SOME EXPERIMENTAL ASPECTS OF DSC DETERMINATION OF KINETIC PARAMETERS IN THERMAL DECOMPOSITIONS OF SOLIDS

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Some particular methods of collecting and treating DSC data for the determination of kinetic parameters in thermal decompositions of solids are suggested. These are mainly concerned with an extrapolation method to avoid the effect of the sample mass; with an approximate method to obtain the activation energy and the exponent of the decay law for runs at constant temperature in which the total area under the thermal curve is not known with accuracy; and with a method to ascertain whether a particular decomposition takes place by a single mechanism or by a sequence of different mechanisms.

The determination of kinetic parameters for thermal decompositions of solids by means of differential scanning calorimetry encounters a number of experimental difficulties. Among these are difficulties connected with the instrument, such as the effect of the sample mass, the effect of the rate of linear advance of temperature (scan speed, ss), the difference in thermal emissivity between the sample and the reference holders, etc.

The aim of the present communication is to suggest experimental devices and particular treatments of data in order to meet and possibly overcome some of the above difficulties.

The results reported have been obtained from a number of thermal decompositions of solids already investigated or under investigation.

As experimental evidence had shown the dependence of kinetic parameters on the mass of the sample, in order to evaluate and eliminate such behaviour, we considered a solid whose decomposition kinetics had previously been studied. Sodium hydrogen carbonate was selected [1—3]. The results obtained (some of the runs have been omitted for clarity) are collected in Fig. 1 where the logarithms of the $n = 1$ rate constant of the equation $d\alpha/dt = k(1 - \alpha)^n$, deduced at constant scan speed by the methods already described [4], are plotted vs. T^{-1} in the Arrhenius diagram. The plots become progressively more curved the higher the mass of the sample; consequently, the activation energy which can be deduced assumes different values in different ranges of fractional decomposition (α), agreeing with the value reported in the literature only in a restricted central portion of the curve. The progressive curving suggested an extrapolation method based on plotting the fractional decomposition attained at a given temperature as a function of mass,

using samples of different mass. Within the limits of error these plots were linear (Fig. 2), and the values of the limiting fractional decomposition at zero mass were obtained by extrapolation. A similar procedure allowed the height (proportional
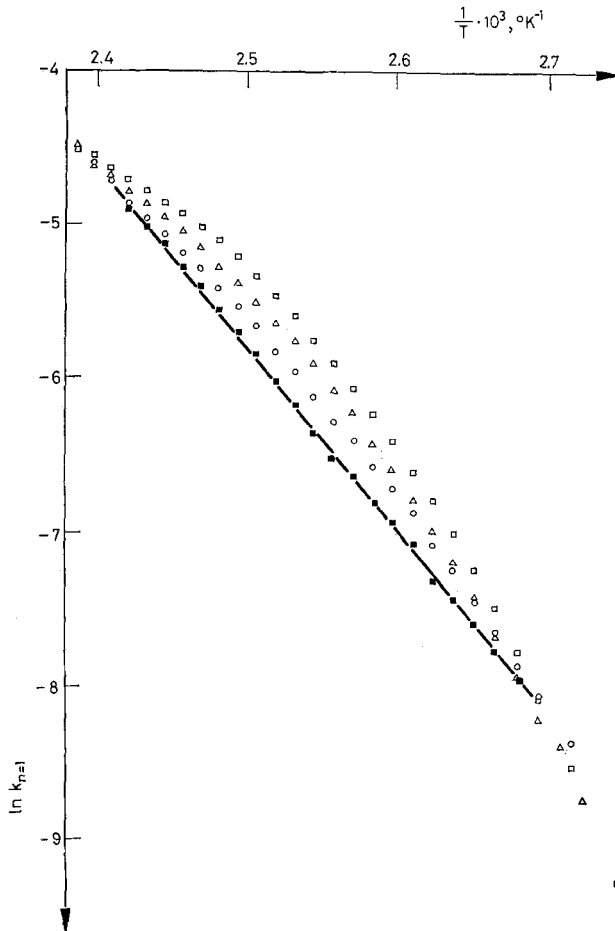

