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AN EXPERIMENTAL INVESTIGATION OF THE THERMAL DECOMPOSITION OF BRUCITE BY THERMOSONIMETRY

KNUT LONVIK
Institutt for Eksperimentalfysikk, N.T.H. Trondheim (Norway)
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ABSTRACT

This paper is a presentation of pure experimental results on the thermal decomposition of brucite, $Mg(OH)_2$, by observations based on thermosonimetry (TS) measurements. The experimental arrangements and methods are briefly described and attention has been given to the determination of the actual signal frequency content. No theoretical conclusions concerning the process mechanism are considered, but the mechanical breaking up of the sample is attributed to an intermittent phenomena of a relaxational character, most probably caused by some kind of temperature barrier.

INTRODUCTION

Reports on the thermal decomposition of brucite, $Mg(OH)_2$, suggest, in many respects, that the process is of a rather specific character. This is partly reflected in the dissymmetry of the temperature deviation peak (DTA) and any extant kinetic equation is unlikely to be explicable. For the dehydroxylation process itself, different theoretical descriptions have been proposed. The object of this paper is not to evaluate the theoretical mechanism involved, but to give new experimental data based on thermosonimetric (TS) measurements. One advantage of this method is the prompt response to any sudden change in the thermomechanical properties of the sample. Under ideal conditions, it would be possible to observe details during the course of the decomposition.

An earlier result from a scanning temperature trace on a piece of unspecified mineral containing brucite, shown in Fig. 1, conveys nothing new except for the expected peaking around 400 °C, probably composed of a group of sub-peaks.

In relation to this preliminary information, a specially selected scan from a new set of refined experiments with brucite mineral, given in Fig. 2, does, however, uncover an interesting feature of a different nature. The immediate conclusion drawn from this observation is the existence of a reaction structure within the temperature deviation peak. It is worth noting that the corresponding pulsed TS activity is located close to the step front of the DTA curve around 400 °C.

TS detection seems to be a useful tool in mapping the relationship during the

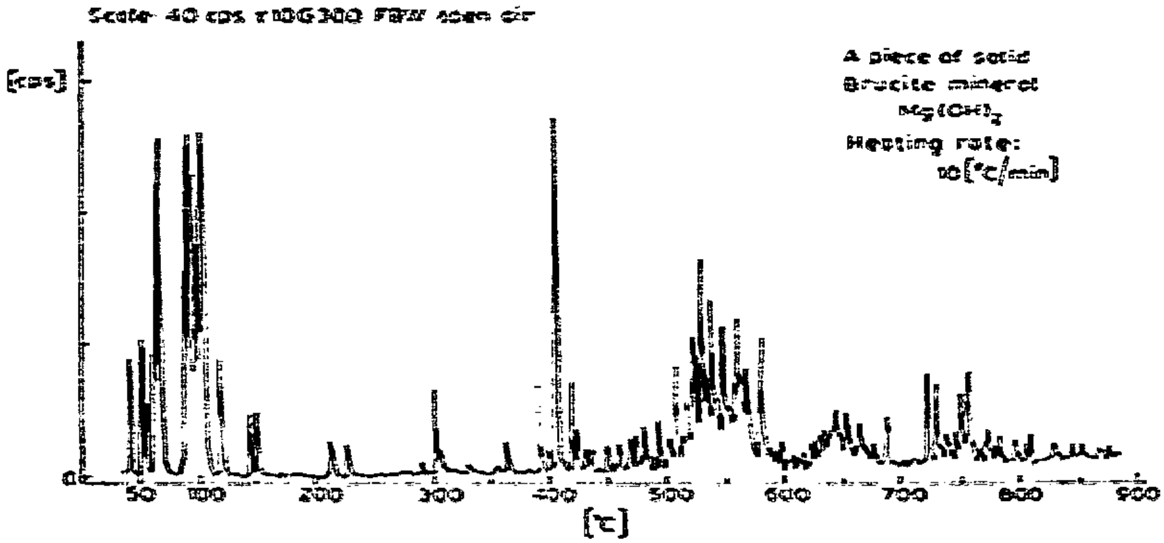


Fig. 1. The course of TS activity from a piece of solid brucite mineral.

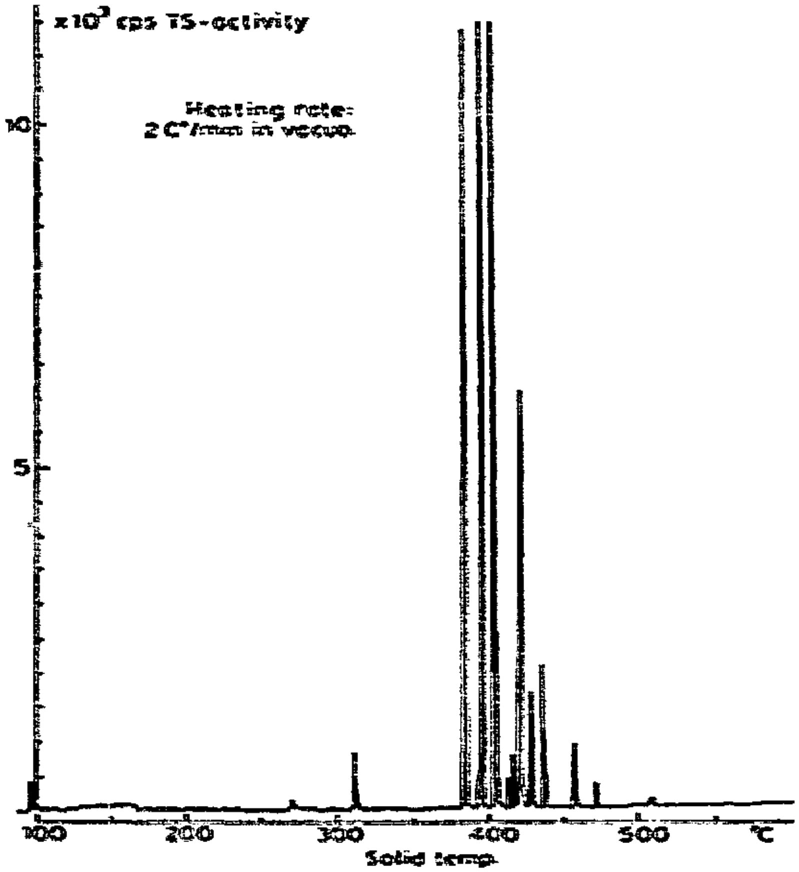


Fig. 2. Characteristic TS activity in a solid piece of brucite mineral (sample D).

course of sample fracture caused by the decomposition of $Mg(OH)_2$. The investigation indicates certain aspects of the working mechanism and supports the assumption of a partly intermittent process.

EXPERIMENTAL

Experimental set-up

The basis of the experimental set-up for these measurements is sketched in Fig. 3. The integral system of the sample on the top of the resonance stethoscope and the signal pick-up cell at the base are performed entirely in a special seismic mount. The temperature reference was read from an interchangeable probe placed in the neighbourhood of the actual sample. A vacuum proof housing sealed off this arrangement from the environmental atmosphere. The rise of the scanning temperature and the inside working pressure were controlled by suitable instrumentation.

