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KINETICS OF SrSO_4 REDUCTION BY MEANS OF $(\text{CO} + \text{CO}_2)$ GAS MIXTURES

KINETYKA REDUKCJI SrSO_4 ZA POMOCĄ MIESZANINY GAZÓW $(\text{CO} + \text{CO}_2)$

Strontium belongs to chemically very active metals. It occurs usually in nature as the sulphate, mostly in celestite form. Strontium sulphate can be processed to strontium or strontium salts of practical importance by different methods. One of them consists in converting strontium sulphate SrSO_4 to strontium sulphide SrS that can in form be used for synthesizing of strontium carbonate or nitrate. However, a direct transformation of SrSO_4 into SrCO_3 during strontium sulphate reduction by $(\text{CO} + \text{CO}_2)$ mixture is also suggested in literature.

The work is aimed to confirm the possibility of this direct transformation. The experiments were carried out within temperature range 1073–1373 K and for varying CO/CO_2 ratio. The obtained results allow to determine the temperature range and the gas compositions in which SrSO_4 is reduced to SrS . However, no direct transformation of strontium sulphate to strontium carbonate was observed under experimental conditions.

Stront należy do metali bardzo aktywnych. Występuje w przyrodzie głównie w postaci minerału siarczanowego zwanego celestynem. Przerób siarczanu strontu na stront metaliczny oraz inne sole wykorzystywane w gospodarce realizowany jest różnymi metodami. Do jednej z nich należy redukcja SrSO_4 do SrS , z którego uzyskuje się inne sole, np. węgiel lub azotan. Spotyka się również w literaturze informacje o bezpośredniej transformacji SrSO_4 do SrCO_3 zachodzącej w procesie redukcji siarczanu za pomocą mieszaniny gazowej $(\text{CO} + \text{CO}_2)$.

Celem tej pracy jest sprawdzenie możliwości tworzenia się SrCO_3 w czasie redukcji SrSO_4 za pomocą mieszaniny gazowej $(\text{CO} + \text{CO}_2)$. Badania przeprowadzono w zakresie temperatur 1073–1373 K dla SrSO_4 przy zmiennym stosunku CO/CO_2 . Otrzymane wyniki pozwoliły określić zakres temperatur oraz skład fazy gazowej, przy których redukcja SrSO_4 zachodzi do SrS . Nie stwierdzono tworzenia się węgla strontu w zakresie stosowanych temperatur procesu oraz składu fazy gazowej.

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1. Introduction

Strontium belongs to chemically very active metals situated in the group of alkaline metals between calcium and barium. It reacts with oxygen, nitrogen, hydrogen and with sulphur creating very strong compounds SrO , SrN_2 , SrH_2 , SrS . In electronics, metallurgy, chemistry and ceramics strontium finds the use both in the metallic form as well as in the form of compounds. The addition of strontium into copper as a deoxidizing agent does not lower its electric conductivity, but it increases its hardness. The addition of Sr to lead in quantities 0.2–0.6 wt. pct., and 0.2 to 2 wt. pct. of tin, increases its hardness and the life time of battery plates.

The compounds of strontium obtained on the industrial scale in the form of nitrate, of sulphate and of carbonate are used in the pyrotechnics, in metallurgy to purify steel from sulphur and phosphorus, in the porcelain-faience industry to obtain of enamel and of glazes, and also in the optical industry in the form of oxide and of phosphate. Also, it should be mentioned that strontium salts are used for the improvement of the quality of dyes, gums, and to purify caustic soda.

Because of the fact, that strontium appears in Nature mostly in the form of sulphate mineral as celestite, this raw material is used for the production of other salts of strontium mostly in the form of SrCO_3 and of $\text{Sr}(\text{NO}_3)_2$. From these salts metallic strontium can be obtained by:

- Thermal decomposition of some strontium compounds
- Electrolysis
- Reduction of strontium compounds.

To obtain strontium compounds from celestite the following methods are used:

- Reduction by carbon
- Sintering with soda
- Leaching in soda solutions.

As a result of the reduction of celestite by means of carbon SrS is formed. It can be leached in Na_2CO_3 or HNO_3 solutions and strontium carbonate or strontium nitrate will be to obtain.

