

## INVESTIGATIONS UNDER QUASI-ISOTHERMAL AND QUASI-ISOBARIC CONDITIONS BY MEANS OF THE DERIVATOGRAPH

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It is proved that under the conditions of dynamic thermoanalytical examinations the course of a decomposition reaction is determined primarily by the gas- and heat-transfer partial processes, i.e. indirectly by the experimental conditions. This raises the question of whether it is justified to make kinetic calculations based on the shapes of similar curves. A new measuring technique is reported which uses a slightly modified Derivatograph. With this new method decomposition reactions can be examined under "quasi-isothermal" and "quasi-isobaric" conditions. The pernicious effects of the gas- and heat-transfer processes are thus eliminated, and the shapes of the curves obtained provide the possibility of studying the decomposition reactions in a new and more thorough way.

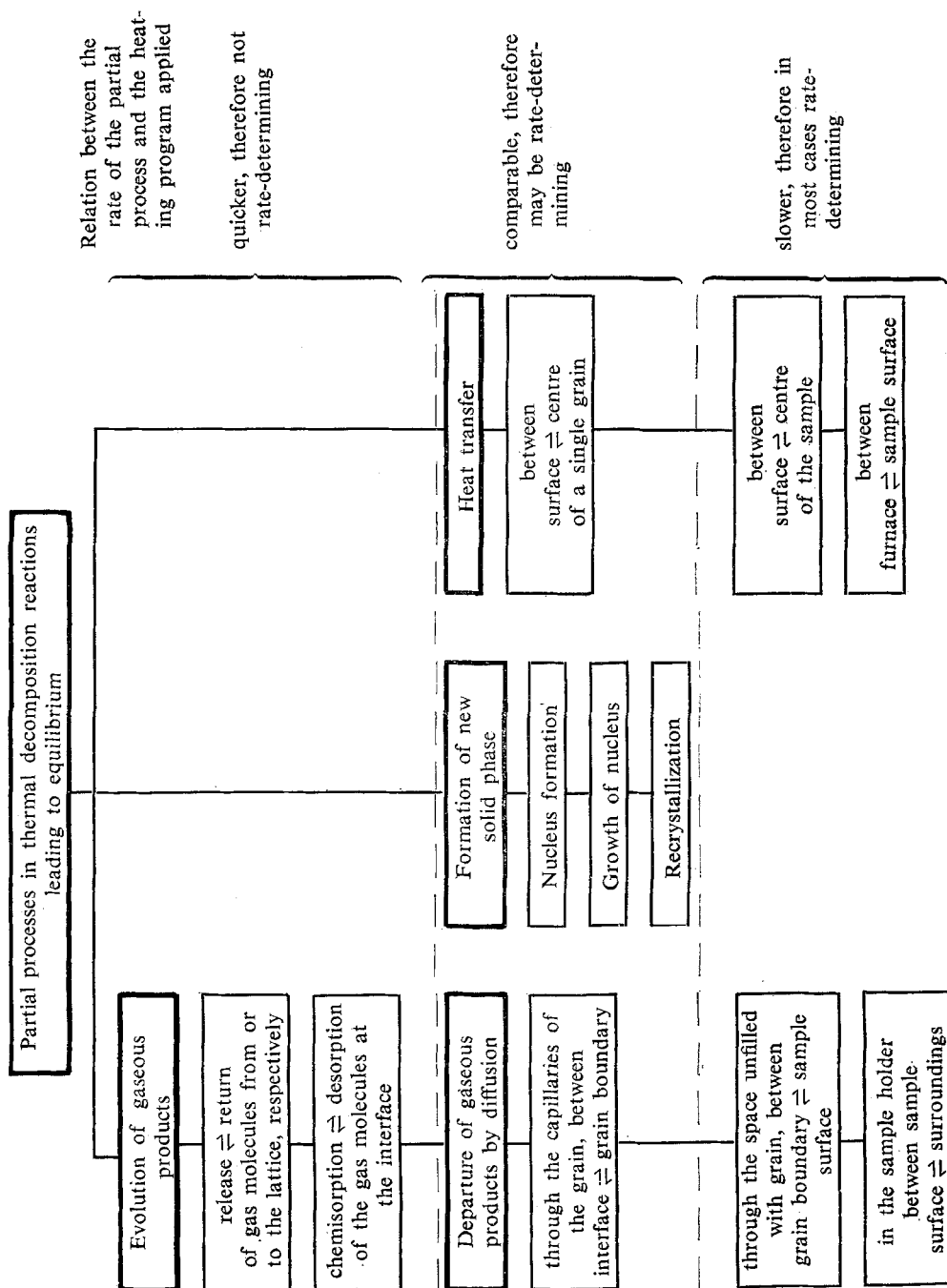
It seems evident that the results of thermoanalytical examinations can be used to draw conclusions on the kinetics and possibly the mechanism of reactions leading to equilibrium. Accordingly, many approximate calculation methods have been elaborated for the determination of reaction order and activation energy. Despite the perfect logic upon which these calculations were generally based, they did not always fulfil expectations. This is due in part to the fact that the thermal curves used for the calculations very often gave a distorted picture of the transformation processes.

Thermal decomposition reactions leading to equilibrium consist of a number of chemical and physical partial processes. These partial processes are usually interdependent on each other in a complex way. Table 1 gives a schematic picture of the correlations. The course of the reaction is determined by the rate of the slowest partial process. If this is commensurable with the heating rate applied, then the transformation with increasing temperature will take place with delay over a more or less broad temperature interval.

Of the many partial processes, only two may be regarded as really chemical. One takes place at the interface as demonstrated in Fig. 1. This process is the release of gas molecules from the lattice and their rebuilding into it. The other is the chemisorption and desorption of gas molecules at the interface. Since both of these processes leading to equilibrium take place extremely rapidly, they do not usually influence the course of the transformation.