Fig. 1. Arrhenius plot for the thermal decomposition of $NaHCO_3$ showing the effect of the sample mass. □ 8.97 mg; △ 6.07 mg; ○ 3.08 mg; ■ 0

to $d\alpha/dt$) at $m = 0$ to be computed. It was therefore possible to obtain the value of $k_{m=0}$ from the equation:

$$k_{m=0} = \frac{\lim\limits_{m \to 0} \dfrac{d\alpha}{dt}}{\lim\limits_{m \to 0} (1 - \alpha)}$$

with $n = 1$ according to the optimization by Beech [3]. The values of $\ln k_{m=0}$ have been plotted in Fig. 1 and a good straight line is obtained for a large range of α. The value deduced for the activation energy agrees with the one already reported, thus showing that the method is effective and can be used when a dependence of kinetic parameters on mass is observed.
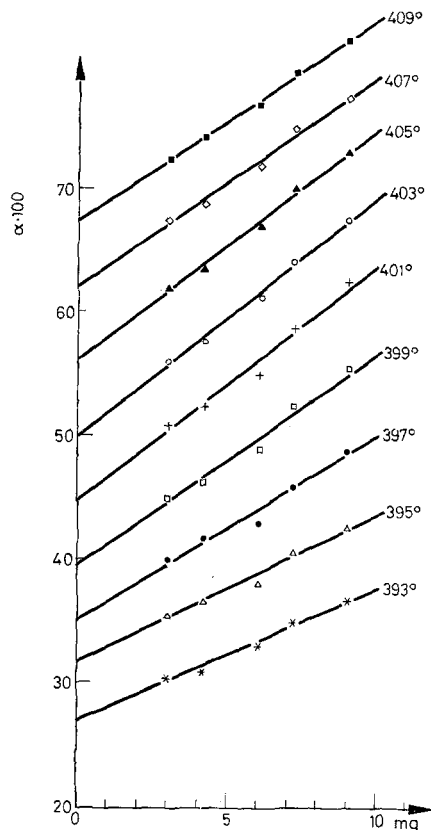

Fig. 2. Extrapolation method to obtain the $\alpha_{m=0}$ value

Another rather common problem is that the analysis of data obtained in experiments with varying temperatures gives linear Arrhenius plots for a number of different kinetic equations, and therefore it becomes impossible to select which particular law is the right one. This is evident, for example, in the case of the monomerization of 9-methyl-10-acetoxyanthracene photodimer (9-Me-10-AcAD), shown in Fig. 3. It appears that "contracting circle", "contracting sphere" and "$n = 1$ decay law" all give good agreement and about the same activation energy. In order to know which is the most probable mechanism responsible for the

observed behaviour (assuming that the same mechanism takes place both at constant and at variable temperature) it was found expedient for these cases to establish a selective criterion making use of the $T = $ const runs.
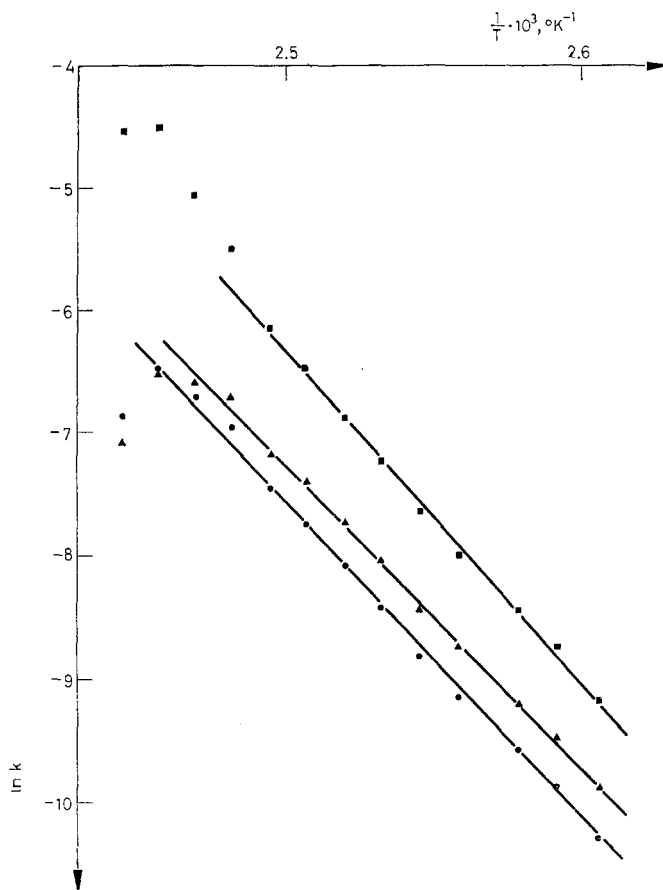

