

KINETICS OF OXIDATION OF “V₅S₈” and V₃S₄

S. K. Basu and M. Taniguchi

DEPARTMENT OF CHEMICAL ENGINEERING, TOKYO INSTITUTE
OF TECHNOLOGY, O-OKAYAMA, MEGURO-KU, TOKYO-152, JAPAN

(Received March 15, 1985)

The kinetics of oxidation of “V₅S₈” and V₃S₄ to V₂O₃ were studied by using both isothermal and nonisothermal thermogravimetry in the oxygen partial pressure range from 1.0×10^{-1} to 1.0×10^{-3} atm. The kinetic equation describing the oxidation process was found to be $kt = 1 - (1 - \alpha)^{1/1.5}$ and was valid for the fraction of sample reacted $\alpha = 0$ to 80–95%. The activation energy was found to be from 45.9 to 27.8 kJ/mol⁻¹ for “V₅S₈”, and from 46.8 to 29.0 kJ/mol⁻¹ for V₃S₄ over the temperature range 375 to 500°. The relationship between rate constant k and PO_2 was also determined.

Precise knowledge about the kinetics and thermal oxidation of metal sulfides is of enormous technological importance, especially for the recovery of metals from sulfide ores and industrial by-products. Although various sulfide systems have been very thoroughly studied, only a few reports on the mechanism and kinetics of thermal oxidation (e.g. ZnS, FeS, MoS₂, NiS, V₂S₃, CuS, PbS, etc.) are available due to the complexity of the oxidation processes. We recently submitted a detailed report [1] on the thermal oxidation of nonstoichiometric “V₅S₈” and stoichiometric V₃S₄, covering a wide range of oxygen partial pressure (PO_2) and temperature. It is clear from that report that the kinetic study of “V₅S₈” and V₃S₄ is not possible either in a flow or in a static atmosphere of O₂ or air, because of the enormous rise in sample temperature due to self-heating during the oxidation. Moreover, the overlapping of different oxidation steps under these oxidation conditions makes it unreasonable to attempt a kinetic study.

In these circumstances, the purpose of the present paper was to find suitable PO_2 and temperature ranges where only a single oxidation reaction takes place without any rise in sample temperature, and then to study the oxidation kinetics of “V₅S₈” and V₃S₄ phases by thermogravimetry (TG).

Experimental

TG-DTA measurements were carried out with a rapid-heating Rigaku-Thermoflex TG-DTA unit. Five, 10 and 20 mg quantities of the sample (250–325 mesh) were weighed accurately in a platinum crucible of 2.5×5 mm diameter, distributed evenly without pressing, and tapped 2 or 3 times on a metal surface for both the isothermal and the nonisothermal methods. High-purity "dead-burnt" α - Al_2O_3 was used as the standard reference material.

The preparation of the samples $\text{VS}_{1.567}$ (" V_5S_8 " phase) and $\text{VS}_{1.34}$ (V_3S_4 phase), the controlling of PO_2 by mixing N_2 -air and N_2 - O_2 , and the characterization of the samples and the reaction products, were performed in the same way as reported in our previous paper [1]. Heating was started at least 30 min after the sample was placed in the TG furnace. Computer work was done with an NEC PC 9801F personal computer.

Results and discussion

Figures 1 and 2 show the TG-DTA traces of the " V_5S_8 " and V_3S_4 phases, respectively, obtained under different oxidizing atmospheres (e.g.

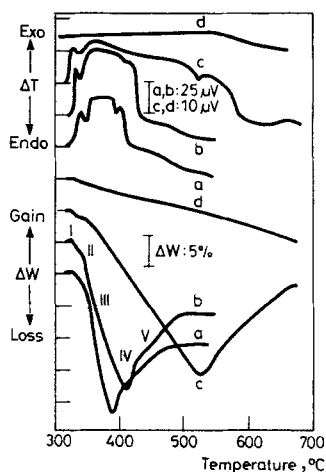


Fig. 1 TG-DTA curves of " V_5S_8 " at 5 deg/min^{-1} (sample: 20 mg, 250–325 mesh; PO_2 : (a) 1.00×10^{-1} , (b) 4.97×10^{-2} , (c) 1.10×10^{-2} and (d) 1.00×10^{-3} atm; gas flow: 2 ml s^{-1})

