Thermochimica Acta, 144 (1989) 209–224
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CONTROLLED TRANSFORMATION RATE THERMAL ANALYSIS: THE HIDDEN FACE OF THERMAL ANALYSIS

JEAN ROUQUEROL

Centre de Thermodynamique et de Microcalorimétrie du C.N.R.S., 26 rue du 141° R.I.A., 13003 Marseille (France)

(Received 16 June 1988; in final form 15 September 1988)

ABSTRACT

Controlled transformation rate thermal analysis is defined here as a general thermoanalytical method where, instead of controlling the temperature (as in conventional thermal analysis), one controls some other physical or chemical property, which is made to follow a pre-determined programme by appropriate heating of the sample. The historical development of the method is reviewed (from the early sixties) together with its analytical, preparative and kinetic applications. Examples given mainly deal with adsorbents, catalysts and ceramics. The paper ends with a list of expected developments.

INTRODUCTION

Thermal analysis, which, in our day, is usually rapid, sensitive and computerized, includes a wide choice of techniques over a broad range of temperature. Nevertheless, the dream of many scientists involved in thermal analysis for analytical purposes or in the thermal preparation of solids (adsorbents, catalysts, ceramics, inorganic or carbon fibres, etc.) is still:

to obtain thermoanalytical curves and kinetic parameters which would be independent of the sample mass (especially when the requirements of satisfactory sampling do not allow the sample size to be decreased at will), of the shape of the crucible and of the location of the temperature sensor, so that they would be, above all, characteristic of the sample studied and not of the experimental arrangement

to have more reproducible thermal preparations, on both the laboratory and the industrial scale

to disentangle the various phenomena occurring in complex thermolyses (i.e. those leading to several gaseous or solid products) by simple and safe processing of the thermal analysis data, and to obtain "meaningful" and useful apparent energies of activation.

In the author's opinion, most of the above wishes can be satisfied by what is described hereafter under the name of controlled transformation rate

0040-6031/89/$03.50

thermal analysis (CRTA) with the aim of giving a unifying presentation of a few modern trends of thermal analysis. These trends, especially those called constant decomposition rate thermal analysis [1] and quasi-isothermal thermogravimetry [2] or quasi-isothermal thermal analysis [3] by their authors, have often been considered different from each other, although, as will be seen, they are basically of the same nature. We think that such a unification is worthwhile to give the thermoanalyst a simpler and clearer picture of what is going on, and to inspire new ideas, especially by cross-fertilization between techniques which are actually closely related.

DEFINITION

A generally accepted definition of thermal analysis is that given in 1969 by the Nomenclature Committee of the International Confederation of Thermal Analysis (ICTA), which defines thermal analysis as "a group of techniques in which a physical property of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme" [4]. Any thermal analysis experiment may therefore be schematically represented as in Fig. 1, which shows that three basic parameters are measured simultaneously: the sample temperature (T) (using the 'thermometer'), the time *t* (using the 'chronometer') and the physical property *X* which depends on the technique selected (using the '*X*-meter'). The two former parameters are linked, by means of the heating control loop,

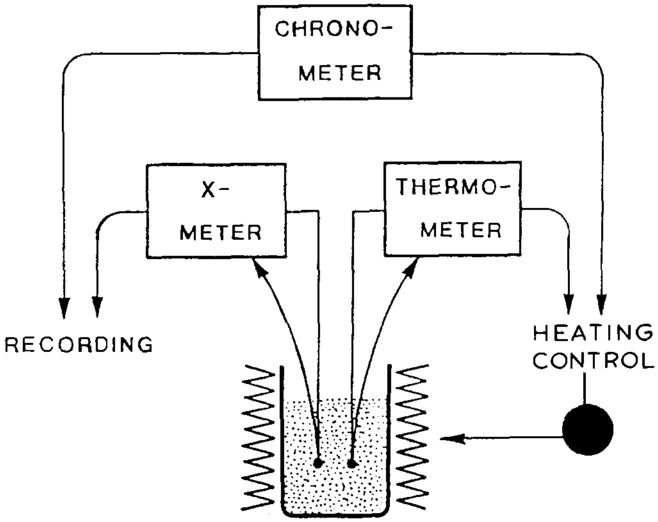


Fig. 1. Principle of conventional thermal analysis (temperature-controlled).

