

CRITICAL EXAMINATION OF SEVERAL PROBLEMS TYPICALLY FOUND IN THE KINETIC STUDY OF THERMAL DECOMPOSITION UNDER VACUUM

J. ROUQUEROL

*Centre de Recherches de Microcalorimétrie et de Thermochimie du C.N.R.S.,
Marseille, France*

After considering several problems peculiar to the kinetics of thermal decomposition under vacuum (formalism, separation of successive steps, influence of residual pressure and of heat or mass transfers) the author suggests, as a possible answer, the use of constant decomposition rate thermal analysis, in association or not with thermogravimetry or calorimetry. The interest of the method is shown for the following measurements: apparent orders of reaction, energies of activation, differential enthalpies of dissociation. It appears to be specially suited to the study of thermal decomposition under high vacuum.

A great deal of quantitative or semi-quantitative information on the thermal decomposition of solids has been obtained during recent years from the development of many thermal analysis apparatuses of high sensitivity. Nevertheless, even to-day, it is often difficult to derive satisfactory kinetic data for these thermal decompositions from the former results. This can be illustrated for the well-known thermal decomposition of calcium carbonate, for which the published activation energies range from 146 to 960 kJ · mole⁻¹ [1]: such a spread emphasizes the special requirements of kinetic studies with regard to the quality of thermal analysis curves. This leads to the two following questions: 1. What conditions must be fulfilled in a thermal decomposition experiment to make it useful for a kinetic study? 2. What is the most advisable procedure: the isothermal one (reported in most treatises on heterogeneous kinetics published to date), or the non-isothermal one, which is increasingly popular and for which several authors have prepared the necessary formalism [2]?

In order to answer these questions at least partly, we shall first review different problems typically linked with the kinetic study of thermal decomposition under vacuum, and then give the way we have chosen to solve them.

A. Problems arising from the kinetic study of thermal decomposition under vacuum

1. Problems peculiar to heterogeneous kinetics

a) Aims and techniques of heterogeneous kinetics

Since studies on heterogeneous kinetics always try, in one way or in another, to follow the advance of a reaction interface, it can be said that the final object is to understand the reaction mechanism on that interface. Nevertheless, this

mechanism is often screened by other phenomena which can be responsible for a limiting step: these must therefore be studied, either to eliminate or to take advantage of them.

In heterogeneous kinetics we try to achieve this goal by studying the influence of various parameters (temperature, pressure, degree of completion of the reaction, properties of the starting sample) on the reaction rate. There is considerable interest in those techniques which display a signal proportional to the reaction rate (like those which allow measurement of heat flow or gas flow). Those allowing the measurement of integral quantities (thermogravimetry for instance) need to be especially sensitive and accurate in order to allow satisfactory derivation of their signal.

b) Problems of formalism

If the degree of completion of the reaction α is defined as the ratio of the mass of starting sample already transformed to the total mass at the beginning of the experiment, the rate of reaction can be written in the form:

$$\frac{d\alpha}{dt} = k(T) \cdot f(1 - \alpha) \cdot g(P).$$

Let us now consider the problems arising when an attempt is made to evaluate the different terms of this relationship from actual experiments.

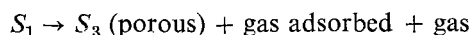
Consider the degree of completion of the reaction α . In the simple case when the thermal decomposition is of the type $S \rightarrow \text{gas}$, the degree of completion of the reaction is given by the relationship:

$$\alpha = \frac{m_0 - m}{m_0}$$

where m_0 is the initial mass of the sample and m its instantaneous mass. In the more usual case of a thermal decomposition of the type $S_1 \rightarrow S_2$ (not porous) + gas, the degree of completion of the reaction can be written:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty}$$

where m_∞ is the mass of the sample at the end of the thermal decomposition. The experimental measurement of m_∞ is often necessary to check whether the thermal decomposition has followed the stoichiometry of the expected reaction. It may well be that in isothermal experiments the reaction does not go to completion: in such a case, m_∞ cannot be correctly measured. Finally, in the more common case of a thermal decomposition of the type:



it becomes very difficult to determine α accurately from the instantaneous mass. It must then be assumed that the percentage of gas adsorbed remains constant

throughout the thermal decomposition. This would be acceptable if at least the temperature and the partial pressure of gas could be kept constant during the thermal decomposition: theoretically, these conditions are only fulfilled in the case of a reaction of formal order zero with respect to $(1 - \alpha)$. Nevertheless, the variation of these two parameters should be reduced as much as possible during a given step of the thermal decomposition.

