

## COMPARATIVE KINETIC AND THERMODYNAMIC STUDY ON THE CHLORINATION OF $V_2O_5$ with $CCl_4$ , $COCl_2$ and $Cl_2$

*I. S. Pap, G. Mink, I. Bertóti, T. Székely, \*I. Z. Babievskaya  
and E. Karmazsin*

RESEARCH LABORATORY FOR INORGANIC CHEMISTRY  
OF THE HUNGARIAN ACADEMY OF SCIENCES, P. O. BOX 132,  
H-1502 BUDAPEST, HUNGARY

\*N. S. KURNAKOV INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY,  
ACADEMY OF THE SCIENCES OF THE USSR, MOSCOW, USSR  
CLAUDE BERNARD UNIVERSITY, DEPARTMENT OF APPLIED CHEMISTRY,  
LYON, FRANCE

(Received February 12, 1988)

The chlorination kinetics of pure vanadia was studied via isothermal thermogravimetric measurements, with  $CCl_4$ ,  $CoCl_2$  and  $Cl_2$  as chlorinating agents. At temperatures where chemical control was predominant, apparent activation energies of 77, 48 and 126  $\text{kJ} \cdot \text{mol}^{-1}$  were obtained for chlorination by  $CCl_4$ ,  $COCl_2$  and  $Cl_2$ , respectively. For interpretation of the conversion vs. time curves in the whole conversion range, a non-uniform particle size distribution was assumed, where the reacting solid phase was considered to be composed of thin plates of different thicknesses. With this model, a fairly good correspondence was obtained between the measured and calculated kinetic curves. Selected thermodynamic calculation data on the  $V_2O_5 + CCl_4$ ,  $V_2O_5 + COCl_2$  and  $V_2O_5 + Cl_2$  systems are presented.

On an industrial scale, vanadium is extracted in the form of pure, volatile  $VCl_4$  from concentrated ores and minerals by high-temperature chlorination with  $Cl_2$  in the presence of carbon [1]. The direct action of gas-phase chlorinating agents such as  $CCl_4$ ,  $COCl_4$ ,  $CO + Cl_2$ , etc. offers a considerable reduction of the reaction temperature. In these reactions, however, the predominant volatile product is  $VOCl_3$ , which is not suitable for the direct production of metallic vanadium. In spite of the great practical and theoretical importance of these types of chlorination, hardly any data are available concerning the kinetics and mechanisms of these reactions [2–4].

In our previous work [5–7], kinetic studies were made on the  $V_2O_5 + CCl_4$  reaction. The aim of the present work is to give comparative data on the thermodynamics and kinetics of the  $V_2O_5 + Cl_2$ ,  $V_2O_5 + COCl_2$  and  $V_2O_5 + CCl_4$  reactions. All the kinetic data referring to this latter process are taken directly or are derived from the results published in [6].

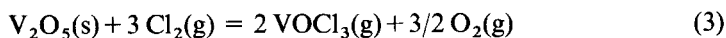
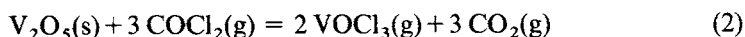
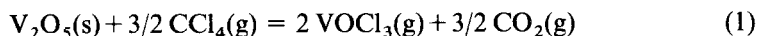
## Experimental

The kinetics of chlorination of pure  $V_2O_5$  (Reanal,  $s^\circ = 3.1 \text{ m}^2 \text{ g}^{-1}$ ) was investigated in the temperature range 400–900 K. The chlorination reactions were carried out in a fused silica reactor coupled with a Mettler semimicro recording balance [8].  $CCl_4$  of pss. purity [6], phosgene and chlorine of 3N purity were used as chlorinating agents. Nitrogen of 4N purity, dried in the usual manner, was used as carrier gas. Before the chlorination, the samples were preheated in situ at 700 K for 30 minutes in an  $O_2$ – $N_2$  mixture. During the measurements, the conditions of a differential-type flow reactor were maintained, a large excess of the inlet active gases being used.

