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KINETIC STUDIES OF THERMAL DECOMPOSITION REACTIONS UNDER QUASI-ISOTHERMAL AND QUASI-ISOBARIC CONDITIONS BY MEANS OF THE DERIVATOGRAPH*

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INTRODUCTION

Numerous approximate-calculation methods have been elaborated in the last two decades, based upon curves recorded by dynamic thermoanalytical techniques, in order to find numerical correlations for the kinetics of the processes. Despite the perfect logic upon which these calculations have mostly been built, they could not always fulfil the expectations. The reason for this is partly due to the fact that the thermal curves upon which the calculations were based very often gave a distorted picture of the transformation processes.

This concerns first of all the thermal decomposition reactions of solids leading to equilibrium. As the scheme in Fig. 1 shows, these transformations are composed of many chemical and physical partial processes, in complicated interactions with one another. The course of the transformation will be determined by the rate of the slowest partial process. Accordingly, if the rate of the partial process in question (*e.g.* growth of nuclei) is commensurable with the heating rate applied, then the transformation will be protracted in time. Consequently, as the partial process is generally strongly temperature-dependent, it will become faster and faster as the temperature increases, causing a distortion in the course of the process.

However, even bigger errors are caused if one of the partial processes defines the rate of the whole transformation; it may be regarded as a process originated by the experimental conditions and is consequently insignificant from the point of view of the kinetics and mechanism of the transformation process. That may be the case, for example, with powdery samples, where the heat transfer between the grains is slow, because they are in poor contact with one another. This slow heat-transfer may cause a significant temperature drop inside the sample. Similarly, the departure of the gaseous decomposition products by diffusion through the space left unfilled by the grains may also influence the course of the decomposition process. Nevertheless, since a strict correlation exists between the experimental conditions (*i.e.* amount, compactness and layer thickness of the sample, shape and size of the sample holder,

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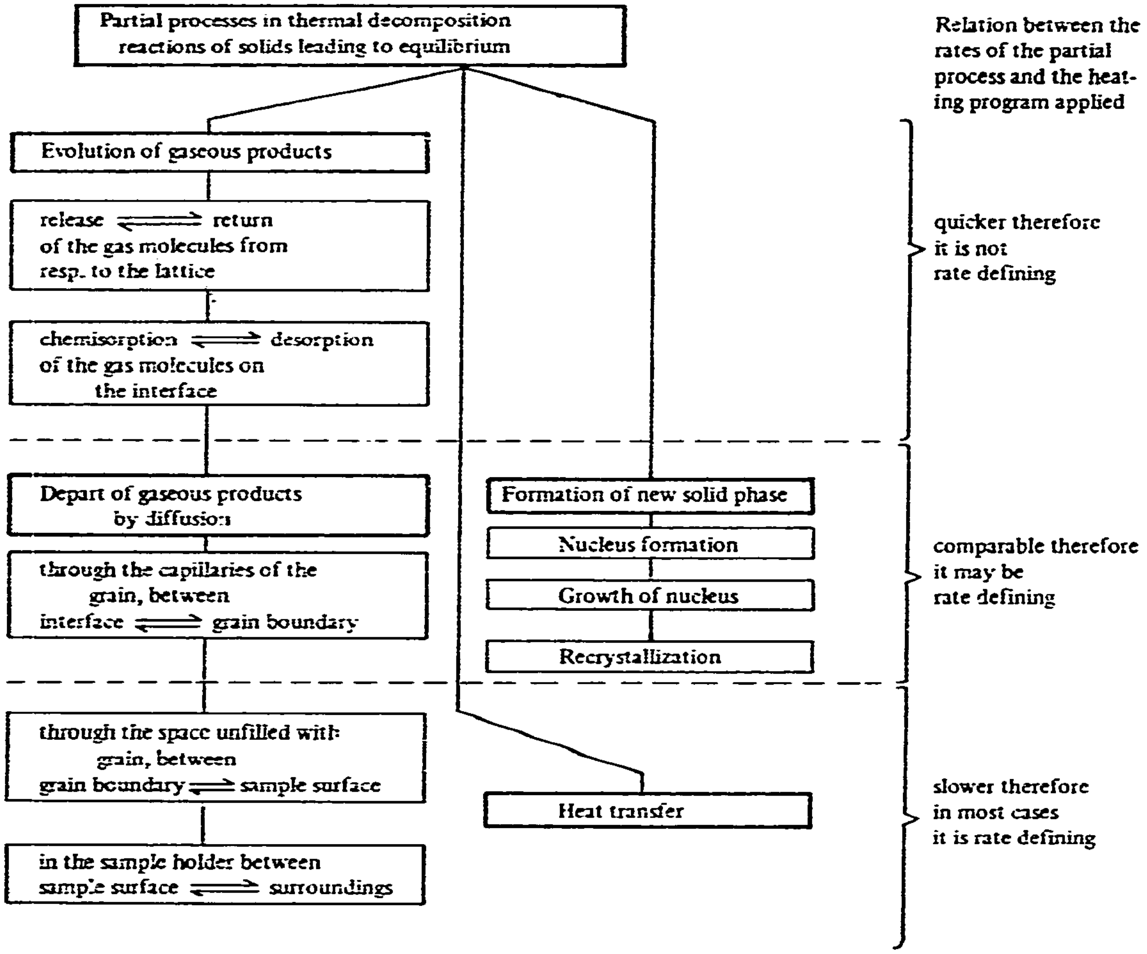

