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KINETICS OF $SrSO_4$ REDUCTION WITH CO

JULIAN PLEWA AND JOZEF STEINDOR

*Institute of Non-ferrous Metals, Silesia Technical University, 8b Krasinskiego Street,
40-019 Katowice (Poland)*

JERZY NOWAKOWSKI

*Institute of Metallurgy of Non-ferrous Metals, Academy of Mining and Metallurgy,
30 Mickiewicza Street, 30-059 Krakow (Poland)*

KRZYSZTOF FITZNER

*Institute for Metals Research, Polish Academy of Science, 25 Reymonta Street,
30-065 Krakow (Poland)*

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ABSTRACT

It has been found that the process of $SrSO_4$ reduction with CO results in SrS formation. Increasing the oxygen content of the reducing gas by adding CO_2 results in $SrCO_3$ formation. Using a 5% CO + 95% CO_2 mixture, $SrCO_3$ was formed during experiments conducted in the temperature range 1240–1420 K. This process was controlled by nucleation and growth with an activation energy of 115 ± 10 kJ mol^{-1}. Application of a 10% CO + 90% N_2 gas mixture resulted in SrS formation. In this case, two stages of the reduction process were distinguished, the first connected with the nucleation and growth and the second apparently controlled by diffusion. Values of the activation energy for both processes are given.

INTRODUCTION

Among the metals occurring in Polish sulfur deposits strontium appears as $SrSO_4$. Because of the great practical value of metallic strontium as well as of some of its compounds, investigations into the possibility of its extraction have been carried out.

The stabilities of the respective phases of the Sr–S–O system have already been established [1]. The results obtained prove that the thermal decomposition of $SrSO_4$ takes place at high temperatures only. According to ref. 2, the temperature at which the thermal decomposition of $SrSO_4$ occurs is 1647 K. However, it could be significantly lower when a reducing agent is present. It was reported [3] that under a hydrogen atmosphere $SrSO_4$ reduction occurs at about 1073 K and that the product is SrS. During the tests by Panek and

Fitzner [1] SrS was obtained at 1073 as well as at 1273 K as a product of $SrSO_4$ reduction by H_2.

It was pointed out elsewhere [4] that during metal sulfide reduction with gaseous agents (H_2 or CO) different products can be formed depending on temperature, atmospheric composition and the metal. According to these factors the products of sulfate reduction can be metals (Ag, Cu, Ni), metal oxides (Mg, Ca), metal sulfides (Na, K), metal sulfide–metal oxide mixtures (Zn, Mg, Ca) or a metal–metal sulfide mixture (Pb). Metal sulfates [4] may also be formed as intermediates.

Generally, with increasing reduction temperature and oxygen potential in the system, the formation of products free from metal sulfides is expected.

In the available literature no information can be found concerning the kinetics of $SrSO_4$ reduction with CO. In order to complement this lack of information, investigations have been carried out on the kinetics of $SrSO_4$ reduction with CO, as well as on the conditions allowing the formation of $SrCO_3$.

EXPERIMENTAL

Materials

$SrSO_4$ was obtained by precipitation from $SrCl_2$ solution with sulfuric acid. $SrCl_2$ of 99.7% purity was purchased from Reachim (U.S.S.R.).

Carbon monoxide, produced from formic acid, was mixed with N_2 or CO_2 (obtained from POLGAZ, Poland) to produce appropriate gas mixtures.

Technique

Reduction kinetics were investigated using a Mettler TA1 thermobalance in a reducing gas flow under atmospheric pressure.

$SrSO_4$ samples $m_0 = 40\ (\pm 1)$ mg were placed on a platinum plate, first as pellets of 6 mm diameter and about 0.5 mm thickness and then as a 0.06–0.088 mm powder. After placing the sample in the thermobalance, the system was evacuated and a gas mixture of known composition was introduced. The flow rate was then determined and the sample was heated up to the required temperature at a rate of 10 K min^{-1}. Therefore, under initial conditions ($t = 0$) the samples were already partly reacted. Once the required temperature had been reached, the weight loss of the sample with time was recorded.

