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 flow 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 flowing 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 \( \mu \)m). We chose a substance subject to polymorphic transformation for the reason that in such transformation the essential conditions of heat transfer 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 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.