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Analysis of the chemical processes occurring in the system $PbSO_4$–ZnS

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Abstract

Research carried out on the interactions between $PbSO_4$ and ZnS, using mixtures with variable molar ratios of $PbSO_4$:ZnS, showed that the process starts at 803 K. It was found that a few reactions occur at the same time, including transformation of zinc sulfide into its oxide and PbS formation; the secondary lead sulfate containing the sulfur from ZnS also appears. The PbS is derived primarily from $PbSO_4$, and some of it contains the sulfur from ZnS.

Keywords: Decomposition; Lead sulfate; Oxidation; Reaction in the state phase; Zinc sulfide

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1. Introduction

In a series of metallurgical processes, attention is paid to the fact that some of the reactions occurring between MSO_4 and MS influence the degree of elimination of sulfur as a gaseous phase as well as the composition of the final gas product. The problem seems quite simple if a sulfate and a sulfide of the same metal react. It was analyzed in Refs. [1–8] for the system $ZnSO_4$–ZnS; for the system $PbSO_4$–PbS, see Refs. [9–12].

In Refs. [6–8, 10, 11], it was reported that the reactions in the analyzed systems run in a few successive stages, like those of the thermal decomposition of sulfates. The starting temperature for the reaction is close to the flash-point of the sulfide in question and is considerably lower than the starting point of the thermal dissociation of the sulfate. From the analysis of the material mentioned above, it is concluded that the rate

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of a chemical process in the system depends to a large extent on the molar ratio MSO_4:MS. An increase in the molar ratio MSO_4:MS impedes the process rate.

The system is more complex if the chemical reactions occur between sulfates and sulfides of different metals. Frents [4] believes that the reaction between $PbSO_4$ and ZnS takes place according to the scheme

$$2ZnS + 2PbSO_4 = 2PbS + ZnSO_4 + ZnO + SO_3 \qquad (1)$$

at temperatures over 860 K. This is not probable as it requires dissociation of the more stable sulfate ($PbSO_4$) and formation of the less durable $ZnSO_4$ by the oxidation of ZnS. In Ref. [12], which reports the results of the reaction between PbS and $ZnSO_4$, the formation of the phases ZnO and $PbSO_4$ is confirmed. The authors [12] suggest the following for the total reaction

$$PbS + 4ZnSO_4 = 4ZnO + PbSO_4 + 4SO_2 \qquad (2)$$

As mentioned above, in the presence of PbS, $ZnSO_4$ is decomposed and not formed.

In Refs. [13, 14], the authors analyze the effect of temperature and the molar ratio $PbSO_4$:ZnS upon the reaction rate. Based on the phase analysis of the products, they suggest that the process can be described by the following total equation

$$ZnS + 3/4\,PbSO_4 = ZnO + 3/4\,PbS + SO_2 \qquad (3)$$

In Refs. [8, 15], the results of the analysis of the contents of ^{35}S from $Zn^{35}S$ in the gaseous and sulfate phases showed that the reactions between $PbSO_4$ and ZnS cannot be presented by one stoichiometric equation only.

This paper is aimed at an exact analysis of the distribution of the sulfate and sulfate sulfur in both solid and gaseous products of the reaction. It is believed that it will provide better knowledge of the chemical processes occurring in the system under investigation.

2. Experimental

The tests were performed on the preparations obtained by mixing the pure ingredients, ZnS and $PbSO_4$, in different molar ratios. The measurements were executed in an inert gas atmosphere under linearly increasing temperature, as well as under isothermal conditions, using a TA-1 thermoanalyzer (Mettler).

Figs. 1 and 2 show typical thermograms for mixtures with various molar ratios of $PbSO_4$:ZnS. A deviation of the DTG curve from the baseline occurs at 803 K which denotes the initiation of the process. This temperature coincides with the starting point of oxidation of ZnS in air [8] and is about 230 K lower than the starting point of the thermal decomposition of $PbSO_4$ given earlier [6], as well as being about 300 K below that determined in Refs. [16, 17].

