summarized in Table 2.

These operations and calculations for curve construction will be computerized in the future, which makes them, beyond all comparison, much quicker and more accurate.

Interpretation of curves Q-DTA_t and Q-TA_T for water

Both curves in Figs 6 and 7 need interpretation. According to both, two processes took place successively. The second process occurred at 100°C, in an isothermal way. Thus it is no doubt that this kind of heat can be identified as the latent heat of water leaving by boiling. It was right to suppose that the heat effect of the other process taking place between 20 and 100°C could be ascribed to the uptake of specific heat by the water. Three arguments support this assumption:

a. Earlier experiments proved that no water vapour could leave the labyrinth crucible before water started to boil at 100°C [1]. Subsequently, however, the temperature of the system could not change till all the water is evaporated. This rule can be extended to the other solvents studied.

b. The above statement is supported by the course of curve Q-TG$_T$ in Fig. 6, as well. That is, no considerable mass decrease can be read from the curve under 100°C. Thus, heat uptake could not have its origin in the evaporation of water before boiling.

c. The establishment that under 100°C curve Q-DTA$_t$ (Fig. 6) and curve Q-TA$_T$ (Fig. 7) correspond to uptake of the specific heat by water, above 100°C to that of its

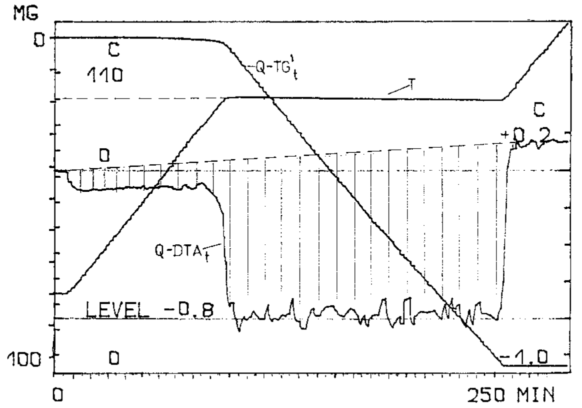

Fig. 6 Examination of boiling water; Recorded by the derivatograph PC, original record

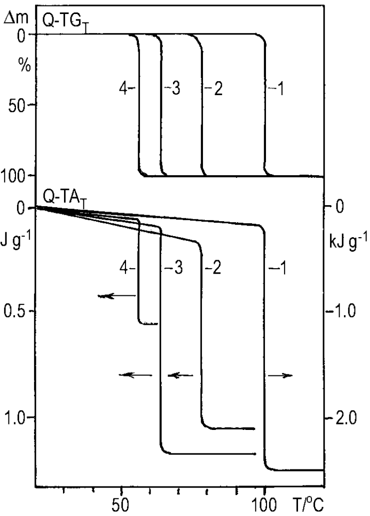

Fig. 7 Q-TA$_T$ and Q-TG$_T$ curves of water (curves 1), ethanol (curves 2), methanol (curves 3), aceton (curves 4)

latent heat can also be proved by the good agreement of the ΔH^{o}_{20} values calculated and taken from literature [7], as is shown in Tables 1 and 2.

Table 1 Latent heat of water–vapour transition

	No.	Measured data/	Literature data [6, 7]/	Difference/	
		J g^{-1}		J g^{-1}	%
$\Delta H_{100°}$	1	2233.5	2257.0	–23.5	–1.0
	2	2264.5		+7.5	+0.3
	3	2260.9		+3.9	+0.2
$\Delta H_{20°}$	1	2482.4	2448.0	+34.4	+1.4
	2	2416.8		–31.2	–1.3
	3	2458.1		+10.1	+0.4

Table 2 Latent heat of solvents. Liquid–vapour transition

Solvent	ΔH	Measured data	Literature data [6]	Difference/	
		J g^{-1}		J g–1	%
Ethanol	$\Delta H_{78.3°}$	864.6	855.0	+9.6	+1.1
	$\Delta H_{20°}$	1050.0	–	–	–
Methanol	$\Delta H_{64.7°}$	1116.6	1099.8	+16.8	+1.5
	$\Delta H_{20°}$	1163.5	1189.8	–26.3	–2.2
Aceton	$\Delta H_{56.1°}$	517.0	521.0	–4.0	–0.8
	$\Delta H_{20°}$	564.1	552.0	+12.1	+2.2

Increase in resolution and selectivity

The following several examples illustrate the high resolution and selectivity of this measuring technique.

