

## KINETICS AND MECHANISM OF THE DECOMPOSITION OF PYRITE UNDER CONVENTIONAL AND QUASI-ISOTHERMAL – QUASI-ISOBARIC THERMOANALYTICAL CONDITIONS

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The kinetics and mechanism of the thermal decomposition of pyrite were examined by the method of quasi-isothermal and quasi-isobaric thermogravimetry (Q–TG). It emerged that by means of this technique the overlapping partial processes of the complicated oxidation and decomposition reactions of pyrite can be separated and studied independently from one another. It was found that the partial reactions  $\text{FeS}_2 = \text{FeS} + \text{S}$  and  $\text{Fe}_2\text{O}_{3-x}(\text{SO}_4)_x = \text{Fe}_2\text{O}_3 + \text{SO}_3$  are endothermic processes taking place quasi-isothermally and leading to equilibrium, while the oxidation  $\text{FeS} + \text{O}_2 = \text{Fe}_2\text{O}_{3-x}(\text{SO}_4)_x$  is an exothermic process which takes place in an oscillating manner in a rather broad temperature interval.

There are few compounds the decomposition of which is influenced by the conditions of thermal analysis to such an extent as in the case of pyrite, or in a broader sense of the chalcogenides. The differences between the simultaneous TG, DTG and DTA curves in Figs 1, 2 and 3 serve as proof of this fact. The only difference between the practical conditions in Figs 1 and 2 (curves 1 traced in air and curves 2 in nitrogen) was that in the case of Fig. 1 the sample was situated in an open crucible, while in the case of Fig. 2 the sample was spread out in a thin layer on the large surface area of a multiplate sample holder. This comparatively small variation in the conditions completely changed the course of the curves. Figure 3 shows that the shape of the curves changed even if, in accordance with the earlier custom, the pyrite sample was diluted with aluminium oxide, which is held to be indifferent.

The thermal decomposition of pyrite has been investigated by many researchers [1–15], in addition to our own work [16–18]. Despite the differences in opinion, in one single thing the view was consistent: the thermal decomposition of pyrite in the presence of oxygen is a rather complicated process composed of several overlapping reactions.

Our earlier experience led us to assume that by means of the quasi-isothermal–quasi-isobaric measuring technique [19–21] we would be able to separate these partial reactions and study them independently from one another. In the present paper we report the results of our investigations in this respect.

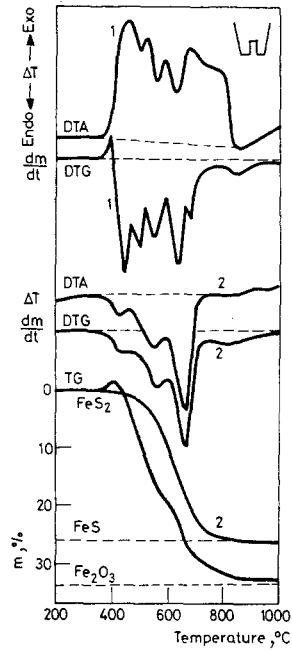


Fig. 1. Simultaneous TG, DTG and DTA curves of pyrite recorded by using an open crucible in  $O_2$  (1) and  $N_2$  (2)

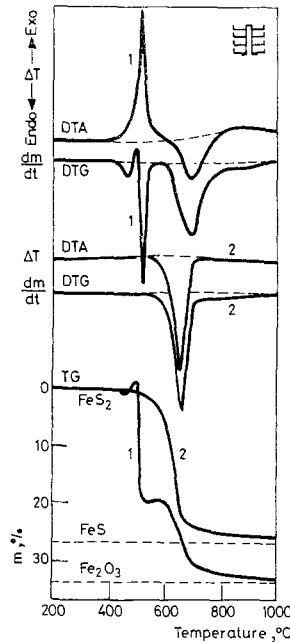


Fig. 2. Simultaneous TG, DTG and DTA curves of pyrite recorded by using the multiplate sample holder in  $O_2$  (1) and  $N_2$  (2)

