CHARACTERISTIC FEATURES OF SULPHIDE MINERAL DTA

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Differential thermal analysis and simultaneous electrical conductivity and evolved gas detection measurements were used to determine temperature intervals and in a number of cases the nature of the recorded transformations of 21 sulphides. For example, along with the thermal dissociation of covellite interaction with copper sulphide impurity is also found. The result of polymorphic pentlandite transformation (610—620°) is vaesite; in the incongruent melting of tennantite (710—735°), lautite and sulphur are formed. Dissociation of sulpharsenides is as follows: cobaltite (885—905°) yields cattierite and sulphur; gersdorffite (800—860°) yields niccolite and pentlandite; and arsenopyrite (670—740°) yields loellingite. Endothermic transformation of pyrite (550—580°) results in destruction of its superficial oxidized film. A thermal change typical for each type of iron monosulphide has been established. A method for the quantitative estimation of sulphides is based upon measurement of the gas evolved during interaction of the sulphide with solid oxidants.

Two lines of approach have been followed in studies on the thermal behaviour of sulphides. Some researchers investigated the processes taking place when the specimens were heated in air [1 — 6], while others worked in inert atmospheres [7 — 10]. In the first case the processes studied involve oxidation of the sulphides in air, and the subsequent dissociation of the products formed. On the other hand, studies of the thermal behaviour of sulphides under conditions excluding their oxidation allow investigation of transformations that are free from the superposition of additional processes.

Several authors, e.g. [4, 7, 8], point out the feasibility of utilizing DTA results for the identification of sulphide minerals. However, data in the literature on the temperature ranges of sulphide oxidation in air are largely inconsistent, and demonstrate the poor reproducibility of the DTA results. This latter finding might be explained by the large number of not readily stabilizable factors that have an effect on the thermal analytical characteristics when sulphides are heated in oxidizing atmospheres. Hence, it appears difficult to solve the problem of thermoanalytical identification in this way. It is obvious that satisfactory reproducibility of thermal analytical data is a basic condition for their successful utilization in the identification of minerals. From this aspect, information on the thermal behaviour of sulphides in inert media appears more useful (in addition, such information is also very interesting from a theoretical viewpoint).

From what has been said, it appears useful to study the characteristic features of the thermal behaviour of some sulphide minerals, with the aim of finding means of obtaining satisfactorily reliable thermal analytical data.

Experimental

The materials studied were sulphides of iron, tin, zinc, copper and other metals, and some sulphides of arsenic, antimony and bismuth, closely associated with the former in many ores, as well as certain polysulphides and sulpho salts.

The basic method used in the present work was complex DTA–evolved gas-detection method with simultaneous recording of the electric conductivity. DTA curves were recorded using a low-frequency NTR-62M recorder that yields temperature difference *versus* time plots.

Serious problems in the execution of differential thermal analysis consist in the necessity to shield the sulphides from the oxidizing action of air, and to protect the material of the thermocouple from the aggressive action of the products formed in the decomposition of the sulphides. We used quartz reaction tubes with capsular cavities at the bottom to hold the junctions of the thermocouples which were introduced from below. Many observations demonstrated that in most cases it is unnecessary to provide an inert gas atmosphere to shield the sulphides from the oxidizing action of air. To achieve conditions preventing oxidation of the sulphides, the specimens were heated in long narrow quartz test tubes (inner diam. 5 mm, length 220 mm). A layer of alumina was spread on top of the specimen, and a tightly-fitting porcelain mandrel was introduced into the test tube. The DTA curves obtained in this manner did not indicate even the slightest exothermic effect that could have evidenced partial oxidation of the specimens. Analysis of the reaction products for sulphate ion demonstrated its absence too.

To study the thermal behaviour of sulphides in an oxygen stream, oxygen was introduced by means of a narrow porcelain tube that extended to the bottom of the reaction vessel. The flow rate of oxygen was controlled by a rheometer, and was about 2 litres per hour.

Good reproducibility of the differential recording was achieved by using the following techniques to ensure uniform heat transfer:

(i) Air was used as reference standard. Thereby, the strictly centered position of the thermocouple junction became unnecessary.

(ii) There was no contact between the wall of the test tube and the block. In order to achieve more uniform heat flow to the specimen and to the reference standard to prevent local overheating and to eliminate the effect of air convection currents in the tubular oven on the recorded data, a special massive block made of heat-resistant steel was used. The penetration depth of the test tubes containing the specimen and the reference standard was controlled by ring-shaped springs made of chromium-nickel alloy wire. To ensure high reproducibility of recording, the test tubes were centered at a constant depth in the openings in the block by means of bushings.

