

INFLUENCE OF REACTING ATMOSPHERE ON ISOTHERMAL DECOMPOSITION OF AMMONIUM METAVANADATE

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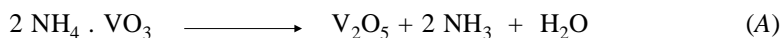
Ammonium metavanadate (AMV) was decomposed under pure oxygen, air, nitrogen, vacuum and controlled humidity, in the temperature range of 453 to 623 K. Three well established limiting conversions appear corresponding to the formation of ammonium tetravanadate at 453 K (50%), ammonium hexavanadate at 503 K (67%), and V_2O_5 at 623 K (100%). Oxidizing atmospheres have a retarding effect at 453 K but an accelerating one at 573 to 623 K, as observed from the reaction limiting time and rate constant. In addition to H_2O and N_2 , oxygen plays an important role in the oxidation of ammonia to N_2 , and in the proton transfer process.

Decomposition of ammonium salts yields volatile NH_3 as a result of the removal of a proton from the NH_4^+ cation. There is a general agreement that the first step is proton transfer with consequent accumulation of H^+ in the neighbourhood of the oxoanions network. This results in the elimination of water accompanied by continued condensation of these anions. Since the decomposition of many ammonium salts evolve NH_3 and H_2O simultaneously (or consecutively) in a 2 : 1 molar ratio, it is often convenient to write the formula of such salts in the form $[m (NH_4)_2O \cdot n (\text{metal oxide}) \cdot x H_2O]$, where m , n and x are integers. Determination of the influence of crystal structure and reactant environment on the deammoniation and dehydration processes is complicated by several solid phase transformations that are characteristic for many ammonium salts¹.

Thermal dissociation of ammonium metavanadate (AMV) was found to proceed in several stages. The reaction is sensitive to the composition and pressure of the prevailing atmosphere. This can be represented as a stepwise decrease in the $(NH_4)_2O : V_2O_5$ ratio¹. The first step (423 to 453 K) yields $(NH_4)_2O \cdot 2 V_2O_5$ (ammonium tetravanadate, ATV), which further reacts to $(NH_4)_2O \cdot 3 V_2O_5$ (ammonium hexavanadate, AHV) at

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453 to 483 K. Both steps occur as a single stage in moist ammonia, since NH_3 and H_2O are the principal products. Finally, AHV decomposes between 533 and 573 K to yield V_2O_5 . The overall reaction is readily reversible²⁻⁵.



Two or three endothermic stages were observed by DTA and DTG, which were supplemented by differential enthalpic analysis (DEA), IR spectroscopy and TG-MS measurements^{2,6-10}. Employing a TG-MS technique, von Sacken and Dahn⁹ observed the decomposition of AMV in the presence of He, O_2 or NH_3 . Below 523 K, the decomposition proceeded with simultaneous release of NH_3 and H_2O in a fixed proportion, regardless of whether the atmosphere was oxidizing or inert. Above 523 K, residual ammonia gas plays an important role as a reducing agent. Its role in reaction increases gradually between 523 and 623 K.

The formation of an ATV intermediate $[(\text{NH}_4)_2\text{V}_4\text{O}_{11}]$ has been ruled out by Range et al., and deWaal et al. in their recent series of studies using IR and Raman spectroscopy¹¹⁻¹⁴. They emphasized that when NH_4VO_3 is heated in air in an open system, the first, and possibly the only, intermediate is ammonium hexavanadate $[(\text{NH}_4)_2\text{V}_6\text{O}_{16}]$. Under dynamic conditions, only two TG clearly separated stages of decomposition occur, corresponding to the formation of AHV and V_2O_5 (refs^{9,10}). However, Brown et al.³⁻⁵ earlier reported the intermediate formation of ATV. Actually, a recent study by von Sacken et al.⁹ revealed that the first TG curve ended with a small kink which appeared as a very sharp DTG peak and corresponded exactly with the ATV-AHV stage weight change. It is a very sharp change that takes place within a limited range of temperature, and is associated with the release of water vapour (as detected by MS data).

The present study reports an isothermal weight loss of AMV determined under controlled oxidizing, inert and humid atmospheres. It covers the whole range of decomposition, 453 to 623 K, in order to assess the influence of the reaction environment on the decomposition kinetics. Four different solid state models of decomposition were tested.

