DETERMINATION OF THE CALIBRATION CONSTANT gK_s IN THE QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS OF POWDERED MATERIALS

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(Received 5 February 1979)

ABSTRACT

In this article, results are presented for the determination of the calibration constant gK_s for the DTA of powdered materials related to the mass and particle size of the samples studied.

It was established that gK_s represents a linear function of the coefficient of thermal conductivity of the samples studied. The determined value of gK_s is not valid for all experiments in quantitative studies of a particular system, but should be corrected depending on changes in the coefficient of thermal conductivity of the sample studied. These dependences are also valid for the DTA of metal systems, i.e. for cases in which the sample is in monolithic form.

INTRODUCTION

Quantitative determination of thermal effects by means of differential thermal analysis (DTA) using ordinary apparatus, is based upon a well-known relation between the area of the DTA peak and the quantity of heat which is liberated or absorbed by the substance studied [1—7]

$$m\Delta H_T^0 = gK_s \int \Delta T \, dt \qquad (1)$$

where m, ΔH_T^0, g, K_s and $\int \Delta T \, dt = S$ represent, respectively, sample mass, specific heat of reaction, constant of geometric shape, thermal conductivity of the sample and area of the DTA peak.

The constant gK_s is often termed the calibration constant, proportionality factor or equipment constant, and in some cases it is denoted by K [7,8].

Because the value of gK_s is related to a very large number of parameters, from the practical point of view, at least for the time being, it is not possible to give a complete mathematical interpretation [3,8].

The classical method for the determination of the calibration constant gK_s for quantitative DTA consists of calculating the constant from the heat change and the area of the DTA peak obtained [2,5,9].

Šatava and Veprek [7] have established that gK_s is a linear function of the thermal conductivity of the sample studied for different physical states of the same sample, which is of interest for DTA systems in the powdered state.

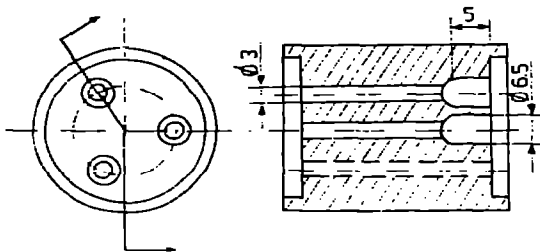The author presents in this article the results of his study on the deter-

Fig. 1. Ni block with dimensions of reaction space.

mination of the constant gK_s for powdered materials with relation to the mass and particle size of the sample studied. This has not been covered very fully in current literature.

EXPERIMENTAL

For experimental studies, the natural minerals magnesite and calcite were ground in an agate mill and separated into particular ranges of particle size through a series of laboratory screens. Samples of particles with average diameters from 18 to 275 μm were studied for both minerals. The purity of the magnesite and calcite samples was 99.5%.

As a reference material, calcined alumina with the same particle size as the sample under study was used. All studies were carried out at a heating rate of 10° min^{-1} in an atmosphere of air using DTA equipment provided with a Ni-block with space for both the studies and reference materials, as shown in Fig. 1.

RESULTS AND DISCUSSION

By solving the basic equation for quantitative DTA eqn. (1), in gK_s we obtain

$$gK_s = \frac{m\Delta H_T^0}{\int \Delta T\, dt} \tag{2}$$

If we represent graphically the relation $m\Delta H_T^0$ as a function of the area of the DTA peaks obtained for different masses of the sample studied, we obtain a straight line from whose slope it is possible to determine gK_s.

The calibration constant gK_s consists of two terms [4,5], i.e. the constant g which represents the geometrical constant, and the constant K_s which characterises the thermal conductivity of the sample. This shows that the calibration constant should be denoted by gK_s and not by K alone, as is often the case in the literature [7,8,10].