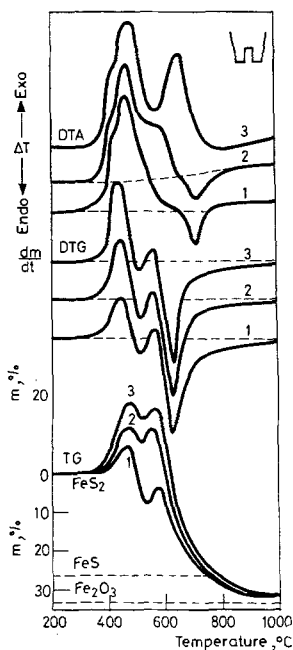


Fig. 3. Simultaneous TG, DTG and DTA curves of mixtures containing alumina and 5% (1) 2% (2) and 1% pyrite in  $O_2$

## Experimental

### Materials

As model substance we selected a radiologically pure, well-crystalline pyrite sample from Gyöngyösoroszi (Hungary). By using conventional gravimetry and our thermogas-titrimetric method [19], we found that the sample contained 50.5% sulphur. We took this value as starting point in our calculations. In the construction of the figures we assumed that our sample contained pyrite of stoichiometric composition equivalent to the above sulphur content. This is of course only a surmise, for pyrite is nearly never completely pure and the mineral is seldom of stoichiometric composition. We further assumed that the impurities in the sample, which were not considered in the course of our calculation method, did not cause measurable weight changes in the temperature range examined.

For dilution we applied four compounds (Figs 8–11): Silica powder prepared from silica glass by powdering; aluminium oxide of analytical purity, heated to  $1000^\circ$  before application; corundum powder prepared by heating analytically pure  $Al_2O_3$  to  $1750^\circ$ , i.e. the temperature of sintering; ferric oxide prepared by heating ferric oxalate heated to  $500^\circ$ .

### *Techniques*

The conventional simultaneous DTA, DTG and TG and the quasi-isothermal—quasi-isobaric thermogravimetric (Q—TG) examinations were carried out by means of a Q—D 1500 derivatograph, produced by the Hungarian Optical Works (MOM), Budapest.

The essence of the quasi-isothermal—quasi-isobaric measuring technique [19—21] lies in a special controller incorporated in the derivatograph [19], which ensures that the transformation takes place at a strictly constant rate some orders of magnitude lower (0.2—0.5 mg/min per 100 mg total weight change) than in the case of conventional dynamic heating techniques. While no transformation occurs the temperature increases rapidly (3—5°/min), whereas during transformations it does not increase at all or only exceedingly slowly (quasi-isothermal).

The application of a “labyrinth crucible” also belongs to the essence of the method. Immediately after the beginning of the reaction, the partial pressure of the gaseous product within this crucible reaches atmospheric pressure, 100 kPa (“self-generated atmosphere”), and it remains constant up to the end of the process (quasi-isobaric).

Experience has shown [19] that if the labyrinth crucible is replaced by a covered, an open or a multiplate sample holder the partial pressure of the gaseous decomposition products in the vicinity of the sample decreases from 100 to 20, 5 or 1 kPa, respectively. These values stay practically constant throughout the whole period of the transformations. In this way the composition of the sample in contact with the gas atmosphere can be changed at preference. This possibility can be utilized advantageously to influence the equilibrium of the reactions, as well as for the study of oxidizing processes.

### *Experimental conditions*

The simultaneous TG, DTG and DTA curves of Figs 1, 2 and 3 were recorded in the conventional way at a heating rate of 10°/min. In the case of Fig. 1 the sample was situated in an open crucible. In the case of Fig. 2 the pyrite was spread out in a thin layer on the surface of a multiplate sample holder and was examined in an atmosphere of air (curves 1) or nitrogen (curves 2). The curves of Fig. 3 were recorded for aluminium oxide mixed with various amounts of pyrite: 5% (curve 1), 2% (curve 2) and 1% (curve 3). The samples were situated in an open crucible and were examined in the presence of air.

The Q—TG curves of Figs 4 and 5 were obtained by means of the quasi-isothermal—quasi-isobaric measuring technique. In order to examine the influence of the concentration of the sample in contact with oxygen, we carried out parallel measurements in air (Fig. 4) and oxygen (Fig. 5) atmospheres, using a crucible without a lid (curves 1 and 2) and the multiplate sample holder (curves 3 and 4). We repeated every measurement in order to obtain information regarding the reproducibility of the curves. Curves 1 and 2, and curves 3 and 4, were traced under identical conditions.