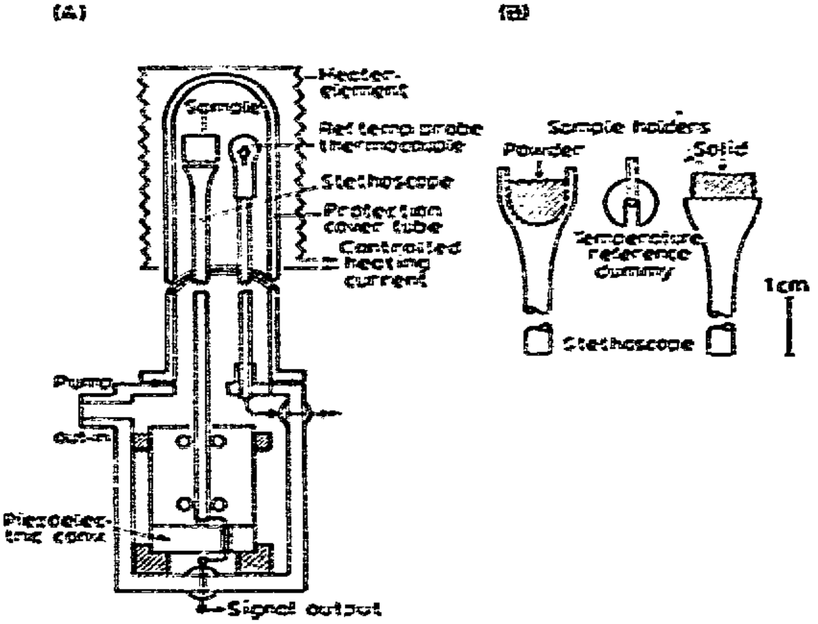


Fig. 3. (A) The experimental set-up. (B) The stethoscope sample holders.

Information detection

The thermomechanical activities in the sample consisted of different types of temperature-dependent sonic vibrations which were picked up by the resonance stethoscope and converted to electrical signals by the use of a piezo-electric cell. These signals are the basic information given and are measured as a function of the surrounding temperature of the sample picked up by the nearby dummy reference sample.

The final result depends, to a certain extent, on the way in which the available electrical signals are handled. These are a succession of bursts of individually damped oscillations with different frequency content. The actual situation is best illustrated by Fig. 4.

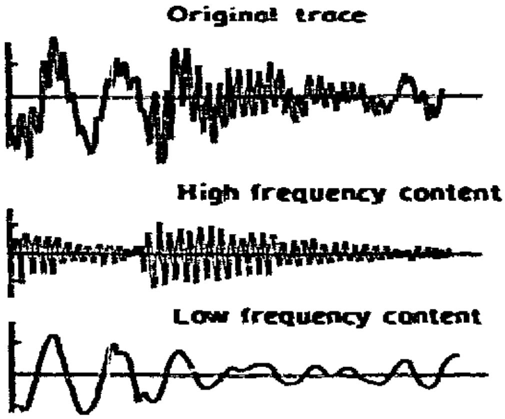


Fig. 4. An example of actual signal bursts. The information is separated according to high and low frequency contents.

The main method of TS detection used in the present experiment was based on the registration of the number of bursts (or waves included) per second (cps) (or by the signal RMS value) of the signals arriving from the electronic adaption. A further improvement to obtain more extensive information would be to have a figure for the frequency content of the signalling itself. The present instrumental set-up therefore includes an electronic circuit to register the main frequency components in the TS burst signal. The occurrence of the individual frequencies is stored and recognised by a distribution versus frequency curve.

Sample description

The present investigation was carried out on various sources of material, the main purpose being to determine the influence of different environmental conditions on the decomposition process.

The following substances were used.

(A) $Mg(OH)_2$ powder

Source, Merck 5870; molecular weight 58.34.

The powder samples, due to their purity, were the centre of interest. The preparation of the samples was carried out by packing the powder into a quartz glass stethoscope holder as pictured in Fig. 3(B). About 1 mg of material was used in each experimental run.

Several problems arose while working at low pressure. There was a tendency for the powder to spill out of the upper open side of the sample holder. The powder was, however, sufficiently stable for measurements to be performed in open air conditions.

(B) Brucite crystal from Lancaster Co. Texas, Pennsylvania

Source, Mineral-geologisk museum in Oslo.

The material was a partly transparent and laminated solid consisting of regular layers of flakes, which, unfortunately, split up during the rise of temperature (300 °C). This is the main cause of additional signals and the reduction in the ability of the

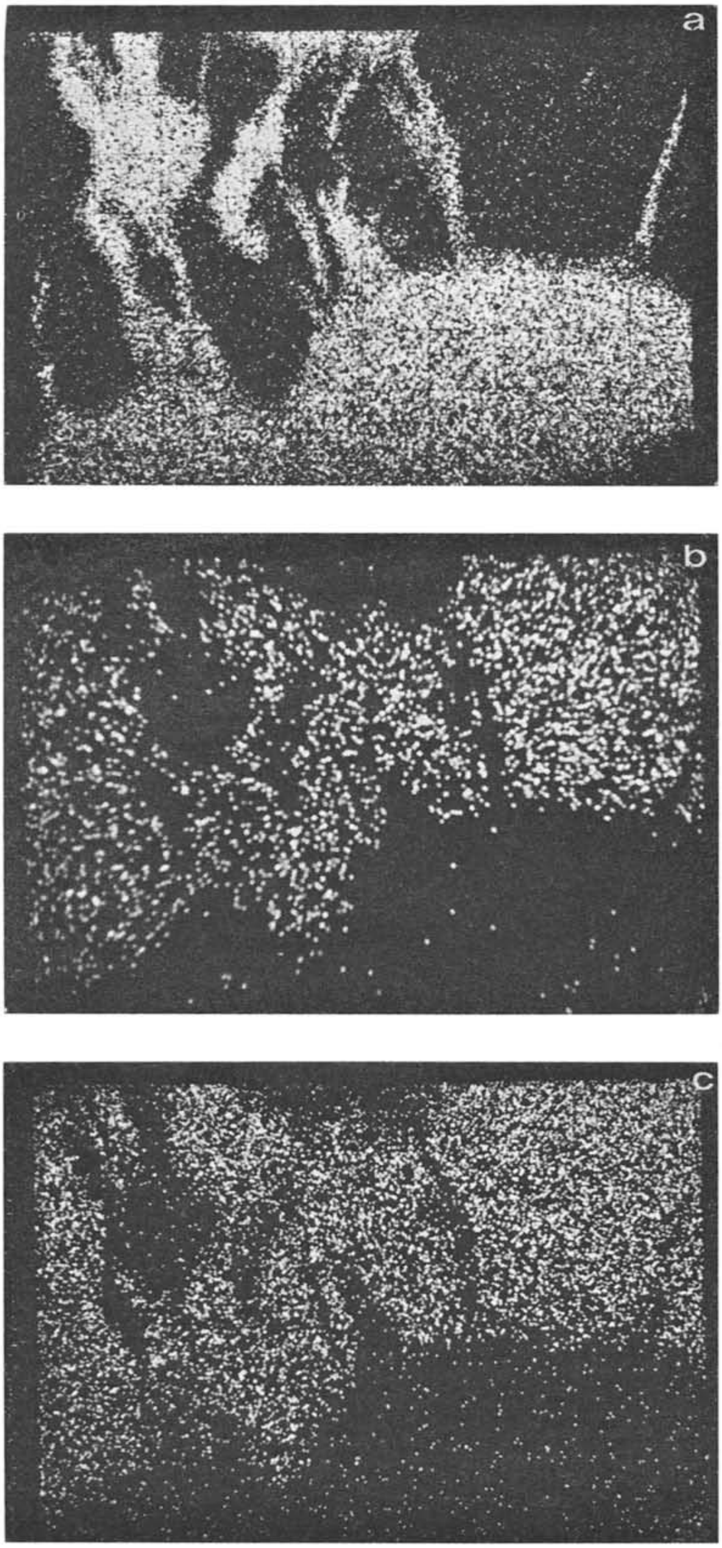


Fig. 5. Microsonde picture of the distribution of magnesium in the brucite sample D shown in Fig. 2 together with the distributions of carbon and calcium ($CaCO_3$). (a) Magnesium distribution, 10 keV, ≈ 235 cps. (b) Calcium distribution, 20 keV, ≈ 11.5 cps. (c) Carbon distribution, 10 keV, ≈ 25 cps.

stethoscope to sense all regions of the sample. The loss of information caused by this situation is difficult to clarify.