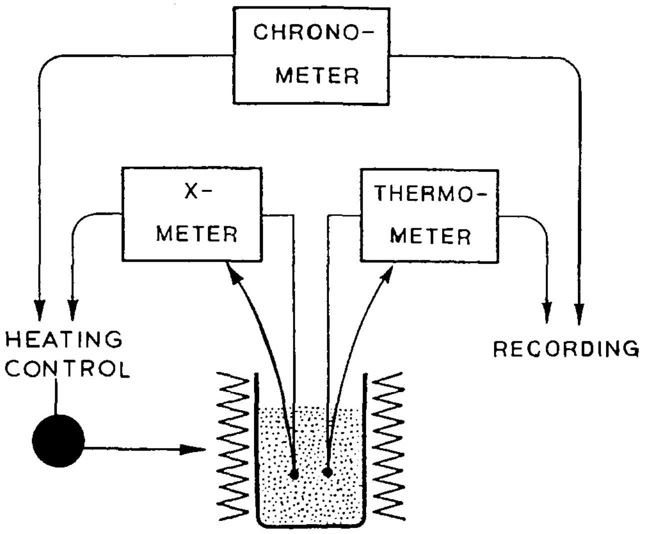


Fig. 2. Principle of controlled rate thermal analysis (X-controlled).

in order to follow a predetermined T vs. t programme, most often linear and therefore not necessarily recorded. The resulting value of X (vs. t or T) is recorded to give the actual thermal analysis curve.

Nevertheless, for more than 20 years another approach has been used to study the thermal behaviour of a substance. Very close to thermal analysis, this approach is in some respects 'the opposite', as may be seen from Fig. 2. The same three parameters (temperature, time and physical property X) are again measured simultaneously, but the operation of the heating control loop is basically different. The pre-determined temperature programme (required in the conventional definition of thermal analysis) no longer exists. The roles of the 'thermometer' and of the "X-meter" are exchanged so that it is now the physical property X which is made to follow a predetermined programme and which controls the heating of the sample. The thermoanalytical information is obtained simply from the recording of T vs. t, since the physical property X follows its predetermined programme and does not necessarily need to be recorded.

To sum up, this thermoanalytical approach makes use of the same measuring devices as conventional thermal analysis, but the operation of the control loop is basically different. Comparison of Fig. 1 and Fig. 2 shows that the conventional and the novel approach may be considered as "opposite" or "symmetrical" or, also, "images" of each other. The difference is clear and there is no way to pass smoothly and progressively from conventional thermal analysis to this new approach. Although, for the reasons just given, one could think of calling it reciprocal thermal analysis, inverted thermal analysis or image thermal analysis, we shall follow recent advice of the Nomenclature Committee of ICTA and call it controlled transformation rate thermal analysis. To make it shorter (when there is no ambiguity, i.e. when it is certain that the rate in question will be taken to be a transformation rate, not a heating rate) it may be called controlled rate thermal analysis which abbreviates to CRTA.

Since the novel approach, as an "image", has just as broad applications as thermal analysis and is a new way to use a similar type of equipment, we suggest starting from the name of the conventional thermal analysis technique as defined by the Nomenclature Committee [4,5], for instance thermogravimetry (TG) or evolved gas analysis (EGA) and simply to add the words controlled rate (or controlled transformation rate in case of ambiguity) to give, for example, controlled rate TG and controlled rate EGA.

Finally, controlled transformation rate thermal analysis can be defined as a general thermoanalytical method where a physical or chemical property X of a substance is modified, following a predetermined programme $X=f(t)$, under the appropriate action of temperature.

HISTORICAL DEVELOPMENT

To the best of our knowledge, the method has its beginnings in the years 1960–1962: J. Rouquerol (in Paris) and J. and F. Paulik (in Budapest) independently had the idea of automating the ultra-slow heating procedure used at that time by a few researchers [6], in order to ensure, if possible, quasi-equilibrium conditions and to increase the resolution of thermal analysis. Rouquerol's idea was to heat the sample in such a way as to control, at any time, the flow of self-generated gas in what is now called evolved gas detection (EGD) equipment (Fig. 3), and the Pauliks' idea was to control the signal of what is now called derivative thermogravimetry (DTG) (Fig. 4, loop I). Rouquerol built equipment and carried out the first experiments of what he calls constant decomposition rate thermal analysis [7]. The Pauliks took out a patent on a "device for an automatic control of the heating programme of thermobalances in the case of stepwise isothermal heating" [8] and, as they themselves reported later, they "made the first attempt in 1962 to develop this technique, but it was only in 1971 that every obstacle to the realization of an appropriate * measuring system could be eliminated" [11]. From the start of the method and during its "infancy", the succession of published documents available to scientists was as follows.

---

* It now seems that the word "industrial" was unfortunately omitted here in the published book (F. and J. Paulik, 1983, personal communication).

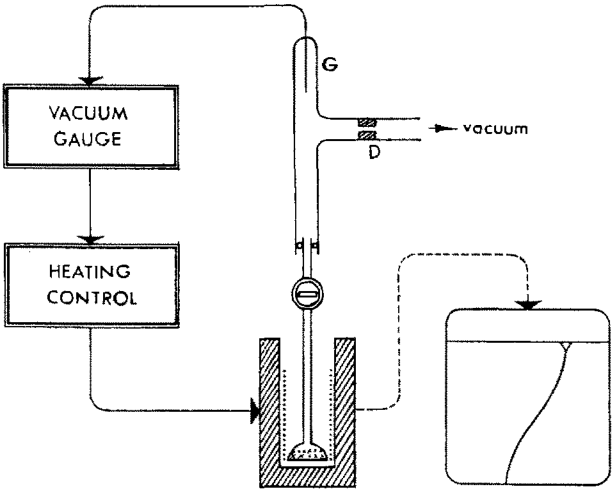


Fig. 3. Principle of the controlled rate EGD system (redrawn according to ref. 1).

