

KINETICS OF THERMAL DECOMPOSITION OF PYRITE IN AN INERT ATMOSPHERE

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The thermal decomposition of pyrite in an inert atmosphere was studied in order to obtain a detailed knowledge of the kinetics and mechanism of the reaction $2\text{FeS}_2 = 2\text{FeS} + \text{S}_2$, which is one of the methods of producing elementary sulphur. The process was studied under isothermal conditions at temperatures of 600, 660, 700, 750, 800 and 850 °C in a nitrogen atmosphere, by means of a thermobalance. The rate-controlling processes were determined and their kinetic parameters were calculated. The optimum temperature for the process was found to be 800 °C.

Pyrite is often a constituent of ores and raw materials used in the production of base metals.

The exploitation of pyrite for the production of elementary sulphur, through the thermal decomposition of pyrite in an inert atmosphere [1], demands a detailed knowledge of the kinetics and mechanism of the thermal reaction.

The purpose of this work was to study the kinetics of the process, but it also illustrates the possibility of using a thermobalance to study the kinetics of chemical and other processes at a gas/solid interface.

Experimental

Material

The pyrite concentrate “Novo Brdo” from the Trepča mine in Yugoslavia, with the mineral, chemical and granulometric compositions given in Tables 1–3, was studied.

The mean particle diameter, r , calculated by means of Eq. (1) [2], was 0,0072 cm.

$$r = \left[\frac{\sum_{i=0}^{i=n} \frac{G_i}{R_i}}{\sum_{i=0}^{i=n} \frac{G_i}{R_i^3}} \right]^{1/2} \quad (1)$$

where: G_i = mass fraction. and

R_i = mean diameter (arith. mean) of particles in individual fraction.

Method

A Stanton thermobalance of decimilligram sensitivity, adapted for work in a gas atmosphere [3], was used in the experiments.

The thermobalance furnace was heated up to a predetermined temperature, which was then held constant. A sample of pyrite was inserted into the furnace, and the loss in weight was recorded against time.

Table 1 Mineral composition of the "Novo Brdo" pyrite concentrate

Mineral	%
Pyrite	80,2
Waste material	13.5
Sphalerite	4.3
Undefined material	1.9
Chalcopyrite	trace
Galena	trace

Table 2 Chemical composition of the "Novo Brdo" pyrite concentrate

Element	%
Fe	37.33
S	42.87
Zn	0.24
Pb	0.48
Mn	0.24
Cu	0.19–0.90
As	0.65
SiO ₂ + CaO + MgO	0.70

Results and discussion

The thermal decomposition of pyrite in an inert atmosphere, which proceeds as follows:

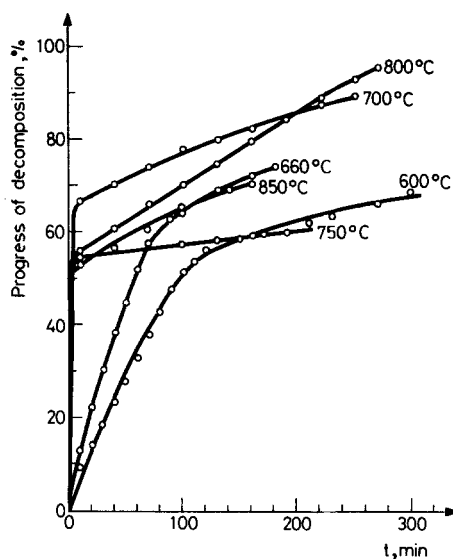


Table 3 Sieve analysis of the "Novo Brdo" pyrite concentrate

Sieve (mesh)	Mass fraction, g	%
28	0.0	0.00
35	1.8	0.62
42	1.3	1.01
60	8.1	6.25
100	39.6	30.93
140	43.4	33.90
200	8.5	6.66
325	17.2	13.43
- 325	5.9	4.60

was studied under isothermal conditions at 600, 660, 700, 750, 800 and 850°, in nitrogen, using 0.5 g pyrite for each experiment. The loss in weight of the samples is plotted as a function of time in Fig. 1, illustrating the degree of the chemical reaction given by Eq. (2).

