ON CERTAIN RELATIONS IN QUANTITATIVE THERMOGRAPHY

Fig. 1.** Diagram of the block and thermocouple mounting:

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Abstract

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ON CERTAIN RELATIONS IN QUANTITATIVE THERMOGRAPHY

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Thermographic analysis is one of the principal methods for determining the phase composition of a number of artificial and natural compounds. However, even at present there is no sufficiently complete development of quantitative relations in thermography. The question has not yet been resolved of the possibility of comparing areas measured on differential curves for substances with different heat-transfer coefficients, since the thermal effect of a phase transformation is proportional to the product of the heat-transfer coefficient K and the area S formed by the deviation of the differential curve during the reaction. By the heat-transfer coefficient is meant here the sum of all factors affecting the rate of heat transfer, i.e., the coefficients of heat exchange, thermal conductivity, heat capacity, the distance from the thermocouple junction to the outer surface of the sample and of the standard, the magnitude of the surface, etc. (^{1}).

Fig. 1. Diagram of the block and thermocouple mounting:
1 –block of heat-resistant steel,
2 –reaction vessel made of Pyrex,
3 –powdered metallic Al,
4 –combined thermocouple,
5 –porcelain tubes,
6 –charge of the substance under investigation.

L. G. Berg (^{1}) proved mathematically that such a comparison of areas on different thermograms for substances with different values of K is possible if the areas are reduced to areas with the same value of K in the following way:

$$S'' = S' \cdot \frac{\Delta t''}{\Delta t'}. \tag{I}$$

Here $\Delta t'$ and $\Delta t''$ are the temperature differences between the furnace and the sample. These quantities can be determined directly from the thermograms.

If, during the process of a phase transformation, the heat-transfer coefficient changes, then the mean heat-transfer coefficient is used, and equation (I) takes the form:

Fig. 2. Heating curves 1, 3, 4, 5, and 8

Figure 1: Fig. 2. Heating curves 1, 3, 4, 5, and 8

$$S'' = S' \frac{\dfrac{\Delta t_1'' + \Delta t_2''}{2}}{\dfrac{\Delta t_1' + \Delta t_2'}{2}} = S' \cdot \frac{\Delta t_1'' + \Delta t_2''}{\Delta t_1' + \Delta t_2'}. \qquad \text{(II)}$$

We carried out an experimental verification of equation (II) by measuring the areas corresponding to the polymorphic transformation of KNO_3. The change in the heat-transfer coefficient was achieved by introducing into the charge of KNO_3 substances with a deliberately sharply different thermal conductivity, in such quantities that the heat capacity of the mixture remained the same in all experiments.

The heating curves were recorded on an electronic automatic recording potentiometer of the EPP-09 type, whose sensitivity was increased by reducing the resistance of the rheochord shunt (from 235 to 4.5 ohms) and increasing the resistance R_{init} in order to shift the beginning of the recording to the extreme left position ([2]). This improvement made it possible to obtain a voltage drop over the entire rheochord of 0.5 mV. The junction of the differential thermocouple was placed directly in the block. Since placing the junction of an ordinary thermocouple strongly affects the magnitude of the area of the peak corresponding to the phase transition, when placing the thermocouple from above it is very difficult to achieve good reproducibility. We used rigid mounting of the thermocouples from below, which strictly fixed the constancy of the junction position. The reaction vessel had an internal pocket at the bottom for placing the thermocouple junction (Fig. 1). Since the magnitude of the area of the peak corresponding to the phase transition increases with increasing sample weight only up to a certain limit, after which it remains constant, we determined this maximum sample weight n_{max}, and in the experiments we used sample weights considerably smaller than n_{max}, which made it possible to obtain the true values of the areas corresponding to the given sample weight.

Fig. 2. Heating curves 1, 3, 4, 5, and 8

Thus, in the course of the study, most of the quantities affecting the rate of heat transfer remained strictly constant, with the exception of the thermal conductivity, which was deliberately varied in each experiment.

The reduction of the areas corresponding to the polymorphic transition of KNO_3 with different values of K (introduction into the KNO_3 sample of chamotte, CuO, metallic Ag and Al) to areas with the same value of K, carried out by us, is given in Table 1. The reduction was made to the area of curve 1. At constant

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Table 1

No.	Substance studied	Δt_1, mm	Δt_2, mm	$\Delta t_{\text{avg.}}$, mm	S, relative units	S reduced, relative units	Relative error, %
1	3 g KNO_3 + 1.5 g chamotte	46.0	59.0	52.50	6.80	–	–
2	Same	48.0	58.0	53.0	7.08	6.98	+2.65
3	3 g KNO_3 + 1.5 g $NaNO_3$	46.0	56.0	51.0	6.50	6.66	−2.06
4	3 g KNO_3 + 3 g CuO	46.0	56.0	51.0	6.56	6.77	−0.44
5	3 g KNO_3 + 1.5 g Al (met.)	39.0	47.0	43.0	5.46	6.66	−2.06
6	Same	44.0	52.0	48.0	6.20	6.72	−1.15
7	3 g KNO_3 + 6 g Ag (met.)	31.5	40.0	35.75	4.70	6.87	+1.03
8	Same	31.5	39.5	35.50	4.6	6.77	−0.44
9	» »	31.5	39.0	35.25	4.66	6.93	+1.91

with the same thermal conductivity, good reproducibility was obtained for the values of the peak areas and of the deviations Δt_1 and Δt_2 of the differential curve from the zero line (Nos. 7, 8, 9).

It is evident from Table 1 that, without such a reduction, the magnitudes of the areas for one and the same amount of substance may differ, depending on the thermal conductivity, by almost a factor of two; for example, $S_1 = 4.6$ and $S_2 = 6.8$ (Nos. 1 and 8). After reduction to area S_2, however, $S_1 = 6.77$, i.e., the absolute error amounts to only 0.03 relative units, and the relative error to 0.45%. In our experiments the constancy of the heat capacities of the mixtures was selected in advance. However, owing to the negligibly small value of the heat capacity relative to the thermal conductivity, the heat capacity may be neglected, since this can only slightly increase the error in reducing the areas.

Thus, in practice such a reduction will make it possible to decrease errors in phase quantitative analysis and will permit the use, for quantitative calculations, of heating curves of different substances on different thermograms, and, all the more, the comparison of thermal effects on one thermogram with an error not exceeding 3%.

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Note: Figure translations are in progress. See original paper for figures.