Up to 850 K, the process runs at a slow rate, corroborated by the slight change in mass with increasing temperature. Above 850 K, an increase in temperature brings about large changes in the mass. Over 1003 K, the DTA curve registers the appearance of a series of endothermic effects accompanied by weight losses. In Figs. 1 and 2, based upon the analysis of the course of the TG, DTG and DTA curves, it may be assumed

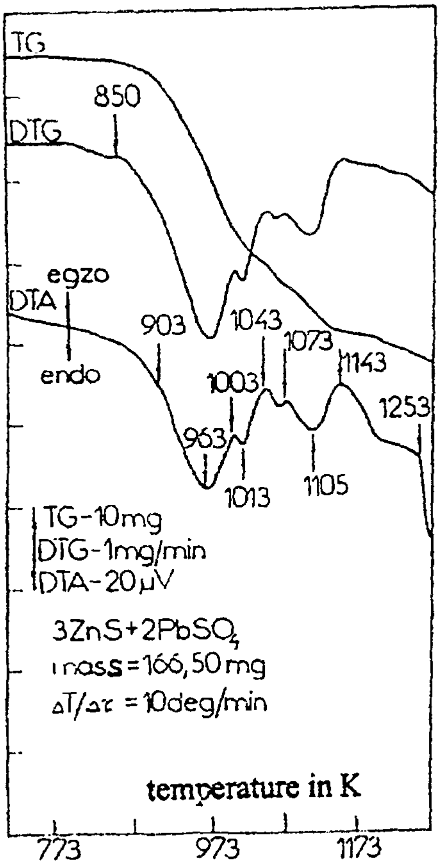

Fig. 1. Thermogram for the mixture $2PbSO_4 + 3ZnS$.

that the process ended at 1143 K. The presence of an appreciable endothermic effect at 1253 K corresponds to the melting of $PbO \cdot PbSO_4$. The appearance of a series of peaks on the DTG and DTA curves attests to the fact that during the interaction of $PbSO_4$ with ZnS, a series of chemical reactions occur at the same time. It would seem that the determination of the intermediate product species in this complex system is the main objective. Their respective effects upon the degree of transformation of zinc sulfide into its oxide are also of importance. This task was performed by carrying out experiments under isothermal conditions; however, the maximum temperature amounted to 948 K. The measurements were made with 1 g samples. These were heated up to the pre-set temperature at a rate of 25 K min^{-1}. The moment at which weight losses were first noted was considered the zero time and this is taken to be the point of reaching the pre-set temperature. The results, weight changes of respective mixtures at 923 K, are presented in Fig. 3. The largest weight losses for the specified processing time were registered for the preparation $PbSO_4 + ZnS$, whereas the smallest was for the $4PbSO_4 + ZnS$ mixture.

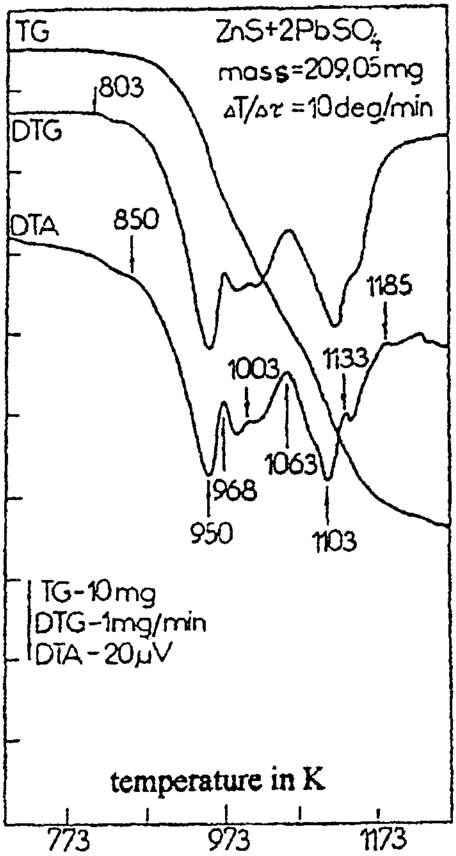

Fig. 2. Thermogram for the mixture $2PbSO_4 + ZnS$.

During the reaction, the preparations changed color from white to dark grey in strict relation with the molar ratio of $PbSO_4$:ZnS, as well as with the changes in the mass. The change in color during the reaction might point to formation of lead sulfide as the primary product. The X-ray phase analysis of the reacted mixtures, in which different degrees of weight losses were obtained, confirmed formation of ZnO and PbS, as well as the disappearance of the primary phases, namely $PbSO_4$ and ZnS. The analysis mentioned above also proved the existence of the phase $PbO \cdot PbSO_4$; its amount depended, however, on the type of preparation and the weight loss achieved in the isothermal test. The X-ray analysis results are collected in Table 1.

