

QUASI-ISOTHERMAL METHODS IN THERMAL ANALYSIS

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ABSTRACT

Compared with conventional non-isothermal analysis, quasi-isothermal methods have the advantages that (1) reaction temperatures can be determined accurately, (2) close-lying reactions can easily be separated, and (3) accurate kinetic data can be determined for each intermediate reaction in a single run. After a short description of the experimental technique, examples of the resolution obtained in quasi-isothermal thermogravimetric studies of thermal decompositions are discussed as well as the advantages obtained in quasi-isothermal dilatometric sintering studies of oxide compacts. Finally, it is demonstrated how kinetic data can be determined from the temperature and weight/length curves recorded in quasi-isothermal thermogravimetric and dilatometric studies.

INTRODUCTION

Quasi-isothermal analysis (QIA) was introduced only a few years ago by Paulik and Paulik [1–3], who used it in connection with thermogravimetric analysis. Since then several publications have shown the usefulness of this method both in thermogravimetric and dilatometric studies (see, for instance, Sørensen [4,5]), whereas its application in its true sense still remains to be demonstrated in differential thermal analysis and differential scanning calorimetry. Compared to conventional non-isothermal methods, QIA has the following advantages:

(1) consecutive but close-lying reactions or phase transformations are easily separated;

(2) for each reaction, the kinetics (controlling mechanism and activation energy) can be determined from the QIA curve without the interference of overlapping reactions.

(3) the reactions take place under nearly isothermal conditions and the kinetic data obtained are more accurate than those obtained by non-isothermal methods.

(4) data for all relevant reactions are obtained in a single run. Much less work is thus involved in this method relative to an isothermal study, which often requires many runs to cover a large temperature range.

The purpose of this paper is, first, to define and describe how this technique operates, then to demonstrate how some of these advantages have been obtained both in thermogravimetric and dilatometric studies, and finally to discuss how QIA curves generally can be interpreted. Most of the examples used here come from the author's previous publications [4–6].

DESCRIPTION OF THE QIA TECHNIQUE

The QIA technique operates in the following way. When the sample during a programmed heating reaches the reaction temperature and a deviation is obtained in the weight (TG) or length curve (dilatometry), a DTG signal proportional to the slope of this curve is produced in the DTG amplifier. With a regulator two limits can be preset for the DTG signal: an upper limit where the heating is stopped when the DTG signal exceeds this limit, and a lower limit where the heating is resumed when the signal again becomes smaller than this limit, which takes place when the reaction is nearly completed. As shown in Fig. 1, two different types of behaviour can be envisaged using the QIA method:

(1) if the rate of the reaction taking place in the sample is so large that the DTG signal remains outside the limits during the whole reaction period, there will be strictly isothermal conditions and the weight/length curve will have the sigmoid form shown in Fig. 1;

(2) if only a small portion of the sample reacts when the reaction temperature is reached, the DTG signal will quickly return to the lower preset limit, the heating will be resumed, and a small portion of the sample will react again, etc. This will cause the DTG signal to fluctuate between the two limits and the weight/length curve obtained in this case will be a straight line. The sample will be heated only a few degrees during each step and the reaction will take place under quasi-isothermal conditions.

A characteristic feature of this method, which makes it unique, is that the overall heating rate is determined by the reactions themselves, whereas in all other thermal analysis methods the heating programme is forced upon the samples and the reactions will take place under a given set of conditions. In a QIA method, the reactions thus take place under conditions that are close to equilibrium, and more accurate and reproducible results must therefore be expected with this method. In order to obtain ideal conditions, however, the

