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THE POSSIBILITY OF A SIMPLE TRANSFORMATION OF THERMOGRAVIMETRIC CURVES

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A simple method is suggested for the Arrhenius-like representation of the thermal decomposition of a wide variety of materials. It consists in the transformation of the TG and the corresponding DTG curves, obtained as a single measurement by a derivative thermobalance. The method consists mainly in the division of the momentary DTG ordinates by the corresponding momentary TG values, the transformation of this value into logarithmic form, and the plotting of the logarithmic expression as a $1/T$ function. In many cases a straight line results testifying to a first-order reaction or a tolerable approximation of it.

The simple method described in this paper has been found useful in evaluating the thermal stabilities of a wide variety of materials.

The method suggested is the calculative or instrumental transformation of thermogravimetric curves obtained with a derivative thermobalance. The first

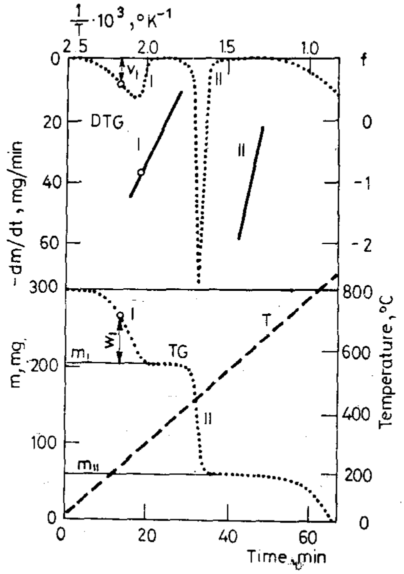

Fig. 1. TG, DTG curves and f lines of the decomposition of $Ca(COO)_2 \cdot H_2O$

step in the transformation method consists in the instrumental (or calculation) division of the momentary DTG (calibrated) values $\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)$ by the corresponding TG values (m) or by the residual weight fraction (W). The second (or parallel) step is the (instrumental) transformation of these values into logarithmic form

$$\log \frac{\frac{\mathrm{d}m}{\mathrm{d}t}}{m} = f.$$

In this way a relative rate constant is obtained in logarithmic form, plotted as a function of the temperature, eliminating the great deviation of the DTG curve from the real kinetic shape. If these data are plotted on a reciprocal temperature scale, in most cases a straight line is obtained, indicating the approximate first order of the decomposition reaction; any deviation from linearity is indicative of different kinetics or complexity. As an example, Fig. 1 illustrates the decomposition of calcium oxalate: the T, TG and DTG curves are given as usual time functions, and the f lines (see the above formula) as reciprocal temperature functions, all in the same diagram. The corresponding TG steps, DTG peaks and lines are marked by I and II. (It must be noted that these f lines are not in the same temperature position as the T and DTG curves for technical reasons.) It can be seen that the function f is not continuous, indicating that the steps of decomposition can be regarded as different reactions where the residual fraction of the material, m (in Fig. 1 w_1), becomes zero at the end of the step and so the expression $\log \frac{\mathrm{d}m/\mathrm{d}t}{m}$ becomes infinite. Figs 2 and 3 similarly illustrate polyethylene decomposition but without the T and TG curves.

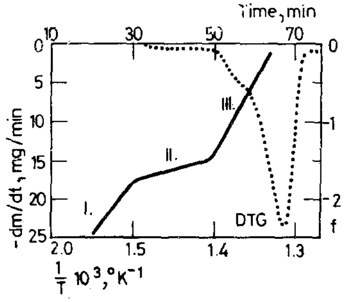

Fig. 2. DTG curve and f lines of polyethylene. Heating rate: 8°/min

Fig. 2 shows an example of a continuous f function, the line consisting of three straight sections, obtained by regarding the whole decomposition as characterized by only one residual material fraction (W). This value therefore becomes zero only at the end, resulting in a continuous line.

In Fig. 3 there is a correction of Fig. 2, on the basis of the three sectional processes marked by the linear sections of Fig. 2, obtained instrumentally. The method can be seen to have increased selectivity. The method outlined above is simple and recommended for practical use, making possible the direct Arrhenius-like interpretation of a number of thermal decomposition in both inorganic and organic systems. It is possible to carry out the measurements instrumentally, by adapter devices attached to the derivative thermobalance, but also by calculation or graphical method. The basic instrument used in these experiments was the Derivatograph.

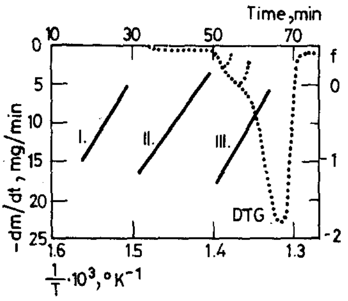

Fig. 3. DTG curve and corrected f lines of polyethylene. Heating rate: 8°/min

It is possible to "linearize" non-linear f functions by choosing a probable reaction order.

The approach by this method is fair in many practical cases, and primarily in the comparative evaluation of the thermal stabilities of materials.

RÉSUMÉ — On propose une méthode simple pour représenter la décomposition thermique d'un grand nombre de substances par une loi analogue à celle d'Arrhenius. La méthode consiste à transformer les courbes TG et TGD obtenues par une mesure unique à l'aide d'une thermobalance comportant un dispositif de dérivation. En premier lieu, on divise les ordonnées de la courbe TGD par les valeurs TG correspondantes puis on exprime ce symbole sous forme logarithmique et finalement on représente cette expression logarithmique en fonction de $1/T$, ce qui donne dans de nombreux cas une droite et prouve ainsi qu'il s'agit d'une réaction du premier ordre ou d'une approximation qui peut être tolérée comme telle.

ZUSAMMENFASSUNG — Eine einfache Methode zur Arrheniusanalogen Darstellung der thermischen Zersetzung vieler Arten von Substanzen wird vorgeschlagen. Sie besteht in der Transformierung der TG- und der entsprechenden DTG-Kurven, welche mit Hilfe einer derivierenden Thermowaage durch eine einzige Messung erhalten worden sind. Die Methode besteht hauptsächlich in der Teilung der bestehenden DTG-Ordinaten durch die entsprechenden TG-Werte, dann in der Transformierung dieses Symbols in die logarithmische Form und schließlich in der Darstellung dieses logarithmischen Ausdruckes als Funktion von $1/T$, wobei in vielen Fällen eine Gerade oder eine annehmbare Näherung einer Geraden erhalten wird, die für eine Reaktion erster Ordnung spricht.

Резюме — Предложен простой метод описания по Аррениусу термораспада большого количества разных веществ. Метод заключается в преобразовании ТГ и соответствующих ДТГ кривых, полученных на дифференциальных термовесах при одном измерении как непосредственные данные измерений. Метод, в основном, заключается в делении актуальных ординат ДТГ на соответствующие величины ТГ, превращении этой величины в логарифмическую форму и, наконец, в преобразовании полученного логарифмического выражения в виде функции 1/T. В большинстве случаев получалось линейное соотношение, свидетельствующее о реакции первого порядка или удовлетворительном приближении к нему.