Fig. 1. Scheme showing the partial processes in the thermal decomposition reactions of solids.

heating rate), the diffusion rate of the gaseous products, the composition of the atmosphere in the space unfilled by the grains and the course of the transformation, one very often obtains curves whose course is perhaps more characteristic of the experimental conditions than of the transformation itself.

Our new method[1-3], called "quasi-isothermal and quasi-isobaric thermogravimetry", makes the course of the thermal decomposition reactions independent of the pernicious effects of heat- and gas-transfer. This is attained partly by means of a special heating control device[12] built into the derivatograph[4,5]. This quickly increases the temperature of the sample so long as no changes occur in it, but establishes, in an indirect way, quasi-isothermal conditions for the time during which transformations connected with weight change are taking place in the sample. Under these conditions, the delaying effect of the slow heat-transfer, exerted upon the process, is eliminated. But the accelerating effect on the partial process starting at a given temperature, exerted by the continuous rise in temperature, will also be eliminated.

On the other hand, our method is based on the application of a sample holder of special shape[2,3], which ensures a self-generated atmosphere in the surroundings of the sample. Because of this, the composition of the gas is standardized, *i.e.* isobaric conditions are produced, which make the course of the thermal curves independent of the influencing effects of experimental conditions.

EXPERIMENTAL

Fig. 2 shows the design and operation of the derivatograph modified for the purpose of these investigations. The device regulates the heating as a function of the rate of weight change.

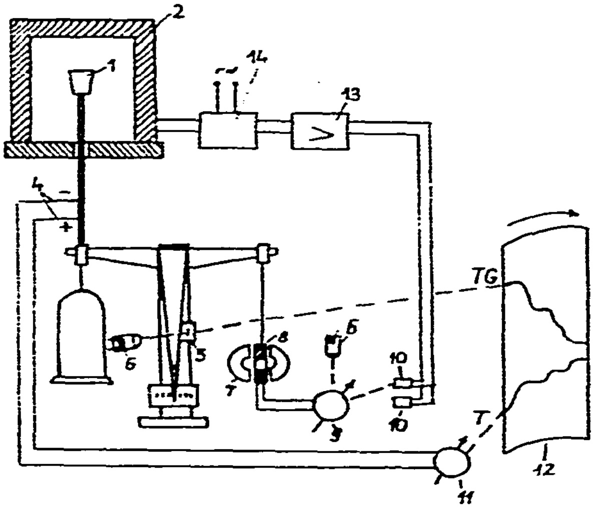

Fig. 2. The modified derivatograph. 1, crucible; 2, furnace; 3, porcelain rod; 4, thermoelement; 5, optical slit; 6, lamp; 7, magnet; 8, coil; 9, galvanometer; 10, double phototube; 11, galvanometer; 12, photopaper; 13, switching device; 14, amplifier.

The voltage of the heating current is raised at a constant rate (0.5–5 °C/min), in the usual way, by the program regulator until the weight of the sample slowly begins to decrease or increase. Because of the weight change, the balance is deflected, and so the light signal of the galvanometer, connected to the poles of the coil of the deriving device, is also 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, while it falls on to one or the other cell when the weight of the sample decreases or eventually increases. The photoelectric current generated in the photocells is amplified, actuating a relay system, which reduces in several steps the voltage of the heating current. Due to the decrease in temperature, the rate of the thermal decomposition is reduced and accordingly, the galvanometer light signal is deflected to a lesser extent. The light signal moves away from the photocell, whereupon the relay system switches on the heating current again and begins to increase stepwise the voltage of the heating current. The process, lasting only a few seconds, will be repeated many times before the end of the thermal decomposition, at which point the temperature of the sample is again increased at the usual heating rate up to the temperature where the next thermal decomposition process starts.

