Note

A method for the experimental determination of the kinetic characteristics of the thermal decomposition processes of inorganic compounds near the upper boundary of the metastable state

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Abstract

Conventional TGA apparatus cannot be applied near the upper boundary of the metastable state of a material because the low heating rates applied result in the material decomposing before high temperatures are achieved. Moreover, under these conditions the mass loss of the sample depends on the mass exchange conditions at its boundary with its surroundings.

A design for the sample container and a new method of heating it are proposed.

Studies of the kinetics of thermal decomposition of materials by thermogravimetric analysis (TGA) methods in standard apparatus with small heating rates, are not possible near the upper boundary of the metastable state of substances, as determined by the condition of the internal stability of the condensed phase $\delta^2 G = 0$. In a standard apparatus (see Fig. 1, A and B), the sample does not completely fill the crucible. In such conditions, the rate of mass loss of the sample depends on the mass exchange conditions at the boundary with the environment. Figure 1 shows, as an example, the experimental data for the kinetics of mass loss of the well known thermolysis process of $CaCO_3$, obtained with a standard derivatograph [1]. A comparison of these data with the dependence of the equilibrium pressure of CO_2 over a sample published in ref. 2, indicates that the thermal decomposition of a substance takes place at low temperatures at which the equilibrium pressure of CO_2 p_∞ is lower than atmospheric pressure, in conformity with the van t'Hoff equation. The mass decrease of a substance in such conditions depends on the pressure p_i, according to the
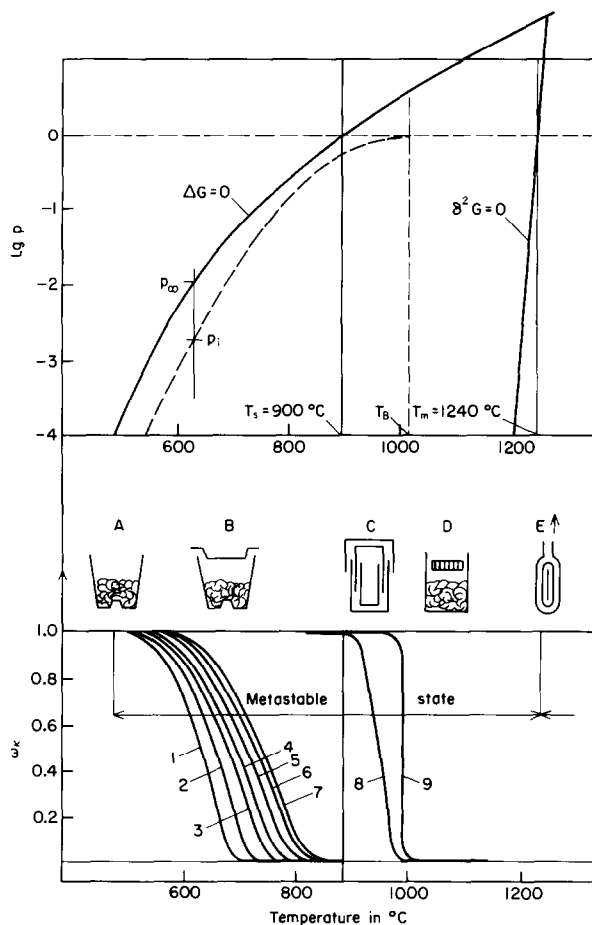
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Fig. 1. Comparison of the derivatograms (1–7) obtained at different heating rates, with zones of metastable and unstable (labile) states, for the example of $CaCO_3$ decomposition. Heating rates: 1, $0.5\,K\,min^{-1}$; 2, $1.0\,K\,min^{-1}$; 3, $2.0\,K\,min^{-1}$; 4, $3.0\,K\,min^{-1}$; 5, $4.0\,K\,min^{-1}$; 6, $5.0\,K\,min^{-1}$; 7, $10\,K\,min^{-1}$. The line $\Delta G = 0$ is the van t'Hoff binodal, $\delta^2 G = 0$ is the boundary of the metastable state, and T_m is the temperature of melting with decomposition. Shapes of vessels: A, open crucible; B, crucible with loosely fitting cover; C, labyrinth packing; D, hypothetical crucible with weightless piston; E, proposed method of packing a sample in parcels. Curves 8 and 9 are kinetic curves obtained at high heating rates of samples (more than $1\,K\,s^{-1}$).

kinetic equation [3]

$$\frac{d\alpha}{dt} = Zf(\alpha)\left(1 - \frac{p_i}{p_\infty}\right)\exp\left(-\frac{E}{RT}\right)$$

where Z and E are parameters, and p_i and p_∞ are the partial pressure of a gaseous product and the equilibrium pressure of this product over a sample.

The values of E and Z depend on p_i and p_∞. Because of the influence of

the pressure p_i on the analytical results, high temperature investigations are not possible, and an approach to the upper boundary of the temperature range of a substance's thermal decomposition cannot be achieved because it decomposes before high temperatures are reached. Another factor which prevents high temperatures from being attained are low heating rates, about 2–20 K min^{-1} in conventional derivatographs.

In refs. 4 and 5, it is shown that an increase in the sample temperature may be achieved by using labyrinth packing of a crucible, instead of a standard cover. In this case, the test temperature may exceed the equilibrium temperature T_s which is 900°C for $CaCO_3$. However, the presence of a gas over the sample at the start of an analysis, even when using labyrinth packing, causes errors in measurements. Theoretically, an ideal situation may be obtained by testing in a cylindrical crucible with a weightless piston which rises as the volume of the gas emitted increases (see Fig. 1, D). An increase in the testing temperature is favoured by an increase in the sample heating intensity, which is small in the case of convective heating.