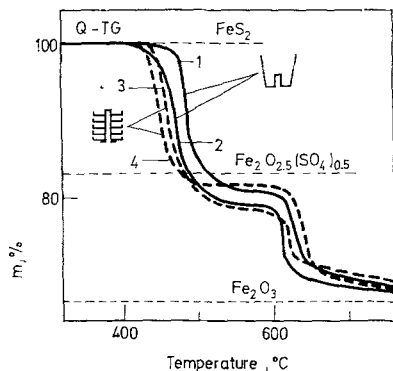


Fig. 4. Parallel Q-TG curves of pyrite recorded in air using an open crucible (1, 2) and a multiplate sample holder (3, 4)

It can be seen from Fig. 7 that the partial processes could only be separated if the pyrite was first decomposed to ferrous sulphide in a nitrogen atmosphere (curves 1-4) and thereafter the oxidation of the sample cooled down in nitrogen was examined in air (curves 6 and 8) or in oxygen (curves 7 and 9). Various types of sample holders were similarly used in these experiments (labyrinth: curve 1; covered crucible: curves 2 and 9; uncovered crucible: curves 3, 7 and 8; multiplate sample holder: curves 4, 5 and 6).

We also studied the question whether interactions occur in an oxygen atmosphere between pyrite and silica (Fig. 8), corundum (Fig. 9), aluminium oxide (Fig. 10) and ferric oxide (Fig. 11), all regarded as inert materials, and if so how these change with the extent of the dilution. We therefore mixed these diluents with 1, 2 and 5% of pyrite.

In the recording of every Q-TG curve the transformation was regulated by the heating controller system at a rate of 0.3 mg/min/100 mg total weight change.

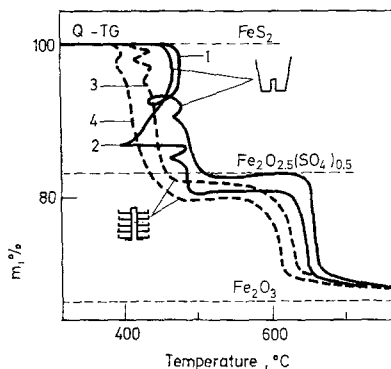


Fig. 5. Parallel Q-TG curves of pyrite traced in  $O_2$  using an open crucible (1, 2) and a multiplate sample holder (3, 4)

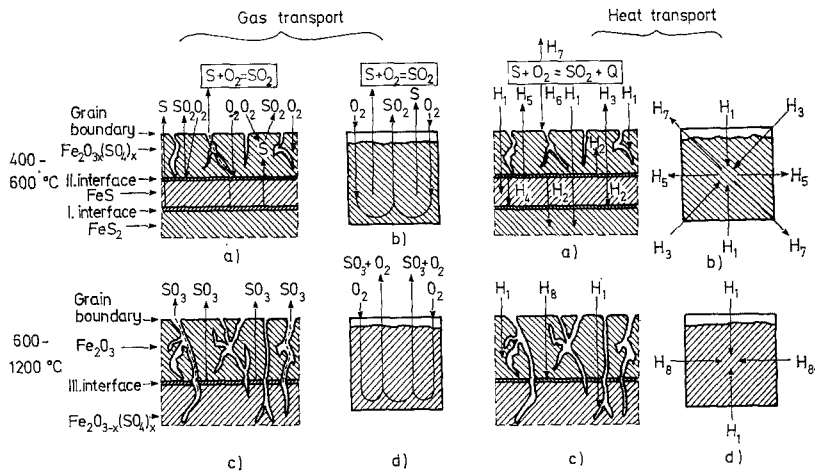


Fig. 6. Phenomenological picture of partial gas and heat transport processes taking place within the grains (a, c) and sample holder (b, d)

