

MECHANISM AND KINETICS OF INORGANIC SULPHATES DECOMPOSITION

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Abstract

Thermal decomposition of different inorganic sulphates are presented. A number of techniques, but mainly TG and DTA, are used to prove the mechanism and kinetics of CaSO_4 , BaSO_4 , $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ under various gas atmospheres. It is shown how the partial pressure of gas components and heating rate may effect the mechanism and kinetic parameters. There are also examples on the effects of some additives and initial treatment on the thermal processes.

On the base of the results obtained some recommendations are given concerning the precautions to be taken into account in the thermal decomposition studies and the sulphur recovering.

Keywords: inorganic sulphates, kinetics, mechanism, thermodynamics

Introduction

The sulphates of Ca, Ba, Al, and Fe have been always a subject of study in respect of their thermo-chemical behaviour as many industrial productions are closely related to their derivation and decomposition [1, 2]. The scaling of big quantities of inorganic debris such as gypsum, barites, etc. leads to sulphur losses and disruption of the ecological balance. On the other hand this requires the development of some new technologies for their processing.

In the present article some results are presented from our analysis, related to the study of mechanism and kinetics of the thermal decomposition of CaSO_4 , BaSO_4 , $\text{Al}_2(\text{SO}_4)_3$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$.

Experimental

Various thermal analysis techniques have been used for the purpose of the study: TG and DTA examinations were made by derivatograph MOM (Hungary), model Q-1500D, with heating rate of 5 K min^{-1} . Zirconium crucibles with 8 mm diameter and 20 mm height, as well as platinum crucible of 8 mm diameter and 1 mm height were used for the test. The experiments were carried out on "Shimadzu-31H" thermal balance. The sample mass was 10 mg. Standard gas mixtures containing H_2 – 1–9 kPa and flow rate of 26 l h^{-1} were also used.

Samples of BaSO_4 , $\text{Al}_2(\text{SO}_4)_3$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ have been studied with characteristics – "chemically pure for analysis". CaSO_4 is produced from preliminary recrystallized phosphoritic (PG)-anhydride (PPG). The complete chemical content of the sulphates used, the conditions of their preliminary processing and the various physico-chemical methods used for characterization of the intermediate and end products of the thermal decomposition have been already described and presented in details in older publications [3–9].

Results and discussion

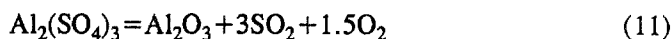
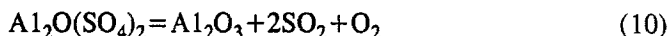
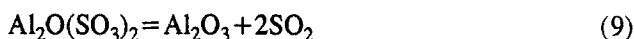
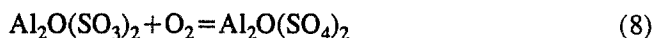
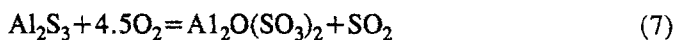
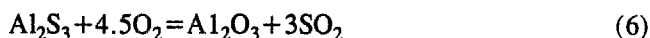
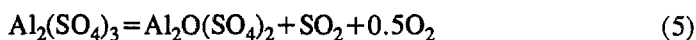
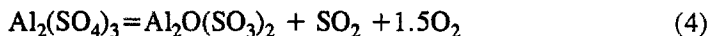
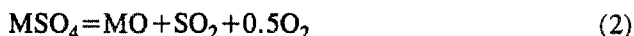
The common sulphate ion defines some general characteristics of the mechanism and the kinetics regularities. However, the different cations and the presence of crystallization water drastically change the conditions of the all possible reactions. As a result of this the mechanism and kinetics of the thermal decomposition processes are affected. Depending on the influence of the metal ion, respectively the stability of the sulphate, those processes are carried out at various temperatures: 1523 K for CaSO_4 and 1653 K – for BaSO_4 ; and at significantly lower temperatures for $\text{Al}_2(\text{SO}_4)_3$ (over 853 K) and for FeSO_4 (over 823 K) [2].

The need to develop clean effective technologies for utilization of larger quantities of waste PG and processing of barites has led in search of some new methods and options for reduction of the higher temperatures at which CaSO_4 and BaSO_4 are decomposed into end products with some consumer's profit, i.e. the respective sulphides [4–11].