Fig. 3. Arrhenius plot illustrating the impossibility of ascertaining which particular law is followed. 9-Me-10-AcAD ■ decay law; ▲ contracting circle; ● contracting sphere

Unless the reaction does not begin at the fixed temperature if nitrogen is not allowed to flow, in a real experiment at $T = $ const there is great uncertainty in the position of the initial base-line owing to the fact that the reaction is going on during the period necessary for the calorimeter to stabilize at the desired temperature. This uncertainty does not allow a precise measurement of the fractional decomposition given by the ratio of the area at time t (A_t) and the total area (A) under the thermal curve. At $T = $ const a decay law, e.g. $d\alpha/dt = k(1 - \alpha)^n$ with

$n = 1, 1/2, 2/3$, can be applied only to those parts of the thermal curve (following the maximum) showing convexity toward the base-line, and so it is possible from the shape of the curve to select a time (usually somewhat before the maximum)
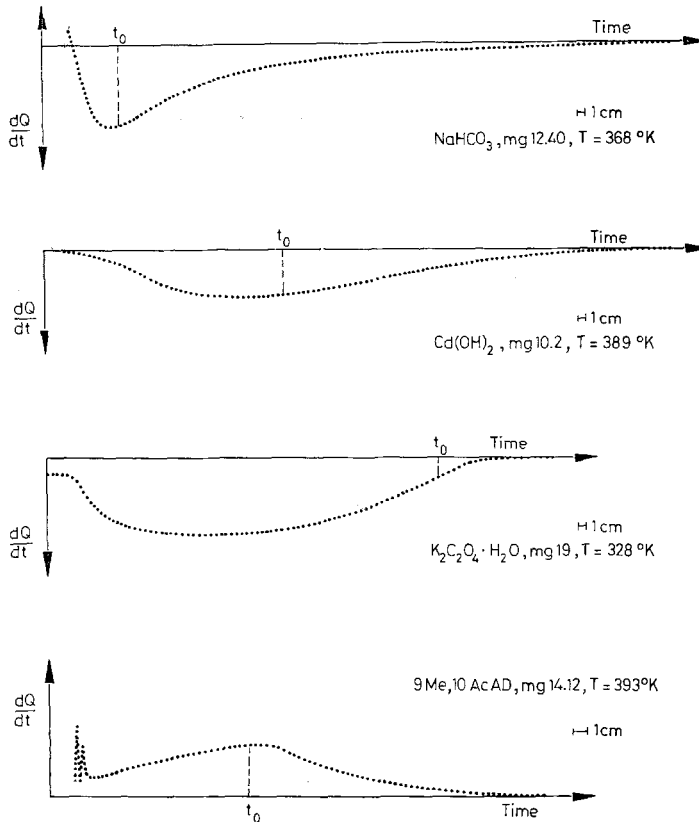

Fig. 4. The extent of the decay region for some reactions investigated at constant temperature

to be used as zero time for the decay. Obviously the range of validity is dependent upon the particular kind of reaction investigated, as shown in Fig. 4. To obtain the values of n and k, the final base-line is extended back to the zero point (this procedure is correct if it is possible to avoid differences in thermal emissivity, as in the case of anthracene dimer monomerization [5] in which the samples were sealed in the usual volatile sample pans), and heights (h_t) and residual areas (B_t) are then measured at times computed starting from the arbitrarily set beginning of the decay. The zero time obviously has an undetermined error Δt. The general law $\mathrm{d}\alpha/\mathrm{d}t = k(1 - \alpha)^n$ is easily integrated to give $1 - (1 - \alpha)^{1-n} = k(1 - n)t$, and substituting $(1 - \alpha)^n$ from the previous relation, with $\mathrm{d}\alpha/\mathrm{d}t = h_t v_c/A$ and