(iii) Instead of the usual platinum-platinorhodium thermocouple, a chromel-alumel thermocouple was used, allowing substantial increase of the sensitivity of the differential recording.

For the recording of DTA and conductivity curves, the weight of the specimens was around $0.3-0.5$ g. For the recording of gas evolution by means of the automated gas burette (L. G. Berg system), larger specimens of $0.5-1$ g were usually taken. The grain size of the specimens was of the order of 0.05 mm. The rate of heating was $10°/$min. Heating was continued up to $950-1050°$.

Results and discussions

To decide the question as to whether it is possible to obtain thermoanalytical characteristics of sulphides sufficiently reproducible to be suitable for identification purposes when heating is carried out in an oxidizing atmosphere, we studied the behaviour of the above-listed minerals in the course of heating.

When sulphide minerals were heated in air, substantial variations were observed in the temperature at which oxidation started, together with large deviations in the temperature ranges in which the oxidation process was recorded. When the sulphides were heated in oxygen, the temperature ranges and the shapes and areas of the thermal effects were found to depend largely on the flow rate of the oxygen, on the grain size of the sulphide and on the mass of the specimen. Thus, reproducible results were difficult to obtain. For these reasons we shall deal in the present work mainly with the behaviour of sulphides heated under conditions that exclude their oxidation.

A study was made of the thermal behaviour of 92 substances, both pure synthetic sulphides and natural minerals of various origins. Thermal analytical data of 21 mineral sulphides, sulphosalts and related compounds (with the exception of thermally inert minerals) are shown in Fig. 1. By studying the thermal behaviour of these minerals in inert media, and identifying the solid phases by means of complex DTA, X-ray, chemical, visual-optical and thermomagnetic analysis, we were able to determine the temperature ranges more accurately, and also, in a number of cases, to give a more correct picture of, or to propose a new scheme for the phase transformations of the minerals studied. In the following, the thermal behaviour will be discussed in detail only as regards those minerals whose investigation resulted in essentially new recognitions of particular interest.

The transition temperature of chalcocite (Cu_2S) into digenite ($Cu_{1.8}S$) is not strictly constant, but varies within the range $315-425°$ for specimens of different origins.

On the basis of data from the literature [7, 8, 11 − 14], one would expect that the DTA curve of copper (II) sulphide (covellite, CuS) would indicate only its dissociation ($2CuS \rightarrow Cu_2S + 0.5S_2$) at a temperature around $500°$. However, DTA curves of both natural and synthetic CuS specimens recorded in purified nitrogen are much more complex. The chemical analysis of all specimens studied demonstrated

the presence of small amounts (up to 4.3%) of copper sulphate. It should be pointed out that, in general, copper(II) sulphide is characterized by the presence of sulphate impurities which are readily formed during storage or grinding, because CuS is one of the most easily oxidizable sulphides, particularly in humid air. For this reason, in addition to the endothermic dissociation effect ($470-500°$), the DTA and gas evolution curves of the natural and synthetic specimens indicate
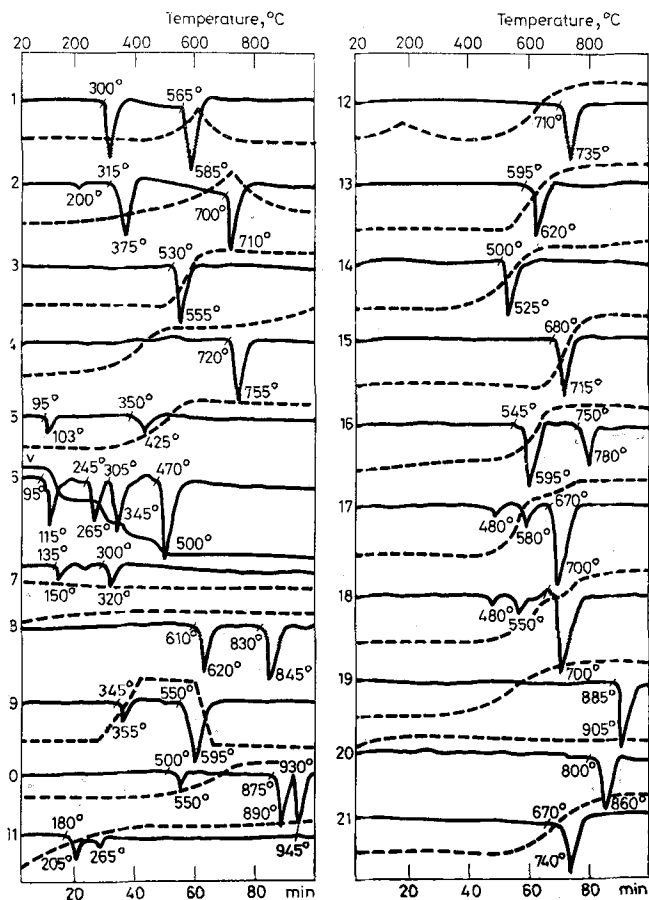