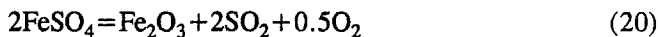
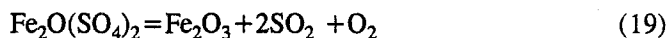
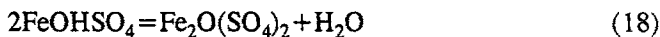
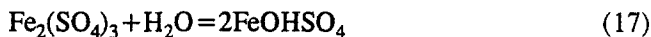
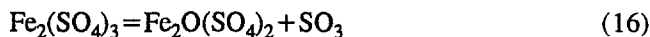
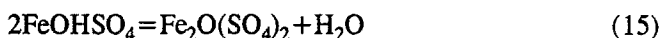
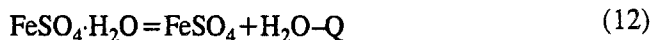
Mechanism the balance of the systems $\text{MSO}_4\text{--MS--MO}$ ($M=\text{Ca, Ba, Fe}$) and $\text{M}_2(\text{SO}_4)_3\text{--M}_2\text{S}_3\text{--M}_2\text{O}_3$ ($M=\text{Al}$) is defined by the influence of the partial pressures of the gaseous components – SO_x , O_2 , H_2O , H_2 , CO , etc. They drastically change the rate and the optimal temperatures of the reactions and it leads to obtaining one or more desirable products [2]. Many of the methods for identifying the thermally-stable inorganic sulphates (CaSO_4 and BaSO_4) [6, 7] are related to the possibility of using various gaseous reducers; with $\text{Al}_2(\text{SO}_4)_3$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ the presence of H_2O and O_2 might change the direction of the process which results in obtaining various intermediate sulphates [2]. Those changes in the mechanisms of the thermal decomposition are not traditional and are defined by the test conditions, but most of all – by the content of the gaseous environment [8, 9]. The production of intermediate sulphates by the thermal decomposition of $\text{Al}_2(\text{SO}_4)_3$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ is described also by Lorant [12], Gallagher [13], etc.

The curves of the thermodynamics of the systems $\text{MSO}_4\text{--MS--MO}$ ($M=\text{Ca, Ba, Fe}$) and $\text{M}_2(\text{SO}_4)_3\text{--M}_2\text{S}_3\text{--M}_2\text{O}_3$ ($M=\text{Al}$) are shown in Figs 1–4. On the phase Kellog-diagrams the areas of stability of the respective oxides, sulphides and sulphates are defined, according to the temperature, P_{SO_2} , P_{SO_3} , P_{O_2} and $P_{\text{H}_2\text{O}}$ for $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (Fig. 4). The temperature intervals show that MSO_3 is not in stable phase and because of this only the areas of MSO_4 , MS and MO are presented in the state's diagrams. The conditions for the calculations are the same as those described in [14].

For the phase diagrams of CaSO_4 and BaSO_4 (Figs 1, 2) the reactions 1–3 are definitive; for the $\text{Al}_2(\text{SO}_4)_3$ – those from 4 to 11:



The areas of stability of the separate phases of the thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ are defined mostly by the reactions (12–20):



CaS and BaS are stable products at relatively lower temperatures and partial O_2 pressures (P_{O_2} , 10^{-9} – 10^{-14} Pa). Lower values of P_{O_2} are normally reached with incomplete burning of natural gas when the reduce-acting components of the systems