After reaction, the preparations were subjected to a more detailed chemical analysis, consisting of an additional determination of the lead present as oxide and sulfate via selective dissolution in ammonium acetate. The results are shown in Table 2. It must be stressed that the chemical composition of the reacted preparations depended only on the registered weight loss. Using the chemical analysis results together with the simultaneously obtained X-ray phase analysis data, the quantities of the respective

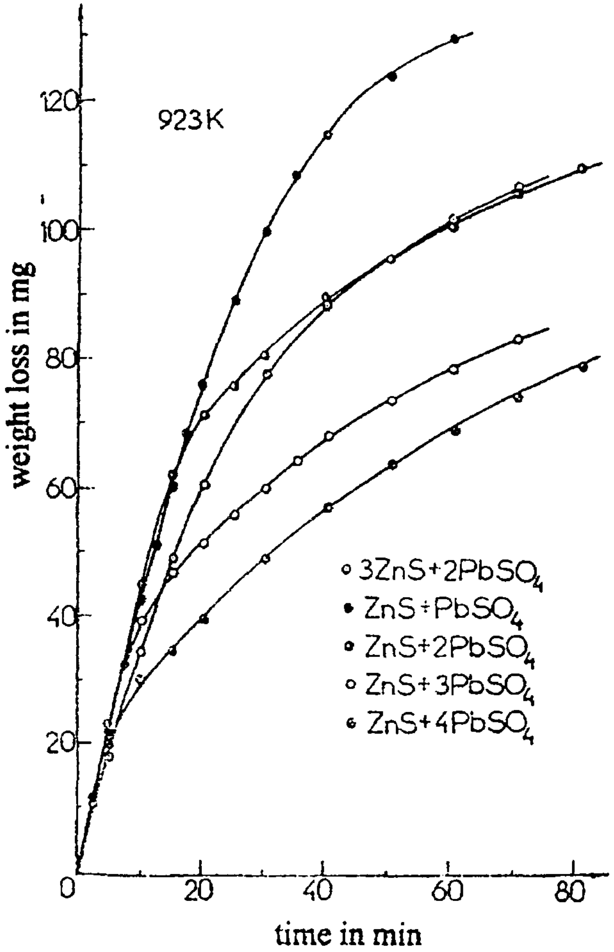

Fig. 3. Relation between weight loss and time of the reaction at 923 K.

phase ingredients in the preparations were found (Table 3). Following these calculations, a quantitative relation between the intermediate (appearing and disappearing) phase ingredients and the relative weight changes of the given preparation can be written. These results also prove that lead(II) oxide, an ingredient of $PbO \cdot PbSO_4$, occurs in all preparations, but its quantity depends on the molar ratio $PbSO_4:ZnS$ and on the relative weight loss. In the preparations having molar ratios of $PbSO_4:ZnS$ up to 2:3, the PbO quantities, irrespective of weight losses, are below 1%. For this reason, it could not be detected in the phase analysis. In the remaining preparations, a successive increase in PbO content with increasing weight losses during the process may be observed.

Formation of large amounts of $PbO \cdot PbSO_4$ is accompanied by increase in PbS content in the preparations. This is confirmed by the calculations made for the

Table 1
Results of the X-ray phase analysis

Preparation	Process temperature/K	Weight loss/%	Phases found
$2PbSO_4+3ZnS$	873	9.50	ZnO, ZnS, PbS, $PbSO_4$
	948	18.10	ZnO, PbS, ZnS, $PbSO_4^*$
$PbSO_4+ZnS$	873	10.10	ZnO, ZnS, PbS, $PbSO_4$
	948	15.18	ZnO, PbS
$2PbSO_4+ZnS$	898	10.32	ZnO, PbS, $PbSO_4$, $PbO \cdot PbSO_4^*$
$3PbSO_4+ZnS$	923	6.50	ZnO, PbS, $PbSO_4$, $PbO \cdot PbSO_4^*$
	948	9.62	ZnO, PbS, $PbSO_4$, $PbO \cdot PbSO_4$
$4PbSO_4+ZnS$	898	4.50	ZnO, PbS, $PbSO_4$, $PbO \cdot PbSO_4^*$
	948	9.96	ZnO, PbS, $PbSO_4$, $PbO \cdot PbSO_4$

Weight loss % = 100 × (weight loss/maximum weight loss).