Small cubic samples of about 5 × 5 × 8 mm were cut from the original crystal and polished at the end facing the sensing head. The samples were held on the converting head of the stethoscope by their own weight. A few of these small pieces were repelled from the sensing head and sometimes jumped off the stethoscope during the splitting of the crystal into flakes.

(C) Brucite mineral (canzoeoli) from Plummertahl in the Tyrol

Source: Geologisk samling N.T.H., Trondheim.

This was a more consistent, solid piece of crystal, not fully transparent, having a weak grayish colour. The samples used in the experiment were of uniform size, as mentioned above, and were cut from the original piece. When inspected from outside the chamber, these pieces seemed to keep their volume and shape during the heating process.

(D) Mineral occurrence of brucite from Långban in Sweden

Source: Geologisk samling, N.T.H., Trondheim.

This piece of mineral was perhaps the most useful material to deal with. It was not transparent but consistent and solid.

A microsonde examination showed the $Mg(OH)_2$ to exist in layers with areas of different carbonates, mainly calcium, within the mother substance as shown in Fig. 5.

Signal handling

A flow diagram for the handling and analysis of the information obtained is shown in Fig. 6. The available temperature and TS activity signals are applied as input to the system. The curves presented are the outputs from (1) the recorder giving a scan of the TS activity versus the chosen reference temperature. The scanning parameter is the nominal rate of the temperature rise programmed by an ordinary temperature controller; (2) the pulse high analyser (PHA) unit finds the density distribu-

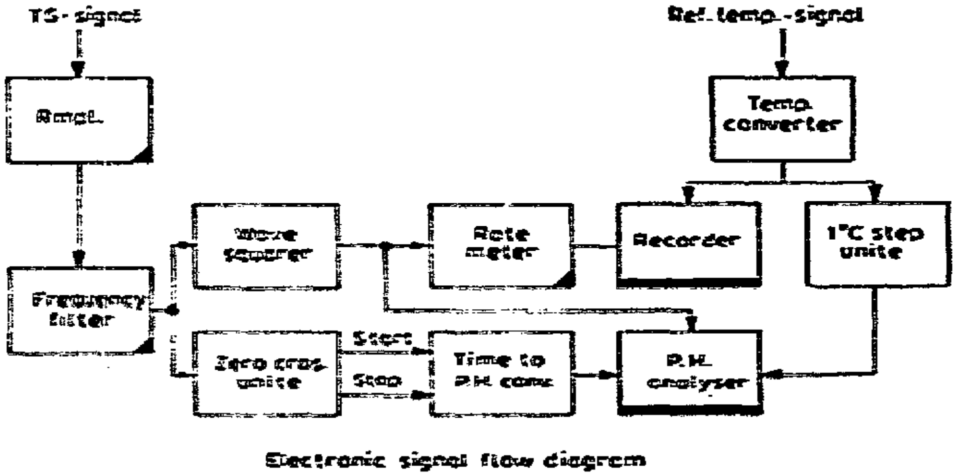


Fig. 6. Electronic signal flow diagram.

tion per 1 °C of the TS activity, and ultimately the zero crossing frequency distribution measured on the applied signal information.

The electronic equipment needed for each step in the signal treatment is given in each block in the diagram. The instrumental conditions were governed by an independent setting of three available adjustments of either the time constant of the ratemeter, the bandwidth of the frequency filtering or the registered sensitivity by the factor of amplification.

RESULTS

(A) Mg(OH)$_2$ powder

The powder samples were measured with different nominal rates of scanning temperature increase at constant pressure. Typical results are presented in Fig. 7 where the thermosonic information is given on the ordinate scale as a function of the temperature of a chosen reference material.

As seen from the curve, the reaction is characterized by a collection of successive sub-peaks around 400 °C. Relative to a reduced working pressure, provided by a vacuum pump (10^{-2} to 10^{-3} torr), the TS information has the same impressive character. The performance of the activity variations seems to be only slightly influenced by a lowering of the environmental pressure. In addition, the TS signals always

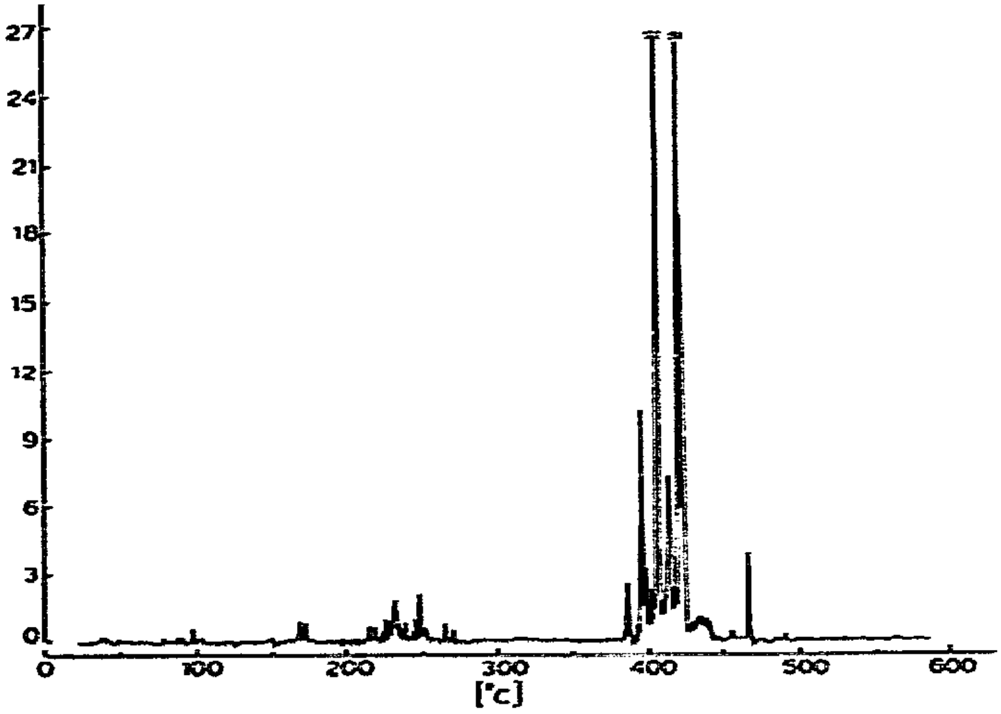


Fig. 7. TS activity of Mg(OH)$_2$ powder.