Fig. 1. DTA curves (solid line), electric conductivity (dotted line) and gas evolution (V) of sulphide minerals in inert atmosphere. 1 — As_4S_4 (realgar); 2 — As_2S_3 (orpiment); 3 — Sb_2S_3 (antimonite); 4 — Bi_2S_3 (bismuthite); 5 — Cu_2S (chalcocite); 6 — CuS (covellite); 7 — $Fe_{1-x}S$ (pyrrhotite); 8 — $(Ni,Fe)_9S_8$ (pentlandite); 9 — HgS (cinnabar); 10 — $CuFeS_2$ (chalcopyrite); 11 — Cu_5FeS_4 (bornite); 12 — $Cu_{12}As_4S_{13}$ (tennantite); 13 — $Pb_5Sb_4S_{11}$ (boulangerite); 14 — $CuPbSbS_3$ (bournonite); 15 — $Pb_3Sn_4Sb_2S_{14}$ (cylindrite); 16 — $Pb_5Sn_3Sb_2S_{14}$ (frankeite); 17 — FeS_2 (pyrite); 18 — FeS_2 (marcasite); 19 — (Co,Fe)AsS)cobaltite); 20 — (Ni,Fe)AsS (gersdorffite); 21 — FeAsS (arsenopyrite)

effects pertaining to the removal of water vapour (95−115° and 245−265 °C) and of sulphur dioxide (305−345 °). With specimens freed from sulphate impurities, DTA curves were obtained which were in agreement with the data for pure CuS in the literature. These curves did not indicate the endothermic effects representing the stepwise dehydration of the sulphate ($CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O \rightarrow CuSO_4$) or its interaction with the sulphide ($7 \, CuS + 2 \, CuSO_4 \rightarrow 5 \, Cu_{1.8}S + 4 \, SO_2$). However, a weak exothermic effect persists. It does not disappear, nor change its size, even when the specimen is heated in nitrogen purified from oxygen and moisture traces. It appears probable that the small percentage of copper oxide present in these specimens (copper cations could be detected in the ammonia extract) leads to a partial oxidation of the sulphide. X-ray analysis of specimens not freed from sulphate impurities indicated the formation of a solid solution of β-Cu_2S in undecomposed CuS, in a proportion of about 1 : 1. Hence the DTA curve of covellite reflects not only the thermal dissociation of the sulphide, but also a number of other transformations resulting from the presence of low-percentage impurities characteristic of the mineral, so that the DTA curve may be well used for the thermoanalytical characterization of the mineral.

Data in the literature on the DTA curves of iron monosulphides ($Fe_{1-x}S$) do not reflect the peculiarities in the thermal behaviour of various monosulphide types [7, 8, 15]. Thermal analytical characteristics obtained in our work allowed the detection of the following specific features for each monosulphide type:

(i) α-Transformation (transition into the rhombic modification at $\sim 149°$) was observed only in the DTA curves of stoichiometric FeS and hexagonal pyrrhotites, but was absent with monoclinic types.

(ii) γ-Transformation involving an increase in magnetic susceptibility (around 200−240°) was recorded only with monoclinic pyrrhotites and specimens of the intermediate type.

(iii) β-Transformation involving a decrease in magnetic susceptibility (around 300°) is distinctly observable with all types of iron monosulphides.

On the DTA curve of pentlandite [$(Ni,Fe)_9S_8$] two endothermic effects (at 610−620° and 830−845°) were recorded; these were found to be reversible when the specimen was cooled. The first transformation corresponds to transition into a more stable modification, viz. a phase close to cubic vaesite [$(Ni,Fe)S_2$]. This phase (whose melting is represented by the second effect) is a solid solution of pentlandite and vaesite.