## Results and discussion

### *Thermodynamic aspects*

The equilibrium conditions for closed systems of  $V_2O_5 + CCl_4$ ,  $V_2O_5 + COCl_2$  and  $V_2O_5 + Cl_2$  were calculated with a computer program developed in the Institute for Inorganic and General Chemistry of the Academy of Sciences of the USSR. The computations showed that under equilibrium conditions the predominant volatile metal compound is  $VOCl_3$ . However, the formation of minor amounts of  $VCl_4$  is also probable. Thus, the overall reactions correspond almost exclusively to the following equations:



The variation in the equilibrium composition of the gas phase with the reaction temperature for "stoichiometric" mixtures in a closed reactor and under atmospheric pressure is illustrated in Figs 1–3. Figures 1 and 2 show that the chlorination with  $CCl_4$  or  $COCl_2$  is highly favoured. Both of these reactions lead to the total gasification of the solid throughout the temperature range investigated. None of the assumed solid residues such as  $VO$ ,  $VO_2$ ,  $V_2O_4$ ,  $V_2O_5$ ,  $V_3O_5$ ,  $V_4O_7$ ,  $VOCl$ ,  $VC$  or  $C$  taken into account in the calculation can achieve an equilibrium concentration of  $10^{-17}$  mol/mol  $V_2O_5$  feed. In the presence of  $Cl_2$  as chlorinating agent, the reaction is not so favoured, but the equilibrium yield of  $VOCl_3$  continuously increases with temperature. At 600 K, which is the lowest temperature used for calculation, the equilibrium composition of the gas phase is

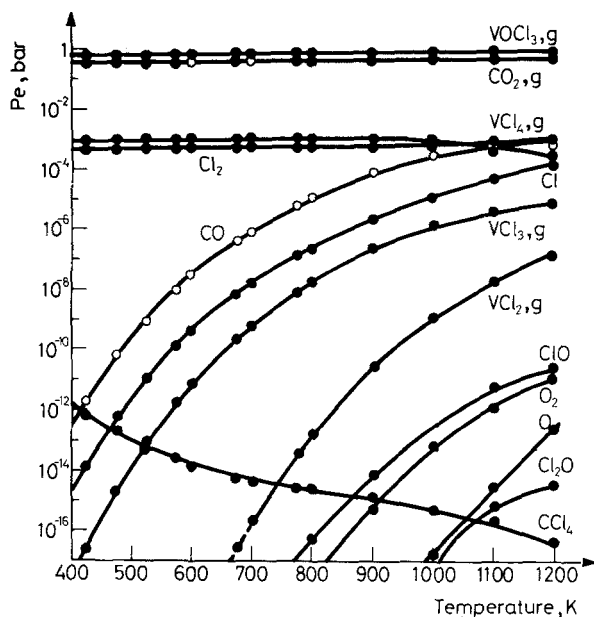


Fig. 1 Equilibrium compositions of the gas phase for the reaction of  $V_2O_5 + CCl_4$  (molar ratio: 1 : 1.5)

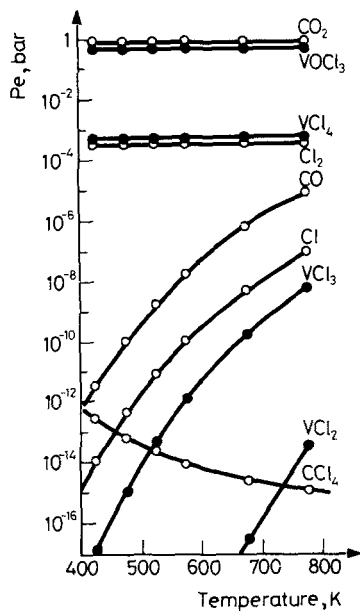


Fig. 2 Equilibrium compositions of the gas phase for the reaction of  $V_2O_5 + COCl_2$  (molar ratio: 1 : 3)