Each plot in Fig. 1 is divided into two clearly separated parts. The first part, from the start of the decomposition reaction up to the deflection point, is a straight line with a slope that increases with the increase of temperature. In the second part, after the deflection point, the slope is not temperature-dependent.

**Fig. 1** Degree of thermal decomposition of pyrite in a nitrogen atmosphere at given temperatures

As a starting point for considering the mechanism of the reaction given by Eq. (2), it was accepted that the rate-controlling process of this reaction could be either a chemical reaction on the FeS_2/FeS interface, or the diffusion of S_2 vapour through the layer of FeS (pyrrhotine).

Farrar and Smith [4] have developed equations that describe the two above-mentioned rate-controlling processes. Thus, when the rate is diffusion-controlled:

$$1/2 + 1/2(1-F)^{2/3} - (1-F)^{1/3} = k \cdot t/r^2 \quad (3)$$

where: k = constant,
 r = mean diameter of a particle, and
 t = time;

and when the rate of process is controlled by a chemical reaction:

$$1 - (1-F)^{1/3} = k' \cdot Vm \cdot t/r \quad (4)$$

where: k' = kinetic constant of the reaction,
 Vm = molar volume of the initial material,
 r = mean diameter of a particle, and
 t = time.

In both equations, F is the degree of the reaction, and is defined by Eq. (5):

$$F = \frac{(S_i - S_t)}{S_i(M_p/M_i - 1)} \quad (5)$$

where: S_i = initial weight of sample,
 S_t = weight of sample at time t ,
 M_i = molecular weight of initial sample, and
 M_p = molecular weight of the product.

The values of F were calculated from the experimental results in Fig. 1, and introduced into Eqs (3) and (4). The cases when straight lines were obtained, the left-hand sides of Eq. (3) or (4) vs. time, are given in Figs 2, 3, and 4.

The first part of the curve from Fig. 1 can be linearized with Eq. (4), which means that in this case the rate-controlling process is the chemical reaction on the FeS_2/FeS interface (Figs 2 and 3). The ends of the straight lines for 600 and 660° show a curvature (Fig. 2), which means that diffusion takes over the control of the process rate, since the layer of FeS becomes thicker.

The second part of the curves from Fig. 1 for the temperatures 600, 660, 700 and 750°, can be linearized by means of Eq. (3) (Fig. 4). In this case, the rate-controlling process is the diffusion of S_2 vapour through a layer of FeS.

The values of the rate constants of the chemical reaction, k' from Eq. (4), are calculated from the slopes of the straight lines in Figs 2 and 3, and are given in Table 4.

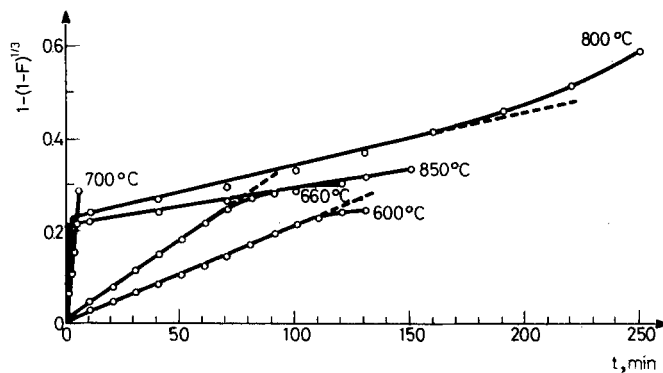


Fig. 2 The weight loss vs. time curves when the rate-controlling process is a chemical reaction on the FeS_2/FeS interface, transformed via Eq. (4)

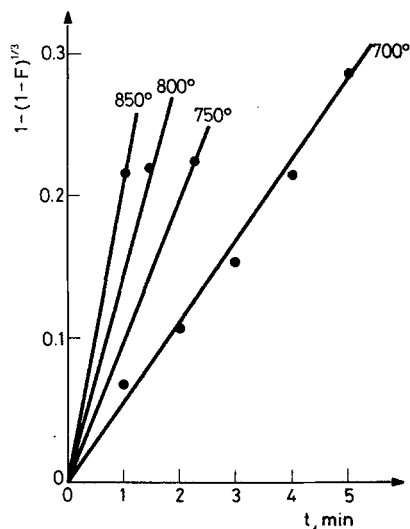


Fig. 3 The weight loss vs. time curves when the rate-controlling process is a chemical reaction on the FeS_2/FeS interface, transformed via Eq. (4)

