THERMOLYSIS UNDER VACUUM: ESSENTIAL INFLUENCE OF THE RESIDUAL PRESSURE ON THERMOANALYTICAL CURVES AND THE REACTION PRODUCTS*

J. ROUQUEROL and M. GANTEAUME

Centre de Recherches de Microcalorimétrie et de Thermochimie du C.N.R.S. 26, rue du 141e R.I.A., 13003 Marseille, France

This paper examines the influence of residual pressures in the range from 10^{-5} to 5 torr on the course of thermal analysis. With the help of examples concerning in particular the thermolysis of gibbsite, $Al(OH)_3$, it is shown that a) the control of residual pressure is of virtually no use unless the rate of decomposition is *also* controlled (otherwise, the TG curves represent a composite phenomenon, which is practically unintelligible); b) the influence of residual pressure may be unexpectedly high both on the shape of the TG curves (and therefore on the apparent kinetic parameters) and on the nature (porosity, structure) of the products.

The influence of the gas atmosphere on a thermal decomposition of the type solid A → solid B + gas is widely accepted. In 1951, Rowland and Lewis [1] in this way explained the usual DTA trace for calcite thermolysis, where the onset of decomposition may be observed as soon as 650° (low partial pressure of CO_2) and where "the reaction progressively becomes more vigourous until a peak is reached at about 925°", the temperature at which the reaction would begin if the furnace had been filled with CO_2 at one atmosphere pressure. In 1960, Garn suggested simplification of the situation by operating under self-generated atmospheres [2], and several devices were proposed and used in order to control the overall pressure, e.g. the "cold sink", especially convenient in the case of water evolution [3], or the discontinuous and automatic gas extractor [4]. Nevertheless, "vacuum" was often considered as *one* pressure at which it may be worthwhile to carry out one experiment in order to complement a set of data obtained under higher pressures. Indeed, various authors, such as Eyraud *et al.* at the time of the first vacuum TG experiments, pointed out the "simplifying" part played by vacuum-operation, which was supposed to eliminate disturbing phenomena such as adsorption or diffusion processes [5] or secondary reactions [6] and to give rise to the simplest mechanism with higher decomposition rate [7]. Now pressures lower than 1 torr, which are usually referred to as "vacuum", actually cover a wide experimental range, down to 10^{-13} torr, whereas the range of medium and

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high pressures goes from about 1 to 10^7 torr. Is the importance of the low pressure range the fiction of a logarithmic representation, or does it cover a physical reality? This is what we shall try to examine here.

Experimental approach

Preliminary remarks

If our goal is to observe the influence of low pressures on thermal decompositions, we must set and control all other parameters able to influence the thermal process. Among these, we must of course mention:

— the grain size and shape,
— the composition of the gas atmosphere,
— the heating rate.

We mention the heating rate since this is a basic parameter in thermal analysis, but in fact we also know that it is *not* a well-defined parameter at the place where the reaction occurs, *i.e.* on the reaction interface. Indeed, at any time of the experiment, the heating rate is responsible for a temperature gradient, itself more or less enhanced or cancelled by the thermal effect due to the reaction enthalpy. Moreover, in one given grain of the sample, the temperature increase normally results in an acceleration of the decomposition rate. Unfortunately, owing to the previously-mentioned temperature gradient (which depends on the thermal conductivity and packing of the sample — which may both vary during the thermal decomposition —, on the pressure and composition of the gas, on the part played by radiation thermal transfers — which are themselves temperature-dependent — and on the rate of decomposition . . .), *the temperature at each point* of the sample and at any time *is normally unknown*, whereas the overall measured decomposition rate is a mean which very often results in the well-known — but not always significant - sigmoïd TG curve. For us to achieve a better insight into the elementary mechanism, just like the grain size or the gas composition, *the decomposition rate must be identical for each grain of the sample.* The reaction interface must advance in each grain at the same rate. This needs a very high homogeneity of temperature and pressure in the sample, which may be obtained either with extremely small samples (with problems of sampling and accurate weighing) or with a procedure giving rise to slow and controlled decomposition rates.