The process of sintering of celestite with soda did not find wider use because of low efficiency of this process.

The leaching of celestite in soda solution in temperature 90–100°C is very common. Technical strontium carbonate, which is precipitates from the solution after purifying from iron and aluminium is the product used for the production of pure strontium carbonate or strontium nitrate.

In order to specify the literature data the investigations of SrSO_4 reduction were carried out. In work [1] the stability of phases in the Sr–S–O system was determined and Gibbs energy of SrSO_4 decomposition was derived. The results presented in this work for SrSO_4 reduction by means of hydrogen in the range of temperatures 1073–1273 K showed the formation of only SrS . In work [2] the temperature of polymorphic SrSO_4 transformation and its enthalpy were determined. Authors of work [3] carried out the investigations of SrSO_4 reduction by means of mixtures of gases (10% CO and 90% N_2)

in the range of temperatures 1120–1280 K and ascertained SrS presence. The investigations of SrSO₄ reduction by means of mixtures of gases (10% CO and 90% CO₂), in the range of temperatures 1280–1400 K showed SrS and SrCO₃ presence in the products. In the range of temperatures 1280–1420 K the reduction by means of mixtures of gases (5% CO and 95% CO₂) showed only SrCO₃ presence. However, no evidence in the form of chemical or phase analysis was presented, on the base of which the existence of these phases was inferred. Also in this work curves illustrating degree of transformation calculated on the ground of mass changes approached the value of 1. This is possible only in case when reduction of SrSO₄ to SrS is completed. Instead, if SrCO₃ is formed then maximum degree of transformation should be 0.5625 from the degree of SrSO₄ reduction to SrS. In case of formation SrS and SrCO₃ simultaneously, what authors [3] suggest, maximum degree of transformation should be situated in the range $0.5625 \leq \alpha \leq 1$. Represented kinetic curves do not fulfill this condition, and so direct SrSO₄ transformation into SrCO₃ wakes serious doubts.

The aim of this work is to determine the influence of the temperature and of the gaseous phase composition (CO + CO₂) on the rate of reduction reaction of SrSO₄ and the determination of the possibility of the formation other phases as a result of reactions, taking place at the SrSO₄ – SrS phase boundary.

2. Experimental part

2.1. Materials and measurements

The investigations of kinetics of SrSO₄ reduction by means of gaseous phase (CO + CO₂) were carried out on pure samples with changing temperature and gaseous component concentrations. The apparatus used for investigations consisted of vertical electric furnace tube with regulation of temperature by means of Pt–PtRh thermocouple introduced from below of the furnace and kept immediately under the examined sample. The investigated sample in the form of powder was placed on special pan of Al₂O₃, which was suspended on the balance. This made possible continuous registration of mass changes during the process with the accuracy of $1 \cdot 10^{-3}$ g. The starting mass of SrSO₄ sample was equal to 0.790 g. Gaseous phase of constant amount and of a predetermined composition, which was controlled by means of rotameter, was flowing from below of the furnace to its top.

The measurements were conducted in the following manner. A determined mass of the sample was introduced into a furnace and heated to the preset temperature. The gaseous phase with the flow rate of 60 dm³/hour was passed. The measurements were conducted to a moment in which the sample reached constant mass. After reduction, the samples were examined by X-ray phase analysis.

2.2. Experimental results and their discussion

The first series of investigations of SrSO_4 reduction as a function of temperature was conducted by means of pure carbon oxide. These results of investigations are presented in Table 1 and are shown in Fig. 1. In all measurements maximum total decrease of mass corresponded to the reaction:



TABLE 1
Mass decrease of SrSO_4 during the reduction by means of CO

Time of the process, min	Temperature of the process, K								
	1073	1085	1098	1110	1123	1138	1148	1173	1223
	Mass decrease, mg								
0	0	0	0	0	0	0	0	0	0
5	6	6	11	10	20	24	40	62	90
10	10	16	28	32	56	72	110	144	196
15	16	26	47	54	90	120	174	202	244
20	21	37	68	80	122	164	218	238	262
25	27	48	86	102	156	202	242	256	270
30	34	59	109	128	188	232	254	262	274
35	40	70	131	160	213	250	261	266	
40	49	82	151	184	238	258	266	268	
45	54	97	176	210	254	262	268	270	
50	62	110	196	230	264	265	271	271	
55	69	125	215	244	268	268		272	
60	78	140	230	254	271	269			
70	94	174	254	264	273				
75	103	188	260	266	273				
80	112	204	264	268	274				
90	132	234	268	270					
100	158	252	270	271					
115	194	262							
130	226	268							
140	244								
160	262								