As regards the temperature function $k(T)$, this can be accepted as following the Arrhenius law, and may then be written in the form:

$$k(T) = a \cdot \exp(-E/RT).$$

This means, of course, that the rate of reaction is limited by a thermally activated phenomenon (which may be for instance gas diffusion in micropores, chemical desorption, or diffusion of ions in the vicinity of the reaction interface).

Let us now come to the pressure function $g(P)$. In practice, it appears advisable to consider not the total pressure, but the difference $P - P_0$ between the equilibrium pressure P_0 of the transformation and the partial pressure P of the same gas in the neighbourhood of the solid. Unfortunately, $g(P_0 - P)$ is a function of two parameters which cannot be dissociated: the temperature (which determines P_0) and the pressure. A means of simplifying the situation is to select a case where P remains negligible compared with P_0 . This can be achieved either by operating under vacuum or by using a gas flow *through* the sample. The function is then simplified to $g(P)$, which may be assumed as P_0^m (m , order with respect to pressure). If it is assumed that P_0 follows Van't Hoff's law we arrive at a relationship of the type:

$$P_0^m = b^m \exp(-m \Delta H/RT).$$

This expression may be included in the temperature function $k(T)$. The reaction rate can then be written as follows:

$$\frac{d\alpha}{dt} = ab^m \exp\left(-\frac{E + m\Delta H}{RT}\right) \cdot f(1 - \alpha)$$

$$\frac{d\alpha}{dt} = A \exp(-E_a/RT) \cdot f(1 - \alpha)$$

where E_a is the apparent energy of activation. The term $m\Delta H$ can be considered as the energy of activation of the "pure" chemical reaction occurring on the reaction interface, whereas the term E concerns another activated step.

c) Problems of isolation

Every time a thermal decomposition includes several steps (as is often observed in inorganic chemistry for hydrates, hydrocarbonates, oxalates, and even hydroxides), it is essential to *separate these stages* as well as possible. It is sometimes useful to seek the pressure and temperature conditions favouring the existence of an intermediate state. Nevertheless, an even more general rule is to keep the

reacting system in a state as close as possible to thermodynamic equilibrium: the best synchronism between the reactions occurring at different points of the sample is then achieved, and the best separation between the successive steps is then observed. This is obtained by means of very low decomposition rates.

After the successive stages are isolated, one must also isolate the influences of the different parameters: this usually leads to a "degeneration" procedure, by which all parameters but one are kept constant.

It must be possible to maintain constant not only the temperature but also the partial pressure of the gas evolved or the degree of completion of the reaction: the latter condition again necessitates low decomposition rates.

2. Problems raised by vacuum experimentation

a) Reasons for vacuum experimentation

The study of thermal decomposition under vacuum (or, more precisely, under low pressure) appears to be advantageous from various aspects.

First of all, when the gas produced by the thermal decomposition is the only gas in the system, it is possible to know its true pressure in the immediate neighbourhood of the sample; this is usually impossible during thermal decomposition in the presence of other gases (carrier gases for instance).

Moreover, if that pressure is low enough, it may be neglected compared with P_0 , in order, as we have seen, to simplify the kinetic study.

At the same time another simplification may result, for instance from the elimination of a limiting step such as desorption: a new aspect of the mechanism

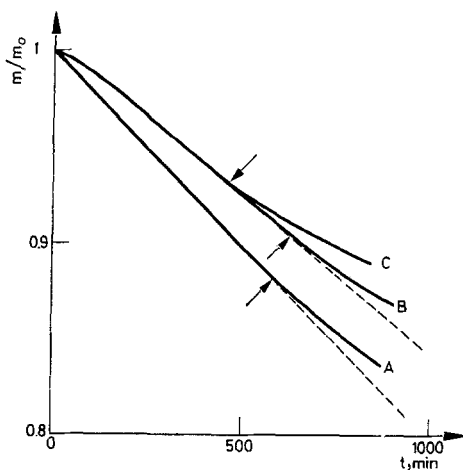


Fig. 1. Study by isothermal thermogravimetry (164 °C) of the thermal decomposition of an industrial gibbsite $\text{Al}(\text{OH})_3$ under low pressure (A: 10^{-5} Torr, B: $3.5 \cdot 10^{-5}$ Torr, C: 10^{-3} Torr)

of the thermal decomposition can then be discerned. Fig. 1 shows how, in the isothermal thermal decomposition (at 164 °C) of a sample of gibbsite $\text{Al}(\text{OH})_3$, the induction period may be completely eliminated (curve A) if the pressure is kept lower than $3.5 \cdot 10^{-5}$ Torr. This involves a second simplification which will be seen later.