From this point of view, it is very instructive to compare the information available from curves in Figs 4. III, 4.IV, 4. V and Fig. 8. As it was shown, it would be very difficult to construct the phase diagram of the $LiNO_3$–KNO_3 system from T, or even from DTA curves taken by the non-isothermal heating method. To the contrary, based on the real break points of the T' curve taken by the Q-DTA study, this does not arise any problems any more, though it is true that the picture on the subsequent transformations is not sufficiently expressive yet. In contrast, curve Q-TA$_T$ visualizing the same information in another form (Fig. 8), not only provides a visual picture

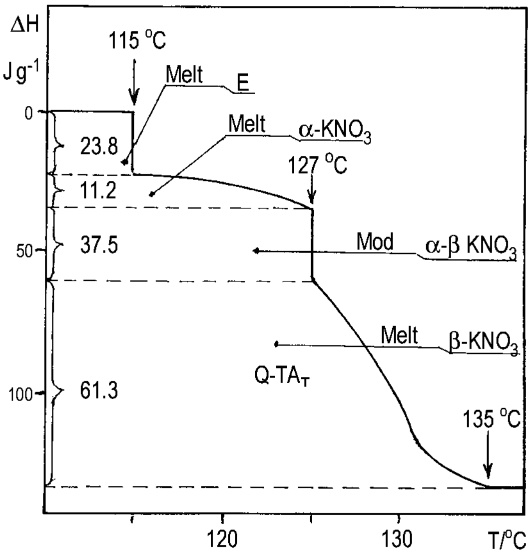

Fig. 8 Q-TA$_T$ curve of LiNO$_3$–KNO$_3$ (51 mol.%) system

about all the details of the process, but also makes possible to determine the enthalpy change caused by the whole and the individual elementary processes.

We have studied the modification change and melting of KNO$_3$ by the conventional DTA method on the one hand, and by the Q-DTA apparatus working under quasi-isothermal conditions, on the other hand. According to the Q-TA$_T$ curve in Fig. 9, the α–β modification change took place isothermally, in a regular way, at 127°C.

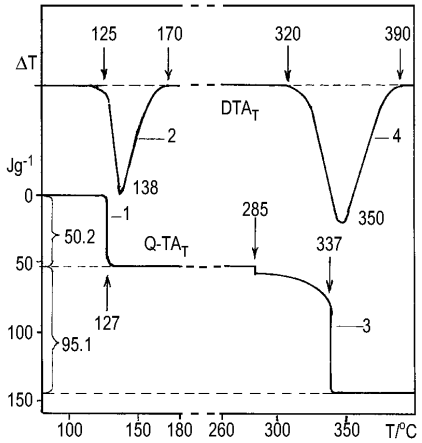

Fig. 9 Q-TA$_T$ and conventional DTA$_T$ curve of α–β modification change (curves 1 and 2) and melting process (curves 3 and 4) of KNO$_3$

Even the first part of the melting curve is surprising. At 285°C, a small, but well-defined break point appeared on the curve 3. Subsequently, at increasing temperature, it took up further heat in an increasing amount. It can be supposed that the ordered crystal structure of β-KNO_3 remaining intact up to 285°C starts to be loosened at this temperature, and this process shows a trend to accelerate by increasing temperature. Reaching the melting point, the sample melted in a strictly isothermal manner. These processes cannot be observed by non-isothermal DTA studies (curve 4) [9–12]. By investigating this sample by other physico-chemical methods, this phenomenon could not be found, either [8]. The measure of enthalpy changes generated by modification change and melting agrees well with literature data [6].