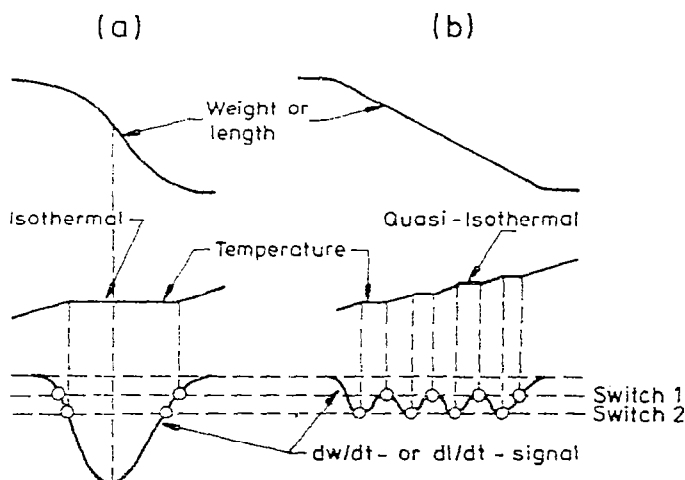


Fig. 1. Principle of quasi-isothermal thermal analysis methods.

equipment must fulfill the following requirements:

- (1) the furnace must operate quickly with no overshoot in temperature;
- (2) heat must be transferred rapidly to the sample and the time lag between the sample and the furnace should be small;
- (3) the temperature distribution must be homogeneous.

That conditions close to equilibrium can be obtained by stepwise heating is also evident from the work of Simonsen and Zaharescu [7], who developed a new differential thermal analysis technique in which the temperature was increased in constant steps — 2°C between each step — whereas the time at each step was manually controlled. In conventional differential thermal analysis melting and phase-transformations usually take place over a substantial temperature range — characteristic ranges are 50 and 80°C for the two types of reactions — but with the stepwise heating method temperature ranges of only 2 – 4°C were obtained, which obviously must improve the accuracy considerably. Furthermore, increased accuracy was obtained by Staub and Perron [8], who introduced stepwise heating in the quantitative differential thermal analysis method used for purity determination. Finally, Flynn and Dickens [9] demonstrated that many of the uncertainties involved in conventional thermal analysis using a constant heating rate are removed in methods where a rate-forcing variable such as temperature is varied in discrete steps. These authors showed also that kinetic data and reaction mechanisms determined by this method for solid state reactions are more realistic than those found by conventional methods.

It is also interesting to compare QIA with the constant rate thermal analysis methods introduced by Rouquerol [10] and Criado et al. [11,12].

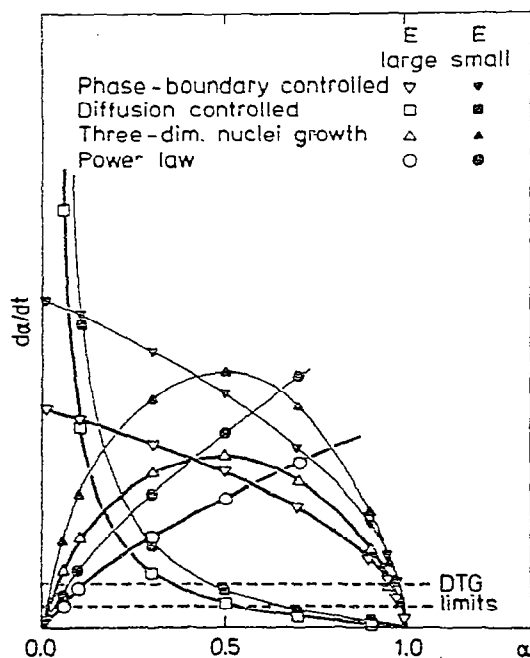


Fig. 2. Reaction rate ($d\alpha/dt$) as a function of degree of conversion (α) for reactions controlled by different mechanisms [14].

Although this method cannot be regarded as isothermal or quasi-isothermal, it certainly has considerable advantages compared to conventional methods using constant heating rates, primarily because the sample is allowed to react under conditions which are close to equilibrium. However, as shown in Fig. 2, it is natural for most reactions to proceed at a changing reaction rate, and by imposing the restriction of a constant reaction rate the reaction must be influenced in an artificial way. In the author's opinion some doubt still exists as to whether strictly equilibrium conditions really are obtained in the constant reaction rate sintering method introduced by Huckabee et al. [13], which also gives conditions closer to equilibrium than those obtained in conventional sintering methods.

