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Thermochimica Acta 246 (1994) 141–152

thermochimica
acta

Oxidation of zinc sulfide by means of zinc sulfate

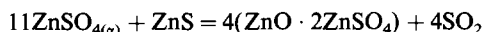
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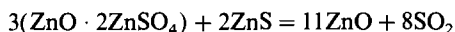
Received 19 November 1993; Accepted 13 April 1994

Abstract

The problems dealt with in this study concern the oxidation of metal sulfides, in particular attention to the reactions between MSO_4 and MS . The paper contains some experimental results obtained in analyzing the interaction between ZnSO_4 and ZnS by means of thermogravimetric analysis, radiomarking using the isotope ^{35}S , X-ray phase analysis and chemical analysis. It was found that irrespective to the molar ratio of ZnSO_4 to ZnS , the process has two stages. In the first stage, the following equation may be applied:



The second stage may be described by the expression



In addition, the effect of the molar ratio of ZnSO_4 to ZnS and of the process temperature on the oxidation rate of ZnS mixed with ZnSO_4 , was determined. The results were compared with those obtained for the oxidation of ZnS in air. The activation energies in both stages of the process were also determined.

Keywords: Binary system; DTA; DTG; Oxidation; Sulphide; TG; Zinc sulphate; Zinc sulphide

1. Introduction

The oxidation of metal sulfides is a complex process occurring in the system M-S-O . During this process, reactions in the system $\text{MSO}_4\text{-MS}$, MS-MO ,

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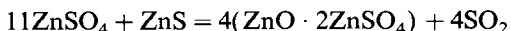
M-MSO₄, between MS, MO, M and the gaseous phase containing oxygen and sulfide oxides, as well as the dissociation of sulfates, take place. They affect the rate of the process, as well as the final composition of the products.

With respect to this, the literature contains most information about the thermal dissociation of sulfates. Few published papers are concerned with analyzing the reactions between sulfides and sulfates of the same metal. The interaction occurring between ZnSO₄ and ZnS has been investigated by Fischer [1] who gives the equilibrium pressures for SO₂ for the reaction

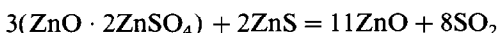


In addition, Ingraham and Kellogg [2] determined the stability conditions of the respective phases in the system Zn-S-O. From thermodynamic computations, the authors assume the existence of the phase ZnO · 2ZnSO₄, resulting from a reaction of the sulfate with sulfide. Cizikov et al. [3] and Frenc [4] believe that the reaction between ZnSO₄ and ZnS is possible via formation of a metal phase. Skackov [5] determined that the reaction starts at about 723 K and that ZnO · 2ZnSO₄ is present during the reaction.

In Refs. [6] and [7], however, it was stressed that the reaction occurring between ZnSO₄ and ZnS, irrespective of the molar ratio of these ingredients, takes place in two subsequent stages. The temperature at the beginning of the first stage is similar to the flash-point of zinc sulfide and is approximately 160 K below the temperature at which the decomposition of the sulfate begins. The second process starts at 873 K. In Ref. [8], a more recent publication, a complex analysis of the chemical process in the system ZnSO₄-ZnS was performed. Based on the thermogravimetric tests made and supplemented with the results of the chemical and X-ray phase analyses, as well as with those of the sulfur distribution in the solid and gaseous products of the reaction, Malinowski [8] found that in the first stage of the process, three simultaneous chemical reactions occur, expressed via the balance equation



In the second stage, two reactions run simultaneously as follows



From recent studies, it has been concluded that the chemical process occurring between ZnSO₄ and ZnS comprises the reactions of thermal decomposition of ZnSO₄, and of oxidation of ZnS by the oxygen from the sulfate. The rates of these processes depend on the grain size and the reciprocal contact existing between the reacting substances arising from their molar ratios in the mixture (MSO₄-MS). This paper is aimed at the determination of the effect of the molar ratio ZnSO₄:ZnS and of the process temperature upon the degree and rate of the transformation of ZnS into ZnO.