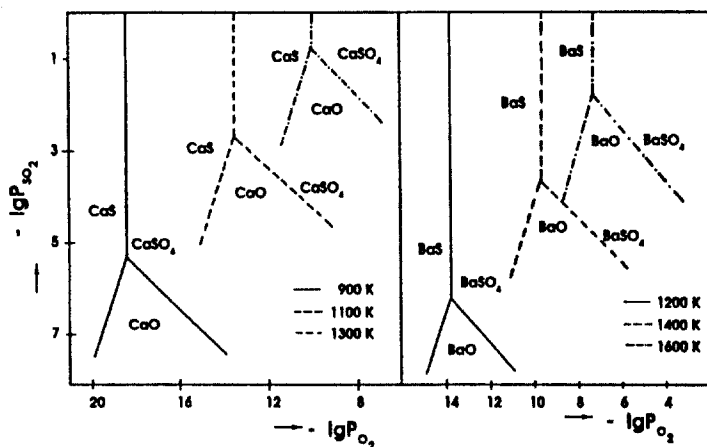


Fig. 1 Phase diagram of the system Ca-S-O and Ba-S-O

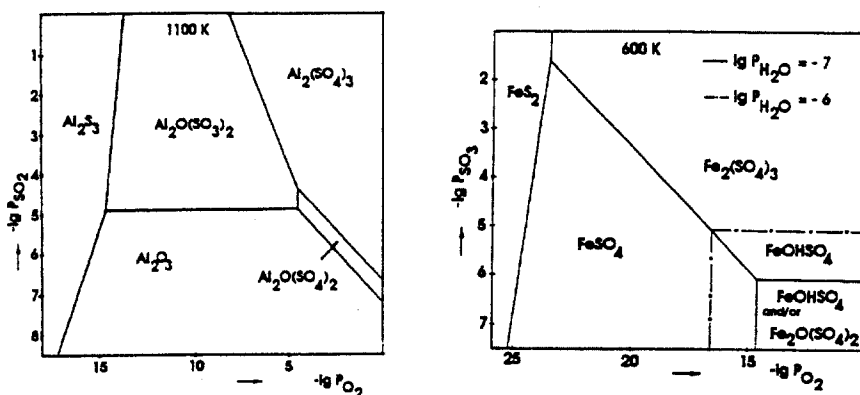


Fig. 2 Phase diagram of the system Al-S-O at $T=1100$ K and Fe-S-O at $T=600$ K

are H₂ and CO. On the other hand, the reduction of P_{O_2} leads to an increase of P_{S_2} (balanced). Obviously, with the P_{SO_2} and temperature increase, P_{S_2} in the gaseous phase will also be increasing. This we need to record when tests for reduction of CaSO₄ and BaSO₄ are being carried out. The partial pressure of O₂ is defined from the balance of the following reactions:



That's why the ratio H₂:H₂O and CO:CO₂ should be also taken into consideration when our goal is to obtain MS or MO during the thermal decomposition of MSO₄.

For $\text{Al}_2(\text{SO}_4)_3$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ the mechanism of the thermal processes is defined with the areas of existing intermediate sulphates – $\text{Al}_2\text{O}(\text{SO}_3)_2$ and/or $\text{Al}_2\text{O}(\text{SO}_4)_2$, FeOHSO_4 and/or $\text{Fe}_2\text{O}(\text{SO}_4)_2$ (Fig. 2). For the oxysulphates of Al the values of P_{O_2} and P_{SO_2} are also critical when we selectively guide the thermal decomposition to the desired intermediate product. Thus, the thermodynamic balance of $\text{Al}_2\text{O}(\text{SO}_3)_2$ is limited from $P_{\text{SO}_2} > 0.64$ Pa for $T=1100$ K; P_{O_2} can vary from 10^{-8} to 10.13 Pa. The stability field's limits of $\text{Al}_2\text{O}(\text{SO}_4)_2$ are defined from the narrow interval in which the values of P_{O_2} reach 10.13 Pa and those of P_{SO_2} vary from 10.13 Pa to 0.33 Pa.

Because of the effects of P_{O_2} , P_{SO_2} and $P_{\text{H}_2\text{O}}$ on the system's thermodynamic balance (Fig. 2) the most sophisticated of all happens to be the state diagram of the system Fe–S–O at 600 K. Depending on the values of $P_{\text{H}_2\text{O}}$ there is also a chance for production of FeOHSO_4 and/or $\text{Fe}_2\text{O}(\text{SO}_4)_2$. Only at $P_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}(\text{balanced})} = 10^{-2}$ Pa at $T=600$ K the stability fields of FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ coincide and this determines the chance of production of both products in balance with the other phases. At $P_{\text{H}_2\text{O}} > 10^{-2}$ Pa or $P_{\text{H}_2\text{O}} < 10^{-2}$ Pa for $T=600$ K thermodynamically stable becomes either $\text{Fe}_2\text{O}(\text{SO}_4)_2$ ($P_{\text{H}_2\text{O}} < 10^{-2}$ Pa) or FeOHSO_4 ($P_{\text{H}_2\text{O}} > 10^{-2}$ Pa).

The experimental studies on the thermal decomposition of BaSO_4 and CaSO_4 prove that by proper regulation of the gaseous components the processes can be carried out in optimal conditions, which the chemical mechanism corresponds to the formation of sulphides or oxide solid products only [5]. The chemical mechanism is more complicated with the presence of some admixtures or additives which might change the physical properties of the solid phase [5, 15].