Garn and Kessler[6], and later Forkel[7], were the first who effectively applied self-generated atmospheres, but many other attempts[8] were also made in this respect. However, according to experience, the realization of a self-generated atmosphere of 100% purity was, even at a high heating rate (5–10°C/min), very difficult. This proved to be an especially difficult task in applying a quasi-isothermal heating program in the case 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 (shown in Fig. 3).

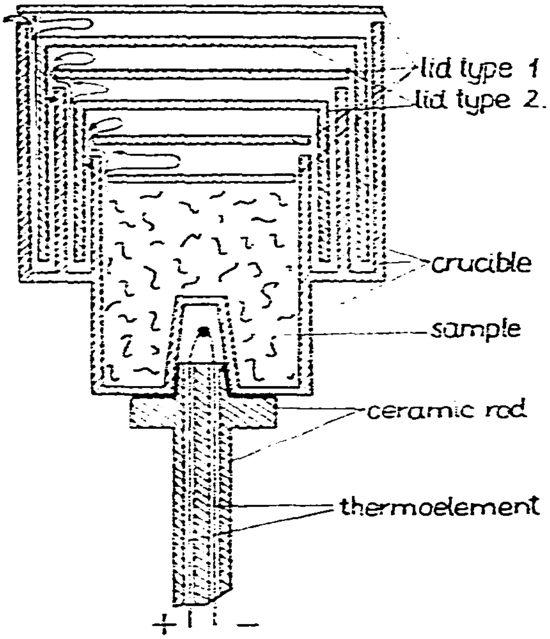

Fig. 3. Diagram of the platinum sample holder.

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.

RESULTS AND DISCUSSION

With the help of the technique described, we have studied, among others, the thermal decomposition of calcium oxalate monohydrate. The change in temperature (*T* curve) and weight (*TG* curve) of the 0.4-g sample was measured as a function of time. The curves obtained are shown in Fig. 4, where curve 1 represents the weight

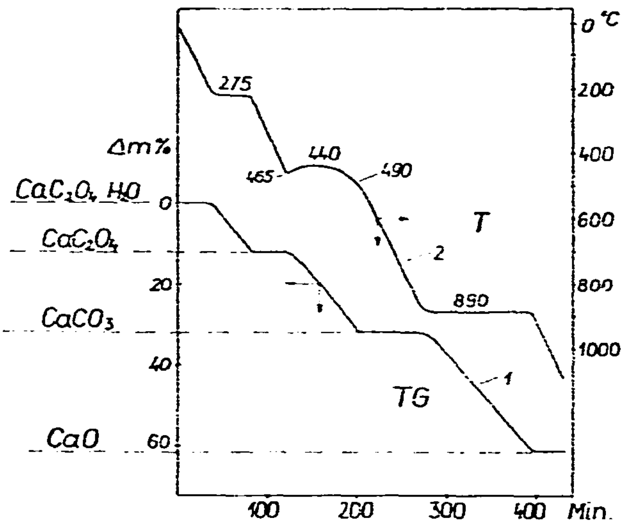

Fig. 4. Change in weight (curve 1) and change in temperature (curve 2) plotted as functions of time for the thermal decomposition of calcium oxalate monohydrate.

change and curve 2 the temperature change. As the course of these curves proves, the temperature of the sample increased with a rate of 5 °C/min up to 275 °C. Then the water of crystallization began to come off. The dehydratation took place slowly (in about 45 min) while the weight of the sample changed with a speed of about 1 mg/min. After the end of the thermal decomposition the temperature increased again with a rate of 5 °C/min until the calcium oxalate anhydride began to decompose. This process took place around 465 °C in about 80 min, while the decomposition of calcium carbonate at 890 °C lasted about 120 min.

Curve 1 in Fig. 5 is a version of the *TG* curve of Fig. 4, plotted as a function of temperature (instead of time) by means of an X–Y recorder. On the basis of the two curves of different shape representing exactly the same process, it can be stated that during either the whole dehydratation process of calcium oxalate monohydrate or the decomposition of calcium carbonate, the temperature of the sample did not change to a greater extent than ±2 °C. We regard this phenomenon as a very remarkable one since it took place spontaneously; namely, the heating regulator only provides directly for the constancy of the rate of weight change.