2. Experimental

Pure substances were used for testing the reaction in the system ZnSO₄-ZnS. The zinc sulfide of regular structure had an average grain size of 0.90 μm. This size was

determined via Fisher's apparatus. Before making the preparations, the zinc sulfate was dehydrated at 770 K so as to secure complete elimination of water of crystallization and at the same time to avoid thermal decomposition of sulfate. For highly higroscopic zinc sulfate, the dehydration was performed directly before making the mixture of zinc sulfate and sulfide. After dehydration, the sulfate was placed in an agate mortar in order to obtain a grain size close to that of zinc sulfide.

From these ingredients ($\text{ZnSO}_4 + \text{ZnS}$), mixtures of different sulfate : sulfide molar ratios were made. At the same time, the composition of the preparations were selected such that they contained both oxygen excess and depletion. Thus, oxygen could participate in the oxidation process of zinc sulfate. The measurements were performed in an inert atmosphere which had been deoxidized at 620 K in a column filled with copper scraps. The gaseous phase flowed through the system at a rate of $5 \text{ dm}^3 \text{ h}^{-1}$. Any increase in this rate had no further effect on the rate of deoxidation. In the tests, the specimen sizes were adjusted to the sensitivity of recording changes in the mass, namely $1 \times 10^{-4} \text{ g}$ with a linear increase in temperature or $1 \times 10^{-3} \text{ g}$ under isothermal conditions. The tests were performed by means of a Mettler TA-1 thermal analyzer which enabled the furnace atmosphere to be exchanged via a vacuum pump.

The experiments were performed at constant heating rate to determine whether the reaction between zinc sulfide and sulfate occurred in one or a few successive stages, like the ZnSO_4 decomposition.

Fig. 1 and 2 show some of the thermograms obtained. The TG, DTG and DTA curves reveal that in the preparations with molar ratios of sulfate : sulfide below 3 : 1, the reaction runs in two successive stages. When the molar ratio $\text{ZnSO}_4 : \text{ZnS}$ exceeds 3 : 1, the reactions occur in three stages. The temperature of the start of the reaction determined by extrapolation of the DTG curve to zero heating rate was in conformity with the flash-point of ZnS being in the range $793 \pm 5 \text{ K}$, whereas that of the second stage was $873 \pm 5 \text{ K}$. The temperature of the initiation of the first process is about 170 K lower than that of the start of the thermal decomposition of zinc sulfate. The temperature at the beginning of the second stage is subject to a shift towards higher values with an increase in the molar ratio $\text{ZnSO}_4 : \text{ZnS}$.

The tests executed with linearly increasing temperature showed that the interaction between ZnSO_4 and ZnS occurs with formation of intermediate compounds that react with the excess substrates in the subsequent stage at higher temperatures. It seems that the basic problem related to such a course is the determination of the nature of the intermediate phases and of the participation of the starting ingredients in their formation which has a direct effect on the degree of zinc sulfide–zinc oxide transformation. In order to determine these relations, each preparation was subject to testing in isothermal conditions in two series of measurements. The first series, related with the first stage, was performed within the temperature range that resulted from tests with linearly increasing temperatures. The maximum testing temperature was about 25 K lower than that of the beginning of the second stage reaction. The first stage was considered complete if the change in mass in particular at high temperatures, in a 10 min interval did not exceed 1 mg. After the first stage, the material was subject to both chemical and X-ray phase analyses. This was the substrate tested in the second stage.