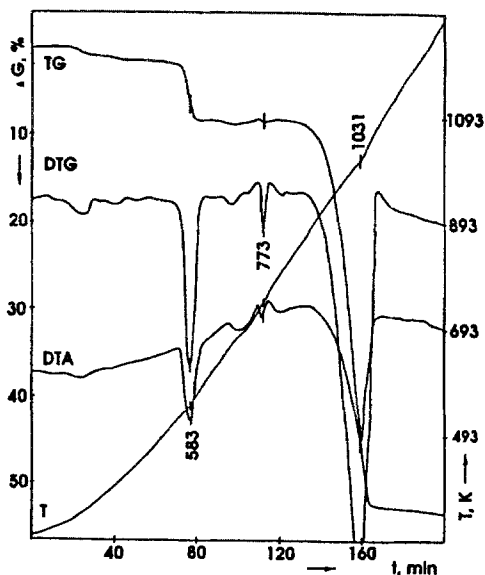


Fig. 3 TG, DTA, and DTG curves of the thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in oxidizing medium at $V=5$ K min^{-1}

The more complicated mechanism of the thermal decomposition of the Fe- and Al-sulphates is defined from the stability of other intermediate products in temperature intervals close (or partially identical) to those of the desulphurization process. Furthermore, the stability of some intermediate processes is in critical dependence even from very small changes of the partial pressures of the gaseous components. The inadequate evaluation of the influence on the oxi-reduction potential of the system and the partial pressure of the water vapours are the reasons for some different views about the mechanism of the thermal decomposition of Fe- and Al-sulphates

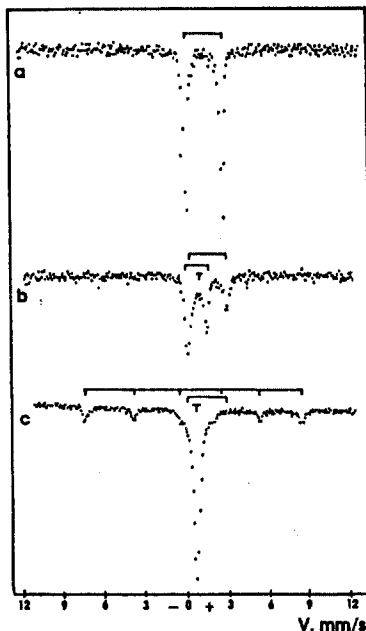


Fig. 4 Mössbauer spectra of the solid products from decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ at: a) initial product; b) $T=605$ K; c) $T=793$ K

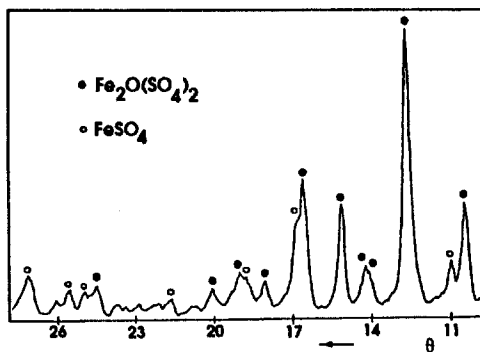


Fig. 5 X-ray pattern of the solid product from decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ at $T=793$ K and $V=5$ K min^{-1}

[16, 17]. According to Gallagher, Safuillin and Neto [13, 18, 19] the oxidation is a two-stage process with parallel dehydration of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and decomposition of FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$.

The TG, DTG and DTA curves of the thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in oxidation medium is shown in Fig. 3. In the temperature interval 545–645 K there are recorded 6.6% of mass, related to the dehydration of the main part of the crystallization water; in the temperature interval 823–1073 K the desulphurization of the sulphate takes place. The recorded lower mass losses (compared with the theoretical values) for the dehydration stage in the temperature interval 545–645 K, as well as the changes in the curve of DTA dependence in the interval 680–823 K are all related to the effect of overlapping one endothermal with one exothermal reactions. The change in the dependences is a base for examination of the intermediate products from the decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ at 605 and 793 K with Mössbauer spectroscopy and X-ray phase analysis (Figs 4, 5).

The data obtained from those analysis show that during dehydration of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ to FeSO_4 in the temperature range of 545–645 K there is a process of oxidation going on, related to the simultaneous production of FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$. The quantity of $\text{Fe}_2\text{O}(\text{SO}_4)_2$ is smaller and this is explained by the fact that during dehydration of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ probably PH_2O gets higher values compared with the balance ones. This defines FeOHSO_4 as the main phase in the temperature interval 545–645 K. With the increase of temperature up to 763–823 K, FeOHSO_4 becomes thermally unstable and decomposes to $\text{Fe}_2\text{O}(\text{SO}_4)_2$ – endothermal reaction. In parallel, there is a second oxidation stage of Fe^{2+} to Fe^{3+} , i.e. direct modification of FeSO_4 in $\text{Fe}_2\text{O}(\text{SO}_4)_2$ – exothermal reaction. The simultaneous progress of both reactions leads to both overlapping of effects of DTA dependence and com-