Preliminary kinetic measurements

During the preliminary stage of kinetic tests the influences on the kinetic curve of the flow rate, the sample mass and the type of sample (i.e. pellet, powder) were investigated. It was found that the process of pressing the pellets affects the course of the process significantly (Fig. 1a); it not only reduces the contact surface but it also increases the resistance to mass transport inside the sample, as is clearly demonstrated by the pattern of the kinetic curves.

In order to reduce the influence of heat and mass transport on the process, a number of measurements were carried out with samples of different weights (Fig. 1b). The kinetic patterns of samples of 40 and 80 mg were found to be similar; thus, it may be assumed that in this case resistance to transport can be disregarded.

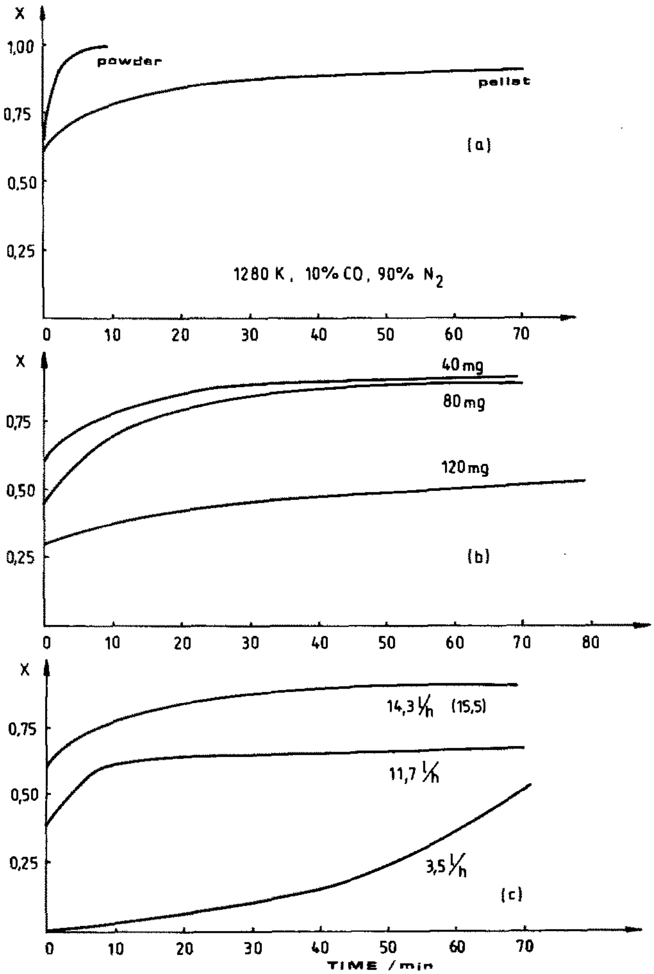

Fig. 1. Influence of (a) the shape of the sample, (b) the weighed amount of the reactant and (c) the flow rate on the kinetic curves.

Figure 1c illustrates the influence of the gas flow rate on the reduction reaction. It shows that under experimental conditions external mass transport can be disregarded for a flow rate > 14 l h^{-1}.

On the basis of these observations subsequent measurements were carried out for 40 mg powder samples at the gas flow rate 15 l h^{-1}.

RESULTS

The influences of temperature and gas composition on the kinetics of $SrSO_4$ reduction were established on the basis of three series of measurements. In Fig. 2 the kinetic curves obtained at various temperatures with 10% CO + 90% N_2 are shown. Analysis of the reaction products revealed SrS formation. The photomicrographs show that the sizes of $SrSO_4$ grains were greater than those of the reduction products (i.e. SrS). $SrSO_4$ grains (A) of different sizes were transformed by reduction into finer grains with numerous voids between them (B). The final form (C) exhibits a significant elimination of gaps and pores.