EXAMPLES

Thermal decompositions studied by quasi-isothermal thermogravimetry

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

It is well known that, on heating, the crystal water of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is released in three steps—two water molecules at $\sim 80^\circ\text{C}$, two at $\sim 120^\circ\text{C}$,

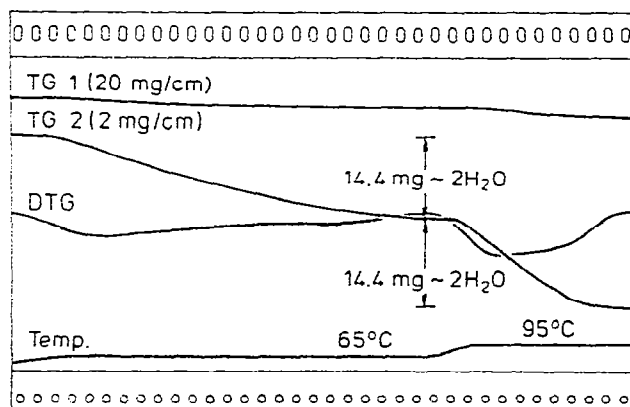
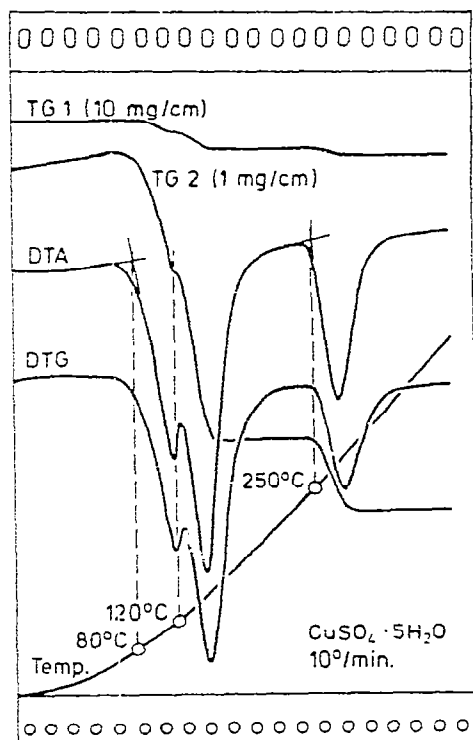


Fig. 3. Thermal decomposition reactions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ determined by conventional non-isothermal simultaneous (TG and DTA) thermal analysis.

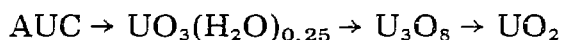
Fig. 4. Quasi-isothermal temperature and weight curves for thermal decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

and the last at $\sim 250^\circ\text{C}$. In conventional thermogravimetric analysis the first two steps overlap considerably, as shown in Fig. 3, and it is impossible to determine quantitatively the amount of water released in the single steps by this method. Using the QIA technique, however, these two steps can be completely separated, as shown in Fig. 4, and the weight change involved in each step can be accurately determined in this manner.

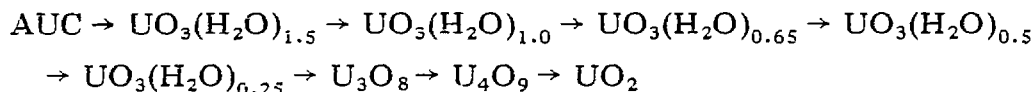
Ammonium uranyl carbonate (AUC)

Ammonium uranyl carbonate (AUC) has become an important intermediate product in the conversion of UF_6 to UO_2 powder, and is used for fabricating fuel elements for nuclear reactors. AUC is the precipitate from a wet chemical process and has to be reduced in a hydrogen atmosphere to UO_2 powder, which is pressed and sintered to UO_2 pellets used in the fuel elements.

The reactions during thermal decomposition and subsequent reduction of AUC have been studied both by conventional and quasi-isothermal thermogravimetry [15]. Comparing the results obtained by these methods the advantages of QIA are clearly demonstrated. Whereas conventional TG showed that the thermal decomposition and the reduction apparently take place in the following steps



the detailed step temperature curve obtained by QIA (Fig. 5) indicated that many more intermediate compounds are possible, i.e.



which demonstrates the good resolution of the QIA method.

