INFLUENCE OF METAL OXIDE ADDITIVES ON THE KINETICS OF ISOTHERMAL DECOMPOSITION OF AMMONIUM METAVANADATE
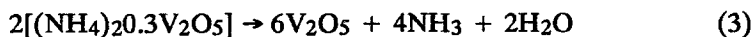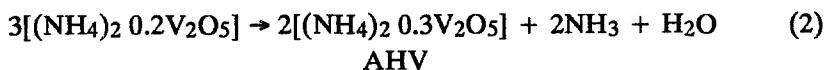
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The kinetics of isothermal decomposition of ammonium metavanadate (AMV) and its mixtures with MgO, CaO, CuO and NiO - in the molar ratio of 2:1 — were investigated. The computer - oriented kinetic analysis of the α-t data reveals the validity of Ginstling-Brounshtein equation to describe these reactions. The accelerating effect accompanying the MgO addition can be attributed to its affinity to abstract protons. In case of CaO, the formation of the relatively stable $Ca(OH)_2$ during the proceeding of the decomposition process results in a retarding effect. On the other hand, the higher calculated E_a value for the AMV + CuO mixture was explained in terms of a solid-solid interaction between CuO and the solid decomposition product, leading to the formation of $Cu_3(VO_4)_2$. According to electronic factors, the effect of NiO addition on the decomposition process was discussed. It was found that the decomposition process is less favourable in presence of p-type semiconducting additive.

The products of thermal decomposition of pure NH_4VO_3 (AMV) or mixed with some metal oxide additives result in catalysts of great importance [1-5]. Additionally, it was reported in several studies [6-10] that the mechanical addition of a foreign substance to metallic salts gives rise to significant changes in the thermochemical reaction behaviour of these salts. These changes may be ascribed to (i) the catalytic action of the additive which accelerate or retard the reaction, and (ii) the chemical interaction occurring between the reactant and the additives to form some new compounds [11]. Extensive information on the behaviour as well as the mechanistic criteria of these reactions is impossible without knowledge of their kinetics. Therefore, the present study is set out to analyze the thermoanalytical data, as obtained in isothermal conditions, of AMV in a pure state or mixed with MgO, CaO, CuO, and NiO in order to evaluate the dif-

ferent kinetic parameters and ascertaining the mechanism describing these thermal processes. Electrical conductivity measurements together with X-ray analysis were used to confirm our results.

Experimental

All the reagents used in the present investigation were of analytical grade (BDH Chemicals). The mixing of ammonium metavanadate (AMV) with metal oxide additives (i.e., MgO, CaO, CuO and NiO) were carried out in an agate mortar. The mixing ratio of these additives to AMV was 1:2. Twenty minutes were needed to obtain a homogeneous mixture. Even in the case without additives the pure AMV sample was also ground for 20 minutes. DTA and TG of AMV were obtained using a 1090 DuPont Thermal Analyzer with a heating rate 10 deg/min. The study of isothermal kinetics of pure and mixed samples was carried out with the aid of a Sartorius Electrobalance (Type 2004 MP6). The sample was placed in a quartz basket suspended from the arm of the balance by means of a quartz wire. The sample temperature was adjusted using a Heraeus Temperature Controller Type TRK. The electrical conductivity measurements were carried out with the aid of a conductivity cell described by Chapman et al. [12] with some modifications. The resistance was measured using a 610 Electrometer (Keithley Instruments) [6]. A Philips X-ray diffractometer, model (PW 1710) was used to record d values for the calcination products of pure AMV and its mixtures. CuK_α radiation was used at 40 kV and 30 mA with a scanning speed of 2 deg/min.