In order to establish the influence of oxygen partial pressure (p_{O_2}) on the kinetics of $SrSO_4$ reduction, N_2 in the gaseous mixture was replaced in two

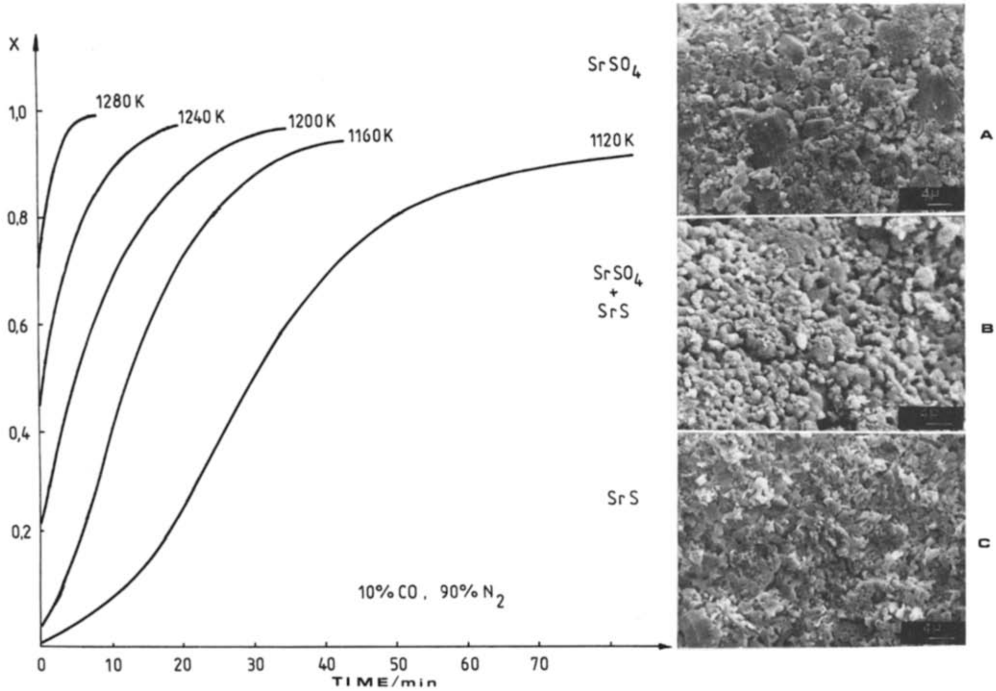

Fig. 2. Influence of temperature on the degree of $SrSO_4$ reduction by 10% CO+90% N_2.