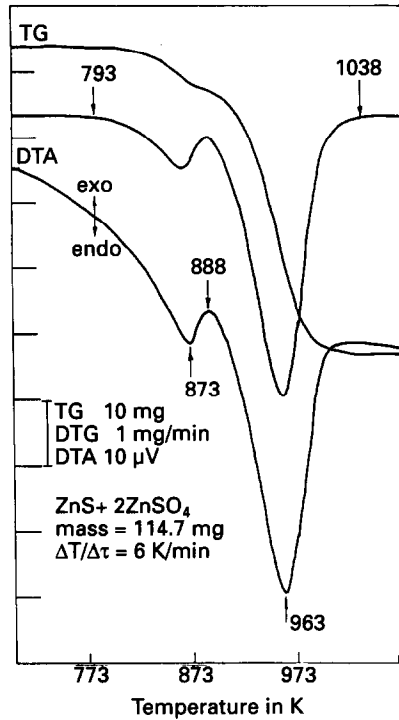


Fig. 1. Thermogram of a mixture of zinc sulfide and sulfate. Molar ratio, $\text{ZnSO}_4:\text{ZnS} = 2:1$.

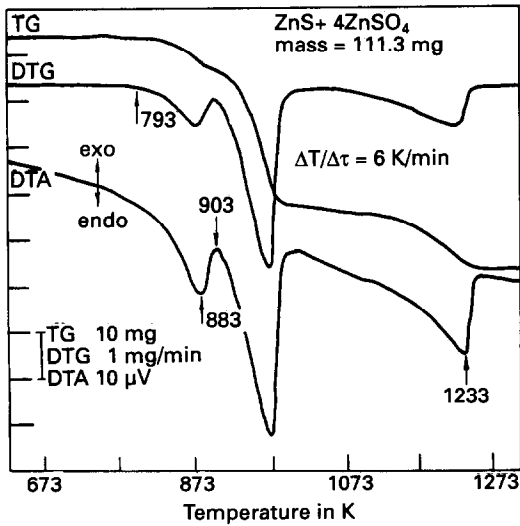


Fig. 2. Thermogram of a mixture of zinc sulfide and sulfate. Molar ratio, $\text{ZnSO}_4:\text{ZnS} = 4:1$.

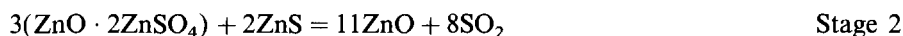
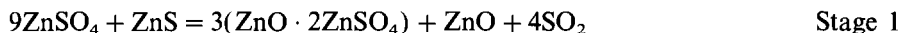
Table 1
X-ray phase analysis results

| Preparation | Phases found in the products after | |
|--------------------------|------------------------------------|-------------------------------|
| | Stage 1 | Stage 2 |
| ZnSO ₄ + ZnS | ZnO · 2ZnSO ₄ , ZnS | ZnO, ZnS |
| 2ZnSO ₄ + ZnS | ZnO · 2ZnSO ₄ , ZnS | ZnO, ZnS |
| 3ZnSO ₄ + ZnS | ZnO · 2ZnSO ₄ , ZnS | ZnO |
| 4ZnSO ₄ + ZnS | ZnO · 2ZnSO ₄ , ZnS | ZnO, ZnO · 2ZnSO ₄ |

Table 2
Results of the chemical analyses of the preparations (ZnSO₄ + ZnS) after the stage given

| Preparation | Relative change mass in % | Stage | Contents of the ingredients in % | | |
|--------------------------|---------------------------|-------|----------------------------------|------------------|------------------------------|
| | | | Zn | S _{tot} | S _{so₂-} |
| ZnSO ₄ + ZnS | 8.85 | I | 54.64 | 22.10 | 9.85 |
| | 26.00 | II | 74.50 | 10.65 | Traces |
| 2ZnSO ₄ + ZnS | 10.90 | I | 52.70 | 19.40 | 12.45 |
| | 32.70 | II | 78.00 | 2.95 | Traces |
| 3ZnSO ₄ + ZnS | 11.95 | I | 50.90 | 18.20 | 13.80 |
| | 35.60 | II | 79.40 | 0.60 | 0.55 |
| 4ZnSO ₄ + ZnS | 12.40 | I | 50.10 | 17.60 | 14.40 |
| | 25.30 | II | 67.30 | 6.40 | 6.32 |