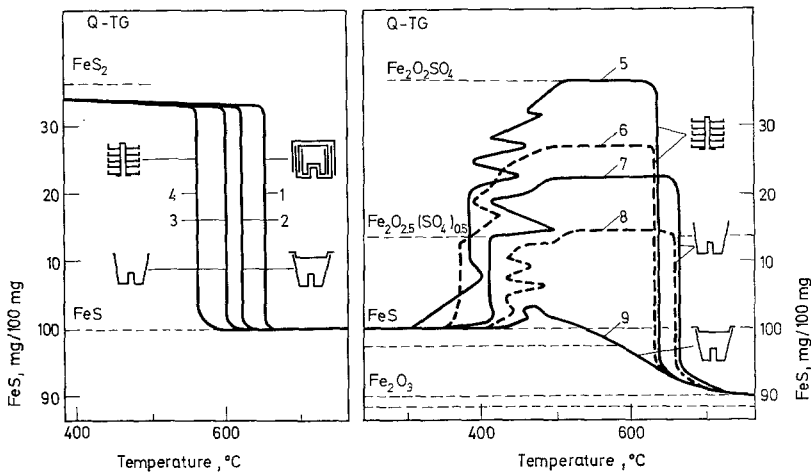


Fig. 7. Q-TG curves of the dissociation of pyrite in  $N_2$  using the labyrinth (1), a covered (2) and an open crucible (3), and the multiplate sample holder (4). Q-TG curves of FeS decomposition product, illustrating its oxidation and the dissociation of the intermediate  $Fe_2O_{3-x}(SO_4)_x$  in  $O_2$  (5, 7, 9) and in air (6, 8), using the multiplate sample holder (5, 6) an open crucible (7, 8) and a covered crucible (9)

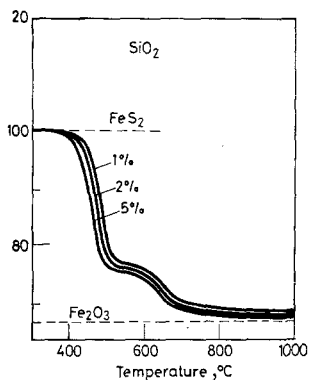


Fig. 8. Q-TG curves of mixtures containing silica and 1%, 2% or 5% pyrite

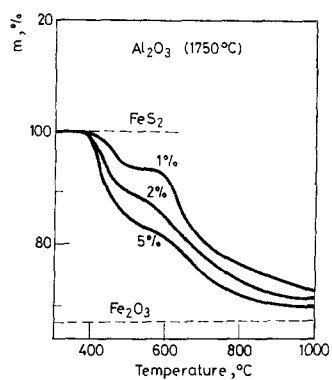


Fig. 9. Q-TG curves of mixtures containing ferric oxide and 1%, 2% or 5% pyrite

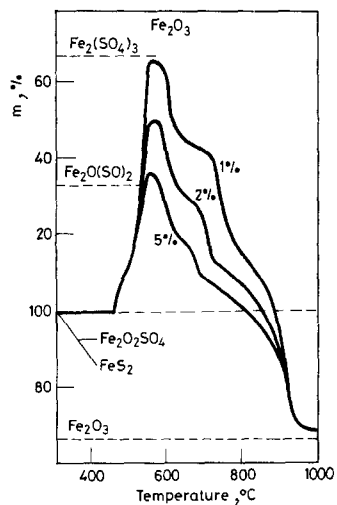


Fig. 10. Q-TG curves of mixtures containing corundum and 1%, 2% or 5% pyrite

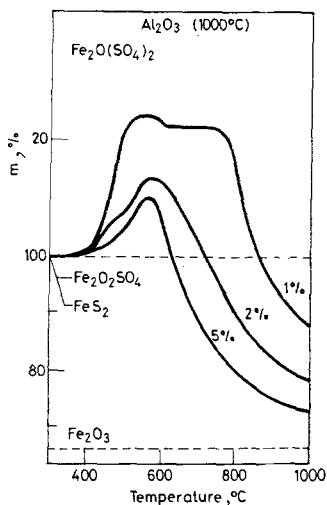


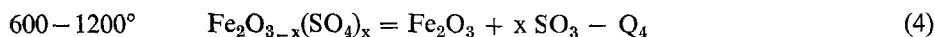
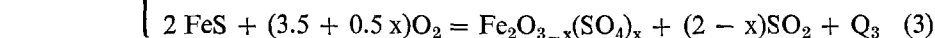
Fig. 11. Q-TG curves of mixtures containing alumina and 1%, 2% or 5% pyrite

### Results and discussion

The idealistic experimental conditions offered by the quasi-isothermal—quasi-isobaric measuring technique remained inefficient for the case of pyrite. This could be concluded by observing the abnormal and uncertain shape of the Q-TG curves in Figs 4 and 5. The curves could not be reproduced, even when the experimental conditions were kept as strictly constant as possible. From case to case the composition of the intermediate  $[\text{FeO}_{3-x}(\text{SO}_4)_x]$  also changed. Apparently, neither this nor the transformation temperature could be influenced by the selected experimental conditions (change of the sample holder or atmosphere). The most conspicuous anomaly was shown by the distorted course of curves 1 and 2 in Fig. 5.