For the study of this question the most appropriate part of the curves is the section representing the thermal decomposition of calcium carbonate. According to literature, the partial pressure of calcium carbonate reaches 1 atm at 895 °C (the mean of 20 literature date). Accordingly, in our case, the decomposition of calcium carbonate taking place at 890 °C means that the compound decomposed at a temperature which can also be interpreted on a physico-chemical basis, *i.e.* at a temperature value which calcium carbonate can only attain if it contacts pure carbon dioxide. We have also observed that the 890 °C decomposition temperature did not change even then, if the measurement was repeated in a carbon dioxide atmosphere instead of air. Judging from the measured value of the decomposition temperature and its spontaneous stabilization, a self-generated atmosphere of perfect purity could be established inside the sample, even at a slow gas evolution (0.5 ml of CO_2/min).

It is significant that between 840 and 890 °C the curve forms a slightly sloping horizontal. This section can be interpreted by suggesting that the decomposition of only 2–3% of the sample was necessary for the carbon dioxide to completely expel the air from inside the sample and the sample holder, respectively.

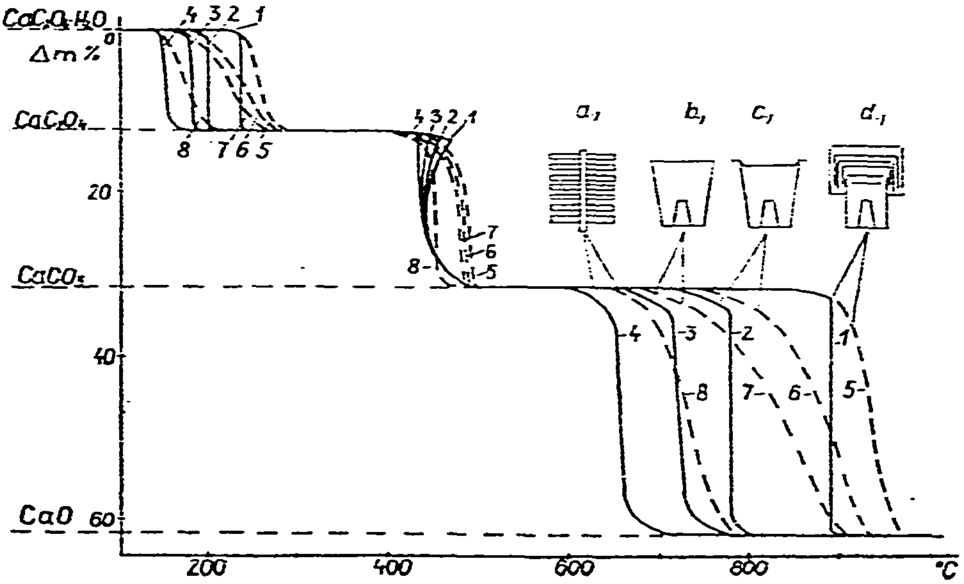

Fig. 5. Change in weight plotted as a function of temperature for the thermal decomposition of calcium oxalate monohydrate. Curves 1–4, using quasi-isothermal heating and curves 5–8, using dynamic heating (10 °C/min). (For explanation of (*a*), (*b*), (*c*) and (*d*), see text.)

In the case discussed, the decomposition of calcium carbonate took place under quasi-isothermal and quasi-isobaric conditions (*i.e.* it occurred under quasi-equilibrium conditions) which means that with the exception of the loss of the gaseous products, the rate of the thermal decomposition has not been influenced by any other process; unlike the case of curve 5 in Fig. 5. This curve was also recorded by using the crucible covered with the sixfold lid, but with programmed dynamic heating, *i.e.* at a heating rate of 10 °C/min. The shape of this curve is completely different; it shows, like other curves recorded using a dynamic heating program, a sigmoid form. The decomposition is significantly shifted in the direction of higher temperatures. The cause of this probably lies not only in the slow heat-transfer, but also in the contribution of other processes to this effect. The significant difference in the shape of curves 1 and 5 in Fig. 5 proves that the realization of a self-generated atmosphere alone does not solve the problem of standardization.