Figure 2 shows the relationship $m\Delta H_T^0 = f(S)$ for different masses of the sample for $MgCO_3$, $CaCO_3$ and $CdCO_3$, the average particle diameters of the samples studied being 20, 18 and 8 μm, respectively. Values of ΔH_T^0 were cal-

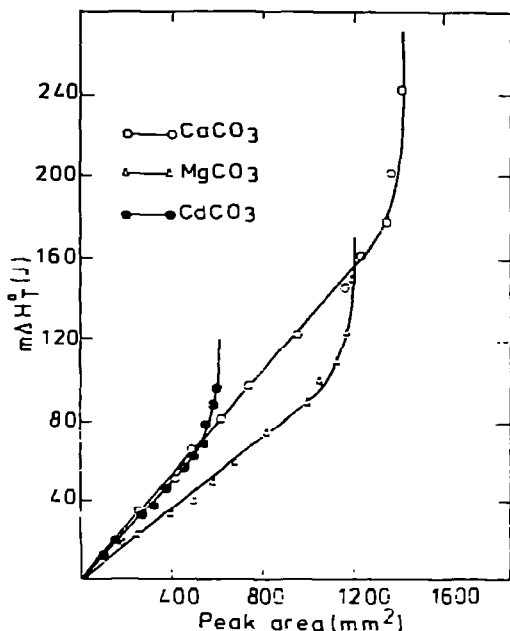Fig. 2. Relationship $m\Delta H_T^0$ with the area of the DTA peak for MgCO$_3$, CaCO$_3$ and CdCO$_3$. (Average particle diameter: MgCO$_3$, 20 μm; CaCO$_3$, 18 μm; CdCO$_3$, 8 μm).
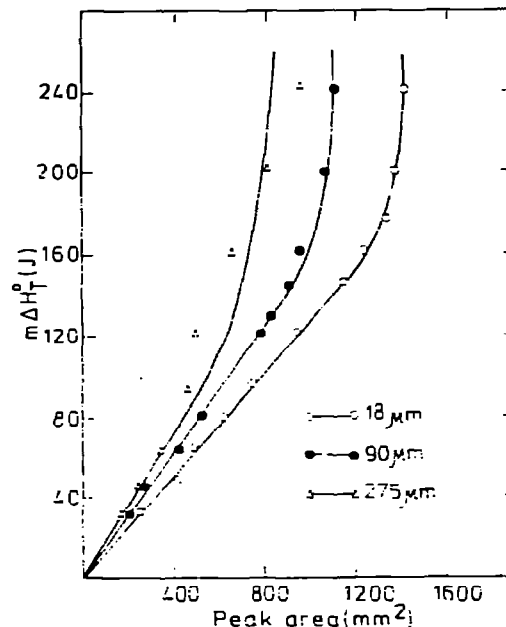
Fig. 3. Relationship of $m\Delta H_T^0$ with the area of the DTA peak for different particle sizes of MgCO$_3$.

culated be͟ ͟d on thermodynamic data for the dissociation reactions of CaCO$_3$, MgCO$_3$ and CdCO$_3$ at temperatures given by the maxima on the DTA curve.

From Fig. 2, it is obvious that after the peak reaches a certain area, the linear relationship $m\Delta H_T^0 = f(S)$ breaks down. This limit is also the limit of validity of the calculated constant gK_s for a given sample and equipment.

The relationships obtained for $m\Delta H_T^0 = f(S)$, shown in Fig. 2, for CaCO$_3$, MgCO$_3$ and CdCO$_3$ show that the linear parts do not coincide, which indicates that for such systems the values for gK_s must be separately determined. Dobovišek [11] states that, for small sample masses, which provide thermal transformations up to 40 J, these relationships do coincide, i.e that for all minerals the same value of gK_s is valid, which would possibly be true for the results shown in Fig. 2. However, carrying out DTA with such small samples increases the probability of errors, because it is more difficult to determine experimental conditions. Consequently, samples of similar size to those used to give the results shown in Fig. 2 are usually used.

