# THE THERMAL DECOMPOSITION OF AMMONIUM METAVANADATE

## II The kinetics and mechanism of the decomposition

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On heating, ammonium metavanadate (AMV) decomposes in several atmosphere-dependent stages. An important decomposition intermediate, ammonium hexavanadate (AHV), may also be prepared by wet-chemical methods and the kinetic parameters for the thermal decomposition of AMV and of the AHV preparation have been obtained. The kinetic study has been supplemented by surface-area measurements and by electron microscopic examination of the surfaces of reactant, intermediate and product crystallites.

On the basis of the type of decomposition curve, the measured activation energies, and the effects of oxygen and water vapour on the decomposition rate, it has been concluded that in vacuum and in inert atmospheres the evolution of ammonia is the rate-determining step, while in oxidizing atmospheres evolution of water is rate determining.

Comparison of the kinetic parameters with thermodynamic data for the decomposi. tion has led to suggestions as to the nature of the activated complexes involved-

The stoichiometries of the various stages involved in the thermal decom po sition of ammonium metavanadate (AMV) have been shown [1] to correspond to a decrease to $V_2O_5$, stepwise in the proportion of ammonia and water, considered as "$(NH_4)_2O$" units, from the initial composition $(NH_4)_2O \cdot V_2O_5$ (i.e., $NH_4VO_3$) to the final product, $V_2O_5$, in vacuum, in air, and in argon. In an atmosphere of ammonia reduction occurs to $VO_2$ at temperatures up to about 400°, and to VN at higher temperatures, 500 — 1500°. The actual intermediates formed and their structural order are dependent upon the prevailing atmosphere [1], see Fig. 1.

The decomposition is an endothermic reaction [2, 3] and, in common with many endothermic decompositions [4, 5], shows a high degree of reversibility [6]. The enthalpy changes for the decomposition have been determined and discussed [3] in terms of the structural order of the intermediates and products of decomposition.

Deschanvres and Nouet [7], using mass-spectrometric methods, studied, over the temperature range 130 — 180°, the kinetics of the first stage of the decomposition of AMV in vacuum, which corresponds to:

$$6NH_4VO_3(s) \rightarrow (NH_4)_2V_6O_{16}(s) + 4NH_3(g) + 2H_2O(g) \tag{1}$$
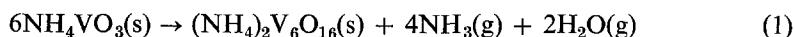
They did not characterize their solid product structurally and, although it has the empirical formula of ammonium hexavanadate ($NH_4V_3O_8$ as it is usually written), this product has been shown [1] to be structurally different (and will be referred to as AHV*) to the product, of the same empirical formula, formed in the second stage of the decomposition in air and in argon, and in the first stage of the decomposition in ammonia (AHV). The infrared spectra and X-ray powder data of all of these last three intermediates correspond to those of the ammonium hexavanadate which can also be prepared from an acidified aqueous solution of ammonium metavanadate [8].
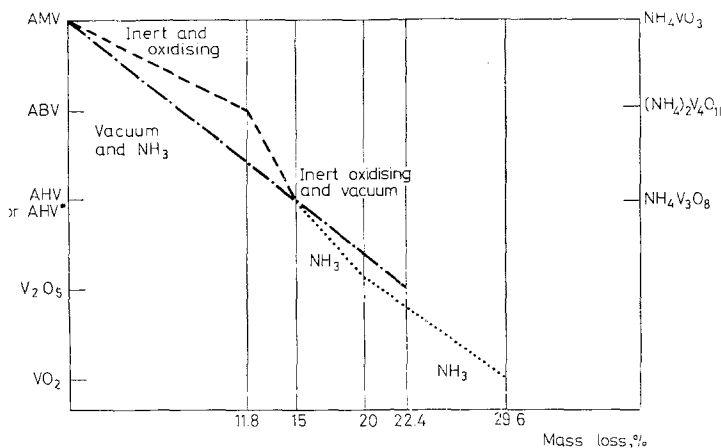


Fig. 1. Schematic representation of the course of the decomposition of AMV in various atmospheres

The present study of the thermal decomposition of AMV was undertaken to determine the kinetic parameters of the various stages involved in the decomposition in various atmospheres, and to investigate the surfaces of the sample particles using electron microscopy, in order to combine this information with the structural information available [1], in an attempt to determine the mechanism of the decomposition. A structural view of the decomposition mechanism is presented in Part III [9].