Table 4 Temperatures of process, kinetic constants of rate-controlling processes, coefficients of diffusion of S_2 vapour through the layer of FeS , and mean diameters of particles

$t, ^\circ\text{C}$	$10^8 k', \text{cm}^{-2} \text{sec}^{-1}$	$10^{11} k, \text{cm}^2 \text{sec}^{-1}$	$10^{10} D, \text{cm}^2 \text{sec}^{-1}$	r, cm
600	1.08	5.46	1.50	0.0072
660	1.80	27.71	3.70	0.0072
700	25.50	65.10	8.24	0.0107*
750	50.00	128.20	18.77	0.0393*
800	105.90			

* mean diameter of sintered particles.

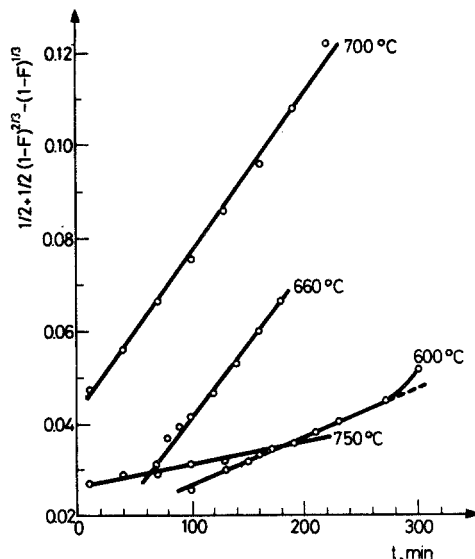


Fig. 4 The weight loss vs. time curves when the rate-controlling process is the diffusion of S_2 vapour through the layer of FeS, transformed via Eq. (3)

The Arrhenius dependence $\ln k'$ vs. $1/T$ is given in Fig. 5. This dependence is represented by two separate straight lines. Line 1 corresponds to the temperature interval 600–660°, and line 2 to the temperature interval 700–850°. This leads to the conclusion that two different phase modifications are involved. Some explanations of this phenomenon can be found in the publication of Bistrov et al. [5], who studied the phase equilibria in the system Fe/S, and found that the composition of a sample at lower temperatures corresponds to the two-phase region pyrite + pyrrhotite, and that this composition does not change up to 717°. In this region the dependence of the S_2 vapour pressure on temperature is given by a straight line: $\log p_{S_2}$ vs. $1/T$.

In the temperature interval 717–1149°, a condensed phase corresponds to the region of homogeneous pyrite.

An attempt can be made to calculate the constant k in Eq. (3) from the slopes of the straight lines in Fig. 4. The slopes first increase between 600 and 660°, and then decrease in the temperature interval 700–750°.

The fact that constant k decreases with temperature can not be accepted, and thus the explanation for the decrease in the ratio k/r^2 must be the increase in the particle diameter due to sintering of the particles.

The plot of k/r^2 vs. $1/T$ is given in Fig. 6. The straight line part of the plot (600–660°) can be extrapolated (broken line). From the extrapolated part of the straight line one can take the values of the ratio k/r^2 for 700 and 750° (values that