Table 2
Results of the chemical analysis of the reacted preparations

Preparation	Relative weight loss/%	Contents of ingredients/%				
		Zn	Pb	Pb in $PbO+PbSO_4$	S	$S_{SO_4^{2-}}$
$PbSO_4+2ZnS$	9.00	28.60	45.40	19.40	16.32	2.97
-	16.60	31.20	49.50	2.40	13.25	0.36
$2PbSO_4+3ZnS$	9.50	24.00	50.75	24.85	14.33	3.80
	16.40	26.05	52.40	7.30	11.25	1.10
	18.50	26.71	56.80	1.45	10.15	0.12
$PbSO_4+ZnS$	10.10	18.30	57.40	29.82	12.30	4.55
	15.82	19.37	61.11	16.60	9.48	2.35
	16.46	19.80	61.90	15.90	9.25	2.10
$2PbSO_4+ZnS$	6.36	10.05	62.50	47.32	11.25	7.25
	8.10	10.25	63.70	44.73	10.34	6.60
	10.30	10.30	65.15	44.41	9.48	6.18
$3PbSO_4+ZnS$	3.20	6.80	63.45	55.85	11.05	8.30
	6.60	7.10	65.92	52.37	10.15	7.65
	9.50	7.36	67.87	56.56	8.64	6.56
$4PbSO_4+ZnS$	2.50	5.25	64.30	58.65	10.90	8.63
	5.10	5.40	66.45	53.85	9.86	7.70
	10.00	5.60	69.74	62.50	8.02	6.82

Table 3
Phase composition of the products deduced from the chemical analysis results

Preparation	Relative weight loss/%	Contents of phase ingredients/%				
		ZnO	ZnS	PbS	$PbSO_4$	PbO
$PbSO_4+2ZnS$	9.00	11.84	28.43	30.01	28.14	0.18
	16.60	24.54	17.10	54.37	3.41	0.07
$2PbSO_4+3ZnS$	9.50	13.27	19.87	29.90	36.00	0.27
	16.40	24.31	9.71	52.06	10.42	0.19
	18.50	29.49	4.50	63.90	1.14	0.72
$PbSO_4+ZnS$	10.10	13.90	10.62	31.84	43.11	0.39
	15.82	23.17	1.01	51.38	22.27	1.49
	16.46	24.52	0.15	53.10	19.90	2.48
$2PbSO_4+ZnS$	6.36	8.29	5.05	17.52	68.69	0.41
	8.10	10.70	2.46	21.90	62.53	2.15
	10.30	12.57	0.30	23.94	58.56	4.73
$3PbSO_4+ZnS$	3.20	4.44	4.81	8.77	78.64	2.27
	6.60	7.79	1.25	15.64	72.48	3.06
	9.50	8.33	1.00	13.06	62.16	15.17
$4PbSO_4+ZnS$	2.50	3.00	4.23	6.58	81.73	2.98
	5.10	6.16	0.67	14.54	72.96	4.30
	10.00	6.77	0.24	8.36	64.62	19.76

$3PbSO_4+ZnS$ and $4PbSO_4+ZnS$ mixtures in which the relative weight change amounted to about 10%. This implies that at low ZnS contents the dominating process is the reaction between lead(II) sulfide, coming into existence as the first phase, and lead(II) sulfate present in excess. As a consequence of this reaction, the intermediate product $PbO \cdot PbSO_4$ [10–12, 18, 19] appears. Then, a system of a different quality emerges in which the reactions occurring between $PbSO_4$ and ZnS play no significant role.

The results obtained and the calculations made regarding the phase composition of the reacted preparations prove that, during the first stage, transformation of ZnS into ZnO with simultaneous formation of PbS and PbO takes place. However, there is no information about reactions that result in the determined products.

This information can be obtained by radiomarking, which enables a quantitative determination of the partition into gaseous and solid products of the isotope ^{35}S introduced into one ingredient of the system. This being a well-established and reliable method, it was decided that ^{35}S would be an ingredient of zinc sulfide. The principles of this measurement method and the procedure for obtaining pure $Zn^{35}S$ were discussed in Ref. [8].

The tests were made with some mixtures in which the mole fraction of ZnS in $PbSO_4+ZnS$ changed from 0.2 to 0.8. The ^{35}S contents in the gaseous and solid phases, as the sulfate sulfur, were calculated from measurements of the activity of a preparation tested [8]. In order to find the ^{35}S level in the gaseous phase, it was passed through a system of washers filled with a solution of hydrogen peroxide. After a suitable weight loss, the process was interrupted and the system was accurately cleansed with a gas for securing full absorption of the evolved gases containing ^{35}S as SO_2. By adding barium chloride, barium sulfate was precipitated from the solution. The ^{35}S level was then determined in this sulfate. To determine the level in the sulfate phase in the reaction products, the latter were treated with hot water or sodium carbonate to dissolve the sulfates; barium sulfate was precipitated from the solution so as to find the ^{35}S level in it.

