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QUANTITATIVE THERMAL ANALYSIS. PART IV. ROLE OF THE STATIONARY GASEOUS MEDIUM IN THE ANALYSIS OF DISPERSE MATERIALS

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In thermal analysis of disperse materials, the gas filling the pores of the samples has an important effect on the determination of heats of phase transformations.

Particularly significant errors, up to 25%, may arise in cases when thermal analysis is carried out in gas atmospheres having high thermal conductivities.

Based on experimental data, a relationship expressing the dependence of peak area on the thermal conductivity of the gas and on the thermal conductivity and particle size of the studied material has been derived. This relationship allows to calculate the possible experimental error and hence to adopt measures for reducing its value.

Owing to the inadequate elaboration of the quantitative thermal analysis of processes accompanied by the formation of a gaseous phase, in such cases researchers are often forced to apply relationships established for solid-phase processes.

In our view, the particular features of heat exchange and mass exchange in a disperse material as a result of the appearance of gaseous products, the form in which they are reflected, the quantitative aspects of the effects, and hence well-founded suggestions as to the necessity and means of eliminating or taking them into account, have not been discussed with satisfactory consistence in the thermal analysis literature [1–7].

The fact that the presence of a gaseous phase in the pores of a disperse material is reflected in the magnitude of the peak areas corresponding to the phase transformations may be considered as reliably established. Gases with higher thermal conductivities increase, and gases with lower thermal conductivities decrease the peak areas [1–4].

The quantitative aspect of this problem, however, i.e. the degree to which peak areas change as a function of the parameters of the disperse system and the gaseous medium, has been much less studied. Reports in the literature on the quantitative evaluation of the effect of the gaseous phase in the thermal analysis of disperse materials are insufficient for the establishment of general relationships. In many cases the data are contradictory, obviously because the experimental apparatus used by the different authors differed in design.

The main objective of the present work was the quantitative evaluation of the effect of the gaseous phase on the quantitative characteristics of the thermal curves, and primarily on the phase-transition peak areas.

In the study of the role of the gas phase (medium) it is necessary to define certain experimental conditions. If the disperse sample is in an atmosphere of some gas, then – in our opinion – the roles of the gas in the pores of the disperse sample and outside the boundaries of the sample must be kept strictly apart, for exactly the same reasons that made it necessary earlier [8] to distinguish between "external" and "internal" experimental parameters.

In the present paper we shall deal only with the role of the gas filling the pores of the sample, and shall attempt to analyze the causes resulting in the particular features of processes accompanied by gas release.

As regards quantitative thermal analysis, i.e. as regards heat determination in our case, three elements must be distinguished in the phase transformation process: (*i*) the effect of the gas filling the pores of the sample and thereby changing heat transfer conditions, (*ii*) the effect of this gas when moving in the pores of the disperse material, and (*iii*) the effect of the change in the mass of the sample, due to part of the sample being transformed into a gas which leaves the reaction zone. In real processes, all three elements take place simultaneously. Their relative share has not yet been determined.

In order to evaluate the degree and establish the relationships for each of the above elements, the experimental conditions must be so chosen that the effect of one element only be separated by eliminating the effects of the other elements, or by providing for their being taken into account by calculation. Accordingly, we decided to study the effects of different gases in the pores of a disperse material on the polymorphous transformation of this material.

The chosen model substance was sodium sulphate and the changes in the peak area corresponding to its polymorphous transformation were studied with various gases. The sample holder consisted of a long tube, with a thermocouple composed of butt-welded chromel and alumel wires extended in its axis. Heat transfer conditions close to those in an infinitely long cylinder were obtained by using a very long sample (height: diameter ratio $>10 : 1$), and also by covering both top and

Table 1

Peak areas corresponding to the polymorphous transformation of sodium sulphate powders having different gravimetric apparent densities, in different gases