EXPERIMENTAL

Material

Ammonium metavanadate used was a 99% pure product of Laborchemie Apolda, with the following trace impurities: insoluble ammonium salts 0.02%, chloride 0.05%, sulfate 0.01%, iron 0.01% and alkali metals (Na + K) 0.3%.

Kinetic Curves

Isothermal weight loss (ITG) curves were determined using a high sensitivity quartz spring balance enclosed in a pyrex tube. This helped to keep the required environment: inert atmosphere (vacuum or

nitrogen), oxidizing atmosphere (air or oxygen) and controlled humidity (0.60 and 2.07 kPa water vapour). In case of experiments under N_2 , O_2 or H_2O vapour, the jacketed spring was primarily degassed below 13 Pa, and then a slow current of either gas was introduced. In case of experiments carried out in air, the system was kept under static air with the degassing stopcock open during the measurements.

Weight changes of 300 mg of AMV were determined at constant temperatures of 453, 573 and 623 K. The data are plotted as x vs time, where x is the weight loss fraction related to the limiting weight loss at 623 K (Figs 1 - 4).

Mathematical Analysis of ITG Curves

Each of the 24 curves was tested by applying four of the well-established kinetic equations for the rate constant k . These are: the first order (F_1) equation, $[-\ln(1-x)]$, second order (SO) equation, $[(1-x)^{-1}-1]$, a contracting spherical geometry (R_3) equation, $[1-(1-x)^{1/3}]$, and three dimensional diffusion controlled (D_3) model, $[1-(1-x)^{1/3}]^2$. A linear regression procedure was adopted throughout using the least squares method. The correlation coefficient ($-r$) and the slope corresponding to the reaction rate were determined in each case. Using the Arrhenius equation correlating $\ln k$ and $1/T$, the respective E_a values were obtained as well as the preexponential factors A .

According to Maciejewski¹⁵, all three kinetic parameters: A , E_a , and the kinetic equation should be considered in order to obtain significant information concerning the progress of the thermal decomposition process.

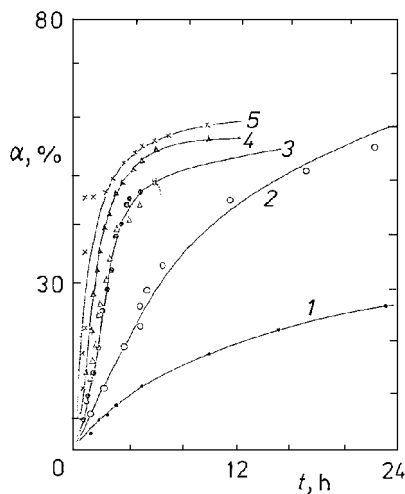


FIG. 1

Isothermal decomposition (α , fraction decomposed) of NH_4VO_3 at 453 K in various reaction atmospheres: 1 O_2 ; 2 air; 3 N_2 ; 4 0.6 kPa H_2O ; 2.07 kPa H_2O ; 5 vacuum

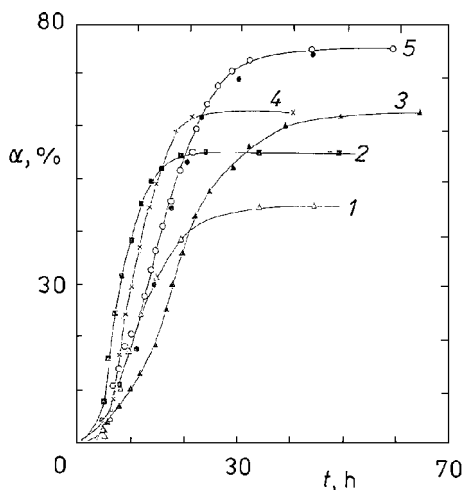


FIG. 2

Isothermal decomposition (α , fraction decomposed) of NH_4VO_3 at 503 K in various reaction atmospheres: 1 N_2 ; 2 0.6 kPa H_2O ; 3 2.07 kPa H_2O ; 4 vacuum; 5 air, O_2

RESULTS AND DISCUSSION

General Isothermal Characteristics

On the basis of the isothermal curves (Figs 1 – 4), the data in Table I were collected with respect to the limiting conversions attained at every temperature and the time needed to reach it. Two gaseous atmospheres seem to play a decisive role during the decomposition in the range of 503 – 623 K. Nitrogen shows retarding action and the oxidizing environment (oxygen supplied as pure or in air) shows an accelerating effect. The reaction following Eq. (A) is rather unexpected because vanadium in oxidation state five is well known for its oxidizing power, whereas NH_4^+ ion can act as a mild reducing agent. In the presence of O_2 , such catalyzing action would contribute to the formation of nitrogen.

