

## **KINETICS OF REDUCTION OF MAGNESIUM SULFATE BY CARBON OXIDE**

*J. Plewa and J. Steindor*

INSTITUTE OF NON-FERROUS METALS, SILESIA TECHNICAL  
UNIVERSITY, KATOWICE, POLAND

The thermodynamic analysis and the results of thermogravimetric investigation of the reduction of magnesium sulfate by carbon oxide are reported.

The isothermal experiments were carried out in the temperature range 640 to 675°. A shrinking-core model was found to fit the reaction rate. An activation energy of  $209.7 \pm 8.6$  kJ/mol was obtained.

Besides the reduction of metallic oxides and metallic sulfides, the reduction of metallic sulfates is one of the chief problems of chemistry and metallurgy. In processes carried out in industry, metallic sulfates present in sulfate minerals and intermediates (dusts, slimes, sintered products) are generally converted into oxides, and the degree of sulfur elimination depends upon the temperature and the presence of other substances. The process is carried out either in an oxidizing atmosphere (thermal decomposition) or in a reducing atmosphere (reduction). In the latter case, the intended effect is reached at lower temperatures. The action of reductants upon metallic sulfates leads to the formation of phases dependent on the temperature and the nature of the metal. The materials may be metals (Pb, Cu, Ag), sulfides (Zn, Pb, K, Na), oxides (Ga, Mg) or basic sulfates (Zn, Pb) [1], the physical and chemical properties being connected with the spatial structure and the bonds in the crystals. Magnesium sulfate is reduced by hydrogen from a temperature of 650° to form magnesium oxide [2].

Habashi et al. [1] estimated the temperature at the beginning of the reduction with hydrogen as 670°, and they observed thermal decomposition at 890°.

According to [2], carbon oxide reacts with magnesium sulfate from a temperature of 700°, with formation of magnesium oxide, CO<sub>2</sub> and COS. Magnesium sulfide is also formed under these conditions.

Krikliyi et al. [3] showed that the reduction of magnesium sulfate may follow different schemes. Magnesium oxide and magnesium sulfide may be formed in the solid phase. The following compounds may be formed in the gaseous phase: sulfur vapor, sulfur dioxide, carbon disulfide, carbon oxysulfide and carbon dioxide.

Theoretical predictions of the course of the reaction in the system initially containing  $\text{MgSO}_4$  and  $\text{CO}$  have been presented in [3]. The kinetics of the reduction has been experimentally studied by examining the influence of the temperature, the rate of flow of the reductant and the characteristics of the reagents.

### Thermodynamic analysis

The stability of particular compounds in the system  $\text{Mg-S-O}$  can be analyzed in a Kellogg's diagram in the coordinate system partial pressure of  $\text{SO}_2$  ( $p_{\text{SO}_2}$ ) as function of the quotient  $p_{\text{CO}_2}$  to  $p_{\text{CO}}$  at constant temperature (Fig. 1). The equilibrium lines in the diagram have been calculated on the basis of the thermochemical data of Barin and Knacke [4]. The results of calcinations of the partial pressures of gaseous compounds at the steady point B in the diagram are given in Table 1.

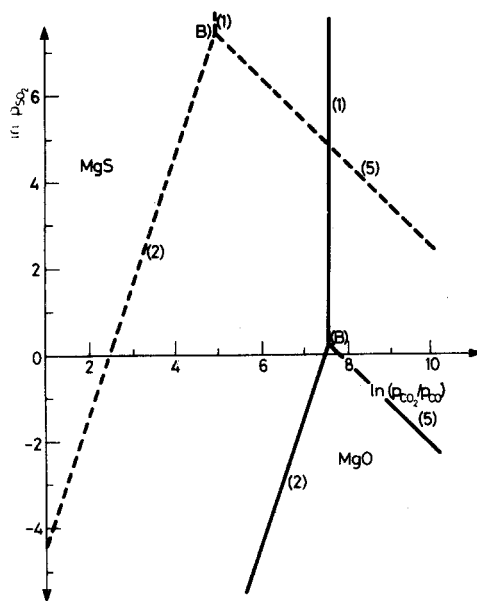


Fig. 1 The predominance area diagram of the  $\text{Mg-S-O}$  system at 527 and 927 °C