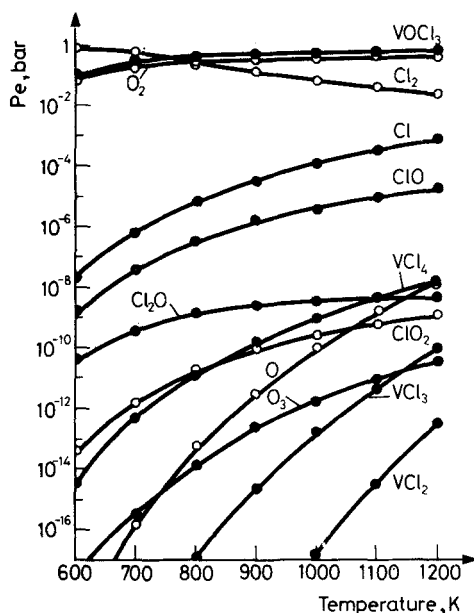


Fig. 3 Equilibrium compositions of the gas phase for the reaction of  $V_2O_5 + Cl_2$  (molar ratio: 1 : 3)

0.09030 bar of  $VOCl_3$ , 0.006778 bar of  $O_2$  and 0.84182 bar of  $Cl_2$ . This means that under flow conditions  $V_2O_5$  can be volatilized by  $Cl_2$  to  $VOCl_3$ , even at a reaction temperature of 600 K.

### Kinetic results

The reaction kinetics was followed by isothermal TG measurements in the temperature ranges 455–540 [6], 400–500 and 770–900 K for  $CCl_4$ ,  $COCl_2$  and  $Cl_2$ , respectively. The partial pressure of the reactive gases was 11.2 kPa for  $CCl_4$  [6], and 10.1 kPa for  $COCl_2$  or  $Cl_2$ . Some characteristic conversion (relative mass loss) vs. time curves are shown in Figs 4 and 5. It can be seen that the reaction with  $COCl_2$  starts with a slight mass gain, attributed to chemisorption or to surface O/Cl exchange reactions. This stage is followed by a steady-state mass loss due to the volatilization of  $VOCl_3$ . At higher temperatures and partial pressures, the TG curves start immediately with a continuous mass loss. Similarly, an initial mass gain was not observed either with  $CCl_4$  [6] or with  $Cl_2$ .

The reaction rate was determined in the steady-state region as the slope of the mass loss vs. time curves related to unit mass. The temperature-dependence of the reaction rate is shown in Fig. 6. It can be seen that the reactions with  $CCl_4$  and  $COCl_2$  start at much lower temperatures (about 400 K) than that, with  $Cl_2$ . The

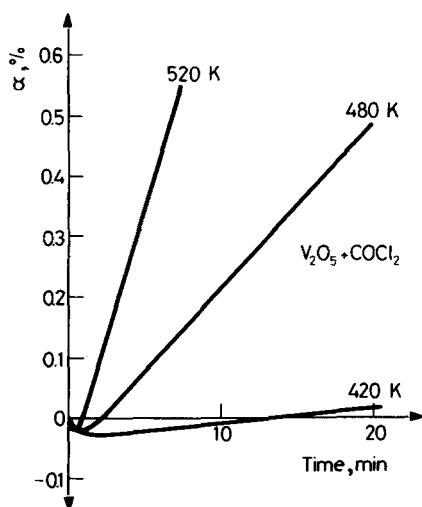


Fig. 4 Conversion vs. time curves for the chlorination of vanadia by phosgene ( $P_{\text{COCl}_2} = 11.8 \text{ kPa}$ )

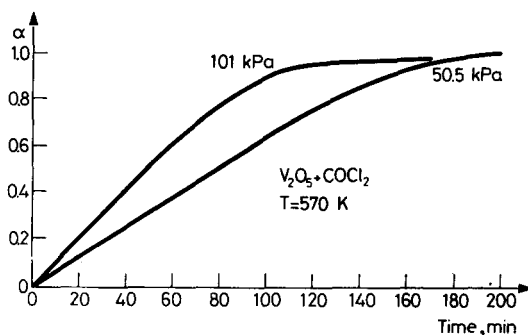


Fig. 5 Conversion vs. time curves for the chlorination of vanadia by phosgene ( $T = 570 \text{ K}$ )