By the statistical method of least squares, the most probable slopes of the straight lines were determined up to the limit of validity of the linear relationship, shown in Fig. 2, and the values for gK_s obtained were CaCO$_3$ 0.12656 J mm^{-2}, CdCO$_3$ 0.12210 J mm^{-2} and MgCO$_3$ 0.08219 J mm^{-2}.

Bearing in mind that thermal conductivity changes with change in sample particle size, one must expect this factor to influence gK_s. Figures 3 and 4 show $m\Delta H_T^0$ as a function of the area of the DTA peak for different particle
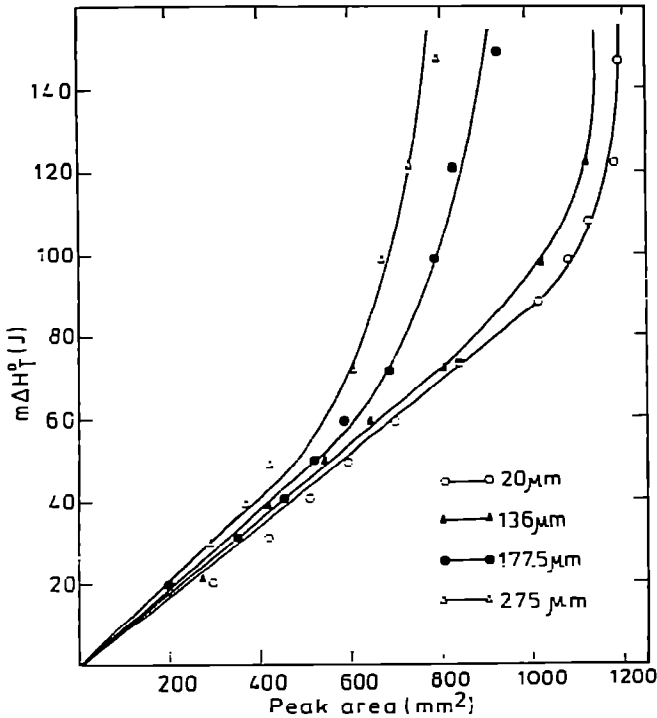
Fig. 4. Relationship of $m\Delta H_T^0$ with the area of the DTA peak for different particle sizes of $CaCO_3$.

sizes of $MgCO_3$ and $CaCO_3$, respectively.

It is obvious that, in both cases, the slope of the linear part of the relationship $m\Delta H_T^0 = f(S)$ changes, as does the limit for maintaining this linear relationship, with change in particle size of the sample studied. Values obtained for gK_s for these two cases are shown in Table 1.

The results obtained show that, in both cases, gK_s increases with the increase in the average particle diameter of the sample. At the same time, it is observed that with the increase in sample particle size, the limit of validity of the linear relationship $m\Delta H_T^0 = f(S)$ is shifted towards smaller areas, i.e.

TABLE 1

Calculated values of gK_s for $MgCO_3$ and $CaCO_3$ of different particle size

Average particle diameter (μm)	gK_s (J mm^{-2})	
	$MgCO_3$	$CaCO_3$
18		0.12656
20	0.08219	
90		0.15689
136	0.08823	
177.5	0.09482	
275	0.10300	0.18120

towards smaller masses of the sample studied. This is considered in greater detail elsewhere.

Because, for DTA powder materials, the porosity of this bulk layer, P, also increases with the change in sample particle size, the coefficient of thermal conductivity, λ, of these samples in the dispersed state would also be changed. This influences K_s and consequently gK_s. The relationship between the porosity of samples of $MgCO_3$, $CaCO_3$ and the reference sample, α-Al_2O_3, used in the bulk layer without compression, and the average particle diameter is shown in Fig. 5.

It may be seen that for $CaCO_3$, with the increase in average particle diameter, porosity decreases up to 90 μm and then maintains a constant value. The same trend is shown by two other samples, but the limit for the case of $MgCO_3$ is about 220 μm and for the case of α-Al_2O_3 about 80 μm.

