

THE QUESTION OF THERMAL DECOMPOSITION OF PYRITE

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The thermal decomposition of monomineral pyrite was studied in an inert atmosphere. From an analysis of the values of the thermal effects, an interpretation of the three physicochemical processes recorded in the thermoanalytical curves is proposed.

Both Paulik [1] and Berg [2] stated that three endothermic effects are observed in the thermoanalytical curves of pyrite: at 450–480°, 530–570° and 630–690°, successively increasing in height. The endothermic effect at 630–690° is interpreted as the thermal dissociation of pyrite and the destruction of its crystal lattice. The transformations at 450–480° and 530–570° however, are, interpreted differently by different researchers. Some authors [3] assume that the effect at 530–570° has no connection with the dissociation of pyrite, while data of other authors [4] indicate that pyrite partially dissociates, yielding pyrrhotine. According to Berg and co-workers [2] the endothermic effect at 450–480° is caused by evolved impurities and gaseous or liquid inclusions, and also by defects in the crystal lattice. The thermal process at 530–570° is attributed by these authors to the evolution of oxidized “non-equivalent” sulfur located on the surface of the pyrite. Simultaneously they observed an increase in magnetic susceptibility, due to the appearance of pyrrhotine.

In the present paper thermoanalytical results obtained with monomineral natural pyrite and analysis of the values of the thermal effects are reported.

Experimental

The initial specimen was obtained by selection under a binocular microscope and contained (in mass per cent) 46% iron, 52% sulfur and 2% quartz. The thermoanalytical curves were obtained using a Hungarian MOM derivatograph, at a heating rate of 10°/min, in a stream of dried and purified helium. To purify the helium, it was passed through sulfuric acid, melted calcium chloride (to remove moisture), and subsequently pyrogallol and copper chips heated to 500° (to remove oxygen). The inert gas was introduced into the upper part of the thermoblock of the derivatograph (above the crucibles holding the sample and the reference

standard) and passed into the lower part by its own pressure. The feed rate was about 1.2 l/h. In this arrangement the exothermic effect corresponding to the oxidation of pyrite did not appear. The weighed pyrite samples were placed in all experiments into ceramic crucibles. The mass of the sample was 520 mg in all cases. Ignited alumina was used as reference material.

For thermal effect calculations the apparatus was previously calibrated using standard substances at the corresponding temperatures. The value of the thermal effect (ΔH , cal) was determined using the DTA peak area. The specific thermal effect was defined as the ratio of the thermal effect and mass loss recorded by the instrument in the course of the transformation in question (ΔP , mg) or as the ratio of the thermal effect and surface area (S , cm^2) of the initial pyrite sample. This surface area was calculated from the average size of the particles in the given class, in accordance with the cubic form of pyrite crystals.

Results

In the DTA curve three endothermic effects were recorded, with maxima corresponding to 480, 540 and 670°. The first effect was characterized by unsatisfactory reproducibility with different pyrite samples, by its absence on repeated heating, by the insignificant mass losses (0.8–1.0% of the initial mass) and by small values of the specific thermal effect (0.2 cal/mg mass loss). The second effect was characterized by somewhat higher mass losses (1.8–2.5% of the initial mass) and higher values of the specific thermal effect (Table 1), accompanied by an increase in the magnetic susceptibility of the sample. On repeated heating, after the sample has been heated to 800–830° and cooled in a helium flow in the derivatograph, the effect is reproduced at a higher level, and the specific thermal effect increases to 1.0–1.3 cal/mg mass loss. The absolute value of the thermal effect decreases proportionally to the total surface area of the particles with increasing particle size from <0.05 to 0.2 mm, and mass losses decrease correspondingly. The ratio of heat effect to mass loss for the second thermal

Table 1

Specific thermal and gravimetric characteristics of the endothermic effect at 540°

	Pyrite particle size, mm		
	< 0.05	> 0.063–0.1	> 0.1–0.2
1. Value of thermal effect, ΔH , cal	9.75	6.25	3.81
2. Mass loss, ΔP , mg	15.0	11.0	6.3
3. $\Delta H/\Delta P$, cal/mg	0.65	0.58	0.57
4. $\Delta H/S$, cal/ cm^2	0.0780	0.0813	0.0855
5. $\Delta P/S$, mg/ cm^2	0.12	0.14	0.15

effect remains practically unchanged, while the ratio of heat effect to initial sample surface area S increases substantially. The ratio of mass loss to initial surface area increases to the same extent (Table 1).

Slight oxidation of the pyrite sample (stopping the helium flow and introducing air for 1–2 seconds at 400°) resulted in a small increase of the second endothermic effect.

The third endothermic effect is distinguished by good reproducibility between different pyrite samples [1–4] and is characterized by the decomposition of pyrite in its whole bulk, accompanied by the evolution of elemental sulfur. Specific heat absorption is 0.9–1.1 cal/mg evolved sulfur, this being in agreement with the results of thermodynamic calculations carried out for temperatures of 500–700° taking into account changes in specific thermal effect (Table 2).