It therefore appears that a minute change in pressure (from $3.5 \cdot 10^{-5}$ Torr down to $1 \cdot 10^{-5}$ Torr) is enough to modify the kinetics of the reaction. The porosity of the resulting alumina was observed to be strongly dependent on the pressure, even when the latter remained within the range usually called vacuum [3]. This is why we believe that the control of pressure during a thermolysis is as important in that range as in the range of higher pressures for which the control is more usual.

b) Problem raised by gas diffusion

Several authors have paid special attention during recent years to the disturbing influence of unavoidable pressure gradients on the kinetics of thermal decomposition. These gradients have to be considered from the aspects of the powder and the grain. In both cases, the lower the pressure the higher the relative importance of the gradients [4].

Let us first consider the pressure gradients within the powder bed. In an approximate estimation, Anderson et al. [5] point out that overpressures of several Torr are often unavoidable even in a sample 1 mm thick which is decomposed "under vacuum". It was shown by Barret [6] that the advance of the reaction interface does not take place in accordance with the dimensions of the grain, but with those of the crucible. It follows that the apparent order of reaction depends only on the shape of the crucible and the arrangement of the powder (Fig. 2).

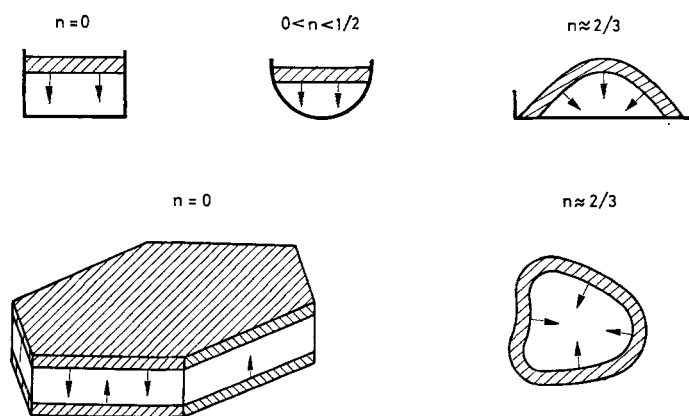


Fig. 2. Formal orders corresponding to different kinds of advance of the reaction interface, either according to the dimensions of the powder (upper part) or to those of the grain (lower part)

It is worth noting that this internal overpressure often blows the sample out of the crucible. This effect may be eliminated by the use of a glass-wool pad or glass-frit: in these circumstances it is not correct to speak of "vacuum". Here again it appears necessary to operate at low decomposition rates (in order to reduce the gradients).

If the conditions are such as to make the pressure gradient in the powder negligible, and to allow a simultaneous reaction of all the grains, it is then necessary to consider the diffusion of gas through the layer of product coating each individual grain. In the case of a porous or microporous ($r < 2$ nm) product, it must be checked that the overpressure in the pores (*i*) does not change the reaction and (*ii*) is the same at any time at all points of the reaction interface. The porosity of the product must therefore be extremely uniform throughout the sample.

c) Problems due to thermal diffusion

Those who are familiar with differential thermal analysis know that the temperature difference between the external surface and the center of the sample, which is only partly measured in DTA, is rarely less than several °K. This difference is due, in part, to the sample not closely following the temperature programme of the furnace. This thermal lag is usually not detected, as a result of the differential arrangement. The other reason for a temperature gradient in the frequent case of an endothermic thermal decomposition is, of course, the cooling occurring from the reaction itself. For a 50 mg sample of magnesium hydroxide arranged in a cylindrical crucible 3.5 mm in diameter (Fig. 3) and dehydrated in 15 minutes, the self-cooling can be estimated to produce a temperature difference ΔT of about 1.5 °K.