Sintering studies by quasi-isothermal dilatometry

The quasi-isothermal technique can also be used successfully in dilatometric studies. As an example of the advantages of quasi-isothermal dila-

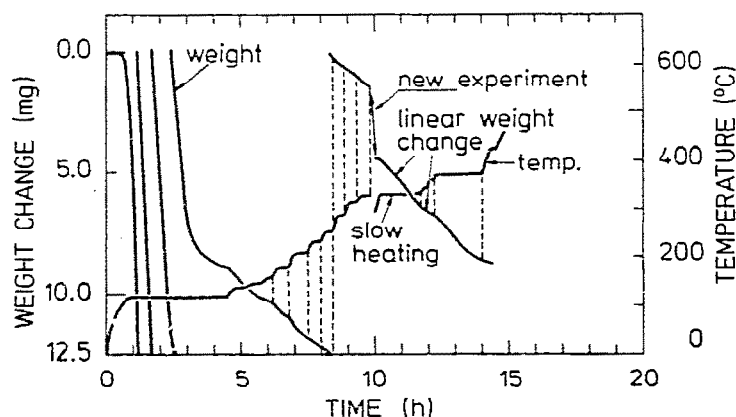


Fig. 5. Weight and temperature curves obtained in a quasi-isothermal thermogravimetric examination of the thermal decomposition of ammonium uranyl carbonate (AUC) in hydrogen.

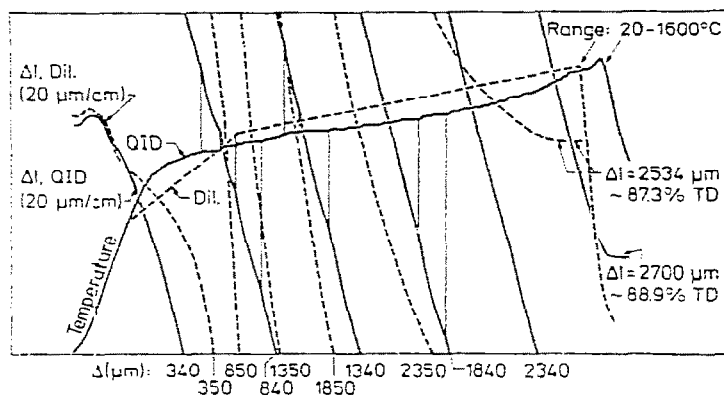


Fig. 6. Length and temperature curves obtained in a non-isothermal and quasi-isothermal dilatometric study of $\text{ZrO}_2\text{-MgO}$ powder compacts.

tomety (QID), the temperature and length (shrinkage) curves recorded in a sintering study of $\text{ZrO}_2\text{-MgO}$ compacts are presented in Fig. 6, where the curves obtained by QID are superimposed on those obtained by conventional (constant heating rate) dilatometry. Comparing these curves it is clear that the heating programme automatically obtained with the quasi-isothermal method is quite similar to that used in the conventional non-isothermal method. It is, however, interesting to note that while the heating programme used in the latter method was selected after several trial runs, the optimum programme could be established from a single QID run. In fact, a larger total shrinkage and thus a higher final density was obtained by QID, indicating that the sintering conditions automatically selected in this method are very close to the equilibrium conditions. The reason for the higher density obtained in QID is probably due to the lower densification rate selected for the first part of the sintering process. For $\text{ZrO}_2\text{-MgO}$ a gas release apparently takes place at lower temperatures, and if the densification proceeds too rapidly these gases will become entrapped, which gives a lower final density.

INTERPRETATION OF QUASI-ISOTHERMAL CURVES

Quasi-isothermal thermogravimetry

Shape and pattern of weight and temperature curves

As shown in Fig. 1, two basic types of behaviour can be expected in quasi-isothermal experiments: (A) the DTG signal remains outside the upper preset limit during a large part of the reaction, and a sigmoid weight curve, but strictly isothermal conditions, will be obtained; (B) the DTG signal fluctuates between the two preset limits and a linear weight change will be obtained. The temperature will increase only a few degrees during each step and quasi-isothermal conditions are obtained.