Results and discussions

Figure 1 shows the TG curve of the non-isothermal decomposition of pure NH_4VO_3 (AMV). Two intermediates appear to be formed, at $\alpha = 0.5$ and 0.67, respectively, before reaching the final product, i. e. V_2O_5. This observation is in accordance with the suggestion [13] that the decomposition of AMV proceeds via a gradual reduction of the ratio of "$(NH_4)_2O$" to V_2O_5 units from the original 1:1 ratio in AMV to pure V_2O_5 according to equations (1-3).

$$6[(NH_4)_2 \ 0.2V_2O_5] \rightarrow 3[(NH_4)_2 \ 0.2V_2O_5] + 6NH_3 + 3H_2O \qquad (1)$$
$$\text{AMV} \qquad\qquad\qquad \text{ABV}$$

$$3[(NH_4)_2 \, 0.2V_2O_5] \rightarrow 2[(NH_4)_2 \, 0.3V_2O_5] + 2NH_3 + H_2O \qquad (2)$$
$$AHV$$

$$2[(NH_4)_2 0.3V_2O_5] \rightarrow 6V_2O_5 + 4NH_3 + 2H_2O \qquad (3)$$

(ABV and AHV indicate ammonium bivanadate and ammonium hexavanadate, respectively.)
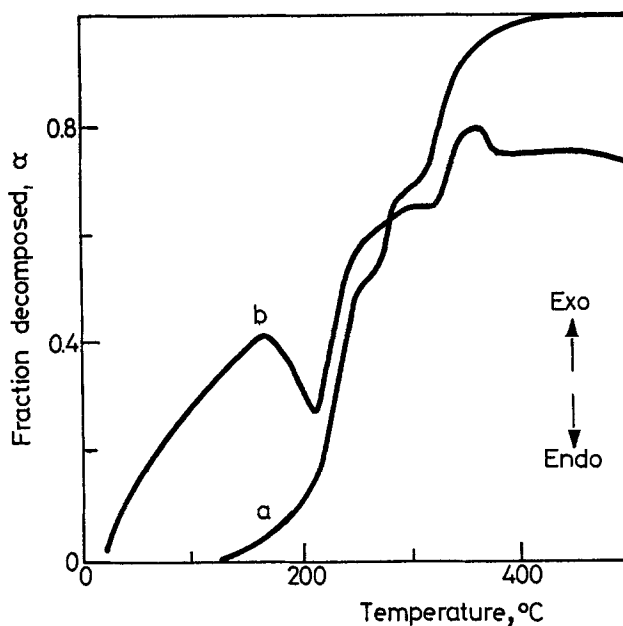