January 1964

First paper on the topic, entitled "A method of thermal analysis under low pressure and at constant decomposition rate" [7]. It gives the principle of the method (based here on the control of the gas flow) and the first

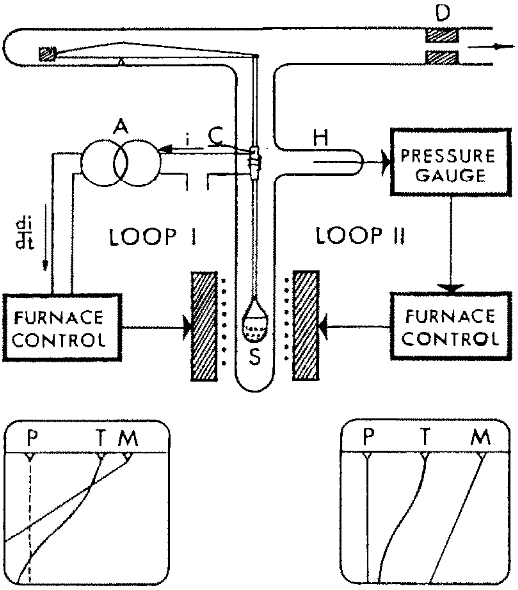


Fig. 4. Two ways to use a thermobalance in the controlled transformation rate thermal analysis mode. Loop I, controlled rate DTG (in accordance with the principle given in ref. 2); loop II, controlled rate EGD linked with TG (as in refs. 9 and 10).

experimental results (thermal analysis of a mixture of aluminium, magnesium and calcium hydroxides and also of a mixture of $CoSO_4 \cdot H_2O$ with $Ca(OH)_2$).

December 1965

The Hungarian patent (based on the control of the DTG signal) becomes available [8] before being extended to other countries, although application for it was made as early as October 1962. It is interesting to note, from the above dates, that both approaches (using a control based either on EGD or on DTG) were thought of independently.

1967

Proposal of the concept of "rate controlled sintering" by Palmour and Johnson [25].

Prior to 1970

The only experimental results available in the literature and able to enter the scope of controlled transformation rate thermal analysis are those obtained with the method devised by Rouquerol and which can also be used in association with TG [9], see Fig. 4, loop II. They deal with the thermal decomposition of aluminium hydroxides [12,13], of uranyl nitrate hydrates [14] and of silica–alumina gels [15].

1970

The general principle of what J. Rouquerol at that time called "constant decomposition rate thermal analysis" is laid down [1], whatever the controlling parameter. This may be, for instance, a flow of gas (self-generated, as in all the experiments reported at that time, or mixed with a carrier gas), a flow of heat (as detected by differential thermal analysis or differential scanning calorimetry), a DTG signal (which is the case considered in the Pauliks' patent, at that time ignored by Rouquerol and not quoted in his paper), or any other parameter directly related to the rate of decomposition of the sample. An estimation is given of the expected sensitivity of the latter arrangement, on the basis of the performances of commercially available DTG systems. It appears that the sensitivity is then ca. 20 times lower than with an EGD-based system using a constriction and a Pirani gauge. Constant decomposition rate thermal analysis may be considered today as a special case (although the major one) of controlled transformation rate thermal analysis, where the physical property selected is made to follow a linear programme so that the rate of transformation is constant. The role of constant decomposition rate in controlled transformation rate thermal analysis is therefore comparable, in importance, with the role of constant heating rate in conventional thermal analysis.

The same year, the first experiment in rate controlled sintering occurs, unfortunately only reported in an abstract form [51].

1971

First publication by F. and J. Paulik [2] of experimental results obtained using the arrangement described in their patent [8] and schematically represented in Fig. 4, loop I. Although this technique clearly enters the scope of the previously defined "constant decomposition rate thermal analysis" [1], it was then given the new name of "quasi-isothermal thermogravimetry" [2]. The similar nature and basic principle of the above methods was pointed out several times [1,10,16–18], since their specific feature is the control of the rate of transformation (and not the ultra-slow heating rate which may be obtained by any conventional thermal analysis method by simply setting an ultra-slow heating rate). Nevertheless, this was even recently apparently not always appreciated (cf. for instance, refs. 19 and 20) which is of course confusing for the reader who would like to understand where the difference does lie. Since a number of similar or related methods were described or renamed in the last two decades, we have found it useful to list, in Table 1, the chronological succession of names proposed in the literature for thermal methods based on the control of the rate of transformation. The reference is that of the paper which, to our knowledge, makes the first use of the name and the year is that of publication. The abbreviations, when given, are those suggested in the same paper. Depending on the definition given, the name refers to a thermal method which may be considered as the "image" of one or more conventional methods of thermal analysis. This is indicated in Table 1 by one or more filled circles following each name. For the sake of conciseness, the abbreviations TA and TD stand for thermal analysis and thermodilatometry respectively. One can see that the first "collective" name was that of "constant decomposition rate thermal analysis (CRTA)" given in 1970 to a general method whose "basic idea is to control the sample temperature so as to keep constant a parameter related to the decomposition rate" (quoted from English abstract of ref. 1). The name was not changed for the case where, for kinetic measurements, the decomposition rate was made to swing between two predetermined values (see ref. 27, page 375). Nevertheless, "improved" or "enlarged" collective names were proposed later as the depth and generality of this approach was increasingly realized. Among them, the relatively recent name of "quasi-static methods" probably deserves a special mention. Its definition is given in ref. 19, page 33 in the following way: "Neither measuring principles nor the results obtained by the techniques discussed [in the first pages of ref. 19] are identical, they are

