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# CHARACTERISTICS OF THE OXIDATION PRODUCTS OF SPHERICAL SAMPLES OF LEAD SULPHIDE IN THE TEMPERATURE RANGE 773—1023 K

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## ABSTRACT

The products obtained from the oxidation of spherical galena and spectroscopically pure (s.p.) PbS samples in air have been studied using a thermogravimetric method. The thermal effects occurring in the course of non-isothermal heating have been identified, and a balance of sulphur oxidized to the gaseous state ($SO_2$ and $SO_3$) and sulphur present in the lead sulphates formed has been drawn. The distribution of individual phases across a sample cross-section, the growth rate of the layer of galena oxidation products during the process and their structure have been determined. It was found that the lead sulphide formed is non-stoichiometric and the type of damage changes in the course of the oxidation process.

## INTRODUCTION

The oxidation of metal sulphides is a heterogeneous process, where such factors as the crystallo-chemical characteristic of sulphides and their oxidation products, the conditions of oxygen chemisorption on the sulphide surface, the possibility of oxygen diffusion towards the reaction surface through the product layer, the chemical affinity of oxygen to metal and sulphur, as well as the eventual existence of defined phases in the Me—S—O system are most essential [1].

According to Margulis [2] oxygen chemisorption results in the formation of MeSO or $MeSO_2$-type sorptive unstable complex compounds. If the latter are sufficiently stable and manage to attach complementary atoms of oxygen before dissociation, they are converted into new complexes of $MeSO_3$ and $MeSO_4$ type. With the enrichment of these complexes with oxygen, the sulphur valence increases from —2 to +6, whereas its ionic radius reduces from 1.82 to 0.29 Å. Consequently, this process facilitates oxygen penetration and thus induces the rebuilding of the crystalline lattice and the generation of a new phase nucleus, namely metal sulphate. On the other hand, metal oxide as the original oxidation product forms in the case when metastable complexes would dissociate at some intermediate step of oxygen chemisorption before having time to transform into sulphate.

The proper oxidation reaction proceeds at the MeS—$MeSO_4$ or MeS—MeO interface, which shifts towards the inner sulphide zone with the growth of the product layer; its determination, however, is not always possible [3].

In the course of the lead sulphide oxidation process, $PbSO_4$ forms as the primary product. According to adsorption—dissociation theory, oxysulphide $PbO \cdot SO_2$ dissociates at a temperature above 873 K [4] along with the formation of basic lead sulphates and the SO molecule desorbed from the reaction surface, which is immediately oxidized to $SO_2$.

The authors of refs. 5 and 6 observed $PbSO_4$ formation in a $N_2$—$O_2$—$SO_2$—$SO_3$ gas mixture and stated that the overall reaction is controlled by the diffusion of $Pb^{2+}$ ions through the sulphate layer. On the other hand, basic lead sulphates form when the sulphur nucleus bursts the superficial layer under the action of increasing pressure [7].

Information about the PbO—$PbSO_4$ equilibrium system was provided by Billhardt's studies [8]. His results allow X-ray identification of basic lead sulphates, as well as the determination of their crystalline parameters and IR absorption spectra. Kellogg and Basu [9] thoroughly investigated the thermodynamic properties of the Pb—S—O system between 800 and 1100 K. They identified and investigated nine equilibria and plotted a phase diagram, according to which the dissociation of basic lead sulphates requires extremely low $SO_2$ pressures unattainable under roasting conditions.

## EXPERIMENTAL

### *Description of the methods adopted and the measurement system*

Investigations of the lead sulphide oxidation process have been carried out following the thermogravimetric method with parallel control of the amounts of $SO_2$ and $SO_3$ educed. Galena and s.p. PbS were used in the studies, their thermal effects in the course of non-isothermal heating being determined by means of a Mettler thermoanalyzer (Fig. 1). X-ray phase analysis separately traced the occurrence of PbS, ZnS, $PbCO_3$ and $CaCO_3 \cdot MgCO_3$ in galena.

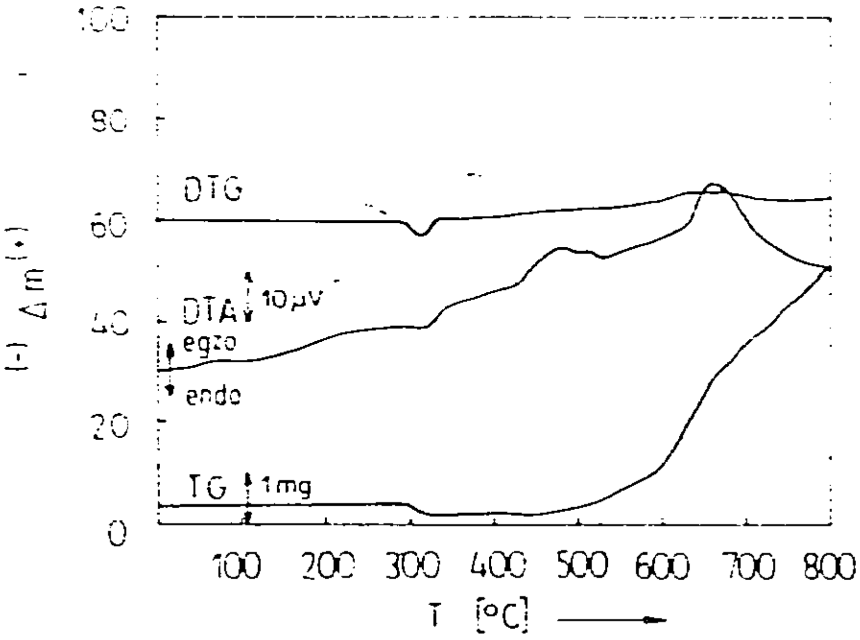

Fig. 1. TG, DTG and DTA curves of galena oxidation in a Mettler thermoanalyser. Heating rate 4°C $min^{-1}$.