We have proposed another design for the sample container and another way of heating it, the conductive method. Instead of a crucible with labyrinth packing, the sample is located in one or several parcels of thin metallic foil inserted into each other; the metal of the foil must not interact chemically with the sample, e.g. aluminium, nickel, gold, etc., Fig. 1, E. The gases emitted move between the foil layers in a complicated way. The dense packing prevents the spread of sample particles and their escape from the parcels. During the test, the sample is always surrounded by the gaseous products of its own thermal decomposition. In this case, up to T_s and near to it, $p_i \approx p_\infty$ and there is practically no mass loss and the reaction does not take place. The decrease in mass begins when p_∞ is considerably greater than p_i, which takes place at temperatures above T_s.

In order to obtain high rates of temperature increase, the sample parcels are placed in contact with a metallic heat-transfer medium [5]. Metallic bars preheated up to the pre-set test temperature have proved to be successful; the sample parcel is held between the ends of the bars. Conductive heating in a heat-transfer medium with a high thermal conductivity, allows sample heating rates of more than 100 K s^{-1} up to the constant test temperature to be obtained, and the thermolysis process to be shifted to temperatures considerably higher than the equilibrium temperature T_s ($T \gg T_s$). In this case, $p_\infty \gg p_i = p_{atm}$. Thus, in the kinetic equation, the factor containing the pressure becomes unity, and the mass exchange conditions do not influence the results of the tests.

Experimental data for the thermal decomposition kinetics obtained by the method of contact heating of samples are given in ref. 6. The test results for some aluminium salts have shown that the intensification of the sample heating has allowed the upper temperature boundary of the metastable
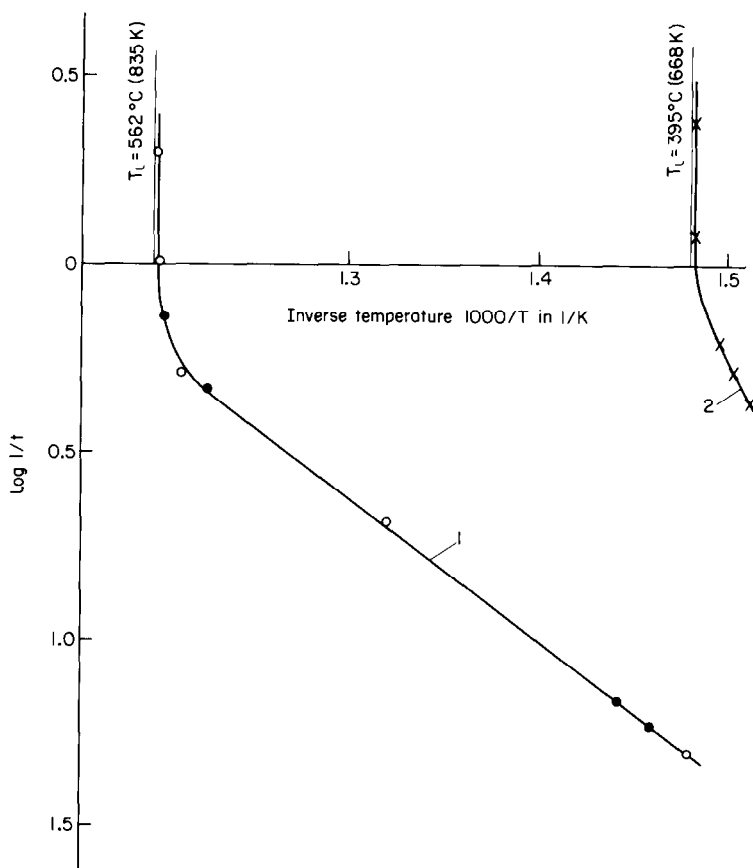
Fig. 2. Temperature dependence of the characteristic time for the termination of the last stage of the thermal decompositions of aluminium nitrate and colemanite plotted in the semi-logarithmic system of coordinates: T_l, temperature of accessible superheating, ○, experimental data from ref. 6; ●, additional studies: 1, aluminium nitrate; 2, colemanite.

state of a substance to be achieved. Such a boundary is marked by a declination in the thermolysis process rate from the rectilinear plot of the Arrhenius equation in semi-logarithmic coordinates. Figure 2 gives such a dependence for the thermolysis of the crystalline hydrate $Al(NO_3)_3 \cdot 9H_2O$. For the final stage of the thermolysis, the activation energy E is 17 kcal mol^{-1} and the pre-exponential factor Z is 1.58×10^4 s^{-1}. The temperature on the line between the metastable and unstable (labile) states of this substance was 835^{+9}_{-5} K, as determined by the position of the vertical asymptote of the plot. The temperatures of accessible overheating of linear polymers [7] and of colemanite mineral [5] have been obtained in a similar way. In contrast to the limiting temperatures of linear polymers, the determined temperature of $Al(NO_3)_3 \cdot 9H_2O$ thermolysis has another physical significance, connected with the loss in stability of the oscillations of anharmonic oscillators of a condensed substance [5].

   The results of thermal analysis with contact heating of samples have been used in the analysis of thermal treatment processes of nitrate solutions obtained after decomposition by nitric acid of different kinds of alkaline aluminosilicate raw materials, including nephenlines. Their nitric acid processing is only economically effective for the thermal treatment of nitrates, including aluminium nitrate, in a nitrogen/oxygen plasma heat-transfer medium. The thermal treatment of nitrates in plasmochemical reactors is notable for the high rates of heating (more than $100\,\mathrm{K\,s^{-1}}$) and thermolysis achieved. Therefore, the above studies could provide an adequate model of a plasmochemical reactor. Plasma/nitric acid processing of alumosilicate raw materials (both natural and contained in industrial wastes) may become a multitonnage source of alumina, a scarce raw material for aluminium production.

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