The increase of process temperature influenced both: the progress of reaction and the shape of obtained dependence. This refers especially to lower temperature ranges, in which the curves of mass decreases exhibit sigmoidal character as a function of time. It would suggest, that after certain degree of transformation, the products accelerate further progress of reaction. This tendency gradually changes with increasing temperature.

Taking into account the character of obtained dependences, which could suggest the formation of new phases during the reduction, which may have catalytic influence on further course of reaction, the process of reduction was conducted in steps, and the obtained products were subjected to X-ray phase analysis. It was done by means of X-ray

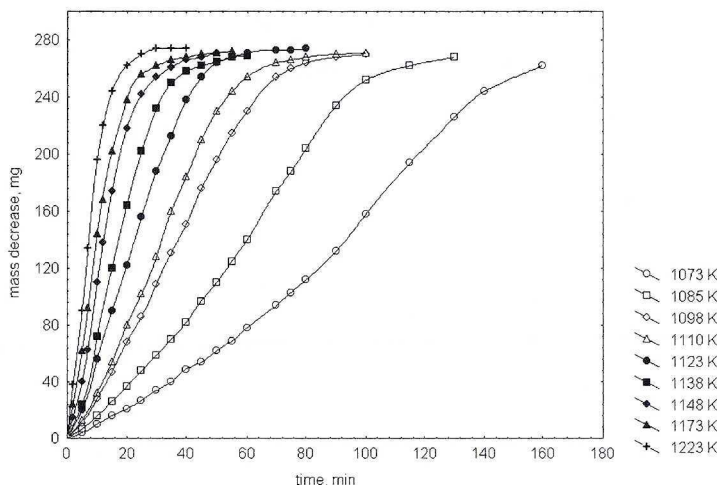


Fig. 1. Mass decrease of SrSO₄ sample during the reduction in pure CO at different temperatures with time

diffractometer XRD 7 using characteristic radiation CoK_α and of Fe filter, in the angle range 2θ from 10° to 80°. The analysis of crystalline phases was performed basing on catalogues [4, 5]. The results of this analysis show, that in the range of transformation degree 0,35 to 0,60 only SrS and SrSO₄ presence was confirmed. Instead, at transformation degree above 0,95 only SrS was identified. Simultaneously, maximum weight loss registered after the end of the process corresponded to mass of oxygen in SrSO₄.

The sequence of experimental series of SrSO₄ reduction by means of gaseous mixtures (CO+CO₂) was conducted, in which the gas concentration changed from 100% to 7,5% by volume in temperature range up to 1373 K. The obtained experimental data are shown in Figs. 2 and 3. The obtained dependences show strong influence of CO concentration in gaseous phase (CO+CO₂) on registered mass changes. It is clear that diminution of CO concentration in gaseous phase results in lowering of the reduction rate.

From comparison of suitable curves from Figs. 2 and 3, obtained for constant concentration of CO in the gas-phase, are may infer profitable influence of temperature on the rate of reaction. It should be noted, that the usage in investigations similar starting masses of SrSO₄ samples at temperature 1373 K resulted in smaller total change of the mass. It could suggest the formation of other phases, eg SrCO₃, what authors of work [3] suggested. To answer this question, the obtained samples in different conditions after the process were analysed by X-ray. Results are gathered in Table 2.

The results of this analysis testify, that process of SrSO₄ reduction runs to SrS independently of temperature and of the composition of gaseous phase. They influence only the reaction rate. Smaller mass decrease observed in temperature 1373 K could be caused by difficulties with diffusion of gaseous reacting substances to the reaction surface due to sintering of solid material.

