A NEW DIFFERENTIAL THERMAL ANALYSIS METHOD

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(Received September 9, 1977)

A new differential thermal analysis method has been developed which allows fast and accurate determinations of phase equilibria in condensed systems between 400 and 1100°. In this method the temperature is increased stepwise, heat effects being determined by analysis of the transient thermoelectric effects after each step. Between steps the temperature is kept constant until equilibrium is attained. The method has been tested in measurements of displacive solid-state transformations and melting points.

In the up-to-date study of phase equilibria, instead of the classical quenching methods which are responsible for the majority of the reliable literature data on this subject, increasing use is being made of dynamic methods such as differential thermal analysis [1].

The success of the quenching method depends upon the preservation of the phase assemblage present at equilibrium upon cooling to room temperature.

The dynamic methods offer two advantages over static methods: since quenching is not involved, it is possible to explore quickly the limits of phase stability, and the danger of a change in phase assemblage during quenching is avoided. However, the greatest difficulty confronting its use is the attainment of equilibrium.

In the case of DTA, in order for a thermal effect to be detected, the temperature must to be varied rapidly, so that a measurable temperature difference arises between the standard and the specimen. This severely restricts the acquiring of subsolidus data, and complicates liquidus investigations where peritectic type reactions occur. To these complications, those associated with supercooling and spurious noise are added.

For the elimination of the disadvantages of both static and dynamic methods, a new differential thermal analysis method has been developed, which allows fast and accurate determinations of phase equilibria in condensed system between 400 and 1100°.

In this method the temperature is increased stepwise, the heat effect being determined by analysis of the transient thermoelectric effects after each step Between steps the temperature is kept constant until equilibrium is attained.

The method worked out, using stepwise increasing of the temperature, has not. been mentioned in the literature so far [2—4].

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Apparatus

The basic instrument used is a Mettler Vacuum Thermoanalyzer. The furnace is specially constructed for fast heat transfer to the sample, reference and controlling thermocouple, and is fed from a special thyristor proportional controller operated by a linear set-point generator.

Furnace

The furnace used is shown in Fig. 1. It consists of a quartz tube 330 mm long with 50 mm outer diameter with an inside heating element supported by hooks made in the tube wall. The heating element is made from 12 m, 1 mm $\oslash$ Kanthal A − 1 wire wound in a double spiral (resistance 18Ω). The quartz tube is surrounded by a cylindrical polished nickel radiation shield.
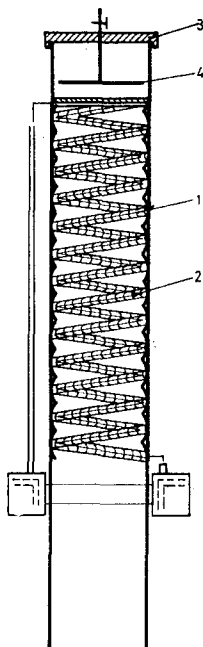

Fig. 1. The furnace: 1. quartz tube; 2. heating element; 3. furnace lid; 4. radiation shield

Sample holder

A modified Mettler sample holder is used. The sample and reference are placed in covered platinum crucibles supported directly by the two junctions of the differential thermocouple. The controlling thermocouple is placed between the crucibles, without a shielding tube.

Controller

The furnace is fed from a Univel TRC − 2 high-performance proportional voltage controller (provided with an adjustable current limit). The output voltage from the controller is a nearly linear function of the voltage difference between the furnace thermocouple and the set-point generator. The slope of this function is adjustable from 0.05 to 1.5 V/μV. The highest possible slope giving no temperature oscillation is used (1.2 V/μV in most cases). The output voltage for zero difference between thermocouple and set-point generator is adjusted to the steady value for the furnace at the relevant temperature.

Set-point generator

A Univel TVP − 2 high-performance linear set-point generator is used, programmed to increase the set-point in steps of 20μV (corresponding to approximately 2°), the time between steps being set manually. The generator is stabilized to 0.0002% for a mains variation of ±15%, and has a resetting tolerance of 0.001% and an accuracy better than 0.025%.

Experimental

The method has been tested in measurements of displacive solid-state transformations and melting points. The work was carried out on both pure compounds and binary and ternary mixtures of salts and oxides. Reagent grade chemicals were used (Table 1).

The mixtures, always amounting to 2 g, weighed out with an accuracy of ±0.0005 g, were finely ground and mixed. The mixed powders were melted and reground three times to attain complete homogenization.

Before measurements, the standard material (Al_2O_3) and the samples were ground to powder of the same particle size and both crucibles were filled by means of a hard packing technique. The mass of samples was ca. 0.5 g.