The results at 923 and 973 K, given in Tables 4 and 5, represent the average ^{35}S contents in the gaseous and sulfate phases corresponding to the determined weight change. It can be concluded that the ^{35}S level in the products depends on the molar ratio of $PbSO_4$:ZnS, the process temperature, and the relative weight loss. A higher $PbSO_4$:ZnS ratio causes a decrease in ^{35}S contents in the gaseous phase and an increase thereof in the condensed sulfate phase.

While analyzing the ^{35}S levels in the products in relation to temperature, it can also be concluded that a higher process temperature favors an increase in the ^{35}S content in the gaseous phase and its decrease in the solid sulfate. These differences amount to a few percent of the approximate weight loss for the preparation given.

The ^{35}S level distribution in the gaseous and sulfate phases supports the view that a series of reactions whose rates drop during the process, take place. A large influence upon the reactions rates is also exerted by the molar ratio $PbSO_4$:ZnS.

3. Discussion of the results

Some tests performed under isothermal conditions showed that an increase in the relative weight loss is accompanied by a simultaneous decrease in the contents of ZnS

Table 4
^{35}S isotope level in the reacted products from the experiment at 923 K

Preparation	Mass/mg	Relative weight loss/%	^{35}S contents/%	
			Gaseous phase	Solid phase
$PbSO_4+4ZnS$	2065	6.29	59	–
	2020	12.11	57	35
$PbSO_4+2ZnS$	1470	8.15	56	9
	1500	16.63	55	30
$2PbSO_4+3ZnS$	1334	9.37	51	10
	1340	18.36	50	26
$PbSO_4+ZnS$	1562	8.00	46	8
	1555	15.68	44	20
$2PbSO_4+ZnS$	2660	4.13	36	6
	2670	8.65	34	15
$3PbSO_4+ZnS$	3477	3.16	32	5
	3480	6.32	28	12
$4PbSO_4+ZnS$	5166	2.52	30	4
	1170	4.64	27	10

Table 5
^{35}S isotope level in the reacted products from the experiment at 973 K

Preparation	Mass/mg	Relative weight loss/%	^{35}S contents/%	
			Gaseous phase	Solid phase
$PbSO_4 + 4ZnS$	2065	6.05	79	5
	3105	11.59	75	32
$PbSO_4 + 2.77ZnS$	1706	6.74	71	5
	1710	14.44	68	30
$PbSO_4 + 2ZnS$	1437	8.56	64	8
	1440	17.22	58	22
$2PbSO_4 + 3ZnS$	1350	11.33	57	8
	1332	17.04	56	20
$PbSO_4 + ZnS$	1120	12.26	49	6
	1120	15.89	46	13
$2PbSO_4 + ZnS$	2086	4.70	39	5
	2190	9.04	33	11
$3PbSO_4 + ZnS$	3512	3.05	36	4
	3520	6.44	32	9
	1498	8.54	28	–
	1498	14.55	22	
$4PbSO_4 + ZnS$	5286	2.53	31	2
	5280	4.37	30	7
	2580	4.64	30	8
	1562	10.54	20	–

and $PbSO_4$ and formation of PbS and ZnO. The calculation of the phase compositions of the reacted preparations suggested (based on the chemical analysis results) simultaneous formation of the phase $PbO \cdot PbSO_4$, the amount of which depended on the composition of the preparations, as well as on the relative mass changes (Table 3).

The results of experiments carried out via the radiomarking method proved that the ^{35}S, from $Zn^{35}S$ is present in the gaseous and sulfate phases. From the isotope values and the results of the chemical analysis, calculations of the distribution of ^{35}S and $S_{SO_4^{2-}}$ in respective products were performed.

The calculated values collected in Tables 6–8 indicate a decrease in the ^{35}S level in the gaseous phase as the molar ratio $PbSO_4 : ZnS$ is increased. The transfer degree of ^{35}S and $S_{SO_4^{2-}}$ into the gaseous phase is of variable character.

The transfer degree of ^{35}S into PbS was also of variable character. It depended on mass changes and the molar ratio $PbSO_4 : ZnS$. The transfer degree of $S_{SO_4^{2-}}$ into PbS showed a decreasing tendency with increasing molar ratios (Tables 7 and 8).