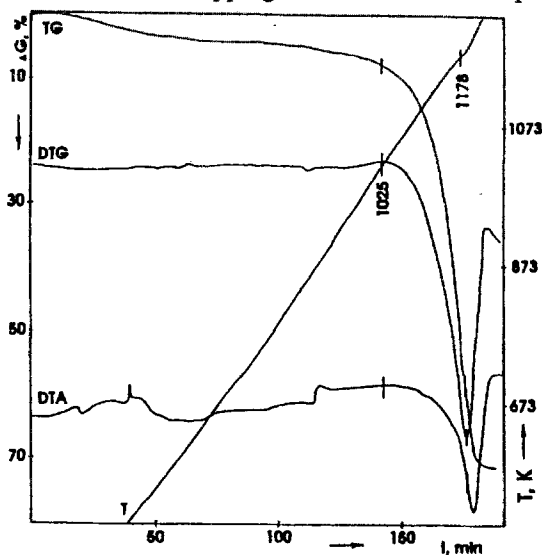


Fig. 6 TG, DTA, and DTG curves of $\text{Al}_2(\text{SO}_4)_3$, heating rate – 5 K min^{-1} ; atmosphere – hydrogen (5 kPa) + argon; weight of sample – 500 mg

compensation for the weight losses. Thus, at $T=823$ K the system's Fe is mainly presented as $\text{Fe}_2\text{O}(\text{SO}_4)_2$. Probably, it is thermally not so stable as FeSO_4 is, so the initial disintegration of its structure explains the presence of certain quantity of $\alpha\text{-Fe}_2\text{O}_3$ at T as low as 793 K (Fig. 4c).

The experimental data definitely shows that the quantity and thermal stability of FeOHSO_4 and $\text{Fe}_2\text{O}(\text{SO}_4)_2$ are defined not only by the temperature, but also by the ratio between the partial pressures of the gaseous components – water vapours and oxygen in the reaction tract. The production of only FeOHSO_4 , or only $\text{Fe}_2\text{O}(\text{SO}_4)_2$ obviously requires the backing of strictly defined test conditions such as temperature, P_{O_2} , $P_{\text{H}_2\text{O}}$, as well as their transport to and out of the system. Upon the obtained results it could be proposed the following process mechanism of the thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in oxidation gas medium: The dehydration with partial oxidation in the temperature interval 563–605 K is defined with reactions 18–20 and the intermediate oxidation at $T=683\text{--}800$ K – with reactions (12–15):

The desulphurization at $T=823\text{--}1073$ K is strictly related to the progress of reactions (19) and (20).

Firstly Lorant [12] points out that the mechanism of decomposition of $\text{Al}_2(\text{SO}_4)_3$ is related to formation of the intermediate compounds $\text{Al}_2\text{O}(\text{SO}_3)_2$ and $\text{Al}_2\text{O}(\text{SO}_4)_2$. For some of the process' stages this has been also confirmed by Pysiak [20, 21].

The TG, DTG and DTA curves of thermal decomposition of $\text{Al}_2(\text{SO}_4)_3$ in medium of 5 kPa H_2 and Ar is shown in Fig. 6. In the temperature interval 883–1263 K the process of desulphurization of the sulphate is in action. The recorded 70.2% mass losses coincide with the theoretical figures for the complete process flow till the production of Al_2O_3 takes place.

One peculiar feature of the thermo-gravimetric dependences, explained also by some old studies [9], is the formation of the intermediate solid phase in the temperature interval 1025–1048 K. The decomposition products at 1178 K are ana-

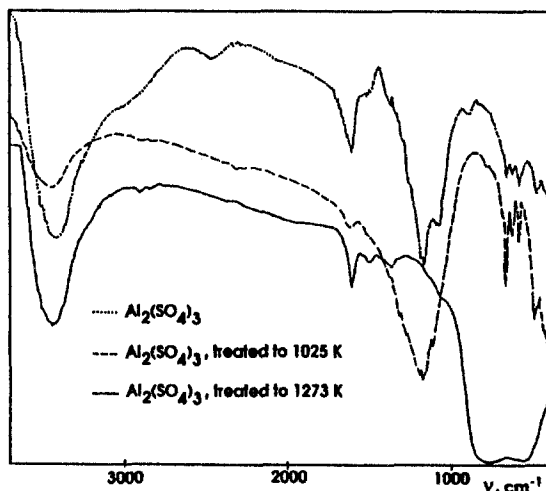


Fig. 7 Infrared spectra of $\text{Al}_2(\text{SO}_4)_3$ + argon

lyzed by IR spectroscopy (Fig. 7). In the IR spectra of the product, as a result of its treatment up to 1178 K, one can find the same absorption triplet in the interval $600\text{--}700\text{ cm}^{-1}$. This proves the bond Al–O–Al and can be eventually related to $\text{Al}_2\text{O}(\text{SO}_4)_2$.