Table 1

Chemical compounds used in the work

Compound	Source	Purity
Ag_2SO_4	NBS	ICTA standard
SiO_2	NBS	ICTA standard
K_2SO_4	NBS	ICTA standard
K_2CrO_4	NBS	ICTA standard
CsCl	Merck	p.a.
KCl	Analar	analytical reagent
Na_2SO_4	Merck	p.a.
$CaSO_4$	Merck	p.a.

The temperature was increased continuously, at a rate of $10-15°$/minute, up to $15-20°$ below the transformation temperatures, when the stepping program was started. The stepping program allows the increasing of the temperature stepwise, in 2° steps. Between steps the temperature was kept constant until equilibrium was attained.

In all cases the classical DTA curves were also recorded. The measurements were made with a heating rate of 10°/minute and a speed of paper transport of 12 inch/hour.

Results and discussion

Pure compounds

Melting point measurements

For discussion of the results obtained in determinations of melting points by the step method, a typical curve, recorded for Na_2SO_4, is presented in Fig. 2. From analysis of the transient thermoelectric effects following each step, it emerges that in the domain of temperatures up to the melting point the recorded DTA curve deviates from the base line at each step. This is due to the difference between the thermal properties of the sample and the reference material. The return to the
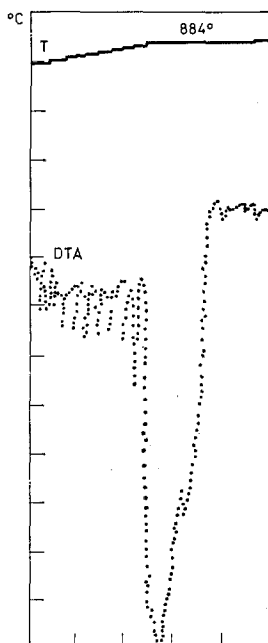

Fig. 2. Step method DTA curve recorded for Na_2SO_4 melting

base line, however, is very fast, the height of deviation for each step is approximately identical and the recorder pen draws a line, not a curve enclosing an area.

At the moment when a new step brings the temperature to the melting point, the recorded deviation is perceptibly higher and the time required to return to the base line is approximately 20 times longer. In this case, the curve described delimits an area with surface proportional to the heat of melting.
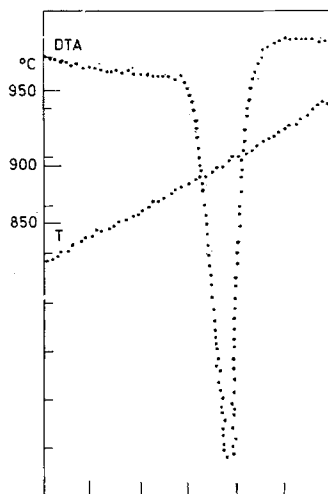

Fig. 3. Classical DTA curve recorded for Na_2SO_4 melting

After melting, the position of the base line is essentially displaced, but the aspect of the recorded curve is similar to that before melting.

All the mentioned changes are achieved within a 2° step. Consequently, in the step method the melting starts and ends at the same temperature, and all the heat of melting is evolved during one single step.

Table 2

Melting temperatures and heats of melting of the compounds employed

Compound	Melting temperature, °C		Heat of melting, mg area/g sample	
	Ref. [5]	Step method	DTA	Step method
CsCl*	641.8	642		
KCl*	770	770		
Na_2SO_4	884	884	216	221
K_2SO_4	1074	1074		

* Strong evaporation

For comparison the classical DTA curve is also shown (Fig. 3). In this latter case there is a 20° temperature interval between the start and the peak of the thermal effect of melting, and the complete melting proceeds within 50°.

All the other analysed samples (Table 2) presented similar behaviour.

The complete melting in one step was proved by comparing the extent of the area delimited by the deviation of the recorded curve during the melting with that obtained by the classical DTA method. The results, presented in Table 2, are in good agreement.

Displacive solid-state transformations

Displacive solid-state transformations have been studied, using the step method, on several ICTA standard materials (Table 1). A characteristic curve, obtained for K_2SO_4 is shown in Fig. 4.
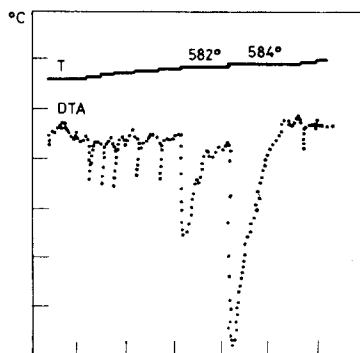

Fig. 4. Step method DTA curve recorded for K_2SO_4 displacive solid-state transformation

Analysis of the transient thermoelectric effects following each step shows the behaviour of the recorded curve to be similar to that of curves recorded for determinations of melting points. In the domain of temperatures below and above the phase transformation, each step entails a small deviation of the recorded curve from the base line. This is explained by the difference between the thermal properties of the sample and the reference material. The return to the base line is very fast, and the heights of the deviations for all steps are approximately equal.