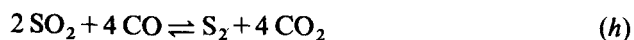
At the invariant point B (where three solid phases coexist:  $\text{MgSO}_4$ ,  $\text{MgS}$  and  $\text{MgO}$ ), a pressure over 1 atm (1 atm = 101,325 Pa) is needed to reach equilibrium at 527° and 927°. Among the above-mentioned gaseous products, the partial pressure of sulfur reaches high values. This problem has been pointed out in [3].

Under equilibrium conditions, the share of sulfur in the gaseous phase may be

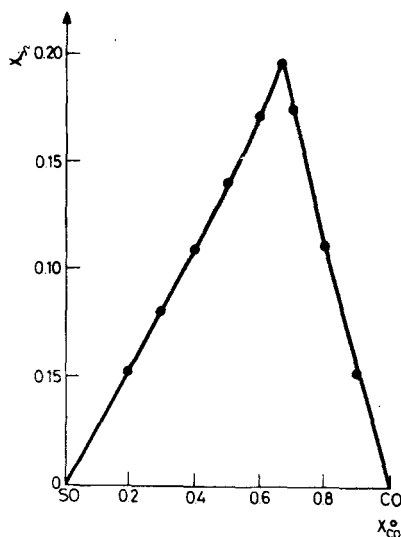
**Table 1** Logarithms of partial pressures of gaseous compounds at steady point B (Fig. 1), in atm (1 atm = 101,325 Pa)

Logarithm of partial pressure of gaseous compound	527 °C	927 °C
$\ln p_{\text{SO}_3}$	0.2687	7.4824
$\ln \left( \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \right)$	7.5684	4.9769
$\ln p_{\text{O}_2}$	-48.9528	-24.7805
$\ln p_{\text{S}_2}$	7.1554	9.3590
$\ln p_{\text{SO}}$	-11.5316	-1.1689
$\ln p_{\text{SO}_3}$	-20.6430	-6.2183

analyzed on the basis of the reaction:

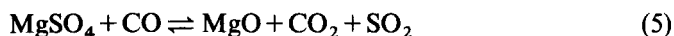


The equilibrium constant of reaction (h) is very high; at 527° and 927°, it reaches values of  $1.05 \cdot 10^{16}$  and  $1.47 \cdot 10^7$ , respectively. When the total pressure is equal to 1 atm (1 atm = 101,325 Pa), the shares of the particular gaseous compounds depend on the temperature and the initial conditions, if we do not take into account other gases [5]. The maximum share of sulfur in the gaseous phase, depending on the initial concentrations ( $x_i^0$ ) of sulfur dioxide and carbon oxide, is presented in Fig. 2. This indicates that sulfur vapor may be present in the gaseous products of the

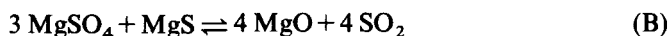


**Fig. 2** Maximum concentration of vapour of sulfur in the system depending on initial concentration  $\text{SO}_2$  and  $\text{CO}$ . Total pressure in the system  $P = 1$  atm (1 atm = 101,325 pA), temperature 927 °C

reduction of magnesium sulfate. In order to determine the condensed products of the reaction, one may apply the method of Jacinto et al. [6], which allows determination of the course of the reaction, depending on temperature and pressure. Under equilibrium conditions, the products of the reaction in a phase diagram adjoin to the area of stability of  $\text{MgSO}_4$  (Fig. 1). At a total pressure of 1 atm, the primary product of the reduction of magnesium sulfate by carbon oxide may be a single phase (magnesium oxide) or a diphasic product (a mixture of magnesium sulfide and magnesium oxide). Magnesium sulfide itself cannot form the product of the reduction of magnesium sulfate by pure carbon oxide at a total pressure of 1 atm. The range of temperature of the reduction of magnesium sulfate to magnesium oxide results from the course of reaction (5), limited by the invariant point B. From the stoichiometry of the reaction:

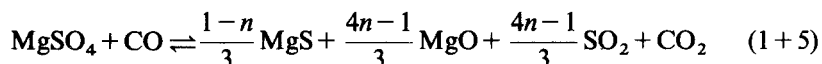


it follows that the maximum pressure of sulfur dioxide is equal to  $p_{\text{SO}_2} = 0.5$  atm. In the reaction:



a pressure of sulfur dioxide  $p_{\text{SO}_2} = 0.5$  atm can be achieved at  $520^\circ$ .

This indicates that at temperatures higher than  $520^\circ$  magnesium sulfate is reduced to magnesium oxide according to reaction (5). However, at temperatures lower than  $520^\circ$ , the result of the reduction of magnesium sulfate is a mixture of magnesium sulfide and magnesium oxide in proportions dependent on the temperature. In this case the reaction may be presented as follows



where  $n$  is a constant dependent on the temperature. The value of  $n$  is calculated by minimizing the free enthalpy (Gibbs function). The presented thermodynamic predictions of the different products of the reduction should be verified experimentally. Measurements of non-balance may also be useful for the verification.

### Kinetic analysis

In order to study the kinetics of the reduction of magnesium sulfate by carbon oxide, series of thermogravimetric measurements were carried out. The mass change of samples of magnesium sulfate in a flow of carbon oxide at an elevated temperature was analyzed. A Mettler TA1 thermobalance, magnesium sulfate

(pure for analysis) roasted at 400°, with a grain size distribution below 0.052 mm, and carbon oxide from formic acid were used.

### Temperature at beginning of reduction

Figure 3 presents the curves of mass decrement (TG), differentials of mass decrement (DTG) and thermal effects (DTA) obtained during the heating of samples of magnesium sulfate in a flow of carbon oxide. Magnesium sulfate with an initial moisture content of 0.7% is reduced from a temperature of 550° under the investigated conditions. The DTA curve is characteristic. Starting from 550°, the DTA curve deflects in the exo direction; then, in the range 630–635–660° it shows an endo effect, and in the range 860–865–900° an exo effect. This may be interpreted in the following way: the deflection of the DTA curve in the exo direction above 550° corresponds to the course of reaction (1 + 5), and the exo effect above 860° corresponds to the course of reaction (B). The endothermic effect above 630°, associated with a considerable mass decrement (DTG peak), may be attributed to the local maximum in the rate of reaction (5).

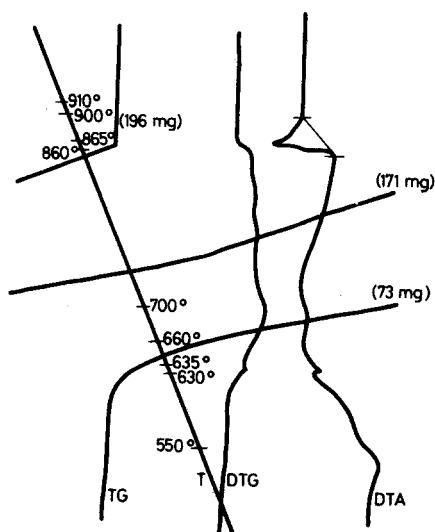


Fig. 3 Thermal curves of magnesium sulfate in carbon oxide. Conditions of measuring:  $m_0 = 300$  mg,  $\beta = 8$  deg/min, alundum crucible macro,  $v = 86.6$  cm<sup>3</sup> Co/min

### Influence of heating rate

The results of polythermic measurements are illustrated in Fig. 4. The course of the kinetic plots is complex. The final mass decrement corresponds to magnesium oxide formation, independently of the heating rate. This indicates that the magnesium sulfide formed in the initial phase of the process is transformed into magnesium oxide according to reaction (B). In later measurements, the initial heating was carried out at a rate of 8 deg/min.