A remarkable, rare phenomenon can be observed in the second section of the curve concerning the dehydration of barium chloride dihydrate, as well. As is shown on curves T' in Fig. 10, Q-TA_T (curves 1,3) in Fig. 11 and Q-TG_T in Fig. 11 (curve 2), the sample lost its first crystal water at 100°C in a regular, i.e. isothermal way. However, the loss of the second water molecule occurred at increasing temperature, i.e. in an irregular way. Two small, beak-shaped formations indicating overheating also appeared on the curves. This indicates that during the second water loss, various, not expected processes take place as well.

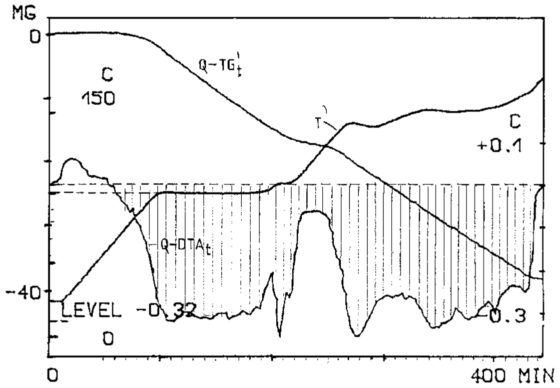

Fig. 10 Dehydration of $BaCl_2 \cdot 2H_2O$; Recorded by the derivatograph PC, original record

It was shown earlier by X-ray investigations that during the loss of the second crystal water molecule, a pseudomorphosis occurs, in other words, crystals keep their external habit, but their structure changes. This phenomenon was studied by thermoanalytical methods only with partial success [13–19], except for Garn [20, 21], who showed that under a pressure of several atmospheres, two, three or even four hardly interpretable peaks appeared, depending on the pressure.

We could reproduce these break points, though under different conditions, and we explained their appearance by other reasons, as well. We assumed that on the DTA curves of Garn, peaks appeared not due to the mere increase of pressure, but owing to the increase in the partial pressure of water vapour.

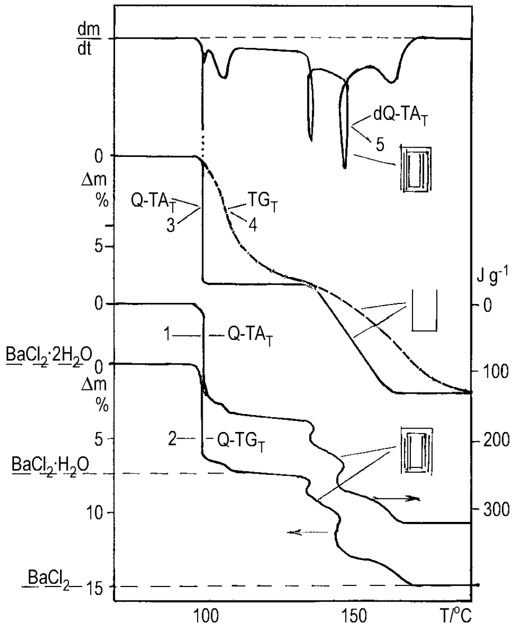

Fig. 11 Dehydration of $BaCl_2 \cdot 2H_2O$; Examined under quasi-isothermal heating, in labyrinth (curves 1, 2 and 5), and in open (curves 3 and 4) crucibles resp. and with non-isothermal heating (curve 4)

The original Q-DTA$_t$, Q-TG$_t$ and T' curves for the dehydration of $BaCl_2 \cdot 2H_2O$ are presented in Fig. 10, whereas those reconstructed are shown in Fig. 11. From above the latter, curves 1, 2 and 5 were taken by using the labyrinth crucible, whereas curves 3 and 4 in an open sample holder. In the labyrinth crucible, i.e. in a pure water vapour atmosphere, the decomposition of monohydrate took place in our experiment also in a step-wise manner, which, considering the high water vapour concentration, made the subsequent formation of several unstable intermediate crystal hydrates probable. This caused the beak-like formations on the Q-TA$_T$ and Q-TG$_T$ curves, and the loop-like ones on the dQ-TA$_T$ curve. The development of pseudomorphous crystal hydrates could take place also at lower water vapour pressures, as for example in our case, when applying an open sample holder (curve 3), but the formation of intermediates could not be finished, and thus their temporary formation and decomposition overlapped totally. This is why the course of curve Q-TA$_T$ became uniform, but not isothermal in open crucible.