TABLE 1

Succession of names proposed in the literature for thermal methods based on the control of the rate of transformation

Year	Ref.	Names proposed	Corresponding "image" conventional method					
			DTA	TG	EGD	TD	EGA	All other methods
1964	7	Low pressure and constant decomposition rate TA			●			
1967	25	Rate controlled sintering				●		
1969	9	TA under given pressure and decomposition rate			●			
1970	1	Constant decomposition Rate TA (CRTA)	●	●	●	●	●	●●
1971	2	Quasi-isothermal quasi-isobaric TG		●				
1977	3	Quasi-isothermal, quasi-isobaric thermodilation				●		
1978	21	Quasi-isothermal dilatometry (QID)				●		
1982	22	Controlled decomposition rate EGA					●	
1982	22	Controlled decomposition rate TA	●	●	●	●	●	●●
1983	23	Isobaric thermal decomposition (ITD)			●			
1983	18	Controlled reaction rate TA (CRTA)	●	●	●	●	●	●●
1983	24	Stepwise isothermal analysis (SIA)		●		●		
1986	19	Quasi-static methods	●	●	●	●		
1986	41	Controlled transformation rate TA	●	●	●	●	●	●●
1987	26	Inverse TA	●	●	●	●	●	●●
1989	[a]	Reciprocal TA, inverted TA image TA	●	●	●	●	●	●●

[a] This work.

only more or less similar. Nevertheless, all these techniques have a common characteristic feature in contrast with conventional dynamic and isothermal methods, viz. they permit transformation to take place at very low rates,

TABLE 2

Relative situation of the fields covered by names proposed in the literature for thermal methods based on the control of the rate of transformation

Controlled transformation Rate TA (applies *to any transformation*, including purely physical and fully reversible)

Controlled reaction Rate TA (applies to chemical reaction but *whatever the programme* selected for the rate of reaction which does not need to be constant)

Controlled decomposition Rate TA (applies to thermal decomposition here again *whatever the programme* selected for the rate of reaction)

Constant decomposition Rate TA (applies *whatever the rate* of decomposition)

Quasi-static methods (applies to one aspect of Controlled transformation Rate DTA, TG, EGD or TD but only in the case when *the rate selected is low enough* to ensure quasi-static s. conditions. Till now, it has only been considered to apply this name to methods where the rate of transformation is d controlled around one or between two constant values)

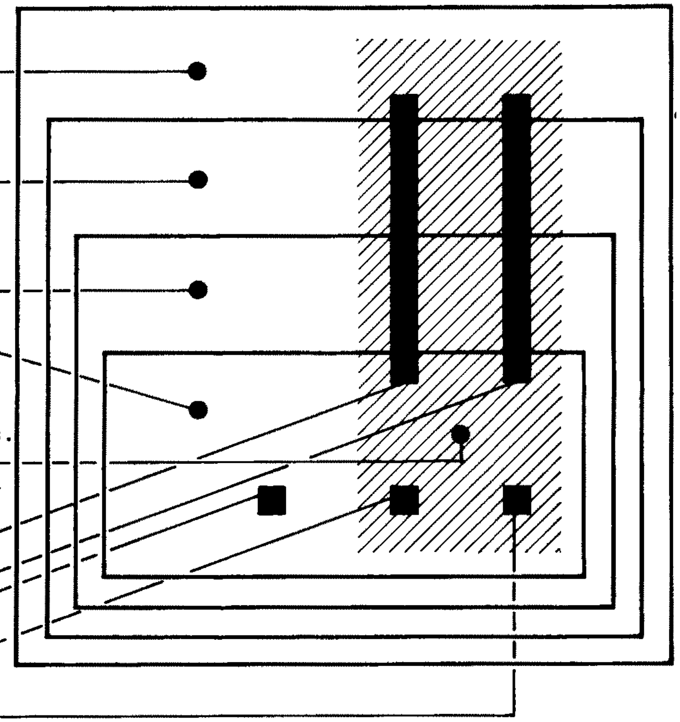
Quasi-isothermal thermodilation "Q-TD"

Stepwise Isothermal Analysis "SIA" ("Image" of both thermodilatometry and TG)

Controlled decomposition rate EGA

Quasi-isothermal, quasi isobaric TG "Q-TG"