Arrhenius representation of the data is shown in Fig. 7. In both cases a fairly good linear relationship was obtained, suggesting that the rate-controlling process does not change in the temperature ranges investigated, i.e. chemical control is predominant. As the calculated pre-exponential coefficient ( $k_0$ ) of the chlorination with  $\text{CCl}_4$  is more than  $10^3$  times higher than that of the chlorination with  $\text{COCl}_2$ , and at the same time the activation energy is also higher for  $\text{CCl}_4$ , the two curves intersect, as can be seen in Fig. 7. The apparent activation energies were calculated from the slopes of the Arrhenius plots. As Table 1 shows, the activation energies are 77, 48 and  $126 \text{ kJ} \cdot \text{mol}^{-1}$  for chlorination by  $\text{CCl}_4$ ,  $\text{COCl}_2$  and  $\text{Cl}_2$ , respectively. The variation in the reaction rate with the partial pressure of  $\text{COCl}_2$  and  $\text{Cl}_2$  is

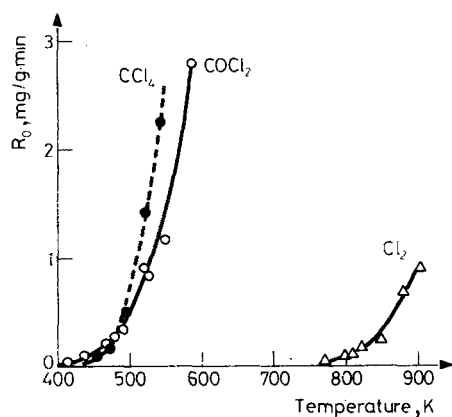


Fig. 6 Temperature-dependence of the reaction rates

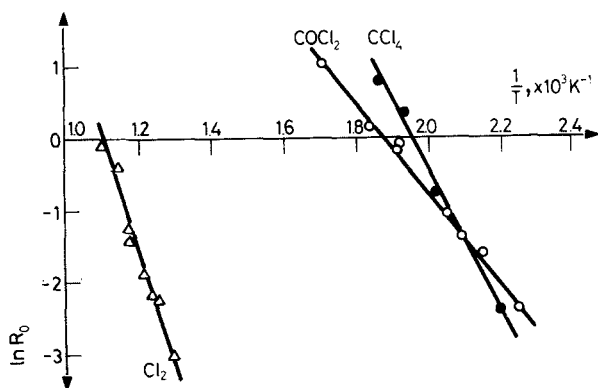


Fig. 7 Arrhenius representation of the reaction rates

Table 1 Apparent activation energies and reaction order for the chlorination of vanadia

	$E, \text{kJ} \cdot \text{mol}^{-1}$		$n$	
$\text{CCl}_4$	77*	(445–540 K)	0.5*	(470 K)
$\text{COCl}_2$	48	(400–570 K)	0.95	(420 K)
			0.77	(460 K)
			0.80	(510 K)
			0.74	(510 K)
$\text{Cl}_2$	126	(770–900 K)	0.5	(795 K)
			0.9	(850 K)

(\* Data for  $\text{CCl}_4$  are taken from [6]).

illustrated in Figs 8 and 9. The results correspond to formal reaction orders of 0.75–0.95 and 0.5–0.9 in  $\text{COCl}_2$  and  $\text{Cl}_2$ , respectively. For the chlorination by  $\text{CCl}_4$ , a reaction order of 0.5 was found [6] (see Table 1). For the reactions with  $\text{COCl}_2$  and  $\text{Cl}_2$ , the data show a linear course in the  $1/R_0$  vs.  $1/p$  representation. Thus, a Langmuir-type rate equation can also be used to describe the dependence of the chlorination on the partial pressure (see Figs 10 and 11).

In order to describe the conversion vs. time curves, various models [9] were tested. As the chlorination curves were closely linear up to a conversion about 70% (see Fig. 5), a fractional order of zero with respect to the solid proved to be the most satisfactory one for describing the time-dependence of the reaction rate. According to its crystal structure,  $\text{V}_2\text{O}_5$  consists of two-dimensional planes bound together by weak van der Waals forces [10], and it therefore forms slabs of relatively small thickness. Thus, the surface of the crystalline particles roughly coincides with that of the sum of the basal and cover plates, i.e. the contribution of the side walls to the surface is negligible. Under steady-state conditions, the linear rate of the reaction perpendicular to the surface is constant ( $-dl/dt = k$ , where  $l$  is the thickness of the slabs and  $k$  is the rate constant). For particles of uniform initial thickness, therefore, the conversion vs. time function can be given by a zero-order kinetic function:

$$\alpha \simeq kt/l_0 \quad (4)$$

where  $l_0$  is the initial thickness of the slabs.