Nucleus formation and nucleus growth may be regarded as a transition between chemical and physical processes. Simultaneously with the departure of the gas

Table 1



molecules, the split chemical bonds recombine to form a more or less ordered aggregate of the molecules of the new solid compound. A certain dislocation of the atoms of the solid phase must be presumed, however. This process is slower than the earlier mentioned ones. For example, the nucleus formation of the freshly formed solid phase begins at a given temperature with a delay, in many cases only after a well measurable induction period. But thereafter both nucleus formation and nucleus growth tend to accelerate strongly. The resultant of the

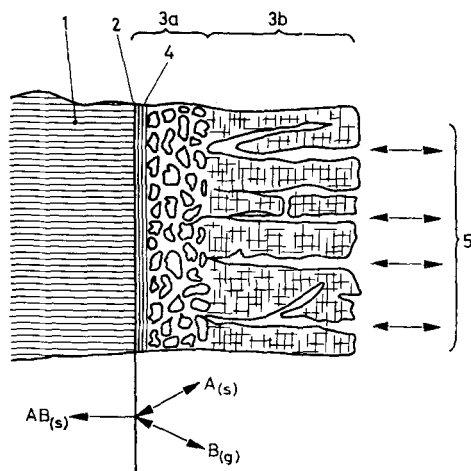


Fig. 1. Structural changes inside a single sample grain in the course of a decomposition reaction of the type  $AB_{(s)} \rightleftharpoons A_{(s)} + B_{(g)}$ . 1. Original solid phase; 2. interface; 3. new solid phase: a) before; b) after the partial recrystallization; 4. nuclei; 5. gaseous products

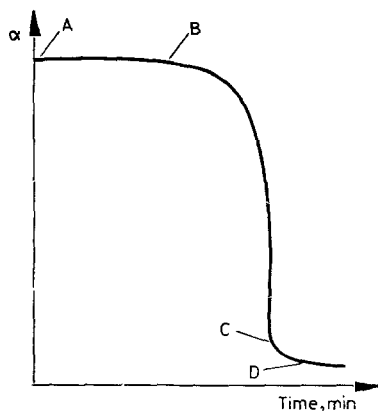


Fig. 2. The course of thermal decomposition if controlled only by nucleus formation and nucleus growth.  $\alpha$  = degree of transformation;  $t$  = time, AB = induction period; BC = main period according to the correlation  $\alpha = kt^n$ ; where  $k$  = constant;  $n = 2-8$ ; CB = decay period

two processes, i.e. the progress of the thermal decomposition, is shown schematically in Fig. 2 for the special case when the reaction is regulated solely by the rate of the two processes mentioned. Apart from the induction period AB and the decay period CD, the progress of the decomposition ( $\alpha$ ) in the main period BC may be defined to a rough approximation by the exponential correlation

$$\alpha = kt^n$$

where  $k$  is the proportionality factor,  $t$  is the time, the exponent  $n$  of which generally varies between 2 and 8.

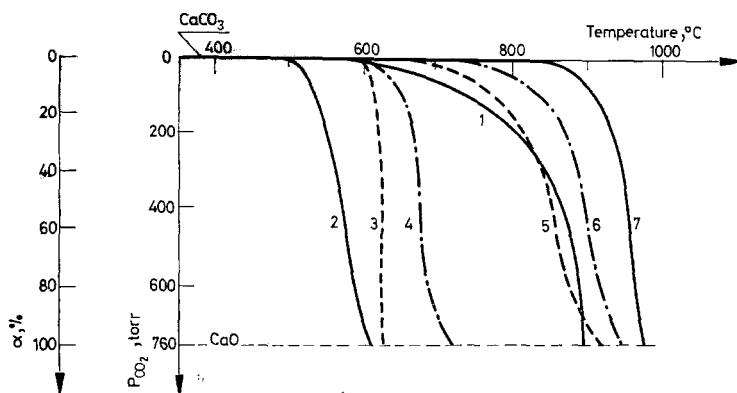


Fig. 3. Thermal decomposition of calcium carbonate in different thermoanalytical examinations.  $\alpha$  = degree of transformation,  $p_{\text{CO}_2}$  = partial pressure of  $\text{CO}_2$ ,  $T$  = temperature. Curves 1: Correlation between partial pressure and temperature; TG curves obtained: 2 in vacuum; 3 by stepwise isothermal heating; 4 by means of the derivatograph on the polyplate sample holder; 5 in the conventional crucible of thermobalances; 6 designed on the basis of the DTA curve; 7 in  $\text{CO}_2$  atmosphere

Though the nucleus formation and nucleus growth may exert a delaying effect upon the transformation in its initial and final stages, due to their significant acceleration they do not usually interfere with the progress of the transformation in its main stage if dynamic thermoanalytical methods are used.

With the progress of the transformation the interface is gradually shifted towards the centre of the grains. Hence, the crust, i.e. the new solid phase surrounding the untransformed centre of the grain, becomes thicker and thicker. This crust is generally of mosaic structure, porous and interlaced with an unbroken capillary network (Fig. 1). Accordingly, the gaseous decomposition products can leave the grains without hindrance. However, in the case of certain compounds the structural ordering of the new solid phase already takes place at the temperature of the transformation. Due to this early recrystallization process the crust becomes compact and can be crossed by the gas molecules only with difficulty. The rate of

departure of the gas molecules across this layer can decrease to such an extent that this process will become the slowest one. Accordingly, in such cases the rate of the departing gas molecules will determine the rate of the whole process.

Many observations and experimental data prove that the shapes of dynamic thermoanalytical curves are determined in the overwhelming majority of cases not by these partial processes but by those gas- and heat-transfer processes which convey the gaseous decomposition products in one direction and heat in the opposite direction between the grain surface and the furnace. However, while the earlier mentioned processes depend primarily on the material properties of the sample, the following ones depend on the given experimental conditions to such an extent that the shape of a thermoanalytical curve is often more characteristic of the conditions than of the transformation itself (Fig. 3). This raises the question of whether it is justified to make kinetic calculations based upon the shapes of similar curves.