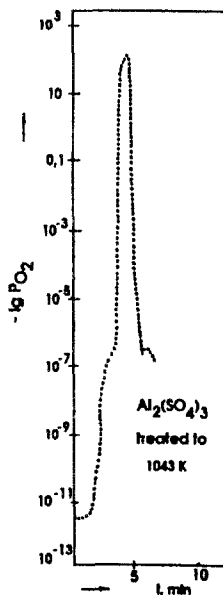


Fig. 8 The relationship between $\lg P_{\text{O}_2}$ and time, obtained during decomposition of $\text{Al}_2(\text{SO}_4)_3$ at $T=1043\text{ K}$, in an atmosphere of hydrogen (1 kPa) + argon

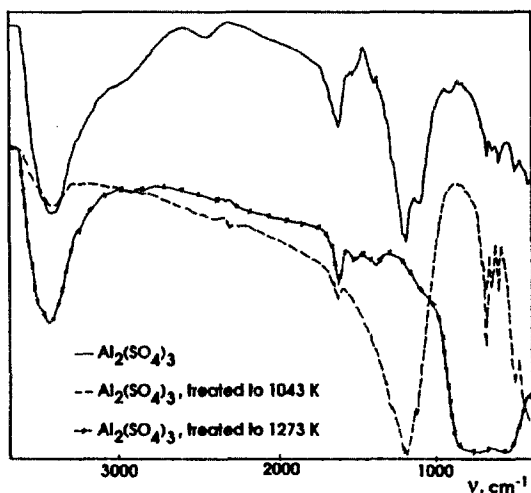


Fig. 9 The infrared spectra of the products of thermal decomposition of $\text{Al}_2(\text{SO}_4)_3$ at different temperatures in an atmosphere of hydrogen (1 kPa) + argon

The production of $\text{Al}_2\text{O}(\text{SO}_4)_2$ is possible by disintegration of $\text{Al}_2(\text{SO}_4)_3$ with precipitation of SO_2 and O_2 in the gaseous phase. This was confirmed with the study of the thermal decomposition of $\text{Al}_2(\text{SO}_4)_3$ by the emf-method [22]. The graphic dependence from alteration of P_{O_2} in the outgoing gases is shown on Fig. 8. The IR-spectra of the solid products are shown on Fig. 9. For only 2.5 min the content of P_{O_2} (Fig. 8) has altered from $2.54 \cdot 10^{-7}$ to $1.28 \cdot 10^2$ Pa. The obtained results show that in the solid phase the reactions are taking place lead to precipitation of O_2 . From the IR-spectra of the products produced at 1043 K, the specific for the bond Al–O–Al absorption triplet at ν -600–700 cm^{-1} is clearly recorded. It confirms that the reaction progressing at 1025–1048 K is related to the formation of $\text{Al}_2\text{O}(\text{SO}_4)_2$.

As a result of those studies, the mechanism of the thermal decomposition of $\text{Al}_2(\text{SO}_4)_3$ could be eventually described with the reactions 5, 10 and 11:

The formation of $\text{Al}_2\text{O}(\text{SO}_4)_2$ and the precipitation of SO_2 and O_2 in the gaseous phase have to be taken into consideration with the kinetic studies and the control of the processes.

Kinetics

The results of the isothermal studies of the processes on thermal decomposition of CaSO_4 , BaSO_4 , $\text{Al}_2(\text{SO}_4)_3$ and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in gaseous medium containing hydrogen are presented in Figs 10–14 and Tables 1–4.

The rate of the thermal process of decomposition of CaSO_4 to CaS can be generally described with an equation of the following type:

$$d\alpha/dt = f_1(T) f_2(\alpha f_3(P_{\text{H}_2})) \quad (23)$$

where: t – time, min; T – temperature, K; α – degree of conversion.

