Thermochimica Acta, 119 (1987) 329–336
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ANALYSIS OF THE CHEMICAL REACTION BETWEEN $PbSO_4$ AND PbS

CZESŁAW MALINOWSKI

Institute of Non-Ferrous Metals Metallurgy, Academy of Mining and Metallurgy, al. Mickiewicza 30, 30-059 Kraków (Poland)

(Received 20 February 1987)

ABSTRACT

The chemical reaction between $PbSO_4$ and PbS at different mole ratios has been studied. The multistage character of this reaction has been established. It has been found that the starting temperature of the reaction is approximately 250 °C lower than the initial temperature of $PbSO_4$ decomposition. The reaction occurring at each stage has been proposed on the basis of phase and chemical analyses. It has been shown that metallic lead can be formed only by the reaction of PbO with PbS only. Therefore the popular statement that $PbSO_4$ combines with PbS to form metallic lead is false. The experimental results have shown that the higher the mole ratio of $PbSO_4$ to PbS the lower the reaction rate.

INTRODUCTION

The chemical reaction between lead sulphate ($PbSO_4$) and lead sulphide (PbS) is very important from the point of view of lead smelting. The first studies on this reaction were carried out in the first half of the twentieth century. They were limited mainly to the determination of the starting temperature as well as of the temperature at which the process proceeds rapidly. It has been shown that the reaction between $PbSO_4$ and PbS can be described by the equations

$$PbS + PbSO_4 = 2Pb + 2SO_2 \tag{1}$$

$$PbS + 3PbSO_4 = 4PbO + 4SO_2 \tag{2}$$

Further investigations [1,2] do not contain new relevant information because they concern the influence of temperature on the reaction rate only according to the stoichiometric reaction. These circumstances, as well as the lack of a theory of oxidation of metal sulphides have prompted the author to study this problem.

0040-6031/87/$03.50

EXPERIMENTAL

Preparations of various mole ratios of $PbSO_4$ to PbS from chemicals of reagent grade purity were used. The base materials, i.e. $PbSO_4$ and PbS were heated at a linearly increasing temperature in an argon atmosphere before mixing. The decomposition of $PbSO_4$ started at 1033 K, while a polymorphic change was observed at 1143 K. DTG and DTA curves showed that some compounds ($PbO \cdot PbSO_4$, $2PbO \cdot PbSO_4$ and $4PbO \cdot PbSO_4$) were formed on thermal dissociation in accordance with literature data. The thermogram obtained on heating PbS was surprising since it suggests some chemical reaction, while the chemical properties of PbS suggest the occurrence of the sublimation process only. Phase and chemical analyses have shown some $PbSO_4$ content in PbS. This content has been taken into account in the preparation of mixtures of assumed $PbSO_4$ to PbS mole ratio. These mixtures were studied at a linearly increasing temperature as well as at constant temperature.

A typical thermogram of a $3PbSO_4$ + PbS mixture is presented in Fig. 1. The shapes of TG, DTG and DTA curves show that the chemical reaction is multistage and that several intermediate products are formed. Thermograms of mixtures of different mole ratios are similar to the one presented. The starting temperature of the chemical reaction of $PbSO_4$ with PbS has been

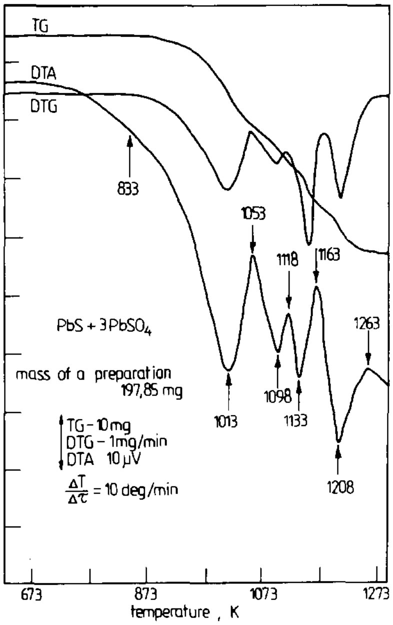

Fig. 1. Thermogram of (PbS + $3PbSO_4$) mixture.

