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Note

Experimental results on the correlation between the areas of DTG and DTA peaks and the sample weight

G. SIRACUSA* AND V. CUCINOTTA
Istituto di Chimica Generale, Università di Catania, Viale A. Doria, 8, 95125 Catania (Italy)
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The determination of the enthalpy change of a process by DTA involves in any case the measurement of the area of the peak corresponding to the considered process.

Also for the evaluation of kinetic data under non-isothermal conditions, owing to the earlier development of DTA with respect to TG, and particularly for processes occurring without weight change of the sample, several methods involve the measurement of the DTA peak area[1-7].

While in kinetic studies an ideal behaviour of the system is generally assumed, in thermodynamic studies the influence of the actual experimental conditions is more carefully considered. Thus, the calibration procedure is practically used only for the

TABLE 1

AREAS (cm^2) OF DTA AND DTG PEAKS FOR REACTIONS (1) AND (2) AND RELATIVE SAMPLE WEIGHTS (mg)

Sample weight (mg)	*Reaction (1)*		*Reaction (2)*	
	DTA	*DTG*	*DTA*	*DTG*
23.2	113	80	65	95
34.7	142	115	80	145
45.7	200	152	120	180
61.3	261	200	150	245
71.2	280	237	185	280
100.5	310	342	290	410
147.0	330	450	415	575
208.3	375	675	602	805
260.0	425	825	755	1015
302.3	440	951	840	1145
330.5	451	1060	860	1275
353.4	475	1115	875	1345
375.4	490	1198	885	1420

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* To whom correspondence should be addressed.

determination of enthalpy changes[8]. However, in all methods, general equations need to be derived, because it is impossible to take into account all the experimental factors, many of which depend on the particular apparatus used.

In this note, we report data concerning the correlation between the area of DTG and DTA peaks and the amount of material analyzed. The data (Table 1) were found for the following reactions of $CaC_2O_4 \cdot H_2O$ in nitrogen atmosphere:

$$CaC_2O_4 \cdot H_2O\,(s) \rightarrow CaC_2O_4\,(s) + H_2O\,(g) \qquad (1)$$

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g) \qquad (2)$$

All experiments were performed with a Mettler thermoanalyzer using a Mettler T-TD2 sample holder, Al_2O_3 as reference material, $\phi = 15\,°C\ min^{-1}$, and the recorder's chart speed is 12 in. h^{-1}.

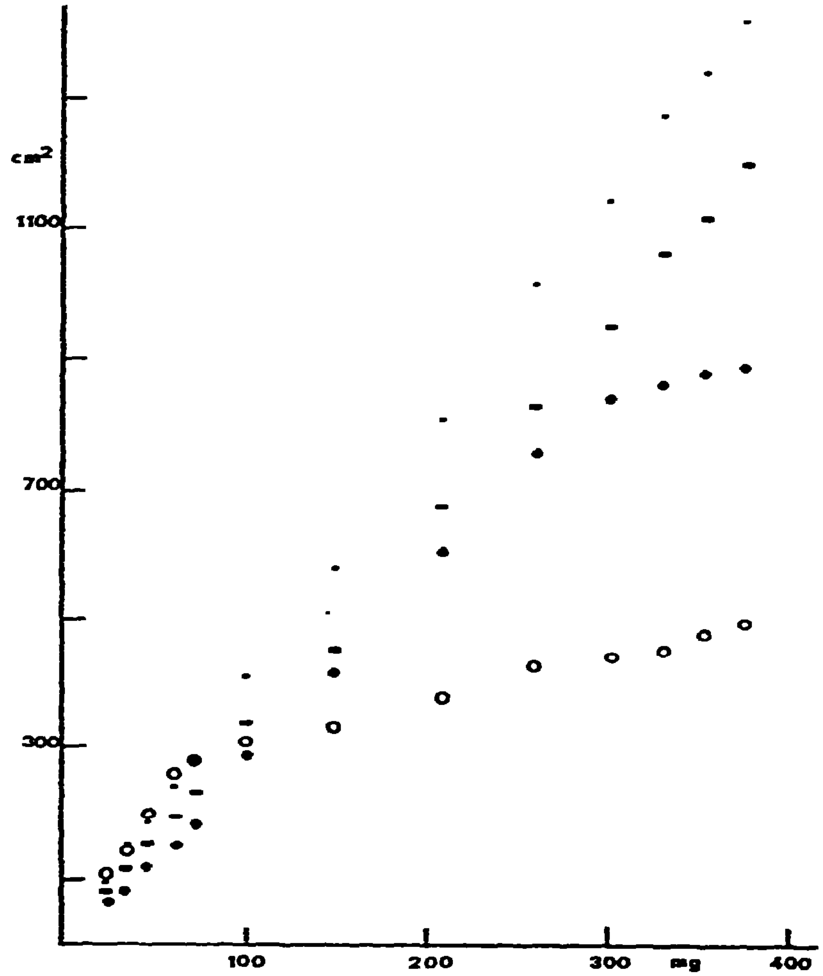

Fig. 1. Plot of areas (cm^2) of DTA and DTG peaks against sample weight (mg). ○ = DTA area of the reaction 1; ■ = DTG area of the reaction 1; * = DTA area of the reaction 2; ● = DTG area of the reaction 2.

Figure 1 shows the results of our measurements. While for the DTG peaks, the linearity between the peak areas and the sample amounts is verified in the entire investigated range, for the DTA peaks we observe a discontinuity. Two straight lines with different slopes can be traced as graphic representation of the correlation between our experimental data. The exact sample weight, which is different for the two reactions can be identified. This allows separation of two ranges of linearity, corresponding to different values of the proportionality constant between the DTA peak areas and the sample weight.

The first suggestion of these results is that, when possible, as for kinetic measurements of processes with a weight change associated, it is preferable to use the DTG curves[9, 10]. For a correct enthalpy change determination, it appears advisable, besides the usual calibration with a process whose ΔH is known, to do an additional calibration of our kind on an adequately wide range of sample weights.

The relationship we have obtained is surprising in some aspects, as it denotes the presence of a point of discontinuity. In our opinion, the sample weight which separates the two ranges of linearity is connected with a particular apparatus and with the considered reaction. Thus, no theoretical "a priori" derivation can be made of this value. Presumably, the characteristics of thermal conductibility inside the sample and between the sample and the thermocouple joint, in relation with the geometrical experimental arrangement determine the discontinuity.

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