Above  $\alpha = 70\%$ , however, a deceleration of the chlorination was observed and the formal zeroth order became insufficient for describing the time-dependence of the reaction rate.

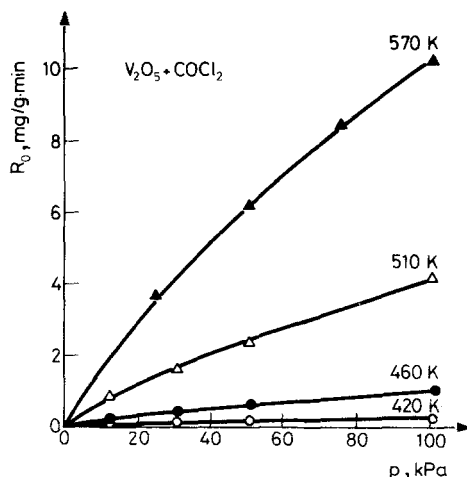


Fig. 8 Partial pressure-dependence of the reaction rate for the chlorination of vanadia by phosgene

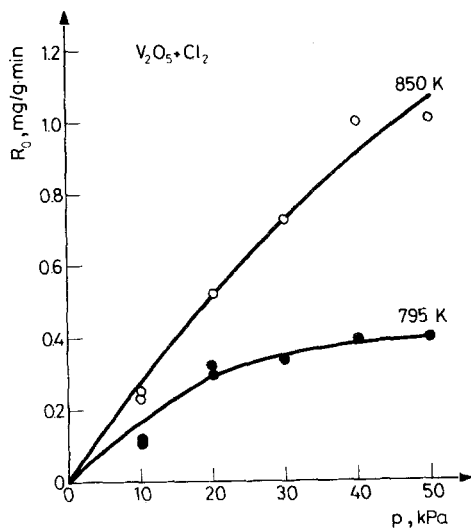


Fig. 9 Partial pressure-dependence of the reaction rate for the chlorination of vanadia by chlorine

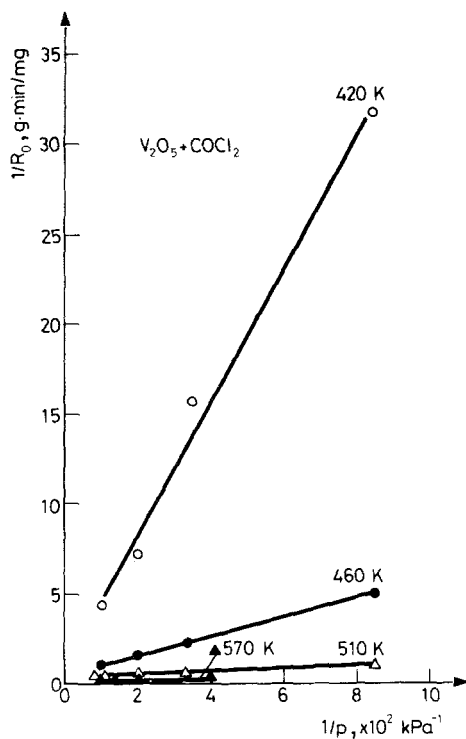


Fig. 10  $1/R_0$  vs.  $1/p$  curves for the chlorination of vanadia by phosgene



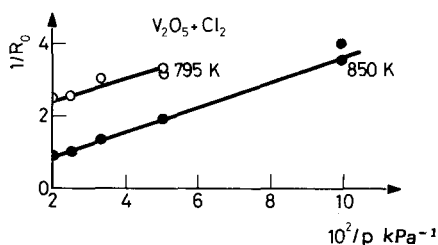


Fig. 11  $1/R_0$  vs.  $1/p$  curves for the chlorination of vanadia by chlorine

It is known that a non-uniform particle size distribution may influence the kinetics of heterogeneous reactions significantly [11]. Several reports have recently been published on the particle size effect [12, 13] and conversion vs. time relationships based on detailed mathematical equations have been predicted for a few special distributions. Similarly, in our previous work [14] the conversion vs. time curves in the chlorination of  $TiO_2$  were interpreted by assuming a special particle size distribution of  $TiO_2$  particles of close to spherical shape.