In looking for the reason for these anomalies, we established the following phenomenological picture regarding the kinetics and mechanism of the decomposition of pyrite.

In an oxygen-free atmosphere one must consider the occurrence of reaction (1)—whereas in the presence of oxygen all four reactions (1–4) must be taken into account. In this latter case the first three reactions occur simultaneously (400–600°)—while the fourth either follows the earlier ones (600–1200°) or often totally overlaps with them (curves 1 in Fig. 1):





The transformation in oxygen is the resultant of numerous heat and gas transport processes. In Fig. 6 we demonstrate the complex interaction of these elementary transport processes by symbolical means. Parts "a" and "c" of the Figure illustrate the grains, while parts "b" and "d" demonstrate the processes taking place within the sample holder.

For the start of a simple endothermic transformation (e.g. reaction 4), the sample must be heated first to the temperature of transformation. For this and the further temperature increase of the sample, the substance must take up the heat amount proportional to the specific heat of its original  $[\text{Fe}_2\text{O}_3-x(\text{SO}_4)_x]$  and new  $[\text{Fe}_2\text{O}_3]$  phases ( $H_1$  elementary heat transport). Once started, the reaction can proceed only at a rate at which the sample is able to absorb the reaction heat necessary for its transformation ( $H_5$ ). In the present simple case the sample takes up these two kinds of heat from its surroundings.

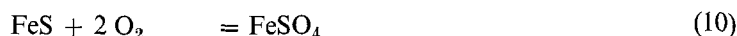
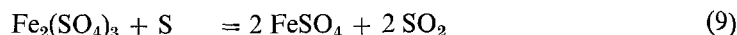
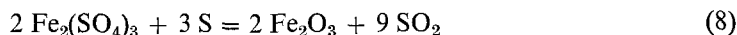
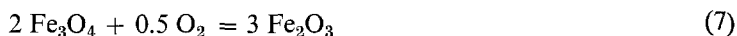
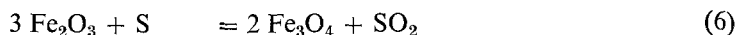
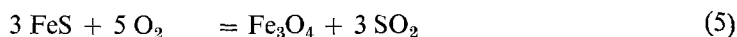
However, in the oxidation of pyrite the situation is more complicated. Reaction (3) produces heat spontaneously. This is consumed partly by the temperature increase of the old ( $\text{FeS}_2$ ) and new  $[\text{FeS}, \text{Fe}_2\text{O}_3-x(\text{SO}_3)_x]$  phases ( $H_2$ ) and partly by the dissociation of pyrite ( $H_4$ ). The excess liberated heat departs in the direction of the surroundings ( $H_3$ ). If the amount of liberated heat is not sufficient, the direction of the heat transport between the grain and its surroundings will be the reverse ( $H_1$  and  $H_3$ ). The combustion of sulphur vapour on the surface of the grains, between them, and outside the sample causes the liberation of further heat. Part of the heat liberated within the sample is absorbed by the substance ( $H_6$ ), while the excess is dispersed in the surroundings ( $H_7$ ).

The two oxidation processes (reactions 2 and 3) together cause a sudden spontaneous increase in sample temperature and the rapid occurrence of the decomposition process if sufficient oxygen can reach interface II, for gas transport processes also participate in the control of the transformation. The transformation commences with the dissociation of pyrite, leading to equilibrium (reaction 1). The liberated sulphur vapour passes through the pores and channels of various sizes in the new phases  $[\text{FeS}$  and  $\text{Fe}_2\text{O}_3-x(\text{SO}_4)_x]$  onto the grain boundary, and from there between the grain onto the surface of the sample. On interface II, sulphur dioxide, too becomes mixed in the stream of sulphur vapour. Oxygen diffuses in the same path, but in the reverse direction, but only a restricted amount of this reaches interface II as the diffusion of oxygen is hindered by the gaseous decomposition products streaming in the opposite direction.

