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Note

Effect of the sample thermal conductivity on the calibration constant in differential thermal analysis

VLADIMÍR ŠATAVA AND OTAKAR VEPŘEK

Joint Laboratory for Silicate Chemistry of the Czechoslovak Academy of Science and the University of Chemical Technology, Suchbatarova 5, 16200 Prague 6 (Czechoslovakia)

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It has been shown by a number of workers$^{1-3}$ that the area of a DTA peak which is defined by the integral

$$A = \int \Delta T dt \text{ [deg.sec]} \tag{1}$$

is directly proportional to the heat of process in study

$$A = \frac{Q}{K} = \frac{q \cdot w}{K} \tag{2}$$

Apparatus·constant K is for a given temperature constant, w is the mass of the reactive component in the sample and q is the heat of reaction per gram of reactant.

The calibration constant depends not only on the geometrical arrangement of the sample and the reference, but also on their thermal properties^{4}.

The classical method for the calibration of a DTA apparatus requires several runs using substances with known heats of transition$^{5-7}$, measurement of peak areas A and consequent calculation of K. Another more accurate method is based on an electrical generation of heat in the sample^{8,9}. All these methods, however, assume that K is a mere function of temperature, but the thermal conductivity of the sample depends also on the nature of the sample. Thermal conductivities of metals are two orders greater than those of ionic crystals. One order difference in the thermal conductivity can be found for a powder and continuous solid materials. The aim of our contribution is to show that this effect is serious enough and cannot be simply neglected.

EXPERIMENTAL

Materials

For our study the phase transition of iron sulphide (FeS) was choosen. Samples having the value of thermal conductivity in a wide region were prepared by using:

(a) compact FeS; (b) powder bed of FeS with different distributions of particle size; (c) mixtures of powdered FeS with SiO_2 (aerosil); (d) powder bed of FeS, the pores of which filled with liquids of different coefficient of the thermal conductivity (in this case the hydrothermal modification of differential thermal analysis was employed).[10]

To reach a high thermal conductivity the melting of indium was used as it proceeds nearly at the same temperature as the transition of FeS.

Measuring devices

Three types of specimen holders were used (see Fig. 1).

The constant heating rate of 10°C min^{-1} was controlled by the commercial Netzsch (G.E.R.) temperature programme controller. For the ΔT vs. t recording (where ΔT is the temperature difference between the sample and the reference and t is time) a high quality potentiometric recorder was used.

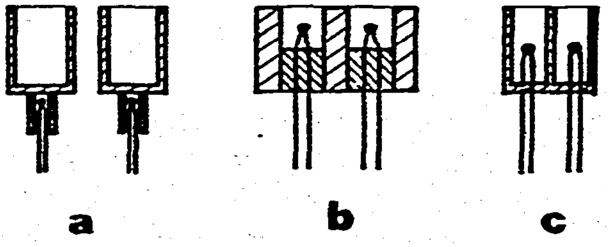

Fig. 1. The sample holders for DTA. (a) = DDK; (b) = Ni-block; (c) = chambers divided by a wall.

The reference material was either powdered α-Al_2O_3 for the investigation of FeS-transition or pure Sn in the case of melting of indium. The baseline of all recorded curves was a horizontal straight line so that the values of peak areas (deg.sec) were determined without any difficulties.

Thermochemical properties of both materials used were taken from Table 1[11].

TABLE 1

	ΔH ($J\ mol^{-1}$)	T (K)	c_0 ($J\ mol^{-1}\ K^{-1}$)
FeS	2.38	411.1	$21.70 + 110.5 \cdot 10^{-3}\ T$
In	3.26	429.3	$21.50 - 17.55 \cdot 10^{-3}\ T$

For the determination of the heat transfer coefficient the method described by Baumgartner[12] and Bohon[13] was applied. It assumes that at the moment when the top of the DTA peak is reached the studied process is finished. The decay of the curve to the baseline can then be described by Newton's cooling law

