QUANTITATIVE THERMAL ANALYSIS, II

DESIGN OF EQUIPMENT AND TECHNIQUE OF QUANTITATIVE THERMAL ANALYSIS

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Some problems on adjustment of the equipment and on data evaluation, in view of the equations derived earlier for the calculation of specific heat and heat of transformation are discussed. It is shown that quantitative determinations are possible also if the adjustment is "non-ideal" and that both air and an inert material, respectively, may be used as reference material.

Comprehensive information and detailed recommendations are to be found in the recent literature on how to select optimum experimental conditions and equipment for thermal analysis [1—3]. In this paper we wish merely to specify some points with respect to experimental technique and equipment design, required by the application of the equations derived earlier [4] for the calculation of specific heat and heat of phase transformation.

1. Design of furnace and sample holder

The most important requirement with respect to furnace and sample holder design is maximum stability of conditions of heat transfer from the heating element to the surface of the sample.

In this paper only classical thermal analysis in its customary execution is dealt with, *viz.* the junctions of the differential thermocouple are immersed in the material under investigation and in the reference material, respectively, and both materials are placed in the cells of the sample holder in test tubes or crucibles.

For stability of heat transfer conditions, an arbitrary position of the sample in the cell is inadmissible since this would affect the heat exchange between the sample and the medium [5], and consequently the quantitative parameters of the thermal curves (area, height, shape and duration of the peaks). For the same reason, it cannot be recommended to fill the space between the test tube and the cell wall with a solid material (alumina, metal chips, etc.). It would be practically impossible to avoid variations in the density of packing of the filler material and these variations would affect the thermal conductivity of the fill substantially.

The design of the furnace and sample holder which were used in our work is shown in Fig. 1.

Heat flows from the sample holder *1* to the sample and reference material respectively (*2*) through ring-shaped air gaps with a width of 0.5—2 mm. Aligning sleeves *3* prevent direct contact of the test tubes *2* with the cell wall in that part of the tube which contains the material. Two-channel porcelain tubes *4* align the junctions. Their depth of immersion is controlled by the rings *5*. The depth of immersion of the test tubes in the cells of the sample holder is controlled by the rings *6*, preventing contact of the test tubes with the bottom of the cell.
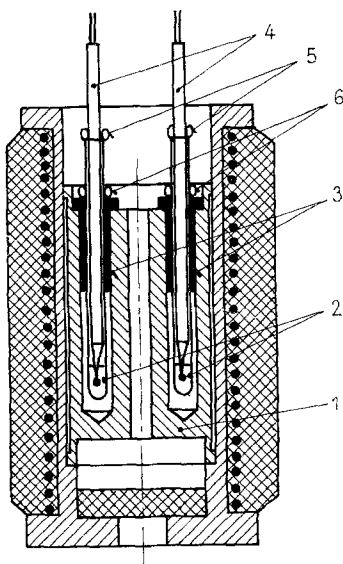

Fig. 1. Design of furnace and sample holder

In the case of equipment operated at relatively low temperatures, the empty space around the test tubes may be filled with a high-boiling liquid. This results in reduced peak heights but thermal effects become sharper so that in many cases effects with slight temperature differences may be distinguished which would be concealed by superposition if normal DTA procedure were applied. A similar effect is obtained by placing the sample directly in the cell. This procedure, however, cannot always be realized, due to the aggressivity of the material being investigated or of its thermal decomposition products.

We wish to emphasize that we are far from considering the outlined design of furnace and sample holder as the best possible solution. This design has been discussed merely by way of example, in the hope that the conclusions based on the analysis of the design in question may prove useful in the analysis of other designs and procedures.

2. Thermocouple

In the U.S.S.R. the use of combined thermocouples [1] is widely accepted and has proved to be fully satisfactory. One disadvantage appearing in some cases is a marked divergence of the differential line from the horizontal (the lower the resistance in the circuit of the simple thermocouple, the higher the angle of deviation). This effect, which is due to the asymmetry of the differential thermocouple, is somewhat inconvenient in quantitative thermal analysis. It can be eliminated by connecting a shunting resistance in parallel with the thermocouple immersed in the reference material. This resistance is approximately equal to the total resistance of the circuit of the thermocouple immersed in the material being investigated. It should be mentioned that "creep" of the differential line is caused in most cases by non-uniform heat transfer to the junctions. This effect can also be eliminated in the same way (i.e. by adjusting the resistances of the circuits). However, primarily one should try to reduce "creep" by a more symmetric arrangement of the test tubes relatively to the heating element.

3. Reference material

In the mathematical treatment of quantitative thermal analysis [4], air was taken as reference material. This assumption was made to eliminate conditions entering the calculation due to the reference material. In addition, an "ideal" course of the thermal curves was assumed for runs without sample and reference material.

In practice, it is possible (though rather difficult in some cases) to obtain such thermal curves. However, the use of air as reference material is certainly not compulsory; any other thermally inert material may be used. The main point is to have a differential curve in which no sample is involved.

Consequently, prior to actual measurements a blank run must be performed to obtain the thermogram "reference material – air".