Considering the $d\alpha/dt$ vs. α curves shown in Fig. 2 for different controlling mechanisms, it will be noted that nucleation (power law) and three-dimen-

sional growth of nuclei can, depending on the activation energy, give type B behaviour in the first part followed by type A behaviour, whereas the opposite will be observed for phase-boundary and especially diffusion-controlled reactions. Each reaction can, therefore, involve several temperature steps and generally the pattern of these steps and the shape of the weight curves are determined by the mechanism controlling the reaction. A detailed study of the temperature and weight curves can thus provide information about the reaction type.

Calculation of activation energies, general

For a reaction involving several steps, the reaction rate, $d\alpha/dt$, at the two DTG limits is given by

$$\left(\frac{d\alpha}{dt}\right)_1 = k_\infty \exp(-E/RT_1) \cdot f_1(\alpha)$$

$$\left(\frac{d\alpha}{dt}\right)_2 = k_\infty \exp(-E/RT_2) \cdot f_2(\alpha)$$

where E is the activation energy, k_∞ is the frequency factor in the Arrhenius equation, T_1 and T_2 are the absolute temperatures at two succeeding temperature steps, and $f(\alpha)$ is a function of α (fraction reacted at time t) describing the reaction mechanism [14].

Assuming that α remains constant during the change in temperature from one isothermal step to the next, it follows that $f_1(\alpha) = f_2(\alpha)$, and the ratio between the two reaction rates becomes

$$C = \exp(-E/RT_1)/\exp(-E/RT_2)$$

or

$$\log C = \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{E}{R} \Delta \left(\frac{1}{T} \right) \quad (1)$$

where C is a constant depending on the DTG value used at the two preset limits (switches 1 and 2 in Fig. 1). In the measurements on AUC discussed above, these were 0.10 and 0.15 mg min^{-1} , respectively, and in this case $C = 0.1/0.15 = 0.66$. According to eqn. (1) the activation energy can thus be calculated directly from the temperature difference between two succeeding steps.

Activation energies and mechanisms of thermal decomposition reactions in AUC

The first step in an evaluation of kinetic data from quasi-isothermal weight and temperature curves is to determine the number of temperature steps involved in the single reactions. Some guidance can be obtained by comparing the characteristic pattern for possible reactions (as discussed in the previous section) with the pattern of the measured temperature curve. The most accurate method, however, is to compare activation energies calculated from the temperature difference between succeeding steps according to eqn. (1). A change in the reaction type will then be indicated by a significant change in the activation energy.

TABLE 1

Activation energies for thermal decomposition reactions of ammonium uranyl carbonate (AUC)

Step	Temp. (°C)	$\Delta(1/T) \times 10^4$ (K ⁻¹)	E (kJ mole ⁻¹)	Reaction
1	116			AUC
2	120	-0.26	57.7	↓ UO ₃ (H ₂ O) _{1.5}
3	139	(-1.18)	(12.7)	UO ₃ (H ₂ O) _{1.5}
4	148	-0.52	28.9	↓
5	158	-0.55	27.3	UO ₃ (H ₂ O) _{1.0}
6	179	(-1.08)	(13.9)	
7	208	-1.35	11.1	Consecutive
8	232	-0.97	15.4	reactions
9	252	-0.75	20.0	UO ₃ (H ₂ O) _{1.0}
10	286	-1.16	13.0	↓
11	316	-0.90	16.7	↓
12	328	(-0.35)	(42.9)	UO ₃ (H ₂ O) _{0.25}

Using this method to evaluate the number of reactions involved in the thermal decomposition of AUC, the activation energies (given in Table 1) which were calculated from the quasi-thermal temperature curve shown in Fig. 5 were obtained. From Table 1 it is clear that several reactions are involved in the thermal decomposition and that a change in the reaction type takes place between steps 2 and 3, 5 and 6, and 11 and 12.