The method adopted covered measurements allowing the determination of product type and quantity as well as the rate process. The measurement unit [10] consisted of four elements (Fig. 2): I, the thermobalance system; II, the system for reactions gas analysis; III, the furnace heating system with temperature control and recording; and IV, the air conditioning system.

The $SO_2$ concentration in waste gases was determined by means of a Junkalor's Infralyt 4 IR absorption analyser. Just after the $SO_2$ concentration dropped below apparatus accuracy (10 p.p.m.), filtration with iodine was adopted, a series of washers (18) being used for the purpose. The values obtained on the analyser were recorded automatically by the recorder (20) at a 0.4 sec frequency designed for analog-to-digital conversion, the obtained digital data being coded on a paper tape after the Consul code. Electronic data processing and organization block (22) transferred successive digital data at a preset rate from the voltmeter (21) to the input of the tape perforator (23). The values coded on the tapes were subjected to processing in a computer. At the same time, the $SO_3$ content in the deposit precipitated from $BaSO_4$ in the washer (16) was determined at defined time intervals. Spherical samples of $\phi$ 10 mm and $g = 3000$ mg were prepared. The experimentally determined air flow intensity did not affect the rate of the process.

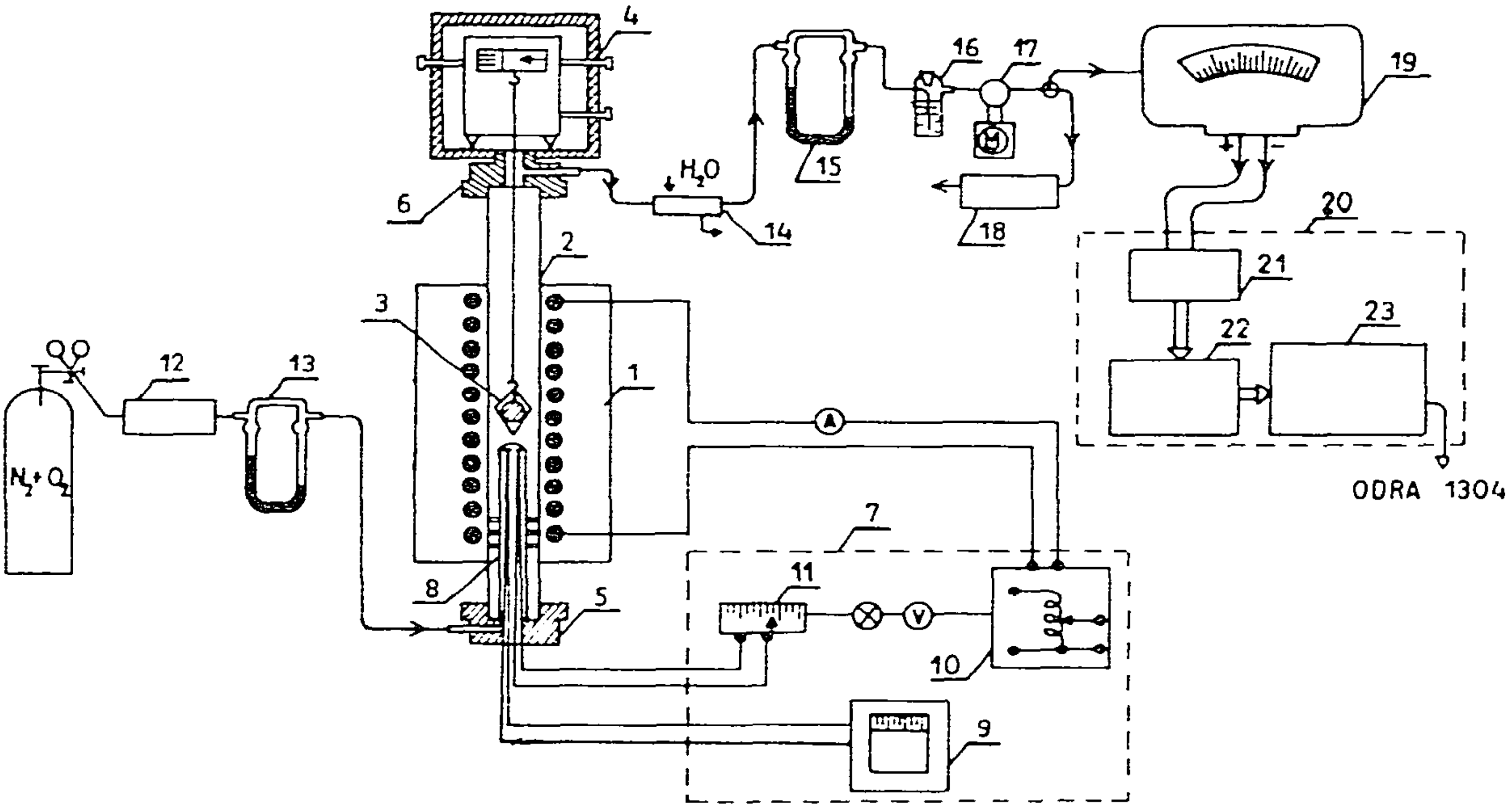

Fig. 2. The measurement system. 1, kanthal resistance furnace; 2, reaction tube; 3, PbS sample; 4, torsion balance with casing; 5, bottom seal with gas entry; 6, upper seal with gas exit; 7, furnace heating system; 8, Pt/Rh—Pt thermocouple; 9, electronic compensator; 10, autotransformer; 11, Galwa temperature controller; 12, air conditioning unit; 13, 15, flow meters; 14, cooler; 16, $BaCl_2$ wash solution; 17, pump; 18, set of iodine wash solutions; 19, Infralyt 4 gas analyser; 20, $SO_2$ concentration recorder; 21, digital voltmeter; 22, electronic data processing block; 23, tape perforator.