TA under given pressure and decomposition rate and Isobaric Thermal Decomposition "ITD"



practically in a quasi-static way. Therefore, the authors propose to use "quasi-static methods" as a collective name, and in addition, for better differentiation, each individual technique could preserve the original name given by the author". This definition refers to the techniques discussed in ref. 19 and which involve, as reported in Table 1, the control of one of the following parameters: heat flow, mass, evolved gas flow or length. In the above paper the name "constant decomposition rate TA (CRTA)" is quoted but is unfortunately misunderstood and limited to what we would call today "controlled rate EGD". Hence the relatively limited number of techniques for which the term "quasi-static methods" is proposed. Also, by essence and by definition, the name is limited to the case, admittedly most interesting, when the transformations "take place at very low rates, practically in a quasi-static way" [19].

This leads us to another representation, aiming to show the overlapping of the names listed in Table 1. This is done in Table 2, where each collective name (or general method) is given a field in the form of a large rectangle marked with a filled circle connected to the name in question (in italics). One sees that, for simple reasons of individual consistency, the scopes of the first four names nicely fit into each other, whereas the fifth (quasi-static methods) covers part of those mentioned above (because of the limitation to low rates and to four techniques). The more specific methods are located with the help of filled squares or rectangles. We can see, for instance, that both "TA under given pressure and decomposition rate" [9] and "quasi-isothermal, quasi-isobaric TG (Q-TG)" [2] are in the fields of both "quasi-static methods" and "constant decomposition rate TA", since we know, using Q-TG, that "the transformations take place at a very low and strictly constant rate" (cf. ref. 19, page 25). On the other hand, "controlled decomposition rate EGA" [22] does not enter the scope of "quasi-static methods", not only because it was not mentioned in the paper introducing these methods [19] but also because, as cleverly pointed out by Stacey (cf. ref. 28, page 243), it is practical "to work at moderately high rates where each particle has within it a concentration gradient; hence, the diffusion limited regime is accessible to investigation as well as the chemical reaction limited regime".

To end this section we may consider that possibly it is not necessary to change any existing names, provided that any new definition (or name) is clearly and explicitly used with reference to the existing body of definitions and names (such as those quoted in Tables 1 and 2), so that the reader is helped instead of being confused when approaching this not yet conventional family of thermal methods.

The further development of the techniques entering the scope of CRTA is given hereafter, together with their main applications.

TYPICAL APPLICATIONS OF CONTROLLED TRANSFORMATION RATE THERMAL ANALYSIS

Analytical applications

In short, CRTA usually allows significant enhancement of the resolution of any thermal analysis equipment. Indeed, a special interest in controlling the rate of the reaction is that one also controls, indirectly, all the gradients (of temperature, of partial pressure of evolved gases, etc.) which originate from the rate of reaction itself. Under these conditions the reaction may take place simultaneously within the whole sample, the degree of synchronism then being limited only by the size of the grains or crystallites of the sample and not by the size of the sample or by the shape of the crucible. This leads to an improved sensitivity and resolution, as we have shown for instance in our earliest publication in the case of a mixture of $CoSO_4 \cdot H_2O$ and $Ca(OH)_2$ or of $Al(OH)_3$ and $Mg(OH)_2$ [7]. Later, excellent examples were given by Paulik and Paulik, such as the thermal decomposition of $CaC_2O_4 \cdot H_2O$ [29].

Thermal preparation of solids

It seems trivial to say that the products of the thermal decomposition of hydroxides, oxalates, carbonates, many other inorganic salts and many organic polymers strongly depend on the thermal path followed by the sample. This thermal path involves the temperature and the distribution of partial pressures in the close vicinity of each individual grain. The only practical way to control this path in a reproducible manner is to keep at least these parameters identical for all the grains at a given time. This requires lowering, at will, the pressure and temperature gradients through the sample, which may be automatically obtained by controlling directly the rate of transformation (in this case a chemical reaction) instead of the heating rate. Striking results were readily obtained in the case of the preparation of microporous aluminas from the thermal decomposition of gibbsite: the maximum nitrogen BET specific surface area of these aluminas could be made to vary from more than 400 $m^2\ g^{-1}$ to less than 40 $m^2\ g^{-1}$, simply by changing the constant partial pressure of water in the vicinity of the gibbsite crystals from 1 Torr to 0.04 Torr [12,16]. It is also possible progressively to increase the width of these micropores, keeping a narrow pore-size distribution simply by carrying out the same heat treatment to a higher extent of transformation. A unique set of nitrogen adsorption–desorption isotherms was thus obtained for a range of beryllium oxide samples whose pore size could be tailor-made to any dimension between 0.8 and 8 nm [30].

The thermal preparation of uranium oxide [14], zirconia [31], scandium oxide [23] and cerium oxide [32] was also carried out, with novel results, by CRTA (incidentally, Fierro et al. [23] call this method, in their context, "isobaric thermal decomposition (ITD)", which once more shows the need for some unifying concepts and terminology). This approach may be used systematically for the thermal decomposition of precursors of catalytic oxides (bulk or supported) and of catalyst supports [33]. It is also worthwhile for preparing reference adsorbents in a highly reproducible state of outgassing, as was recently done [34].