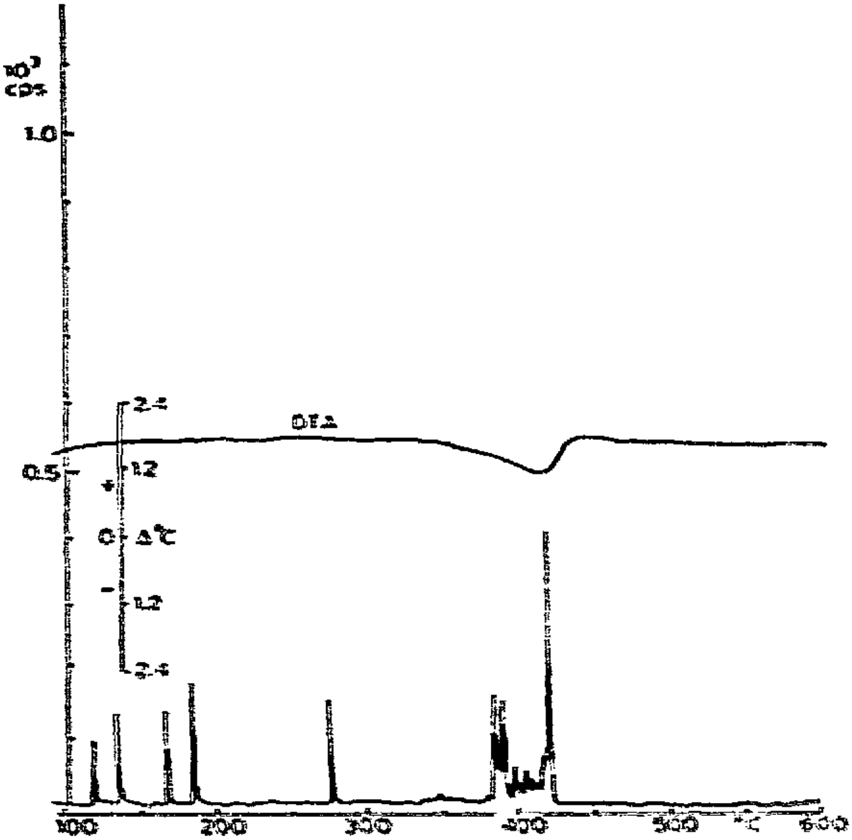


Fig. 8. Simultaneous recordings of the TS activity and DTA peak of $Mg(OH)_2$. Heating rate, 2 °C/min; range, 10 kc=1 Mc.

appear within a limited temperature range of 30 °C. As expected, the starting point of TS signals is immediately lowered on the scale of reference temperature by about 50 °C for a nominal scanning rate of 2 °C/min.

The conclusion drawn is the common feature of several sub-peaks, intervals with concentrations of bursts spread regularly on the reference temperature scale within a definite temperature region.

Note when reading the course of the activity change on the graphs, that the intensity (cps) was often cut in the ordinate direction caused by a saturation of the pen recorder due to the high amplification. This was done to emphasize the interesting information at the onset (the precursor zone) and the end of the process.

The recordings given in Fig. 8 are a comparison of the actual TS curves, relative to a simultaneous recording of the temperature deviation peak for different rates of nominal temperature rise in open air conditions. A reading from these curves confirms that the TS signalling occurs on the front of the thermal peak. In this connection, it is worth mentioning that the true thermomechanical breaking up of the sample was momentarily given as a TS activity. The thermal deviation peak, however, merely reflected a combined picture of the variations in the heat transaction and changes in the thermal property of the "sample".

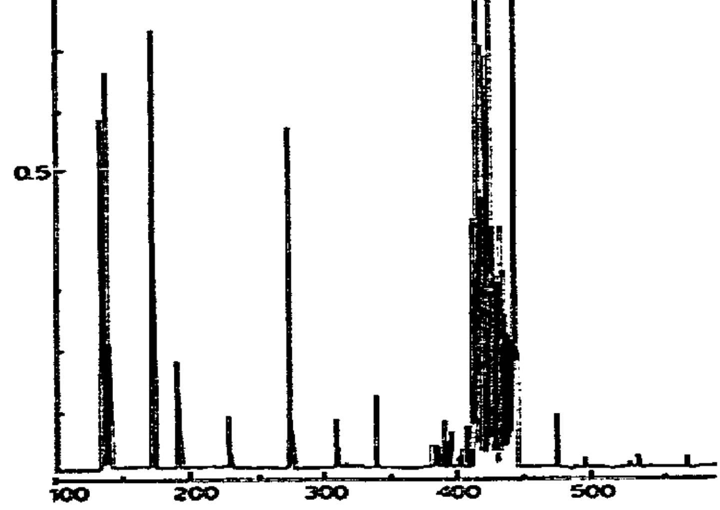
The advantage of TS scanning was better resolution in detecting the definitive fact of a material break up and in that sense represented a more differentiated course of the process in question. The measurement of the temperature deviation peak, on the other hand, contained rather integral information. For that reason, it was possible to focus interest more closely on the details within the measured activity region.

Figure 9(A) and (B) show some ratemeter registrations as well as an enlargement of the actual decomposition range. This was made possible by a simultaneous recording of the number of signal events per 1 °C versus a reference temperature and, in fact, represents a type of density distribution of the TS activity. The choice of a different temperature reference in this connection was not of importance.

The resolution of sub-peaks usually varied somewhat from registration to registration. This was a natural statistical effect and depended on the condition of the sample and the detection efficiency in relation to the choice of the instrument settings.

The pronounced feature of a marked peaking at the beginning and end of the actual TS registrations was assumed to indicate the real start and finish of the physical breaking up of the sample. The amplitudes between these two edging peaks seemed, on the average, to be smaller and partly masked because of lack of resolution.

In this actual experiment, the breaking up of the sample seemed to take place in steps. Therefore, the fracturing effect was thought to be mainly initiated within a limited "surface region" of an actual fresh part of the sample. After this partial con-



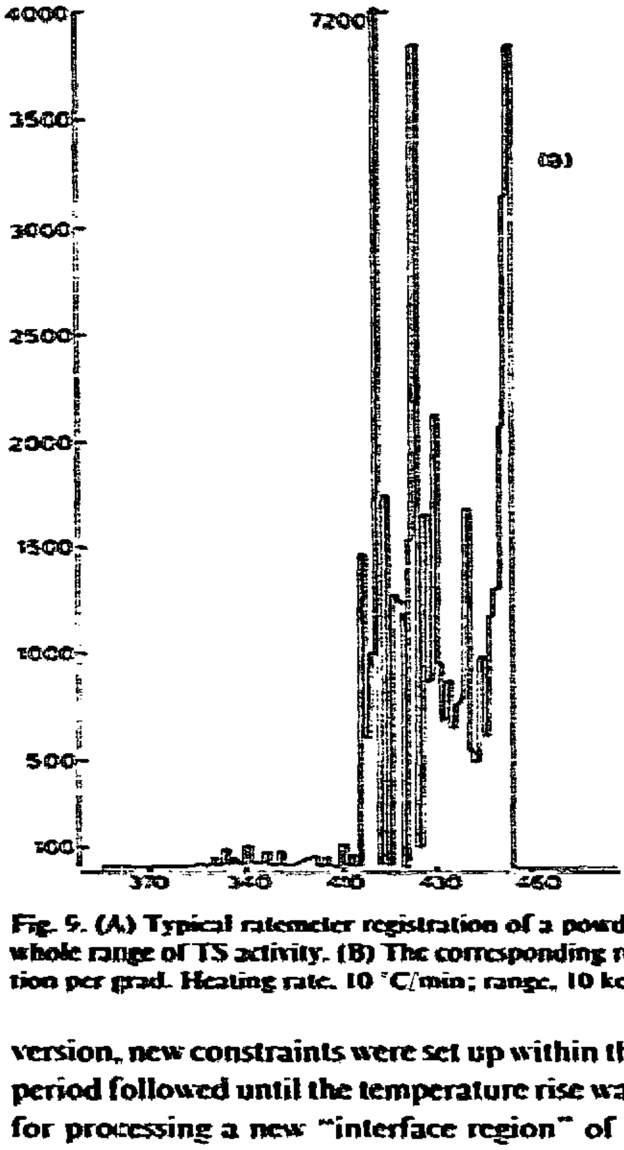


Fig. 9. (A) Typical ratemeter registration of a powder sample showing marked sub-peaking over the whole range of TS activity. (B) The corresponding resolution of the TS-active area as signal distribution per grad. Heating rate, 10 °C/min; range, 10 kc–1 Mc.

version, new constraints were set up within the layer of unreacted material. A revealing period followed until the temperature rise was high enough to overcome the conditions for processing a new "interface region" of an intermediate part of the sample. This procedure continued as the temperature increased within the sample, changing the inside tension during the partial transformations of the sample into periclase.