According to the rules of physical chemistry, in the case of thermal decomposition reactions there exists a strict correlation between the pressure of the gaseous product and the temperature of the system. This correlation defines the state of the system only in a closed system, at equilibrium and under isothermal conditions, but if the system is an open one and its change of state is examined under non-isothermal conditions and in the presence of air, as is the case with thermoanalytical investigations in general, then the problem becomes more complicated. In such investigations both the partial pressure of the gaseous product in contact with the solid phase and the temperature of the sample change continuously during the whole transformation process. The changes in the partial pressure take place in accordance with the experimental conditions, while those in the temperature depend on the heating program, but the changes are such that if possible the equilibrium correlation should prevail between them. Of course, one can speak here only of numberless, quasi-equilibrium states, changing from moment to moment.

Let us take the example of calcium carbonate, and examine how the composition of the gas atmosphere changes within the sample, between the grains [1, 2]. The correlation between the decomposition pressure and temperature is demonstrated by curve 1 in Fig. 3. When the decomposition of calcium carbonate begins at a given temperature, the carbon dioxide set free will expel some of the air from the space not filled up by grains. If the partial pressure of carbon dioxide in this space approaches the value of the decomposition pressure corresponding to the given temperature, the decomposition will slow down, or even stop when this value is attained. Meanwhile the temperature of the sample will of course change continuously in accordance with the heating program, and so the actual equilibrium decomposition pressure will change too, until the decomposition is complete. Meanwhile the mixture of carbon dioxide and air continuously diffuses outwards from the sample and the air of the furnace diffuses into the inside of the sample.

Thus, the course of the decomposition will be determined (within the limits defined by the correlation between decomposition pressure and temperature) by

the double gas diffusion equilibrium between the centre and the surface of the sample, and between this latter and the surroundings. This means that the decomposition is influenced mainly by those experimental conditions which exert an effect upon this equilibrium, such as the amount of sample, its layer thickness and compactness, the airing of the furnace, the shape and size of the sample holder, whether the crucible is covered or not, and so on.

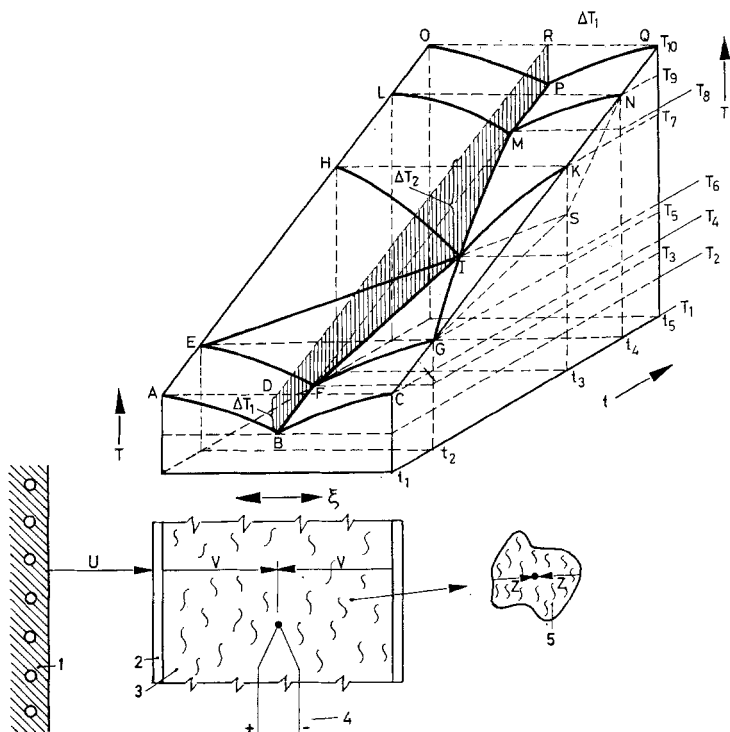


Fig. 4. The temperature change along the cross-section of the sample in the case of a dynamic heating program.  $T$  = temperature;  $\xi$  = space coordinate;  $t$  = time;  $\Delta T$  = temperature drop. 1. Furnace; 2. sample holder; 3. sample; 4. thermoelement; 5. a single grain of the sample. Time and temperature of the beginning ( $t_2, T_5$ ), maximum rate ( $t_3, T_6$ ) and end ( $t_4, T_8$ ) of an endothermal reaction. Heat-transfer between furnace and sample surface ( $U$ ), surface and centre of the sample ( $V$ ), surface and centre of a single grain ( $Z$ )

The significant difference in the shape of the curves in Fig. 3 can in part be explained by this. All these curves demonstrate the thermal decomposition of calcium carbonate, but under different experimental conditions, since the measurements were carried out by using different thermoanalytical methods.

A further complication arises from the fact that the temperature of the sample not only changes constantly, but also shows further differences from the heating program which are impossible to check.

The heat conductivities of powdery substances are generally poor. Due to this, a significant temperature drop usually exists between the surface and centre of the sample during dynamic thermoanalytical measurements. This change of temperature ( $T$ ) as a function of the space coordinate ( $\xi$ ) and time ( $t$ ) is shown in Fig. 4 in a three-dimensional space coordinate system.

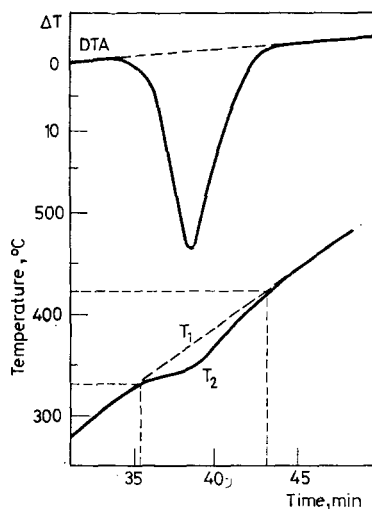


Fig. 5. DTA and T curves for the melting of potassium nitrate.  $T_1$  = temperature change measured in the reference material,  $T_2$  = that in the sample. Weight of the sample = 2 g; heating rate =  $10^\circ\text{C}/\text{min}$ ; sample holder = crucible of the Derivatograph

The temperature difference ( $\Delta T_1$ ) between the surface and centre of the sample is illustrated by the section indicated with the points DBRP. Under normal conditions this difference usually amounts to about  $10^\circ$ , but the temperature drop ( $\Delta T_2$ ) may become even  $40\text{--}50^\circ$  in cases when an endothermic reaction takes place in the sample, as demonstrated by the section FIM. This phenomenon is well known; the method of differential thermal analysis is based upon the measurement of just this particular change in the sample temperature.