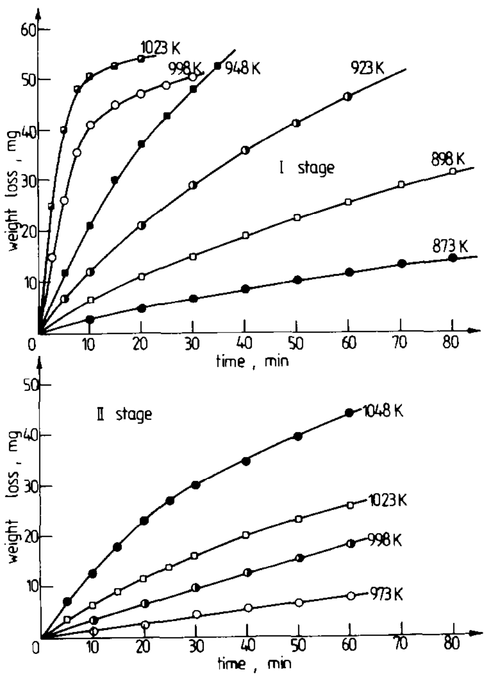

Fig. 2. The mass reduction of ($PbS + 3PbSO_4$) mixture vs. time in stages I and II of reaction at different temperatures.

determined. It was found that it is approximately 250° lower than the starting temperature of $PbSO_4$ decomposition [3].

Isothermal studies have been carried out to identify the products of each stage of the reaction. Mixtures were heated to the desired temperature at a rate of 25° min^{-1}. The temperatures of the isothermal studies were chosen on the basis of the analysis results at a linearly increasing temperature, and the necessity of selective reaction at every stage was taken into account.

TABLE 1

Chemical analysis of the products of stages I and II of the reaction

Mixture	Reaction stage	Content (wt.%)			
		Pb_{total}	$Pb_{(PbO+PbSO_4)}$	S_S	$S_{(SO_4^{2-})}$
$2PbSO_4 + PbS$	I	80.08	60.20	3.06	4.67
$3PbSO_4 + PbS$	I	78.83	67.10	1.82	5.35
$4PbSO_4 + PbS$	I	78.33	70.64	1.20	5.62
$2PbSO_4 + PbS$	II	83.70	60.05	2.88	2.84
$3PbSO_4 + PbS$	II	84.46	72.44	0.91	3.40
$4PbSO_4 + PbS$	II	84.40	74.60	0.25	3.50

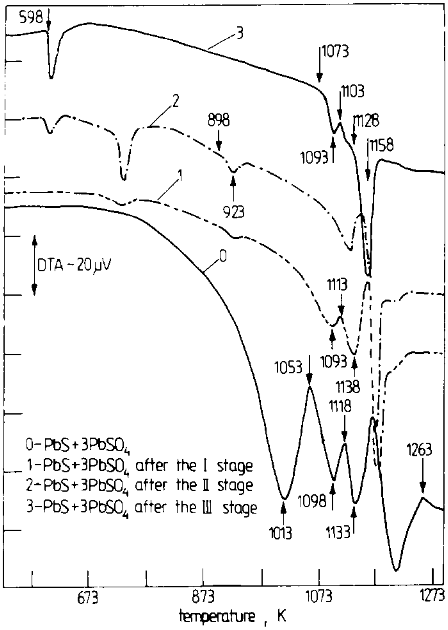

Fig. 3. Comparison of DTA curves of ($PbS + 3PbSO_4$) mixture: curve 0, initial; curve 1, after stage I; curve 2, after stage II; curve 3, after stage III.

The mass reduction of the $3PbSO_4$ + PbS mixture vs. time and temperature is presented in Fig. 2. A significant influence of temperature on the chemical reaction rate is observed. A decrease in the mass reduction rate after reaching a certain reduction level, especially at high temperatures, was also observed. It makes possible the selective investigation of each stage of the reaction. The sequence of phase formation during the chemical reaction has been studied. The products of one stage were used as substrates for reaction rate studies in the next stage. The chemical composition of the products of stages I and II of the reaction is presented in Table 1. Some metallic lead was found in the products of stage II of the reaction. This fact has made the investigation of further stages impossible because of the inhomogeneity of the mixture and the possibility of significant errors. Typical DTA graphs of the products after stages I, II and III are presented in Fig. 3.