The ^{35}S level in the sulfate phase requires further discussion. The calculation results prove that in the preparations in which the molar ratio $PbSO_4 : ZnS$ does not exceed 1 : 1, a low value of the index is computed for a high ^{35}S level in the sulfate phase. This arises from a low level of sulfate sulfur in the after-reaction mixtures. Moreover, a decrease in the transfer degree into the sulfate phase with increasing weight loss is observed.

Table 6
Average ^{35}S level in the gaseous phase in relation to changes in the mass of the mixtures

Preparation	Process temperature 923 K		Process temperature 973 K	
	Relative weight loss range/%	Average ^{35}S contents/%	Relative weight loss range/%	Average ^{35}S contents/%
$PbSO_4+4Zn^{35}S$	0–6.29	59	0–6.05	79
	6.29–12.11	55	6.05–11.59	71
$PbSO_4+2.77Zn^{35}S$	–	–	0–6.74	71
	–	–	6.74–14.44	65
$PbSO_4+2Zn^{35}S$	0–8.15	56	0–8.56	64
	8.15–16.63	54	8.56–17.22	52
$2PbSO_4+3Zn^{35}S$	0–9.37	51	0–11.33	57
	9.37–18.36	49	11.33–17.04	54
$PbSO_4+Zn^{35}S$	0–8.0	46	0–12.26	49
	8.0–15.68	42	12.26–15.86	36
$2PbSO_4+Zn^{35}S$	0–4.13	36	0–4.70	39
	4.13–8.65	32	4.70–9.04	26.5
$3PbSO_4+Zn^{35}S$	0–3.16	32	0–3.05	36
	3.16–6.32	24	3.05–6.44	28
	–	–	6.44–8.54	15.7
	–	–	8.54–14.55	13.5
$4PbSO_4+Zn^{35}S$	0–2.52	30	0–2.53	31
	2.52–4.64	23	2.53–4.64	29
	–	–	4.64–10.54	12.1

Table 7
Distribution of ^{35}S and $S_{SO_4^{2-}}$ in the products from the experiments at 923 K

Preparation	Relative weight loss/%	Distribution of ^{35}S in the products/%				Distribution of $S_{SO_4^{2-}}$ in the products/%		
		Gaseous phase	ZnS	PbS	$PbSO_4$	Gaseous phase	PbS	$PbSO_4$
$PbSO_4+2ZnS$	9.00	19.55	66.07	12.61	2.33	31.00	31.62	37.38
	16.60	35.52	34.71	27.95	0.70	58.18	38.55	3.27
$2PbSO_4+3ZnS$	9.50	22.84	55.75	18.77	3.24	33.02	23.08	43.90
	16.40	38.77	25.19	33.10	1.91	56.99	32.82	10.18
$PbSO_4+ZnS$	10.10	28.25	38.91	28.25	5.58	34.80	19.47	45.73
	15.82	43.12	3.47	47.57	5.96	55.65	24.49	19.85
$2PbSO_4+ZnS$	6.36	24.17	21.98	28.13	15.60	22.86	10.11	67.03
	8.10	30.37	16.26	32.44	18.66	29.32	13.36	57.32
$3PbSO_4+ZnS$	3.20	15.99	47.96	11.28	12.54	11.47	8.21	80.31
	6.60	28.86	11.91	35.44	26.96	25.01	8.80	66.19
$4PbSO_4+ZnS$	2.50	15.24	54.88	3.66	13.82	9.01	7.72	83.21

Table 8
Distribution of ^{35}S and $S_{SO_4^{2-}}$ in the products from the experiments at 973 K

Preparation	Relative weight loss/%	Distribution of ^{35}S in the products/%				Distribution of $S_{SO_4^{2-}}$ in the products/%		
		Gaseous phase	ZnS	PbS	$PbSO_4$	Gaseous phase	PbS	$PbSO_4$
$PbSO_4+2ZnS$	9.00	22.21	66.15	10.46	1.89	35.64	35.98	38.31
	16.60	37.60	34.71	26.08	0.49	54.01	42.29	3.69
$2PbSO_4+3ZnS$	9.50	25.57	55.75	17.17	2.17	28.97	25.53	45.53
	16.40	43.68	25.19	29.62	1.60	50.64	38.72	10.64
$PbSO_4+ZnS$	10.10	30.61	38.91	27.82	2.53	32.29	19.91	47.80
	15.82	45.10	3.47	47.34	3.22	53.64	24.75	21.61
$2PbSO_4+ZnS$	6.36	25.05	21.98	31.65	10.44	22.42	8.24	69.34
	8.10	30.11	16.26	37.80	13.41	29.45	10.66	59.89
$3PbSO_4+ZnS$	3.20	17.87	47.96	11.60	10.66	10.84	8.10	81.05
	6.60	19.43	11.91	47.96	20.06	27.16	4.42	68.42
$4PbSO_4+ZnS$	2.50	15.85	54.88	10.57	6.91	8.86	6.28	84.86