## Experimental

The apparatus used has been described earlier [1]. The series of isothermal decompositions used to determine the stoichiometry of the various stages of the decomposition in vacuum and in the other atmospheres were extended to the limits of temperature which still gave conveniently measurable rates of decomposition.

Electron micrographs were obtained using an Akashi TRS-80 instrument. Samples were prepared using a two-stage replication technique, pre-shadowed with gold and palladium at $cot^{-1}2$.

Surface areas were determined by the BET method using krypton adsorption.

## Results

The isothermal $\alpha$-time curves for all of the stages of the decomposition in vacuum (where $\alpha$ is the fraction of the total mass-loss for the particular stage) were deceleratory throughout, as illustrated in Fig. 2, curve A, for the first stage of the decomposition in vacuum at 123°. This type of $\alpha$-time curve will be referred to as "Type I".

In the presence of a surrounding atmosphere, the decomposition curves comprised an initial approximately linear region ($0.01 < \alpha < 0.6 \pm 0.1$) followed by a deceleratory region as illustrated in Fig. 3, curve A, for the first stage of the decomposition in argon at 163°. This type of $\alpha$-time curve will be referred to as "Type II".
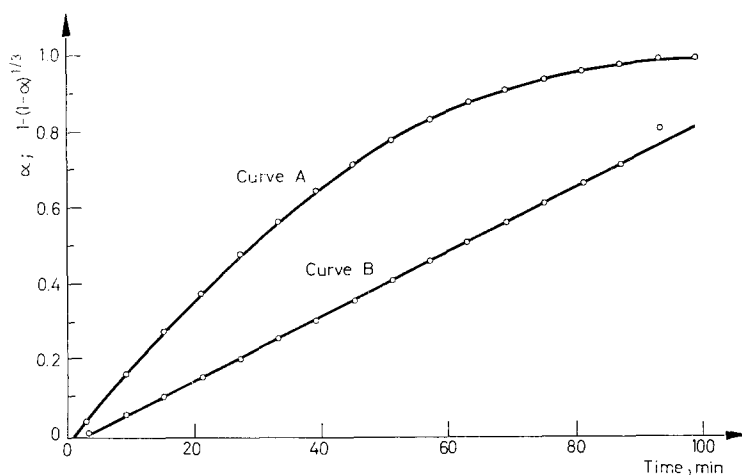


Fig. 2. AMV decomposition curve — "Type I" (first stage of the decomposition in vacuum at 123°) Curve A: $\alpha$ — time plot; Curve B: contracting volume plot

The usual mathematical expressions for kinetic models of solid decompositions [4, 5, 10−12] were tested on selected $\alpha$-time values and the contracting volume equation:

$$1 - (1 - \alpha)^{1/3} = kt + C \tag{2}$$

was found to apply over virtually the complete "Type I" curve (Fig. 2, curve B) and over the deceleratory region of the "Type II" curve (Fig. 3, curve C), with

the constants $k$ and $C$, of course, having different values for each particular stage and each particular temperature.

Arrhenius plots of the rate constants, $k$, obtained from equation (2) and directly from the slopes of the linear regions, yielded the apparent activation energies, $E$, and pre-exponential factors, $A$, for the various stages of the decomposition, which are listed in Table 1. The activation energies for the two regions of the "Type II" curves were virtually identical, which suggests that the same process is rate-determining throughout such stages.
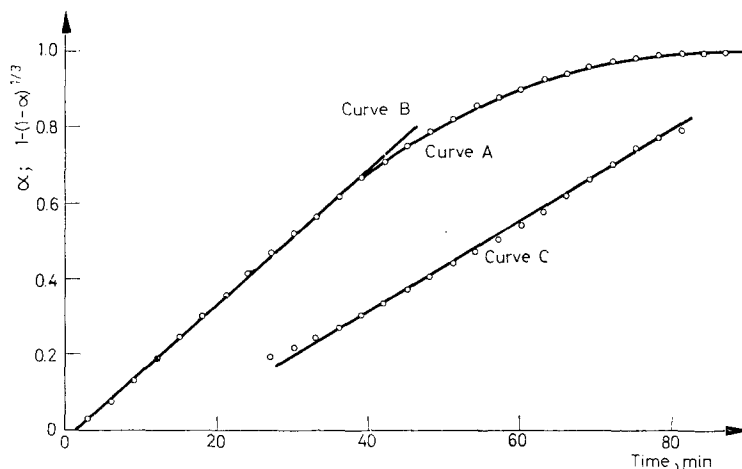


Fig. 3. AMV decomposition curve — "Type II" (first stage of the decomposition in argon at 163°) Curve A: $\alpha$ — time plot; Curve B: linear region; Curve C: contracting volume plot

Self-cooling is often a problem in studying the rates of endothermic decompositions but the small samples used (12 mg) and the resulting reasonable linearity of the Arrhenius plots, show that any self-cooling effect is not marked.