Fig. 1 TG (a) and DTA (b) curves for pure AMV

Further evidence for this suggestion is obtained by examining the DTA curve (Fig. 1). Two endothermic peaks can be easily distinguished, the first is a broad one starts at 180° and the onset of the second peak at 280° indicating a coincidence with the starting temperature of stages(1) and (3) in the TG curve. The DTA curve also shows an exothermic peak follows the decomposition process which can be attributed to (i) the oxidation of the last traces of ammonia trapped in V_2O_5 product, and/or (ii) the recrystallization effect [14].
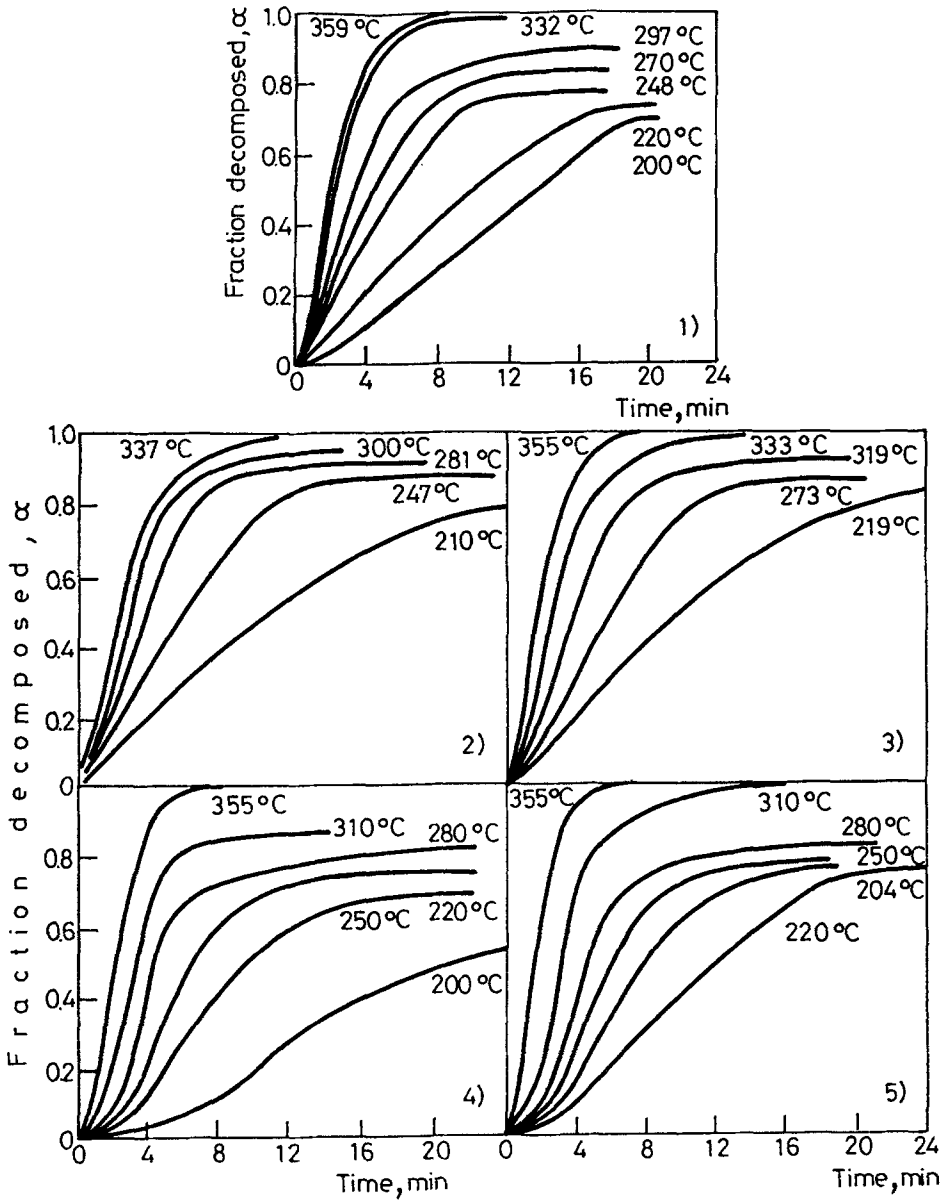
Fig. 2 α *vs. t* curves for the isothermal decomposition of pure AMV and its mixtures with MgO, CaO, CuO and NiO (1-5 respectively)

In order to elucidate the kinetic parameters of the reaction, the thermal decomposition of AMV was studied in an isothermal condition. Figure 2 shows the α–t curves obtained in the temperature range 200-360°. The computer-oriented kinetic analysis of the isothermal decomposition reaction was performed for each set of α and t data according to the various kinetic equations cited in Table (1).

Table 1 Kinetic equations examined in this work

Reaction model	$g(\alpha) = kt$	Function symbol
One-dimensional diffusion	α^2	D1
Two-dimensional diffusion	$\alpha + (1 - \alpha)\ln(1 - \alpha)$	D2
Jander equation, three-dimensional diffusion	$\left(1 - (1 - \alpha)^{1/3}\right)^2$	D3
Ginstling-Brounshtein equation, three-dimensional diffusion	$\left(1 - \frac{2}{3}\alpha\right) - (1 - \alpha)^{2/3}$	D4
Two-dimensional phase boundary reaction	$\left(1 - (1 - \alpha)^{1/2}\right)$	R2
Three-dimensional phase boundary reaction	$\left(1 - (1 - \alpha)^{1/3}\right)$	R3
First-order kinetics	$-\ln(1 - \alpha)$	F1
Random nucleation: Avrami equation	$\left(-\ln(1 - \alpha)\right)^{1/2}$	A2
Random nucleation: Erofeev equation	$\left(-\ln(1 - \alpha)\right)^{1/3}$	A3