Finally, at higher temperatures it was extremely worthwhile to prepare sintered ceramics by what we would now call controlled transformation rate thermodilatometry. By avoiding the formation of trapped pores (usually resulting from the excessive densification rates obtained in the case of conventional heating programmes), this allows us, for instance, to obtain a sintered alumina with a smaller and much more homogeneous grain size at lower final temperatures (ca. 100 ° C lower) than with a conventional heating programme, as shown by Huckabee and Palmour [48]. In a similar way (but now controlling the rate of sintering between two preset limits by appropriate increments of temperature), Sorensen successfully studied the sintering of UO_2 [49,50] and CeO_2 [24].

Kinetics of thermal decomposition

This is possibly the field in which CRTA is most novel and powerful. The novelty is such that a specialist of the now conventional methods of studying the kinetics of thermal decomposition might be embarrassed about the validity of this unconventional approach. Indeed here, instead of imposing the temperature conditions and measuring the resulting rate of reaction one does exactly the reverse. But this, of course, does not change anything in the relationship which may exist (when all other "influencing parameters" are kept constant) between the rate of reaction and the temperature. This is the relationship which is looked for, in view of analysis and interpretation, in terms, for instance, of chemical reaction at the reacting interface, diffusion of the gaseous products through the solid ones, recrystallization of the latter and final desorption of the former. The validity and significance of the relationship which is arrived at closely depend on our exact knowledge of the "influencing parameters" mentioned above and of their values at any point in the reacting system. This means that any unknown gradient in temperature, gas composition (or pressure) and porous structure of the solid products is a real limit to our kinetic understanding. This is where CRTA is especially worthwhile, since it allows us to lower at will these gradients by an appropriate control of the rate of reaction, so that one local measurement of the above-quoted parameters may hold for the whole sample. In other words, the experimental conditions of the reaction under study may be satisfactorily controlled.

Another feature of kinetic interest in this approach is that it lends itself to powerful and periodical analysis of the thermal reaction by applying the "rate-jump" method. Here, the rate of transformation is made to swing between two pre-selected values, conveniently chosen, for instance, with a ratio of 1 : 3 or 1 : 4. Correspondingly, the heating control loop changes the sample temperature in such a way that the desired rates are successively obtained. Any set of 2 successive rates of transformation and 2 successive temperatures for a sample whose experimental conditions are otherwise virtually unchanged (atmosphere composition and pressure, extent of reaction and porosity of the solid products) allows a meaningful "temperature factor of the reaction" to be reached, which may be expressed, if desired, as an "apparent energy of activation" of the reaction. An immediately interesting feature of this temperature factor is that, since it may be measured 20 or 30 successive times during a single experiment, it may detect any change in the course of the reaction mechanism, even before it has any physico-chemical meaning. Following these lines, CRTA was applied to kinetic studies involving calcium carbonate (the unavoidable reference sample!) [27,35,36], precipitated silica-gel (to follow its dehydroxylation mechanism) [37], carbonates of Mg, Sr and Ba [38], Cu–Zn hydroxycarbonate solid solutions [39], gibbsite and boehmite [40]. Not only thermal decompositions but any thermally activated transformation may be studied in this way, as carried out by Stacey who followed the reduction of copper or nickel catalysts in a flow of $H_2 + He$, using a fluidized bed technique under atmospheric pressure [28]. The comparison between the CRTA approach and the conventional ones was carried out systematically on several occasions, so that there is now enough material to evaluate the meaning and value of this method [35–37,38,41]. Sorensen's "stepwise isothermal analysis" [21] also causes the transformation rate to swing between two pre-set limits, but with the extra condition of a stepwise variation of the sample temperature. During each temperature step the transformation rate decreases automatically from the high to the low pre-selected, known limit, hence giving a useful kinetic analysis. The differences between the kinetic approach we proposed [10,27] and Sorensen's approach are (i) that, whereas we suggested switching from rate 1 to rate 2 and staying a while at each of them once they are obtained, in Sorensen's method the reaction rate is never allowed to stabilize, and (ii) that the existence of isothermal steps in the latter method makes it, at first glance, more amenable to a conventional analysis, although the "loose control" of the rate of transformation has the effect that some advantages of CRTA (which allows a careful control and knowledge of the influencing parameters) may partly be lost. It may be pointed out that the idea of directly using the original temperature programmer of the thermal analysis equipment and of actuating this programmer in steps to keep the rate of reaction within the preset limits is especially suited for carrying out CRTA without over-modifying conventional thermal analysis equipment. We found it useful in our first kinetic study by CRTA [27], as did Sorensen [21].