At the moment when a new step brings about the phase transformation, the recorded deviation is perceptibly higher and the time required to return to the base line is essentially longer.

The difference between the curve recorded for the displacive solid-state transformation of K_2SO_4 and the curves obtained in determinations of melting points originates from the fact that in the former case the full transformation could never be achieved in one single step. The complete displacive solid-state transformation of K_2SO_4 occurs in two steps of 2°.

For comparison, Fig. 5 presents the classical DTA curve. In this case the peak width covers an 80° temperature interval.

Table 3 shows the results obtained with the step method in determinations of displacive solid-state transformations of several other ICTA standard materials. In all these cases the full transition proceeds in two steps of 2° (never completely in one). However, the temperature intervals in which the transitions are complete are smaller than those obtained using the classical DTA method.
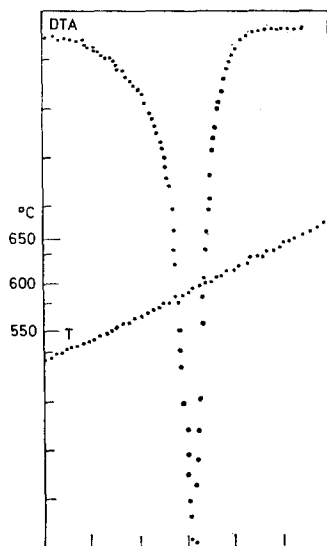

Fig. 5. Classical DTA curve recorded for K_2SO_4 displacive solid-state transformation

Table 3

Phase transformation temperatures and heats of transition of the compounds employed

Compound	Phase transformation temperature, °C				Heat of transition, mg area/g sample	
	T_{onset}	T_{peak}	T_{eq} [6]	Step method	DTA	Step method
Ag_2SO_4	424	433	430	424—426	139.13	134.24
SiO_2	571	573	573	572—574	22.00	23.60
K_2SO_4	582	588	583	582—584	97.25	98.29
K_2CrO_4	665	673	665	666—668	100.00	97.80

The complete phase transformation in two steps of 2° was proved by comparing the areas delimited by the deviations of the recorded curves during the phase transformations with those obtained by the classical DTA method. The results are presented in Table 3, and display good agreement.

In the step method, the difference in the shapes of the DTA curves in the cases of solid-state transitions and melting results from the thermal gradient of the furnace used. In the case of melting, the first quantity of material which melts equalizes the temperature in the crucible (by a capillarity effect) and the melting proceeds in one single step.

Binary and ternary mixtures

In the case of binary and ternary mixtures, the step method has been tested for determinations of solidus and liquidus temperatures.

A characteristic curve, obtained for a ternary salt mixture of composition presented in Table 4, is shown in Fig. 6.
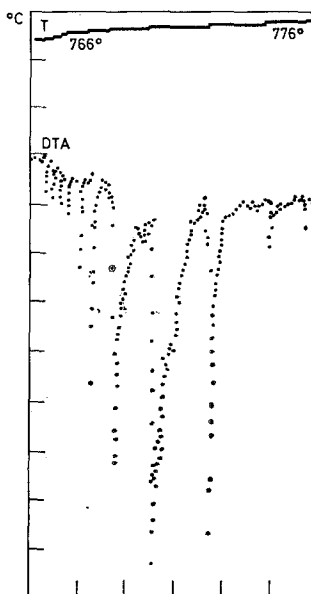

Fig. 6. Step method DTA curve recorded for the melting of ternary salt mixture (50—35)

Within the temperature range where any phase transformation occurs, the shape of the recorded curve is similar to that previously described, a small and short deviation being displayed after each step.

When the solidus temperature is attained in a new step, a quantity of mixture starts to melt, the curve presents a higher deviation and, on its return to the base line, delimits an area. Within the melting interval, each 2° step causes a new quantity of material to melt and determines a new, higher deviation of the recorded curve and a slow return to the base line.

When all the material has melted, the recorded curve again shows a small and short deviation, similarly to those before melting.