The results show that the Ginstling-Brounshtein equation gives the best fit of data with a correlation coefficient very close to unity. Estimation of E_a values according to Arrhenius equation provides a straight line broken at 280° (Fig. 3), indicating more than one stage to be involved in this decomposition process. This also confirms that stages 1 and 2 in the suggested mechanism are kinetically overlapped, with E_{a1} and E_{a2} values of 41.55 and 20.15 kJ·mol^{-1}, respectively.

Computer-oriented kinetic analysis also indicates the maintenance of Ginstling-Brounshtein equation to be valid for describing the mechanism by which AMV decomposes in presence of metal oxide additives. For studying the effect of metal oxide additives on the thermal decomposition of AMV, the kinetic parameters characterizing the decomposition of AMV in presence of each additive were calculated.

Table 2 Kinetic parameters of isothermal decomposition for pure AMV and its mixtures

System	E_{a_1} kJ·mol^{-1}	E_{a_2} kJ·mol^{-1}	$E_{total} = \left(E_{a_1} + E_{a_2}\right)$ kJ·mol^{-1}	A_1 sec^{-1}	A_2, sec^{-1}
Pure AMV	41.55	20.15	61.70	$191 \cdot 10^{-2}$	$2 \cdot 10^{-2}$
2 AMV + MgO	38.16	–	38.16	$104 \cdot 10^{-2}$	–
2 AMV + CaO	25.57	53.61	79.18	$4 \cdot 10^{-2}$	$161 \cdot 10^{-1}$
2 AMV + CuO	17.49	104.47	121.96	$11 \cdot 10^{-3}$	$35 \cdot 10^{6}$
2 AMV + NiO	15.83	64.02	79.85	$5 \cdot 10^{-3}$	$2 \cdot 10^{2}$

The variation of E_{a1} values, as shown in Table 2, indicates clearly that the presence of all metal oxide additives enhances the first decomposition stage of AMV. Contrary, the second stage seems to be retarded as detected from the interrelation between the E_{a2} values, with an exception observed in case of AMV + MgO mixture. These findings could be explained in terms of Garn's [15] conception, that for reactions described by the above equation, nucleation, followed by surface diffusion, occurs at a temperature below that needed for bulk diffusion. This concept was developed by Searcy and Beruto [16]. They stated that the steady decomposition rates for any particular reaction depend not only on the rate of a surface step of the gaseous component of the reaction, but also on the rates of three additional necessary steps: (i) diffusion of the eventual gaseous reaction product along the interface reactant and solid product, (ii) diffusion of the solid component of the reaction along the portions of reactant phase which are fronted by pores, and (iii) transfer of the solid reaction component from the reactant phase to the solid product phase across interfaces between the reactant and the solid product phase. Accordingly, the observed decrease in E_{a1} values (belongs to the first stage) is consistent with the suggestion that the metal oxide additives serve, in the early stage of decomposition, as a diluent and lead to promote the escape of the gaseous product. The increasing order of this effect is NiO > CuO > CaO > MgO. Thus, the influence of the additives on this stage seems to be due to physical effect and not to a chemical one. The same conclusion was realized for similar systems [17].