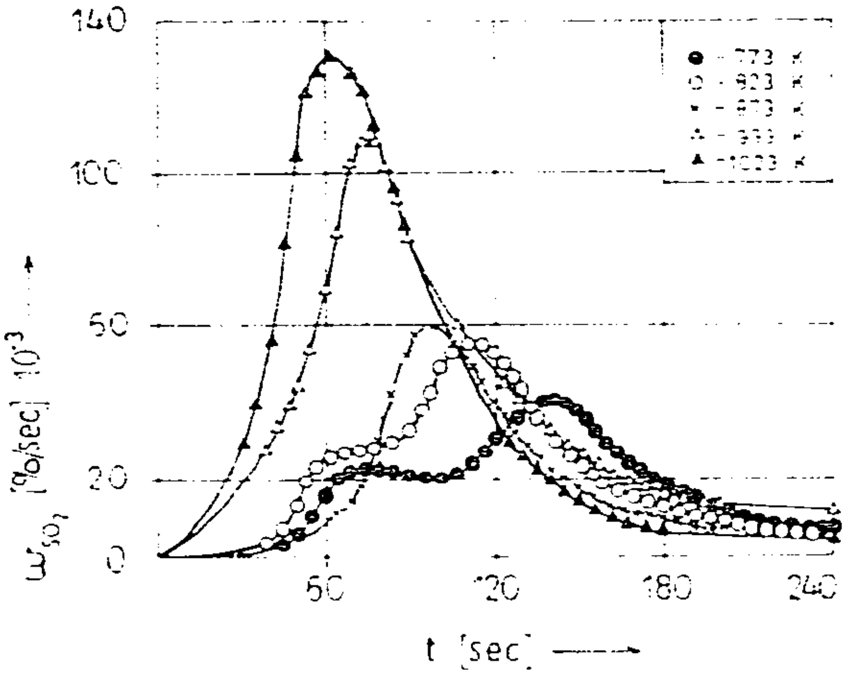

Fig. 3. Rate of $SO_2$ eduction at the initial period of galena oxidation.

## *Test results and their analysis*

With the purpose of computing every single measurement error, the results were subjected to statistical analysis [11] (assumed 0.05 significance level) and standard deviations were plotted on the graphs. The computed values of $SO_2$ evolution rate ($\omega_{SO_2}$) at the initial period of galena oxidation are plotted in Fig. 3. A rate increase at higher temperatures and a simultaneous time reduction occurring at maximum values, followed by an abrupt hampering of the process by the product layer in formation have been noticed.

The oxidation products determined, arranged in the order of the intensity of their occurrence in the samples are listed in Table 1.

With temperature rise of the process, basic lead sulphates with an increasing $PbO/PbSO_4$ mole ratio were formed. In the oxidation products, the α-2 $PbO \cdot PbSO_4$ form was identified, the intensity of its lines slightly diverging from those of the β form [8].

On the basis of the amounts of sulphur oxidized to the gaseous state and determined analytically in the lead sulphates formed, balances have been drawn relevant to sulphur content in the samples analysed [12]. The results are plotted by way of example in Fig. 4. Direct proportionality has been sug-

TABLE 1

X-Ray phase analysis of the oxidation products of galena and s.p. PbS

| *T* (K) | Oxidation products |
|---|---|
| 773 | $PbSO_4$ |
| 823 | $PbSO_4$, $PbO \cdot PbSO_4$ |
| 873 | $PbSO_4$, $PbO \cdot PbSO_4$, α-2 $PbO \cdot PbSO_4$ |
| 933 | $PbO \cdot PbSO_4$, α-2 $PbO \cdot PbSO_4$ |
| 1023 | $4PbO \cdot PbSO_4$, α-2 $PbO \cdot PbSO_4$, $PbO \cdot PbSO_4$ |