Once the extent of the individual intermediate reactions is known, $\alpha (= \Delta W_t / \Delta W_{\max})$ and $d\alpha/dt$ can easily be calculated at constant temperature for selected temperature steps, and using a $\log d\alpha/dt - \log f(\alpha)$ plot the mechanism controlling the reaction can be determined. Taking the $\text{AUC} \rightarrow \text{UO}_3(\text{H}_2\text{O})_{1.5}$ conversion as an example, a linear relationship could be

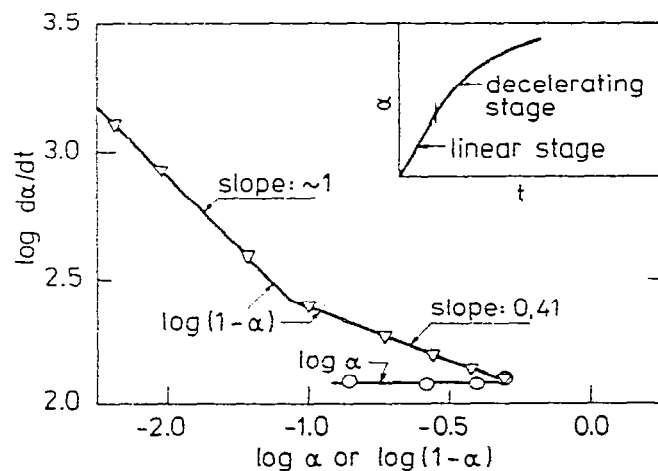


Fig. 7. Log-log plot for the $\text{AUC} \rightarrow \text{UO}_3(\text{H}_2\text{O})_{1.5}$ conversion step.

obtained only when $\log d\alpha/dt$ was plotted against $\log \alpha$ and $\log (1-\alpha)$ (Fig. 7), indicating that the first part of this conversion is controlled by one- and two-dimensional phase boundary movement, respectively [$f(\alpha) = \text{constant}$ and $f(\alpha) = (1 - \alpha)$]. No data are available in the literature on the isothermal decomposition reactions of AUC. However, a lot of work has been done on ammonium diuranate (ADU) [17] and, for instance, in the work of Ball et al. [18] it was concluded that the thermal decomposition of ADU is controlled by a one-dimensional diffusion mechanism [$f(\alpha) = \alpha^{-1}$] with an activation energy of 42 kJ mole⁻¹. It has been observed that the activation energy strongly depends on the modification of UO₃ being formed — formation of amorphous UO₃ for instance, requires 113 kJ mole⁻¹ — which can explain the higher activation energy observed in this study. However, the reason for the difference between the two observed reaction mechanisms is not clear, but Ball et al. [18] did use the less precise non-isothermal thermogravimetric technique in their investigation. Finally, in a recent study Hälldahl and Sørensen [19] determined the activation energy of the first part of thermal decomposition of AUC to be 79.5 ± 6.9 kJ mole⁻¹. This is somewhat higher than that given in Table 1, but again a non-isothermal technique with high heating rates ($\sim 130^\circ\text{C min}^{-1}$) was used in this study, making these activation energies less precise.

Quasi-isothermal dilatometric (QID) sintering studies

Theory

Sintering of a powder compact is an activated process which involves several stages. From experiments with model systems, equations describing the different stages have been proposed but generally none of these can fully describe the complicated and, to some extent, overlapping processes taking place in a “real” powder compact. For a preliminary study of a sintering process by QID the following very general equation proposed by Thümmeler and Thomma [20] can therefore be used

$$\frac{\Delta l}{l_0} = (Kt)^n = [(Z \exp - Q/RT) t]^n \quad (2)$$

where Δl is the shrinkage, l_0 is the initial length of the specimen, K is the Arrhenius constant with the pre-exponential factor Z and the activation energy Q , T and t designate the temperature and time, respectively, and n is an exponent which characterizes the sintering process. According to this equation, isothermal plots of $\ln \Delta l/l_0$ vs. $\ln t$ should give a straight line with a slope equal to n . However, this was not the case, with the experimental data obtained in the study of CeO₂—Gd₂O₃ compacts discussed below, which gave a straight line only when Δl was plotted against t ; the equation to be used for QID data in this case must be

$$\Delta l = Kl_0 t = Z \exp(-Q/RT) l_0 t \quad (3)$$

The slope of this line is Kl_0 and according to

$$\ln(Kl_0) = \ln Z + \ln l_0 - Q/RT \quad (4)$$

the activation energy can thus be determined from the slope of the straight line obtained by plotting $\ln(Kl_0)$ vs. $1/T$. From eqn. (4) the pre-exponential factor can also be determined when l_0 and Q are known.