Not only the described heat and gas transport processes, but also the experimental conditions, such as the amount of the sample, its compactness and dilution, the shape and size of the sample holder, the heating rate, the ventilation of the furnace, etc., exert great effects on the progress of the transformations.

In addition to the above-mentioned processes, depending on the experimental conditions, i.e. the oxygen amount passing into the inside of the grains, many other kinds of partial oxidation and reduction reactions may take place between the solid phases and the gases diffusing through them. These partial reactions may change the

composition of the new phase transitionally, or even permanently. Some of these characteristic cases are represented by the following examples:



The mechanism of the outlined transport processes offered an explanation for both the diverse shapes of the conventional thermoanalytical curves (Figs 1 and 2) and the anomalies of the Q-TG curves in Figs 4 and 5, and it also provided a new starting point for our further investigations.

As Fig. 7 demonstrates, we repeated the examinations under quasi-isothermal-quasi-isobaric conditions but first the pyrite was decomposed in a nitrogen atmosphere (curves 1-4) and thereafter in the presence of oxygen we examined the oxidation of ferrous sulphide (section between 300 and 500° of curves 5-9) as well as the decomposition of the intermediate  $\text{Fe}_2\text{O}_{3-x}(\text{SO}_4)_x$  (section between 640 and 660° of curves 5-9). In this way we were able to separate the heat and gas transport processes in space and time and eliminate their pernicious interactions.

In interpreting the course of these curves, we may state that the dissociation of pyrite is a process leading to equilibrium, since the decomposition temperatures varied with the different sample holders and their sequence corresponded to the sequence of changing partial pressure of sulphur vapour (100, 20, 5 and 1 kPa) depending on the sample holders applied. In the labyrinth crucible, in the presence of sulphur vapour at 100 kPa partial pressure, the decomposition occurred at 650°. In all four cases the transformation under the given conditions took place in a quasi-isothermal way. From this it follows that the reaction was not a complex one and its progress was not hindered by physical obstacles either (such as a small porosity compact structure of the new phase).

Curves 5-9 show that the oxidation of pyrite started at about 350° and ended at approximately 500°. However, even under these conditions the progress of the transformation remained rather capricious and oscillating. It seemed improbable that this was also caused by the lability of the heat and gas transport processes. The assumption that the heating control system is not suitable for the examination of such spontaneous exothermic reactions could be excluded, since earlier we were able without difficulty to diminish by some orders of magnitude the rate of decomposition of nitrocellulose, which decomposes far more violently than pyrite, and no similar anomalies could be observed in those Q-TG curves [22]. Consequently, the following explanation seemed to be the most probable.

The surface energies on the grains may be very different. Active sites may be created by lattice distortions, foreign lattice elements incorporated in the lattice, chemisorption of gases, oxidation of surface lattice elements, etc. The nucleus formation always begins at the sites of highest activity and only after these sites are occupied can the formation of newer nuclei begin at sites of progressively lower activities. This graduality creates differences which generally cannot be expressed in terms of time or temperature. However, in special cases this condition may be expressed in the thermoanalytical curves. For example, if a heat-producing oxidation process is the subject of examination, if there is a great difference in the activities of the sites of the nuclei, and if the material has a very low heat conductivity, then it may occur that the partial transformation processes take place at various temperatures and at various times in various isolated points of the sample, without initiating the transformation of the whole material.

Pyrite is a characteristic example of such substances. It was earlier observed [15] that the oxidation of a suitably prepared pyrite sample gave rise in the DTA curve not to a large exothermic peak, but to a series of numerous needle-shaped peaks. Consequently, the supposition seems justified that in the present case the abnormal course of curves 5–9 in the interval 350–500° in Fig. 7 was caused by the different activities of the nucleus sites.

From a comparison of the shapes of curves 5–9 it can be stated that the sulphate content of the intermediate  $\text{Fe}_2\text{O}_{3-x}(\text{SO}_4)_x$  increased if the examination was carried out not in air (curves 6 and 8) but in oxygen (curves 5 and 7), or if the multiplate sample holder (curves 5 and 6) was used instead of the crucible (curves 7 and 8).