It can be seen in Fig. 4 that when the transformation in the sample begins at a given temperature ( $T_5$ ) the temperature increases only in the external layer with a uniform rate ( $G\text{--}N$ ), while in the centre of the sample the temperature increase practically stops ( $T_5\text{--}T_6$ ) for time ( $t_2\text{--}t_3$ ) until the transformation is completely finished. Meanwhile the sample must take up (under otherwise unchanged conditions) an increased amount of heat from the furnace space ( $U$ ). The amount of heat required corresponds in this case not only to the specific heat but also to the reaction heat of the material. This heat transfer needs time. The sample and sample holder take up heat from the furnace partly by the intermediation of air and partly by absorption of the infrared rays. It is well known, however,

that these two kinds of heat transfer processes can convey heat only to a limited extent. The sample has to forward the heat taken up by its outer layers towards its centre (V) too. The upper limit of this process is defined by the heat conductivity of the substance. Accordingly, it takes time ( $t_2 - t_3$ ) until the whole section of the sample can be transformed. After the transformation is complete, a further time ( $t_3 - t_4$ ) passes before the temperature drop ( $\Delta T_2$ ) within the sample is restored to its original normal value ( $\Delta T_1$ ). The two processes together usually take 5–10 minutes under normal conditions. Consequently, it is a rare case when no influence is exerted upon the process of the decomposition by heat transfer.

The proof of this can be seen in Fig. 5 which shows the DTA and  $T$  curves of the melting of 2 g potassium nitrate taken by means of the Derivatograph using a heating rate of 10 °/min. This example was chosen because it is well known that the melting of pure substances should take place at a strictly constant temperature. This process means the instantaneous collapse of the lattice, which is not influenced by any other process but heat transfer. As shown by the DTA curve, the melting of the substance took place in about 8 minutes in the temperature interval 340–430°.

A temperature drop exists not only within the sample but within the individual grains too. This latter can be neglected because the two temperature drop values differ from one another by many orders of magnitude, like the dimension of the sample and grains.

For the sake of completeness we should like to mention two circumstances regarding this problem. In our experience the temperature of the sample does not increase linearly, even in the outer layers, while transformation occurs in the substance as has just been supposed (GKN), but in a way somewhat similar to line GSN in Fig. 4. The heat conductivity of the substance is generally greater, so that the establishment of such a great temperature difference between surface and centre cannot be supposed. We have also observed that the temperature of the crucible changes practically as the outer layers of the sample do, if the wall of the sample holder is thin and its heat capacity is relatively low. Accordingly from the point of view of heat transfer, sample and sample holder form a uniform connected system.

The pernicious effects of heat- and gas-transfer can be eliminated with the help of our recently elaborated method [3–6]. This method is called “quasi-isothermal and quasi-isobaric thermogravimetry”. The new technique is based in part on an earlier developed special heating control device [7]. This makes use of the deriving system of the Derivatograph in the control of the heating program. This increases the temperature of the sample quickly so long as no changes occur in it, but establishes quasi-isothermal conditions by indirect means for the time during which transformations associated with weight change take place in the sample. In this way, the delaying effect of the slow heat-transfer upon the process is eliminated and the temperature drop within the sample is reduced to a minimum. The method is further based on the application of a sample holder of an appropriate shape [8] which ensures a self-generated atmosphere in the surroundings of the



sample. Due to this, the composition of the gas is standardized, i.e. quasi-isobaric conditions are produced, which make the shapes of thermal curves independent of the effects of experimental conditions.

Fig. 6 shows the principle of operation of the Derivatograph modified for this purpose [7]. The voltage of the heating current is raised at a constant rate (0.5–5 °/min) by the heating regulator in the conventional way, until the weight of the sample begins slowly to decrease or increase. The balance and hence the light

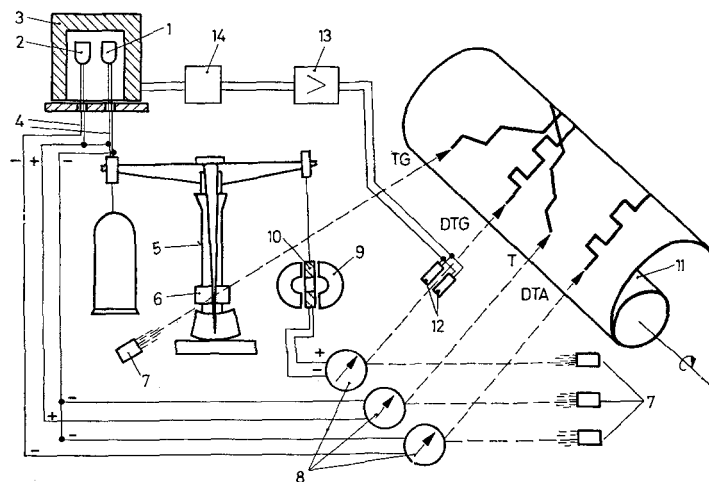


Fig. 6. Derivatograph operating with quasi-isothermal heating program. 1. Sample; 2. reference material; 3. furnace; 4. thermoelements; 5. balance; 6. optical slit; 7. lamps; 8. galvanometer; 9. magnet; 10. coil; 11. photopaper; 12. double phototube; 13. switching device; 14. program regulator

signal of the DTG galvanometer are then deflected. Light-sensitive instruments, e.g. two photocells, are placed in the path of the light signal. In the case of weight stability, the light signal stays between the two light cells. When the weight of the sample decreases, the signal falls onto one of the light cells. The photoelectric current generated in the photocells is amplified and actuates a relay system, which reduces the voltage of the heating current in several steps. Due to the decrease in temperature, the rate of the decomposition is reduced, and accordingly the DTG galvanometer light signal is deflected to a lesser extent. The light signal moves away from the photocell and the relay system again begins to increase the voltage of the heating current stepwise. The process lasts only a few seconds and is repeated many times before the decomposition is finished. After the end of the reaction the temperature of the sample is again increased with the conventional heating rate until the next decomposition reaction begins.