A sample of "recombined" AMV, prepared by reacting the $V_2O_5$ decomposition product with damp ammonia [6], decomposes for a second time in air at more than twice the rate of the original sample. Repeated recombinations and decompositions do not increase the rate of decomposition further [13]. Decomposition of the "recombined" AMV proceeds via structurally less-ordered intermediates, and the formation of AHV has been suggested [6] as the point of maximum structural order in the decomposition of AMV. This is irretrievable on recombination.

The decomposition of the AHV sample prepared from solution, $AHV_{soln}$, was compared with the further decomposition of the various decomposition intermediates of the same empirical formula. The activation energies and pre-exponential factors for these decompositions under a variety of conditions are listed in Table 2.

Table 1

The thermal decomposition of AMV

| Atmos-phere | Stage | Temp. range, °C | Empirical formula of product | | Activation energy, E, kJ mol$^{-1}$ | | Pre-exponential factor A, s$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | formula | abbre-viation | Region | Value | |
| Vacuum | 1 | 105—135 | $NH_4V_3O_8$ | AHV* | cont. sphere | 129 | $45 \times 10^{15}$ |
| | 2 | 135—155 | $NH_4V_4O_{10.5}$ | — | cont. sphere | 160 | |
| | 3 | 165—200 | $V_2O_5$ | — | cont. sphere | 98 | |
| Inert | 1 | 160—180 | $(NH_4)_2V_4O_{11}$ | ABV | linear | 138 | $15 \times 10^{15}$ |
| | | | | | cont. sphere | 132 | $10 \times 10^{15}$ |
| | 2 | 180—210 | $NH_4V_3O_8$ | AHV | cont. sphere | 106 | |
| | 3 | 270—300 | $V_2O_5$ | — | linear | 119 | |
| | | | | | cont. sphere | 120 | $1.7 \times 10^{11}$ |
| Oxidizing | 1 | 150—180 | $(NH_4)_2V_4O_{11}$ | ABV | linear | 171 | $15 \times 10^{20}$ |
| | | | | | cont. sphere | 176 | $12 \times 10^{20}$ |
| | 2 | 180—210 | $NH_4V_3O_8$ | AHV | linear | 134 | |
| | | | | | cont. sphere | 131 | |
| | 3 | 260—300 | $V_2O_5$ | — | cont. sphere | 143 | $1.8 \times 10^{13}$ |
| Ammonia | 1 | 165—190 | $NH_4V_3O_8$ | AHV | linear | 136 | $8 \times 10^{15}$ |
| | | | | | cont. sphere | 142 | $1 \times 10^{15}$ |
| | 2 | 280—300 | $NH_4V_6O_{15}$ | — | cont. sphere | 335 | |
| | 3 | 340—360 | $VO_2$ | — | cont. sphere | 282 | |

Table 2

Activtiaon energies and frequency factors for the decomposition of each of the AHV's in each of the atmospheres

| Sample | Atmosphere of subsequent decomposition | E, kJ mol$^{-1}$ | A, s$^{-1}$ |
|---|---|---|---|
| AHV$_{soln}$ (prepared as in ref. [8]) | Vacuum | 120 | $5.3 \times 10^9$ |
| | Inert | 190 | $5.2 \times 10^{15}$ |
| | Oxidizing | 141 | $1.7 \times 10^{11}$ |
| AHV$_{oxid}$ (prepared in air) | Vacuum | 118 | $1.9 \times 10^{10}$ |
| | Inert | 153 | $5.1 \times 10^{11}$ |
| | Oxidizing | 143 | $1.8 \times 10^{13}$ |
| AHV$_{inert}$ (prepared in oxygen) | Vacuum | 65 | $6.2 \times 10^4$ |
| | Inert | 120 | $9.8 \times 10^{11}$ |
| | Oxidizing | 92 | $1.7 \times 10^{11}$ |

Pre-irradiation of AMV with gamma rays from a ^{60}Co source to a dose of 100 Mrad showed no detectable effect on the kinetics of the thermal decomposition.