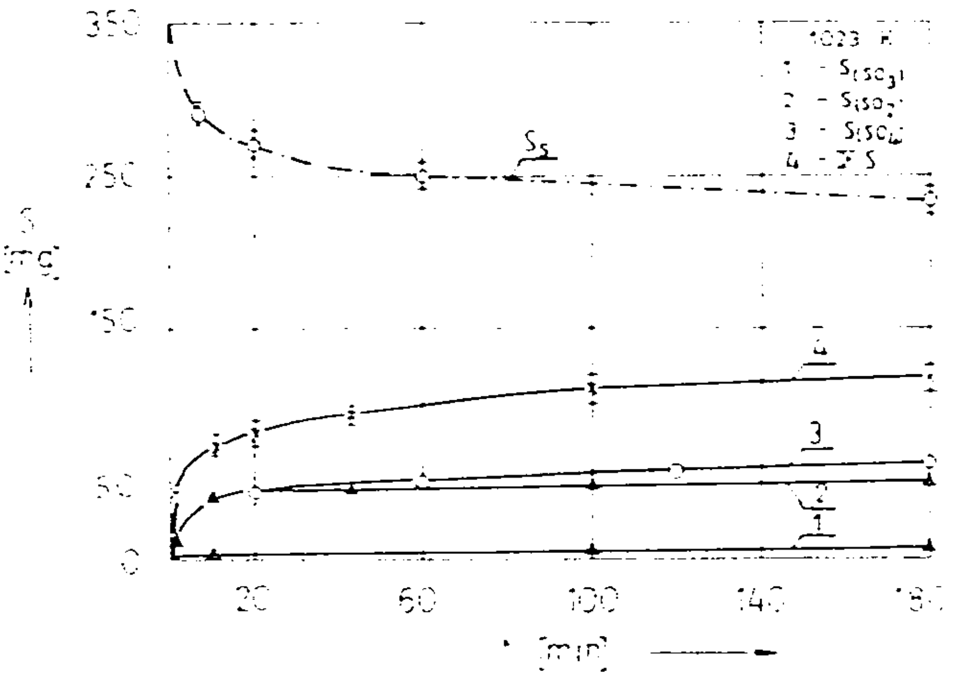

Fig. 4. Amount of sulphur oxidized to $SO_2$ and $SO_3$ during the process, as well as of $SO_4$ in lead sulphates. Galena, temperature 1023 K.

gested between process temperature and the ratio of the amounts of sulphur oxidized to the gaseous state $SO_2/SO_3$, whereas the amount of sulphur present as sulphate depends on the kind of solid phases in formation. Such a procedure allowed the determination of the overall degree of oxidation for lead sulphide; this was quite unachievable with only sample weight changes taken into account, as is suggested in refs. 13—15.

On the basis of the thermogravimetric study results, analysis of $SO_2$ and $SO_3$ gases and chemical analysis of $SO_4$ in samples, their weight changes $\Delta g$ have been computed [10], the latter being a consequence of the formation of respective final products of oxidation reactions with atmospheric oxygen [16,17].

$$PbS + 2\ O_2 = PbSO_4 \qquad (1)$$

$$2\ PbS + \tfrac{7}{2}\ O_2 = PbO \cdot PbSO_4 + SO_2 \qquad (2)$$

$$3\ PbS + 5\ O_2 = 2\ PbO \cdot PbSO_4 + 2\ SO_2 \qquad (3)$$

$$5\ PbS + 8\ O_2 = 4\ PbO \cdot PbSO_4 + 4\ SO_2 \qquad (4)$$

$$PbS + \tfrac{3}{2}\ O_2 = PbO + SO_2 \qquad (5)$$

$$PbS + O_2 = Pb + SO_2 \qquad (6)$$

The composition of PbS is generally non-stoichiometric with a damaged anionic sub-lattice [18]. Consequently, the "*p*" type conduction of the materials examined has been determined [10]. Non-stoichiometric excess sulphur contained in lead sulphide dissociates rapidly and sublimes from the sample during the initial period of 150 sec, oxidizing in the air stream to $SO_2$ (Fig. 3) and, consequently, the unoxidized nucleus of the sample becomes $PbS_{1-x}$ of "*n*" type electric conduction.

The thermogravimetric curve is thus a result of the process of lead sulphate formation as well as of the changes in the type of damage occurring in the lead sulphide according to the equation

$$p + [S_i''] \xrightarrow{T} n + [V_s^{\bullet\bullet}] \qquad (7)$$

where, $p$ = concentration of vacancies; $[S_i'']$ = concentration of bi-negative sulphur anions in interstitial sites; $n$ = concentration of electrons within the conduction band; and $[V_s^{\bullet\bullet}]$ = concentration of ionized vacancies in the anionic sub-lattice.

The $\bar{x}$ thickness of the formed layer of oxidation products of galena has been measured by means of a Pladun polarizing microscope. The results are plotted in Fig. 5 with the assumption that the rate of layer increment is inversely proportional to the time of the process and has a hampering effect on the development of the latter.

Sample micro-regions have been examined in order to investigate whether the process course is zonal as well as if the examined macro-layer has thoroughly reacted. A Cameca Ms 46 X-ray analyser was used for the determination of the linear content of lead and sulphur. The zonal character of oxidation was noticed on the macro-scale, the products building up in layers on every single PbS grain and thus hampering further penetration of oxygen into the sample nucleus. Consequently, in the case of galena, a thoroughly reacted layer was found only at 1023 K, separated from the unoxidized nucleus by a gap approximately 60-μm wide (Fig. 6). 4 PbO · $PbSO_4$ sulphate contained in the products crystallizes in the monoclinic system [19], is characterized by a high coefficient of compactness [10,13] and has a strong hampering effect on the course of the process (Fig. 5). On the other hand, unoxidized PbS grains have sometimes been found in the layers at lower temperatures and sulphates of a lower PbO/$PbSO_4$ mole ratio due to their higher porosity did not present such a serious hindrance for gaseous reactants.