After achieving constant weight at the stage of the process considered, the preparations were subject to X-ray phase analysis using an iron-filter cobalt lamp, the angle range being 2θ from 10° to 100° . The compounds listed in Table 1 were detected. Chemical analysis of the preparations at the end of the process (Table 2) indicate a decrease in the sulfide sulfur with a decreasing level of sulfate sulfur. This would confirm the oxidation of ZnS by oxygen derived from the sulfate. Because zinc sulfate is decomposed gradually with formation of intermediate ZnO · 2ZnSO₄, and at the same time oxidation of ZnS to ZnO occurs by means of the oxygen evolved during the decomposition, the products after the first stage, apart from ZnS and ZnO · 2ZnSO₄, should also include ZnO. In the second stage, decomposition of ZnO · 2ZnSO₄ to ZnO and the equivalent oxidation of ZnS to ZnO take place. These processes may be described by the balance equations



If the hypothesis presented is correct, and the respective stages have been completed, then the change in mass of the preparations calculated according to the balance equations should be in conformity with the experimental data. These results are collected in Table 3.

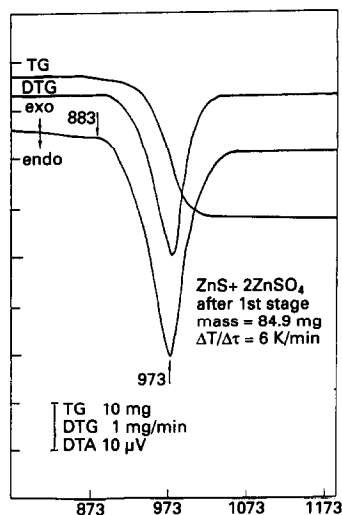
Table 3

Relative mass losses calculated and obtained experimentally for the preparations

| Preparation | Relative mass loss of the preparations in % | | | |
|--------------------------|---|--------------|----------|--------------|
| | Stage 1 | | Stage 2 | |
| | Computed | Experimental | Computed | Experimental |
| ZnSO ₄ + ZnS | 10.84 | 8.85 | 24.32 | 25.90 |
| 2ZnSO ₄ + ZnS | 13.39 | 10.90 | 30.92 | 32.70 |
| 3ZnSO ₄ + ZnS | 14.66 | 11.93 | 33.52 | 35.52 |
| 4ZnSO ₄ + ZnS | 15.24 | 12.40 | 22.96 | 25.40 |

Analyzing the obtained results, a difference between the experimental and computed values is apparent. The relative changes in mass obtained experimentally in stage 1 are less than the computed values. In stage 2 of the process, these relations are inverted. Thus, it may be suggested that either the process is not completed in stage 1 or that additional compounds cause a relative change in the mass of the specimens which is less than the computed change.

Firstly, in order to explain the ambiguities, the products obtained after stage 1 were subjected to thermogravimetric tests. It was believed that if the first stage was not over, it would be reflected in the TG, DTG and DTA traces. Fig. 3, for example shows a thermogram of a preparation after the first stage. The curves confirm that the previous stage has ended.

Fig. 3. Thermogram of a preparation (2ZnSO₄ + ZnS) after the first stage.

Another possible reason for the lower changes in sample mass during stage 1 is oxidation of zinc sulfide to $\text{ZnO} \cdot 2\text{ZnSO}_4$. In consequence of such a reaction, part of the sulfide sulfur would be oxidized to sulfur from $\text{ZnO} \cdot 2\text{ZnSO}_4$. It is also probable that $\text{ZnO} \cdot 2\text{ZnSO}_4$ is formed as the result of a reaction between zinc oxide sulfate.