In Fig. 5, curves recorded under other experimental conditions can also be seen. While curve 1 was recorded with a quasi-isothermal heating program and using the new sample holder covered with the sixfold lid (*d*), curves 2–4 were traced using the conventional crucible of the derivatograph[4,5], covered (*c*) and uncovered (*b*), and the polyplate sample holder (*a*), respectively. In the latter case the sample was spread out on the plates in very thin layers[5,9]. Curves 5–8 were recorded using the same sample holders but with the dynamic (10°C/min) heating program. The shape of these curves recorded under different experimental conditions is also remarkable. One can observe, for example, that the thermal decomposition of calcium carbonate is taking 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; though in the latter case the decomposition temperature is lower. In this case, the steady state of the temperature means that according to the given circumstances, the diffusion of the carbon dioxide released took place from the inside of the sample with the same speed as the diffusion of air towards the inside of the sample, so that in the space not filled with grains, the composition of the mixture of air and carbon dioxide was constant. Meanwhile the decomposition temperature was determined by the decreased partial pressure of carbon dioxide. On the basis of the correlation between decomposition pressure and temperature it could be calculated, from the magnitude of the decomposition temperatures, that the sample was counterbalanced at 150 torr partial pressure of carbon dioxide in the covered crucible (curve 2), at 20 torr in the uncovered crucible (curve 3), and at 5 torr on the polyplate sample holder (curve 4).

On the basis of the above observations, we can state that by using the new technique (the quasi-isothermal heating program and the crucible with the sixfold lid) such experimental conditions can be created under which the endothermic decomposition reactions, leading to an equilibrium, will take place at a constant temperature, provided they are reactions of zero order, *i.e.* their course is defined exclusively by the rate of evolution of the gaseous products.

Accordingly, the decomposition of both calcium oxalate monohydrate and calcium carbonate took place as zero-order reactions under the experimental conditions of the decomposition traced by curve 1 in Fig. 5. But the process represented by curve 2 also came close to a reaction of zero order. According to the shape of the curve, the decomposition of calcium oxalate anhydride could by no means be qualified as a zero-order reaction, which is understandable since the reaction does not lead to an equilibrium.

With the following few examples we wish to demonstrate some characteristic types of transformation, rather than analyse these ones more deeply.

The *TG* curve in Fig. 6 shows the thermal decomposition of nickel hexammine chloride using the quasi-isothermal heating program and the sample holder with the sixfold lid. The shape of the curve shows the sample decomposed in three separate steps at 180, 320 and 360°C, respectively. All the three decomposition reactions took place under quasi-isothermal conditions, *i.e.* in the given case they were reactions of zero order. As can be seen, the temperature of the sample temporarily increased at the beginning of the decomposition to 185°C. This section of the curve probably represents the induction period of the delayed nucleus formation. However, after the formation

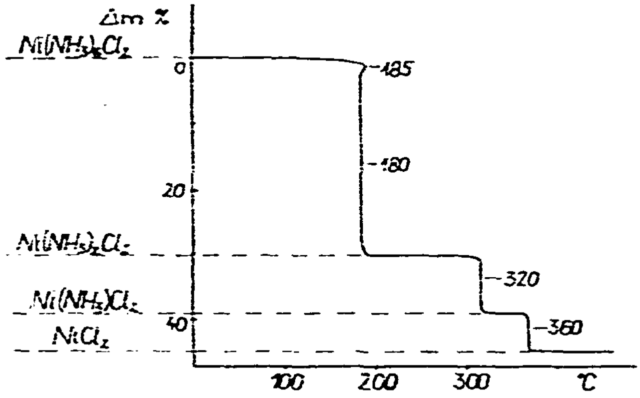

Fig. 6. Change in weight plotted as a function of temperature for the thermal decomposition of nickel hexammine chloride.

of a sufficient number of nuclei, no further obstacle existed, so that the reaction could take place according to the rate of weight change (1 mg/min) defined by the heating regulator, and the course of the curve later became regular and the decomposition temperature lower.