Gas species	Thermal conductivity of gas, $\frac{\text{cal}}{\text{cm} \cdot \text{sec. degree}}$	Peak area, degree·sec, at apparent densities of				
		1.219 (490–370 μm)	1.250 (370–250 μm)	1.314 (250–230 μm)	1.341 (230–180 μm)	1.481 (180–96) μm)
Carbon dioxide	$7.94 \cdot 10^{-5}$	795.4	797.5	799.3	800.0	805.0
Nitrogen	$9.49 \cdot 10^{-5}$	789.9	791.8	794.1	796.2	801.1
Air	$9.83 \cdot 10^{-5}$	790.0	790.0	794.0	784.6	799.4
Oxygen	$10.39 \cdot 10^{-5}$	785.7	788.1	790.3	792.5	799.4
Helium	$53.73 \cdot 10^{-5}$	661.0	667.1	676.6	676.6	707.0
Hydrogen	$67.17 \cdot 10^{-5}$	631.2	636.4	649.9	653.4	682.1

bottom ends of the sample with a layer of finely-ground quartz. This sample shape was chosen with the aim of eliminating the effects of gas change at the extremities of the sample. Thus, all changes occurring when the gas was changed could be ascribed to the change in heat transfer conditions between the centre and surface of the sample. The gas atmosphere surrounding the samples and reference standards was identical in all experiments.

Peak areas obtained with different particle sizes and with different gases are presented in Table 1. The apparent (gravimetric) density of the material was selected to characterize the material, instead of the particle size. The corresponding particle sizes are given in parentheses.

All experimental data in Table 1 are the arithmetical means of the results of six experiments.

Table 1 convincingly demonstrates the dependence of the peak area on the gas species: hydrogen and helium cause a sharp decrease in the peak area. To a certain extent, the dependence of the peak area on particle size can also be recognized in Table 1.

General evaluation of the results relating to the effects of both factors was attempted by using the simplest possible mathematical description of the observed phenomena.

According to Melling [9], the peak area S can be expressed as a function of the thermal effect H of the phase transformation, and the thermal conductivity λ and the density γ of the sample:

$$S = K \cdot H \frac{\gamma}{\lambda} \tag{1}$$

By writing Eq. (1) once for a monolithic (pore-free) sample and again for a porous sample, and by combining these equations, we find

$$S = S_{\mathrm{M}} \frac{\gamma \cdot \lambda_{\mathrm{M}}}{\gamma_{\mathrm{M}} \cdot \lambda} \tag{2}$$

where symbols with the subscript M refer to the monolithic sample, and symbols with no subscript to the powder.

Let us now write Eq. (2) for the cases when the interstices between the powder particles are filled with carbon dioxide and hydrogen, respectively:

$$S_{\mathrm{CO_2}} = S_{\mathrm{M}} \frac{\gamma \cdot \lambda_{\mathrm{M}}}{\gamma_{\mathrm{M}} \cdot \lambda_{\mathrm{CO_2}}} \quad \text{and} \quad S_{\mathrm{H_2}} = S_{\mathrm{M}} \frac{\gamma \cdot \lambda_{\mathrm{M}}}{\gamma_{\mathrm{M}} \cdot \lambda_{\mathrm{H_2}}}$$

By solving the above expressions as a system of equations, we obtain

$$\frac{S_{\mathrm{CO_2}}}{S_{\mathrm{H_2}}} = \frac{\lambda_{\mathrm{H_2}}}{\lambda_{\mathrm{CO_2}}} \tag{3}$$

Here $S_{\mathrm{CO_2}}$ and $S_{\mathrm{H_2}}$ are the peak areas obtained when the pores in the sample are filled with carbon dioxide and hydrogen, respectively, while $\lambda_{\mathrm{CO_2}}$ and $\lambda_{\mathrm{H_2}}$ are the thermal conductivities of the powder when its pores are filled with carbon dioxide and hydrogen, respectively.

To utilize Eq. (3) for the analysis of our experimental data, a mathematical equation must be found which describes the dependence of the thermal conductivity of the sample on its physical characteristics, viz. the particle size, the thermal conductivity of the solid material of the particles, and the thermal conductivity of the gas in the interstices between the particles.

For this purpose, we applied the simplest relationship, based on the rule of additivity, for the thermal conductivity of disperse materials [10]:

$$\lambda = \frac{\gamma}{\gamma_M}\left(\lambda_M + \frac{\gamma_M + \gamma}{\gamma}\lambda_g\right) = \frac{\gamma}{\gamma_M}(\lambda_M + P\lambda_g) \tag{4}$$

where λ_g is the thermal conductivity of the gas phase and P is the porosity.

