

USE OF GRAPHITE TO IMPROVE HEAT DETERMINATIONS BY DIFFERENTIAL SCANNING CALORIMETRY

G. G. T. GUARINI, R. SPINICCI and D. DONATI*

*Institute of Physical Chemistry, University of Florence, Firenze, *Centro di studio del C.N.R. sulla chimica e la struttura dei composti eterociclici e loro applicazioni, c/o Institute of Organic Chemistry, University of Florence, Firenze, Italy*

(Received November 21, 1972; in revised form March 20, 1973)

The presence of graphite is demonstrated to reduce the influence of thermal emissivity on the evaluation of heat changes for reactions of the type: $A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}}$ by differential scanning calorimetry.

A kinetic study of reactions of the type $A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}}$ by means of a differential scanning calorimeter requires to ensure the free escape of the gaseous product in order not to alter in an irreproducible way the shape of the thermal curve. Therefore covers both in the sample pan and on the sample holders are usually avoided.

However this generates a dissimmetry between the sample and the reference parts of the calorimeter sensor which has hardly an effect if any on the heat measurements if thermal events happening in a narrow temperature interval and with no change in mass and composition (like first order phase transitions) are considered, but is important if the heat in play in a solid \rightarrow solid + gas reaction (that is a thermal event happening in a large temperature interval and involving mass and composition changes) is to be determined.

Under these conditions the heat of reaction, as determined by DSC, that is in a temperature interval [1], appears to be dependent on the mass of the sample and on the rate of linear advance of the temperature (scan speed, SS). As an example for the reaction $\varepsilon \cdot \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}$ values more and more unreasonable ranging from 12,000 cal/mol (11 mg; SS = 4 K/min) to 43,000 cal/mol (2.5 mg; SS = 0.5 K/min) have been obtained by means of our Perkin-Elmer DSC-1b.

Rogers and Morris [2] have pointed out that a variation of thermal emissivity can cause base-line drift and therefore give rise to misleading results. Assuming the variation in thermal emissivity as responsible for the observed results, we have considered the measured heat change as the sum of two terms:

$$\Delta Q_{\text{measured}} = \Delta Q_{\text{reaction}} + \Delta Q_{\text{emissivity}}$$

where $\Delta Q_{\text{emissivity}}$ is independent of sample size and may be due mainly to the increase and change in composition of the emitting surface as a result of the reaction. Because of such a heat change, the usual tracing of a straight base-line

from the beginning to the end of the reaction results in an erroneous value of the area under the peak and thus of the heat of transformation.

Fig. 1 gives an actual DSC curve for the reaction $\text{Cd}(\text{OH})_2 \rightarrow \text{CdO} + \text{H}_2\text{O}$, showing the variation in height of the base-line before and after the reaction. Three different base-lines are shown in the Figure: base-line a) is the usual straight line from the beginning to the end of the thermal event; base-line b) is obtained assuming that the height variation is mainly due to the change in thermal capacity on going from reactants to products [3]; and base-line c) is the one proposed in

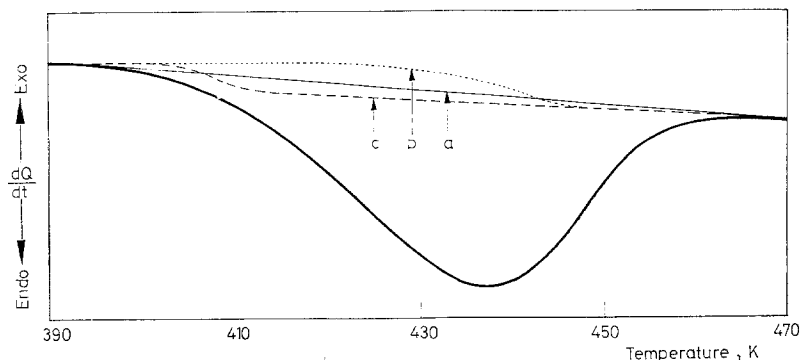


Fig. 1. Actual DSC curve of the decomposition of $\text{Cd}(\text{OH})_2$, showing the three possible interpolated base-lines (see text)

this work. The peculiar shape of the latter is postulated assuming that initially the thermal emissivity is due to the surface of the reactant, but (as the decompositions of solids usually take place from the surface towards the inner part) after a very small fraction of the decomposition has occurred, the emitting surface is already formed by the product. Such an emissivity variation is independent of the mass of the sample and depends only on the geometry of the container and on the increase of surface area due to the fragmentation of the external portion of the reactant.

As the reaction takes place from a temperature T_1 to a temperature T_2 at a certain value of the scan speed, from the Stefan-Boltzmann law $dQ/dt = k\epsilon sT^4$ (where dQ is the heat radiated in time dt at a temperature T from a surface of area s and emissivity coefficient ϵ) we may write:

$$Q = k\epsilon s \int_0^t (T_1 + SSt)^4 dt = \frac{k\epsilon s}{SS} \int_{T_1}^{T_2} T^4 dT = \frac{k\epsilon s}{5SS} (T_2^5 - T_1^5) \quad (1)$$

and substituting $SS = \frac{T_2 - T_1}{t}$

$$Q = \frac{k\epsilon st}{5(T_2 - T_1)} (T_2^5 - T_1^5) = \frac{k\epsilon st}{5} (T_2^4 + T_2^3 T_1 + T_2^2 T_1^2 + T_2 T_1^3 + T_1^4).$$