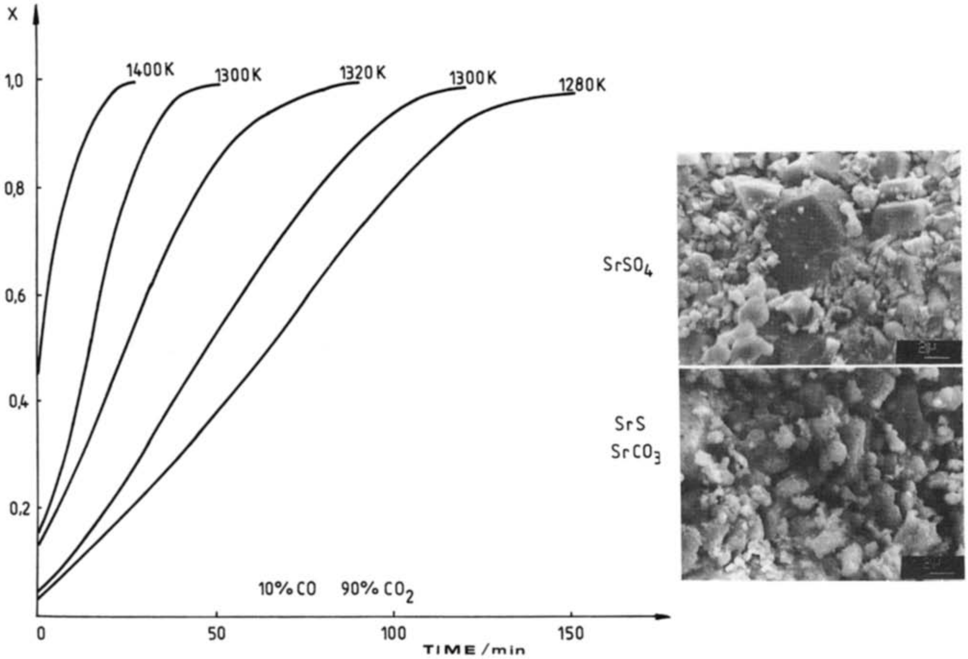

Fig. 3. Influence of temperature on the degree of $SrSO_4$ reduction by 10% CO+90% CO_2.

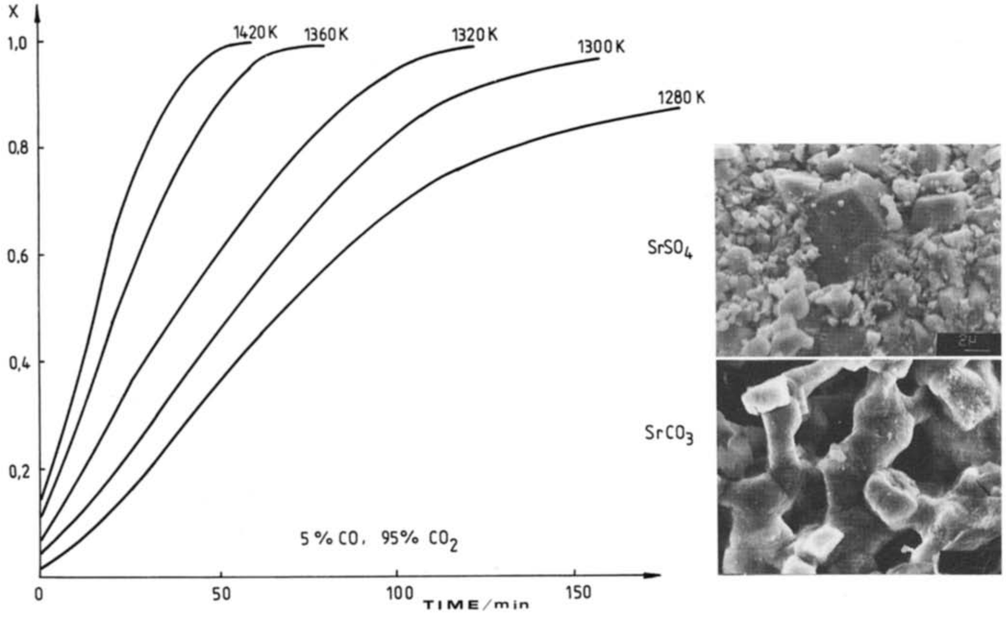

Fig. 4. Influence of temperature on the degree of $SrSO_4$ reduction by 5% CO+95% CO_2.