Experimental procedure

From what was said above, one may guess that we do not advocate a method in which the heating rate is constant, but a method in which the rate of decomposition is low and constant. The general method ("Constant decomposition rate thermal analysis") was described elsewhere [8]. In its principle, *this method only*

needs to monitor the heating of the sample with any parameter depending on the rate of decomposition: for instance, a flow of evolved gas, a DTG signal or also a thermal flow. Soon afterwards Paulik and Paulik [9], applying a former idea they had [10], developed the DTG approach, which they called "quasi-isothermal thermogravimetry". This approach is the most convenient under medium and high pressures, but in the low pressure range the gas flow control is more sensitive
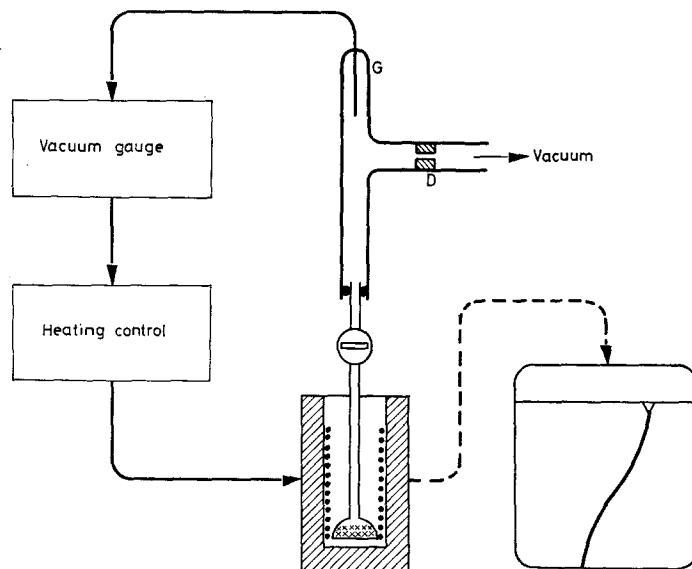

Fig. 1. Principle of the gas pressure and gas flow control used by the authors (constant decomposition rate thermal analysis). *G:* pressure gauge, *D:* diaphragm

and adds the advantage of a *pressure control,* as is easily understood from the diagram of Fig. 1. We currently use this technique for pressure controls in the range from 10^{-5} to 5 torr and for decomposition rate controls corresponding to a mass loss as low as 1 *micro*gram per minute, if necessary.

Typical results

Influence of residual pressure on thermoanalytical curves

Figure 2 shows two TG curves obtained for identical amounts of gibbsite, $Al(OH)_3$, but under different "vacuum" conditions [8]. The lower curve, obtained by conventional TG, shows that the main part of the dehydration takes place from 150 to 300°. The upper curve, obtained by the method described above, shows a nearly vertical fall, the dehydration taking place from 170 to only 200°. The latter curve clearly indicates a nearly zero-order reaction, which is explained by

the advance of a constant-area reaction interface, parallel to itself and to the larger side of the flat, hexagonal, gibbsite elementary crystals, themselves conglomerated into larger grains [11]. Because of the uncontrolled residual pressure and temperature gradients, the conventional TG curve is completely misleading: these gradients drown any mechanism at the elementary particle scale. This complete change of shape of the TG curve is very similar to that observed shortly later under atmospheric pressure by Paulik and Paulik, either with calcium carbonate [9] or with calcium oxalate monohydrate [12], with the help of their "labyrinth-shaped crucible" which ensured a good atmosphere control.
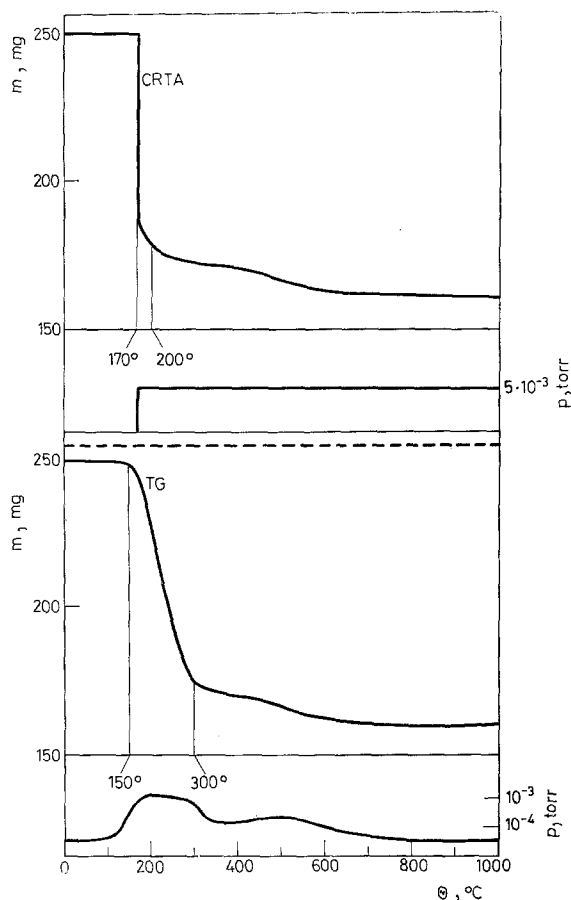