The shape of the grains and the uniformity of their distribution on sample

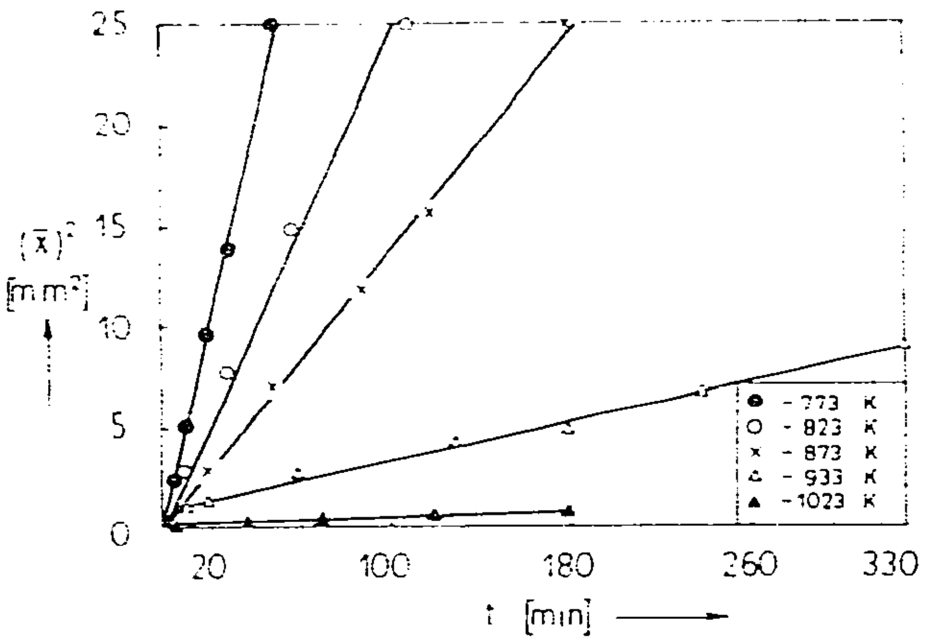

Fig. 5. Linear relationship between the thickness of the layer of oxidation products of galena and the time at the respective temperatures.

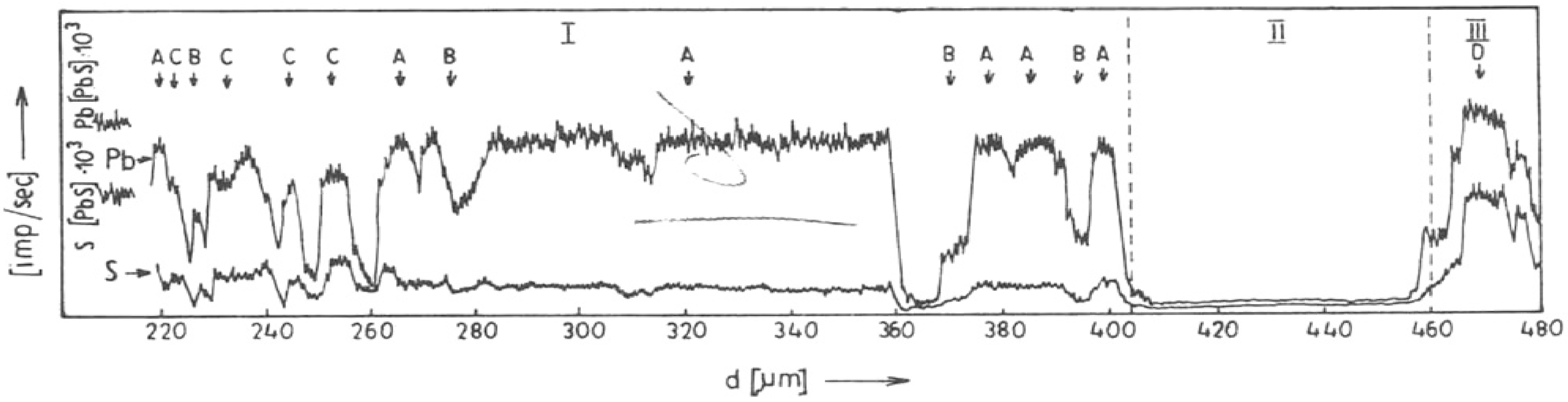

Fig. 6. Results of galena examination in an X-ray microanalyser. Temperature 1023 K; oxidation time 150 min. Zone I, thoroughly reacted: A, 4 PbO · $PbSO_4$, B, α-2 PbO · $PbSO_4$; C, PbO · $PbSO_4$. Zone II, the gap separating the product layer from the unoxidized nucleus of the sample. Zone III, unoxidized nucleus: D, PbS.

fractures were examined in a Jeol electron microscope, the fractures being vacuum powdered with a thin layer of gold. The structures obtained are shown by way of example in Figs. 7—10.

In order to obtain an equation describing the kinetics of the oxidation of compact material with the formation of a solid product, several models have been designed for the process [20]. However, the matter becomes complicated when, as the result of the reaction between solid and gas, some solid phases form in addition to gaseous products, since these facts had been not