Analyzing the results obtained, it is necessary to allow for error resulting from the difference in the ^{35}S level in the preparations considered to be 100% and the sum of the ^{35}S amounts in the phases examined. In the extreme cases, this difference is below $-12.4+3\%$ of the sulfide sulfur. Assuming that in the calculations the sulfate sulfur was totally balanced, the difference appearing here should be referred to the total sulfur level in the preparations. The balance error then lies within the limits of $-3.7+0.7\%$ of the total sulfur.

The transfer degree of ^{35}S and $S_{SO_4^{2-}}$ into the gaseous phase depends on the molar ratio $PbSO_4$:ZnS, the process temperature and the relative weight loss (%) of the mixtures. From the data collected in Tables 6–8, the ^{35}S and $S_{SO_4^{2-}}$ levels in the gaseous phase and their transfer degree into this phase, for any preparation given, depend on the transformation degree of zinc sulfide into its oxide. In order that the error be as small as possible, the analysis was carried out for a weight loss that corresponded to a constant transformation degree of zinc sulfide into its oxide. The results for 973 K are shown in Fig. 4. The course of the plots proves that increasing the ZnS molar fraction in ($PbSO_4$ + ZnS) gives an increase, then a decrease in the transfer degree of ^{35}S and $S_{SO_4^{2-}}$ into the gaseous phase. The point of intersection of the straight line plots coincides with the molar fraction in ($PbSO_4$ + ZnS) equal to 0.57. It is constant and does not depend on the temperature of the process and the relative mass change. It corresponds to the ZnS molar fraction in ($PbSO_4$ + ZnS) according to the stoichiometric expression

$$ZnS + \tfrac{3}{4}PbSO_4 = ZnO + \tfrac{3}{4}PbS + SO_2 \qquad (4)$$

From the results of the radiomarking experiment, the process occurring between $PbSO_4$ and ZnS was analyzed. If in the system mentioned only reaction (4) took place, then the gaseous phase ought to contain 100% of the ZnS sulfur irrespective of the molar ratio $PbSO_4$:ZnS. Transfer of ^{35}S into lead sulfide and sulfate was not apparent

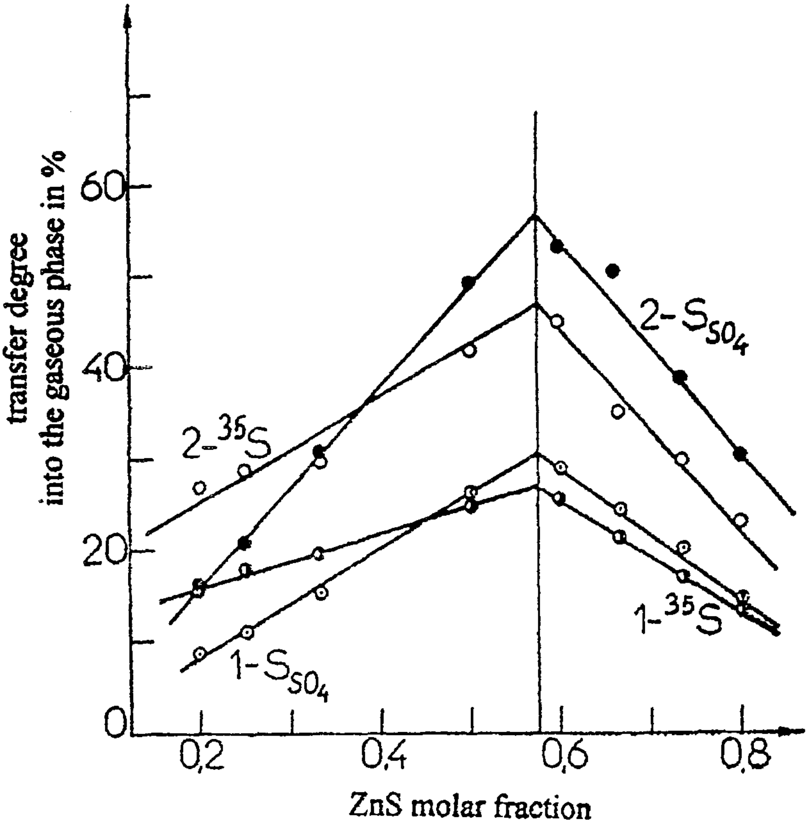

Fig. 4. Transfer degree of ^{35}S and $S_{SO_4^{2-}}$ into the gaseous phase versus the ZnS molar fraction in $PbSO_4 + ZnS$ at 973 K: 1, for a 50 % degree of conversion of ZnS into ZnO; 2, for a 90 % degree of conversion of ZnS into ZnO.