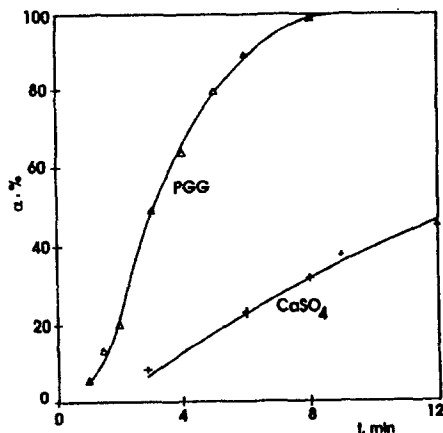


Fig. 10 Correlation of the reduction degree of PGG and pure CaSO_4 with the time, at $T = 1113$ K and $P_{\text{H}_2} = 10$ kPa

At a constant temperature and partial pressure of the hydrogen, Eq. (23) takes on the appearance:

$$d\alpha/dt = kf'(\alpha) \quad (24)$$

where

$$k = f_1(T)f_2(P_{H_2}) \quad (25)$$

After processing with the test data it was established that for some cases best matching was found when the equation of "contracting surface" was used:

$$kt = 1 - (1 - \alpha)^{1/2} \quad (26)$$

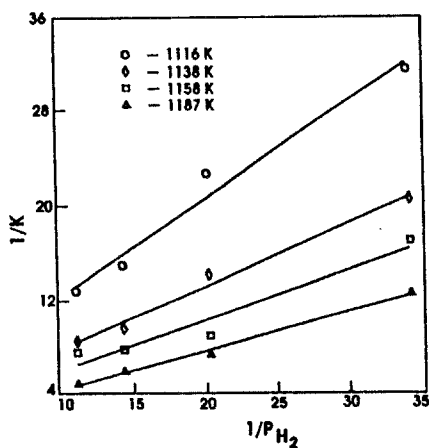


Fig. 11 Plots of $1/K$ vs. $1/P_{H_2}$ at different temperatures for PGG

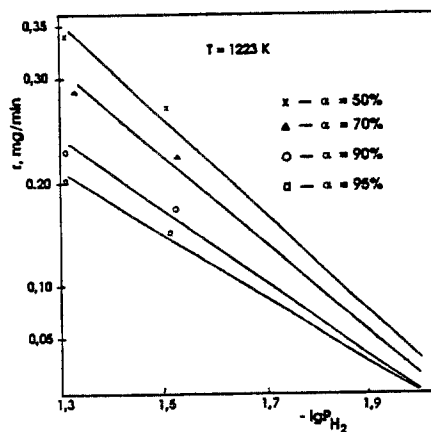


Fig. 12 Correlation of the reduction rate of $BaSO_4$ with $\lg P_{H_2}$ at $T = 1223$ K

The respective values for the rate constant and correlation index are presented in Table 1. At a constant temperature $f_1(T) = K_0 = \text{const}$, Eq. (25) looks like this:

$$K = K_0 f_2(P_{H_2}) \quad (27)$$

Figure 11 presents the dependence of $1/K$ on $1/P_{H_2}$ at constant temperature. As it is seen the data is shown as a straight line. The same result can be also obtained if $f_2(P_{H_2})$ is:

$$f_2(P_{H_2}) = P_{H_2} / (1 + BP_{H_2}) \quad (28)$$

Therefore Eq. (27) is transformed into:

$$K = K_0 P_{H_2} / (1 + BP_{H_2}) \quad (29)$$

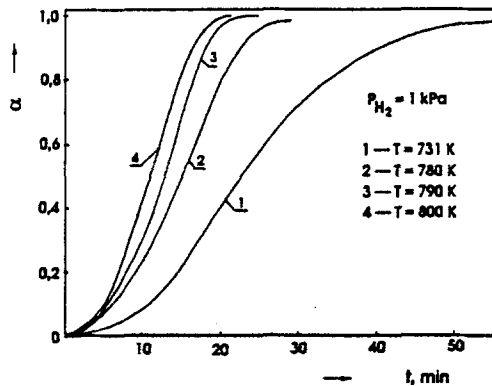


Fig. 13 Correlation of the decomposition degree of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in medium of hydrogen (1 kPa) + argon at various temperatures

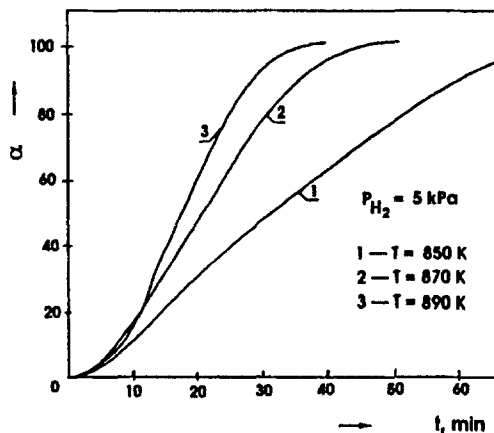


Fig. 14 Correlation of the decomposition degree of $\text{Al}_2(\text{SO}_4)_3$ in medium of hydrogen (5 kPa) + argon at various temperatures

The respective numerical values of K_0 and B are presented in Table 2. Thus, the obtained values of K_0 depend only on the temperature. On that base we get values of the kinetic parameters for the process of thermal decomposition of CaSO_4 in gaseous medium containing 7 kPa hydrogen (Table 4).