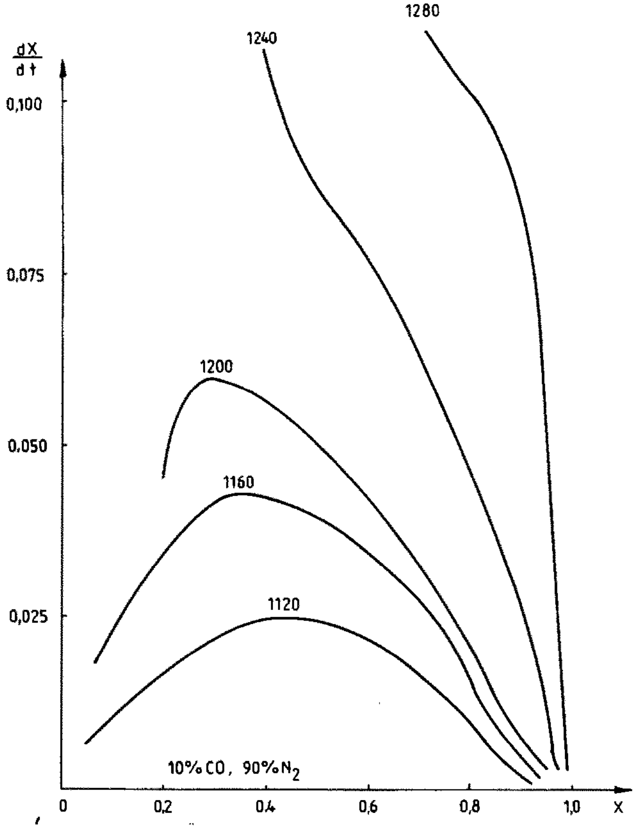

Fig. 5. Influence of temperature on the degree of $SrSO_4$ reduction by 10% CO + 90% N_2.

subsequent experimental runs by CO. Experimental results obtained with 10% CO + 90% CO_2 are shown in Fig. 3. The resulting condensed products contained $SrCO_3$ and SrS, the proportion of the latter not exceeding 15%. The micrographs of product grains (SrS and $SrCO_3$) show that no sintering ocurred here. The spaces between the grains are quite significant.

Figure 4 shows the kinetic curves obtained as a result of reduction with 5% CO + 95% CO_2.

Phase analysis of the products revealed the presence of $SrCO_3$ and small amounts of SrS. The carbonate grains appear as big rounded lumps with large spaces between them. The number of gaps and pores is greater than in the case of SrS.

Analysis of the kinetic curves obtained for various gas mixtures reveals that the reduction reaction attained its maximum rate in many cases (Figs. 5–7). In such cases an adequate description of the kinetic curves may be obtained by using Avrami–Erofe'ev equations concerning the phenomena of nucleation and nuclei growth. Considering the various forms of the Avrami–Erofe'ev equation [6], it has been found that the best representation

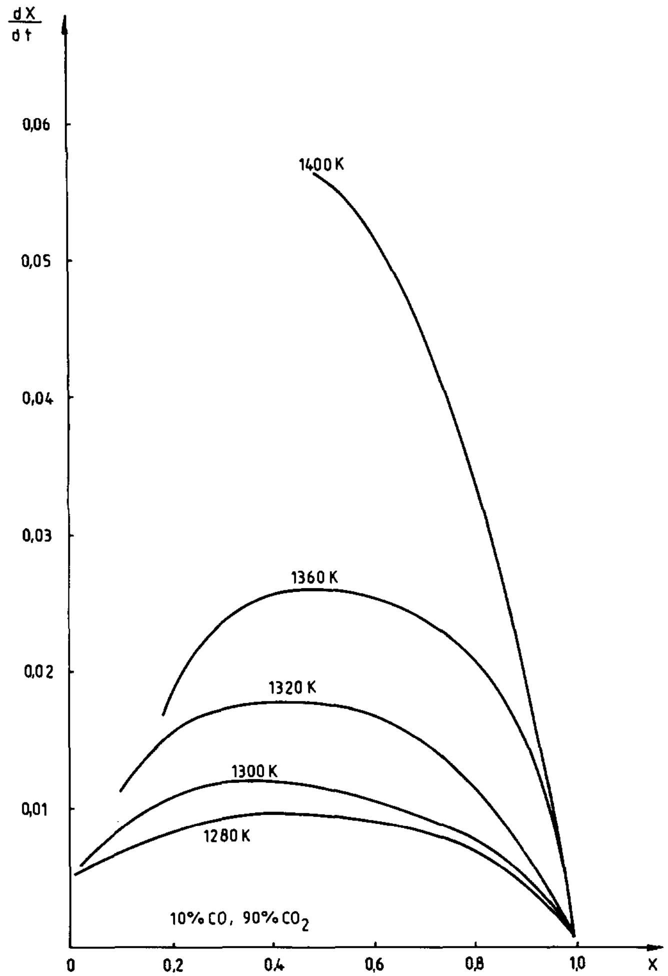

Fig. 6. Influence of temperature on the degree of $SrSO_4$ reduction by 10% CO + 90% CO_2.