Incongruent melting of tennantine ($Cu_{12}As_4S_{13}$) at 710−735° yields lautite (CuAsS) and sulphur.

For cubic iron disulphide (pyrite, FeS_2) some researchers report the presence of one endothermic effect, i.e. dissociation [7, 8, 16−19], while others observed two [20, 21] or three [6, 9] endothermic effects, successively increasing in size. Some authors refer to the pulsating nature of the dissociation, while others contest a relation of the first two transformations with any change in the lattice of the mineral. Our own results of complex DTA for six pyrite specimens indicated the pres-

ence of endothermic transformations in the temperature ranges 455−480°, 550−580° and 670−700°. The first two transformations, accompanied by an increase in both conductivity and gas phase volume above the sample, were clearly discernible with all investigated pyrites, and appear again when a specimen first heated up to 640° is repeatedly heated. The first transformation (which disappears after many heating cycles and whose temperature range is not strictly constant in the case of specimens of different origins) might be caused by the removal of impurities, by defects of the crystal lattice, or by the removal of gaseous or liquid inclusions. The second transformation, which is accompanied by a larger effect and by a larger loss in weight, is much more stable: the effect is retained almost unchanged after a great number of heating cycles up to 600−620° and continued heating under isothermal conditions. Further, additional grinding leads to a sharp increase of the effect. Simultaneously, an increase in magnetic susceptibility is observed, as a result of increasing amounts of magnetic pyrrhotite being formed. Substantial differences in the amounts of impurities, e.g. arsenic, do not affect the thermal effect. However, reduced pressure in the system causes a shift of the effect towards lower temperatures, and when pyrite is being heated mixed with sulphur, or the powder is washed with hot water, the transformation at 550−580° almost completely disappears. None the less, the mechanisms of the processes causing the endothermic effects at 550–580° and 670−700° are probably essentially different. While the size of the high-temperature effect is practically independent of grain size, the latter plays a decisive role in the lower-temperature effect, indicating that a relationship exists between this transformation and the specific surface area of the system being heated. While in the high-temperature effect the decomposition of pyrite proceeds in the total bulk of the crystal, the lower-temperature transformation is a non-equilibrium process taking place on the surface of the particles. This concept is also supported by the highly-dispersed state of the pyrrhotite formed (Debye diagrams of pyrite reveal a characteristic granular structure, which is absent from the lines of pyrrhotite). The mechanism of this transformation may be explained as follows. Pyrite, in contrast to the overwhelming majority of sulphides, has a molecular structure, i.e. it contains, as structural elements, $(S_2)^{2-}$ dumbbells disposed at the edges of the cubic cell of pyrite and extending in the directions of its solid diagonals. While both parts of the dumb-bells are energetically equivalent in the interior of the crystal, their equivalence is not retained on the surface of the particles. As a result, the energy required to disrupt the dumb-bells will be lower at the surface of the particles. This "non-equivalent" sulphur will be oxidized in the grinding operation in air, and will form an oxidized film on the surface. This process corresponds to the effect at 550−580°. The presence of free sulphur or washing with hot water (0.67% sulphur was found in the filtrate) destroys this film, while prolonged grinding enhances the formation of "non-equivalent" sulphur, which will subsequently be removed during heating.

With rhombic iron disulphide (marcasite, FeS_2), in addition to the thermal transformations described, a weak polymorphous transition into pyrite takes place which is not always determinable in the DTA curve. It was recorded with only

two specimens (at $560-576°$ and at $595-600°$), and can therefore not be utilized for a reliable identification of rhombic iron disulphide when this mineral is associated with pyrite in commensurable amounts.