The experiments for CaSO_4 and BaSO_4 are carried out in order to establish the optimal partial pressure of the hydrogen for the reduction progress. The results of those tests (Tables 1 and 2) for CaSO_4 (from phosphogypsum PGG) confirm that optimal conditions for the reduction of CaSO_4 are: $P_{\text{H}_2}=7$ kPa and $T=1138$ – 1158 K. If temperature is further raised, the production of CaS decreases with all values of P_{H_2} . The reason for this is that the quantity of CaO increases in the solid phase.

For BaSO_4 the optimal results for the reduction process carried out with hydrogen are: temperature interval 1148–1223 at $P_{\text{H}_2}=5$ kPa (Table 3).

Table 1 Experimental data and results for CaSO_4 (PGG) decomposition

No.	T/K	$P_{\text{H}_2}/\text{kPa}$	Content/ %	$K(\text{Eq. (26)})/\text{K min}^{-1}$	Coefficient of correl.
1	1116	9	96.7	0.07787	0.9881
2	1116	7	95.5	0.06678	0.9867
3	1116	5	94.0	0.04428	0.9863
4	1116	3	88.9	0.03189	0.9958
5	1138	9	96.7	0.11732	0.9861
6	1138	7	96.5	0.10455	0.9922
7	1138	5	95.9	0.07067	0.9980
8	1138	3	96.3	0.04902	0.9950
9	1158	9	96.7	0.13162	0.9930
10	1158	7	96.6	0.12861	0.9973
11	1158	5	94.1	0.11199	0.9806
12	1158	3	91.8	0.05914	0.9959
13	1187	9	93.0	0.20250	0.9988
14	1187	7	92.4	0.16658	0.9941
15	1187	5	88.9	0.13477	0.9904
16	1187	3	80.6	0.07997	0.9775

Table 2 Values of K_0 and B indexes in Eq. (29)

T/K	K_0/min^{-1}	B	Coefficient of correl.
1187	3.69365	0.99720	
1158	2.38625	4.54726	0.9690
1138	1.91243	5.12791	0.9931
1116	1.23932	5.29233	0.9877

Table 3 Mass losses and conversion degree of BaSO₄, depending on temperature and time

<i>T</i> /K	<i>P</i> _{H₂} /kPa	Content of BaS/%	<i>α</i> /%	<i>t</i> /min
1148	3	47.7	69.3	280
1148	5	48.1	69.3	202
1173	3	78.7	85.7	270
1173	5	86.8	87.5	199
1198	3	79.0	91.2	195
1198	5	93.5	91.2	182
1223	3	85.2	97.0	190
1223	5	98.3	98.4	147

Table 4 Kinetic parameters of the thermal decomposition of CaSO₄, BaSO₄, Al₂(SO₄)₃ and FeSO₄·H₂O in gaseous medium, containing hydrogen and argon

No.	Compound	<i>P</i> _{H₂} /kPa	<i>T</i> _{interval} /K	Kinetic equation	<i>E</i> _a /kJ mol ⁻¹	<i>n</i>	Pre-exp. multiplier/min ⁻¹
1	CaSO ₄ (PPG)	7	1138–1158	$kt = 1 - (1 - \alpha)^{1/2}$	138.3	2	6.59
2	BaSO ₄	5	1148–1223	$kt = 1 - (1 - \alpha)^{1/3}$	101.5	3	1.46
3	Al ₂ (SO ₄) ₃	5	850–890	$kt = [-\ln(1 - \alpha)]^{1/2}$	102.2	2	4.69
4	FeSO ₄ ·H ₂ O	1	731–800	$kt = [-\ln(1 - \alpha)]^{1/2}$	54.7	2	2.45

With decline of the thermal stability of the sulphates – Al₂(SO₄)₃ and FeSO₄·H₂O, the optimal temperature interval of the reduction process is decreased to 850–890 K for Al₂(SO₄)₃. For FeSO₄·H₂O, in parallel with the temperature, *P*_{H₂} is also decreased to 1 kPa.

Conclusion

The studies carried out on the mechanism and kinetics of various inorganic sulphates show the variety and the specific characteristics of the process of their thermal decomposition. According to the type, chemical content of the initial sulphates and the test conditions, the possibility for unfolding the thermal processes at a different chemical mechanism and kinetic parameters is proved. They could be successfully conducted by controlling the partial pressure of the gaseous components and the oxi-reductional potential of the specific systems.

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