There exist numerous methods for the calculation of the coefficient of thermal conductivity of the dispersed system, depending on the thermal conductivity of the monolithic material and on the powder density. According to Berg et al. [12], Krisher's equation gives the most acceptable results for the calculation of the coefficient of thermal conductivity of the dispersed system. Krisher's relation is based on the rule of additivity

$$\lambda = \lambda_m \frac{100 - P}{100} + \lambda_g \frac{P}{100} \tag{3}$$

where λ_m is the coefficient of thermal conductivity of the monolithic material, λ_g is the coefficient of thermal conductivity for the gas in the intermediate area and P is the porosity of the layer.

In the calculation of λ, the coefficient λ_m for $MgCO_3$ was calculated at a temperature of 873 K and for $CaCO_3$ at a temperature of 1073 K. The gas in
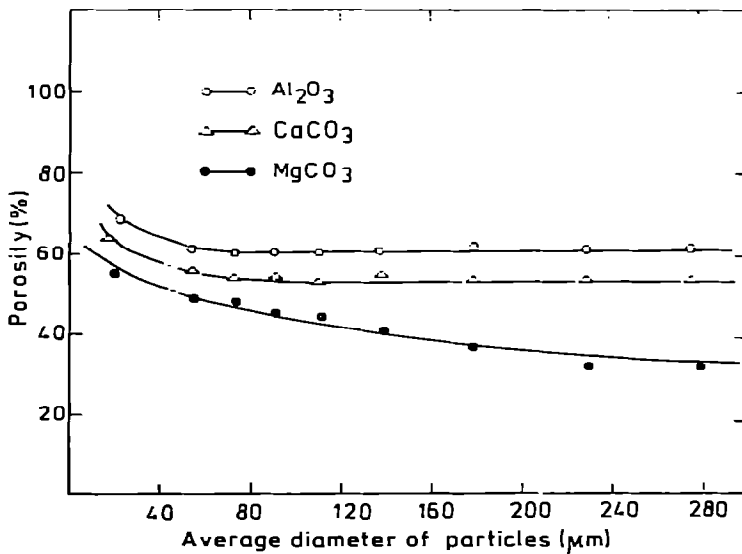

Fig. 5. Relationship of the porosity of samples of $MgCO_3$, $CaCO_3$ and α-Al_2O_3 with average particle diameter.

the intermediate space was CO_2 in both cases. This is liberated during dissociation and its coefficient, λ_g, was also determined.

Coefficients of thermal conductivity were calculated for different sample particle sizes of $MgCO_3$ and $CaCO_3$, and the relationship of gK_s to the coefficient of thermal conductivity of the sample is given in Fig. 6.

From the relationships shown, it is obvious that gK_s increases linearly with increase in the coefficient of thermal conductivity of the sample. Because gK_s was always determined from the linear part of the slope of $m\Delta H_T^0 = f(S)$, it may be taken that the geometric parameter, g, was maintained at a constant value and that the resultant increase in gK_s with the increase in the coefficient of thermal conductivity of the sample was due to a change in the constant K_s.

By using the results of Rosina [13] and Peev [14] for gK_s in their study of melting in pure metals and their alloys, coefficients of thermal conductivity for monolithic materials were calculated at certain reaction temperatures and Fig. 7 shows the corresponding relationship $gK_s = f(\lambda)$.

The relationships obtained show, in both cases, a linear relationship between gK_s and the coefficient of thermal conductivity of the sample studied.

Šatava and Veprek [7] have also obtained a linear relationship $gK_s = f(\lambda)$ for the DTA of FeS and the melting of indium using the same apparatus for the differing physical states of samples studied, this having caused the change in the coefficient of thermal conductivity of the sample.