(B) Pennsylvanian brucite

Results obtained from samples taken from a piece of brucite from Pennsylvania are represented by a selected curve given in Fig. 10(A) and (B). The additional effect seen here was the splitting up of the structure of flakes in the solid samples in the temperature range from 220 to 360 °C. The sample physically swelled and the TS activity measured was most probably related to a release of the interface shearing stress between the flakes.

The reaction under investigation did not immediately manifest any particular, new feature. The general impression was still a spread of TS information, composed of several sub-peaks, within a somewhat broader temperature area (roughly 50 °C).

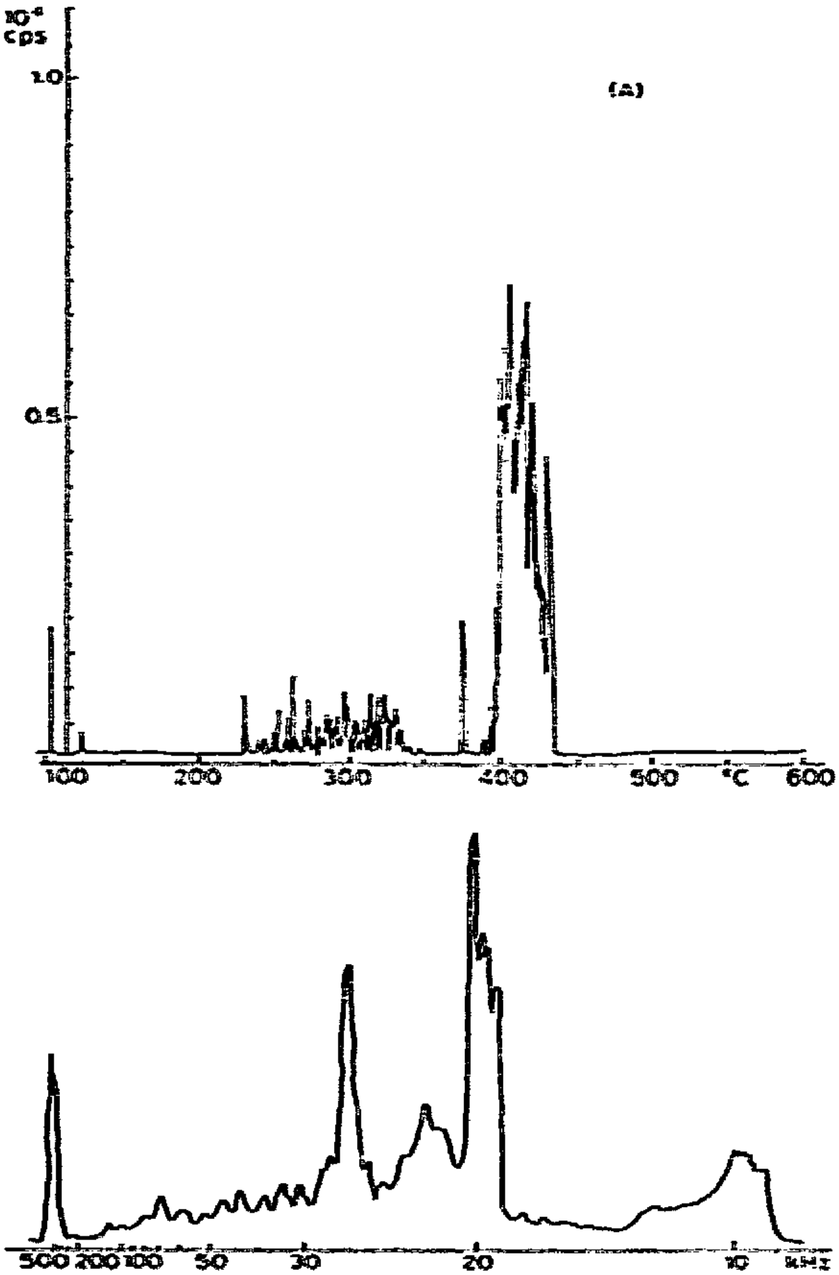


Fig. 10. (A) TS activity of a solid piece of Pennsylvanian brucite crystal. (B) Simultaneous recording of the number distribution of the signal zero crossing frequency. (A) and (B), heating rate, 2 °C/min; pressure, 10^{-2}–10^{-3} torr; range, 20 kc–1 Mc.

The scale resolution on the x-axis was too small to resolve fully the single sub-peaks.

To obtain an idea of the frequency composition of the TS signals at different temperature scanning rates, simultaneous registration was performed on the distribution of the TS signal zero crossing frequency number as given in Fig. 10(B). The existence of differences, the character of which it is too early to define, was the only conclusion drawn.