Sintering of $CeO_2-Gd_2O_3$ compacts

As an example, the temperature and length curves recorded during the QID measurement on a $CeO_2-Gd_2O_3$ compact are shown in Fig. 8. The shrinkage (Δl) determined at each isothermal step from these curves, is shown as a function of time in Fig. 9, and obviously a straight-line relationship is obtained for all steps in accordance with eqn. (3). In some cases, however, the slope of this line changes before the densification is complete at a step (4 and 11), indicating a change in the kinetic parameters for the sintering process. Finally, $\log(Kl_0)$ values calculated from the slope of these lines are plotted vs. $1/T$ in Fig. 10 and a new set of straight lines is obtained from which the activation energy and the pre-exponential factor can be calculated according to eqn. (4). From the values obtained (given in Table 2) it can be concluded that the sintering process takes place in several stages, each with a characteristic activation energy and pre-exponential factor. The mechanism controlling the sintering process at these stages cannot, however, at present be determined by this method but a more detailed analysis has been planned for a later study.

CONCLUSION AND RECOMMENDATIONS

From the examples described here it can be concluded that quasi-isothermal thermogravimetry and dilatometry can be very useful in studies of solid state reactions. Compared to conventional non-isothermal thermal analysis, these methods give the following advantages: (1) better accuracy because the experimental conditions automatically selected by these

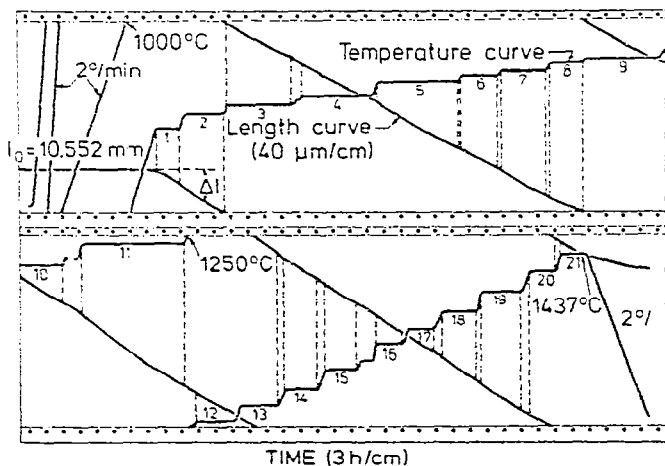


Fig. 8. QID curves (temperature and shrinkage) recorded during sintering of $CeO_2-Gd_2O_3$ (35%) powder compacts.