In order to determine the concurrent reaction, radiomarking testing using the sulfur isotope ^{35}S was applied. It was expected that the determination of the ^{35}S level from zinc sulfide in both gaseous and solid products would simplify the identification of the reaction responsible for the differences between the computed and experimental masses. Preparation of Zn^{35}S for the tests was according to Ref. [8]. The quantitative determination of the proportion of ^{35}S derived from zinc sulfide in the gaseous and solid products of the process was assessed from the standards which were different in specific activities and identical in shape and surface to the specimens under investigation. The tests were carried out in the same conditions as the preparations with various molar ratios of ZnSO_4 to ZnS . The results are presented in Table 4.

The experimental data (Table 4) show that the ^{35}S level in gaseous SO_2 reaches a value of 25% and that there is no relation between the molar ratio of $\text{ZnSO}_4:\text{ZnS}$ and the mass loss. The ^{35}S level in the sulfate phase falls within experimental error and indicates that there is no transfer of ^{35}S from zinc sulfide to sulfate. Therefore, under the conditions of the investigation, there was no oxidation of ZnS to $\text{ZnO} \cdot 2\text{ZnSO}_4$. $\text{ZnO} \cdot 2\text{ZnSO}_4$ was formed as a consequence of a reaction between ZnO resulting from ZnS during its oxidation, and zinc sulfate. This was proved experimentally. The assumption that $\text{ZnO} \cdot 2\text{ZnSO}_4$ is formed from zinc oxide and

Table 4
 ^{35}S contents in the gaseous and sulfate phases

| Preparation | Temperature in K | Initial mass of preparation in mg | Relative change in the specimen's mass in % | ^{35}S contents in % | |
|-------------------------------|---------------------|--|--|-------------------------------|------------------|
| | | | | Gaseous phase | Sulfate phase |
| ZnS | 973 | 239.8 | 16.14 | 99 ± 3 | – |
| $\text{ZnSO}_4 + \text{ZnS}$ | 848 | 2889 | 4.39 | 23.7 ± 1.5 | 0.2 |
| | 848 | 1668 | 7.79 | 25.2 ± 2 | 0.4 |
| | 923 | 1350 | 14.22 | 24.5 ± 2.1 | 0.3 |
| $2\text{ZnSO}_4 + \text{ZnS}$ | 848 | 2904 | 5.41 | 24.3 ± 1.5 | 0.25 |
| | 848 | 2794 | 7.07 | 23.5 ± 1.5 | 0.7 |
| | 848 | 2723 | 9.95 | 23.7 ± 1.8 | 0.3 |
| $3\text{ZnSO}_4 + \text{ZnS}$ | 923 | 2856 | 20.31 | 26.4 ± 1.6 | 0.6 |
| | 848 | 2683 | 6.70 | 23.1 ± 1.6 | 0.4 |
| | 848 | 2520 | 10.36 | 24.2 ± 1.4 | 0.5 |
| $4\text{ZnSO}_4 + \text{ZnS}$ | 923 | 2863 | 25.39 | 25.2 ± 2 | 0.2 |
| | 848 | 1792 | 9.49 | 24.3 ± 1.8 | 0.5 |
| | 923 | 1823 | 20.46 | 23.5 ± 1.3 | 0.8 |
| | 923 | 2823 | 21.78 | 24.4 ± 2 | 0.4 |

sulfate results in agreement between the computed and experimentally obtained changes in mass in the respective stages.

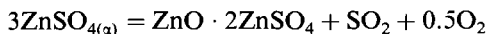
3. Discussion of the results obtained

The thermogravimetric experiments showed that, irrespective of the molar ratio of zinc sulfate:zinc sulfide, the process proceeds in two stages, beginning at a temperature convergent with the ZnS flash-point, about 160 K below the initial temperature of the thermal dissociation of the sulfate.