Let us now suppose that, in order to measure the energy of activation of the former thermal decomposition, a second experiment is carried out at a decompo-

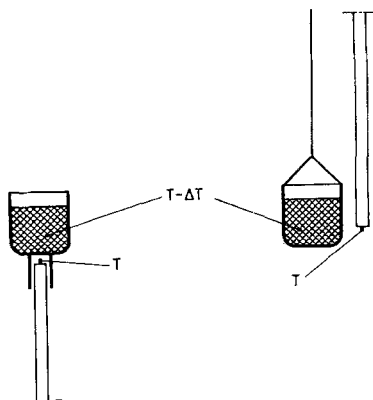


Fig. 3. Temperature difference between the temperature detector (T) and the middle of the sample ($T - \Delta T$)

sition rate 5 times lower and at a temperature 10 °K lower. The temperature gradient in the sample will be 5 times smaller and the error made with the temperature detector will be decreased to 0.3 °K. The mean temperature variation of the sample will therefore be measured with an error of about 0.5 °K. The resulting error in the energy of activation will be about 5%, even in the favourable case where the sample is small. The error would be 3 times bigger for a 150 mg sample. This example shows again the usefulness of a low reaction rate procedure.

B. A possible answer: constant decomposition rate thermal analysis

1. Principle and technique

a) General principle

It has been seen that several problems in the kinetic study of the thermal decomposition of solids (isolation of steps, keeping of the degree of completion of the reaction close to a given value, gas diffusion and thermal diffusion) can be solved if the thermal decomposition rate dx/dt is controlled and kept at low value. This is achieved by means of a special type of thermal analysis: instead of the usual control of the furnace heating to follow a temperature programme, a quantity directly related to the decomposition rate is kept constant. This quantity may be, for instance, a gas flow, a thermal flow, or a signal of derivative thermogravimetry [7]. The advantage of perfectly measuring and controlling the decomposition rate in a kinetic study can easily be conceived.

b) A constant and self-generated gas flow apparatus

The arrangement of such an apparatus is given in Fig. 4. The sample is permanently connected to the pumps through a diaphragm D. The residual pressure (from the gas evolved) is measured by means of the gauge G. To keep constant the flow of gas through the diaphragm, the up-stream pressure must be kept constant. This is achieved by *monitoring the furnace heating by the output signal of the gauge*. It follows that the thermal decomposition is then carried out both under constant residual pressure and at constant decomposition rate (since the gas flow through the diaphragm originates only in the thermal decomposition). The recording of the sample temperature as a function of time, that is to say as a function of the mass lost by the sample, is in many respects similar to a thermogravimetric recording. The possibilities of such an apparatus have been mentioned elsewhere [7].

c) Association with thermogravimetry

One way of associating thermogravimetry with constant decomposition rate thermal analysis is to monitor the heating of the furnace by means of a signal of derivative thermogravimetry. This is represented in Fig. 5 by "Loop I".

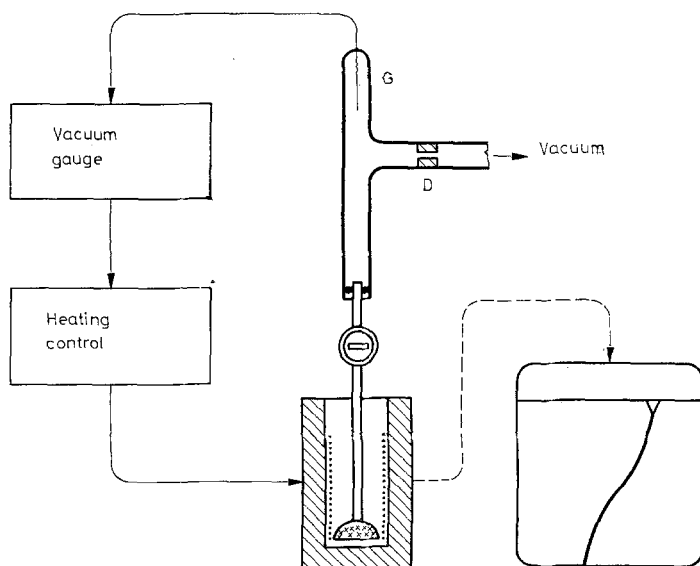


Fig. 4. Principle of a thermal analysis apparatus working under a constant self-generated flow of gas