Let us write Eq. (4) for a powder whose pores are filled with hydrogen $\left(\lambda_g^{H_2} = 67.17 \cdot 10^{-5} \frac{\text{cal}}{\text{cm.sec.degree}}\right)$, and again for a powder whose pores are filled with carbon dioxide $\left(\lambda_g^{CO_2} = 7.94 \cdot 10^{-5} \frac{\text{cal}}{\text{cm.sec.degree}}\right)$, and substitute the values obtained into Eq. (3). This leads to

$$\frac{S_{CO_2}}{S_{H_2}} = \frac{\lambda_M + \left(\frac{\gamma_M}{\gamma} - 1\right)\lambda_g^{H_2}}{\lambda_M + \left(\frac{\gamma_M}{\gamma} - 1\right)\lambda_g^{CO_2}} \tag{5}$$

From Eq. (5) and the experimental data listed in Table 1, it is possible to calculate λ_M, that is, the thermal conductivity of the substance in the monolithic form containing no gas inclusions. Let us utilize, for example, the following values:

$$S_{CO_2} = 800.0 \quad S_{H_2} = 653.4 \quad \gamma_M = 2.70 \quad \gamma = 1.341$$

$$\lambda_g^{H_2} = 67.17 \cdot 10^{-5} \quad \lambda_g^{CO_2} = 7.94 \cdot 10^{-5}$$

yielding a value of $\lambda_M = 264.1 \cdot 10^{-5}$ cal $\cdot$ cm^{-1} $\cdot$ sec^{-1} $\cdot$ degree^{-1}.

Using the found value for λ_M, the value of S_M is then calculated from Eq. (2):

$$S_M = 824.3$$

The knowledge of λ_M and S_M allows utilization of Eq. (2) to find the general relationship between the peak area, the density of the disperse material, and the thermal conductivity of the gas filling its pores, since consideration of the physical meaning of the values λ_M, S_M and γ_M discloses that they are independent of both the disperse state of the powder and the gas species. The calculated peak areas are presented in Table 2.

The agreement between the data in Tables 1 and 2 is rather good, as shown by Fig. 1.

Table 2

Calculated peak areas for the polymorphous transformation of sodium sulphate at different gravimetric densities and in gases having different thermal conductivities

Thermal conductivity of gas, $\frac{\text{cal}}{\text{cm}\cdot\text{sec}\cdot\text{degree}}$	Calculated peak area, degree·sec, at densities of					
	1.00	1.10	1.219	1.30	1.40	1.481
$5 \cdot 10^{-5}$	798.6	802.2	805.8	807.8	809.9	811.7
$10 \cdot 10^{-5}$	774.4	781.2	788.0	792.0	795.9	799.4
$30 \cdot 10^{-5}$	690.8	707.4	724.3	734.5	744.8	753.8
$50 \cdot 10^{-5}$	623.6	646.3	670.2	684.7	699.9	713.2
$70 \cdot 10^{-5}$	568.2	594.9	623.5	641.2	660.0	676.7

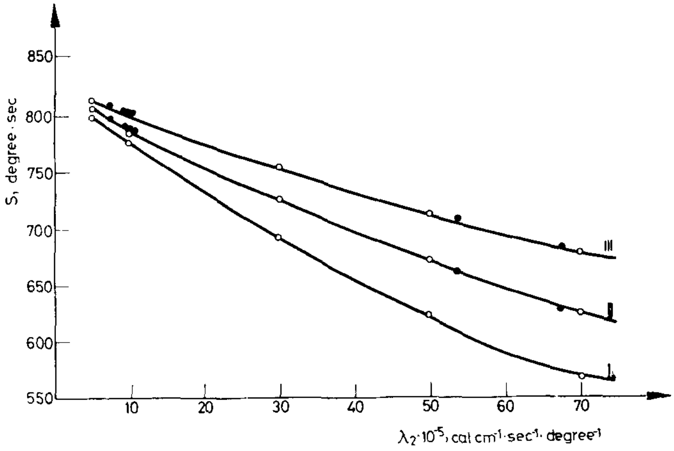

Fig. 1. Peak area S corresponding to the polymorphous transformation of sodium sulphate *vs.* thermal conductivity λ_g of the gas phase, at different gravimetric densities of the powder. I. $\gamma = 1.000$ g/cm^3. II. $\gamma = 1.219$ g/cm^3. III. $\gamma = 1.481$ g/cm^3
o — calculated points, ● — experimental points