which means that the process in the system comprises many simultaneous reactions. It was assumed that, apart from reaction (4), the following also occur

$$2PbSO_4 = PbO \cdot PbSO_4 + SO_2 + \tfrac{1}{2}O_2 \quad (5)$$

$$PbO \cdot PbSO_4 + Zn^{35}S = Pb^{35}S + PbSO_4 + ZnO \quad (6)$$

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

$$2Pb^{35}S + \tfrac{7}{2}O_2 = PbO \cdot Pb^{35}SO_4 + {}^{35}SO_2 \quad (8)$$

$$Zn^{35}S + \tfrac{3}{2}O_2 = ZnO + {}^{35}SO_2 \quad (9)$$

Reactions (5), (7) and (8) may be combined to yield

$$7PbSO_4 + PbS = 4(PbO \cdot PbSO_4) + 4SO_2 \quad (10)$$

$$14PbSO_4 + 2Pb^{35}S = 7(PbO \cdot PbSO_4) + PbO \cdot Pb^{35}SO_4 + 7SO_2 + {}^{35}SO_2 \quad (11)$$

Should only reactions (5) and (6), as well as (9), occur in the system tested, the ^{35}S level in the gaseous phase calculated based on the oxygen balance, would amount to 25%. The sulfur ^{35}S should not occur in the sulfate phase. Transfer of ^{35}S to the sulphate phase takes place during oxidation of PbS [20]. The results in Refs. [10–12] prove some possibilities of a reaction between $PbSO_4$ and PbS. Those reactions decrease the ^{35}S level in the gaseous phase. The appearance of ^{35}S in the sulfate phase attests to the fact that during the reaction a secondary phase containing lead sulfate is formed. The stoichiometric equations for reactions (10) and (11) indicate formation of $PbO \cdot PbSO_4$. An absence or a small amount of this compound is attributed to reaction (6). This has been tested and the results are reported in Ref. [8].

The results obtained show that during the reaction between $PbSO_4$ and ZnS, a decisive role in the transformation process ZnS → ZnO is played by reactions (4) and (6), and indirectly by (10) and (11). For a high ^{35}S level in the gaseous phase, reaction (4) plays an important role even after formation of the reaction products, which prevents direct contact between the reacting phases. It is also corroborated by an increase in ^{35}S-free PbS content. In the course of the process, the rate of this reaction decreases and this results in a change in the ^{35}S level in the gaseous phase.

4. Conclusions

Interaction in the system $PbSO_4$–ZnS starts at a temperature close to the flash point of zinc sulfide. It is 260–300 K below the temperature of thermal dissociation of lead(II) sulfate. First of all, a conversion of zinc sulfide into its oxide takes place, as well as PbS and $PbO \cdot PbSO_4$ being formed.

Radiomarking experiments showed that the sulfur level in the gaseous phase (as SO_2) and coming from zinc sulfate depends on the molar ratio $PbSO_4$:ZnS, the relative weight loss, and the process temperature. The maximum degree of transfer of sulfide-sulfur and sulfate-sulfur to the gas phase was obtained for the molar ratio of 0.57.

It was found that during the reaction between $PbSO_4$ and ZnS, a series of chemical reactions takes place at the same time; these reactions are expressed by the stoichiometric equations (4)–(11). It was also proved that during the reaction a secondary lead(II) sulfate is formed, containing sulfur from ZnS.

The PbS formed on $PbSO_4$ grains by reaction (4) can lead to the product $PbO \cdot PbSO_4$ by reaction (10). Simultaneously, ZnS reacts with the appearing phase and eventually ZnO, PbS and $PbSO_4$ are formed. This explains the absence of larger amounts of the phase $PbO \cdot PbSO_4$ in the products in the presence of ZnS. During the process, the extent of reaction (4) diminishes and reactions (6), (10) and (11) begin to play a significant role.

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