*Electron microscopy*

Samples of AMV, and of the AHV prepared from solution, were examined before and after decomposition under various conditions.

The original AMV, Fig. 4 (a), consisted mainly of fairly well-formed crystallites with smooth surfaces and edges, some intergrowth and attachment and very little irregular material. The crystallites of AHV Fig. 4 (b) are similar in size to those of AMV but are less regular. The faces of the crystallites are generally smooth with some fine "needle" type growth and the edges are rounded.

After decomposition of the AMV sample in vacuum to $V_2O_5$ Fig. 4 (c), the basic crystalline form is retained with some smooth faces, while others show considerable pitting. Fracture of some of the crystallites does occur (either during decomposition or during replication) and the surfaces exposed are very rough. There is also a considerable amount of material of small particle size.

The $V_2O_5$ product of AMV decomposed in nitrogen, Fig. 4 (d), is similar in appearance to that decomposed in vacuum, although the crystallites seemed less susceptible to fracture.

The micrographs of the product formed on decomposing either AMV or AHV to $V_2O_5$ in air (Fig. 4 (e) and (f)) show extreme roughening of the surfaces. The crsytallites are well-formed and show little tendency to crumble.

The BET surface areas of these and related samples are listed in Table 3.

Table 3

The surface areas of various intermediates and products

|  | Sample | Surface area $m^2g^{-1}$ |
|---|---|---|
| 1 | $NH_4VO_3$ (AMV) | 0.365 |
| 2 | $V_2O_5$ from 3rd stage in air | 5.26 |
| 3 | $V_2O_5$ from 3rd stage in vacuum | 25.9 |
| 4 | (3) annealed in air | 27. 6 |
| 5 | $V_2O_5$ from decomposition of AHV in air | 2.86 |
| 6 | $V_2O_5$ from decomposition of AHV in vacuum | 3.20 |
| 7 | $V_2O_5$ from Hopkins and Williams | 3.15 |
| 8 | AHV prepared from solution | 1.30 |
| 9 | AHV from 2nd stage in air | 3.82 |
| 10 | AHV* from 1st stage in vacuum | 18.58 |

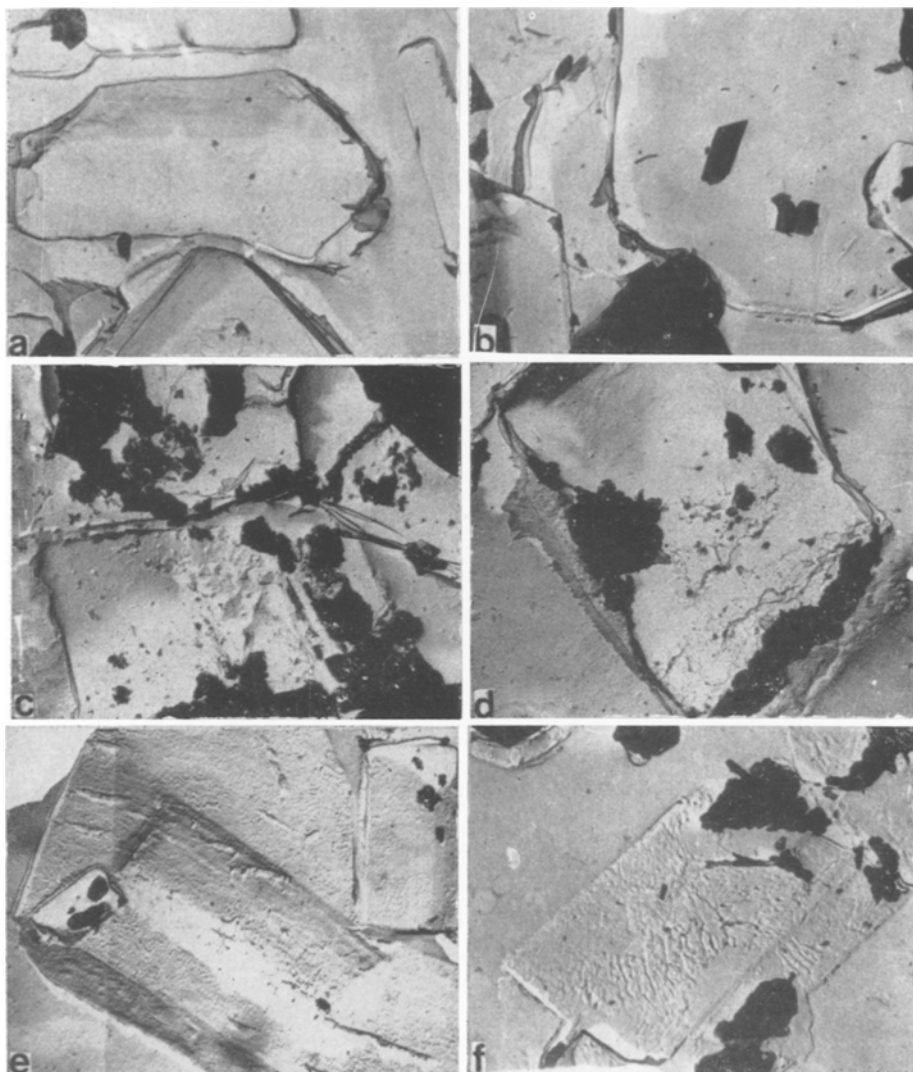The structural changes during the "recombination" reaction have been discussed [6].