of the experimental data is given by the so-called F2 equation in the following form:

$$\frac{dx}{dt} = \bar{k}2(1-x)[-\ln(1-x)]^{1/2} \tag{1}$$

$$[-\ln(1-x)]^{1/2} = a + kt \tag{2}$$

where x is the degree of reaction calculated as specific mass decrement, k, $\bar{k}$ are the rate constants and a is a constant determined by the initial conditions ($t = 0$, $x = x_0$). During mathematical analysis it was discovered that eqn. (1) does not provide an accurate description of kinetic curves obtained at 1120, 1160 and 1200 K for the samples reduced by 10% CO + 90% N_2, where the product was SrS.

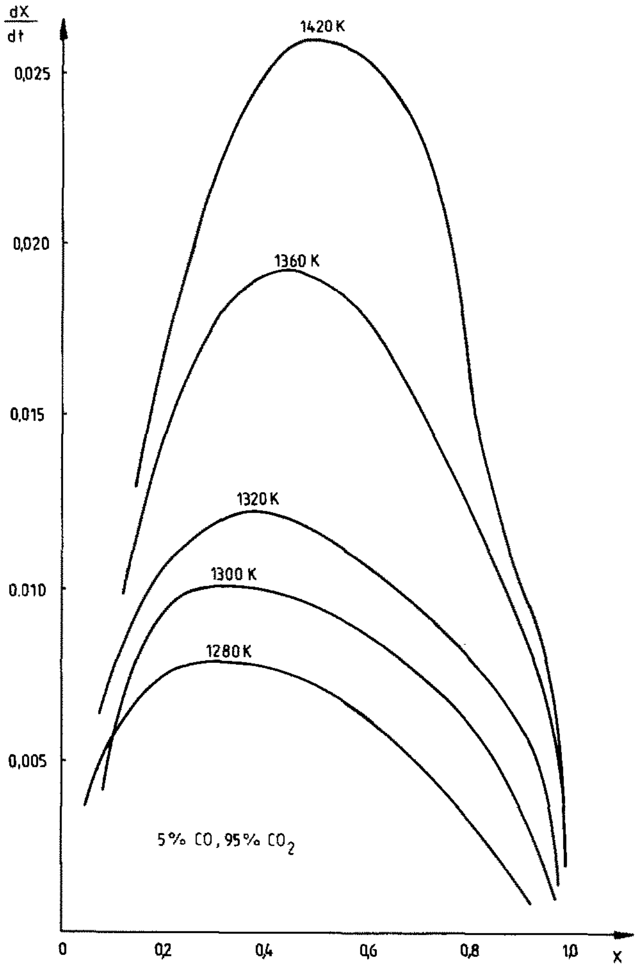

Fig. 7. Influence of temperature on the degree of $SrSO_4$ reduction by 5% CO + 95% CO_2.

As the photomicrographs revealed a sintering of the product grains, one can assume that this process will be reflected by the kinetic curves, from which it follows that the reduction reaction was significantly hampered at the end of the process.