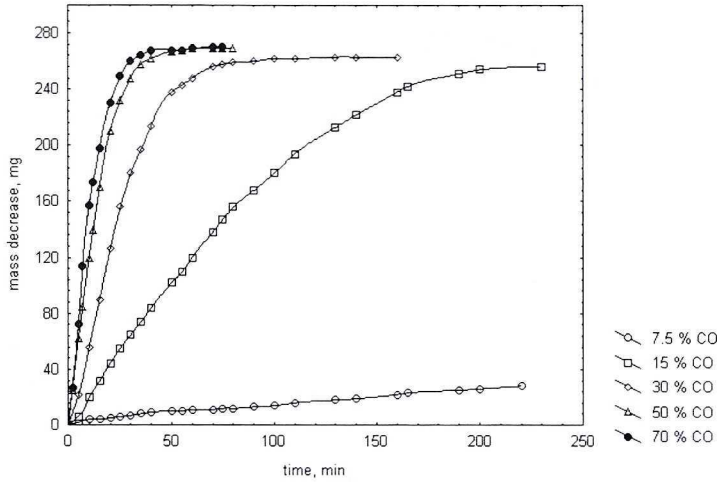


Fig. 2. Time dependence of a mass decrease of SrSO_4 sample on CO concentration in gaseous phase ($\text{CO} + \text{CO}_2$) at temperature 1248 K

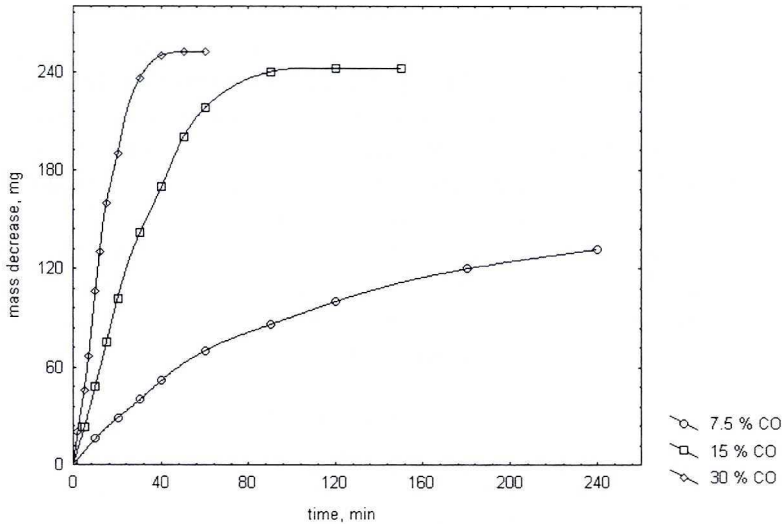


Fig. 3. Time dependence of mass decrease of SrSO_4 sample on CO concentration in gaseous phase ($\text{CO} + \text{CO}_2$) at temperature 1373 K

After the ascertainment, that process of SrSO_4 reduction runs to SrS , independently of temperature and of gaseous phase composition, extent of conversion expressed by the relation

$$\alpha = \frac{\Delta m_{\text{prakt}}}{\Delta m_{\text{teoret}}} \cdot 100\%, \quad (2)$$

where: Δm_{prakt} – registered change of the mass of the sample during the process
 Δm_{teoret} – theoretical maximum change of mass calculated from quantity of oxygen in mass of the sample
 was calculated.

TABLE 2

Results of X-ray phase analysis

Temperature of the process, K	CO content in gaseous phase, %	Time of the process, min	Total change of SrSO ₄ mass, mg	Identified phases
1183	15	270	242	SrS, SrSO ₄ -little
1223	15	300	256	SrS, SrSO ₄ -little
	7.5	315	23	SrSO ₄ , SrS-little
1298	15	180	244	SrS, SrSO ₄ -little
	7.5	150	66	SrS, SrSO ₄
1373	7.5	240	132	SrS, SrSO ₄

The results of these calculations are shown in Figs. 4–5.

Similar character of these dependencies was obtained under other conditions of the process. The maximum of a degree of reaction course obtained the level of 95% in temperature 1373 K, in the face missing of other phases, can be explained by the occurrence of sintering of pulveraceous material, which efficiently stopped transportation of reacting substances to the surface of the reaction.