Fig. 4. Electron micrographs. Samples before decomposition: (a) AMV × 7100; (b) AHV$_{soln}$ × 14,200. V$_2$O$_5$ product of AMV decomposition: (c) in vacuum × 21,300; (d) in nitrogen × 21,300. V$_2$O$_5$ product of the decomposition in air of: (e) AMV × 14,200; (f) AHV$_{scln}$ × 14,200

## Discussion

The inhibiting effect of a gaseous atmosphere on the decomposition, which has been shown to be endothermic [3] and reversible [6], is evident from the fact that decomposition in vacuum, where gaseous products are continuously removed, commences at a measurable rate some 50° below the temperature required for

the decomposition in the various gases. The shape of the isothermal $\alpha$-time curves is also altered from "Type I" for all stages in vacuum, to "Type II" for all stages in gaseous atmospheres (except the third stage of decomposition in oxidizing atmospheres).

The contracting volume equation (2), which applies over the complete "Type I" curve and over the deceleratory region of "Type II" curves, is based on the model of a narrow size-range of particles (in the simplest cases spheres or cubes) which decompose by initial rapid coverage of the surface with product, followed by progression of the reactant/product interface inwards, at constant rate, towards the centre of the particle. With continuous rapid removal of gaseous products it appears that this model is closely obeyed. The movement of the reactant/intermediate I interface is followed by a similar process for the intermediate/ I/intermediate II interface, and so on, with little overlap of the stages. This is confirmed by the separation of the differential enthalpic analysis peaks [3] even at high heating rates (20 K min⁻¹).

From electron micrographs it is evident that even in the later stages of the decomposition the external shape of the crystallites has been maintained although the surface area accessible to krypton has increased by a factor of at least ten (Table 3). This implies that pores and/or channels have developed in the material during decomposition. The increase in surface area is greatest during decomposition in vacuum, and infrared and X-ray data show the disordered nature of the vacuum-formed intermediates.

When the removal of gaseous product is impeded by the presence of a surrounding atmosphere, the decomposition follows a different course, via more structurally-ordered solid intermediates. In general, it is proposed that the linear region in the "Type II" $\alpha$-time curves has its origin in the effect of the ordering or recrystallization process on the rate of evolution of the gaseous products. The decomposition is a higly reversible process [6] and so when the time during which the gaseous products remain close to the solid product is extended on account of the presence of a surrounding atmosphere, several successive recombinations and decompositions result in an ordered solid product. This is supported by the X-ray and infrared data [1] and the fact that the surface areas of the intermediates and products formed in the presence of a surrounding atmosphere are less than those encountered in the vacuum decomposition.

The detailed decomposition will be discussed, as far as possible, in terms of stages with similar reactants and products, see Fig. 1.

*The decomposition of AMW to ABV*

In inert atmospheres this step has an activation energy of 133kJ mol⁻¹, and this is increased to 176kJ mol⁻¹ in air or in oxygen. The presence of water vapour in the inert atmosphere slightly decreases the rate of decomposition at a particular temperature, but does not alter the activation energy. In moist air the activation energy rises to 220kJ mol⁻¹. The pre-exponential factors also increase.

