QUANTITATIVE THERMAL ANALYSIS V.
ROLE OF THE FLOWING GAS PHASE IN THE ANALYSIS
OF DISPERSE MATERIALS

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In the analysis of disperse materials, the thermophysical characteristics (rate, thermal conductivity, thermal capacity) of the gas flowing through the pores of the sample are of great importance in determinations of the heats of phase transformations. We have found that the peak areas corresponding to the phase transformations may either decrease or increase with increasing flow rate of the gas. The largest errors (as high as 15%) caused by gas flow in the pores of the disperse material occur when the thermal conductivities of both the solid material and the gas in which the analysis is performed are low. The experimentally derived relationship between the peak area, the flow rate and thermal conductivity of the gas, and the dispersity and thermal conductivity of the solid phase permits calculation of the possible error, and hence application of measures for its reduction.

Gas flow through a layer of disperse material occurs when the disperse material undergoes thermal dissociation or decomposition and the gas evolved leaves the sample. Gas fow through a layer of disperse material also takes place in thermal analysis in a flowing gas atmosphere, utilized as an independent technique in the study of many chemical reactions.

According to existing concepts [1–4], the gas evolved in the course of the reaction has a substantial effect on the peak area of the DTA curve. The gas flow changes the heat transfer coefficient in the mass of the sample, and consequently changes the areas of the peaks in the differential curve utilized in calculations of phase transformation heats. There is reason to assume [4, 5] that with increasing flow rate of the gas the thermal conductivity of the gas phase will increase, due to the increased heat transfer by convection. The rate of gas evolution in thermal dissociation (and hence the flow rate of the gas in the pores of the disperse material) will depend on the rate of heat transfer to the transformation front, i.e. on the heating rate.

If, with increasing flow rate of the gas, the overall thermal conductivity of the sample also increases, then (for one and the same sample of the investigated substance) the peak area should decrease with increasing heating rate.

The objective of this work was to investigate the effects of the thermophysical characteristics of the lowing gas (rate, thermal conductivity, thermal capacity) on the peak area corresponding to the phase transformation. The substance chosen was sodium sulphate powder, the samples differing in degree of dispersity (particle size: 100 to 500 μm). We chose a substance subject to polymorphic transformation for the reason that in such transformation the essential conditions of heat transfer
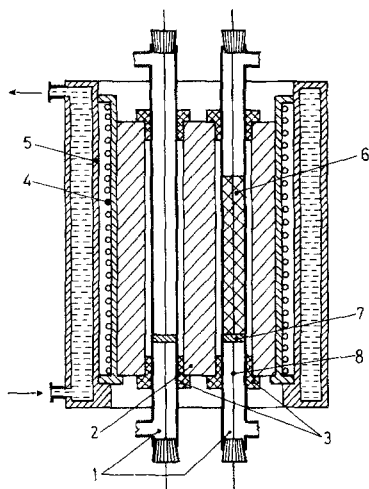

Fig. 1 Apparatus used in the experiments

remain unchanged, similarly to processes with gas evolution [6], with the exception of the gas flow, which in our experiments was generated artificially and controlled within the required limits. Another advantage was that sodium sulphate particles do not adhere to one another in repeated heating-cooling cycles, and hence the peak area decrease caused by the the change of contact thermal conductivity is negligible.

The effect of the rate of gas flow through the sample was studied with the traditional arrangement of thermal analysis, i.e. with the junction of the thermocouple located at the centre of the sample. The experimental apparatus is shown in Fig. 1. The sample holders were quartz tubes *1* (internal diam. 7 mm) located in the metal block *2*. To ensure stable heat exchange conditions, the tubes were centred in the block by means of the sleeves *3*, made of thermally insulating material. To lead off heat from the external side of the heater *4*, water was cycled through the heat exchanger shell *5*. In the central part of the quartz tube containing the sample *6*, a thin porous diaphragm *7* was inserted, on which the substance to be investigated was charged. A thin (0.2 mm) butt-welded chromel-alumel thermocouple *8* extended along the axis of the tube. The height of the sample was ten times its diameter. The cell with the reference material (air) was identical in design.

This cell arrangement provided heat transfer conditions close to those in an infinitely long cylinder [7]. To measure the flow rate of the gas, a previously calibrated liquid differential manometer was used, installed at the outlet of the gas from the quartz tube containing the sample.

The gas used for the experiment was previously heated to the temperature of the phase transformation with a metal tube-and-shell heat exchanger, although some researchers [8] state that the gas passing through the disperse material layer will already attain the temperature of this material at a distance of four times the particle diameter.