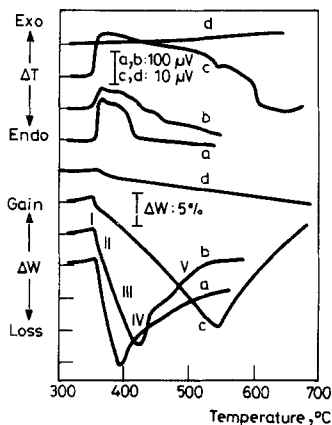
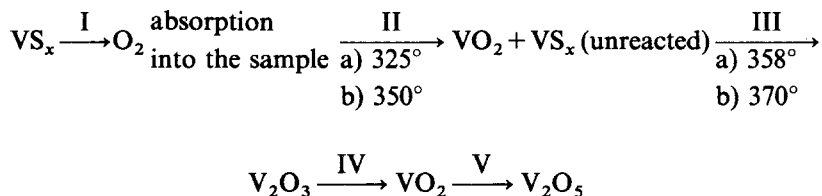


Fig. 2 TG-DTA curves of V_3S_4 at 5 deg/min^{-1} (sample: 20 mg, 250–325 mesh; PO_2 : (a) 1.00×10^{-1} , (b) 4.97×10^{-2} , (c) 1.10×10^{-2} and (d) 1.00×10^{-3} atm; gas flow: 2 ml s^{-1})

$PO_2 = 1.0 \times 10^{-1} - 1.0 \times 10^{-3}$ atm) and at a heating rate of 5 deg/min^{-1} . All the TG traces except curve *d* show 5 weight change steps, whereas the DTA curves (except curve *d*, in which the reaction was very slow and was incomplete) show 3 exothermic peaks corresponding to steps II, III and IV. These phenomena, which are in accordance with the X-ray powder diffraction patterns of the products in different steps, indicate that the principal oxidation reaction sequence is the same as that reported before [1], which is given below:



where $x =$ a) 1.567 for the “ V_5S_8 ” phase and b) 1.342 for the V_3S_4 phase. However, unlike the previous case [1], no abnormal rise in sample temperature was noticed during the progress of the reaction in step III. Also, when a heating rate higher than 10 deg/min^{-1} was used, no VO_2 was formed, and the samples were oxidized stoichiometrically to V_2O_3 in the first oxidation step, which is shown in Fig. 3.

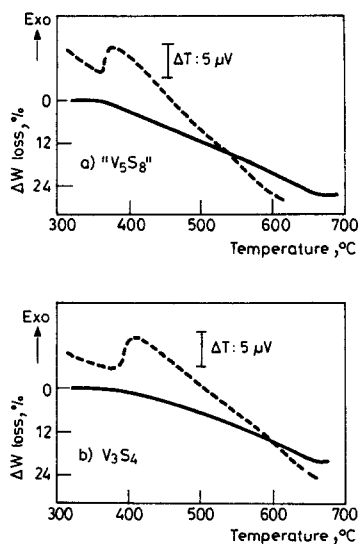
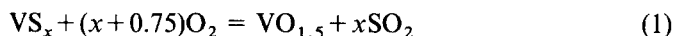


Fig. 3 TG-DTA curves of (a) “ V_5S_8 ” and (b) V_3S_4 at 20 deg min^{-1} (sample: 5 mg, 250–325 mesh; PO_2 : 1.10×10^{-2} atm; gas flow: 2 ml s^{-1})

From the above result it is concluded that an isothermal kinetic study of the oxidations of "V₅S₈" and V₃S₄ to V₂O₃ according to Eq. (1)



can be carried out safely at temperatures over 375°, since below this temperature there is a possibility of the formation of VO₂. This result also shows that a nonisothermal kinetic study regarding Eq. (1) is possible if a higher heating rate is used.