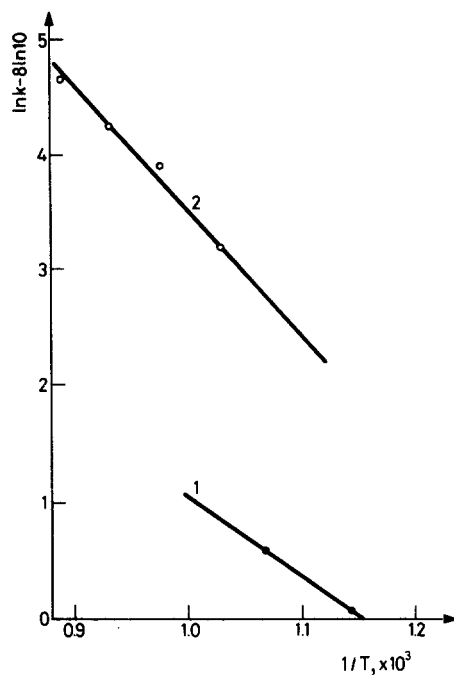


Fig. 5 Temperature-dependence of the kinetic constant of the thermal decomposition of pyrite, k'

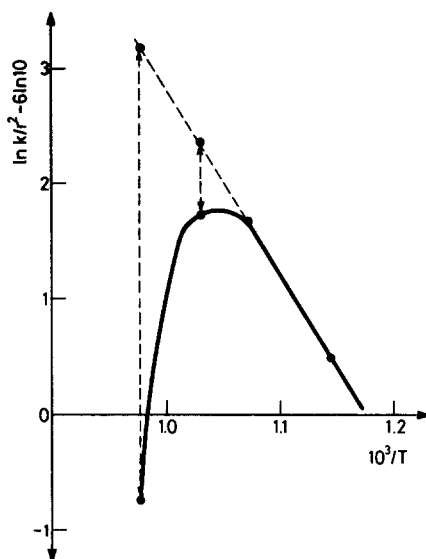


Fig.6 Temperature-dependence of the ratio k/r^2 (Eq. (3))

correspond to the hypothetical case where sintering does not occur). If these values are now divided by the experimentally determined values of k/r^2 , for given temperatures, one can calculate the mean sintered particle diameter by inserting into the ratio the value of r calculated with Eq. (1). The calculated values of the mean diameter of the sintered particles are given in Table 4.

The sharp decrease in the slopes of the straight lines for 800 and 850° in Fig. 2, which obey Eq. (4) over their entire length can be ascribed to the effect of sintering. The slope of the straight line for 850° is lower than that at 800°, which means that the diameter of the particles is higher, and that sintering is occurring.

The change from diffusion rate control to chemical control at 800 and 850° can mean either that the structure of FeS changes and allows easier diffusion, or that the rate of diffusion exceeds the rate of the chemical process.

The experimental results permit study of the diffusion process in the case where it is the rate-controlling process (Fig. 4), and the coefficients of diffusion S_2 vapour through the layer of FeS can also be calculated.

The diffusion coefficients are calculated by means of Eq. (6), developed on the basis of Fick's second law and modified for the case of a sphere [6]:

$$(1 - \alpha) = (6/\pi^2) \sum_{i=1}^{i=n} (1/n^2) \cdot \exp(-n^2 \cdot \pi^2 \cdot D \cdot t/r^2) \quad (6)$$

where: α = degree of diffusion process,
 D = diffusion coefficient,
 r = diameter of a particle, and
 t = time.

If a diffusion process can be represented with only the first term of the

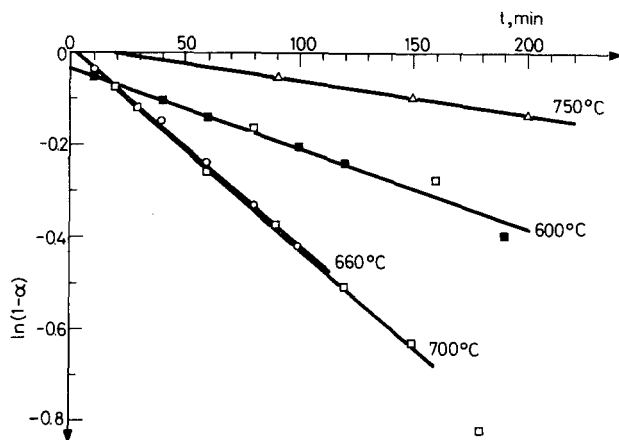


Fig. 7 Representation of the diffusion of S_2 vapour through the layer of FeS according to Eq. (6)