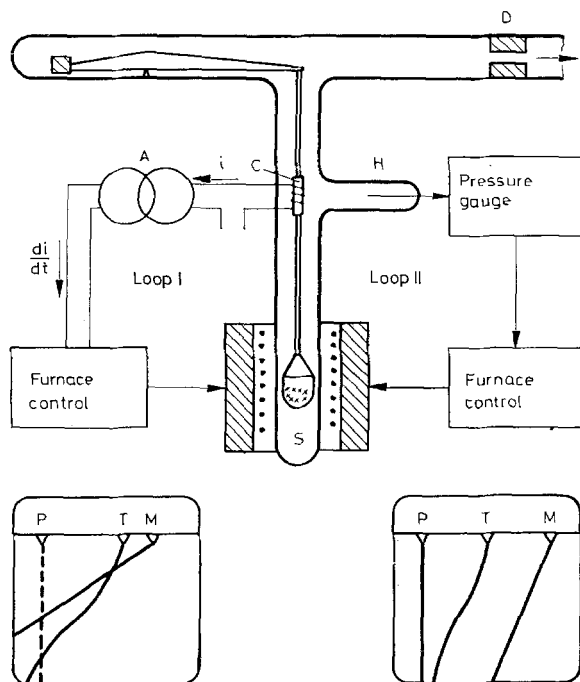


Fig. 5. Two means of association of thermogravimetry with thermal analysis at constant decomposition rate (Loop I: by controlling the signal of derivative thermogravimetry; Loop II: by controlling the flow of gas)

This kind of association was adopted by Paulik and Paulik [8] in their "quasi-isothermal" arrangement. Nevertheless, the sensitivities of the balance and of the deriving system call for a minimum decomposition rate [7].

A second possible way is to control the gas flow generated by the thermal decomposition [9], as represented in Fig. 5 by "Loop II". The lower the pressure, the higher the sensitivity of the control: for instance, during the recording of Curve I

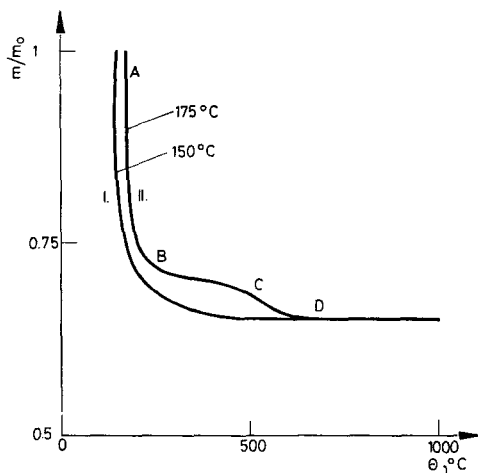


Fig. 6. Thermal analysis of gibbsite $\text{Al}(\text{OH})_3$ at constant decomposition rate (Curve I: $P = 4 \cdot 10^{-6}$ Torr; $m = 30$ mg; $dm/dt = 0.15$ mg \cdot h $^{-1}$. Curve II: $P = 1.5 \cdot 10^{-2}$ Torr; $m = 230$ mg; $dm/dt = 3.5$ mg \cdot h $^{-1}$)

in Fig. 6 ($P = 4 \cdot 10^{-6}$ Torr) the gas flow was kept, without the least trouble, at 0.15 mg \cdot h $^{-1}$, that is to say at a level about 100 times lower than that achievable by a derivative thermogravimetry system.

In our opinion, the choice between these two types of control depends on the pressure range selected for the experiment: for pressures higher than 10^{-2} Torr, Loop I may be more suitable, whereas for pressures lower than 10^{-2} Torr, Loop II leads to a much higher sensitivity.

2. Application to the kinetic study of thermal decomposition

a) Measurement of the formal order of a reaction

In order to bring out the meaning of the formal order of a heterogeneous reaction, let us write down again the expression of the reaction rate:

$$\frac{d\alpha}{dt} = k(T) \cdot f(1 - \alpha).$$

This expression holds when the pressure above the sample is negligible compared with the equilibrium pressure. The term $k(T)$ which includes the apparent energy of activation, can be assimilated to a "specific rate of advance of the interface" in the definition given by Delmon [10] (number of moles transformed per unit interface area per unit time).