One of the main advantages in using air as reference material is that the position of the junction in the empty test tube need not be controlled very strictly since slight differences have a negligible effect on the zero line. On the other hand, if a thermally inert material is used, accidental variations of the position of the junction, the weight of the reference material or its thermophysical characteristics cause serious errors in the results.

The use of air as reference material is connected with another disadvantage which, however, may turn out to be an advantage. If air is used, the differential curve is extremely sensitive to all accidental changes of conditions during the measurement. If a reference material other than air is used and this material is well chosen, a much more "beautiful" thermogram will be obtained, at the cost, however, of concealing the experimenter's mistakes and negligence. Thus, for example, with a well-chosen reference material no change occurs in the differential

line (in the absence of thermal effects) when the rate of heating changes, whereas if air is used the deviation between the differential curve and the zero line increases. From a purely formal point of view this may not look nice. However, the change in the curve can easily be distinguished from thermal effects if a temperature curve is registered simultaneously.

4. Adjustment of the equipment

Adjustment is performed during the blank run "air-air" and consists in approximating the differential line as closely as possible to the zero line. In the case of the equipment shown in Fig. 1, a differential line lying higher than the zero line is corrected by slightly lifting the junction in the test tube for the reference material. In itself, as mentioned earlier, the displacement of the junction has little effect on the position of the differential line. However, lifting the porcelain tube is equivalent to reducing the mass of the test tube (i.e. of inert material). This mass reduction affects the course of the differential curve substantially.

If the differential line lies below the zero line, this is corrected by lowering the thermocouple in the test tube for the reference material.

Adjustment could also be performed by changing the height of the junction in the test tube for the sample (in the opposite sense). Such a procedure, however, cannot be recommended. A change of position of the junction in the sample is undesirable for several indirect reasons (visual comparison of the curves is made difficult due to changes in the height and shape of the peaks).

Adjustment can easily be checked by switching the differential thermocouple on and off periodically during the adjustment run. If adjustment is correct, the light beam of the galvanometer and the slide of the potentiometer are not affected.

The deviation of the differential line from the zero line can be reduced within certain limits by varying the resistance in the circuit of the thermocouple immersed in the reference material, i.e. air.

After adjustment, graduation of the temperature curve, the differential curve and the time axis is performed. This is necessary to obtain the quantities involved in the equations in the required units. It is evident that the graduation of the differential curve, as opposed to the temperature curve and the time axis, need not be very exact. Errors in the graduation of the differential curve do not affect the calculation of heat of transformation substantially since the error is present both in the numerator and in the denominator of the equation $\left(\dfrac{S}{dt}\right)$.

5. Succession and number of measurements

The investigation of a material the specific heat of which is unknown includes the following thermograms:

1 — thermogram "air-air" or "reference material-air" (Fig. 2B).

2 — thermogram "air-sample" or "reference material-sample" (Fig. 2A).

3 — thermogram of a mixture of the material being investigated with an unreactive diluent the specific heat of which is known, i.e. "air-mixture" or "reference material-mixture" (Fig. 2C).
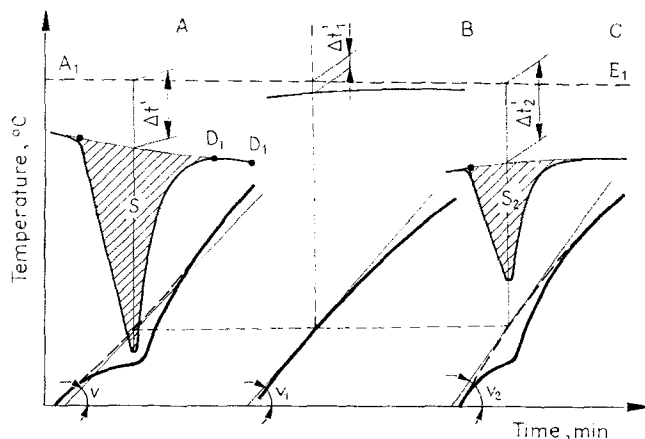

Fig. 2. Experimental data for the calculation of specific heat and heat of transformation

The thermogram "air-air" (or "reference material-air") is needed to establish the differential line in the absence of the sample. If the adjustment was correct, the differential line in the thermogram "air-air" will be identical with the zero line or very near to it. In the thermogram "reference material-air", the differential line will be above the zero line.

During the measurements, no adjustment of the equipment is permitted. Should faults of the previous adjustment be detected, these will be taken into account in the calculations as shown later.

The thermograms "air-sample" and "air-mixture" (Figs 2A and 2C) furnish the data for the equations derived in [4].

In series of routine tests, if the experimenter is certain that the reproducibility of the thermal curve without sample is satisfactory, it is sufficient to perform a blank run ("air-air") from time to time to check stability of adjustment.

In Fig. 2, all experimental data required for calculating the specific heat and the heat of transformation of the material under investigation are presented. It should be noted that the thermal curves in Fig. 2 exhibit all characteristic defects which are frequently encountered in practice, viz. non-linearity of heating, different heating rates in each experiment, incorrect adjustment of the equipment.