Kinetic study

Isothermal method

i) α vs. t plot

The samples were oxidized isothermally between 375 and 525°, selected from the nonisothermal analysis. The TG traces were obtained as plots of percentage weight loss vs. time (t); a typical example is shown in Fig. 4. A minor correction was needed

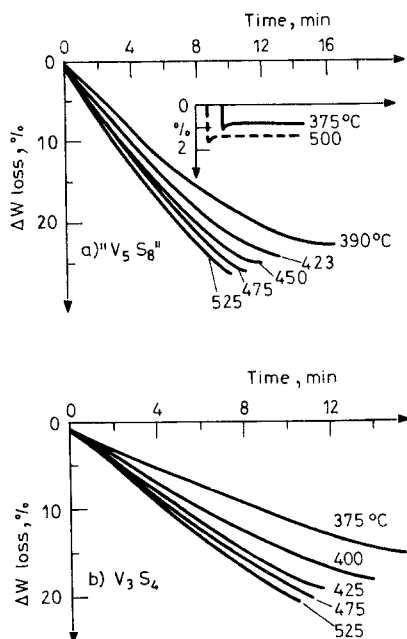


Fig. 4 TG traces of (a) "V₅S₈" and (b) V₃S₄ when heated isothermally at a PO_2 of 4.97×10^{-2} atm (sample: 20 mg, 250–325 mesh; gas flow: 2 ml s⁻¹). The insert in (a) shows the TG curves when α -Al₂O₃ was used in place of sample

to derive the α vs. t data from these plots, since when the TG furnace temperature was raised instantaneously (ca 10 s) to a predetermined temperature, the TG pen initially recorded a sudden loss (ca 1–1.5% with a full-scale sensitivity of 10 mg). This phenomenon was then checked by using an equal amount of calcined α -Al₂O₃ in lieu of the sulfide sample, and a similar effect (insert in Fig. 4a) was observed, which is considered to be a characteristic of the rapid-heating TG-DTA unit. Consequently, the α vs. t data were always derived by deducting the amount of this initial weight loss, recorded during the quick rise of temperature, from the % weight loss in question.

ii) Rate equation

The rate of oxidation with respect to time is given by

$$\frac{d\alpha}{dt} = k'f(\alpha) \quad (2)$$

$$F(\alpha) = kt \quad (3)$$

The functions $F(\alpha)$, derived from the differential forms of the standard rate equations [2, 3], are listed in Table 1. The correct rate equation is considered to be the one which gives the best straight-line fit when plotted against time.

A computer program was developed to test all the rate equations in Table 1 for the best straight-line fit. It was found from Fig. 5 that rate equations (3) and (4) (i.e. two- and three-dimensional phase boundary reactions, respectively) give good straight-line fits at lower temperatures, whereas Eq. (5) gives straight lines for the

Table 1 Kinetic expressions tested for the oxidation reaction

Rate equation no.	$F(\alpha)$ (integral form)	Rate equation no.	$F(\alpha)$ (integral form)
1	α	12	$[-\ln(1-\alpha)]^{1/3}$
2	$-\ln(1-\alpha)$	13	$[-\ln(1-\alpha)]^{1/4}$
3	$1-(1-\alpha)^{1/2}$	14	$[-\ln(1-\alpha)]^{3/4}$
4	$1-(1-\alpha)^{1/3}$	15	$[-\ln(1-\alpha)]^{2/3}$
5	$1-(1-\alpha)^{2/3}$	16	α^2
6	$(1-\alpha)^{-1/2} - 1$	17	$(1-\alpha) \ln(1-\alpha) + \alpha$
7	$-(1-\alpha)^3$	18	$[1-(1-\alpha)^{1/3}]^2$
8	$\alpha^{1/2}$	19	$1-2/3\alpha-(1-\alpha)^{2/3}$
9	$\alpha^{1/3}$	20	$[(1/(1-\alpha)^{1/3}) - 1]^2$
10	$\alpha^{1/4}$	21	$\ln \alpha/(1-\alpha)$
11	$[-\ln(1-\alpha)]^{1/2}$	22	$\ln \alpha/(1-\alpha) = k \log(t)$