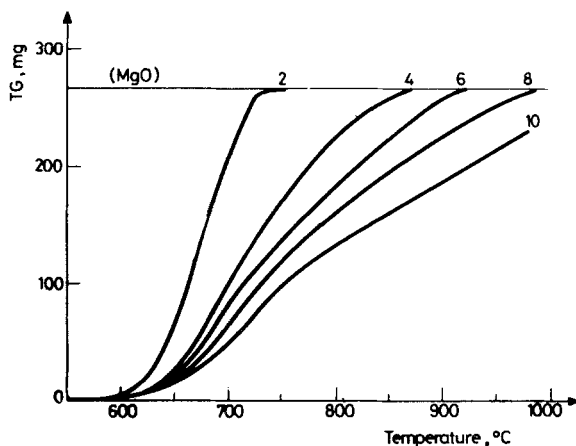


Fig. 4 Mass change in the function of temperature for the reduction of magnesium sulfate in the flow carbon oxide for different velocities of heating ( $\beta$ ),  $m_0 = 400$  mg,  $v = 86.6$  cm<sup>3</sup> CO/min

### Influence of flow rate

The influence of the rate of flow of carbon oxide in the course of the reaction in the range 20–238 cm<sup>3</sup>/min is presented in Fig. 5. It follows from Fig. 5 that the rate of the reaction and the time of the total reaction do not depend on the flow rate if this is higher than 180 cm<sup>3</sup>/min. A flow rate of 238 cm<sup>3</sup>/min was used in a series of isothermal measurements for elimination of the effect of external mass transportation.

### Influence of reaction temperature

The influence of the temperature on the course of the reaction of magnesium sulfate reduction by carbon oxide was studied at different temperatures in the range

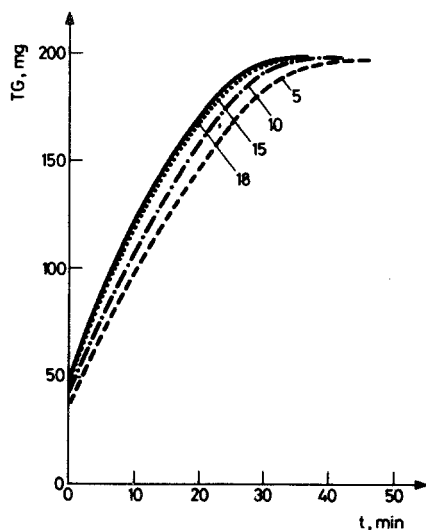


Fig. 5 Mass change in the time function for the reduction of magnesium sulfate by carbon oxide for different intensities of flow,  $m_0 = 300$  mg, temperature 700 °C,  $v$  in SKT

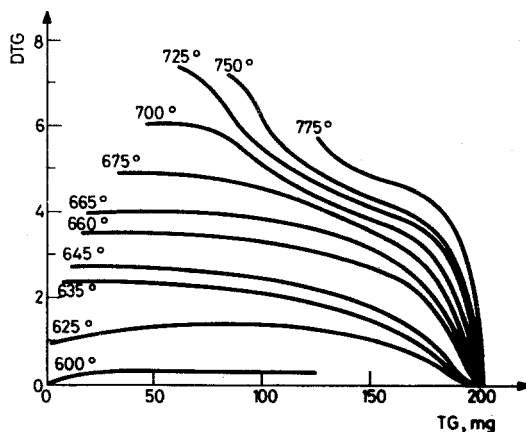


Fig. 6 The change of the velocity of mass decrement in the function of mass decrement for the reduction of magnesium sulfate by carbon oxide for different temperatures,  $m_0 = 300$  mg,  $v = 238$  cm<sup>3</sup> CO/min

625–775°. As shown in Fig. 6, an increase of temperature increases the rate of the reduction. The final mass decrement corresponds to magnesium oxide formation. The shapes of the presented DTG–TG kinetic plots depend on the temperature of the reaction. The fact that the kinetic plots have different shapes may be attributed to the different limiting stages.