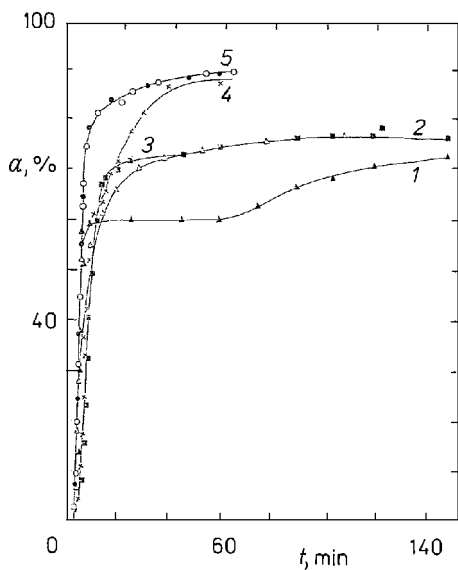
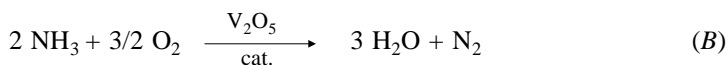


FIG. 3

Isothermal decomposition (α , fraction decomposed) of NH_4VO_3 at 573 K in various reaction atmospheres: 1 0.6 kPa H_2O ; 2 N_2 ; 3 2.07 kPa H_2O ; 4 vacuum; 5 air, O_2

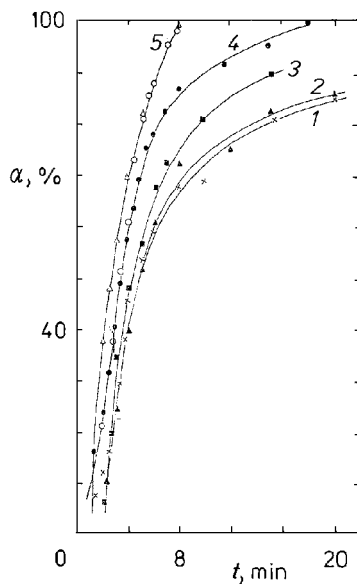


FIG. 4

Isothermal decomposition (α , fraction decomposed) of NH_4VO_3 at 623 K in various reaction atmospheres: 1 N_2 ; 2 0.6 kPa H_2O ; 3 2.07 kPa H_2O ; 4 vacuum; 5 air, O_2

This step would be logically accelerated by excess oxygen and inhibited to a great extent by the presence of N_2 or H_2O vapour. Their high partial pressure in the surrounding atmosphere suppresses the evolution of NH_3 and H_2O by respective adsorption on the decomposing solid surface.

In the TG-MS results of von Sacken and Dahn⁹, ammonia was detected in the evolved gas at 453 – 523 K and 573 – 623 K in inert (He) atmosphere. In the presence of O_2 it appeared only in the first stage whereas N_2 evolved in the second temperature range, accompanied with a higher proportion of H_2O .

Thus, in the presence of oxygen (or air) or nitrogen the evolution of ammonia is suppressed, with pure O_2 having the most pronounced effect. This appears clearly at the lowest temperature of 453 K (Table I). At and beyond 503 K the principal product is H_2O and in this case the presence of vacuum or oxidizing atmospheres contributes to its formation and removal. Naturally, humid atmospheres will retard this stage (Table I). Nitrogen plays an almost identical role in retarding reaction, being one of the product gases, but to a limited degree. For example at 623 K the formation of V_2O_5 is completed in 8 – 18 min in the presence of oxygen, air or under vacuum, whereas in humidity or N_2 this is attained after 90 – 150 min.

Comparison of the Reaction Rate Constants

Tables II and III summarize the estimated rate constants and the respective correlation coefficients ($-r$) evaluated by applying the four above mentioned kinetic equations. The calculated rate constants always decrease in the order SO , F_1 , R_3 and D_3 .

TABLE I
Limiting conversion of AMV under various atmospheres and respective time, t , of its attainment

Atmosphere	453 K		503 K		573 K		623 K	
	α^a , %	t , h	α^a , %	t , h	α^a , %	t , h	α^a , %	t , h
Vacuum	50	2.75	62.7	1.00	87	1.00	100	0.30
2.07 kPa H_2O	50	3.6	63.0	1.08	77	2.50	100	2.50
0.60 kPa H_2O	50	6.0	57.0	1.50	73	2.50	100	1.50
Nitrogen	50	7.0	50.0	2.33	77	1.83	100	2.00
Air	50	16.0	66.7	0.50	90	1.10	100	0.28
Oxygen	30	30.0	67.0	0.50	90	0.50	100	0.13

^a Fraction decomposed.