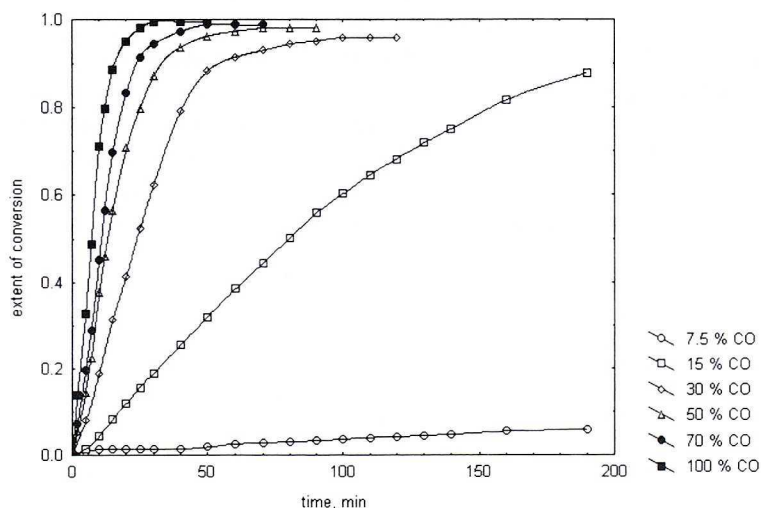


Fig. 4. Time dependence of a degree of SrSO₄ reduction on CO concentration in gaseous phase (CO+CO₂) at temperature 1223 K

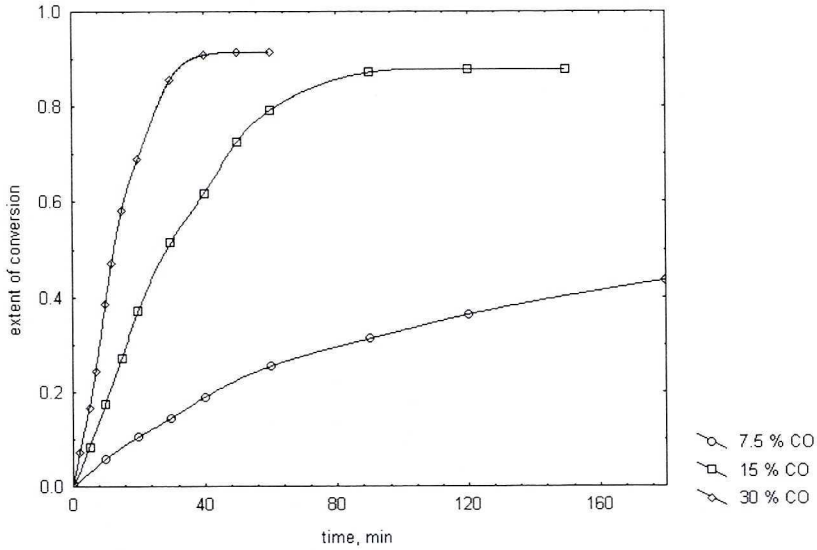


Fig. 5. Time dependence of a degree of SrSO_4 reduction on CO concentration in gaseous phase ($\text{CO} + \text{CO}_2$) at temperature 1373 K.

3. Discussion

To describe the process in a wide range of reaction degree, for different measuring variants, calculations of the obtained experimental data with different models found in literature [6, 7] were done. Equations assuming rate limiting steps due to reaction rate on the surface between phases SrSO_4 – SrS as well as with processes of transportation of gaseous reacting species across the layer of products of reaction to the surface of phase boundary. In this of last case Jander equation was used, in spite of the fact that it assumes constancy of the reaction surface. The initial calculations showed narrow range of agreement between experimental points and applied model and large divergence of first ordinate resulting from the accepted equation, which was calculated for the time of the process equal zero.

Best fitting of experimental points was obtained using the equation in the form:

$$1 - (1 - \alpha)^{\frac{2}{3}} = k \cdot t, \quad (3)$$

where: α – extent of conversion

k – constant proportional to reaction rate

t – time of the process.

This assumes that rate limiting process results from the transportation of reacting species across the layer of reaction products. At simultaneously changing surface of reaction (what happens during investigation of reaction rate of single samples, eg. spherical, cylindrical) the thickness of this layer is proportional to the sizes of a change of the surface during reaction. The results of the calculations are presented in Table 3.