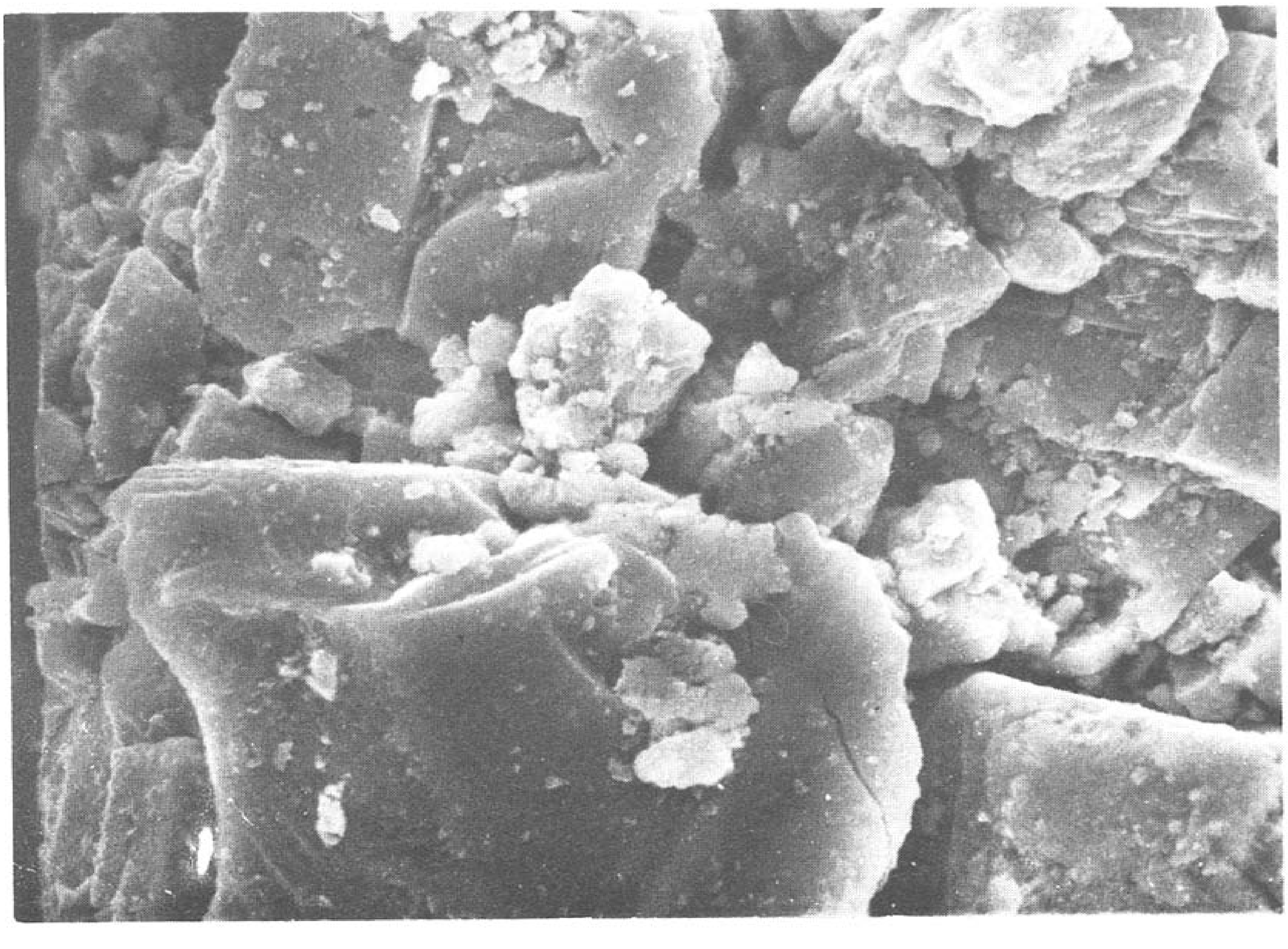

Fig. 7. A fracture of a galena sample under an electron microscope at 3000 × magnification.

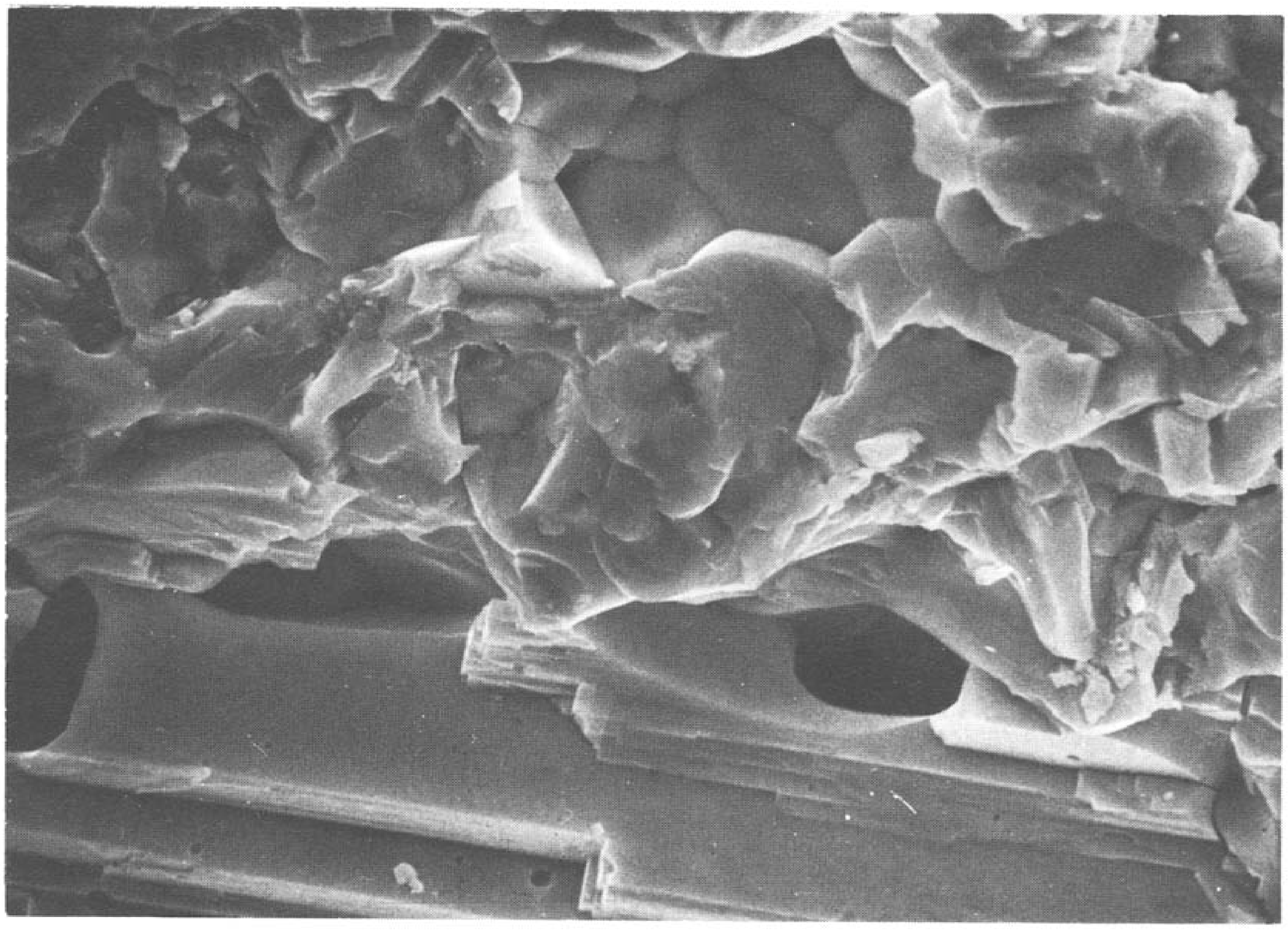

Fig. 8. Structure of the thoroughly reacted layer of galena oxidation products after 150 min at 1023 K. 3000 × magnification.