In this case, the term $f(1 - \alpha)$ represents the variation of the interface area as a function of the degree of completion of the reaction, that is to say as a function of the volume of the undecomposed sample. If we write:

$$f(1 - \alpha) = (1 - \alpha)^n$$

we see that the formal order n , which gives the relationship between surface and volume, is really characteristic of the advance of the interface in the solid.

Let us now consider the case of a constant decomposition rate thermal analysis. We can write:

$$\frac{d\alpha}{dt} = \text{constant } C = k_{10} \exp(-E/RT) \cdot (1 - \alpha)^n.$$

Hence:

$$n \log(1 - \alpha) = E/RT + \log k_{10} - \log C$$

and then:

$$\log(1 - \alpha) = E/nRT + B.$$

It will therefore be necessary only to plot $\log(1 - \alpha)$ as a function of $1/T$ to obtain, for each individual mechanism, a segment of line of slope E/nR . To find the order n one must know E , except in the simple, but not uncommon case when the seg-

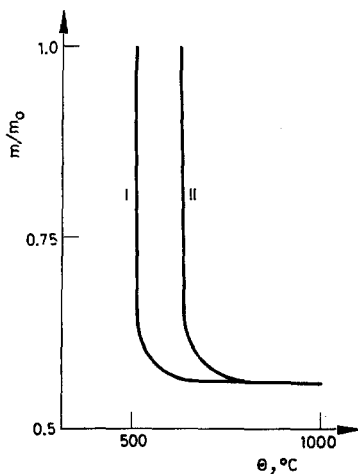


Fig. 7. Thermal analysis of precipitated calcium carbonate, at constant decomposition rate. (Curve I: $P = 10^{-4}$ Torr; $m = 50$ mg; $dm/dt = 0.2$ mg \cdot h $^{-1}$. Curve II: $P = 0.5$ Torr; $m = 5$ mg; $dm/dt = 20$ mg \cdot h $^{-1}$)

ment of line is vertical, which means that $n = 0$ and that the reaction interface progresses parallel to itself with a constant area. This is the result obtained for instance from part AB both of curves in Fig. 6 for the thermal decomposition of an industrial gibbsite sample $\text{Al}(\text{OH})_3$ at two different pressures ($4 \cdot 10^{-6}$ Torr and $1.5 \cdot 10^{-2}$ Torr). Such a low change of pressure is enough to change the mechanism: part CD corresponds to the thermal decomposition of a small amount of boehmite $\text{AlO}(\text{OH})$ previously formed in the experiment at $1.5 \cdot 10^{-2}$ Torr. This shows the importance of pressure control, even in the range of "vacuum".

b) Measurement of the activation energy of a thermal decomposition

Fig. 8 illustrates various ways of measuring the activation energy of a thermal decomposition.

The main advantage of the non-isothermal method (with constant heating rate) is rapidity, and it is now widely developed [2]. Nevertheless, it is not trouble-free. First of all, the change in dissociation extent between points A and B (be-

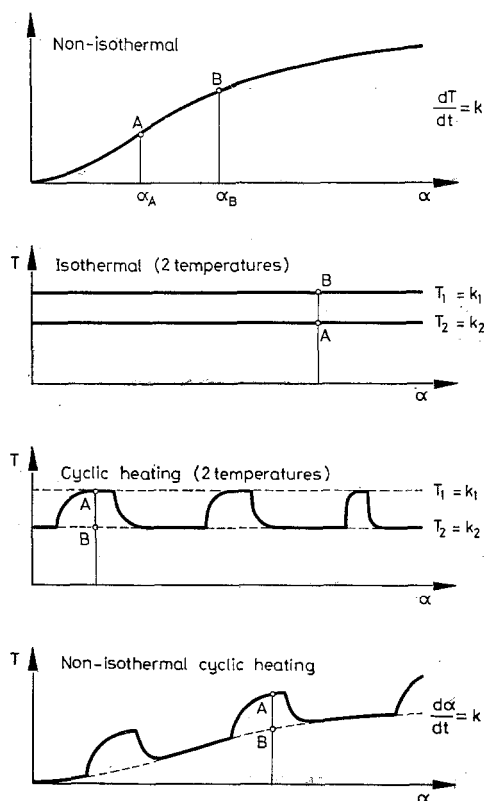


Fig. 8. Different ways of measuring the activation energy of a thermal decomposition

tween which the measurement is carried out) cannot always be neglected: one must then know the corresponding change of the function $f(1 - \alpha)$. Moreover, the constant heating of the sample does not take place without temperature and pressure gradients which may be important and may appreciably alter the kinetics.