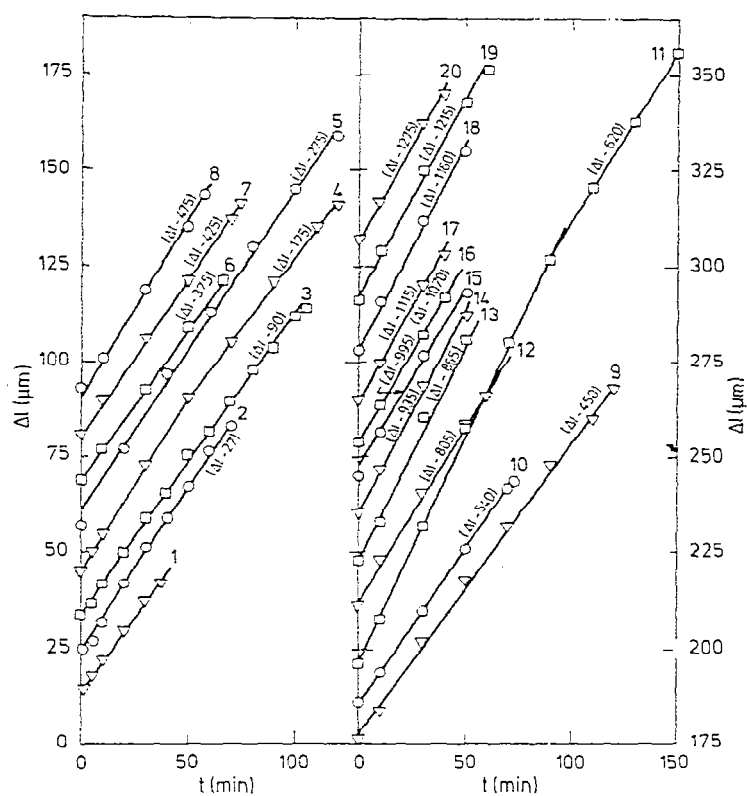


Fig. 9. Shrinkage (Δl) as a function of time determined from Fig. 8.

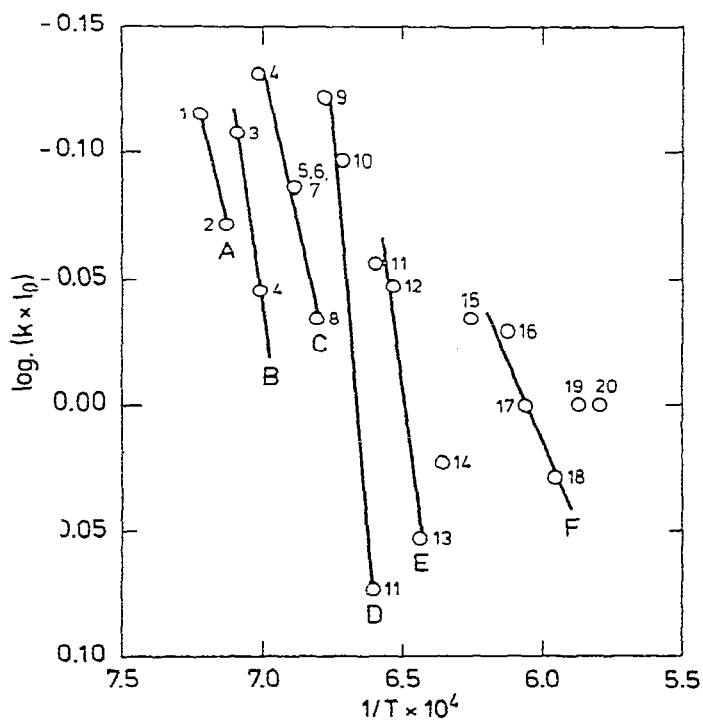


Fig. 10. Arrhenius plot of $\log(Kl_0)$ vs. $1/T$ for sintering of a $\text{CeO}_2\text{-Gd}_2\text{O}_3$ (35%) compact. The number indicated at each point is the step number used in Figs. 8 and 9.

TABLE 2

Calculation of activation energies and pre-exponential factors for sintering stages of $\text{CeO}_2\text{—Gd}_2\text{O}_3$ compacts

Curve No. *	E (kcal mole ⁻¹)	Z (min ⁻¹)
A	22.37 (1) **	0.247
B	39.22 (4)	88.51
C	28.03 (8)	1.33
D	49.57 (11)	1.58×10^3
E	32.95 (13)	4.71
F	13.26 (17)	5.42×10^{-3}

* See Fig. 10.

** Figures in parentheses indicate step numbers used in Figs. 8 and 9.

methods are closer to equilibrium, (2) improved resolution because the heating is stopped as soon as the reaction temperature is reached, (3) more reliable kinetic data because each reaction takes place under isothermal or nearly isothermal conditions, and (4) a very simple and straightforward evaluation of the activation energy for the single reactions.

However, a more detailed analysis, especially of shrinkage curves, is required in order to evaluate fully the capability of these methods and there is still room for improving the experimental technique. Instead of the electronic DTG amplifiers used in studies described here, it would certainly be advantageous to use computer techniques, which can respond more correctly and quickly to weight or length (shrinkage) changes.

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