EXPECTED DEVELOPMENTS

"Simple" controlled rate thermal analysis

As stated in the definition and principle section, the heating of the sample may be controlled by any parameter linked to the rate of the thermally activated transformation. This opens the way to a large number of partly unsuspected possibilities. We may list the following parameters among those not yet used, to our knowledge, to control the rate of the thermal analysis: thermal properties of the sample (thermal conductivity of diffusivity, heat capacity, enthalpy, etc.), electrical properties (electrical conductivity, electrical permittivity, surface charge, pH, piezoelectric effect, etc.), magnetic properties (magnetic permeability, magnetic moment, NMR or EPR frequency or intensity), optical and electromagnetic properties (frequency or intensity of reflected, transmitted, absorbed or emitted radiation, in the IR, visible, UV, X-ray or microwave range, etc.), acoustic properties (resonance frequency, velocity of sound, damping of vibrations, etc.) and dimensional properties (not only the overall length, as in dilatometry, but also structure parameters as obtained from diffraction techniques (X-ray, electron or neutron diffraction)).

The word "sample" is used above with a broad meaning: it may include the whole sample or only part of the reactants or products. Some of the parameters indicated may, for instance, apply either to a solid phase or to a fluid phase (or to both).

Controlled rate thermal analysis coupled with simultaneous measurements

A most rewarding way to use CRTA is to link it with the simultaneous measurement of one or more other parameters among those listed above, to which may be added the mass of the sample and the composition and pressure of the evolved gas. The great interest in that linkage is that each linked measurement draws a large benefit (in resolution and in ease of interpretation) from the well-controlled conditions of CRTA, so that its performance is very often enhanced. The number of possible linkages is very large, but we have found it interesting to list, in Table 3, a few of those which either have been investigated already (the reference is then given in brackets) or which we think are both worthwhile and feasible (although the work still needed for their development must not be underestimated). The names of these coupled techniques are straight-forward. Examples are controlled rate EGA coupled with gravimetry (but not "with TG", since the heating programme and principle remain that of controlled rate thermal analysis), reciprocal TG coupled with analysis of the evolved gas (but not "with EGA" for the same reason as above), controlled rate thermodilatometry coupled with X-ray diffraction, etc. Incidentally, one sees here that the use of the terms "quasi-static" or "quasi-isothermal" would not only limit

TABLE 3

Examples of a controlled transformation rate thermal analysis method linked with another measurement [a]

2nd parameter measured	Parameter controlled				
	Total gas flow, using controlled rate EGD	Partial gas flow, using controlled rate EGA	Mass, using controlled rate TG	Length, using controlled rate TD	Heat flow, using controlled rate DTA
Mass	[9,46]	○			○
Composition of evolved gas	[42]	[22,47]	[44]	○	○
X-ray analysis	○	○	○	○	○
IR absorption	○	○	○	○	○
Flow of evolved gas			○	○	○
Length	○	○			○
Heat flow	[43]	○	[45]	○	

[a] Examples with a reference in square brackets have been investigated; those with an open circle are, in the author's opinion, worth investigation.

the scope of these methods (as remarked concerning Table 2) but would not tell us automatically (except if we add an extra rule) which is the controlling parameter. For instance, it is not obvious that both in a "Q-TG" and in a "Q-TG/Q-DTG/Q-DTA" experiment (Q standing for quasi-static [19]) the controlling parameter is the DTG signal, although these initials are only seen in the second name.

Anyway, we think that years (or perhaps decades) are still necessary to extend the controlled rate thermal analysis approach to fields where the best is still to be drawn from it.

REFERENCES

1 J. Rouquerol, J. Therm. Anal., 2 (1970) 123.
2 J. Paulik and F. Paulik, Anal. Chim. Acta, 56 (1971) 328.
3 J. Paulik and F. Paulik, Proc. Int. Conf. Therm. Anal., 1977, Kyoto, 1 (1977) 75.
4 R.C. Mackenzie, J. Therm. Anal., 13 (1978) 387.
5 G. Lombardi (Ed.), For Better Thermal Analysis, ICTA, 1980.
6 C. Eyraud, R. Goton and M. Prettre, C. R. Acad. Sci., 238 (1954) 1028.
7 J. Rouquerol, Bull. Soc. Chim. Fr., (1964) 31.
8 L. Erdey, F. Paulik and J. Paulik, Hungarian Patent No. 152197, registered 31 October 1962, published 1 December 1965.
9 J. Rouquerol, in Thermal Analysis, Academic Press, New York, 1969, Vol. 1, p. 281.
10 J. Rouquerol, J. Therm. Anal., 5 (1973) 203.
11 J. Paulik and F. Paulik, in G. Svehla (Ed.), Comprehensive Analytical Chemistry, Elsevier, Amsterdam, 1981, vol. XII, part A, p. 48.