The isothermal method allows comparison of the decomposition rates of two samples decomposed to the same extent. However, this method cannot be recommended when the properties of the product (for instance its structure, its porosity or its composition) depend on the temperature of the thermal decomposition: in that case, the two systems considered (represented by points A and B in Fig. 8) are not really similar. Comparison of the two former methods has been carried out by several authors, with varying conclusions (for instance [11]).

The cyclic heating method avoids the drawback mentioned for the isothermal method, since the same sample is used for all the measurements [12]. Nevertheless, as for any isothermal method, the choice of the temperatures is critical, and it is not always possible to achieve complete thermal decomposition.

The method we suggest [13] tries to associate the theoretical advantages of the cyclic heating method and the practical advantages of the non-isothermal one. Here, the thermal decomposition rate is alternately brought to two different levels by the control of the pumping rate by means of two different diaphragms or by means of an adjustable valve. The result is a series of values of $d\alpha/dt$ and T allowing measurement of the energy of activation throughout the thermal decomposition: the apparatus automatically supplies the increase of temperature necessary for completion of the thermal decomposition.

c) Measurement of the differential enthalpy of thermal dissociation

Most kinetic studies of thermal decomposition employ the measurement of mass. Those which depend only on the measurement of heat do not seem so safe, since they do not allow an estimation of the degree of completion of the reaction α unless an assumption is made as to the relationship linking the heat evolved or absorbed to the mass of sample transformed [14]. On the other hand, we believe that the measurement of the heat of reaction may be really useful provided it is (i) associated with a measurement of mass; (ii) carried out under conditions which allow the derivation of a change of state function (enthalpy or internal energy) and (iii) "differential" enough (and therefore leading to results of the type dQ/dn) to follow the advance of the reaction.

The former conditions have been fulfilled, over a limited range of temperature, by associating differential scanning calorimetry with constant decomposition rate thermal analysis [15]. Although the technique is not straightforward, the principle is simply to replace the furnace of Fig. 4 by a calorimeter (here, a differential scanning calorimeter using two Tian-Calvet thermopiles). Due to the constant pressure, the measured thermal flow dQ/dt is closely related to the enthalpy change dH/dt of the sample. Moreover, since the decomposition rate is constant, the recorded signal is proportional not only to dH/dt but also to dH/dn , the differential

(or "partial") enthalpy of the thermal dissociation is recorded directly. Recordings obtained from the same gibbsite sample as previously (here, $P = 1$ Torr) have already been published [15]. These clearly show two successive mechanisms: the first is related to the partial dehydration into crystalline boehmite $\text{AlO}(\text{OH})$ ($dH/dn = 50 \text{ kJ mole}^{-1}$) whereas the second must be assigned to the dehydration of gibbsite into a partly hydrated ρ -alumina ($dH/dn = 80 \text{ kJ mole}^{-1}$).

Conclusion

Most of the preceding remarks lead us to the following conclusion: if the "vacuum" procedure is able to simplify the conditions of a thermal decomposition and to bring out new aspects of the dissociation mechanism, then the requirements of a real vacuum procedure are extremely critical. Decomposition rate and residual pressure have indeed to be carefully controlled, as otherwise it may be venturesome to draw conclusions on the advance of the reaction interface.

The advocated method (constant decomposition rate thermal analysis), which may be associated with thermogravimetry (as was done by Paulik and Paulik [8] or by ourselves [9, 13]), or with calorimetry, attempts to combine the theoretical value of the isothermal method with the practical value of the non-isothermal one: we think that this is a field deserving further exploration.