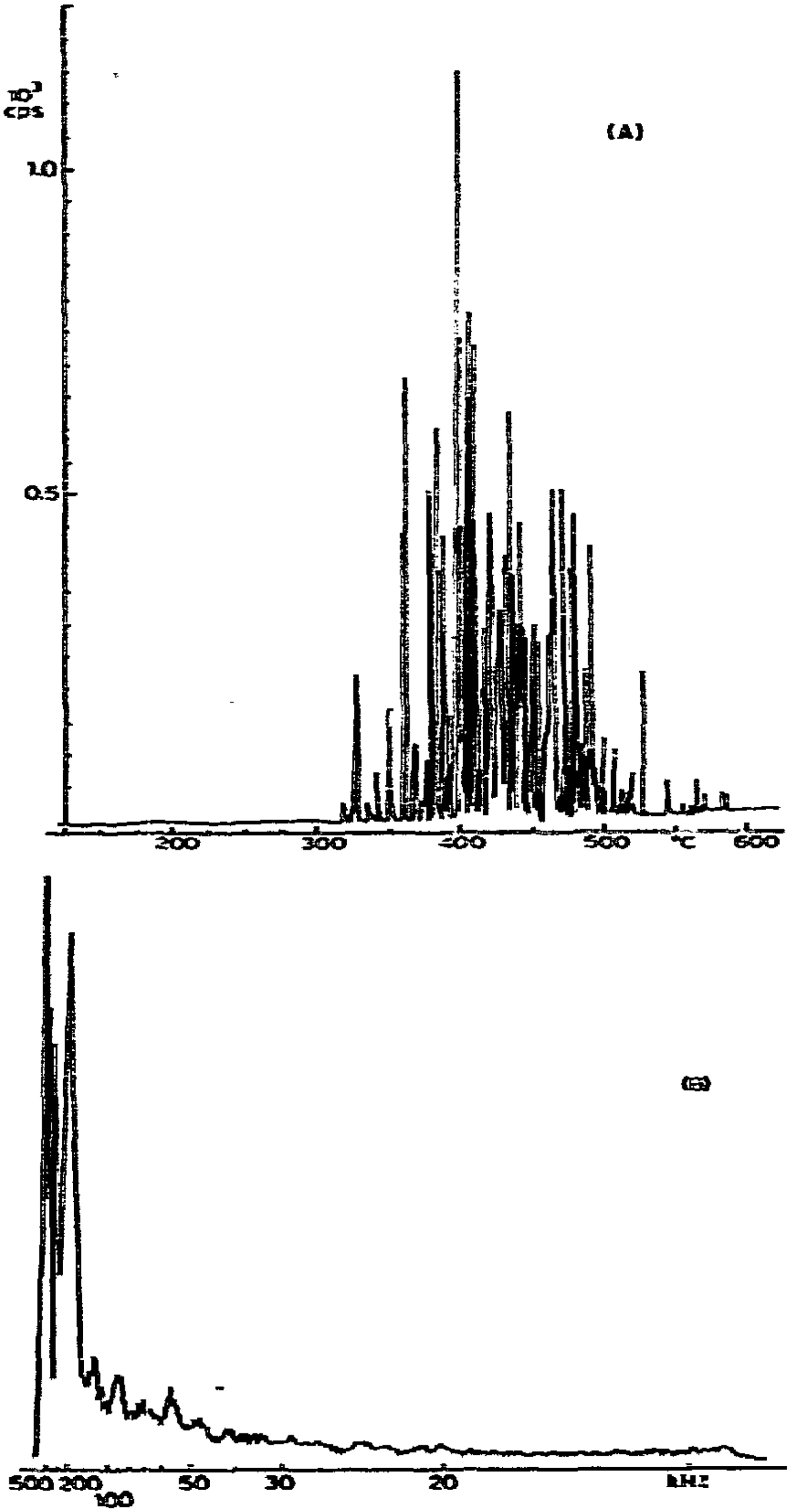


Fig. 11. (A) TS activity of a crushed brucite crystal. (B) Corresponding distribution of the frequency components. (A) and (B), heating rate, 2 °C/min; pressure, 10^{-2}-10^{-3} torr; range, 30 kc-1 Mc.

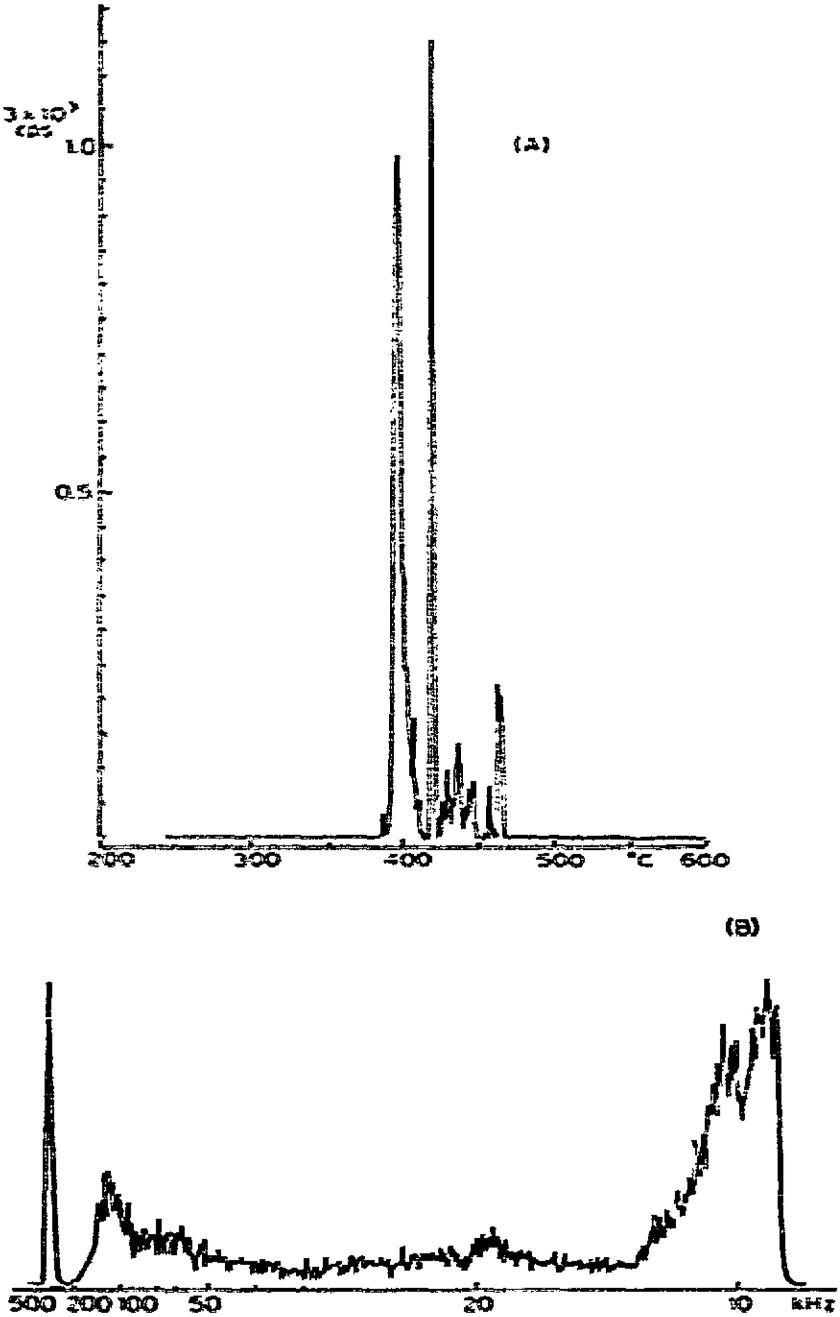


Fig. 12. (A) TS activity of a piece of brucite mineral (sample D) for the lower frequency range. (B) Distribution of signal frequency components. (A) and (B), heating rate, 2 °C/min; pressure, 10^{-2}-10^{-3} torr; range, 7-200 kc.

(C) Brucite from the Tyrol

The results of the brucite samples from the Tyrol are represented by the TS curves taken with a very high frequency cut, beside the mixed conditions, as noted in Fig. 11(A) and (B). The reason for this was to test the influence of the selection of instrument parameters on the apparent detectable information.