In the calculation, the equations for specific heat and heat of transformation remain unchanged but more complex expressions must be used instead of Δt and Δt_2, due to the above-mentioned defects of the curves:

$$\Delta t = \Delta t' \pm \frac{V}{V_1} \Delta t_1' \tag{1}$$

$$\Delta t_2 = \Delta t_2' \pm \frac{V_2}{V_1} \Delta t_1' \tag{2}$$

where $\Delta t_1'$ is the deviation of the differential curve from the zero line $A_1 - E_1$ in the blank run (Fig. 2B). If this curve lies below the zero line, the sign "minus" is used, in the opposite case the sign "plus" is applied.

First, the specific heat of the material under investigation is calculated using the equation

$$C = \frac{S_2 V_2 \, \Delta t}{SV \, \Delta t_2 - S_2 \, V_2 \, \Delta t} \frac{1-n}{n} C_d \tag{3}$$

and then the heat of transformation

$$q = S \frac{V}{\Delta t} C . \tag{4}$$

Table 1

Experimental data for the calculation of specific heat and heat of transformation

Material	NH_4NO_3	KNO_3	NH_4Br	NH_4Cl	Na_2SO_4	$KClO_4$
Diluent (n = 0.5)	Al_2O_3	Al_2O_3	KBr	KCl	Al_2O_3	Al_2O_3
Transition temp. °C	125	128	138	184	240	300
Exptl. data						
S °C/min	4.13	15.66	11.08	14.49	12.22	24.18
V °C/min	5.72	6.02	5.29	5.41	5.01	6.16
Δt °C	0.51	2.06	0.985	1.235	1.225	1.183
S_2 °C/min	2.21	7.76	5.35	7.04	5.65	11.29
V_2 °C/min	5.71	5.79	5.73	5.43	4.86	5.88
Δt_2 °C	0.52	1.712	0.937	0.950	1.068	1.054
Lit. data						
C_d cal/g °C	0.2271	0.2273	0.1089	0.1738	0.2430	0.2516
C cal/g °C	0.2490	0.2850	0.2090	0.3840	0.2750	
q cal/g	12.51	12.88	7.83	19.26	12.8	22.2
Calcd. data						
C cal/g °C	0.2543	0.2790	0.1389	0.3018	0.2600	0.2539
ΔC %	+2.1	—2.2	—33.5[a]	—21.2[a]	—5.8	
q cal/g	11.52	12.68	7.86	19.12	13.0	34.3
Δq %	—9.5	—2.5	+0.4	—0.7	+1.5	+54.5
Mass of sample, g	0.09	0.36	0.40	0.27	0.30	0.35

[a] The substantial difference between the calculated values and the literature values may possibly be due to the inaccuracy of the latter. In the opinion of the editors of the manual [8], the quoted values may be too high.

If the interpolation of the differential curves to the point of maximum deviation of the differential curve should lead to great inaccuracy in the value of Δt, other measuring points, e.g. the range $D_1 - D_2$ may be chosen. However, it should be kept in mind that the measuring point of Δt must lie after the thermal effect and as near as possible to the latter. In the calculation a value of the specific heat of the diluent for the temperature corresponding to the measuring point of Δt must be used.

It goes without saying that a further error is introduced into the calculation by choosing the measuring point of Δt in the described manner since, as it were, coefficient of heat transfer is taken for conditions which do not correspond to the temperature at which the transformation actually proceeds. The value of this error can be estimated e.g. from the data in [6] and [7].

In Table 1, experimental results, calculated data and literature data for specific heat and heat of transformation are listed for various materials. In calculating heat of transformation, not the literature data for specific heat but the values calculated by means of Eq. (3) were used. Literature data for specific heat and heat of transformation were taken mainly from the manual [8].

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RÉSUMÉ — On discuté divers problèmes relatifs à la mise au point de l'appareillage et à l'évaluation des données, dans l'optique des équations déduites précédemment pour le calcul de la chaleur spécifique et de la chaleur de transformation. On montre qu'il est possible de faire des déterminations quantitatives même si la mise au point n'est pas idéale et que l'on peut utiliser comme substances de référence l'air aussi bien qu'un corps inerte.

ZUSAMMENFASSUNG — Gewisse Probleme des Adjustierens der Ausrüstung und der Auswertung der Daten in Hinsicht auf die früher abgeleiteten Gleichungen zur Errechnung der spezifischen und Umwandlungswärmen wurden besprochen. Man bewies, daß quantitative Bestimmungen auch bei "nichtidealem" Adjustieren möglich sind bzw. daß Luft und Inertstoff gleichwie als Referenzstoffe dienen können.

Резюме. — Рассмотрены некоторые вопросы, связанные с настройкой аппаратуры и порядком обработки результатов. Рассмотрение этих вопросов дано с точки зрения практического применения выведенных ранее расчётных уравнений для удельной теплоты фазовых превращений и теплоёмкостей веществ. Показано, в частности, что количественные определения возможны и в случае «неидеальной» настройки аппаратуры, а также с применением эталона или без него.