In order to describe the chlorination curves of vanadia in the whole conversion range, the assumption of a non-uniform particle size distribution is proposed, where the reacting particles are considered to be thin plates of different thicknesses. During the reaction, the smaller slabs are fully chlorinated, and the relatively low rates measured at high conversions are attributed to the reaction of the remaining particles of greater size. On the basis of this model, the conversion of the particles of

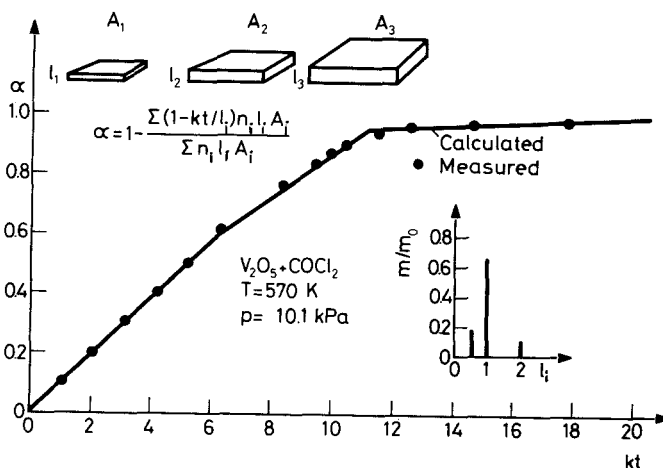


Fig. 12 Calculated and measured conversion vs. time curves and the proposed particle size distribution

different thicknesses can be calculated via the following equation:

$$\alpha \simeq 1 - \frac{\sum n_i l_i A_i (1 - kt/l_i)}{\sum n_i l_i A_i} \quad (5)$$

where  $n_i$  and  $l_i$  are the number and the initial thickness of the particles, and  $A_i$  is the area of the basal plates. With the assumption of a model distribution (Fig. 12) consisting of three types of plates, the conversion vs. time curves were calculated and a fairly good correspondence of the calculated and measured curves was obtained. Thus, the chlorination of  $V_2O_5$  can be regarded as the reaction of thin plates of three different sizes.

## Conclusions

The chlorination reactions of vanadia with  $COCl_2$  and  $CCl_4$  are thermodynamically highly favoured. In both cases, the predominant gaseous products are  $VOCl_3$  and  $CO_2$ . The reactions become measurable at about 400 K. The reaction with chlorine is not so favoured. The thermodynamically stable products are  $VOCl_3$  and  $O_2$ , and the equilibrium yield increases moderately with temperature. Thus, in a flow reactor above 750 K, where the rate becomes appreciable, this reaction can also be utilized.

In the chemical control region, the apparent activation energies for  $CCl_4$ ,  $COCl_2$  and  $Cl_2$  are 77, 48 and 126  $\text{kJ} \cdot \text{mol}^{-1}$ , respectively. In this region the chlorination is of half order in  $CCl_4$ , while the reaction orders for  $COCl_2$  and  $Cl_2$  are 0.75–0.95 and 0.5–0.9. The conversion vs. time curves were described with a kinetic model in which the particles were considered to be thin plates of three different thicknesses. With this model, a fairly good correspondence was obtained between the measured and calculated curves.

## References

- 1 R. J. H. Clark, D. Brown; *The Chemistry of Vanadium, Niobium and Tantalum*, Pergamon Press, 1975.
- 2 S. I. Timofeev, U. T. Brunov, L. A. Niselson, K. U. Tretyakova, F. U. Koslov, Yu. A. Raikov, S. U. Rakitin: *Nauchn. Trudy Gos. Nauchno-Issl. Proekt. Inst. Redkomet. Prom.*, 42 (1972) 87.
- 3 R. G. Yankelevich and I. A. Sheka, *Ukr. Khim. Zh.*, 34 (1968) 58.
- 4 V. I. Sonin, N. I. Vorobev, YU. A. Raikov and O. C. Polyachenok, *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk*, 2 (1971) 88.
- 5 G. Mink, B. Pödör and I. Bertóti, *Travaux ICSOBA*, 12 (1982) 239.
- 6 G. Mink, I. Bertóti and T. Székely, *React. Kinet. Catal. Lett.*, 27 (1985) 33.
- 7 G. Mink, I. Bertóti, C. Battistoni and T. Székely, *React. Kinet. Catal. Lett.*, 27 (1985) 39.