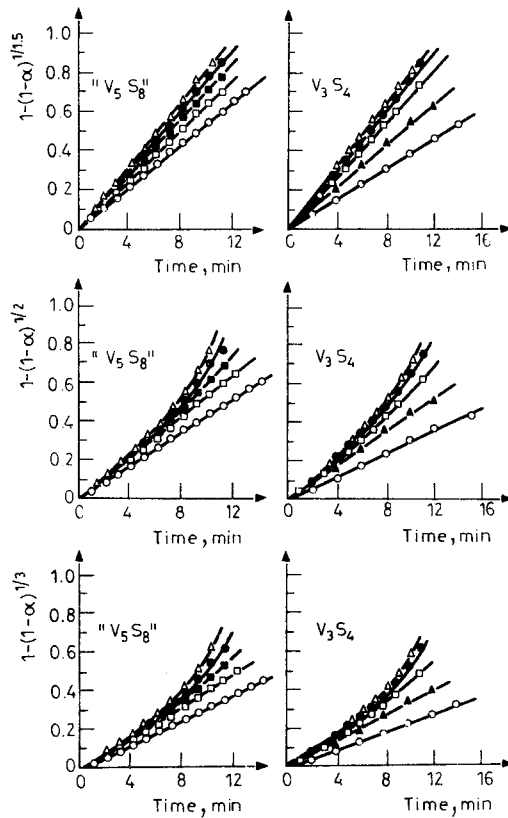


Fig. 5 Plots of $F(\alpha)$ vs. time for " V_5S_8 " and V_3S_4 at (○) 375, (◻) 390, (▲) 400, (◻) 425, (■) 450, (●) 475 and (△) 525° (sample: 20 mg, 250–325 mesh; PO_2 : 4.97×10^{-2} ; gas flow: 2 ml s^{-1})

whole range of temperatures examined, and is valid for $\alpha=0$ to 80–95%. It is therefore assumed that rate equation (5), which corresponds to an "index of reaction" [4] (superficially analogous to order of reaction) of $m = 1/3$ (z and $\beta=1$), indicating the unidirectional kinetics of a sphere, controls the oxidation reaction represented by Eq. (1).

iii) Influence of amount of samples

Different amounts of samples, e.g. 5, 10 and 20 mg, were oxidized at a fixed PO_2 ($4.97 \times 10^{-2} \text{ atm}$) to check the effect of the sample amount on Arrhenius parameters E and A , and the plots are shown in Fig. 6. It is seen that the gradient E and intercept A of the plot of $\ln k$ vs. the inverse of temperature (K) decrease with

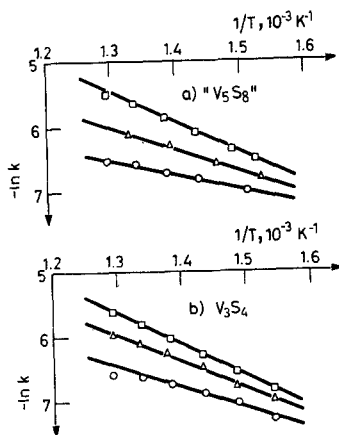


Fig. 6 Arrhenius plots of (a) "V₅S₈" and (b) V₃S₄ (sample: (□) 5 mg, (△) 10 mg and (○) 20 mg, 250–325 mesh; PO₂: 4.97 × 10⁻² atm, gas flow: 2 ml s⁻¹)