12 J. Mayet, J. Rouquerol, J. Fraissard and B. Imelik, Bull. Soc. Chim. Fr., (1966) 2805.
13 A. Baumer and M. Ganteaume, C. R. Acad. Sci. 266 (1968) 120.
14 G. Chottard, J. Fraissard and B. Imelik, Bull. Soc. Chim. Fr., (1967) 4331.
15 J. Kermarec, J. Fraissard, J. Elston and B. Imelik, J. Chim. Phys., 65 (1968) 920.
16 J. Rouquerol and M. Ganteaume, J. Therm. Anal., 11 (1977) 201.
17 J. Rouquerol, in Proc. Workshop on the State of the Art of Thermal Analysis, Gaithersburg, MD, May 21-22, 1979, NBS Special Publication 580, 1980, p. 133.
18 J. Rouquerol, in Proc. 5th Meeting of AICAT, AICAT, Trieste, 1983, p. 18.
19 F. Paulik and J. Paulik, Thermochim. Acta, 100 (1986) 23.
20 O.T. Sorensen, Thermochim. Acta, 50 (1980) 163.
21 O.T. Sorensen, J. Therm. Anal., 13 (1978) 429.
22 G. Thevand, F. Rouquerol and J. Rouquerol, in B. Miller (Ed.), Thermal Analysis, John Wiley and Sons, New York, 1982, Vol. 2, p. 1524.
23 J.L.G. Fierro, S. Mendioroz and J. Sanz, J, Colloid. Interface Sci., 93 (1983) 487.
24 O.T. Sorensen, in Proc. 5th Meeting of AICAT, AICAT, Trieste, 1983, p. 25.
25 H. Palmour, III, and D.R. Johnson, in G.C. Kuczynski, N.A. Hooton and C.F. Gibbon (Eds.), Sintering and Related Phenomena, Gordon and Breach, New York, 1967, p. 779.
26 J. Rouquerol, Thermochim. Acta, 110 (1987) 221.
27 F. Rouquerol and J. Rouquerol, in H.G. Wiedemann (Ed.), Thermal Analysis, Vol. 1, Birkhäuser, Basel, 1972, p. 373.
28 M.H. Stacey, Anal. Proc. 22 (1985) 242.
29 F. Paulik and J. Paulik, J. Therm. Anal., 5 (1973) 253.
30 F. Rouquerol, J. Rouquerol and B. Imelik, in J.M. Haynes and P. Rossi-Dori (Eds.), Principles and Applications of Pore Structural Characterization, Arrowsmith, Bristol, 1985, pp. 213.
31 M.J. Torralvo, Y. Grillet, F. Rouquerol and J, Rouquerol, J. Chim. Phys., 77 (1980), 125.
32 J.L.G. Fierro, Reactivity of Solids, 1985, p. 35.
33 J. Rouquerol, in Proc. 1st Franco-Venezuelian Symposium on Catalysis, 1984, Intevep. S.A., Caracas, p. 247.
34 F. Rouquerol, J, Rouquerol, G. Thevand and M. Triaca, Surf. Sci., 162 (1985) 239.
35 J.M. Criado, F. Rouquerol and J. Rouquerol, Thermochim. Acta, 38 (1980) 109.
36 D. Dollimore, G.A. Gamlen, J. Rouquerol, F. Rouquerol and M. Reading, in D. Dollimore (Ed.), Proc. 2nd Europ. Symp. Therm. Anal., Aberdeen, 1981, Heyden, London, 1981, p. 99.
37 F. Rouquerol, S. Regnier and J. Rouquerol, in Proc. 4th ICTA, Budapest, 1974, p. 313.
38 J.M. Criado, F. Rouquerol and J. Rouquerol, Thermochim. Acta, 38 (1980) 117.
39 M.H. Stacey and M.D. Shannon, in P. Barret and L.C. Dufour (Eds.), Reactivity of Solids, Elsevier, Amsterdam, 1985, part B.
40 M.H. Stacey, Langmuir, 3 (1987) 681.
41 J.M. Criado, A. Ortega, J. Rouquerol and F. Rouquerol, Bol. Soc. Esp. Ceram. Vidr., 25 (1986) 407; 26 (1987) 3.
42 G. Goujon, thesis, no. A.O. 11021, University of Marseille, 1975, p. 107.
43 M. Ganteaume and J, Rouquerol, J. Therm. Anal., 3 (1971) 413.
44 F. Paulik and J. Paulik, Anal. Chim. Acta, 67 (1973) 437.
45 J. Paulik, F. Paulik and M. Arnold, Hungarian Scientific Instruments, 59 (1985) 57.
46 J. Rouquerol and L. Davy, Thermochim. Acta, 24 (1978) 391.
47 J. Rouquerol, Pure and Applied Chemistry, 1985, vol. 57, no. 1, p. 69.
48 M.L. Huckabee and H. Palmour, III, Am. Ceram. Soc. Bull., 51 (7) (1972) 574.
49 M. El Sayed Ali and O. Toft Sorensen, in B. Miller (Ed.), Thermal Analysis, Proc. 7th Int. Conf. on Thermal Analysis, Wiley, 1982, p. 344.
50 M. El Sayed Ali, O. Toft Sorensen and L. Halldahl, J. Therm. Anal., 25 (1982) 175.
51 R.A. Lawbon and H. Palmour, III, Abstract in Am. Ceram. Soc. Bull., 49 (8) (1970) 753.