It was shown from the above discussion that the presence of metal oxide additives results in physical effects which lead to a pronounced lowering of the E_{a1} value for AMV decomposition. The situation appears to be different in case of the E_{a2} values, c. f. Table 2. It clearly indicates a remarkable increase of E_{a2} values in presence of metal oxide additives, compared with that obtained for pure AMV. Only one exception could be observed, addition of

MgO offers one value of E_a, where all the deduced rate constants lie on the same Arrhenius line. This value is smaller than the overall activation energy obtained for pure AMV.
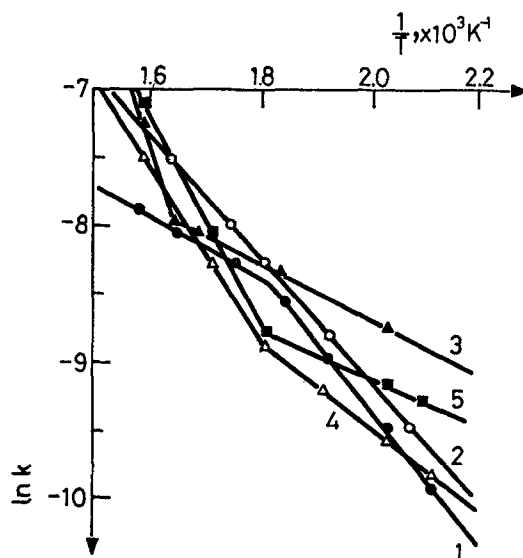

Fig. 3 Arrhenius plots for the isothermal decomposition of pure AMV and its mixtures with MgO, CaO, CuO and NiO (1-5 respectively)

Combining the foregoing finding, for AMV + MgO mixture, with the proton transfer nature characterizing the decomposition reaction of ammonium salts [18], together with the conclusion obtained from Ginstling-Brounshtein equation (i.e., the chemical reaction at the phase boundary is considerably faster than the transport process, and thus the reaction is a bulk-diffusion controlled [15]), we can conclude that the affinity of MgO to abstract protons, offers an additional factor, being chemically in nature, acting throughout the proceeding of the thermal decomposition of AMV. This gives an explanation for the observed decrease in the E_a value for AMV + MgO mixture as compared with that for pure AMV. It also reflects the enhancement role of MgO on the decomposition process. In addition, it is important to decide that the occurrence of two consecutive processes, which are the abstraction of protons [19] to form $Mg(OH)_2$ and the dehydration of the pre-formed $Mg(OH)_2$ to MgO, keep MgO active throughout the whole decomposition process of AMV. In contrast to the ac-

celerating effect of MgO, CaO addition shows a higher E_{a2} value indicating a retarding effect. X-ray diffraction pattern for the calcination products of AMV + CaO, at 380° (Fig. 4), reveals the existence of $Ca(OH)_2$ instead of CaO in the original mixture. Thus, the retarding effect of CaO can be ascribed to the formation of the relatively stable $Ca(OH)_2$ which makes the abstraction of protons more difficult.
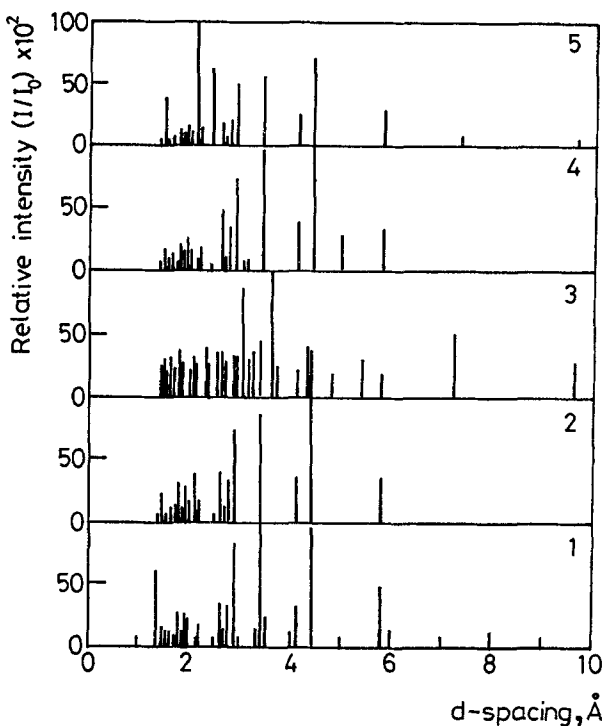