DISCUSSION

An attempt to determine the conversion dependence on the time and on the $PbSO_4$ to PbS mole ratio was carried out on the basis of the mass reduction of mixtures as well as the phase and chemical analyses of products. The direction of the chemical reaction in every stage has been assumed, taking into account some published data [4–6].

The following reactions have been assumed in stage I:

$$2PbSO_4 = PbO \cdot PbSO_4 + SO_2 + 1/2O_2 \quad (3)$$

$$2PbS + 7/2O_2 = PbO \cdot PbSO_4 + SO_2 \quad (4)$$

Stage II of the reaction is the decomposition of basic lead sulphate and the oxidation of excess PbS, according to the scheme

$$2(PbO \cdot PbSO_4) = PbO + 2PbO \cdot PbSO_4 + SO_2 + 1/2O_2 \quad (5)$$

$$2PbS + 7/2O_2 = PbO \cdot PbSO_4 + SO_2 \quad (6)$$

The theoretical composition of the products of stages I and II was calculated on the basis of the assumed reaction scheme. The calculated results are presented in Table 2. Very good conformity of the calculated chemical composition of the products of stages I and II with the results of chemical analyses (Table 1) is observed. Some discrepancies in the compared values occur after stage II, especially in the case of lead content in the form of ($PbO + PbSO_4$). It has been caused, according to thermogravimetric analysis (Fig. 3), by metallic lead formation owing to the reaction of PbO and PbS:

$$2PbO + PbS = 3Pb + SO_2 \quad (7)$$

The phase composition of the products was calculated on the basis of the results of chemical analyses and compared with that calculated theoretically. The composition calculated theoretically is presented in Table 3. The amount of metallic lead was calculated by subtraction of the amount of lead combined in the form of PbO + $PbSO_4$ and PbS from the total lead content. PbS and $PbSO_4$ amounts were calculated on the basis of the sulphide and sulphate sulphur content. The lead balance after stage I is more precise, with an error of ±0.1%. The chemical analysis seems to be correct as the total content of components is higher than 99%.

TABLE 2

Theoretical composition of the products of stages I and II of the reaction

Mixture	Reaction stage	Content (wt.%)				Mass reduction (%)
		Pb_{total}	$Pb_{(PbO+PbSO_4)}$	S_S	$S_{(SO_4^{2-})}$	
$2PbSO_4 + PbS$	I	80.47	61.31	2.96	4.73	8.65
$3PbSO_4 + PbS$	I	79.76	68.37	1.76	5.28	9.55
$4PbSO_4 + PbS$	I	79.34	71.78	1.05	5.60	10.07
$2PbSO_4 + PbS$	II	85.07	69.44	2.86	2.41	5.41
$3PbSO_4 + PbS$	II	84.88	77.95	1.07	3.21	6.03
$4PbSO_4 + PbS$	II	84.77	83.03	0.27	3.42	6.40

TABLE 3

Phase composition of different mixtures after stages I and II of reaction

Mixture	Reaction stage	Content (wt.%)				Total content of components (%)	$Pb_{(PbO)}$: $Pb_{(PbSO_4)}$
		PbO	$PbSO_4$	PbS	Pb_{met}		
$2PbSO_4 + PbS$	I	32.27	44.25	22.87	—	99.46	0.99
$3PbSO_4 + PbS$	I	34.97	50.69	13.60	—	99.26	0.94
$4PbSO_4 + PbS$	I	36.89	53.25	8.97	—	99.11	0.94
$2PbSO_4 + PbS$	II	44.88	26.91	21.53	5.00	98.32	2.27
$3PbSO_4 + PbS$	II	54.32	32.21	6.80	6.13	99.46	2.29
$4PbSO_4 + PbS$	II	55.95	33.16	1.87	8.18	99.16	2.29

The ratio of lead in the form of oxide to that in the form of sulphate ($Pb_{(PbO)} : Pb_{(PbSO_4)}$) has also been calculated. It should be equal to unity after stage I of the reaction and 2.75 after stage II according to theoretical calculations. However, chemical analysis has shown that this ratio is approximately unity after stage I and much lower than 2.75 after stage II. It seems to confirm the reaction of PbO with PbS. It has been assumed, on the basis of calculations carried out and the conformity of chemical and phase analyses with theoretical considerations, that the assumed course of the reaction in stages I and II is correct.