We may thus conclude that the final stage of the reduction reaction was controlled in this case by diffusion. Therefore, the curves obtained have been divided into two groups: The first described by F2 equation and the second by the equation suggested by Jander [6]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{3}{2}\bar{k}\frac{1}{(1-x)^{-2/3} - (1-x)^{-1/3}} \tag{3}$$

$$\left[1 - (1-x)^{1/3}\right]^2 = a + kt \tag{4}$$

TABLE 1

Results of fitting experimental data to the model kinetic equations [a]

T(K)	x_0	x_k	Model	k	$S(k)$	$\bar{k}$	$S(\bar{k})$	a	$S(a)$	r
10% CO+90% N_2										
1120	0.0070	0.8000	F2	0.024498	0.000435	0.022913	0.004551	0.0787	0.0128	0.998586
	0.8000	0.9158	D4	0.003641	0.000297	0.038311	0.001639	0.0164	0.0210	0.983726
1160	0.0458	0.7898	F2	0.041916	0.001073	0.040936	0.007167	0.2505	0.0189	0.996097
	0.7898	0.9442	D4	0.010802	0.000522	0.011141	0.018294	0.0715	0.0183	0.993057
1200	0.2156	0.7764	F2	0.050951	0.002137	0.053576	0.011058	0.5294	0.0180	0.995633
	0.7764	0.9704	D4	0.017368	0.000633	0.019159	0.004961	0.10197	0.0165	0.996039
1240	–	–	–	–	–	–	–	–	–	–
	0.4449	0.9858	D4	0.030257	0.000783	0.036735	0.014304	0.0179	0.0086	0.997663
1280	–	–	–	–	–	–	–	–	–	–
	0.6577	0.9958	D4	0.086374	0.003584	0.095298	0.042026	0.0888	0.0161	0.996721
10% CO+90% CO_2										
1280	0.0233	0.9767	F2	0.011722	0.000310	0.012697	0.003882	0.1376	0.0272	0.995151
1300	0.0189	0.9773	F2	0.015004	0.000361	0.017804	0.007078	0.1528	0.0208	0.995994
1320	0.1195	0.9891	F2	0.020003	0.000187	0.022506	0.006859	0.3638	0.0092	0.999257
1360	0.2293	0.9890	F2	0.034981	0.001256	0.035981	0.022219	0.4257	0.0364	0.995312
1400	0.4642	0.9838	F2	0.052217	0.001962	0.061742	0.028502	0.8249	0.0182	0.993014
5% CO+95% CO_2										
1280	0.0172	0.9783	F2	0.008382	0.000287	0.008121	0.002225	0.2181	0.0219	0.998045
1300	0.0425	0.9635	F2	0.011982	0.000109	0.011402	0.001459	0.2383	0.0083	0.999392
1320	0.0761	0.9645	F2	0.013925	0.000320	0.015401	0.005801	0.2923	0.0183	0.996331
1360	0.1190	0.9908	F2	0.021515	0.000551	0.020872	0.014398	0.3114	0.0258	0.995997
1420	0.1450	0.9949	F2	0.033129	0.001044	0.044017	0.024281	0.3334	0.0338	0.995073

[a] T, temperature; x_0 initial and x_k final degree of reaction; k, $\bar{k}$, rate constants; a constant in eqns. (2) and (4); $S(k)$, $S(\bar{k})$, $S(a)$, standard deviations of the respective constants; r coefficient of linear correlation.

TABLE 2

Parameter values in the Arrhenius equation

T range (K)	Model	E_a (kJ)	$S(E_a)$ (kJ)	ln k_0	S (ln k_0)	r
10% CO + 90% N_2						
1120–1200	F2	102.8	25.4	7.3853	2.6439	0.970674
1120–1280	D4	218.6	19.3	17.9272	1.9429	0.988484
10% CO + 90% CO_2						
1280–1400	F2	189.6	5.5	13.3706	0.5011	0.998722
5% CO + 95% CO_2						
1240–1420	F2	115.0	9.6	6.2948	0.8714	0.989812

T, temperature; E_a, activation energy; S ( ) standard deviation; k_0, pre-exponential factor; coefficient of linear correlation.

This co-called D4 equation (3) was derived under the assumption of diffusional control of the reaction rate. The results of fitting the experimental data to the selected models are shown in Table 1. These results demonstrate the accuracy of the data obtained by use of the adopted models.