Experiments were performed with carbon dioxide, air and helium, in order to cover a thermal conductivity interval as wide as possible. The flow rates of the gases were varied from zero to the rate at which the substance began to be entrained by the gas flow.

For modelling of a process accompanied by gas evolution, the direction of the gas flow was upwards, as in real conditions. On the basis of preliminary considerations regarding the change in thermal conductivity of the sample when gas flows through it (in agreement with the opinion of other authors [4, 5]), it may be noted that with increasing flow rate of the gas, the heat exchange between the individual layers of the sample will increase, and thus the thermal conductivity will increase, which should be reflected in a decrease in peak area for one and the same sample. However, when the gas was introduced from below, the peak areas increased successively with increasing flow rate of the gas through the sample. When the arrangement was changed insofar as the gas was introduced from above, the peak areas in fact decreased with increasing flow rate.

Experimental data relating to the effect of the flow rate w (ml/s) on the peak area S (K·s) are summarized in Table 1 (experimental conditions: sodium sulphate particle size $0.250 < d < 0.300$ mm; gas introduction from above and from below). The flow rate was calculated as the ratio of the volumetric gas consumption to the internal cross-sectional area of the tube. All values for peak areas are means from 9 measurements. Mean errors are indicated at the bottom of the Table.

The results in Table 1 clearly indicate that gas introduction from above or from below acts in different ways on the peak area: introduction from below results in a peak area increase, while introduction from above leads to a peak area decrease, corresponding to increasing thermal conductivity.

In the described experiment, the thermal conductivity of the sample consists not only of the conductive, but also of the convective thermal conductivity of the flowing gas phase, and the latter cannot be neglected as was done in our earlier paper [9].

Table 1 Experimental peak areas corresponding to the polymorphic transformation of sodium sulfate
(particle size $0.25 < d < 0.30$) at different gas flow rates

Gas	$S, K \cdot$ at w, ml/s				
	0	1.8	3.6	5.0	7.5
Gas introduction from above					
CO_2	793.2	771.4	739.2	691.2	652.6
air	784.2	770.6	745.2	708.1	676.3
He	641.2	640.1	629.6	609.4	596.1
Mean error	0.32	0.46	0.54	0.73	1.05
Gas introduction from below					
CO_2	791.9	797.4	815.3	821.4	829.4
air	785.6	787.0	808.9	817.8	823.3
He	641.0	648.7	677.5	686.7	706.5
Mean error	0.37	0.62	0.81	1.33	1.87

The heat transfer by the gas flow can be expressed by the following equation [8]:

$$\lambda_{conv.} = G \cdot C_p \frac{d}{2} \tag{1}$$

where G is the gas consumption by mass, C_p is the specific thermal capacity of the gas, and d is the diameter of the test tube with the sample.

Assuming that the share of heat transferred by the gas flow in the radial direction is proportional to the total amount of heat transferred by the gas flow, Eq. (1) can be written in the following form:

$$\lambda_{conv.} = K_1' \cdot G \cdot C_p \frac{d}{2} = K_1 \cdot w \cdot \varrho \cdot C_p \tag{2}$$

where K_1' and K_1 are coefficients characterizing the share of the heat flow transferred by the gas in the radial direction; w is the flow rate of the gas, and ϱ is the density of the gas.

The effective thermal conductivity of the sample in the radial direction may be written in the form

$$\lambda_{eff} = \lambda + K_1 w \varrho C_p \tag{3}$$

where (from [9])

$$\lambda = \lambda_{cond.} = \frac{j}{J_M} \left(\lambda_M + \frac{j_M - j}{j_M} \lambda_{gas} \right)$$

Equation (3) shows that the gas flow should increase the effective thermal conductivity and hence reduce the peak areas recorded in the DTA curves. However, the experimental data in Table 1 demonstrate that, when the direction of gas flow is upwards (which is the case in real processes), the peak areas increase, and the experimental data accord with the theoretical concept only when the gas is introduced from above.