DDC and DSC studies under quasi-isothermal conditions

Dynamic differential (DDC) and differential scanning calorimeters (DSC) can easily be redesigned according to the invention [5]. Such a reshaping seems to be necessary. It is namely true that the peaks of DDC and DSC curves have a narrower temperature interval as compared to that on the DTA curves, thus the error in the measurement of transformation temperature decreases, and the resolution and selectivity of the study increases, but as the heating program is not isothermal, the character of curves remains also non-isothermal, together with all the consequences originating from this fact.

It should be noted that according to this invention [5], the calibration of the further developed DSC apparatus becomes more simple and more reliable. As it is known, in the case of certain type of DSC apparatus, calibration is performed not by means of a standard, but, in a well-justified manner, by a known value of watt current transferred to the sample.

References

1 F. Paulik, J. Therm. Anal. Cal., 58 (1999) 711.
2 J. Paulik and F. Paulik, Simultaneous Thermoanalytical Examinations by Means of the Derivatograph, in W. W. Wendlandt (ed.) Vol. XII, of Wilson-Wilson's Comprehensive Analytical Chemistry (ed. G. Svehla) Elsevier, Amsterdam 1981.
3 F. Paulik, Special Trends in Thermal Analysis, Wiley, Chichester 1995.
4 J. Paulik, F. Paulik and M. Arnold, Hung. pat. N^o: 194.405/1985 patents in USA. UK. France, Germany, Switzerland.
5 F. Paulik, E. Bessenyey-Paulik and K. Walther-Paulik, Hung. PCT (HU 98) 00041 patents applied in Europe and USA.
6 D'Ans Lax Taschenbuch für Chemiker und Physiker III. ed. Springer, Berlin 1967.
7 N. A. Lange, Handbook of Chemistry IX. ed. Handbook Publ. Inc. Sandusky, Ohio 1956.
8 Gmelins Handbuch der Anorganischen Chemie, Kalium, Vol. 22, 278, 503. Verlag Chemie, Weinheim.
9 A. Rokosz, J. Paulik, F. Paulik and L. Erdey, Acta Chim. Sci. Hung., 56 (1968) 221.
10 G. Liptay, Atlas of Thermoanalytical Curves. Vol. I-V. Akadémiai K., Budapest 1971.
11 F. Solymosi, Magy. Kém. Foly., 74 (1968) 145.
12 J. Simon, S. Gál and L. Erdey, Acta Chim. Acad. Sci. Hung., 66 (1970) 175.
13 Gmelins Handbuch der Anorganischen Chemie, Barium, Vol. 30. 184, Erg. 339 Verlag Chemie, Weinheim.
14 H. J. Borchardt, J. Chem. Educ., 39 (1956) 103.
15 H. J. Borchardt and F. Daniels, J. Physic. Chem., 61 (1957) 917.
16 J. Paulik, F. Paulik and L. Erdey, Anal. Chim. Acta, 41 (1968) 170.
17 W. W. Wendlandt and E. L. Simons, Thermochim. Acta, 3 (1972) 171.
18 J. Paulik and F. Paulik, Hung. Sci. Instr., 34 (1975) 15.
19 F. Paulik and J. Paulik, J. Thermal Anal., 16 (1979) 339.
20 P. D. Garn, Thermoanalytical Methods of Investigation, Academic Press, New York 1965.
21 P. D. Garn, Anal. Chem., 37 (1965) 77.