TABLE 3

Values of parameters calculated for equations of regression

Conditions of SrSO ₄ reduction process			A	k · 10 ²	R
Temperature, K	Composition of the gaseous phase, %				
	CO	CO ₂			
1073	100	-	-0.0099	0.3310	0.9963
1085			-0.0164	0.5772	0.9950
1098			-0.0170	0.9623	0.9945
1110			-0.0221	1.1537	0.9934
1123			-0.0225	1.7423	0.9958
1138			-0.0369	2.4261	0.9944
1148			-0.0397	3.3897	0.9937
1173			-0.0133	3.8541	0.9973
1223			-0.00088	5.3556	0.9964
1173	70	30	-0.0192	2.7756	0.9982
	50	50	0.0044	1.4956	0.9994
	30	70	0.0097	0.7022	0.9988
	15	85	0.0025	0.3305	0.9994
1223	70	30	-0.0124	3.4467	0.9950
	50	50	-0.0151	2.7929	0.9961
	30	70	-0.0145	1.5964	0.9982
	15	85	-0.0005	0.4436	0.9981
	7.5	92.5	0.0045	0.0193	0.9904
1248	70	30	-0.0002	3.9959	0.9953
	50	50	0.0133	2.9247	0.9972
	30	70	-0.0115	1.6655	0.9973
	15	85	0.0042	0.5150	0.9990
	7.5	92.5	0.0021	0.0503	0.9954
1298	30	70	0.0136	1.9592	0.9961
	15	85	-0.0032	0.7068	0.9985
	7.5	92.5	0.0014	0.1909	0.9970
1373	30	70	-0.0103	2.8462	0.9964
	15	85	0.0093	1.1722	0.9973
	7.5	92.5	0.0079	0.2939	0.9959

In accordance with introduced equation (3). for $t = 0$, the value of the first ordinate should be zero. The calculations showed, that first ordinate was slightly different. that is to say eq. 3 well describes the process. Also. the high value of the coefficient of correlation R testifies about this. The application range of the accepted equations with reference to the degree of the course of reduction reaction was different under different conditions of the process. It is shown in following Figs. (6-8). in which values of an extent of conversion 0.5 and 0.7 were set. The obtained values show, that application range of the accepted equations increases with temperature of the process and with CO concentration in gaseous phase (CO+CO₂). This is connected immediately with the

obtained dependences represented in Figs. 1–2, which show sigmoidal course (especially in lower temperatures of reduction) which does not complies to accepted equation.

The calculated values of regression coefficients, which are proportional to constants of reaction rate permitted the determination of their dependences on CO concentration in gaseous phase ($\text{CO} + \text{CO}_2$) for different temperatures. The illustration of obtained results is shown in Fig. 9. It shows, that these dependences have straight-line character in the application range of equation (3).

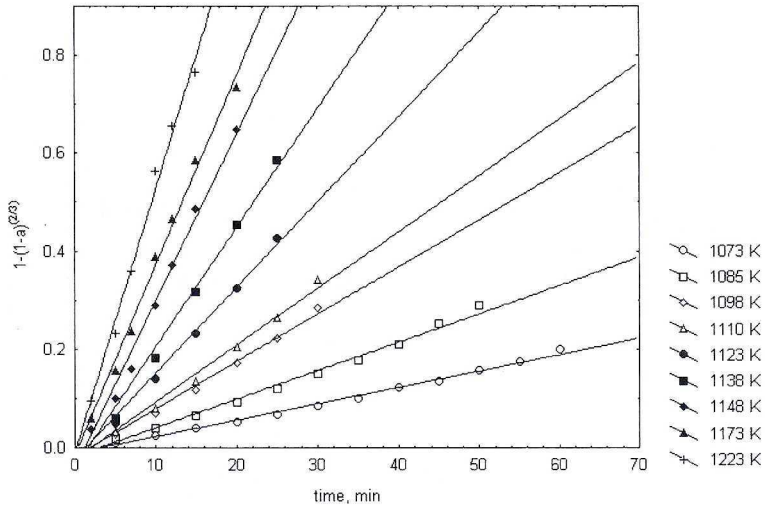


Fig. 6. Fit of eq. 3 to experimental points obtained for SrSO_4 reduction by means of CO in different temperatures