To explain this phenomenon, we assumed that, in addition to the increase in thermal conductivity of the sample described by Eq. (3), there is also a change in the thermal conductivity of the sample connected with a change in contact between the particles of the solid phase. The contact thermal conductivity of the solid phase is proportional to the contact area between the particles constituting the solid phase. Gas flow in the pores of the disperse material generates pressure in the particle layer by reason of the hydrodynamic pressure of the gas flow. A change in pressure leads to a change in contact area between the particles, and hence to a change in the contact conductivity of the solid phase. The pressure is expressed by the equation (from [8])

$$\Delta P = \frac{G^2 \eta a l}{2 g \varrho F^3} \tag{4}$$

where G is the consumption of gas by mass, η is the viscosity of the gas, a is the surface area of particles in the layer per unit volume, l is the length of the sample, g is gravitational acceleration, ϱ is the density of the gas, and F is the share of free space in the layer. The value expressed between j and j_M for the monolayer, has the form [8]

$$\frac{6j \cdot j_M^2}{(j_M - j)^3}$$

According to the Fourier law, the heat transfer is proportional to the contact surface, and according to Hooke's law, the contact surface is proportional to the pressure between two solid particles. Hence, the change in contact thermal conductivity will be expressed by

$$\lambda_{cont} = K_2 \cdot \frac{3 G^2 \eta j \cdot j_M^2}{g \varrho (j_M - j)^3} = K_2 \frac{w^2 \varrho \eta j \cdot j_M^2 \lambda}{g (j_M - j)^3} \tag{5}$$

and the effective thermal conductivity of the sample may then be expressed in the following manner:

$$\lambda_{eff} = \lambda + K_1 w \varrho C_p \pm K \cdot w^2 \frac{\varrho \eta j \cdot j_M^2 \lambda}{g (j_M - j)^3} \tag{6}$$

The sign in Eq. (6) must be chosen in accordance with the flow direction of the gas. Equation (6) can be simplified for the actual case of the experimental data listed in Table 1:

$$\lambda_{eff} = \lambda + A w \pm B w^2 \tag{7}$$

where $A = K_1 \varrho C_p$ and $B = K_2 \dfrac{\varrho \eta j \cdot j_M^2 \lambda}{g(j_M - j)^3}$. Let us now substitute Eq. (7) into the

expression (from [9]) for the peak area $S = S_M \dfrac{j \lambda_M}{j_M \lambda_{\text{eff}}}$; this will result in

$$S = S_M \frac{j \lambda_M}{j_M(\lambda + Aw \pm Bw^2)} \tag{8}$$

The values S_M, λ_M and λ in Eq. (8) can be determined as described in our earlier paper [8]. For the actual case discussed, utilizing the peak area values when the pores of the disperse material are filled with air and helium, respectively, we find

$$\lambda_M = 104.7 \frac{W}{mK}; \ \lambda = 45.6 \frac{W}{mK}; \ S_M = 803.7 \ K \ s$$

Substituting the experimental peak area values for any two experimental points into Eq. (8), we can find the values of the coefficients A and B:

$$A = 0.23 \cdot 10^{-2}, \quad B = 0.128 \cdot 10^{-2}$$

Thus, Eq. (8) for the case discussed will assume the form

$$S = \frac{S_M j \cdot \lambda_M}{j_M(\lambda + Aw \pm Bw^2)} = \frac{358\,570}{456 + 0.023w \pm 0.0128w^2} \tag{9}$$

The theoretical curves plotted on the basis of Eq. (9) are shown in Fig. 2.Curve *I* represents peak area *vs.* air flow rate for the case when air is introduced from below, and curve II that for air introduction from above. Experimental points denoted by o from the data in Table 1 are also presented in the Figure. Supplementary investigations relating to the relationship of peak area *vs.* gas flow rate at different degrees of dispersity for the polymorphic transformation of sodium sulphate also provided experimental results in satisfactory agreement with theory.

Analysis of the data in Fig. 2 reveals that the peak areas calculated through Eq. (8) agree fairly well with the experimental results. Deviations in curve I at maximum flow rate, above which the gas flow will begin to entrain particles, may be explained by the sample becoming less compact at such high gas flow rates; the gravimetric density of the sample, appearing as a constant in Eq. (6), will then decrease, and hence the peak area will also decrease in Eq. (8). The height of the sample column measured under such conditions was noticeably higher than the height measured under immobile gas phase conditions. The phenomenon begins even at flow rates of the order of 4–6 ml/s. In real processes with heat absorption, such high rates of gas evolution occur very rarely. For instance, the mean rate of gas evolution in the thermal dissociation of calcium carbonate, $CaCO_3 \rightarrow CaO + CO_2 + \Delta H$, at a heating rate of 0.18 deg/s is 0.8 ml/s.

The flow rate of the gas was determined from the gas evolution curve recorded with the automated Berg gas burette system.