On the basis of the calculated values of the reaction rate constants, activation energies were determined for the respective experimental runs according to the Arrhenius equation; values are reported in Table 2. It can be noted that the activation energy values obtained are rather high owing to the strong influence of temperature. Moreover, activation energy depends on the composition of the reducing atmosphere, which is related to the reduction products obtained.

4. CONCLUSIONS

On the basis of the results of the present investigation, the following conclusions can be drawn.

(1) $SrSO_4$ can be transfromed into SrS or $SrCO_3$ or a mixture of both these phases at temperatures above 1050 K under the influence of CO. The outcome of this reduction depends on the CO_2–CO concentration ratio in the gas phase, i.e. on p_{O_2}.

Fig. 8 illustrates the equilibrium composition of the gaseous phase obtained as a result of $SrSO_4$ reduction with CO at 1300 K and $p_0 = 101\ 325$ Pa. It was assumed that solid phases do not form solutions. It follows from this diagram that within the area above the line (c) the products contain SrS, whereas within the shaded area (Fig. 8) the conditions ensure $SrCO_3$ formation. A very narrow area where SrO can be formed (below line (c)) is characterized by very low SO_2 partial pressures.

(2) When the gas mixture containing 10% CO + 90% N_2 is used at temperatures in the range 1120–1280 K, reduction resulted in SrS formation.

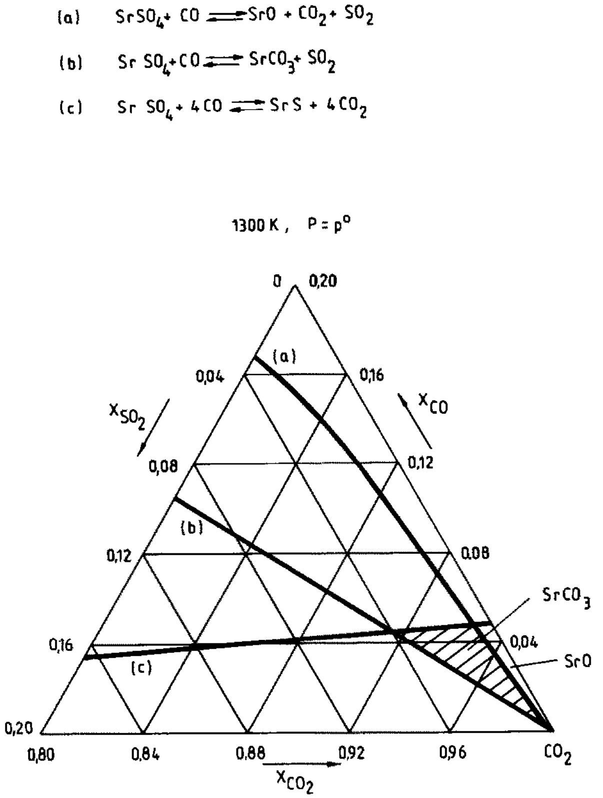

Fig. 8. Equilibrium composition of the gaseous phase in the system where different reduction reactions of $SrSO_4$ by CO are taking place. Thermochemical data taken from ref. 5 were used in the calculations.

Kinetic curves were of a sigmoidal type, but their shape was variable. Thus, the first stage of the reaction is probably controlled by a nucleation process with an activation energy 102.8 (±25.4) kJ mol^{-1}, and the final one by a diffusion process with an activation energy 218.6 (±19.3) kJ mol^{-1}.

(3) Between 1280 and 1400 K, reduction with 10% CO + 90% CO_2 resulted in the formation of a two-phase mixture: $SrCO_3$ and SrS. This process is probably controlled only by nucleation with an activation energy 129.6 (+5.5) kJ mol^{-1}.

(4) Between 1240 and 1420 K, a single product, $SrCO_3$, can be obtained by reduction with 5% CO + 95% CO_2. In this case also it was assumed that the reaction rate is controlled only by the nucleation process with an activation energy 115.0 (±9.6) kJ mol^{-1}.

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