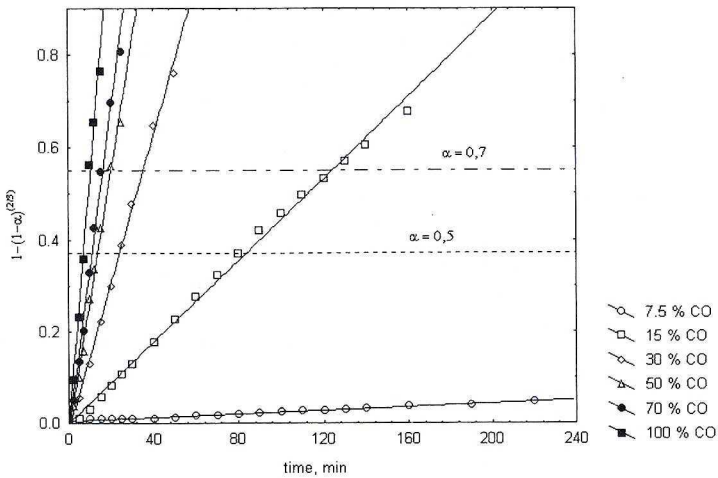


Fig. 7. Fit of eq. 3 to experimental points obtained for SrSO_4 reduction in temperature 1223 K by means of mixtures of gases ($\text{CO} + \text{CO}_2$)

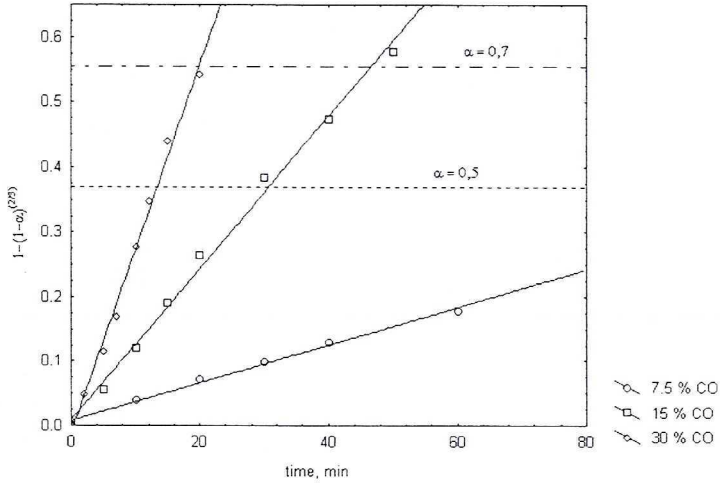


Fig. 8. Fit of eq. 3 to experimental points obtained for SrSO_4 reduction in temperature 1373 K by means of mixtures of gases ($\text{CO} + \text{CO}_2$)

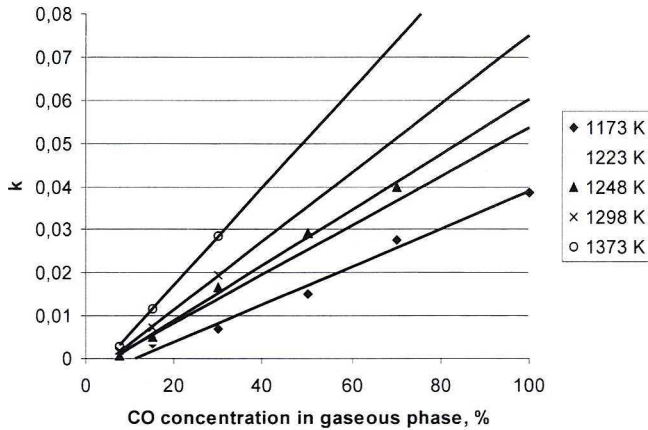


Fig. 9. Dependence of regression coefficients of equation (3) on CO concentration in gaseous phase for different temperatures

To find the mathematical function describing the represented dependencies a linear equation in the form

$$k = B + D \cdot C_{\text{CO}}, \quad (4)$$

was accepted.