In cases when the gas evolution rate is so high that the compactness of the sample begins to decrease and partial entrainment of the solid phase by the gas starts, it is
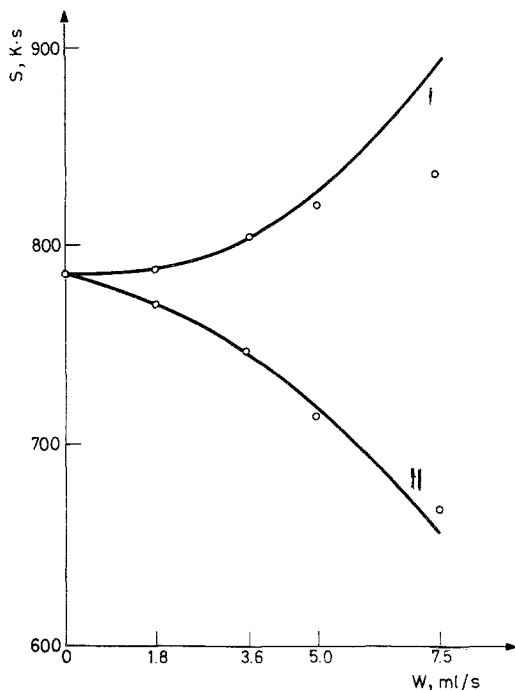

Fig. 2 Peak area *vs.* rate of gas introduction from below and above, resp.
I — introduction from below; II — introduction from above; o — experimental data

recommended that special techniques be applied in the determination of heats of reaction by thermal analysis. For instance, the use of a design in which the gas flow, during gas evolution, exercises a positive pressure on the sample instead of making it less compact. Dilution of the sample with a thermally inert substance will likewise reduce the error in heat of reaction determinations, since it reduces the amount of gas evolved and also heat and mass exchange with the surrounding medium. To correct the results at high rates of gas evolution, further terms would have to be introduced into Eq. (8), taking into account the decrease of density. The difficulty involved is that in real processes the rate of gas evolution is variable, and hence the density of the disperse material in the course of gas evolution varies too.

When the data in Table 1 are considered, it should be noted that a flow of gas having a higher thermal conductivity leads to a lesser increase in the overall thermal

conductivity of the sample than does a flow of gas with a lower thermal conductivity. For instance, a helium flow from above at a rate of 5 ml/s causes a peak area decrease of 5%, while a carbon dioxide flow at the same rate give a decrease of 13%.

The reasons for this difference in the effects of thermal conductivity by convection are the differing properties of the gases, and in particular, differences in density, viscosity and thermal capacity. Changes in contact thermal conductivity are more noticeable for the flow of a gas with a higher thermal conductivity. It was stated earlier [9] that, with increasing thermal conductivity of the solid phase, the effect of the thermal conductivity of the gas phase will be less expressed. In the case of the flowing gas phase, this conclusion is confirmed. In heat of reaction determinations through peak areas of DTA curves, the greatest errors due to the effect of the flowing gas phase will occur when substances with low thermal
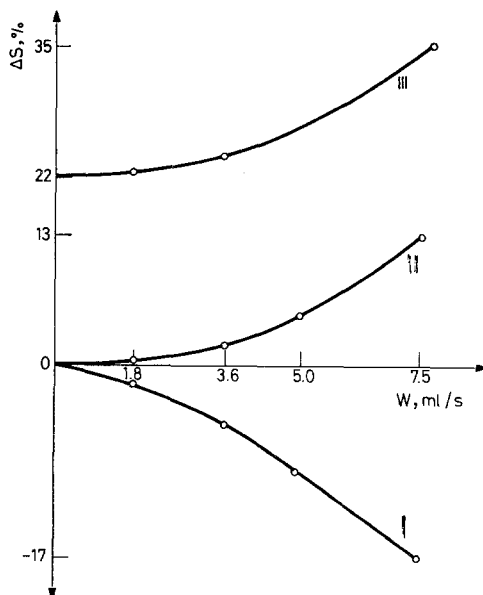

Fig. 3 Possible errors in determinations of heat of reaction by peak area, due to the exchange of the atmosphere from helium to carbon dioxide and to gas flow.
I — introduction from above; II — introduction from below; III — total error at the most unfavourable conditions

conductivities are investigated and the thermal conductivity of the gas evolved in also low.

Via Eq. (8), the error in heat of reaction determinations through peak areas can be quantitatively expressed if the role of gas flow is ignored. If thermal analysis is

carried out in an atmosphere of the gas evolved in the thermal dissociation of the sample, and the flow rate of the gas through the sample is w, the percentage error is expressed by the formula

$$\Delta S = \frac{|S_{\text{flow}} - S_{\text{static}}|}{S_{\text{static}}} \, 100 = \left| \frac{\lambda}{\lambda + Aw \pm Bw^2} - 1 \right| \cdot 100 \qquad (10)$$

where λ is the thermal conductivity of the sample in the event of an immobile gas phase [9].