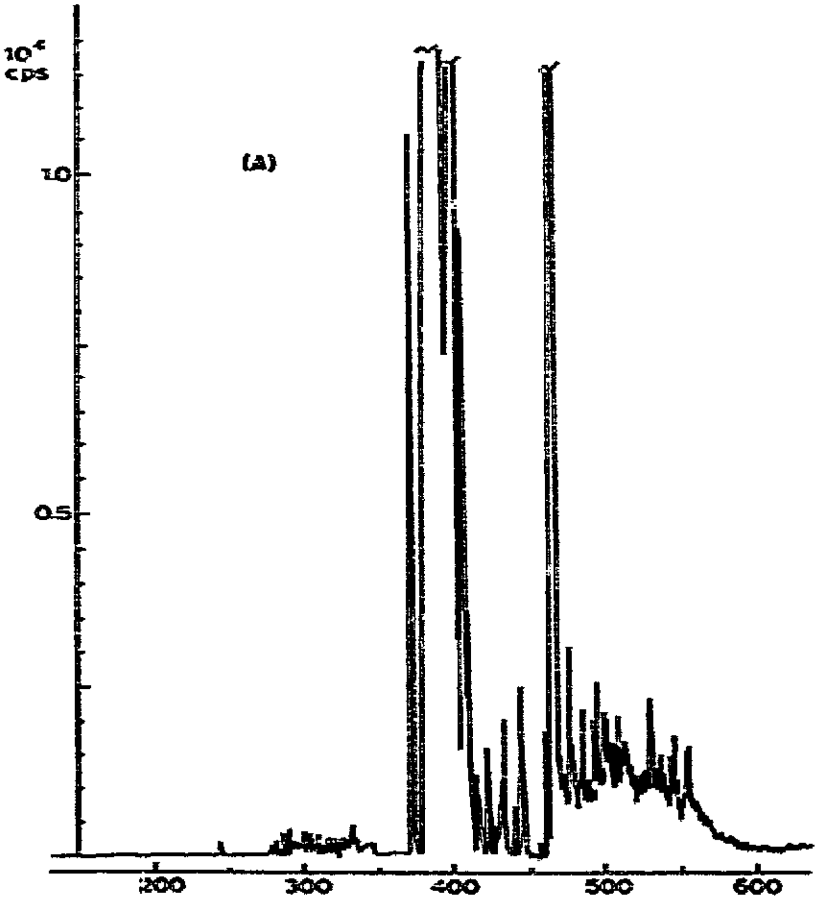
The detection of TS signals in the high frequency mode of operation had a broader temperature performance. The different working conditions of the sample did not noticeably change the common image. The frequencies in the area of 200 kHz seemed to be more dominant. The experiments also showed that the lower frequencies (under 20 kHz) were probably best suited to the specific detection of the fracturing processes following the dehydration in question.

The higher frequency content would also reflect on the change in the other physical properties of the solid (heat capacity, expansion, etc.).

Apart from the statistics in the amplitudes, an overall evaluation would still give the impression of a pulsed character. A conceivable smoothing of the recorded values (averaged with respect to the temperature) would lead to an integral curve more like the shape of the temperature deviation peak.

(D) Långban brucite

Determinations made on brucite mineral from Långban are presented by the curves given in Fig. 12(A) and (B). Concerning the dehydration process itself, these examples scarcely supply any new information other than that the TS activity was grouped around 400 °C with a range of roughly 30 °C and contained a series of in-



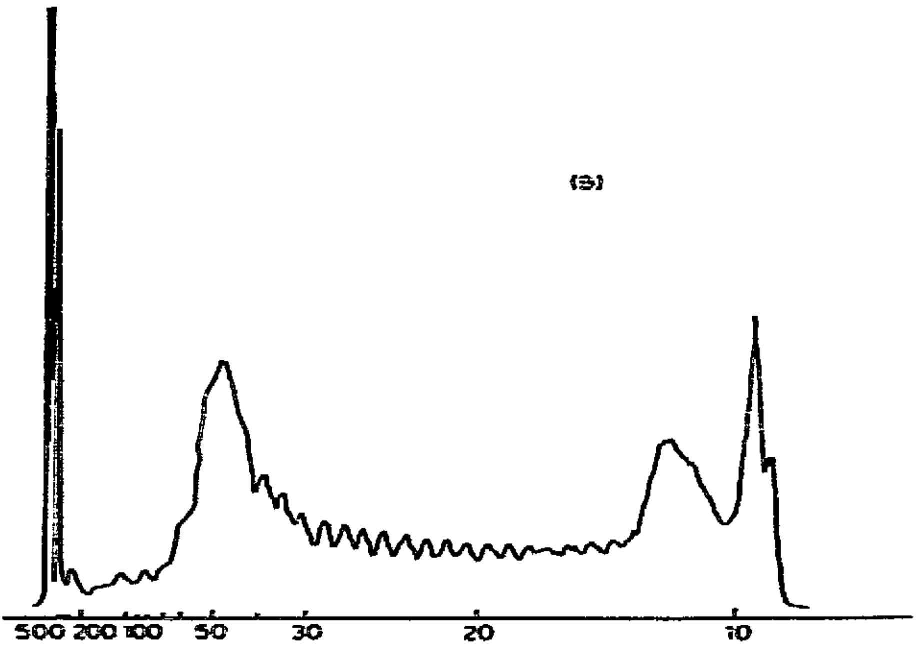


Fig. 13. (A) TS activity of a piece of brucite mineral (sample D) recorded with an expanded signal band width. (B) Corresponding zero crossing frequency distribution showing a definite contribution of higher frequency components. (A) and (B). heating rate. 2 °C/min: pressure. 10^{-2}–10^{-3} torr: range. 6 kc–1 Mc.

dividual sub-peaks. In this connection, the change of frequency band width showed an effect on the course of information. In the high frequency mode, as given in Fig. 13(A) and (B), extra TS activity was picked up around 300 °C and there was also a special wide plateau above 500 °C.

The particular reaction in question was more pronounced in the lower frequency range as shown in Fig. 12(A).

It is not possible at the present time to quote any preference in the system of special signal frequencies related to the specific detection of the dehydration process itself. No doubt that valuable information is hidden in the distribution of the frequency content of the TS signals.

During research on this type of brucite material, peculiar rotational movements of the solid sample on the stethoscope head were observed depending on specific temperature levels. This effect was discovered due to unexpected TS activity in the 700 °C region. A more detailed report on this strange behaviour will be given on another occasion.

GRAPHICAL EVALUATIONS

When the experimental results were known, the question arose of the existence of a real differentiation in the decomposition activity into separate periods. The spread of sub-peaks can best be estimated by the distribution mode of recordings

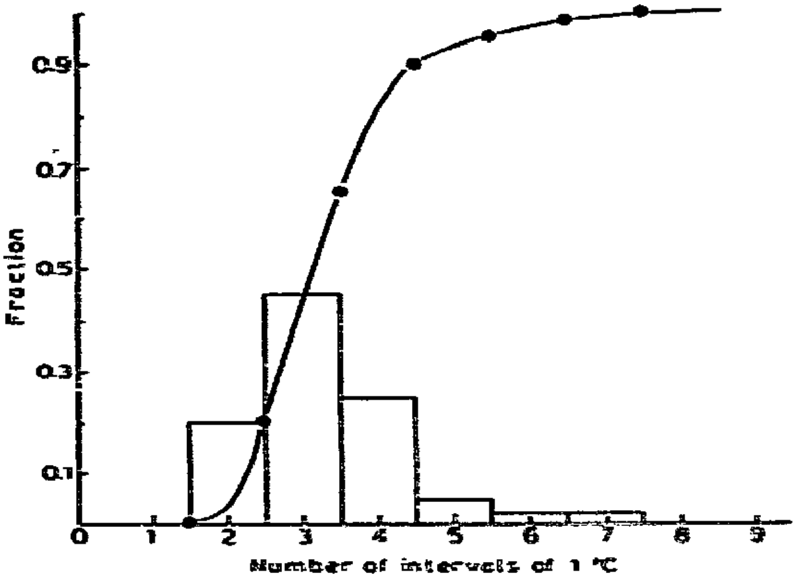


Fig. 14. Histogram and distribution of 1 °C separation intervals between sub-peaks during the decomposition of $Mg(OH)_2$ powder.