Table 2

Specific thermal effects of some chemical reactions at 500–700°

Chemical reaction	$\Delta H/\Delta P$, cal/mg
1. $\text{FeS}_{3s} = \text{FeS}_s + 1/5 \text{S}_{5g}$	1.00
2. $\text{FeSO}_{4s} = \text{FeO}_s + \text{SO}_{2g} + 1/2 \text{O}_{2g}$	0.40
3. $2 \text{FeSO}_{4s} = \text{Fe}_2\text{O}_{3q} + 2\text{SO}_{2g} + 1/2 \text{O}_{2s}$	0.15
4. $3 \text{FeSO}_{4s} = \text{Fe}_3\text{O}_{4s} + 3 \text{SO}_{2g} + \text{O}_{2g}$	0.41
5. $\text{Fe}_2(\text{SO}_4)_{3s} = \text{Fe}_2\text{O}_{3s} + 3 \text{SO}_{2g} + 3/2 \text{O}_{2s}$	0.50

It was observed that the absolute value of the third endothermic effect decreased slightly when the second endothermic effect was increased (by using smaller pyrite particles in the experiment, or by slight oxidation of the sample). For the three size classes (<0.05 to 0.2 mm) presented in Table 1; whose thermal effects at 540° decrease from 9.75 to 3.81, the corresponding values at 670° were found to be 121.0, 131.5 and 142.7 cal. This finding indicates that the decomposition of oxide films on the surface of the pyrite particles at 540° does not control the value of the thermal effect. This is also evidenced by our finding that the second endothermic effect $\left(\frac{\Delta H}{\Delta P} = 0.7 \text{ cal/mg}\right)$ can be recorded with pyrite samples previously washed with hot water. In addition, on the repeated heating of samples previously heated to 800° and cooled in the derivatograph, the third endothermic effect decreases substantially or disappears completely. In the latter case, only the second effect at 540–550°, with a value of 1.0–1.3 cal/mg is recorded.

A comparison of experimental and thermodynamic calculated thermal effects (Table 1 and 2) shows that the specific thermal effect of the decomposition of iron(III) sulfate (Table 2, No. 5) is closest to the experimentally found values of the effect at 540°, for a single heating. Assuming that all the mass loss and the total thermal effect at 540° is due to the decomposition of iron(III) sulfate, then, insofar as the enthalpy of the stepwise dissociation of the compounds, e.g.

$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \rightarrow \text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \rightarrow \text{Fe}_2\text{O}_3 \cdot n\text{SO}_3$, relative to one mole of the gaseous substance is constant [5], the composition of the oxides on the surface of pyrite, according to the reported data, should correspond to compositions ranging from $\text{Fe}_2\text{O}_3 \cdot 2\text{Fe}_2(\text{SO}_4)_3$ to $\text{Fe}_2\text{O}_3 \cdot 1.15\text{Fe}_2(\text{SO}_4)_3$, depending on the particle size of the samples. The presence of such compounds on the surface of the initial pyrite should change the ratio of sulfur to iron in the initial mineral from 1.14 to 1.10–1.11, while the actual ratio in the studied specimens was 1.13. What appears most probable is the assumption that not only is the oxide film decomposed at 540° , but partial dissociation of pyrite also takes place; there is removal of “non-equivalent” disulfide sulfur on the surface of the pyrite, the existence of which has been assumed by Berg [2]. By comparing the specific thermal effect $\Delta H/\Delta P$ of the second endothermic effect for pyrite samples in their initial state and for samples washed with hot water, one can calculate the mass of the oxide film and its thickness, since it assumes the cubic shape of the particles. The values for the three size classes in Table 1 are (in order of decreasing particle size): 3.2, 3.9 and $4.1 \cdot 10^{-5}$ cm, i.e. the thickness of the oxide film remains practically unchanged.

On the basis of our experimental data, one may conclude that the first endothermic effect in the thermoanalytical curves of pyrite in an inert gas stream at atmospheric pressure appears to be connected with the elimination of gaseous-liquid inclusions.

The second effect at 540° is related to the decomposition process of the iron oxide sulfate film on the surface of the mineral (according to literature data the decomposition starts at 480°) and subsequent dissociation of pyrite, involving the removal of disulfide sulfur on its surface and formation of pyrrhotine on the freshly-formed surface. The specific thermal effect of the removal of disulfide surface sulfur is 0.7 cal/mg or 22.4 kcal/gram-atom sulfur.

The third effect consists of the dissociation of pyrite in its total bulk, yielding pyrrhotine and subsequently also troilite. Apparently pyrrhotine crystals also have a surface sulfur layer, on account of which, on repeated heating of the sample, pyrrhotine is decomposed into troilite at $540-550^\circ$, the specific thermal effect of this transformation being 1.0–1.3 cal/mg or 32–42 kcal/gram-atom sulfur.

References

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RÉSUMÉ — On a étudié la décomposition thermique de la pyrite, en atmosphère inerte. On propose une interprétation des trois processus physicochimiques enregistrés sur les courbes thermoanalytiques, qui repose sur l'analyse des effets thermiques.

ZUSAMMENFASSUNG — Die thermische Zersetzung von monomineralem Pyrit wurde in inerte Atmosphäre untersucht. An Hand der Analyse der Werte der thermischen Effekte wird eine Beschreibung dreier, in den thermoanalytischen Kurven festgehaltener physikalisch-chemischer Vorgänge vorgeschlagen.

Резюме — При исследовании термического разложения мономинерального пирита в инертной атмосфере с анализом величин тепловых эффектов предложена интерпретация трех физико-химических процессов, зафиксированных на термограмме.