In the results shown in Fig. 7, straight lines 1 and 2 do not coincide because the results presented were obtained on different equipment, with
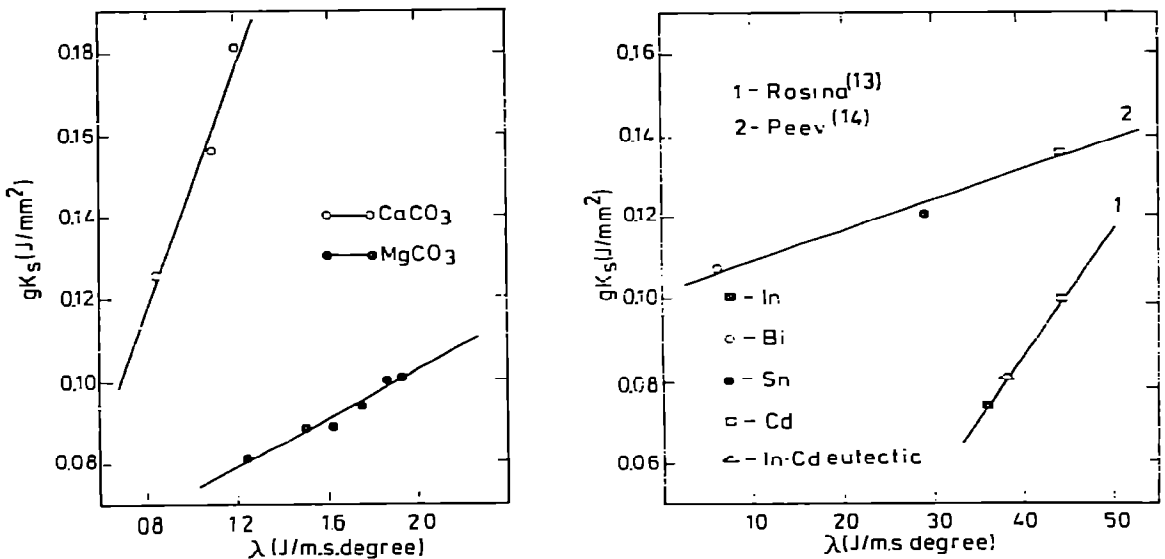

Fig. 6. Relationship of gK_s with the coefficient of thermal conductivity of the sample for $CaCO_3$ and $MgCO_3$.

Fig. 7. Relationship of gK_s with the coefficient of thermal conductivity of the sample for metal systems.

different conditions for the thermal conductivity and measurement of slopes.

Although studies of the DTA of $MgCO_3$ and $CaCO_3$ were carried out on the same equipment, it may be seen that the results do not coincide (see Fig. 6), which is not the case with the results of Rosina and Peev (Fig. 7) and the studies of Šatava and Veprek [7]. In these studies, the results of the different systems studied by DTA give peaks at approximately the same temperatures, which means that the conditions of thermal conductivity from a block at the top of the thermocouple were approximately the same. However, in the DTA of $MgCO_3$, the peak appears at a temperature of 873 K, and for $CaCO_3$ at a temperature of about 1100 K. The more pronounced increase of gK_s as a function of λ for the case of $CaCO_3$ is the result of changed conditions in the thermal conductivity compared with $MgCO_3$. In the case of $CaCO_3$, because of the much higher temperature at which the reaction proceeds, heat transfer in the system is mostly by emission, which is not the case for $MgCO_3$ because of the much lower reaction temperature. This shows that the calculated coefficient of thermal conductivity, λ, in the case of $CaCO_3$ does not represent a realistic value, taking into account that it is calculated in the same way as for $MgCO_3$, but is much higher.

The much faster increase in gK_s against the increase in the coefficient of thermal conductivity obtained for $CaCO_3$ as compared with $MgCO_3$ agrees with the theoretical suggestion of Smaić [15] about the relationship of gK_s with temperature ($gK_s \approx gh + 4T^3 q_{em} \sigma$).