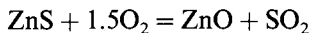
X-ray phase analysis also showed that $\text{ZnO} \cdot 2\text{ZnSO}_4$ is formed in stage 1, whereas zinc oxide is formed in stage 2. The radiomarking tests proved that the ^{35}S level as SO_2 in the gaseous phase reaches a value of 25%, irrespective of the molar ratio of zinc sulfate:sulfide. This confirms the equivalent oxidation of ZnS to ZnO via the oxygen derived from the sulfate. Moreover, it was shown that during this process there is no oxidation of zinc sulfide to $\text{ZnO} \cdot 2\text{ZnSO}_4$. It was proved that the product of the first stage is $\text{ZnO} \cdot 2\text{ZnSO}_4$ which results from the decomposition of zinc sulfate in consequence of a reaction between ZnO and ZnSO_4 . In the second stage, zinc oxide is formed from a reaction between ZnS and $\text{ZnO} \cdot 2\text{ZnSO}_4$.

From the results obtained, it was assumed that in the first stage of the process the following reactions can be considered

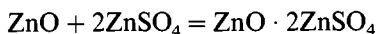
Thermal decomposition of zinc sulfate



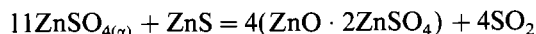
Oxidation of zinc sulfide



Formation of $\text{ZnO} \cdot 2\text{ZnSO}_4$

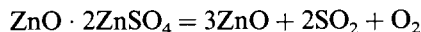


Regarding the oxygen balance, in the first stage the process may be expressed by the total reaction

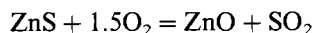


The process occurring in the second stage comprises the following reactions.

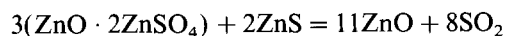
Thermal decomposition of $\text{ZnO} \cdot 2\text{ZnSO}_4$



Oxidation of sulfide to zinc sulfate



The process in the second stage may be expressed by the balance reaction



The second stage of the process ends when ZnS has been completely oxidized to ZnO, or when $\text{ZnO} \cdot 2\text{ZnSO}_4$ has been completely decomposed. This depends on the molar ratio of ZnSO_4 :ZnS.

The assumed course of the process in the 1st and 2nd stages was in conformity with the experimental data regarding the chemical composition, the phase composition and the contents of sulfide sulfur in the gaseous phase. From the recorded changes in mass in the isothermal tests, it was possible to compute the oxidation number of zinc sulfide. Typical results of these computations are illustrated in Figs. 4 and 5 (stage 1) and Figs. 6 and 7 (stage 2). The results obtained prove that for a given molar ratio of zinc sulfate:zinc sulfide, a change in the temperature of the process influences appreciably the oxidation number of zinc sulfide in both the 1st and 2nd stages. The data obtained also indicate that at a given temperature an increase in the molar ratio of ZnSO_4 :ZnS from 1:1 to 3:1 decreases the oxidation number of zinc sulfide.

The activation energy calculated for the first stage ranges from 230 to 240 kJ mol^{-1} , whereas that for the second ranges from 205 to 210 kJ mol^{-1} . These values