Fig. 2. Influence of pressure and heating conditions on the "vacuum" TG curve of 250 mg, industrial gibbsite. Above: constant residual pressure and constant decomposition rate, (13.5 mg h^{-1} g^{-1}; below: conventional dynamic vacuum TG experiment (heating rate; 0.5 K min^{-1}) (from [8])

Figure 3 allows comparison of the influences of residual pressure (left side) and of grain size (right side) on the TG curves of gibbsite, and illustrates the need of a careful control of all parameters. A higher grain size (50–80 μm) and a higher water vapour residual pressure (5 torr) have similar influences: they give rise to a bump (cde) in the curve, which is explained by the thermal decomposition (de) of a boehmite, AlO(OH), phase previously formed (ab). This boehmite formation
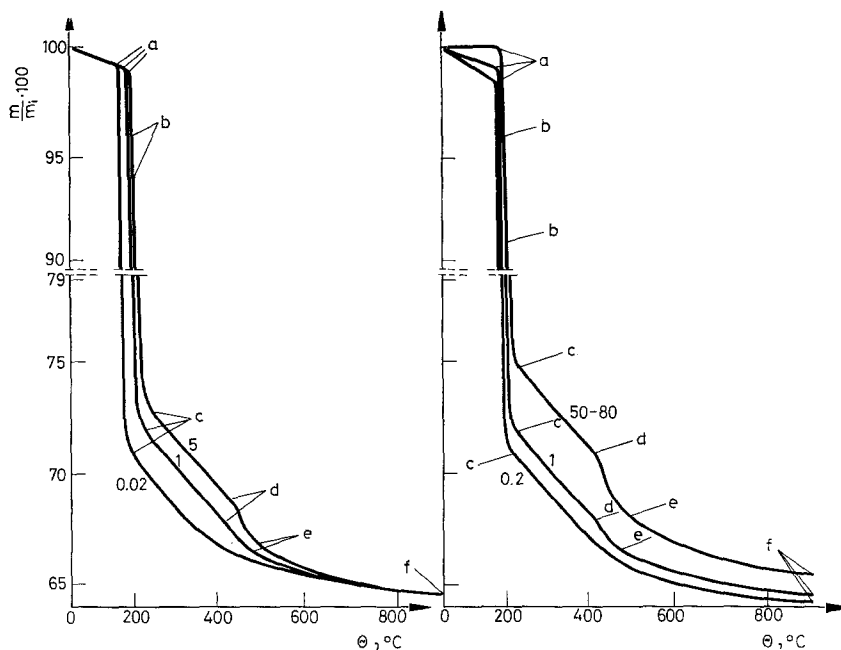

Fig. 3. Influence of residual pressure (left side) and of grain size (right side) on the TG curve of gibbsite (decomposition rate: 11.5 mg h^{-1} g^{-1}). Left side: 1 μm grain size sample, pressures indicated in torr; right side: 1 torr pressure, grain size indicated in μm (from [13])

is possible because of the hydrothermal conditions which may be found in the core of the crystals; under a constant decomposition rate, the temperature necessary for this transformation may be reached if the rate of departure of water vapour is lowered (i) by a small surface area and/or (ii) by a difficult desorption (obtained by an increase in pressure). In the examples given, the specific surface area varies from 0.14 to 15 m^{2}g^{-1}, and the pressure range is one at which strong water adsorption on micropores may already be observed.