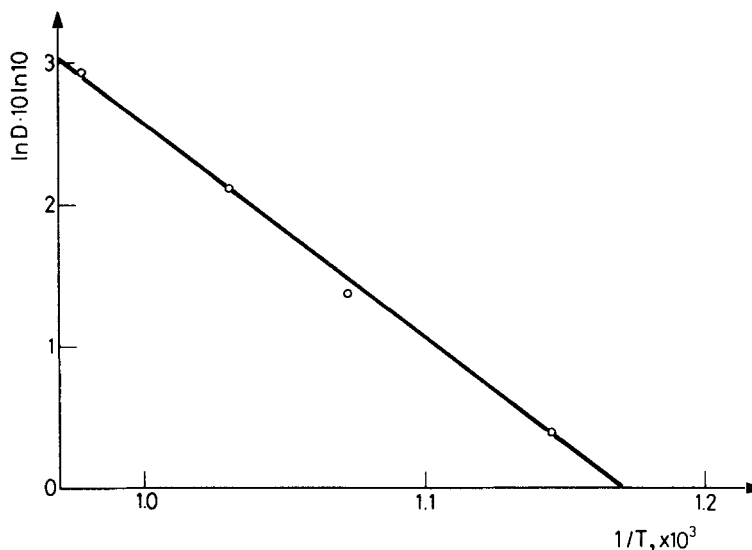


Fig. 8 Temperature-dependence of the coefficients of diffusion, D , of S_2 vapour through the layer of FeS

exponential sequence given by Eq. (6), then the plot $\ln(1 - \alpha)$ vs. time should give a straight line whose slope is $\pi^2 \cdot D/r^2$ (case $n = 1$).

The values of α were calculated from the weight loss vs. time curves (Fig. 1).

In the cases where the diffusion was the rate-controlling process, the total weight loss of the sample was calculated for the time period from the moment of the start of diffusion, taken as $t = 0$, up to the theoretical end of the process. The value of α for a given time t was calculated from the weight loss up to time t divided by the total weight loss.

The plots of $\ln(1 - \alpha)$ vs. t for 600, 660, 700 and 750° are given in Fig. 7.

The diffusion coefficients D can be calculated from these slopes, using for r the values calculated via Eq. (1) for the case of the slopes of the straight lines for 600 and 660°, and the values from Table 4 for 700 and 750°. Calculated values of D are given in Table 4.

The plot of $\ln D$ vs. $1/T$ gives a straight line (Fig. 8), and shows Arrhenius behaviour. This indicates that the diameters of the sintered particles were correctly calculated.

In conclusion, it can be stated that the optimum temperature of the process is 800°, where it is 95% complete in 270 min. The rate is slowed down by diffusion at lower temperatures, and by sintering at higher temperatures, which starts at 660–700° and increases with the elevation of temperature. The sintering of the particles slows down the rates of both diffusion and chemical processes.

References

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Zusammenfassung — Es wurde die thermische Zersetzung von Pyrit in inerte Atmosphäre bestimmt, um detaillierte Informationen über Kinetik und Mechanismus der Reaktion $2\text{FeS}_2 = 2\text{FeS} + \text{S}_2$, einer der Darstellungsreaktionen von elementarem Schwefel zu erlangen. Der Vorgang wurde mittels einer Thermowaage unter isothermen Bedingungen bei Temperaturen von 600, 660, 700, 750, 800 und 850 °C untersucht. Es wurden die geschwindigkeitsbestimmenden Schritte bestimmt und deren kinetische Parameter errechnet. Als Optimumtemperatur für diesen Prozeß erwies sich 800 °C.

Резюме — Термическое разложение пирита в какой-либо инертной атмосфере было изучено с целью детального знания кинетики и механизма реакции $2\text{FeS}_2 = 2\text{FeS} + \text{S}_2$, являющейся одним из методов получения элементарной серы. Процесс был изучен с помощью термовесов в изотермических условиях в атмосфере азота при температурах 600, 660, 700, 750, 800 и 850 °C. Определены скорости определяющих процессов и вычислены их кинетические параметры. Найдено, что оптимальной температурой процесса является 800°.