The relationship based on the additivity rule (Eq. 4) was used for the calculation of λ_M, S_M and λ, because it is the simplest. Other relationship describing the dependence of the thermal conductivity of a disperse material on the thermal conductivity of the monolithic material and the density of the powder have also been reported [10]. Additional calculations were made using the Krischer equation:

$$\lambda = \lambda_M \frac{100 - P}{100} + \lambda_g \frac{P}{100,},$$

the Riban equation:

$$\lambda = \lambda_M(1 - P)^{2/3} + \lambda_g P^{2/3},$$

the Starostin equation:

$$\lambda = \frac{\lambda_M^2 P^{2/3} + (\lambda_g - \lambda_M)\lambda_M}{\lambda_M + (P^{2/3} - P)(\lambda_g - \lambda_M)}$$

and the Russel equation:

$$\lambda = \frac{\lambda_M P + \frac{\lambda_M}{\lambda_g}(1 - P^{2/3})}{P - P^{2/3} + \frac{\lambda_g}{\lambda_M}(1 - P^{2/3} + P)}$$

The values of λ_M and S_M calculated via these equations are presented in Table 3.

Let us first make a comparison only for the values of the thermal conductivity of the monolithic substance, λ_M. This comparison indicates that the additivity rule and the Krischer and Riban equations yield the most probable values for the thermal conductivity of sodium sulphate. No exact thermal conductivity values for sodium sulphate could be found in the literature. However, substances that are closely similar to it, e.g. glass, porcelain and graphite, have thermal conductivities in the range $100 \cdot 10^{-5} - 1000 \cdot 10^{-5}$ $\mathrm{cal \cdot cm^{-1} \cdot sec^{-1} \cdot degree^{-1}}$.

Table 3

Values of λ_M and S_M calculated by using different equations for the thermal conductivity of the powder

	Value calculated with the				
	additivity	Krischer	Riban	Starostin	Russel
	equation				
$\lambda_M, \frac{\mathrm{cal}}{\mathrm{cm \cdot sec \cdot degree}}$	$264.1 \cdot 10^{-5}$	$264.8 \cdot 10^{-5}$	$1600 \cdot 10^{-5}$	$2.11 \cdot 10^{-5}$	$2.09 \cdot 10^{-5}$
S_M, degree · sec	824.3	824.3	255.0	1660	1831

The values obtained with the Starostin and Russel equations are evidently too low: according to literature data, materials like asbestos and cork, that are marked thermal insulators, have thermal conductivities of the order of $10 \cdot 10^{-5} - 30 \cdot 10^{-5}$ $\mathrm{cal.cm^{-1} \cdot sec^{-1} \cdot degree^{-1}}$.

Comparison of the calculated peak area values S_M corresponding to the polymorphous transformation of sodium sulphate if the sample were monolithic restricts the number of applicable equations to two: the additivity and Krischer equations. The low value of S_M calculated by means of the Riban equation is inconsistent with the fairly clear tendency of the experimental data in Table 1: the peak area increases with increasing density.

It is possible that at very low densities, or at densities close to that of the single crystal, some other equation, e.g. the Riban equation or the equations of Eucken, Nekrasov, Torkar or Bogomolov [10] (that we did not test) might yield a better approximation. In our opinion, however, the studied density range (45–55% of the density of the single crystal) embraces the majority of the cases occurring in DTA practice, viz. particle sizes of 100–500 μm, and hence it may safely be assumed that for thermal analysis, the additivity and Krischer equations are the most suitable.

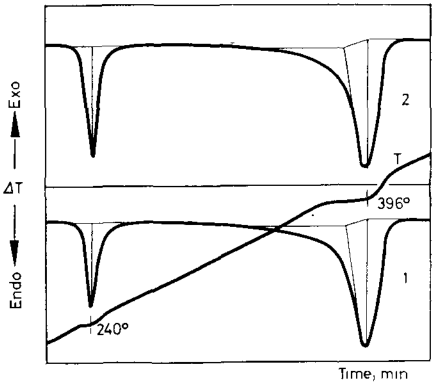

Fig. 2. DTA curves of a 3:1 parts by weight mixture of sodium sulphate and cadmium carbonate powders. 1. in helium, 2. in carbon dioxide

Based on the additivity equation, a quantitative estimation of the possible error in the thermal effect caused by ignoring the role of the gas filling the pores of the disperse sample may be attempted.