Rouquerol [9–11] recently elaborated an investigation method the aim of which was similar to the above-mentioned one, but which differs from it with

regard to the measuring technique. By means of Rouquerol's method investigations can be carried out in vacuum, in contrast to our method, in the course of which thermal decomposition reactions take place at atmospheric pressure in a self-generated gas atmosphere. This difference may cause great changes in the kinetics and mechanisms of decomposition reactions, and therefore the two kinds of method may advantageously supplement each other in the deeper investigation of similar problems.

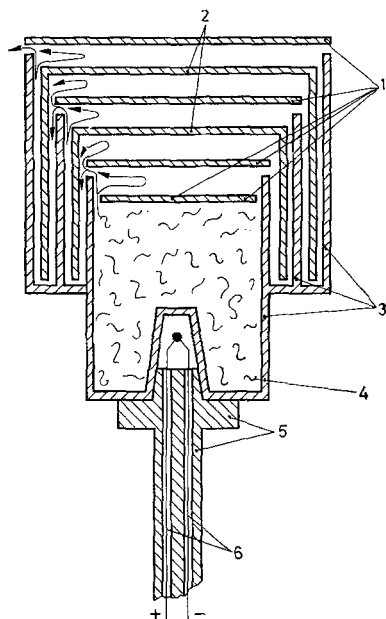


Fig. 7. Labyrinth crucible. 1. Lid, type a; 2. lid, type b; 3. crucible; 4. sample; 5. corundum rod; 6. thermoelement

Garn and Kessler [12] and later Forkel [13] were the first who effectively applied self-generated atmospheres, but many other attempts [14] have been made in this respect. It was found that even at a high heating rate, for example  $5-10^\circ/\text{min}$ , the achievement of a self-generated atmosphere of 100% purity was rather difficult. This proved to be an especially troublesome problem in applying a quasi-isothermal heating program, when the gas-evolution is slower by more than one order of magnitude. In spite of the many difficulties, we at last succeeded in getting good results with the help of our specially shaped platinum sample holder [8], shown in Fig. 7. The crucible is covered with six well-fitting lids in such a way that the gaseous decomposition products are forced to leave through a long and narrow labyrinth.

With this new method we have studied among others the decomposition of nickel hexammine chloride. The change in temperature ( $T'$ ) and weight of the sample ( $TG'$ ), the rate of the weight change ( $DTG'$ ) and the changes in the temperature difference between sample and reference substance ( $DTA'$ ) were measured

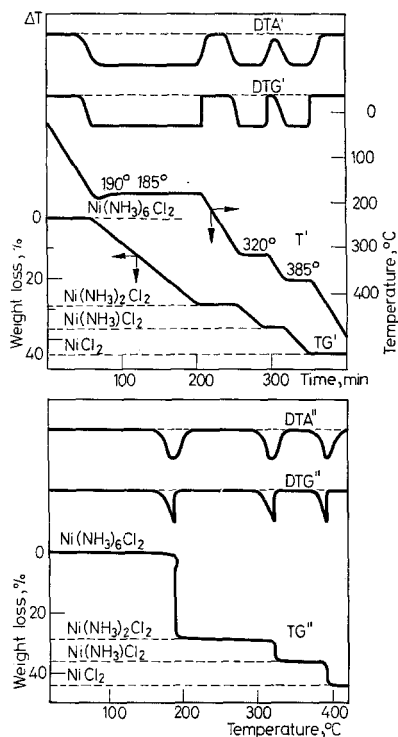


Fig. 8. Thermal decomposition of nickel hexammine chloride under "quasi-isothermal" and "quasi-isobaric" conditions. Curves recorded as a function of time:  $T'$  temperature change;  $TG'$  weight change ( $\Delta m$ );  $DTG'$  rate of weight change ( $\frac{dm}{dt}$ );  $DTA'$  temperature difference ( $\Delta T$ ) between sample and reference material. Curves recorded as a function of temperature:  $TG''$  weight change ( $\Delta m$ );  $DTG''$  rate of weight change ( $\frac{dm}{dt}$ );  $DTA''$  temperature difference ( $\Delta T$ ) between sample and reference material

partly as functions of time, and partly as functions of sample temperature ( $TG''$ ,  $DTG''$ ,  $DTA''$ ). The curves in Fig. 8 were obtained with a temperature increase of the sample at a rate of  $3^\circ/\text{min}$  up to  $190^\circ$ . The decomposition of the substance began at this point. In several minutes the temperature of the sample fell spontaneously to  $185^\circ$ , and did not change until the first stage of the thermal decomposition was completely finished. This lasted about 140 minutes. Meanwhile the weight of the sample changed at a strictly constant rate of about  $0.6 \text{ mg}/\text{min}$ , and a

temperature difference of about  $0.5^\circ$  could be observed between sample and reference. After the first stage of the decomposition was complete, i.e. four ammonia molecules were evolved, the temperature again increased at a rate of  $3^\circ/\text{min}$ , up to the beginning of the next thermal decomposition process. The second and third decomposition processes took place in a similar way as the first, at  $320^\circ$  and  $385^\circ$ , respectively, one ammonia molecule being evolved in each.