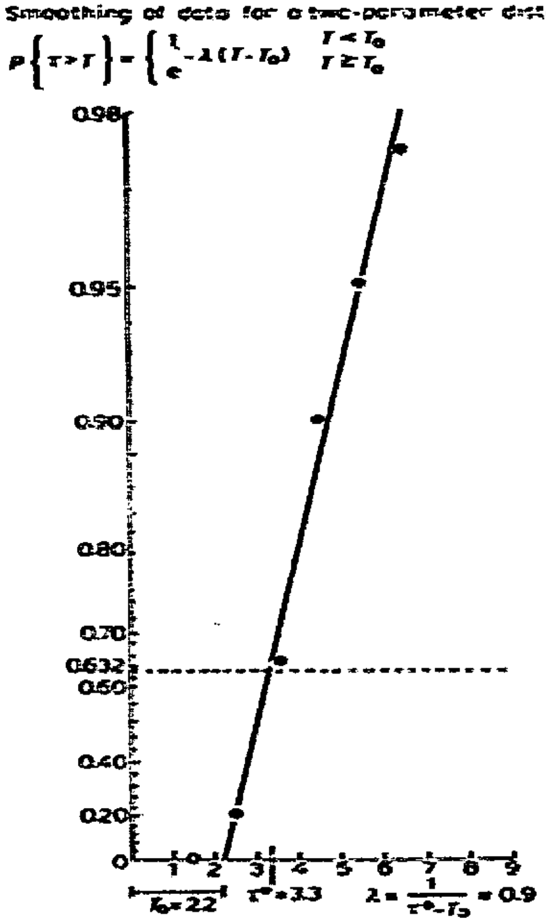


Fig. 15. Temperature threshold for start of signals estimated from data given in Fig. 14.

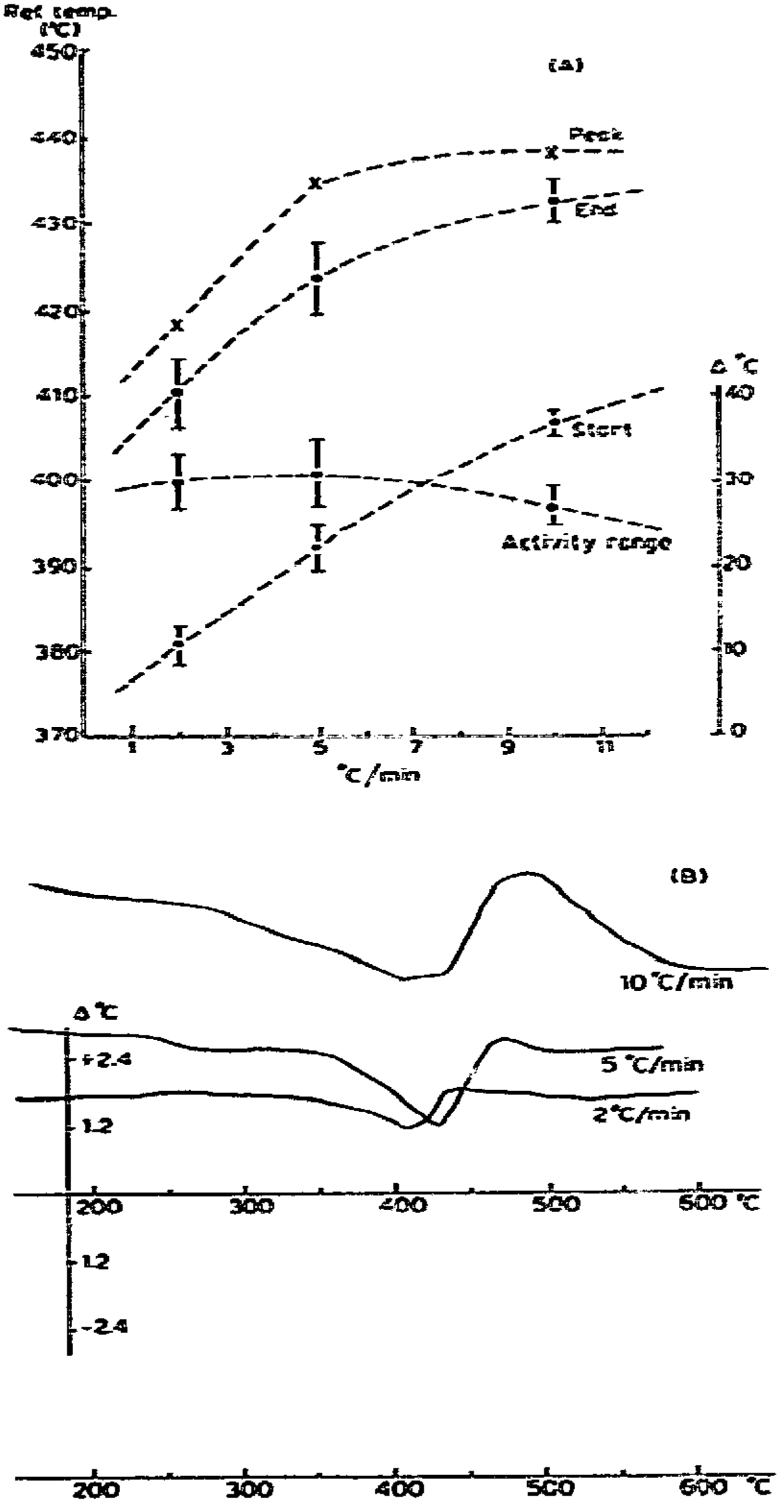


Fig. 16. (A) Graphical presentation of the estimated start and end points of the TS activity zone as a function of the nominal heating rate. The temperature range of the decomposition of $Mg(OH)_2$ powder on the temperature reference scale is nearly constant. (B) The DTA peak position and drift relative to the temperature at different heating rates.

from the powder samples. The figures used in the calculation were read from the individual curves and the graph of the corresponding statistical distribution of these results is drawn in Fig. 14. The adaptation of the data to the theoretical model given in Fig. 15 shows a statistically significant temperature separation between bursts of reaction (sub-peaks). The analysis points to an absolute temperature threshold (dead zone) of relaxation of 2.2°C and that the interval between the reaction push is most probably 3.3°C (on the average about 3°C). The average number of sub-peaks in this calculation is calculated to be 9, including the readable smaller peaks.

An average value of the "beginning and ending" position of the activity range has been calculated from readings on the actual curves. By extrapolation to a nominal zero temperature scanning rate, the activity zone is still found to have a definite width for the course of reaction. The dependency on the heating rate within the limits given does not seem to be significant as shown in Fig. 16.

From these derivations, we presume that the decomposition process can scarcely progress continuously through the sample. The evaluations may be based on the possibility of a partly reversible process governed by some kind of barrier effect.

CONCLUSIONS

The dynamic measurements on the TS activity caused by the dehydroxylation of the present $Mg(OH)_2$ samples suggests that the process has a stepwise behaviour.

Any endothermic transformation does (on the "surface") alter the heating condition locally (of the inside substance) until the reaction is partly accomplished. To what extent this particular situation affects these measurements is not fully understood. Statistically, this investigation does, however, introduce an average delay of 3°C (relative to the reference scale) between successive bursts of reactions in the powder sample. This indicates that a temporary interface may build up within the material and that a certain barrier has to be exceeded to promote the further transition of the sample.

The recorded interstage is, macroscopically, a balancing of the mutual conversion of different forms of energy (thermal, chemical, mechanical). An extrapolation of the dynamic observations to nominal zero rate of heating (slowly against constant working temperature) did not seem to alter this picture.

Finally, there is reason to believe that the decomposition, even on a microscale, will proceed as a relaxational oscillation between two temperature levels 3°C apart.

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