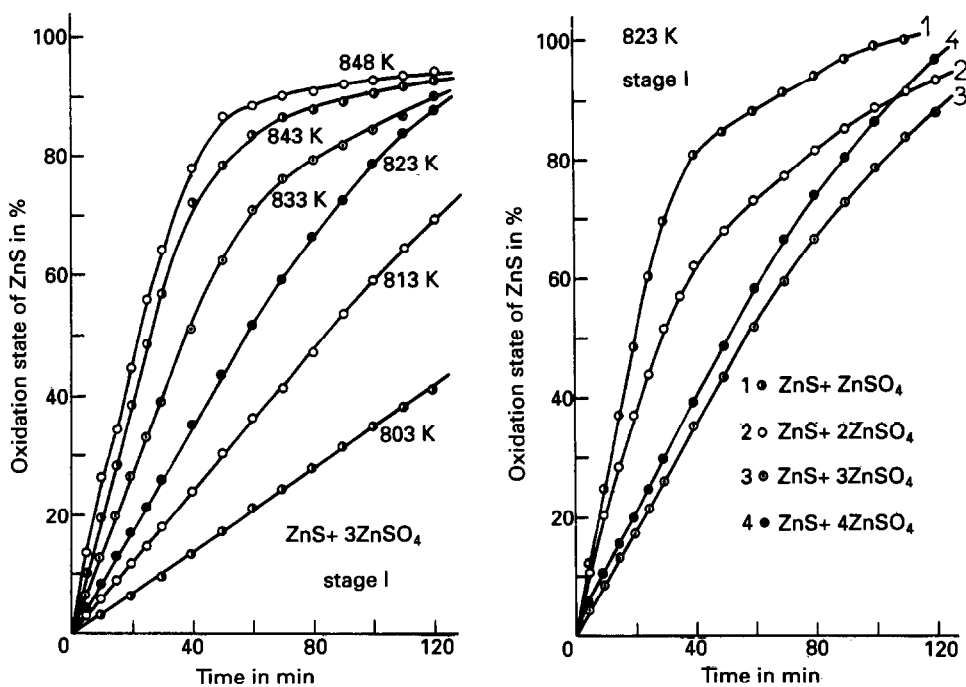


Fig. 4. Relation between the oxidation state of ZnS in the preparation ($3\text{ZnSO}_4 + \text{ZnS}$) and temperature and time in the first stage.

Fig. 5. Relation between the oxidation state of ZnS, and time and molar ratio ZnSO_4 :ZnS at 823 K in the first stage.

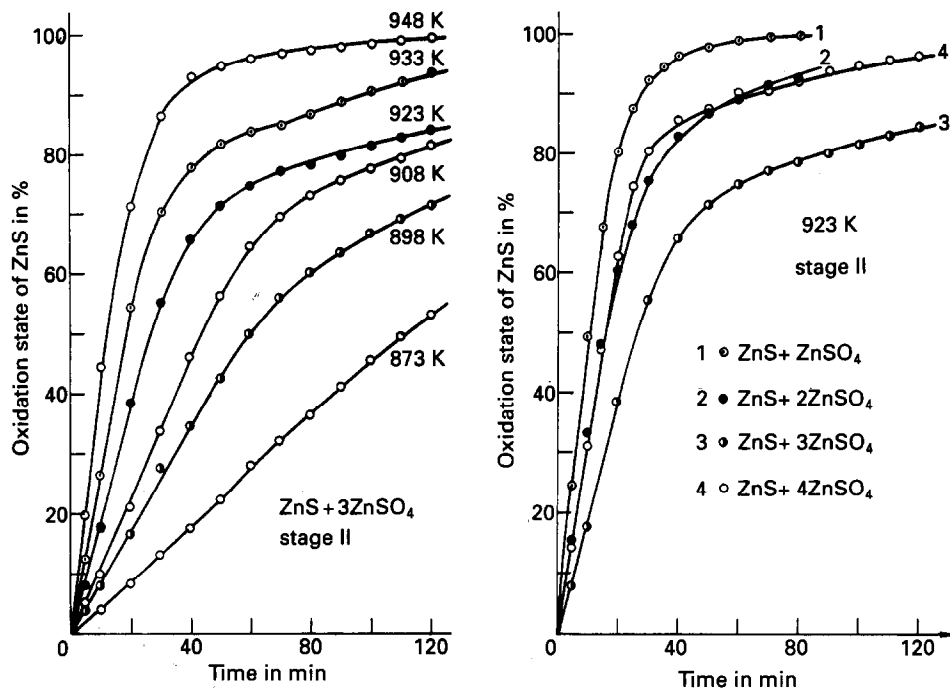


Fig. 6. Relation between the oxidation state of ZnS in the preparation ($3\text{ZnSO}_4 + \text{ZnS}$), and time and temperature in the second stage.