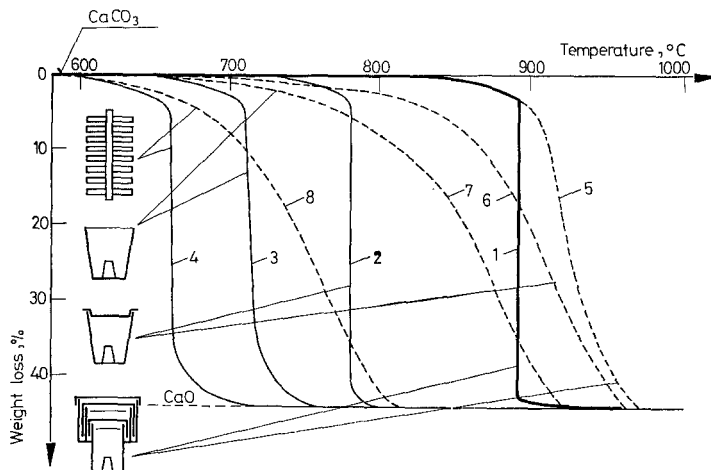


Fig. 9. Decomposition of calcium carbonate. Sample holders used in recording curves 1 and 5: labyrinth type; curves 2 and 6: covered crucible; curves 3 and 7: uncovered crucible; curves 4 and 8: polyplate type. Heating program used in recording curves 1–4 quasi-isothermal; decomp. rate  $0.6 \text{ mg/min}$ ; curves 5–8 dynamic; heating rate  $10^\circ\text{C/min}$ . Weight of sample ca.  $450 \text{ mg}$

It was observed that during the three decomposition processes of nickel hexamine chloride the temperature of the sample never changed to a greater extent than  $1-2^\circ$ . This is rather remarkable, the more so because this phenomenon is a spontaneous one, since the heating control device used provided directly only for the constancy of the rate of weight change.

This problem can perhaps be studied most easily on the example of calcium carbonate. The partial pressure of carbon dioxide above calcium carbonate reaches 1 atm at  $895^\circ$  (the mean of 20 literature data). Let us call this the normal decomposition temperature. It can be seen from curve 1 in Fig. 9 that the decomposition of calcium carbonate at  $890^\circ$  means that the compound decomposed practically at this normal decomposition temperature, which calcium carbonate can attain only if it is in contact with pure carbon dioxide. In this case too the temperature of the sample did not change until the decomposition was complete.

From the measured value of the decomposition temperature and its spontaneous stabilization, the conclusion could be made that in the present case the decomposition of calcium carbonate took place under quasi-isothermal and quasi-isobaric, i.e. under quasi-equilibrium conditions.

The same cannot be said in the case of curve 5 in Fig. 9. This curve was also recorded by using the crucible covered with the sixfold lid, but with programmed dynamic heating at a rate of  $10^{\circ}/\text{min}$ . Because of this, the shape of this curve is completely different; like other curves recorded using a dynamic heating program, it has a sigmoid form. The decomposition is shifted significantly in the direction of higher temperatures.

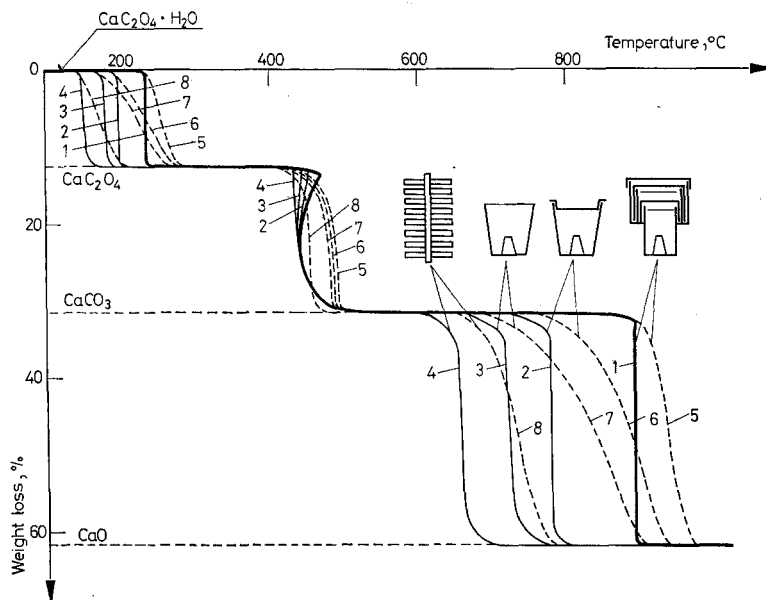


Fig. 10. Decomposition of calcium oxalate monohydrate. Sample holder used in recording curves 1 and 5: labyrinth type; curves 2 and 6: covered crucible; curves 3 and 7: uncovered crucible; curves 4 and 8: polyplate type. Heating program used in recording curves 1-4 quasi-isothermal; decomp. rate  $0.6 \text{ mg}/\text{min}$ ; curves 5-8 dynamic; heating rate  $10^{\circ}\text{C}/\text{min}$ . Weight of sample ca. 320 mg

This is probably due to the fact that, as mentioned above, under the given experimental conditions the poor heat conductivity of the sample means that it can take up only a certain heat amount and transfer it towards its own centre. Thus, the decomposition processes, which generally need a significant amount of heat, can take place only during a protracted period, in a more or less broad temperature range. The significant difference in the shapes of curves 1 and 5 in Fig. 9 proves that the achievement of a self-generated atmosphere alone does not solve the problem of standardization.

Fig. 9 also shows curves recorded under other experimental conditions. Curves 2-4 were recorded using the conventional crucible of the Derivatograph [2], covered and uncovered, and the polyplate sample holder [1], respectively. In the latter case the sample was spread out on the plates in very thin layers.