Our results demonstrated that the decomposition products of sulphoarsenides, in addition to arsenic sulphides, metallic arsenic and pyrrhotite, include
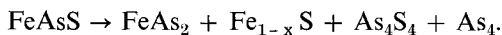
(a) in the case of cobaltite ($885-905$ °C), cattierite (CoS_2) and sulphur:

$$(Co, Fe)AsS \rightarrow CoS_2 + Fe_{1-x}S + As_4S_4 + As_4 + S_2$$
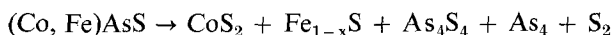
(b) in the case of gersdorffite ($800-860°$), niccolite ($NiAs$) and pentlandite:

$$(Ni, Fe)AsS \rightarrow NiAs + (Ni, Fe)_9S_8 + Fe_{1-x}S + As_4S_4 + As_4$$
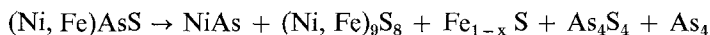
(c) in the case of arsenopyrite ($670-740°$), a phase close to lœllingite ($FeAs_2$):

$$FeAsS \rightarrow FeAs_2 + Fe_{1-x}S + As_4S_4 + As_4.$$

The good reproducibility of the DTA results and the specific nature of the thermal transformations allow one to obtain sufficiently reliable thermoanalytical characteristics for the majority of sulphides and sulphide minerals, independently of the genesis of their occurrence. However, the thermal inertness of a number of sulphides, e.g. ZnS, PbS, MoS_2 etc., particular conditions rendering separation of the sulphides from the embedding rock extremely difficult, and the presence of thermally-active impurities limit the potentials of DTA considerably, if this method is restricted to the study of sulphides in inert media only.

Searching for a procedure for the thermoanalytical determination of sulphides exempt from the above-listed defects, we succeeded in developing a method termed "solid oxidizing additive method" (author's Certificate No. 280978, dated June 23, 1970). The addition of a solid oxidizing agent to the sulphide results in the appearance, in the DTA curve, of an exothermic oxidation effect characteristic for the sulphide. Moreover, oxidation starts at a strictly defined temperature for each sulphide and sulphide mineral and for a given oxidizing agent (in contrast to gaseous oxidizers). This finding allows one to utilize the temperature at which oxidation starts as a characteristic for thermoanalytical identification. The major advantage of this method consists in the possibility of accurate dosage of the oxidizing agent, and of the reliable homogeneity of its distribution within the specimen.

It was found that the most suitable criterion for identifying sulphide minerals by the solid oxidizing additive method is the temperature at which the exothermic effect of the oxidation begins. We studied the dependence of this characteristic on the grain size of the mineral and determined the optimum grain size range ($0.20-0.16$ mm). The starting temperature of oxidation varies for different sulphides and may serve as a means for the qualitative identification of a given sulphide in the specimen. The starting temperature also depends on the type of the solid oxidizing agent. In Table 1, values of the starting temperatures of oxidation are listed for a number of sulphide minerals and several oxidizing agents (CuO,

V_2O_5, MnO_2). Greatest differences between temperatures were found with CuO, which from this point of view, therefore, appears to be the most suitable oxidizing agent.

If the data in Table 1 are utilized it is possible to determine which sulphide is contained in the specimen to be analyzed. For this purpose, the DTA curve of a mixture of the specimen with copper oxide is taken, and (using the Table) the

Table 1

Starting temperature of sulphide mineral oxidation by solid oxidizing agents

No.	Chemical formula	Name of mineral	Starting temperature of oxidation, °C		
			CuO	MnO_2	V_2O_5
1	As_2S_3	Orpiment	200	145	390
2	CuS	Covellite	250	240	280
3	$Pb_5Sb_4S_{11}$	Boulangerite	300	280	430
4	$Pb_5Sn_3Sb_2S_{14}$	Frankeite	310	270	400
5	Sb_2S_3	Antimonite	335	150	380
6	$CuFeS_2$	Chalcopyrite	350	270	450
7	HgS	Cinnabar	350	290	400
8	FeS_2	Pyrite	380	135	450
9	MoS_2	Molybdenite	400	160	510
10	$Cu_{12}As_4S_{13}$	Tennantite	400	250	520
11	Cu_5FeS_4	Bornite	410	280	480
12	FeS	Troilite	420	420	450
13	$Fe_{1-x}S$	Pyrrhotite	420	430	450
14	$(Ni, Fe)_9S_8$	Pentlandite	420	420	480
15	FeS_2	Marcasite	420	400	470
16	FeAsS	Arsenopyrite	430	320	420
17	Cu_2S	Chalcocite	430	280	300
18	PbS	Galenite	500	275	530
19	ZnS	Sphalerite	570	390	500
20	(Co, Fe)AsS	Cobaltite	670	570	650

sulphide to which the recorded temperature corresponds is found. If the recorded temperature at which oxidation starts could correspond to several sulphides, another DTA curve of a mixture with another oxidizing agent will allow selection of the mineral in question among those found previously.