Among other results illustrating similar situations, we may refer, for instance, to those obtained by Acher et al. [14] who observe a drift which may reach 75 K on the TG dehydration curve of kaolinite when the water vapour pressure is increased from 10^{-3} to 47 torr (with the use of a "cold sink"). These authors are

aware of the fact — often disregarded — that the starting vacuum of 10^{-6} torr cannot be maintained when the reaction begins. As Garn [15] points out: "it is popularly supposed that if one withdraws gases from a chamber by continuous pumping, the pressure is everywhere equal to the indicated pressure . . . If there is a source of gases, the supposition is invalid". In another work dealing with serpentine dehydroxylation [16] the same authors explain the strong influence of low water pressures on the apparent activation energy by a fractional coverage (depending on temperature and pressure) of the reacting surface by chemisorbed water. A similar explanation holds for the dehydroxylation of silica gels, for which the conventional isothermal method for determining the apparent activation energy under vacuum does not yield a reproducible result: the amount of adsorbed water (strongly dependent on pressure in the low pressure range) plays an important part in the dehydroxylation process. Only with the constant decomposition rate method (used with a residual pressure of $5 \cdot 10^{-5}$ torr) could a clear correlation be found between the apparent energy of activation of the dehydroxylation and the extent of dehydroxylation (itself linked with the surface hydroxyl concentration) [17].

A last curious example of the strong influence of low pressures on a dehydration is known as the Smith—Topley effect [18] : instead of increasing steadily as the pressure is lowered, the rate of dehydration goes through a minimum for a given low pressure (usually located between 0.1 and a few torr). Much work was recently carried out by Watelle et al. [19] on this effect, also recently observed by Dollimore et al. in the case of magnesium oxalate dihydrate dehydration [20]. Nevertheless, it seems that the phenomenon is only observed under highly irreversible conditions, and that it may be explained, by the thermodynamics of irreversible phenomena, in terms of heat and mass tranfers [21]. To illustrate the ideas, let us say that the phenomenon is observed when the rate of advance of the reaction interface is of the order of magnitude of at least 1 mm per hour. In the experiments reported in Figs 1 to 3, even the higher rate of advance of the reaction interface (coarse $0.14 \text{ m}^2\text{g}^{-1}$ sample, 11.5 mg $\text{h}^{-1}\text{g}^{-1}$ decomposition rate, left side of Fig. 3) is 25 times lower.

Influence of residual pressure reaction products

Figures 4 and 5 give a striking illustration of the influence of low water vapour pressures on the texture of the reaction products. The specific surface areas were measured by the BET method, using nitrogen as the adsorbate and *keeping the sample in the same glass bulb for the thermal analysis and for the adsorption measurements;* this is indeed an interesting feature of the constant decomposition rate thermal analysis with pressure control: at the end of the thermolysis the sample is kept under vacuum in its bulb, and it may be attached later to a gas volumetric apparatus. Under these experimental conditions, which completely avoid any water re-adsorption, the influence of water vapour pressure during the dehydroxylation is as follows:

a) the maximum specific surface area available to nitrogen drops from $430 \text{ m}^2\text{g}^{-1}$ (obtained under 5 torr) down to $40 \text{ m}^2\text{g}^{-1}$ (obtained under $4 \cdot 10^{-2}$ torr); moreover, under $2 \cdot 10^{-4}$ torr no increase at all in the specific surface area was observed for an extent of reaction of 60%;
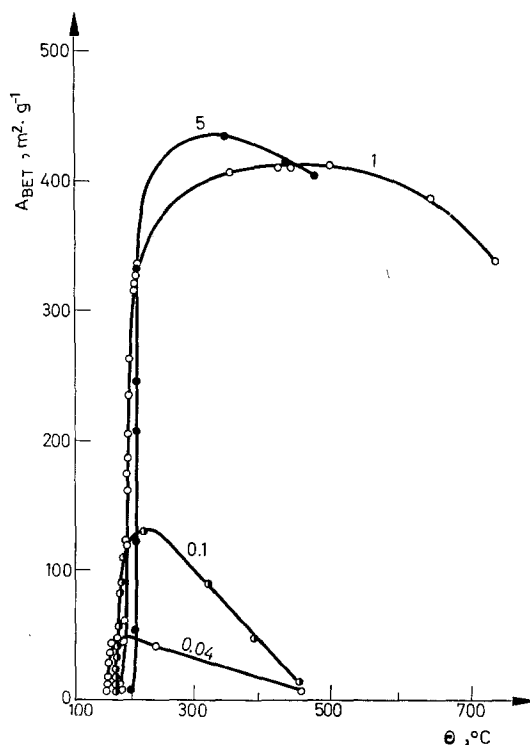