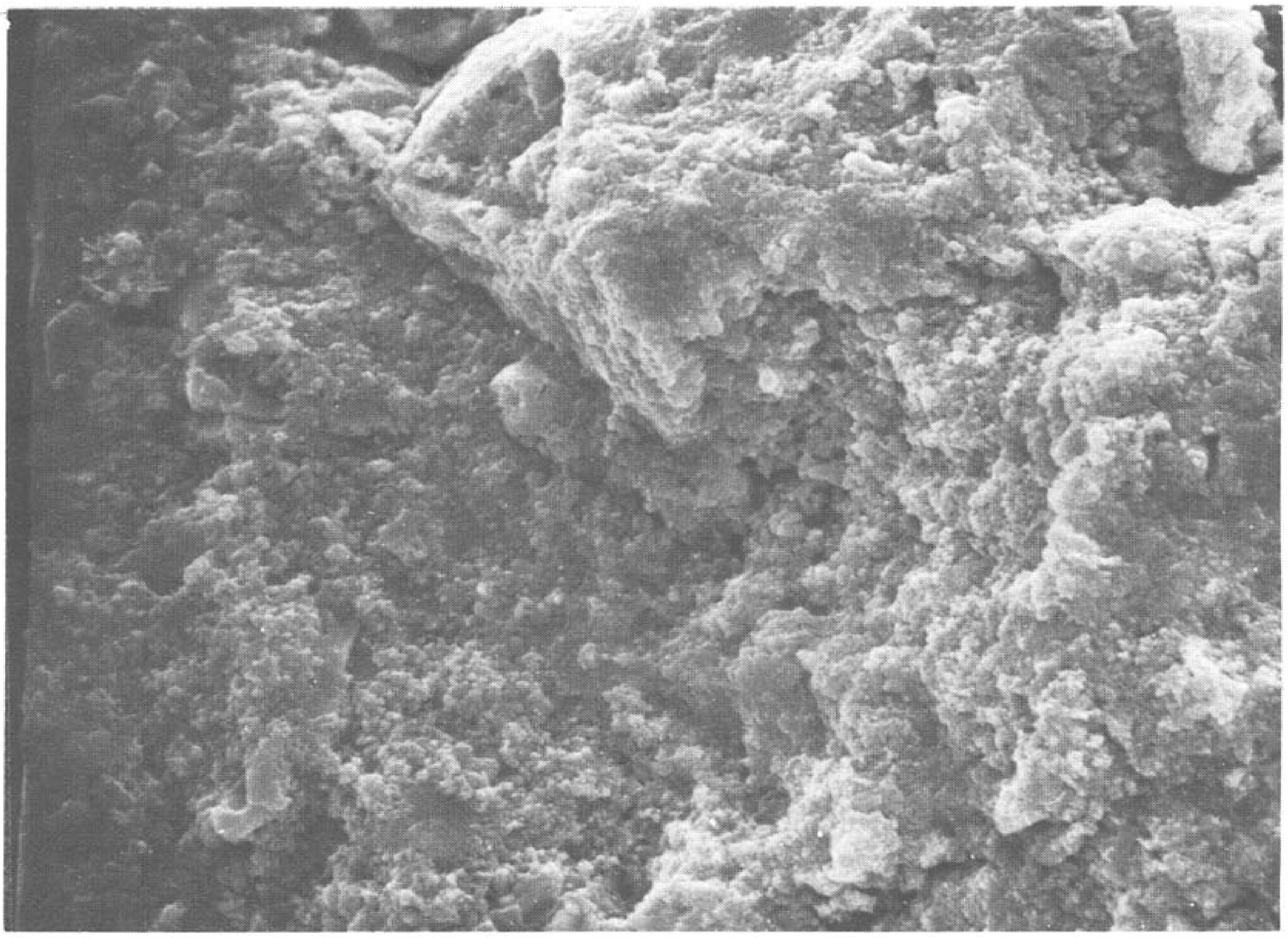

Fig. 9. A fracture of s.p. PbS sample under an electron microscope at 3000 × magnification.