### Characteristic features of reactants

Scanning photos of magnesium sulfate are presented in Fig. 7. The grains of magnesium sulfate have the shape of crumbled plates of different sizes. Grains of this type generally form a layer permeable to gases.

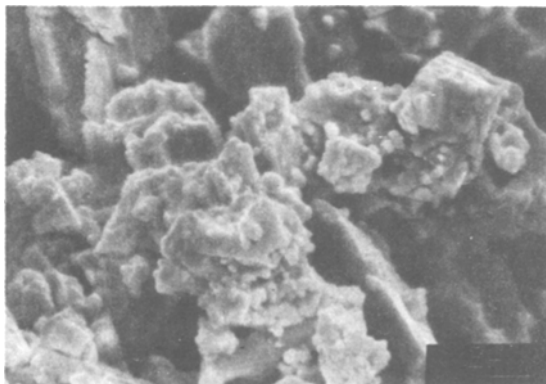


Fig. 7 Scanning electron micrograph showing the crystallites in magnesium sulfate particles

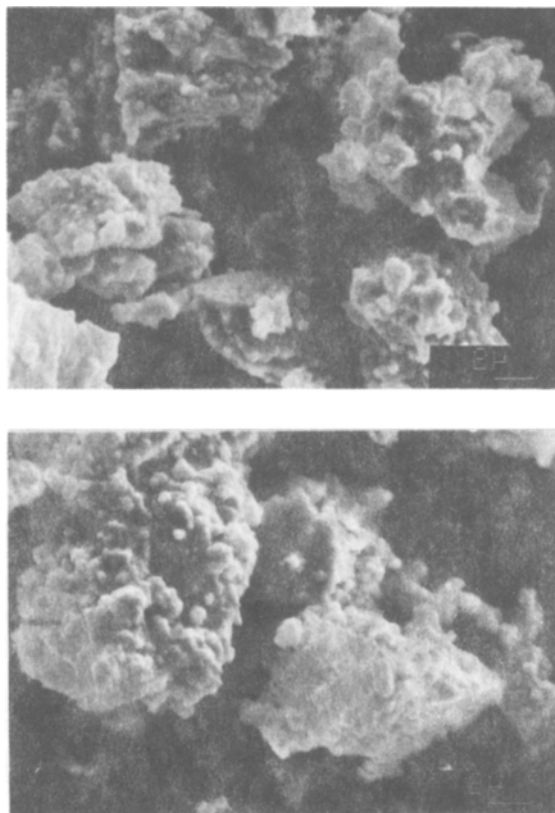
The grains of the reaction products are presented in Fig. 8. The product obtained at 600° (Fig. 8a) was a partially reduced sulfate in which  $\text{MgSO}_4$ ,  $\text{MgO}$  and  $\text{MgS}$  were detected on X-ray phase analysis. A similar phase composition was observed in slightly reduced samples, when magnesium sulfide occurred in a non-crystalline form. Figure 8b presents the reduction product obtained at 700°. In this case, phase analysis detected only magnesium oxide. In both cases, the grains of the products were smaller than the grains of the substrate, i.e. magnesium sulfate. The newly obtained fine grains of the products may form a layer weakly permeable to gases, especially in the process of sintering.

### Interpretation of results

In this paper magnesium sulfate was heated in an atmosphere of carbon oxide. Initially, small amounts of magnesium sulfide were observed among the products in all cases. Under the conditions of measurement, this phase is formed and is stable at temperatures of 550–625°. There is an inconformity with theoretical predictions in this respect, because it has been calculated on the basis of analysis that magnesium sulfide is not formed above 520°.