*The decomposition of ABV to AHV*

Once again, the activation energy for this step in oxidizing atmospheres (133kJ $mol^{-1}$) is higher than in inert atmospheres (106kJ $mol^{-1}$).

*The decomposition of AMV directly to AHV-type intermediates*

The intermediate AHV,* product of the first stage of the decomposition in vacuum, and 'normal' AHV, formed in ammonia, have been shown to be structurally different [1] but the activation energies, 129kJ $mol^{-1}$ (vacuum) and 139kJ $mol^{-1}$ (ammonia) are close enough to suggest that the energy requirements for similar processes are being represented, irrespective of the degree of order of the product. These activation energy values are similar to those for the first stage of the decomposition to ABV in inert atmospheres (133kJ $mol^{-1}$) which suggest that it is only in the presence of an oxidizing atmosphere that the initial mechanism common to the other decomposition conditions is altered.

The results of Deschanvres and Nouet [7] for the first stage of the decomposition in vacuum are different, in several aspects, to those of the present study. Their $\alpha$-time curves correspond more closely to our "Type II" curves and although they applied the contracting envelope equation, equation (2), to their results the fit obtained was relatively poor. The reported temperature range over which the first stage of the decomposition in vacuum occurred is also some 40° higher than the present study. The apparent activation energy found for this stage, 129kJ $mol^{-1}$, is, however, in fair agreement with that now reported, 117kJ $mol^{-1}$.

Trau [14] obtained an activation energy of 200kJ $mol^{-1}$ from TG measurements on the first stage of the decomposition in air. Although they did not isolate the ABV intermediate, Subba Rao and Mulay [15] report an activation energy of 180kJ $mol^{-1}$ for AMV $\xrightarrow{\text{air}}$ AHV, and 163kJ $mol^{-1}$ for AHV $\xrightarrow{\text{air}}$ $V_2O_5$.

*The mechanism of the initial decomposition of AMV*

The linear region in "Type II" curves, which has already been discussed in general terms, extends furthest (to $\alpha \approx 0.8$) in an ammonia atmosphere, which suggests that it is hindrance of the evolution of $NH_3$ rather than of $H_2O$, which influences the extent of the linear region. The activation energies for linear and deceleratory regions are virtually identical and it is suggested that the rate determining step in vacuum and inert atmospheres is the evolution of $NH_3$.

Initial decomposition on the surface of the crystallites and along dislocation lines creates pores in the material; $NH_3$ and $H_2O$ diffuse to the internal surfaces of these pores. Once the pressure of $NH_3$ in these pores and channels has risen to such a point that decomposition via the formation of further pores is no longer more rapid than evolution of the product gases from the external surface of the crystallites (in inert atmospheres and ammonia), or where the material is so porous (e.g. as a result of the extensive breaking-up of larger crystallites which

occurs in vacuum [7]) that there is no difference between evolution from the pores and from the "external" surface, then the product-reactant interface advances inwards into the remaining undecomposed material in the particles in the form of a contracting envelope.

The increased activation energy for the initial decomposition of AMV in oxidizing atmospheres and even more so in moist oxidizing atmospheres, suggests that under these conditions a different process is rate-determining. It is suggested that this is the evolution of $H_2O$. The activation energy for the evolution of $H_2O$ might be expected to be higher than that for the evolution of $NH_3$, since the generation of $H_2O$ involves the fracture of strong $V-O$ bonds while the generation of $NH_3$ merely requires the fracture of hydrogen bonds.

It is to be expected that there will be considerable interaction between partially decomposed AMV and oxygen as oxygen is readily chemisorbed on a $V_2O_5$ surface $(100-480°)$ [16] and the ability of the oxygen atoms in the $V_2O_5$ lattice to exchange with adsorbed oxygen or water is well known [17–19]. Activation energies for adsorption of oxygen on $V_2O_5$ of from 28 to 65kJ mol$^{-1}$, as surface coverage increases, have been reported [16], while activation energies for the exchange processes, which may be controlled by either the dissociation of adsorbed oxygen molecules or the breaking of $V-O$ bonds, were between 155 and 195kJ mol$^{-1}$ [18]. Such interactions in oxidizing atmospheres can well be expected to alter the mechanism of the AMV decomposition. $V_2O_5$ is an $n$-type semiconductor and chemisorption of oxygen is an "electron-withdrawing" process, which suggests that either the evolution of $NH_3$ from $NH_4^+$ is facilitated, or the evolution of $H_2O$ is hindered, by the decreased availability of electrons in oxidizing atmospheres.