- 8 I. Bertóti, A. Tóth, I. S. Pap and T. Székely, *Thermal Analysis, ICTA 80, Vol. 2*, Birkhaeuser Verlag, Basel, Boston, Stuttgart, 1980, p. 235.
- 9 J. H. Sharp, G. W. Brindley and B. N. Achar, *J. Amer. Ceram. Soc.*, 49 (1966) 379.
- 10 L. Fiermans, P. Claws, W. Lambrecht, L. Vandebroucke and J. Vennik, *Phys. Stat. Sol.*, (a), 59 (1980) 485.
- 11 C. H. Bamford and C. F.H. Tipper (Ed.), *Comprehensive Chemical Kinetics Vol. 22*, Elsevier, Amsterdam, 1980, p. 72.
- 12 R. A. Ramachadran and M. P. Dudukovic, *Chem. Eng. Sci.*, 39 (1984) 669.
- 13 M.P. Dudukovic, *Ind. Eng. Chem. Process Des. Dev.*, 23 (1984) 330.
- 14 G. Mink, I. S. Pap, I. Bertoti, T. Székely and E. Karmazsin, *Reactivity of Solids*, (in press).

**Zusammenfassung** — Mittels isothermen Thermogravimetrie-messungen wurde die Kinetik der Chlorierung von reinem Vanadiumoxid mit  $\text{CCl}_4$ ,  $\text{COCl}_2$  und  $\text{Cl}_2$  als Chlorierungsmittel untersucht. Bei Temperaturen mit vorherrschender chemischer Kontrolle wurde für die Chlorierung mit  $\text{CCl}_4$ ,  $\text{COCl}_2$  bzw.  $\text{Cl}_2$  Bruttoaktivierungsenergien von 77, 48 bzw. 126 kJ/mol erhalten. Zur Interpretation der Konversion-Zeit-Diagramme im gesamten Conversionsbereich wurde eine nichteinheitliche Teilchengrösseverteilung angenommen, namentlich den Bestand der reagierenden Festphase aus dünnen Plättchen unterschiedlicher Dicke. Mit diesem Modell konnte eine recht gute Übereinstimmung zwischen errechneten und ermittelten kinetischen Kurven erhalten werden. Einige thermodynamische Rechenbeispiele für die Systeme  $\text{V}_2\text{O}_5 + \text{CCl}_4$ ,  $\text{V}_2\text{O}_5 + \text{COCl}_2$  und  $\text{V}_2\text{O}_5 + \text{Cl}_2$  wurden gegeben.

**Резюме** — С помощью изотермических термогравиметрических измерений была изучена кинетика реакции хлорирования чистой пятиоксида ванадия такими хлорирующими агентами, как  $\text{CCl}_4$ ,  $\text{COCl}_2$  и  $\text{Cl}_2$ . При температурах, где доминировал химический контроль кажущиеся энергии активации при хлорировании  $\text{CCl}_4$ ,  $\text{COCl}_2$  и  $\text{Cl}_2$ , соответственно равнялись 77, 48 и 126 кдж·моль<sup>-1</sup>. Для интерпретации кривых в координатах превращение — время во всем интервале превращений, было предположено неоднозначное распределение размера частиц и где считалось, что реакционная твердая фаза состоит из тонких пластинок неодинаковой толщины. С этой моделью было получено чрезвычайно хорошее совпадение между измеренными и вычисленными кинетическими кривыми. Представлены отдельные вычисленные термодинамические данные для систем  $\text{V}_2\text{O}_5 + \text{CCl}_4$ ,  $\text{V}_2\text{O}_5 + \text{COCl}_2$  и  $\text{V}_2\text{O}_5 + \text{Cl}_2$ .