$\text{Fe}_2\text{O}_{3-x}(\text{SO}_4)_x$  is formed not only in the course of ferrous sulphide oxidation but also during the oxidation of pyrite (Figs 1–3, 5, 6). However, in this latter case the TG or Q–TG curve illustrates the resultant of two effects of opposite signs i.e. the weight loss caused by the departure of sulphur and the weight increase due to the uptake of oxygen.

The decomposition of  $\text{Fe}_2\text{O}_{3-x}(\text{SO}_4)_x$  took place in an isothermal way, at 640° on the multiplate sample holder, and at 660° in the crucible. For the sake of comparison we also examined the decomposition of an analytically pure  $\text{Fe}_3(\text{SO}_4)_2$  sample of theoretical composition under quasi-isothermal and quasi-isobaric conditions. The decomposition of this compound also took place isothermally on the multiplate sample holder, in the open crucible, in the covered crucible and in the labyrinth sample holder at 640, 660, 680 and 730°, respectively. Accordingly, the decompositions of  $\text{Fe}_2\text{O}_{3-x}(\text{SO}_4)_x$  and of pure  $\text{Fe}_2(\text{SO}_4)_3$  took place in the same way and led to equilibrium in both cases.

Several conclusions could be drawn from our experiments with pyrite mixed with various ballast materials, so far considered indifferent [15]. The Q–TG curves of Figs 8–11 show that the sulphur dioxide and sulphur trioxide liberated in the oxidation of pyrite react with aluminium oxide and ferric oxide and are bound to a lesser or greater extent. The binding power of ferric oxide is higher than that of aluminium oxide. It is evident that the binding power of aluminium oxide previ-

ously heated to the temperature of sintering is lower than that of aluminium oxide heated to 1000°. The silica powder proved to be really indifferent.

From the above, the following conclusions can be drawn:

In the examination of mineral substances one has to consider the appearance of secondary reactions if aluminium oxide or ferric oxide is formed in the course of the experiment [23].

The thermoanalytical curves of samples diluted with aluminium oxide are modified (e.g. the curves in Fig. 3 in comparison with the curves in Figs 1 and 2).

The reliability of weight change measurements decreases in the case of thermobalances in which the sample and aluminium oxide reference are situated side by side on the balance.

Further in TG measurements it has to be taken into account that the aluminium oxide reference may bind sulphur trioxide.

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ZUSAMMENFASSUNG — Autoren untersuchten die Kinetik und den Mechanismus der thermischen Zersetzung von Pyrit durch quasi-isotherme und quasi-isobare Thermogravimetrie (Q—TG). Es stellte sich heraus, daß sich überlagernde Teilprozesse der komplizierten Oxydations- und Zersetzungsprozesse von Pyrit mit Hilfe dieser Technik absondern und unabhängig voneinander untersuchen lassen. Es wurde festgestellt, daß die Teilreaktionen  $\text{FeS}_2 = \text{FeS} + \text{S}$  und  $\text{Fe}_2\text{O}_{3-x}(\text{SO}_3)_x = \text{Fe}_2\text{O}_3 + \text{SO}_3$  endotherme Prozesse sind, die quasi-isotherm verlaufen und zu einem Gleichgewicht führen, während die Oxydation  $\text{FeS} + \text{O}_2 = \text{Fe}_2\text{O}_{3-x}(\text{SO}_4)_x$  ein exothermer Prozeß ist, der oszillierend in einem ziemlich breiten Temperaturintervall verläuft.

Резюме — Квазиизотермическим и квазиизобарным термогравиметрическим (Q—ТГ) методами исследована кинетика и механизм термического разложения пирита. С помощью этих методов могут быть разделены и изучены независимо друг от друга налагающиеся частичные процессы сложных реакций окисления и разложения пирита. Установлено, что частичные реакции  $\text{FeS}_2 = \text{FeS} + \text{S}$  и  $\text{Fe}_2\text{O}_{3-x}(\text{S}_2\text{O}_4)_x = \text{Fe}_2\text{O}_3 + \text{SO}_3$  являются эндотермическими, происходящие в квазиизотермическом режиме. Реакция окисления  $\text{FeS} + \text{O}_2 = \text{Fe}_2\text{O}_{3-x}(\text{SO}_4)_x$  является экзотермическим процессом, колеблющимся в широком температурном интервале.