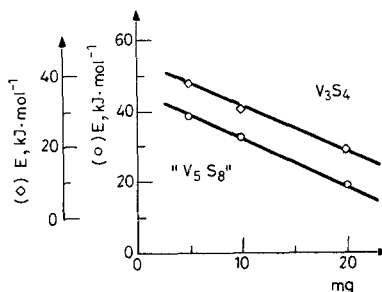


Fig. 7 Plots of activation energy E (kJ mol⁻¹) vs. amount of sample (mg) for (○) "V₅S₈" and (◇) V₃S₄ (PO₂: 4.97 × 10⁻² atm; temperature range: 375–500°)

increase of the sample amount. The variation of E with sample amount is shown in Fig. 7. Figure 6 also reveals that the reaction temperature had less effect on the rate constant k when 20 mg of sample was used, whereas the rate of change of k with respect to temperature improved noticeably with decrease of the sample amount. This is due to the fact that, when a larger amount of sample is used, a thick powder layer is formed and the gas exchange, i.e. the removal of the product SO₂ gas and the access of O₂ from the bulk gas flow to the reaction interface, are hindered, especially when the initial reaction rate increases with the increase of isothermal setting temperature. The gas exchange conditions are improved when a small amount of sample is used or when the flow rate of the reacting gas is increased, which on the other hand enhances the reaction rate. However, the latter can not be done since the construction of the TG-DTA apparatus does not permit the use of a flow rate greater than 2 cm³ s⁻¹. Consequently, 5 mg of sample was used for the determination of E and A ; Arrhenius plots at four different PO₂ values are shown in Fig. 8 for both "V₅S₈" and V₃S₄.

iv) Dependence of E and A on PO₂

The values of E and A were determined by using the least-square method, and are listed in Table 2. It is seen that both E and A increase with the increase of PO₂, that they are almost the same for "V₅S₈" and V₃S₄, and that they vary similarly with PO₂. These results indicate that the sulfur composition in "V₅S₈" and V₃S₄ has almost no effect on the rate of oxidation.

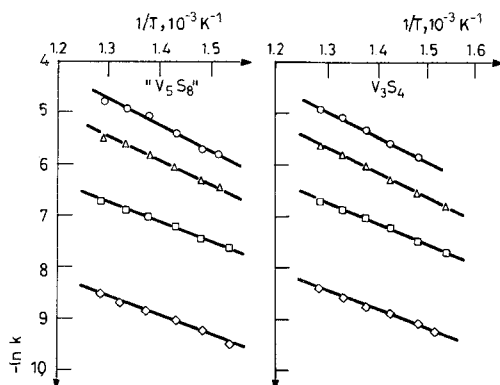


Fig. 8 Arrhenius plots of "V₅S₈" and V₃S₄ (sample: 5 mg, 250–325 mesh; PO₂: (○) 1.00 × 10⁻¹, (△) 4.97 × 10⁻², (□) 1.10 × 10⁻² and (◇) 1.00 × 10⁻³ atm; gas flow: 2 ml s⁻¹)

Table 2 Values of E (kJ mol⁻¹) and A (s⁻¹) for "V₅S₈" and V₃S₄ at different PO₂

PO ₂ , atm	E		A		Method
	"V ₅ S ₈ "	V ₃ S ₄	"V ₅ S ₈ "	V ₃ S ₄	
1.00 × 10 ⁻¹	45.90	46.81	11.63	11.31	isothermal
4.97 × 10 ⁻²	38.77	38.49	1.81	1.43	
*1.10 × 10 ⁻²	30.97	33.18	0.146	0.212	
1.00 × 10 ⁻³	27.75	29.00	0.014	0.019	
*1.10 × 10 ⁻²	32.27	42.18	0.095	0.437	nonisothermal

v) Dependence of rate constant k on PO₂

Figure 9 shows the plot of $\log k$ vs. $\log PO_2$. It is seen that k varies only slightly with temperature at a definite PO₂, but increases linearly with the increase of PO₂. From this plot, the relationship between k and PO₂ was determined as

$$k = c'(PO_2)^{0.782 \pm 0.022} \text{ for "V}_5\text{S}_8", \quad (4)$$

and

$$k = c''(PO_2)^{0.712 \pm 0.024} \text{ for V}_3\text{S}_4 \quad (5)$$

It is evident from this result that, unlike many other sulfides, the rate of oxidation of vanadium sulfides depends much more on PO₂ than on temperature under the present experimental conditions.