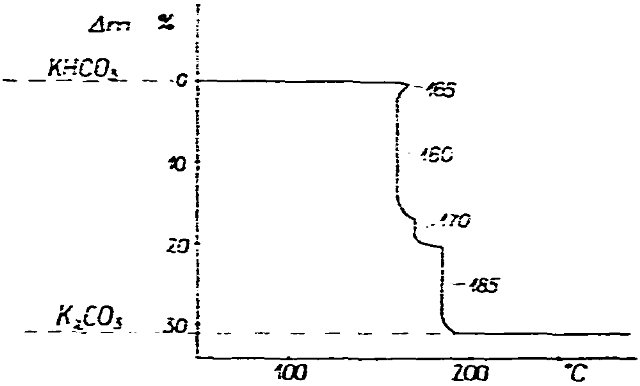

Fig. 7. Change in weight plotted as a function of temperature for the thermal decomposition of potassium hydrogen carbonate.

As can be seen in Fig. 7, a delayed nucleus-formation (165 °C) also introduces the decomposition of potassium hydrogen carbonate, but this curve shows other irregularities too. The curve represents the decomposition of potassium hydrogen carbonate as a process taking place in three steps.

With the help of our simultaneous thermogravimetric and thermo-gas-titrimetric method[10], we have shown before that in the course of the thermal decomposition of this compound, the carbon dioxide and the constituent water were set free in an identical manner[11]. Consequently, the chemical reaction is a uniform one, but its course becomes a gradual one because of the influence of another, unknown process.

During the individual partial processes the temperature (160, 170 and 185°C) remained constant, with the exception of the initial and final periods of the processes. From this fact we concluded that the unknown influence does not change the reaction order, so it also remains zero order in this case.

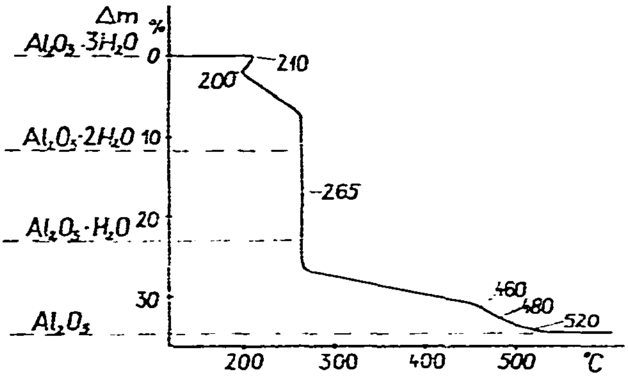

Fig. 8. Change in weight plotted as a function of temperature for the thermal decomposition of an industrial alumina hydrate.

The thermogravimetric curve in Fig. 8 is also of some interest. This is a plot of the decomposition of an industrial alumina hydrate sample with the help of the new technique. According to X-ray investigations the sample was of gibbsite crystal structure. It is known that industrial alumina hydrates generally decompose gradually in three steps, so that first *ca.* two-thirds of a water molecule, then one and two-thirds molecules and finally, another two-thirds of a molecule are removed. In the course of our earlier investigations we found that this proportion may change depending on the conditions of the production. But these changes always take place in such a way that the amount of water removed in the first and third steps changes in equal proportion[12], demonstrating that a strict correlation exists between the two processes.

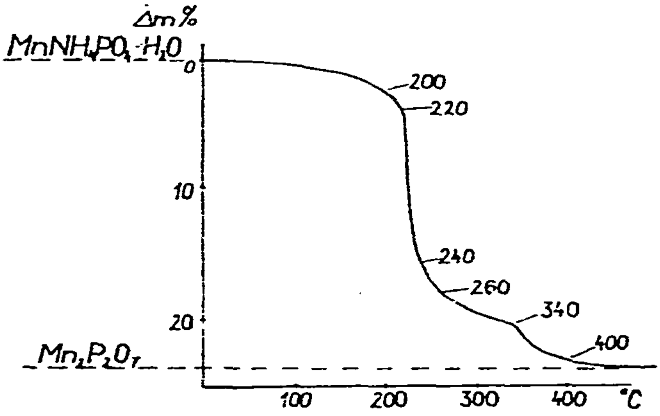

Fig. 9. Change in weight plotted as a function of temperature for the thermal decomposition of manganese ammonium phosphate monohydrate.

The course of the curve shown in Fig. 8 may support this observation, since only the second step of the thermal decomposition looks like a reaction of zero order, while the reaction order of the first and third decomposition steps is different.

Using the example of the decomposition of manganese ammonium phosphate monohydrate (Fig. 9), we wish to demonstrate a reaction type where the temperature does not get even temporarily into a steady state; consequently, the decomposition does not take place as a zero-order reaction. That means that the rate of the decomposition is not defined by the rate of the gas transfer, but by the rate of another process.

ACKNOWLEDGMENT

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