$\alpha = A_t/A$, $A = A_t + B_t$ and v_c = chart speed, the following equation is obtained in which the uncertainty in the zero time is taken into account:

$$\frac{B_t}{h_t v_c} = \frac{1}{k} - (1 - n)\Delta t - (1 - n)t .$$

Thus, if the left hand side is plotted vs. time, a straight line of slope $(1 - n)$ and intercept $1/k - (1 - n)\Delta t$ results. For a number of decompositions studied we have found values for k^{-1} ranging from 2000 to 10 000 s, and assuming 300 s as a reasonable value for Δt, we see that in the worst case ($n = 0.5$) we get a 7.5% error in the value determined for the rate constant. It is then possible, from several runs at different temperatures, even without a precise knowledge of α, to obtain an approximate value for the activation energy to be compared with the one obtained from variable temperature runs. It is to be emphasized, however, that the above method is applicable only if the shape of the thermal curve and the k value allow the approximations introduced. In any case the value found for n is the right one.

Another common feature is that a single decomposition of a particular solid takes place following a number of different kinetic stages (e.g. according to the Mampel theory). If such a decomposition is performed at a certain scan speed, the superimposition of kinetic stages, already present at constant temperature, may be so extended that normal data analysis does not allow distinction between them. In these cases the following treatment of the data is useful. Let us write

$$d\alpha/dt = A \cdot f(\alpha) \cdot \exp (-E/RT)$$

and take the logarithm: $\ln (d\alpha/dt) = \ln A + \ln f(\alpha) - \dfrac{E}{RT}$. The method is slightly different depending on whether constant temperature or variable temperature runs are used.

a) Constant temperature. In this case we need only to measure the heights (h_t) from the base-line, for the same value of the fractional decomposition, of a number of thermal curves obtained at different temperatures using the same sensitivity and amount of sample. The next procedure is to plot $\ln (h_t v_c/A)$ vs. T^{-1}. Provided the plot is linear, the activation energy for that particular value of α is obtained regardless of the form of $f(\alpha)$. As the procedure can be repeated for several values of α, it can be ascertained whether the activation energy is constant in the whole range of α, indicating a single mechanism, or different E_a values are obtained in different ranges of fractional decomposition.

b) Variable temperature. It is necessary to take advantage of the fact that a particular value of the fractional decomposition will be found at different temperatures if different scan speeds are used; in fact

$$\alpha_{(T)} = \frac{1}{ss} \int_{T_{in}}^{T} \frac{d\alpha}{dt} \, dT$$

and $f(\alpha)$ assumes the same value at different temperatures. We have found it useful to plot $\ln (h_t v_c/A)$ and T (°K) vs. α for a number of thermal curves at different scan speeds on the same graph (Fig. 5) in order to interpolate between the measured values. Again the plot of values of $\ln (h_t v_c/A)$ measured at a certain α vs. the corresponding T^{-1} values will give the activation energy at that particular α and the same considerations apply as for constant temperature.
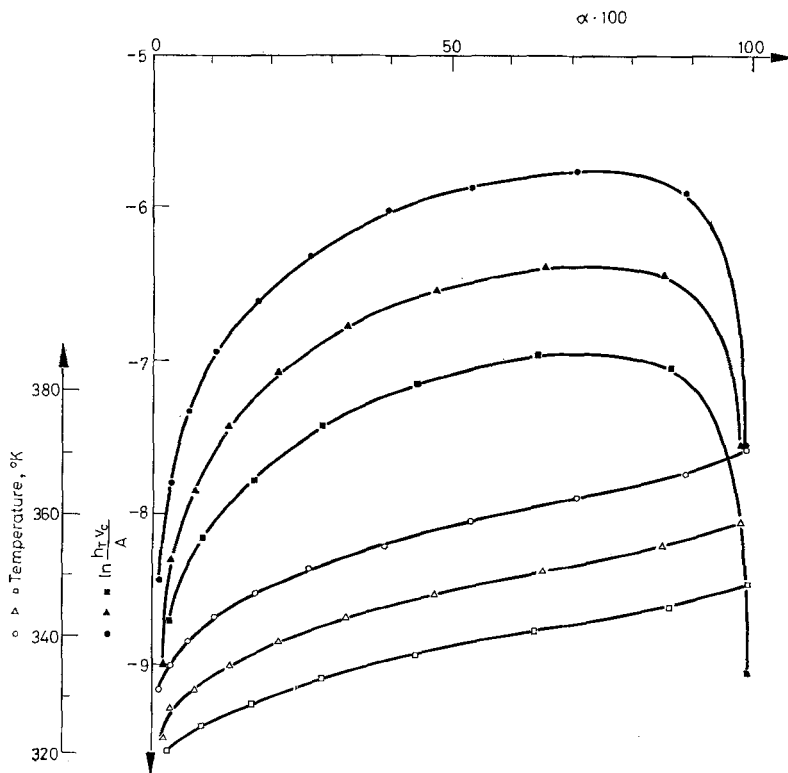