Magnesium sulfide reacts with magnesium sulfate, especially at temperatures





**Fig. 8** Scanning electron micrograph showing the crystallites in the products of reduction at 600 and 700 °C

higher than 625°. Accordingly, this phase cannot be observed in the final products obtained at higher temperatures. The kinetic plots present the formation of these products as a function of time. The kinetic plots obtained at 600 and 625° have a sigma shape, manifested as a maximum in the DTG–TG system. This should be connected with control of the reaction rate by nucleation. For the temperature range 640–675°, the reduction leads to magnesium oxide formation, and the shape of the kinetic plots in the DTG–TG system (Fig. 6) gives evidence of control of the reaction rate by a chemical reaction.

The above hypothesis results from application of the method of differentiating kinetic models under isothermal conditions. However, the kinetic plots obtained at 700, 725, 750 and 775° may indicate a control of the reaction rate which varies in the course of time. The products obtained at these temperatures became sintered. The changes in the degree of reaction as a function of time for fixed temperatures are

presented in Fig. 9. Equation R3 (model of a contracting core with control at the boundary of the phases) was applied to describe the kinetic plots from the range 640–675°:

$$1 - (1 - \alpha)^{1/3} = k_R t \quad (\text{R3})$$

where  $\alpha$  is the degree of reaction,

$k_R$  is a constant of the rate of the reaction, and

$t$  is time.

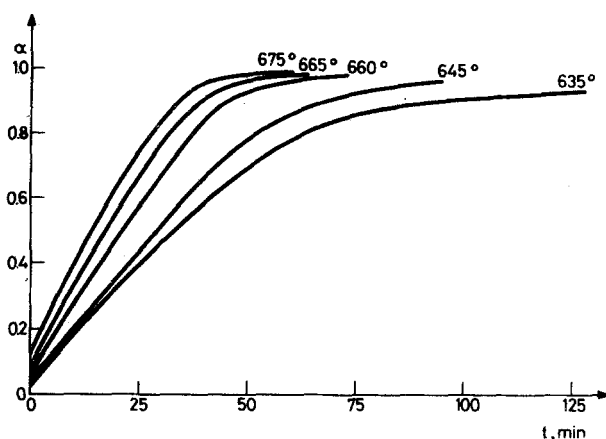


Fig. 9 The change of the degree of the reaction in the function time for the reduction of magnesium sulfate by carbon oxide for different temperatures

The results of matching a model kinetic equation (R3) with the experimental data from the range 640–675° are given in Table 2. The model of a contracting core describes these experimental data satisfactorily. Attempts to describe the experimental data from the range 700–775° by means of the model equations D (diffusive control) and M (mixed control) did not give satisfactory results. The

Table 2 Matching of model kinetic equations with experimental data obtained at 640–675 °C

Temperature	$a_0$	$S(a_0)$	$k_R$	$S(k_R)$	$r$
640	$1.81 \cdot 10^{-2}$	$1.09 \cdot 10^{-2}$	$5.4640 \cdot 10^{-3}$	$2.3332 \cdot 10^{-4}$	0.989236
650	$1.50 \cdot 10^{-2}$	$5.79 \cdot 10^{-3}$	$7.7243 \cdot 10^{-3}$	$1.4021 \cdot 10^{-4}$	0.997865
660	$1.10 \cdot 10^{-2}$	$1.73 \cdot 10^{-2}$	$10.5838 \cdot 10^{-3}$	$4.4484 \cdot 10^{-4}$	0.987853
670	$2.76 \cdot 10^{-2}$	$2.07 \cdot 10^{-2}$	$13.4845 \cdot 10^{-3}$	$6.6986 \cdot 10^{-4}$	0.982996
675	$0.49 \cdot 10^{-2}$	$0.96 \cdot 10^{-2}$	$15.2098 \cdot 10^{-3}$	$4.1078 \cdot 10^{-4}$	0.995292