When several sulphides are found to be present in the specimen, thermoanalytical diagnosis will, of course, be more complex, and will require special measures. The study of the thermal behaviour of some paragenetic associations of sulphide minerals frequently found in nature revealed that (even in the absence of oxidation) it is by no means always feasible to utilize the main advantage of DTA, viz. that the mineralogical composition of the specimen can be determined without the necessity of separating the individual phases.

The method of thermal analysis using solid oxidizing agents widens the potentials not only of qualitative, but also of quantitative characterization of specimens containing sulphide compounds. Quantitative determinations can be based on the heat of reaction of the oxidation process, or on the volume of gas evolved and the weight loss. The presence of embedding-rock impurities in the specimen does not, in general, interfere with the determination of the minerals by the proposed method.

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Résumé — Vingt et un sulfures ont été étudiés par ATD ainsi qu'à l'aide de mesures simultanées de conductivité électrique et de détection des gaz émis pour définir les intervalles de température des transformations enregistrées et, dans un certain nombre de cas, la nature de celles-ci. On a trouvé par exemple que la dissociation thermique de la covellite s'accompagnait d'une interaction avec le sulfure de cuivre comme impureté. La transformation polymorphique de la pentlandite (610—620°) fournit de la vaesite; la fusion incongruente de la tennantite (710—735°) conduit à la formation de lautite et de soufre. La dissociation des sulfoarséniures donne les résultats suivants: pour la cobaltite (885—905°) — cattiérite et soufre, pour la gersdorffite (800—860°) — niccolite et pentlandite, pour l'arsénopyrite (670—740°) — loellingite. La transformation endothermique de la pyrite (550—580°) est le résultat de la destruction de sa couche superficielle oxydée. On a établi la succession des effets thermiques typiques pour chaque type de monosulfure de fer. Une méthode pour l'estimation quantitative des sulfures repose sur la mesure des gaz émis lors de l'interaction du sulfure des oxydants solides.

ZUSAMMENFASSUNG — Differentialthermoanalyse kombiniert mit elektrischen Leitfähig-keits- und Gasentwicklungsmessungen wurde zur Bestimmung der Temperaturintervalle und in einigen Fällen zur Erfassung der Art der Umwandlungen von 21 Sulfiden eingesetzt. Z. B. wird die thermische Dissoziation von Covellite von einer Reaktion mit Kupfersulfid-Verun-reinigungen begleitet. Die Umwandlung von polymorphem Pentlandit ergibt Vaesit (610— 620°); bei inkongruentem Schmelzen von Tennantit (710—735°) entstehen Lautit und Schwe-fel. Die Dissoziation der Sulfarsenide verläuft wie folgt: für Cobaltit (885—905°) — Cattierit und Schwefel, für Gersdorffit (800—860°) — Nikkolit und Pentlandit, für Arsenopyrit (670—740°) — Loellingit. Die endotherme Umwandlung des Pyrits (550—580°) führt zur Zerstörung seiner oxidierten Oberflächenschicht. Eine thermische Reihenfolge, typisch für die einzelnen Eisenmonosulfide, wurde beobachtet. Eine Methode zur quantitativen Ab-schätzung der Sulfide beruht auf der Messung des bei der Reaktion von Sulfiden und festen Oxidantien entwickelten Gases.

Резюме — Использование методов комплексного ДТА позволило уточнить температурные интервалы и в ряде случаев природу термических превращений 21 сульфида. Так, для ко-веллина зарегистрировано наряду с термической диссоциацией взаимодействие его с продуктом дегидратации обязательной примеси — сульфатом меди. Полиморфное превращение пентландита (610—620°) ведет к образованию ваэсита; при инконгруент-ном плавлении теннантита (710—735°) образуются лаутит и сера. Продуктами разложения сульфоарсенидов наряду с сульфидами мышьяка, металлическим мышьяком и пирротином являются следующие: для кобальтина (885—905°) — каттиерит и сера, для герсдорфита (800—860°) — никелин и пентландит, для арсенопирита (670—740°) — леллингит. Эндо-термическое превращение пирита (550—580°) объясняется разрушением его поверхност-ной окисленной пленки. Установлены термические превращения, характерные для каждого типа моносульфида железа. Количественный анализ сульфидов основан на измерении количества газовой фазы при взаимодействии сульфидов с твердыми окислителями.