Next, the conversion has been calculated as the ratio of the mass reduction observed to that calculated. Conversion at 923 K is presented in Fig. 4.

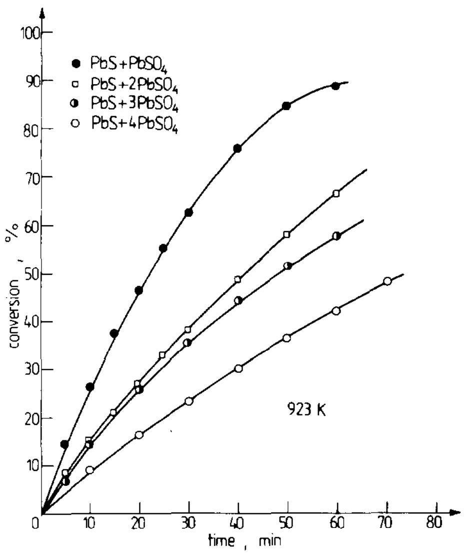

Fig. 4. Influence of $PbSO_4$: PbS mole ratio on the conversion in stage I of reaction at 923 K.

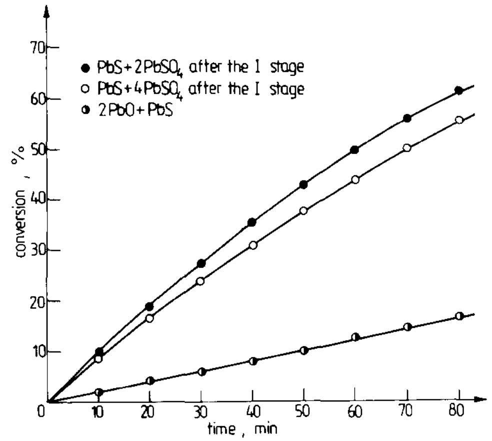

Fig. 5. Influence of $PbSO_4$: PbS mole ratio and of the 2PbO + PbS reaction on the conversion in stage II at 1023 K.

It can be concluded that the higher the $PbSO_4$ to PbS ratio, the lower the conversion. The temperature dependence of the conversion can be observed in Fig. 2.

Kinetic curves of different specimens are presented in Fig. 5. A comparison of the kinetics of reactions PbS + $2PbSO_4$ and PbS + $4PbSO_4$ with that of 2PbO + PbS leads to the conclusion that the latter reaction can be very important in the process studied and can influence the chemical composition of the products.

CONCLUSIONS

The thermogravimetric studies lead to the following conclusions.

(1) It has been shown that the chemical reaction between $PbSO_4$ and PbS is multistage. The final product of stage I of the reaction is $PbO \cdot PbSO_4$, while those of stage II are $2PbO \cdot PbSO_4$ and PbO, at all $PbSO_4$ to PbS mole ratios. Simultaneously with the $PbSO_4$ decomposition, the equivalent PbS oxidation to basic lead sulphate occurs.

(2) The $PbSO_4$ to PbS mole ratio has a great influence on the reaction rate, especially in stage I of the reaction: the higher the mole ratio, the lower the reaction rate.

(3) Metallic lead can be formed by the reaction of PbO with PbS only, so its formation is possible in stage II after PbO formation. Therefore the popular statement that $PbSO_4$ combines with PbS to form metallic lead is false, because this reaction is realized in some stages with basic lead sulphate formation.

REFERENCES

1 G.S. Frents, Okislenie Sulphidov Metallov, Izd. Nauka, Moscow, 1964.
2 V.D. Ponomarev, Izobrannye Trudy. Khimia i Tekhnologia Tyazholykh Tsvetnykh Metallov. AN Kaz. SSR. Inst. Metallurgii i Oboghashcheniya, Alma-Ata, 1975.
3 C. Malinowski, T. Karwan, K. Malinowska and K. Tarosinska, Prace Instytutu Metalurgii Metali Niezelaznych AGH, 1983–1984, unpublished results.
4 M. Bugajska and T. Karwan, Z. Nauk. AGH. Metalurgia i Odlewnictwo, 690, z. spec. 57 (1978) 77.
5 M. Bugajska and T. Karwan, Arch. Hutn., 24(2) (1979) 183.
6 H.W. Billhardt, J. Electrochem. Soc., 117(5) (1970) 690.