*The decomposition of AHV to $V_2O_5$*

The AHV sample prepared from solution, AHV$_{soln}$, decomposes markedly slower than either of the two AHV intermediates (the products of the second stages in inert and in oxidizing atmospheres) under the same conditions. This is to be expected on account of the relatively defective structure of the decomposition intermediates.

The activation energies and pre-exponential factors for the formation of $V_2O_5$ from the various AHV intermediates under a variety of conditions, listed in Table 2, suggest that the effect of oxygen, discussed above, is not confined to participation during a decomposition stage, but may also be "built in" to some extent in a preceding stage and be noticeable during further decomposition in non-oxidizing atmospheres

For each particular AHV sample the activation energy for further decomposition is least in vacuum and greatest in an inert atmosphere. For any particular atmosphere, the activation energy is least for AHV prepared in an inert atmosphere and greatest for AHV prepared from solution. The effect of an oxidizing atmosphere is intermediate in both series.

There appear to be two main factors influencing the value of the activation energy for decomposition.

(i) the degree of structural order of the AHV sample, and

(ii) the effect of an oxidizing atmosphere.

The $AHV_{soln}$ and $AHV_{oxid}$ may be considered to have had a similar oxidizing pretreatment i.e. previous interaction of the surface with the solution in the one case and with air in the other. $AHV_{inert}$ has, however, undergone no such interaction in its formation. The activation energies for the decomposition in vacuum of $AHV_{soln}$ and $AHV_{oxid}$ are similar and higher than that for $AHV_{inert}$.

In an oxidizing atmosphere the above order is the same while in an inert atmosphere the activation energy for the decomposition of $AHV_{soln}$ (surface area = 1.30 $m^2g^{-1}$) is greater than that for the decomposition of $AHV_{oxid}$ (surface area = 3.82 $m^2g^{-1}$). Hence the hindering effect of the inert atmosphere on the evolution of the gaseous products emphasises the effect of structural order.

*The further decomposition of AHV in ammonia*

Further decomposition involves partial reduction of the "$V_2O_5$ units" with a 'final' product of $VO_2$ [1]. The two distinguishable stages have high apparent activation energies (Table 1) and are undoubtedly complex processes which may be explicable in terms of simpler consecutive or competitive steps [20].

*Activated complexes*

The fact that the reverse of the overall decomposition, i.e. the reaction of $V_2O_5$ with ammonia and water to form AMV [6], takes place in a single stage with a very low activation energy ($5-10$ kJ mol$^{-1}$) suggests that the activation energies for the reverse of each decomposition stage are all low and that for each stage

$$\Delta H_{dec} \approx E$$

The values of the enthalpy changes accompanying each decomposition stage have been determined [3] by differential enthalpic analysis. The measured values are dependent upon the sample mass and have been reported per mole of "$(NH_4)_2O \cdot V_2O_5$". The activation energies, however, refer to a mole of activated complex [21] for the particular stage.

If $\Delta H$ for a particular stage, based on one "$(NH_4)_2O \cdot V_2O_5$ unit", is scaled in terms of an integer $n$ in such a way that $n\Delta H$ is as close as possible to $E$ for the stage, without exceeding $E$, then $n$ will indicate the number of "$(NH_4)_2O \cdot V_2O_5$ units" on which the formula of the activated complex for the stage is based.

For the first stage of the decomposition in inert atmospheres, $\Delta H$ is $\approx 110$kJ [mol$(NH_4)_2O \cdot V_2O_5]^{-1}$ and $E$ is $\approx 135$kJ mol$^{-1}$, so that the activated complex is based on $(NH_4)_2O \cdot V_2O_5$. For the second stage in inert atmospheres, $\Delta H$, although variable, is approximately half that of the first stage, while $E$ is only

2

slightly less than for the first stage, so that the activated complex is now based on $(NH_4)_2O \cdot 2V_2O_5$. For the third stage $\Delta H$ is very small referred to 1 mole of $(NH_4)_2O \cdot V_2O_5$ ($< 10kJ$) while $E$ remains at approximately on the same level as before. In view of the values of $\Delta H$ from 67 to 75 kJ $[mol(NH_4)_2O \cdot V_2O_5)^{-1}$ obtained for the decomposition of $AHV_{soln}$ it was proposed [3] that the $\Delta H$ value of $< 10kJ$ was the resultant of an endothermic decomposition process and concurrent exothermic recrystallization processes. $E$ for the decomposition of $AHV_{soln}$ is $\approx 190kJ$ $mol^{-1}$, so $n \approx 3$ and the activated complex is then of the form $(NH_4)_2O \cdot 3V_2O_5$.