Fig. 4 XRD for the calcination product, at 380°C, of pure AMV and its mixtures with MgO, CaO, CuO and NiO (1-5 respectively)

Concerning the AMV + CuO mixture, it was detected from the X-ray pattern that a solid-solid interaction must be occurred. The resulting new phase is characterized by d spacings 7.26, 2.87 and 2.56 Å to be $Cu_3(VO_4)_2$ (Ref. 20). Thus, the high E_{a2} value in AMV + CuO mixture corresponds to two simultaneous processes, the first leads to the formation of the final decomposition product of AMV and the second belongs to the interaction between the solid product and CuO. It is not possible to assume the same

behaviour for the AMV + NiO mixture; the appearance of only NiO lines in the X-ray pattern with no indication to any other new phase (except of course V_2O_5) gives a support for this assumption. The higher E_{a2} value for this mixture allows us to believe that the decomposition of AMV in presence of such semiconducting additive can be affected by electronic factors, it becomes less favourable in presence of p-type semiconductor additives [21] (i. e. NiO). Based on a charge transfer mechanism [22], it is plausible to suggest that the rate limiting step for AMV decomposition, in presence of NiO, is the release of H_2O which depends primarily on the combination of O^{2-} species with the abstracted protons.

$$2H^+ + O^{2-} \rightarrow H_2O \qquad (4)$$

The presence of p-type semiconducting additive retards this reaction, possibly due to the formation of gaseous oxygen.

$$O^{2-} \rightarrow \tfrac{1}{2}O_2 + 2e \qquad (5)$$

$$2 \mid e \mid^{\cdot} + 2e \rightarrow null \qquad (6)$$
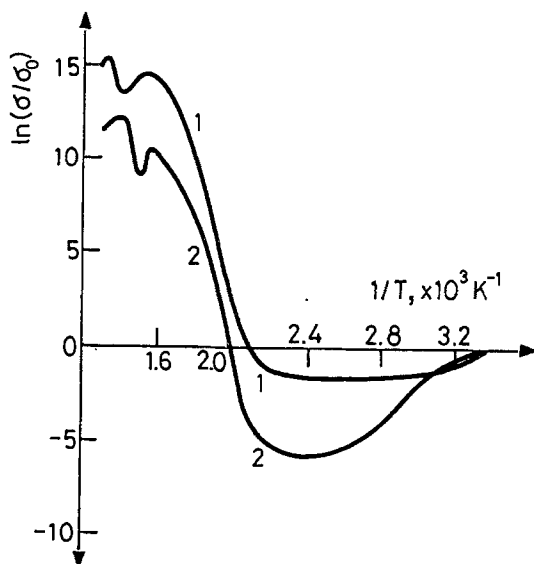

Fig. 5 Variation of ln σ/σ_0 vs. $1/T$ for pure AMV (1) and AMV + NiO mixture (2)

The expected consumption of the electrons produced in step (5) by the positive holes in NiO lattice structure tends to decrease the electrical conductivity as expressed in step 6. This conclusion find support from a comparative in situ measurements of electrical conductivity during the thermal decomposition of both pure AMV and AMV + NiO mixture (Fig. 5).