According to this, for a sample in the powdered state whose geometry remains unchanged, gK_s increases linearly with the increase in the coefficient of thermal conductivity caused by the increase in particle size of the sample. The same increase in gK_s for two different samples is only possible when the transformations are carried out at approximately the same temperature. If, for different samples, transformations are carried out at different temperatures, it is necessary, in the determination of the coefficient of thermal conductivity, to take into account all parameters referring to heat transfer at those temperatures.

These results show that, in the DTA of powdered materials, particular attention must be paid to the determination of gK_s. Apart from temperatures at which transformations are carried out, which must be approximately the same for the sample studied and the sample which is used for the determination of gK_s, attention must also be paid to the coefficients of thermal conductivity, which must also be as close together as possible. In the DTA materials in the powdered state, there is a possibility of adjusting the coefficient of thermal conductivity of the sample by choosing a favourable particle size. This means that, by choosing the particle size of the sample studied, it is possible to adjust the value of its coefficient of thermal conductivity so that it may be approximately equal to the coefficient of thermal conductivity of the sample which is used to determine gK_s for the given equipment.

However, it must be pointed out that the geometric factor, g, should be maintained at a constant value all the time. Figure 8 shows the relationship of gK_s with the sample mass for several different samples with the same particle size, which means that the coefficient of thermal conductivity is the
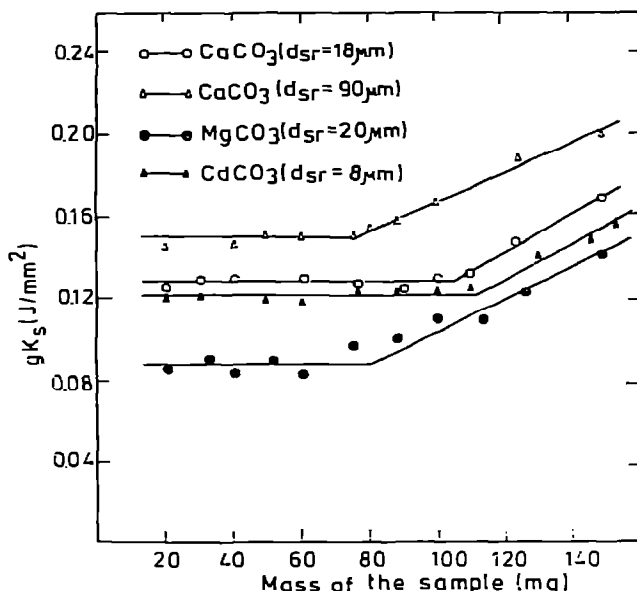
Fig. 8. Relationship of gK_s with sample mass.

same, i.e. K_s in the constant gK_s.

From the relationship given, it is obvious that, with the increase in sample mass up to a certain limit, gK_s has a constant value (geometric factor is constant) and with further increase in the sample mass, gK_s increases because of the change in the sample geometry, so that the resulting increase in gK_s is the result of the increase in the geometric constant, g.

Results shown in Fig. 8 also show that the limit of the constant value for gK_s, with the increase in the sample mass, differs for different particle sizes of the same sample and that these limits coincide with the limits of the linear relationship $m\Delta H_T^0 = f(S)$ shown in Figs. 2—4.

According to this, in the quantitative DTA of powdered materials, apart from given facts referring to temperatures at which transformation are carried out, coefficients of thermal conductivity which must be taken into account in the determination of the constant gK_s and the use of this constant for quantitative determinations, one should also taken into the account the maximum sample mass below which the geometric factor would not have any influence on gK_s.

Results obtained show that the calibration constant gK_s is a linear function of the coefficients of thermal conductivity of the sample. This shows that, in quantitative determinations in a system, it is not possible to use a single value for gK_s, but . `is value must be corrected for each experiment, depending on changes in the coefficient of thermal conductivity of the sample studied.

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