References

1. D. M. SPEROS and R. L. WOODHOUSE, *J. Phys. Chem.*, 72 (1968) 2846.
2. C. D. DOYLE, *J. Appl. Polymer Sci.*, 15 (1961) 285.
J. ZSAKÓ, *J. Phys. Chem.*, 72 (1968) 2406.
A. W. COATS and J. P. REDFERN, *Nature*, 201 (1964) 68.
E. S. FREEMAN and B. CARROLL, *J. Phys. Chem.*, 62 (1958) 394.
J. ŠESTÁK, *Proceedings of the 3rd ICTA, Davos, Switzerland, 1971 Vol. 2., p. 3*, Birkhäuser, Basel-Stuttgart 1972.
V. ŠATAVA, *ibid. Vol. 2., p. 373*.
3. J. MAYET, J. ROUQUEROL, J. FRAISSARD and B. IMELIK, *Bull. Soc. Chim. France*, (1966) 2805.
4. B. DELMON, *Introduction à la cinétique hétérogène*. Paris, Editions Technip. 1969. Publications de l'Institut Français du Pétrole, p. 168.
5. P. J. ANDERSON, R. F. HORLOCK and R. G. AVERY, *Proc. Brit. Ceram. Soc.*, 3 (1965) 33.
6. P. BARRET, *Proc. 4th Int. Symp. React. Solids, Amsterdam, 1960*, p. 178.
7. J. ROUQUEROL, *J. Thermal Anal.*, 2 (1970) 123.
8. J. PAULIK and F. PAULIK, *Anal. Chim. Acta*, 56 (1971) 328.
F. PAULIK and J. PAULIK, *Anal. Chim. Acta*, 60 (1972) 127.
9. J. ROUQUEROL, in "Thermal Analysis", Academic Press, New York, 1969 Vol. 1, p. 281.
10. B. DELMON, *ibid. ref. 4*, p. 77.
11. B. CARROLL and E. P. MANCHE, *Thermochim. Acta*, 3 (1972) 449.
J. SIMON, E. BUZÁGH and S. GÁL, *Proceedings of the 3rd ICTA, Davos, Switzerland, 1971, Vol. 2, p. 393*, Birkhäuser, Basel-Stuttgart 1972.
12. J. H. FLYNN, in "Thermal Analysis", Academic Press, New York, Vol. 1, 1969 p. 1111.
13. F. ROUQUEROL and J. ROUQUEROL, *Proceedings of the 3rd ICTA, Davos, Switzerland, 1971, Vol. 1, p. 373*, Birkhäuser, Basel-Stuttgart, 1972.
14. H. J. BORCHARD and F. DANIELS, *J. Am. Chem. Soc.*, 79 (1957) 41.
H. J. BORCHARD, *J. Inorg. Nucl. Chem.*, 12 (1960) 252.
15. M. GANTEAUME and J. ROUQUEROL, *J. Thermal Anal.*, 3 (1971) 413.

RÉSUMÉ — Après des considérations sur les différents problèmes liés à la cinétique de la thermolyse dans le vide (formulation, séparation des processus successifs, influence de la pression résiduelle, de la chaleur et du transfert de masse) l'auteur recommande l'emploi de l'analyse thermique à vitesse de décomposition constante associée ou non à la thermogravimétrie ou à la calorimétrie. La méthode présente un intérêt spécial dans le cas de la détermination de l'ordre apparent des réactions, des énergies d'activation et des enthalpies différentielles de dissociation.

ZUSAMMENFASSUNG — Nach einer Übersicht verschiedener Probleme der Kinetik der thermischen Zersetzung unter Vakuum (Formeln, Trennung der aufeinander folgenden Stufen, Einfluß des restlichen Druckes, der Wärme und des Massentransports) wird als beste Möglichkeit die Verwendung der Thermoanalyse mit konstanter Zersetzungsgeschwindigkeit mit oder ohne Thermogravimetrie oder Kalorimetrie vorgeschlagen. Die Methode ist von besonderem Interesse bei der Bestimmung von scheinbaren Reaktionsordnungen, Aktivierungsenergien, Differentialenthalpien von Dissoziation.

Резюме — После рассмотрения некоторых проблем, присущих кинетике термолитза под вакуумом (формализация, разделение последовательных стадий, влияние остаточного давления и тепло- или массопередача) автор предлагает, в качестве возможного решения, использовать термический анализ с постоянной скоростью распада с сочетанием или без сочетания с термогравиметрией или калориметрией. Преимущество метода показано для следующих измерений: кажущиеся порядки реакции, энергии активации, дифференциальные энтальпии диссоциации. Повидимому, метод специфично применим для изучения термолитза под высоким вакуумом.