$$g(\alpha) = a_0 + k_R t.$$

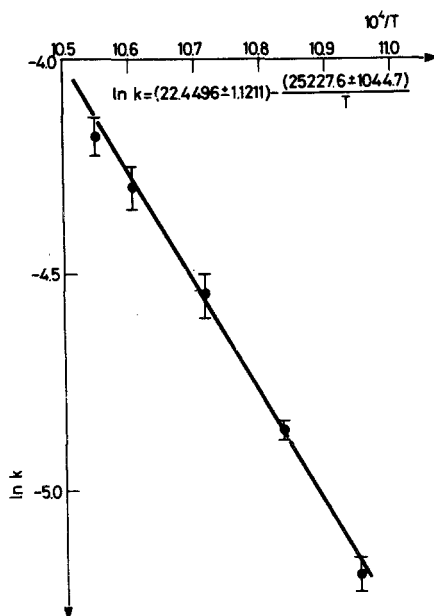


Fig. 10 Arrhenius plot of rate constants obtained from reduction magnesium sulfate by carbon oxide

energy of activation was determined from the Arrhenius equation on the basis of the constant values of the rate of the reaction shown in Table 2. This parameter has a value  $E_a = 209.7 \pm 8.6$  kJ/mol and applies to the control of reaction (5) at the boundary of the substrate product phases.

### Conclusions

It has been proved on the basis of the results obtained in this paper that magnesium sulfate is reduced by carbon oxide from 550°, to form magnesium sulfide and magnesium oxide. The formation of magnesium sulfate is theoretically unjustified above 520°. It has been proved experimentally that the temperature above which magnesium sulfate is not formed is 625°. In the course of the reduction reaction, the grains of the products are smaller than the grains of the substrate. The control of the rate of the reduction reaction varies as a function of temperature. It can be observed that there is rather nucleation control at 600 and 625°, whereas control by a chemical reaction may be noted in the range 640–675°. At higher temperatures, diffusion plays an important role and change of the control rate according to time at constant temperature takes place. To describe the kinetic plots obtained at temperatures of 640–675°, a model of a contracting core has been used. The energy of activation of the reaction is  $209.7 \pm 8.6$  kJ/mol.

## References

- 1 F. Habashi, S. A. Mikhail and K. Vo Van, *Can. J. Chem.*, 54 (1976) 3646.
- 2 Gmelins Handbuch der Anorganischen Chemie, System-nummer 27, Magnesium, Verlag Chemie, GmbH, Berlin, 1938, p. 214.
- 3 D. Krikliivi, O. S. Klimovich and M. F. Shpak, *Zh. Prikl. Khim.*, 57 (11) (1984) 2433.
- 4 I. Barin, O. Knacke and I. Kubaschewski, *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, New York, 1977.
- 5 W. Ptak and M. Sukiennik, *Archiwum Hutnictwa*, 16 (1) (1971) 3.
- 6 N. Jacinto, S. N. Sinha, M. Nagamori and H. Y. Sohn, *Metallurgical Transactions, B*, 14B (1983) 136.
- 7 J. Plewa, J. Norwicz, N. Hajduk and M. Romańska, *Thermochem. Acta*, 46 (1981) 217.

**Zusammenfassung** — Es wird über thermodynamische Analyse und Resultate einer thermogravimetrischen Untersuchung der Reduktion von Magnesiumsulfat mit Kohlendioxid berichtet. Die isothermen Experimente wurden im Temperaturbereich 640 bis 675° durchgeführt. Zur Erklärung der Reaktionsgeschwindigkeit wurde eine Shrinking-Modell gefunden. Es wurde eine Aktivierungsenergie von  $209.7 \pm 8.6$  kJ/mol erhalten.

**Резюме** — Приведен термодинамический анализ и результаты термогравиметрического исследования реакции восстановления сульфата магния окисью углерода. Изотермические измерения проведены в интервале температур 640–675°. Найдено, что скорость реакции описывается моделью сжимаемой активной зоны. Вычислена энергия активации равная  $209,7 \pm 8,6$  кДж/моль.