Table 4

Solidus and liquidus temperatures in ternary $CaSO_4 - Na_2SO_4 - K_2SO_4$ system

No.	Sample	Composition, %			Solidus temperature, °C			Liquidus temperature, °C			Melting interval	
		$CaSO_4$	Na_2SO_4	K_2SO_4	Ref. [7]	Ref. [8]	Step m.	Ref. [7]	Ref. [8]	Step m.	Ref. [7]	Step m.
1.	40—40	40	25	35	776	—	772	799	827	786	23	15
2.	50—40	40	30	30	776	—	766	782	808	772	6	6
3.	50—35	35	32.5	32.5	783	—	766	804	800	776	21	10
4.	40—35	35	25	40	782	—	787	820	813	800	38	13

Similar curves were obtained in all cases when mixtures of salts were tested. The compositions of some of the analysed mixtures are presented in Table 4. In Fig. 7 the recorded curve for one of them (40—40) is to be seen.

Analysis of the recorded curves reveals that the step method gives the possibility to obtain both the solidus and liquidus temperatures through the same determination. The solidus temperature can be considered the temperature at which the first higher deviation of the curve occurs, and the liquidus temperature the temperature where the last higher deviation is recorded.

The results obtained for the studied mixtures have been compared with the corresponding data from the literature [7, 8]. Generally, the melting interval measured using the step method is smaller than the interval measured with the classical thermoanalytical method, since the step method ensures better conditions of obtaining equilibrium.

The curves obtained for the same samples, but recorded under different conditions (with or without lid, melted before recording, and so on) are very similar,
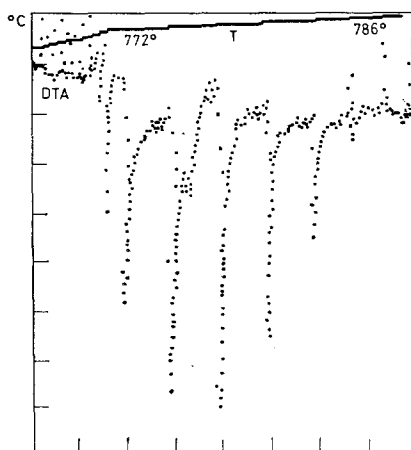

Fig. 7. Step method DTA curve recorded for the melting of ternary salt mixture (40—40)

and the start and the end of melting occur at the same temperature. In this way, the very good reproducibility of the step method is demonstrated.

The lower temperature limit for which the sensitivity of the step method is still satisfactory is about 400°. This temperature limitation is a consequence of the fact that at this temperature and below, the contribution of the radiative thermal transfer to the sample in the total thermal transfer is too small.

Conclusion

A new differential thermal analysis method has been developed. According to this method the temperature is increased step-wise, heat effects being determined by analysis of the transient thermoelectric effects after each step.

The success of the method depends upon the fast heat transfer to the sample, reference and controlling thermocouple, and it needs a very homogeneous temperature in the furnace employed.

The method has been tested, with good results, in measurements of displacive solid-state transformations and melting points in condensed systems between 400 and 1100°.

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RÉSUMÉ — Une nouvelle méthode d'analyse thermique différentielle a été mise au point. Elle permet de déterminer de façon rapide et exacte les équilibres de phases dans des systèmes condensés, entre 400 et 1100°. Selon cette méthode, on augmente graduellement la température en déterminant les effets thermiques par analyse des effets thermoélectriques intermédiaires après chaque palier. A chaque palier, on maintient la température constante jusqu'à ce que l'équilibre soit atteint. On a contrôlé la méthode par l'étude de changements de phases displacifs dans l'état solide et par mesure de points de fusion.

ZUSAMMENFASSUNG — Eine neue Methode der Differentialthermoanalyse wurde entwickelt, welche rasche und genaue Bestimmungen von Phasengleichgewichten in kondensierten Systemen zwischen 400° und 1100° ermöglicht. Bei dieser Methode wird die Temperatur stufenweise erhöht und die Wärmeeffekte durch Analyse der thermoelektischen Übergangseffekte nach jeder Stufe bestimmt. Zwischen den Stufen wird die Temperatur bis zum Erreichen des Gleichgewichts konstant gehalten. Die Methode wurde bei Messungen von Verschiebungsumsetzungen in festem Zustand und von Schmelzpunkten erprobt.

Резюме — Разработан новый метод дифференциального термического анализа, который позволяет проводить быстрые и точные определения фазового равновесия в конденсированных системах между 400° и 1100°. Согласно этому методу температура поднимается ступенчато, а тепловые эффекты определяются с помощью анализа промежуточных термоэлектрических эффектов после каждой ступени. Между стадиями температура поддерживается постоянной для тех пор пока устанавливается равновесие. Метод апробирован при измерении твердотельных превращений и точек плавления.