Fig. 7. Relation between the oxidation state of ZnS, and time and molar ratio $\text{ZnSO}_4:\text{ZnS}$ at 923 K in the second stage.

are lower than the activation energy of the decomposition of zinc sulfate [9–13] and higher than that for the oxidation of zinc sulfide in its regular structure, ($111.6 \text{ kJ mol}^{-1}$) [41].

A constant, high activation energy value might suggest that the rate of the reaction between zinc sulfate and sulfide is the limiting factor. The direct contact of zinc sulfate and sulfide facilitates its decomposition, and also considerably accelerates the oxidation of zinc sulfide. This results from a direct comparison of the oxidation kinetic curves for zinc sulfide in air (Fig. 8) with the results of oxidation of ZnS by ZnSO_4 . The data presented indicate that the oxidation of ZnS in air occurs more slowly and requires higher temperatures. The use of appreciable amounts of Al_2O_3 as a neutral additive to facilitate contact between sulfide and sulfate caused no significant change in the oxidation rate. This may indicate that the oxidation of ZnS in a mixture with sulfate occurs in consequence of the release of atomic oxygen during the decomposition of the sulfate.

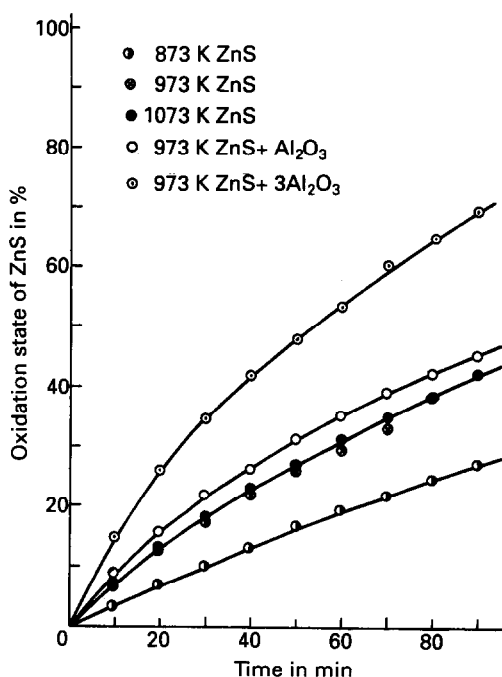


Fig. 8. Relation between the oxidation state of ZnS in air, and time at various temperatures and weight ratios of ZnS:Al₂O₃.

4. Summary

Analyses of the chemical reaction between ZnSO₄ and ZnS showed that it occurs in two stages. It starts at a temperature convergent with the flash-point of zinc sulfide. During the process and simultaneously with the decomposition of zinc sulfate, an equivalent oxidation of zinc sulfide to zinc oxide takes place. The product of the first stage is ZnO · 2ZnSO₄ which is a consequence of the decomposition of sulfate and of a reaction between the resultant zinc oxide and sulfate. The phenomena occurring in the first stage may be described by the balance reaction $11\text{ZnSO}_{4(x)} + \text{ZnS} = 4(\text{ZnO} \cdot 2\text{ZnSO}_4) + 4\text{SO}_2$. In the second stage, the decomposition of ZnO · 2ZnSO₄ in the presence of ZnS, as well as an equivalent oxidation of ZnS to ZnO, takes place, expressed as $3(\text{ZnO} \cdot 2\text{ZnSO}_4) + 2\text{ZnS} = 11\text{ZnO} + 8\text{SO}_2$. At the end of the process, if there is an excess of ZnO · 2ZnSO₄ in relation to ZnS, a third stage related to the thermal decomposition begins.

The oxidation rate of ZnS is strongly affected by the molar ratio of ZnSO₄ to ZnS. On increasing this ratio, the oxidation rate of ZnS decreases. The oxidation rate of ZnS by the oxygen derived from the sulfate is a few times higher than that in air atmosphere.

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