If thermal analysis is carried out in a gas atmosphere having a thermal conductivity λ_g^1, whereas the thermal conductivity of the gas released in the course of the studied process is λ_g^2, then, only as the result of the thermal conductivity change of the gas in the pores of the sample, the possible relative error will be

$$\Delta S = \frac{\lambda_g^2 - \lambda_g^1}{\lambda_g^2 + \dfrac{\gamma}{\gamma_M - \gamma}\lambda_M} \cdot 100$$

where γ, γ_M and λ_M have the same meanings as above, viz. the density of the powder, and the density and thermal conductivity of the solid particles of the powder, respectively.

For an experimental estimation of the error that may arise when the role of the gas filling the pores of the disperse material is ignored, the following experiment was made.

A 3 : 1 mixture of sodium sulphate and cadmium carbonate powders was submitted to thermal analysis in carbon dioxide and helium atmospheres, respectively (Fig. 2). It was found that the area of the peak corresponding to the dissociation of the carbonate was the same (within the reproducibility limits of the experiment) on the thermogram taken in helium (plot 1) as on that taken in carbon dioxide (plot 2). In contrast, the area of the peak corresponding to the polymorphous transformation of sodium sulphate was found to be larger by 25% on the thermogram taken in carbon dioxide than on that taken in helium. Thus, the experiment gave a quantitative illustration of the possible error in heat determination, if the role of the gas filling the pores of the disperse material is ignored.

The great relative error when thermal analysis is carried out in a gas atmosphere of high thermal conductivity indicates that particular caution must be taken in calibration.

When thermal analysis is carried out in air, nitrogen, oxygen or carbon dioxide, and the gas released as a result of thermal decomposition does not differ greatly, with regard to its thermal conductivity, from the gas atmosphere, the possible relative error (as indicated by the above-discussed experimental and theoretical data) does not exceed 3 – 5%.

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Résumé — Dans l'analyse thermique des matériaux dispersés, le gaz contenu dans les pores des échantillons joue un rôle important dans la détermination des chaleurs de transformation de phases.

Des erreurs particulièrement notables, jusqu'à 25 p.c., peuvent se produire si l'analyse thermique s'effectue dans des gaz de conductivité thermique élevée.

A partir des données d'expérience, on déduit une corrélation entre la surface des pics et la conductivité thermique du gaz ainsi que la conductivité thermique et les dimensions des particules du matériau étudié. Cette corrélation permet de calculer l'erreur d'expérience possible et, par suite, de faire des mesures pour réduire sa valeur.

ZUSAMMENFASSUNG — Bei der thermischen Analyse disperser Substanzen ist das die Poren der Proben ausfüllende Gas von entscheidendem Einfluß auf die Bestimmung der Phasenumwandlungswärmen. Besonders bedeutende Fehler, bis zu 25%, können auftreten, wenn die thermische Analyse in Gasatmosphären erhöhter Wärmeleitfähigkeit durchgeführt wird.

Aus Versuchsergebnissen wurde ein Zusammenhang abgeleitet, welcher die Abhängigkeit der Peak-Fläche von der Wärmeleitfähigkeit des Gases und der Wärmeleitfähigkeit und Teilchengröße der untersuchten Substanz zum Ausdruck bringt. Dieser Zusammenhang gestattet die Berechnung des möglichen Versuchsfehlers und daher auch Maßnahmen zur Herabsetzung seines Wertes.

Резюме — При анализе дисперсных материалов для определения теплот фазовых превращений большое значение имеет газовая среда, заполняющая поры образца.

Особо существенные погрешности определения, достигающие 25%, могут возникнуть в тех случаях, когда термический анализ производится в атмосфере высокотеплопроводных газов.

Выведенная на основе экспериментальных данных зависимость площади пиков от теплопроводности газов и теплопроводности и дисперсности исследуемого материала позволяет обоснованно рассчитать возможные ошибки определений и на этой основе принять меры к уменьшению величин этих ошибок.