Figure 3 demonstrates the possible error in heat of reaction determinations via the DTA peak area. Curve I shows the error possible in the results when thermal analysis is performed in a carbon dioxide gas flow introduced from above, and curve II that for a gas flow introduced from below. Curve III illustrates the possible error when thermal analysis is performed in helium and, as a result of dissociation, carbon dioxide gas is evolved at different rates (e.g. thermal dissociation at different heating rates).

Analysis of curves I and II demonstrates that, which increasing gas flow rate, the possible relative error increases, by reason of the thermal conductivity change of the sample due to gas flow. Curve III demonstrates the possible error under the most unfavourable conditions: the thermal conductivity of the sample changing due to the gas change in its pores from helium to carbon dioxide, and also decreasing by reason of the flow of a low-conductivity gas.

The rate of gas evolution in real endothermic processes at relatively low heating rates does not usually exceed 3–4 ml/s. In this case, the possible error is small. However, as shown by curve III, the overall error, due to the exchange of helium by carbon dioxide (a case frequently occurring in practice) and to the carbon dioxide flow, may reach values as high as 35%.

Conclusions

1. According to theoretical concepts, the thermal conductivity of a gas increases with its flow rate, and hence the overall thermal conductivity of a disperse material should increase, resulting in a decrease of peak area. However, the experimental data have demonstrated that, with increasing flow rate of the gas through the sample, peak areas may either increase or decrease.

2. The assumption was made that, besides the increase of thermal conductivity due to the gas flow, another phenomenon will also bring about a change in the thermal conductivity of the sample; this is the change in the contact between the particles of the solid phase, due to the gas flow. When gas is introduced from above, both effects will act in the direction of increasing overall thermal conductivity and

hence decreasing peak area. However, when the gas is introduced from below, it will loosen the contact between the particles and thereby decrease the overall thermal conductivity. This occurs to a greater extent than its increase due to the gas flow, so that the the peak area will increase.

3. Processing of the experimental data led to the mathematical relationship for the peak area *vs.* the flow rate and thermal conductivity of the gas and the thermal conductivity and dispersity of the solid phase. With increasing dispersity, the gas flow will act to a greater extent on the peak area. A reduced thermal conductivity of the solid and gas phases will act in a similar manner.

4. The largest errors due to the gas flow will occur when both the solid and the gas have low thermal conductivities; for most real endothermic processes, the error will not exceed 15%.

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Zusammenfassung — Bei der Analyse disperser Materialien sind die thermophysikalischen Kenndaten (Geschwindigkeit, Wärmeleitfähigkeit, Wärmekapazität) des durch die Poren der Probe strömenden Gases für die Bestimmung der Phasenübergangswärmen von großer Wichtigkeit. Wir haben festgestellt, daß die den Phasenübergängen zuzuschreibenden Peakflächen mit steigender Strömungsgeschwindigkeit des Gases entweder kleiner oder größer werden. Die größten durch die Gasströmung in den Poren verursachten Fehler (bis zu 15%) treten dann auf, wenn sowohl die Wärmeleitfähigkeit des Festkörpers als auch die des Gases, in dem die Analyse ausgeführt wird, niedrig sind. Die experimentell abgeleitete Beziehung zwischen der Bergfläche, der Strömungsgeschwindigkeit und Wärmeleitfähigkeit des Gases und der Dispersität und Wärmeleitfähigkeit der festen Phase erlaubt die Berechnung des möglichen Fehlers und damit das Ergreifen von Maßnahmen zu dessen Verringerung.

Резюме — При анализе дисперсных материалов для определения теплот фазовых превращений большое значение имеют теплофизические характеристики (скорость, теплопроводность, теплоемкость) газа, движущегося сквозь поры образца.

Согласпо проведенным исследованиям площади пиков, соответствующие фазовым превращениям, с увеличением скорости движения газа через образец могут как уменьшаться, так и увеличиваться. Наиболее существенные ошибки, вызванные движением газа через поры дисперсного материала и достигающие 15%, могут произойти в тех случаях, когда твердое вещество и газ, в атмосфере которого производится анализ, обладают плохой теплопроводностью.

Выведенная на основе экспериментальных данных зависимость площади пика от скорости движения и теплопроводности газа, а также от дисперсности и теплопроводности твердой фазы позволила рассчитать возможную ошибку и на этой основе принять меры к ее уменьшению.