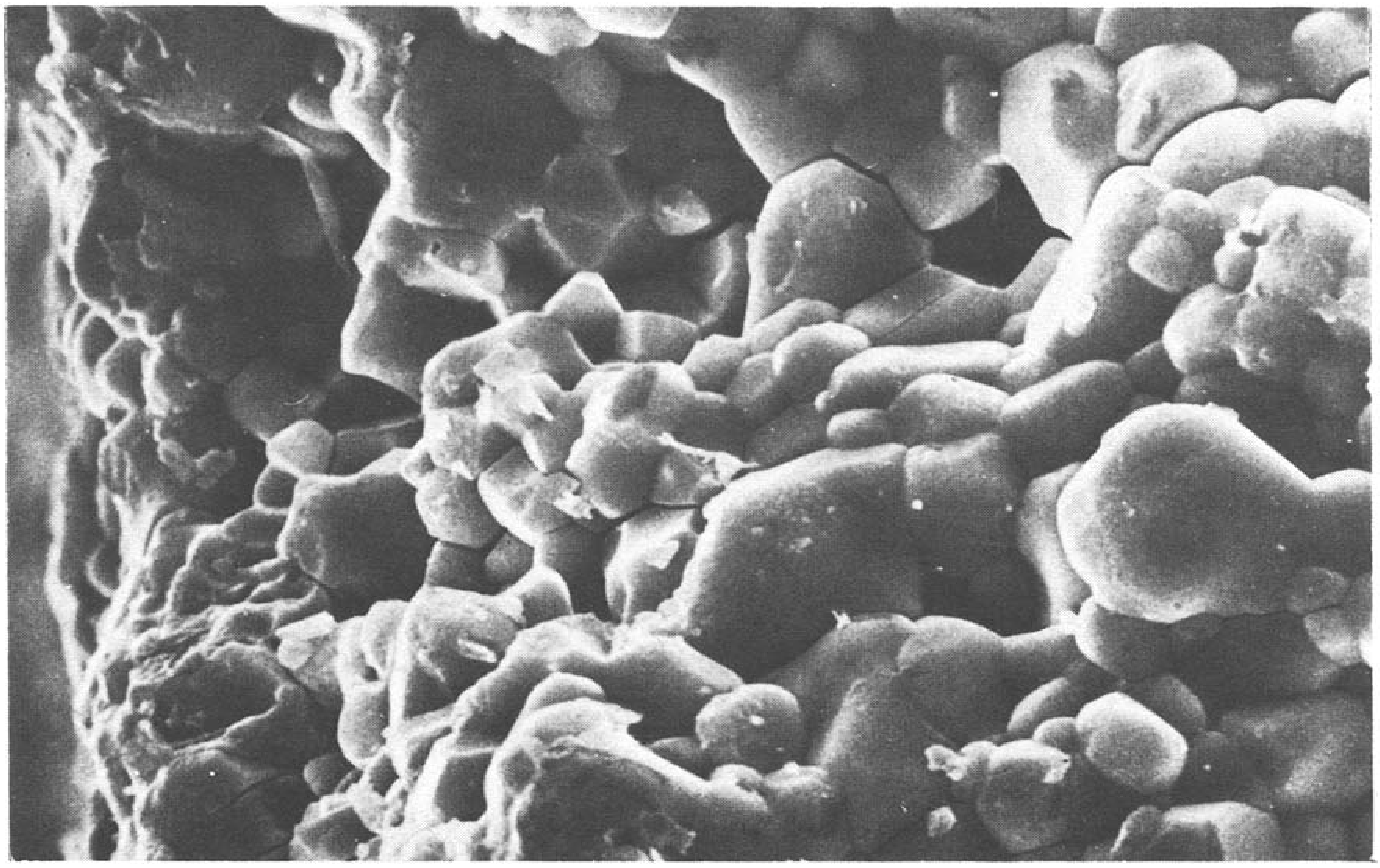

Fig. 10. Structure of s.p. PbS sample oxidized at 1023 K for 150 min. 3000 × magnification.

taken into account in the former models [21]. Consequently, attempts to find agreement between the experimental values of the amount of sulphur oxidized during the process and the results of theoretical equations failed. A linear relation of the curves representing the building up of the product layer on the spherical galena samples was, however, achieved. This fact may be explained by the diffusion course in the solid hampering the rate of the process.

## CONCLUSIONS

The results of thermogravimetric investigations of the oxidation of lead sulphide with parallel control of the amount of gases formed as well as with the identification of solid products led to the following conclusions.

(1) Between 773 and 1023 K, lead sulphates of the following types form successively: $PbSO_4$, $PbO \cdot PbSO_4$, $\alpha$-$2\,PbO \cdot PbSO_4$, and $4\,PbO \cdot PbSO_4$.

(2) The building up of the product layer on galena samples is concomitant with the process course on a micro-scale and the individual phases are arranged topochemically on PbS grains within a temperature range of 773—933 K.

(3) The tetrabasic lead sulphate ($4\,PbO \cdot PbSO_4$) is a compound of high compactness coefficient with the most serious hampering effect on galena oxidation at 1023 K.

(4) The linear dependence of the build-up rate of the galena oxidation

product layer evidences a diffusional hampering of the process at respective temperatures.

(5) The shape and the size of the grains, as well as the uniformity of their distribution on galena and s.p. PbS fractures affect the structure of the products.

(6) The degree of oxidation determined as the amount of sulphur oxidized to ($SO_2$ + $SO_3$) and $SO_4$ in the lead sulphates formed is an indication of the degree to which lead sulphide reacted.

(7) Non-stoichiometric excess sulphur present in PbS oxidizes during the initial process step, initiating a change of the lead sulphide from $PbS_{1+y}$ to $PbS_{1-y}$, this resulting in a change of the electric conduction of the kind "*p*" → "*n*".

(8) The experimental thermogravimetric curve is a consequence of the coincidence of two processes: (a) dissociation and sublimation of non-stoichiometric excess sulphur and its oxidation in an air stream to $SO_2$ and $SO_3$ and (b) reactions of lead sulphide oxidation in galena resulting in the formation of solid products (lead sulphates).

(9) The kinetic models of Pilling and Bedworth, Ginstling, Crank and Carter found in the literature [20,21] and relevant to heterogeneous solid—gas reactions do not describe the process of lead sulphide oxidation, since they do not take into account the formation of several solid phases at a given temperature: a determination of the quantitative ratio between them has been unachievable hitherto. Respective lead sulphates are characterized by a differentiated crystallographic structure, as well as by porosity and molecular volume, this impeding additionally the interpretation of the kinetics of this process.

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