It appears then that the activated complex for each stage of the decomposition in inert atmospheres (where removal of gaseous products is inhibited, but interference from oxygen is absent) contains one "$(NH_4)_2O$ unit" together with increasing proportions of $V_2O_5$ and could be represented as

$$
\begin{array}{ccc}
NH_3H & & V \\
& \diagdown \; O \; \diagup & \\
NH_3H & \diagup \quad \diagdown & V
\end{array}
$$
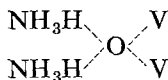
The enthalpy change accompanying decomposition is approximately 35kJ $[mol(NH_4)_2O]^{-1}$ and the energy barriers to be surmounted are of the order of 125 to 175kJ.

The detailed structural changes involved are to be discussed [9].

<div align="center">*</div>

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RÉSUMÉ — Par chauffage, le métavanadate d'ammonium (AMV) se décompose en plusieurs étapes qui dépendent de l'atmosphère. Un produit intermédiaire important de la décomposition est l'hexavanadate d'ammonium (AHV) qui peut aussi être obtenu chimiquement par voie humide. On a pu ainsi déterminer les paramètres cinétiques de la décomposition thermique de l'AMV et de la préparation d'AHV. On a complété l'étude cinétique par des mesures de surface et par l'examen au microscope électronique des surfaces des cristallites du composé initial, du produit intermédiaire et du produit préparé.

En utilisant la courbe de décomposition, les énergies d'activation mesurées et les effets respectifs de l'oxygène et de la vapeur d'eau sur la vitesse de la décomposition, on a pu conclure que dans le vide et en atmosphère inerte, c'est le départ de l'ammoniac qui détermine la vitesse de le réaction, tandis qu'en atmosphère oxydante, c'est le départ de l'eau.

La comparaison des paramètres cinétiques avec les données thermodynamiques de la décomposition a permis d'émettre des hypothèses sur la nature des complexes activés mis en jeu.

ZUSAMMENFASSUNG — Beim Erhitzen wird Ammonium-Metavanadat (AMV) in verschiedenen Stufen zersetzt, welche von der Atmosphäre abhängen. Ein bedeutendes Zersetzungszwischenprodukt, Ammoniumhexavanadat (AHV), kann auch durch naß-chemische Methoden hergestellt werden. Die kinetischen Parameter für die thermische Zersetzung von AMV und das AHV-Präparat wurden ermittelt. Die kinetischen Untersuchungen wurden durch Oberflächenmessungen ergänzt, sowie mit der elektronenmikroskopischen Prüfung der Oberflächen der reagierenden Substanz, der Zwischen- und den Endprodukt-Kristalliten.

Der Typ der Zersetzungskurve, die ermittelten Aktivierungsenergien und die Wirkung von Sauerstoff und Wasserdampf auf die Zersetzungsgeschwindigkeit lassen die Annahme zu, daß im Vakuum und in inerter Atmosphäre die Entwicklung von Ammoniak die geschwindigkeitsbestimmende Stufe ist, während in oxidierenden Atmosphären die Wasserentwicklung geschwindigkeitsbestimmend ist.

Der Vergleich der kinetischen Parameter mit thermodynamischen Daten der Zersetzung führte zu Annahmen bezüglich der Beschaffenheit der mitwirkenden aktivierten Komplexen.

Резюме — Изучен распад метаванадата аммония (АМВ). Важным промежуточным продуктом распада является гексаванадат аммония (АГВ) который может быть получен также химическим методом. Установлены кинетические параметры термораспада АМВ и получения АГВ. Изучение кинетики дополнилось измерением плоскости и электронномикроскопическим исчытанием плоскости реагента промежуточного продукта и кристаллов конечного продукта.

На основании типа кривой распада установлена энергия активации и влияние кислорода и вояного пара на скорость распада. Пришли к выводу, что в вакууме и в инертном газе выделение аммиака является определяющим шагом скорости, а в окисляющей атмосфере выделение воды определяющий фактор.

Сравнение кинетических параметров с термодинамическими данными привело к предположениям относительно природы включенных активированных комплексов.