Curves 1–4 were obtained using quasi-isothermal heating, and curves 5–8 with a dynamic heating program. It can be observed in curve 3 for example that the decomposition of calcium carbonate takes place not only in a self-generated atmosphere, but also in the open sample holder, at a more or less constant temperature if the quasi-isothermal heating program is applied. In this case the steady

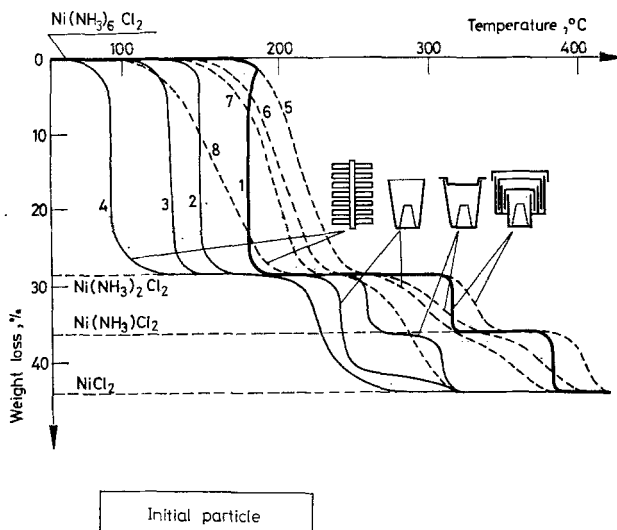


Fig. 11. Decomposition of nickel hexammine chloride. Sample holders used in recording curves 1 and 5: labyrinth type; curves 2 and 6: covered crucible; curves 3 and 7: uncovered crucible; curves 4 and 8: polyplate type. Heating program used in recording curves 1–4 quasi-isothermal; decomp. rate 0.6 mg/min; curves 5–8 dynamic; heating rate  $10^\circ\text{C}/\text{min}$ . Weight of sample ca. 370 mg

state of the temperature means that, in accordance with the given conditions, the diffusion of the carbon dioxide released from the inside of the sample occurred at the same rate as the diffusion of air towards the inside of the sample. Thus, in the space not filled by grains, the composition of the mixture of air and carbon dioxide was constant.

To summarize, our new heating control device ensures that the rate of departure of the gaseous decomposition products does not differ from a certain preselected constant value. This is achieved in such a way that a temperature difference is established between furnace space and sample, such that under given conditions the sample should take up from its surroundings as much heat as necessary for the decomposition to take place at the desired rate. Now, if it is observed that the temperature of the sample spontaneously assumes a constant value, this proves directly that a quasi-equilibrium exists between the solid phase and the gas-atmosphere. It also indicates indirectly that the reaction rate is determined solely by the

heat-transfer, i.e. by the rate of physical process independent of the concentration. Consequently, the process is independent of the concentration. Consequently, the process is a reaction of zero order. In contrast, if a spontaneous change is observed in the sample temperature during the transformation, this means that the progress of the reaction is not determined by the uniform heat-transfer but by another slower and concentration-dependent process, such as the rate of nucleus formation and growth, etc. In such a case the process cannot be qualified as a zero-order reaction.

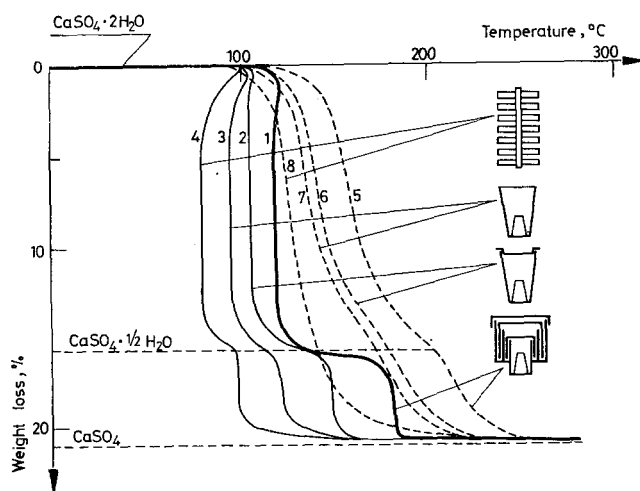


Fig. 12. Decomposition of calcium sulphate dihydrate. Sample holders used in recording curves 1 and 5: labyrinth type; curves 2 and 6: covered crucible; curves 3 and 7: uncovered crucible; curves 4 and 8: polyplate type. Heating program used in recording curves 1–4 quasi-isothermal; decomp. rate 0.3 mg/min; curves 5–8 dynamic; heating rate 10 °C/min. Weight of sample ca. 460 mg

On this basis it can be stated that the decomposition of calcium carbonate took place as a zero-order reaction under the experimental conditions applied in the recording of curve 1 in Fig. 9. The decomposition recorded in curves 2, 3 and 4 can also be qualified as nearly zero-order reactions in spite of the fact that the decomposition temperatures differed strongly from the value of the normal decomposition temperature.

The following few examples illustrate several types of characteristic transformations.

Fig. 10 shows the thermal decomposition of calcium oxalate monohydrate under different experimental conditions. On the basis of the earlier-mentioned considerations, the first and third decomposition processes of this substance approached zero order in the case of curves 2, 3 and 4. Naturally, this conclusion is only valid for curves obtained under given conditions, for example at a given decomposition

rate. In contrast, the shapes of the curves representing the second process show that the decomposition of anhydrous calcium oxalate can by no means be qualified a zero-order reaction; this is understandable, since it is well known that this reaction does not lead to equilibrium.

The TG curves in Fig. 11 show the decomposition of nickel hexamine chloride under similarly varied experimental conditions. Under the conditions for curve 1, all the three decomposition processes were reactions of zero order. It can be

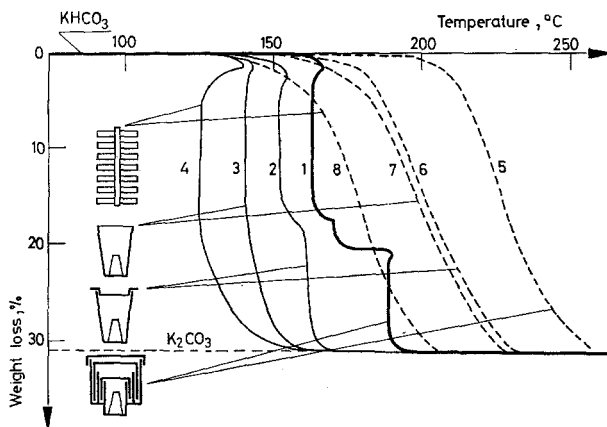


Fig. 13. Decomposition of potassium hydrogen carbonate. Sample holders used in recording curves 1 and 5: labyrinth type; curves 2 and 6: covered crucible; curves 3 and 7: uncovered crucible; curves 4 and 8: polyplate type. Heating program used in recording curves 1–4 quasi-isothermal; decomp. rate 0.6 mg/min; curves 5–8 dynamic; heating rate 10°C/min. Weight of sample ca. 600 mg

seen in curve 1 that at the beginning of the decomposition the temperature of the sample increased temporarily to 190°. This section of the curve probably represents the induction period of the delayed nucleus formation. After the formation of a sufficient number of nuclei the reaction can take place at the rate defined by the heating regulator at a lower temperature, so the temperature spontaneously fell to 185°.