$$\frac{dT}{dt} = -\frac{\mathscr{H}}{wc_p}\Delta T \tag{3}$$

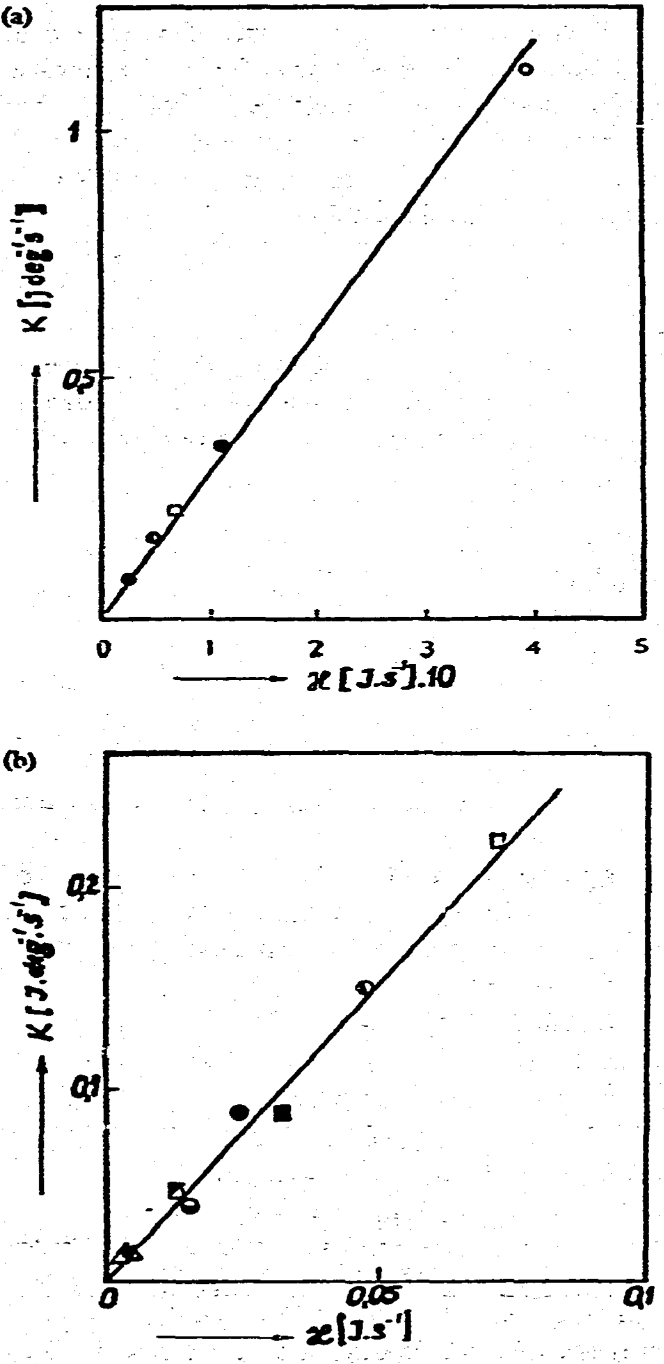

Fig. 2. (a) Plot of the calibration constant $K=\Delta H/A$ vs. apparent heat transfer coefficient $\varkappa$. (b) The range of small values of $\varkappa$.

Type of sample holder (see Fig. 1a): Δ, melting of indium; ▲, transition of FeS in a powder bed; ▲, transition of FeS in the mixture with aerosil.

Type of sample holder (see Fig. 1b): □, melting of indium; ■, transition of FeS in a powder bed; ◩, transition of FeS in the mixture with aerosil.

Type of sample holder (see Fig. 1c): ○, melting of indium; ●, transition of FeS in a powder bed; ⊖, transition of FeS in the mixture with aerosil; ◐, transition of FeS in a powder bed saturated with toluol; ◑, transition of FeS in a powder bed sturated with water.

where ΔT is the difference between the temperatures of the sample and the reference, $\mathcal{H}$ is the coefficient of heat transfer, w is the mass of the sample and c_p is the specific heat.

Integrating eqn (3) we obtain

$$\log \Delta T = -\frac{\mathcal{H}}{wc_p} \cdot t + \alpha$$

where α is an integration constant. Hence the plot of log ΔT vs. time yields a straight line, the slope of which equals $-\mathcal{H}/wc_p$.

The value of $\mathcal{H}$ calculated from this slope is directly proportional to the value of calibration constant as determined through the peak area measurement. This is because both values are proportional to the thermal conductivity of the sample.

RESULTS AND DISCUSSION

The plot of K vs. $\mathcal{H}$ given on Fig. 2 illustrates our experimental measurements on three types of the sample holders shown in Fig. 1. It can be seen that only for the DDK system the calibration constant is practically independent of the thermal conductivity of the sample. Using the other system of experimental arrangement (Figs. 1b and c), the value of K is variable and must be determined for each type of material by a new calibration procedure.

On the other hand we can observe that the DTA peak itself gives sufficient information for the determination of K if the heat capacity of the sample is known. The decay period of the DTA peak provides the value of $\mathcal{H}$ and from the plot K vs. $\mathcal{H}$ the corresponding value of K can then be established. Therefore, a single DTA run is sufficient to carry out a quantitative measurement.

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