References

1 D. C. Agarwal, P. C. Nigam and R. D. Srivastava, J. Catal., 55 (1978) 1.
2 A. Bielanski, J. Piwowarczyk and J. Pozniczek, J. Catal., 113 (1988) 334.
3 J. Haber, A. Kozlowska and R. Kozlowski, J. Catal., 102 (1986) 52.
4 E. Iwamatsu, K. I. Aika and T. Onishi, Bull. Chem. Soc. Jpn., 59 (1986) 665.
5 A. Satsuma, A. Hattori, K. Mizutani, A. Furuta, A. Miyamoto, T. Hattori and Y. Hurakami, J. Phys. Chem., 93 (1989) 1484.
6 A. M. El-Awad, A. A. Said and K M. Abd El-Salaam, Thermochim. Acta., 126 (1988) 17.
7 A. M. El-Awad and R. M. Mahfouz, J. Thermal Anal., 35 (1989) 1413.
8 T. Ishii, K. Kamada and R. Furuichi, Kogyo Zasshi, 74 (1971) 854.
9 S. Shimada, R. Furuichi and T. Ishii, Kogyo Zasshi, 74 (1971) 2006.
10 T. Ishii, R. Furuichi and K. Kamada, Bull. Fac. Eng. Hokkaido Univ., 67 (1973) 137.
11 K. Mocala and J. Ziolkowski, J. Solid State Chem., 69 (1987) 299.
12 P. R. Chapman, R. H. Griffith and J. D. F. Marsh, Proc. R. Soc., London Ser. A, 224 (1954) 419.
13 M. E. Brown and B. V. Stewart, Thermal Analysis Proc. 3rd ICTA Davos (1971) (Ed. by H. G. Wiedmann), Brikhauser Verlag, Basel, (1972), Vol. 2, p. 313.
14 L. Berg, "Differential Thermal Analysis I", Ed. R. C. Mackenzie, Academic Press, London (1970) 346.
15 P. D. Garn, "Thermal Analysis: Comparative Studies on Materials", Ed. by H. Kambe and P. D. Gern, John Wiley & Sons, New York - London - Toronto, (1974) 100.
16 A. W. Searcy and D. Beruto, J. Phys. Chem., 80 (1976) 425.
17 R. Furuichi, T. Ishii, Z. Yamanaka and M. Shimokawabe, Thermochim. Acta., 51 (1981) 245.
18 C. H. Bamford and C. F. H. Tipper, "Comprehensive Chemical Kinetics", Elsevier, Amsterdam, Vol. 22 (1980) 195.
19 F. Feund and V. Sperling, "Thermal Analysis", Proc. 3rd ICTA Davos (1971) (Ed. by H. G. Wiedmann), Birkhauser Verlag, Basel, (1972), Vol. 2, p. 381.
20 Powder Diffraction File (Inorganic Compounds), Ed. by W. F. McClune, JCPDS, PA, (1978).
21 W. K. Rudloff and E. S. Freeman, J. Phys. Chem., 74 (1970) 3317.
22 E. S. Freeman and D. A. Anderson, Nature, 206 (1965) 378.

Zusammenfassung — Es wurde die Kinetik der isothermen Zersetzung von Ammonium-metavanadat (AMV) und von Gemischen aus AMV mit MgO, CaO, CuO und NiO im Molverhältnis 2:1 untersucht. Eine computergestützte kinetische Analyse der -t Daten erwies die Gültigkeit der Ginstling-Brounshtein-Gleichung zur Beschreibung dieser Reaktionen. Der beschleunigende Effekt bei Zugabe von MgO kann dessen Neigung zum Entzug von Protonen zugeschrieben werden. Im Falle von CaO führt die Bildung von relativ stabilem $Ca(OH)_2$ während des Zersetzungsvorganges eher zu einer Verlangsamung. Die hohen berechneten E_{a2}-Werte für das AMV + CuO-Gemisch können mit einer Feststoff-Feststoff-Wechselwirkung zwischen CuO und dem festen Zersetzungsprodukt erklärt werden, wobei $Cu_3(VO_4)_2$ gebildet wird. Der Einfluß von NiO-Zugabe auf den Zersetzungsprozeß wurde hinsichtlich elektronischer Faktoren diskutiert. Man fand, daß die Gegenwart von p-Halbleiterzusätzen für den Zersetzungsvorgang weniger günstig ist.