Fig. 4. Development of the specific surface area of a gibbsite sample (grain size: 1 μm) during its thermal decomposition under various water vapour pressures (in torr) and at a constant decomposition rate (16 mg h^{-1})

b) apart from a first stage (5% of the decomposition, during which the boehmite phase is formed), the specific surface area is a linear function of the mass loss.

Both observations are interpreted by a mechanism where the micropores of the product are drilled in the gibbsite crystal at the site of very narrow "structural channels" in the gibbsite structure. These channels are parallel to each other (and perpendicular to the reaction interface) and the final micropore diameter depends on the mobilities of the Al^{3+} and H^+ ions: these mobilities increase with the decomposition temperature, itself depending on the pressure. As regards the decomposition temperature, we may notice that in a general case (which also holds here) it depends (for a given extent of reaction) on:

a) the equilibrium pressure of the system, which must reach a value higher than

the surrounding pressure (supposed to be of the same gas). These variations of (equilibrium) temperatures with (equilibrium) pressures may be derived from the Van't Hoff equation if we know the reaction enthalpy (if only one gas is produced, then $\dfrac{\partial}{\partial T}\ln p = -\dfrac{\Delta H_2}{RT}$). For instance, if the equilibrium pressure of the reaction $CaCO_3 \rightarrow CaO + CO_2$ is 10^{-4} torr at $500°$ (from a curve given in [22]) and if
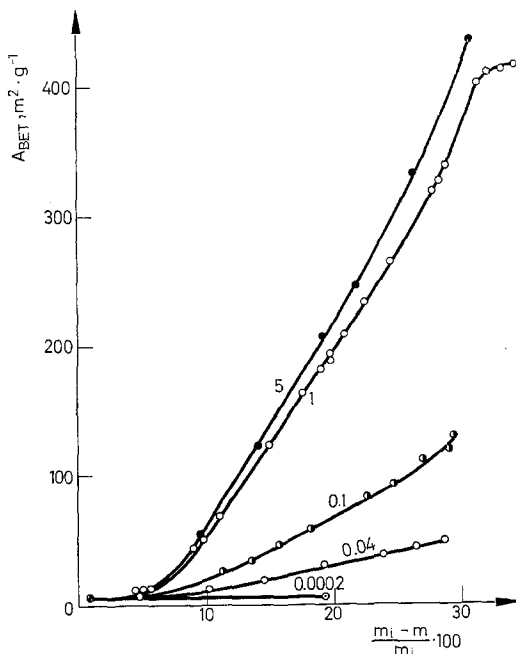

Fig. 5. Same as Fig. 4 but plotted versus the mass loss (as a percentage of the initial mass m_i)

the enthalpy of reaction is 160 kJ mole^{-1}, then under 1 torr the equilibrium temperature ought to be $950°$: actually, this is around the decomposition temperature observed under 1 atmosphere pressure. Our predictions fail because even with very low decomposition rates the system is not under equilibrium conditions and because of the two following parameters;

    b) the affinity of the solid product for the gas evolved;

    c) the actual reaction rate, linked with the decomposition temperature through the apparent activation energy.

    In other words, the decomposition temperature depends on the pressure through the equilibrium pressure of the reaction and through the equilibrium pressure of the secondary adsorption.