Two different values of E , i.e. E_1 and E_2 (for high and low temperatures, respectively), are reported for ZnS [5], FeS [6], V₂S₃ [7], etc. For the sake of comparison these are given in Table 3. For "V₅S₈" and V₃S₄ we observed only one

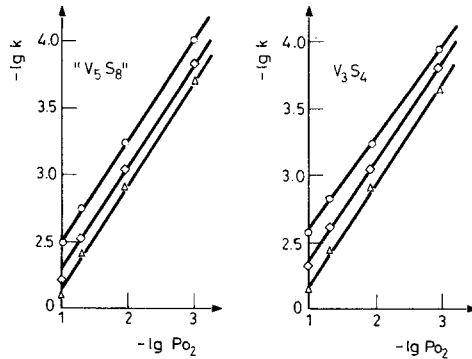


Fig. 9 Plots of $-\log k$ vs. $-\log PO_2$ for “ V_5S_8 ” and V_3S_4 (sample: 5 mg, 250–325 mesh; temperature: (O) 400, (\diamond) 450 and (Δ) 500°)

Table 3 Literature values of E for different sulfides. E_1 and E_2 are for low and high temperatures, respectively, whereas T is the temperature of the reflection point

Sample	E_1 , kJ mol $^{-1}$	E_2 , kJ mol $^{-1}$	T°	Ref.
ZnS	209.2	20.9	605	[5]
FeS	129.0	47.8	500	[6]
V_2S_3	168.6	29.3	330	[7]

value of E at each pressure, and these are very close to the values of E_2 presented in Table 3. It is interesting to note that the results obtained in the temperature range (375–500°) examined in the present study resemble those for E_2 , i.e. those in the high-temperature range. Furthermore, for MoS_2 only one value of E has been reported; using a pelleted sample of MoS_2 , Zelikman et al. [8] calculated E as 57.5 kJ mol $^{-1}$, whereas Cardoen [9] determined a value of 176.4 kJ mol $^{-1}$ over the temperature range 492–670°. This fact suggests that a very strict comparison of the results on solid-gas reaction kinetics is not possible, since the parameters in solid-gas reactions depend on a great variety of factors, including sample preparation, the size and material of the sample pan, the internal construction of the furnace, the gas flow rate, etc. On the basis of the above discussion, it can be concluded that the values presented in Table 2 for “ V_5S_8 ” and V_3S_4 are quite reasonable.

Nonisothermal study

Although it is well known that reliable results can generally be obtained from a nonisothermal kinetic study when a lower heating rate is employed, in the present study a lower heating rate can not be used, since the sample would oxidize partially to VO_2 before the formation of V_2O_3 starts, according to Eq. (1). Therefore, a

heating rate of 20 deg min^{-1} and a PO_2 of $1.10 \times 10^{-2} \text{ atm}$ were used to verify the accuracy of the reaction mechanism observed in the isothermal method. The TG curves are shown in Fig. 3, and E and A were determined for Eq. (1) by employing the graphical method of Coats and Redfern [10]. The general equation for this method is

$$\ln [F(\alpha)/T^2] = \ln \frac{AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{RT} \quad (6)$$

where $F(\alpha)$ is the function observed for the isothermal method, R is the gas constant and a is the linear heating rate. E and A are obtained by plotting $\ln [F(\alpha)/T^2]$ against $1/T$. In this case, for both " V_5S_8 " and V_3S_4 the plots (Fig. 10) yield almost perfect

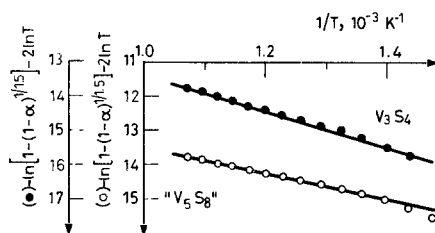


Fig. 10 Coats and Redfern's linearization plots ($\ln F(\alpha) - 2 \ln T$ vs. $1/T$) for " V_5S_8 " and V_3S_4 (sample: 5 mg, 250–325 mesh; PO_2 : $1.10 \times 10^{-2} \text{ atm}$; gas flow: 2 ml s^{-1} ; heating rate: 20 deg min^{-1})

straight lines, and the values of E and A (Table 2) agree well with those obtained from the isothermal study, indicating the exactness of the observed mechanism. For higher PO_2 , the straight-line relationships for the plots are as nearly perfect as those shown in Fig. 10, but the variation in E and A is somewhat greater.