Where: k – constant in equation (3), which is proportional to rate reaction

B – first ordinate

D – regression coefficient of the accepted equation

C_{CO} – CO concentration in the gaseous mixture ($CO + CO_2$), %.

Results of these calculations are presented in Table 4.

TABLE 4
Values of the regression parameters obtained for equation (4)

Temperature of process, K	$B \cdot 10^2$	$D \cdot 10^3$	R
1173	-0.4769	0.436	0.9928
1223	-0.2934	0.566	0.9956
1248	-0.3774	0.640	0.9979
1298	-0.4353	0.793	0.9989
1373	-0.5431	1.132	0.9999

Using the calculated values the dependence of a degree of $SrSO_4$ reduction on time in constant temperature can be determined. independently on CO concentration in the gaseous phase ($CO + CO_2$).

Since the investigation of kinetics of chemical reaction aims at the determination of activation energy, values of which infer about the limiting factors of reaction, Arrhenius dependence was calculated for several CO concentrations in gaseous phase and values of activation energy were derived. These values are gathered in Table 5.

TABLE 5
Calculated values of the activation energy

CO concentration in gaseous phase ($CO + CO_2$), %	Range of temperatures, K	Value of the activation energy, kJ/mol
100	1073–1148	300.7
	1148–1223	72.1
30	1223–1373	54.7
15	1173–1373	84.9

The calculated values of the activation energy show, that it depends on CO concentration in gaseous phase and on temperature range of $SrSO_4$ reduction process. The value of the activation energy of the process in the temperature range 1073–1148 K shows, that it proceeds in the kinetic area. Above this temperature, all values of the activation energy are similar and about three times lower from the previous one,

independently on CO concentration in gaseous phase. The value of this energy may suggest, that the reaction rate is limited by the transportation of reacting substances to the surface of SrSO_4 -SrS phase boundary across the layer of reaction products.

4. Conclusions

The obtained experimental results and the performed calculations allow to formulate, the following conclusions:

1. The obtained dependences of a degree of SrSO_4 reduction by means of CO show sigmoidal character, especially at temperatures up to 1173 K, which would suggest autocatalytic character of reaction. Maximum rate of reaction, at which inflection of curves occur takes place at different degree of reduction, which depends on temperature. Above temperature 1173 K the reaction rate is so large, that autocatalytic character of curves can be neglected.

2. The process of SrSO_4 reduction by means of either CO or $(\text{CO} + \text{CO}_2)$ mixtures can be described by equation (3) in the wide range of the reduction degree. The agreement of this equation with the experimental curves increases with increasing temperature.

3. It was demonstrated, that the rate of reduction reaction is proportional to CO concentration in gaseous phase, for the predetermined temperature.

4. The determined value of the activation energy of SrSO_4 reduction reaction by means of CO is about 300 kJ/mole in the range of temperatures 1073–1148 K, i.e. the process runs in kinetic area. Above these temperatures, the determined value of the activation energy is at average 71 ± 14 kJ/mole, for different CO concentrations in gaseous phase $(\text{CO} + \text{CO}_2)$. This would suggest, that in this temperature range, the reaction rate of SrSO_4 reduction is limited by processes of transportation of gas-reacting substances to the surface of SrSO_4 -SrS phase boundary.

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REFERENCES

- [1] Z. Panek, K. Fitzner, *Thermochemica Acta* **113**, 359–368 (1987).
- [2] M. Sukiennik, J. Torres, J. Mendez, *Thermochemica Acta* **334**, 57–66 (1999).
- [3] J. Plewa, J. Steindor, J. Nowakowski, K. Fitzner, *Thermochemica Acta* **138**, 55–66 (1989).
- [4] Powder Diffraction File Search Manual Inorganic, ICPDS, 1979.
- [5] Powder Diffraction File, Sets 1–32, ICPDS, 1974.
- [6] W. Jost, *Chem. Engrs. Science* **2**, 5 (1953).
- [7] Habashi Fathi, *Chemiker Ztg. Chem. Appar* **93**, 5 (1969).
- [8] Cz. Malinowski, *Archives of Metallurgy* **28**, 2 193–207 (1983).

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