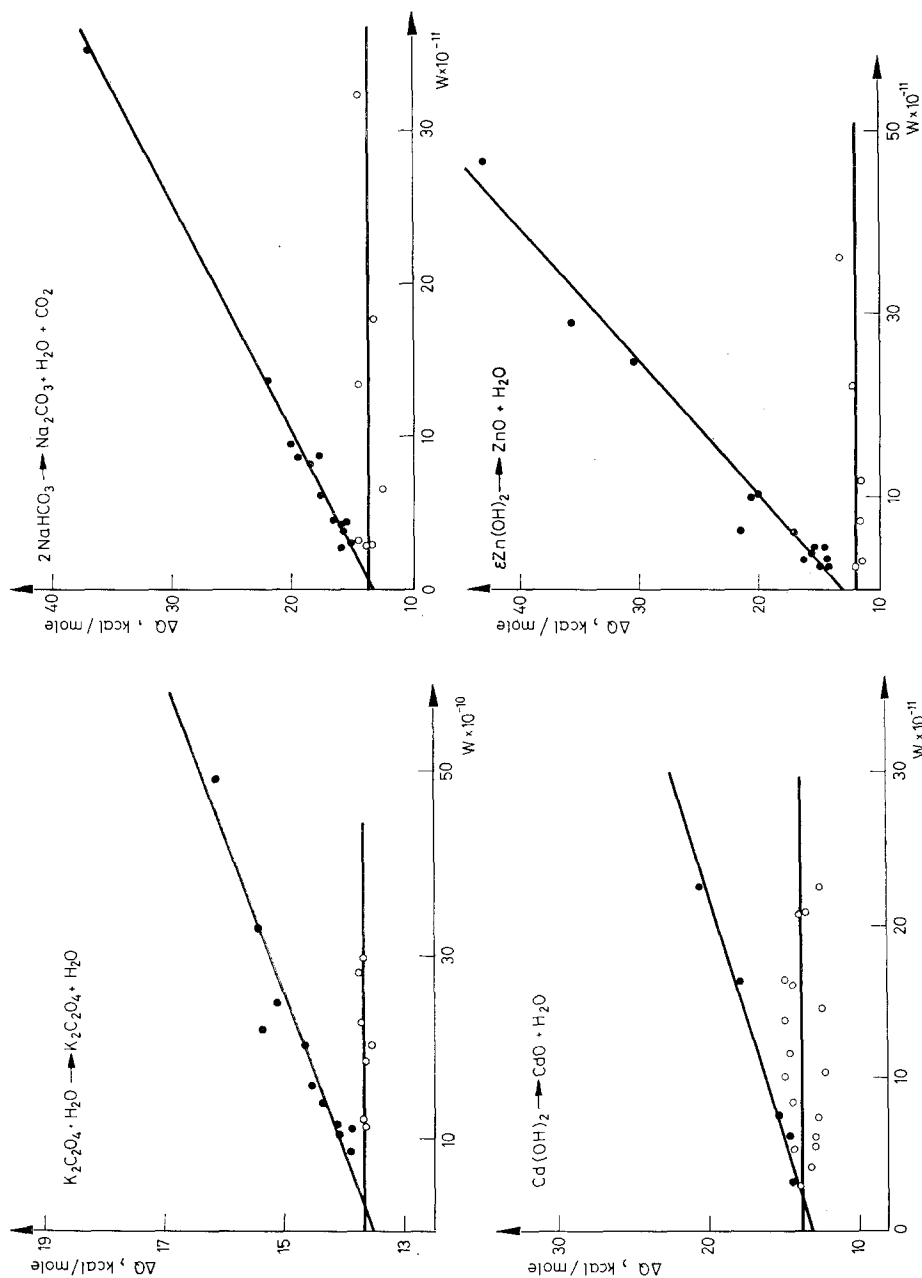


Fig. 2. Plot of the measured heat of reaction as a function of W for experiments performed with (\circ) and without (\bullet) graphite addition

Assuming a proportionality between $\Delta Q_{\text{emissivity}}$ and the change $\Delta(\varepsilon s)$ in emissivity and surface area on going from reactants to products, we get:

$$\Delta Q_{\text{emissivity}} (\text{cal}) = k' \frac{\Delta(\varepsilon s)}{SS} (T_2^5 - T_1^5)$$

where k' is a new proportionality constant. Substituting into (1):

$$\Delta Q_{\text{measured}} (\text{cal/mol}) = \Delta Q_{\text{reaction}} (\text{cal/mol}) + k' \frac{\Delta(\varepsilon s) M}{SS m} (T_2^5 - T_1^5) (\text{cal/mol})$$

with m the mass of a sample having molecular weight M . On plotting $\Delta Q_{\text{measured}}$ (cal/mol) vs. $\frac{T_2^5 - T_1^5}{SS m} = W$, therefore, a straight line should result, giving $\Delta Q_{\text{reaction}}$ as the intercept.

We have verified our hypothesis for a number of compounds and the results are reported in Fig. 2 (●).

If, by some means, it is possible to keep ε and s constant during a run so that $\Delta(\varepsilon s) = 0$, then $\Delta Q_{\text{measured}} = \Delta Q_{\text{reaction}}$ is independent of the mass and the scan speed.

The use of graphite has allowed us to obtain such a result. If a thin layer of graphite powder is added on top of the sample and in the reference pan, there is no difference in emissivity between sample and reference and reactant and product. The results obtained are plotted in Fig. 2 (○) and show the effectiveness of the device.

For the cases we have taken into consideration, the use of graphite, besides leading to an almost total elimination of the dependence of the heat change on mass and scan speed, gives the base-line a good linearity in the temperature interval in which the reaction takes place, owing to the elimination of every difference in emissivity. Moreover, the kinetic parameters which may be deduced from DSC curves obtained in the presence of graphite appear not to be perceptibly altered [4], showing that the escape of the gaseous product through the thin graphite layer is almost free.

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Work supported by the Italian Consiglio Nazionale delle Ricerche (C.N.R.).

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