Fig. 5. Plot to obtain intermediate values of $\ln (h_t v_c/A)$ and the corresponding temperature at constant α. $K_2C_2O_4 \cdot H_2O$ 8.5 mg. $ss = 1$ °K $\cdot$ min^{-1} ■ □; $ss = 2$ °K $\cdot$ min^{-1} ▲ △; $ss = 4$ °K $\cdot$ min^{-1} ● ○

It should be noted, however, that the above method gives reliable results when the total area under the thermal curve is known with accuracy, a task which is possible only when a number of conditions are fulfilled, namely:

i) it is often necessary to use samples of the same mass;

ii) it is useful to operate with the same sensitivity, particularly for runs at variable temperature;

iii) the sample and reference should have the same thermal emissivity throughout the whole experiment.

While items i) and ii) are easily fulfilled, as regards iii) we have found it useful to add a thin layer of graphite in both the sample and the reference pans [6].

Owing to the number and complexity of factors affecting the shapes of thermal curves, some of which have been taken into account in this communication, it appears that the claimed possibility of obtaining kinetic parameters from a single run at variable temperature is to be considered with great suspicion, at least when the thermal decomposition of solids is concerned.

<p style="text-align:center">*</p>

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RÉSUMÉ — On propose quelques méthodes particulières pour rassembler et traiter les données de l'analyse calorimétrique différentielle (DSC) dans le but de déterminer les paramètres cinétiques de la décomposition des corps solides. Ces méthodes comportent surtout une extrapolation afin d'éviter l'influence de la prise d'essai, une approximation afin d'obtenir l'énergie d'activation et l'exposant de la loi de décomposition pour les expériences effectuées à température constante dans lesquelles la surface totale délimitée par la courbe n'est pas connue avec exactitude, et enfin un moyen de s'assurer si une décomposition particulière est due à un seul mécanisme ou à une succession de divers mécanismes.

ZUSAMMENFASSUNG — Einige besondere Methoden der Sammlung und Verarbeitung von DSC-Daten zur Bestimmung kinetischer Parameter bei der thermischen Zersetzung von Festkörpern werden vorgeschlagen. Diese befassen sich hauptsächlich mit einer Extrapolationsmethode um die Wirkung der Einwaage zu vermeiden; mit einer Annäherungsmethode um die Aktivierungsenergie und den Exponenten des Zersetzungsgesetzes von Versuchen bei konstanter Temperatur zu erhalten, bei welchen die Gesamtoberfläche unter der thermischen Kurve nicht genau bekannt ist; und mit einer Methode zur Bestimmung ob eine bestimmte Zersetzung durch einen einzigen Mechanismus oder durch eine Reihenfolge verschiedener Mechanismen herbeigeführt wird.

Резюме — Предложены некоторые конкретные методы сбора и обработки данных ДСК для определения кинетических параметров термораспада твердых веществ. Эти методы в основном связаны: с экстраполированием, чтобы избежать эффекта массы образца; с методом приближения, чтобы получить энергию активации и экспоненту закона распада для процессов, происходящих при постоянной температуре, когда общая площадь под кривой точно неизвестна; с методом, дающим возможность установить, происходит ли данный распад по простому механизму или имеет место последовательность различных механизмов.