    The influence of water vapour on recrystallisation processes has often been pointed out, even at low pressures (for instance in the case of magnesium hydroxide

decomposition [3]). In the case of the 1 μm gibbsite sample, at the end of the main dehydroxylation stage (*i.e.* at point "*c*", Fig. 3) we obtain:

— a completely amorphous alumina (from the X-ray diffraction pattern) if the dehydroxylation takes place under $4 \cdot 10^{-2}$ torr,

— a slightly crystallized alumina (ρ-alumina, with one weak peak at 1.40 Å) under 1 torr,

— an even better crystallized χ-alumina under 1 atmosphere.

Concluding remarks

In conclusion, we should like to draw attention to the following points:

1. Vacuum alone is not enough to give good kinetic data. As noted by Garn, in an ordinary vacuum experiment "It is . . . likely that the reaction is actually proceeding at a pressure which is substantially above that of the vacuum chamber . . . This means that the decomposition kinetics as learned in hard vacuum may have little meaning." However, we have experienced that the kinetic data are strongly simplified if the three following conditions are fulfilled:

a) *self-generated atmosphere* (operation under a dynamic vacuum is only a particular case);

b) *constant pressure control* (especially to control the extent of secondary adsorption);

c) *low rate of decomposition;* the best way to achieve the latter is to control and to keep constant the rate of decomposition, and therefore to use constant decomposition rate thermal analysis.

2. It is important to focus our attention on the thermoanalytical curves, since these are the raw experimental material from which the understanding of a decomposition mechanism may start. Nevertheless, above all, we must avoid starting from too raw a material, *i.e.* too raw a curve. These curves, which are based on a macroscopic measurement, must be representative of the elementary process taking place in each elementary grain of the sample. This cannot be achieved if conditions b) and c) above are not fulfilled.

3. The ease of handling of most thermal analysis apparatus normally leads to quick experiments. Unfortunately, thermal analysis is not a passive experiment: it destroys the sample and, in order to yield clear information on the destruction process, it must perform it progressively and slowly. Just as the biologist who finds it normal to follow the rhythm of life in his experiments, the physicochemist could ask himself, before any thermoanalytical experiment, whether, for a clear understanding, the sample needs some care in the introduction of the necessary stresses and some time in the observation.

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Résumé — On examine l'influence des pressions résiduelles comprises entre 10^{-5} et 5 torrs sur le cours des décompositions thermiques. Grâce à des exemples concernant en particulier la thermolyse de la gibbsite $Al(OH)_3$ on montre: a) qu'un contrôle de la pression résiduelle n'est utile que si l'on peut *aussi* contrôler la vitesse de décomposition (sans quoi les courbes de TG représentent un phénomène composite inextricable); b) que l'effet de la pression rési- duelle peut être extrêmement important, aussi bien sur la forme des courbes de TG et donc sur les paramètres cinétiques apparents) que sur la nature (porosité, structure) des produits

Zusammenfassung — Der Einfluß von Restdrücken zwischen 10^{-5} und 5 torr auf thermische Zersetzungen wird geprüft. An Hand von Beispielen, insbesondere hinsichtlich der Thermoly- se von Gibbsit $Al(OH)_3$ wird gezeigt, daß a) eine Regelung des Restdruckes nur dann von Nutzen ist, wenn auch die Zersetzungsgeschwindigkeit geregelt werden kann (ansonsten stellen die TG-Kurven ein nicht zu entzifferndes komplexes Phänomen dar) und daß b) die Wirkung des Restdruckes äußerst bedeutend sein kann, sowohl hinsichtlich der Gestalt der TG-Kurven (also der scheinbaren kinetischen Parameter), als auch der Beschaffenheit (Porosität, Struktur) des Produkts.

Резюме — Исследовано влияние остаточных давлений в области от 10^{-5} до 5 торр на ход термического анализа. С помощью примеров, касающихся термолиза спеиального $Al(OH)_3$, было показано: а) контроль остаточного давления почти бесполезен, если ско- рость разложения не контролируется (в противном случае, кривые ТГ представляют слож- ное явление, практически неразборчивое), б) влияние остаточного давления может быть неожиданно большим как на форму кривых ТГ (и следовательно на кажущиеся кинети- ческие параметры), так и на природу (пористость, структура) этих продуктов.