Similarly, the nucleus formation also began with a delay in the case of calcium sulphate dihydrate, as shown in curves 1–4 of Fig. 12. When the polyplate sample holder was used, i.e. the experiments were carried out in the presence of a relatively limited amount of vapour, nucleus formation began with special difficulty. In this case the temperature fell by more than 20° after the beginning of the reaction. The extent to which the two dehydration partial processes are separated from each other is also remarkable, as can be seen in curve 1.

A strange irregularity can be observed in Fig. 13. Curve 1 shows the decomposition of potassium hydrogen carbonate to be a three-step process. With our simul-



taneous thermogravimetric and thermo-gas-titrimetric method we have shown that in the course of the decomposition carbon dioxide and constituent water are set free under the strictest parallelism. Consequently, the chemical reaction itself is a uniform one, but for an unknown reason its course becomes stepwise.

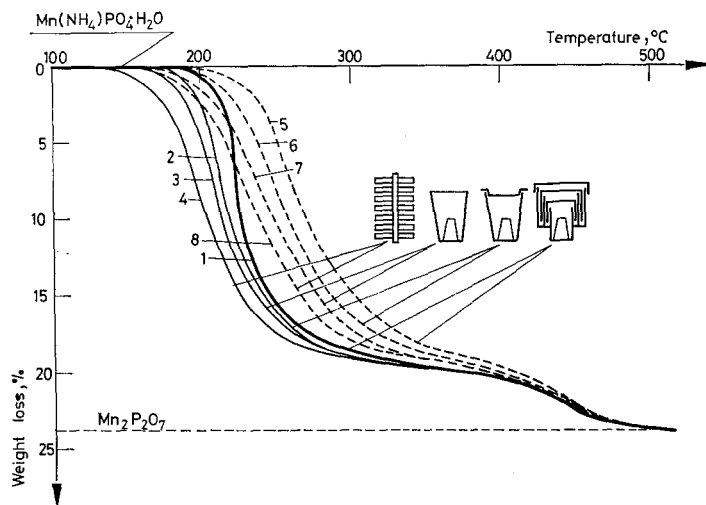


Fig. 14. Decomposition of manganese(II) ammonium phosphate. Sample holder used in recording curves 1 and 5: labyrinth type; curves 2 and 6: covered crucible; curves 3 and 7: uncovered crucible; curves 4 and 8: polyplate type. Heating program used in recording curves 1-4 quasi-isothermal; decomp. rate 0.15 mg/min; curves 5-8 dynamic; heating rate 10 °C/min. Weight of sample ca. 150 mg

The example of manganese ammonium phosphate monohydrate in Fig. 14 demonstrates a reaction type where, with the use of the new measuring technique, the temperature does not get into a steady state even temporarily; consequently, the decomposition does not take place as a zero-order reaction. On the analogy of other compounds of phosphorus it may be assumed that the thermal decomposition of manganese ammonium phosphate monohydrate is not a single decomposition reaction but a complex polycondensation process, which in itself could account for the irregular shape of the curves in Fig. 14.

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RÉSUMÉ — En se référant à leurs résultats d'expérience, les auteurs montrent que dans les conditions des études thermoanalytiques dynamiques, le déroulement des réactions de décomposition est déterminé par des processus partiels de nature diverse et avant tout par les échanges gazeux et calorifiques, c'est-à-dire indirectement, par les conditions expérimentales. La question se pose donc de savoir s'il est justifié d'effectuer des calculs cinétiques sur de telles courbes. Les auteurs rendent compte d'une nouvelle technique de mesure à l'aide du "Derivatograph" légèrement modifié. Elle permet de suivre les réactions de décomposition dans des conditions "quasi isothermes" et "quasi isobares". Les effets pernicioux mentionnés ci-dessus sont alors éliminés et les courbes offrent la possibilité d'étudier les réactions de décomposition d'une façon nouvelle plus approfondie.

ZUSAMMENFASSUNG — An Hand ihrer Versuchsergebnisse beweisen die Autoren, daß unter den Bedingungen dynamischer thermoanalytischer Prüfungen der Verlauf der Zersetzungsreaktionen von den verschiedenen Teilvorgängen vor allem durch die Gas- und Wärmeübertragungsvorgänge, d.h. in indirekter Weise durch die Versuchsbedingungen bestimmt wird. Dadurch wird jedoch die Frage gestellt ob kinetische Berechnungen aufgrund ähnlicher Kurven gerechtfertigt sind. Die Autoren berichten über eine neue Meßtechnik, welche mit Hilfe des Derivatographen nach geringfügigen Änderungen desselben vorgenommen werden kann. Die neue Methode gestattet die Prüfung der Zersetzungsreaktionen unter "quasi-isothermen" und "quasi-isobaren" Bedingungen. Da durch diese Technik die schädliche Wirkung der obenerwähnten Gas- und Wärmeübertragungsvorgänge ausgeschaltet werden kann, bieten die erhaltenen Kurven eine Möglichkeit zum Studium der Zersetzungsreaktionen in einer neuen und eingehenderen Weise.

Резюме — На основании результатов эксперимента авторы доказали, что в условиях динамических термоаналитических испытаний протекание реакций распада определяется частными процессами газо- и теплопереноса. Ставится вопрос о справедливости кинетических расчетов, основанных на подобных кривых. Авторы сообщают о новой технике измерений, которую легко осуществить на дериватографе после его незначительной модификации. Новый метод даст возможность изучать реакции распада в «квази изотермических» и «квази изобарных» условиях. Этот метод исключает эффекты наложения, связанные с процессами газо- и термопереноса.