Conclusions

(1) The rate equation for the thermal oxidations of " V_5S_8 " and V_3S_4 to V_2O_3 is $kt = 1 - (1 - \alpha)^{1/1.5}$, which expresses a unidirectional reaction of spherical particles.

(2) The rate constant increases linearly with the increase of PO_2 and is less dependent on temperature.

(3) The activation energy E and pre-exponential factor A also increase with the increase of PO_2 and remain almost unchanged for " V_5S_8 " and V_3S_4 .

(4) The relationship between rate constant k and PO_2 is

$k = c'(PO_2)^{0.782 \pm 0.022}$ for "V₅S₈", and

$k = c''(PO_2)^{0.712 \pm 0.024}$ for V₃S₄

The above conclusions have been drawn from the experimental results obtained for the temperature range 375 to 500° and the PO₂ range 1.0 × 10⁻¹ to 1.0 × 10⁻³ atm.

* * *

The authors wish to thank Dr. T. Uchida for his computer programming assistance.

References

- 1 S. K. Basu and M. Taniguchi, *J. Thermal Anal.*, 29 (1984) 1209.
- 2 J. Šestak and G. Berggren, *Thermochim. Acta*, 3 (1971) 1.
- 3 A. Bhatti and D. Dollimore, *Thermochim. Acta*, 78 (1984) 55.
- 4 J. H. Taplin, *J. Am. Ceram. Soc.*, 57 (1974) 140.
- 5 T. Wada and K. Niwa, *J. Chem. Soc. of Japan, Pure Chem. Section (Nippon Kagaku Zasshi)* 76 (1955) 1285.
- 6 F. T. Bumazhnov, *Zap. Leningr. Gorn. Inst.*, 42 (3) (1963) 90.
- 7 M. Taniguchi and S. Ohara, *Proc. 7th Inter. Conf. Thermal Anal.*, 1 (1982) 113.
- 8 A. N. Zelikman and L. V. Belaevskaya, *J. Inorg. Chem. USSR*, 10 (1956) 2256.
- 9 C. Cardoen, University of Utah, Ph. D. Thesis, June 1969.
- 10 A. W. Coats and J. P. Redfern, *Nature (London)*, 201 (1964) 68.

Zusammenfassung — Die Kinetik der Oxydation von „V₅S₈“ und V₃S₄ zu V₂O₃ wurde mittels isothermer und nicht-isothermer Thermogravimetrie bei Sauerstoffpartialdrücken von 1 · 10⁻¹ bis 1 · 10⁻³ atm untersucht. Die den Oxydationsprozeß beschreibende kinetische Gleichung

$$kt = 1 - (1 - \alpha)^{1/1.5}$$

ist bis zu einem Umsatzgrad von 80–95% gültig. Im Temperaturbereich von 375–500° liegt der Wert der Aktivierungsenergie für „V₅S₈“ zwischen 45,9 und 27,8 kJ mol⁻¹ und der für V₃S₄ zwischen 46,8 und 29,0 kJ/mol⁻¹. Die Beziehung zwischen der Geschwindigkeitskonstante k und PO₂ wurde ebenfalls ermittelt.

Резюме — Используя изотермическую и неизотермическую термогравиметрию изучена кинетика окисления «V₅S₈» и V₃S₄ до V₂O₃ при парциальном давлении кислорода от 0,1 до 0,003 атм. Реакция окисления описывается кинетическим уравнением $kt = 1 - (1 - \alpha)^{1/1.5}$ для области степени превращения 0–80–95%. Значения энергий активаций в области температур 375–500° для «V₅S₈» находятся в интервале 45,9–28,8 кдж · моль⁻¹, а для V₃S₄ — 46,8–29,0 кдж · моль⁻¹. Определена также взаимосвязь между константой скорости k и парциальным давлением кислорода.