In case of reactions carried out in air or oxygen, the best linearization is generally observed when adopting the F_1 and R_3 models. Under vacuum and in N_2 , the SO and D_3 mechanisms seem to describe the reaction better. Unsatisfactory or poor linearization is observed in most experiments carried out in humid atmospheres. This could be due to the backward reaction effects governing the decomposition especially in the presence of the released gas products.

Comparison of the k values reveals an identical trend for the effect of the reaction environment on the course of decomposition. Thus at 453 K the highest rate constants are observed under vacuum and N_2 . The lowest k values pertain to air or O_2 atmospheres. At 573 and 623 K, this is reversed, the decomposition rate becoming higher in the presence of oxidizing atmospheres and lower in N_2 .

TABLE II
Isothermal rate constants, k (m^{-1}), of AMV decomposed under various atmospheres at 453 and 503 K

Model	Parameter	Air	Oxygen	Vacuum	Nitrogen	0.60 kPa H_2O	2.07 kPa H_2O
453 K							
F_1	$-r$	0.9747	0.9818	0.9629	0.9962	0.9706	0.9608
	k	$4.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	$3.9 \cdot 10^{-3}$	$3.1 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$
SO	$-r$	0.9991	0.9891	0.9820	0.9962	0.9872	0.9832
	k	$9.1 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	$5.8 \cdot 10^{-3}$	$4.3 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$	$4.3 \cdot 10^{-3}$
D_3	$-r$	0.9985	0.9989	0.9945	0.9809	0.9962	0.9928
	k	$4.4 \cdot 10^{-5}$	$7.6 \cdot 10^{-6}$	$2.7 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$
R_3	$-r$	0.9648	0.9785	0.9545	0.9953	0.9634	0.9499
	k	$1.1 \cdot 10^{-4}$	$5.5 \cdot 10^{-5}$	$1.1 \cdot 10^{-3}$	$9.2 \cdot 10^{-4}$	$5.4 \cdot 10^{-4}$	$7.7 \cdot 10^{-4}$
503 K							
F_1	$-r$	0.9967	0.9705	0.9863	0.9864	0.9936	0.9598
	k	$4.9 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$	$5.4 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$	$5.8 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$
SO	$-r$	0.9761	0.9689	0.9955	0.9936	0.9870	0.9843
	k	$9.3 \cdot 10^{-2}$	$8.6 \cdot 10^{-2}$	$9.8 \cdot 10^{-2}$	$3.8 \cdot 10^{-2}$	$8.4 \cdot 10^{-2}$	$3.6 \cdot 10^{-2}$
D_3	$-r$	0.9625	0.9527	0.9910	0.9932	0.9648	0.9786
	k	$4.6 \cdot 10^{-3}$	$4.2 \cdot 10^{-4}$	$4.8 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$3.7 \cdot 10^{-2}$	$1.7 \cdot 10^{-3}$
R_3	$-r$	0.9979	0.9677	0.9807	0.9832	0.9944	0.9187
	k	$1.3 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$	$8.6 \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$	$4.2 \cdot 10^{-3}$

Variations of E_a and A with the Prevalent Environment of the Reaction

The activation energies evaluated from the Arrhenius relations using k values in the full temperature range, are presented in Table IV. These data exhibit three features:

1) The four tested kinetic laws exhibit small variations in E_a although the sequence SO, D₃, F₁ and R₃ can be observed.

2) With the exception of N₂ and high humidity, linearization of the four temperature data points is fairly unsatisfactory.

3) The values of E_a increase in the sequence: N₂, vacuum, humidity, air, oxygen.

According to deWaal et al.¹³, the generalized Avrami–Erofeev equation can be put in the form

TABLE III
Isothermal rate constants, k (m⁻¹), of AMV decomposed under various atmospheres at 573 and 623 K

Model	Parameter	Air	Oxygen	Vacuum	Nitrogen	0.60 kPa H ₂ O	2.07 kPa H ₂ O
573 K							
F ₁	$-r$	0.9922	0.9802	0.9644	0.9622	0.9701	0.9942
	k	0.1905	0.1949	0.0723	0.0635	0.1023	0.1229
SO	$-r$	0.9720	0.9822	0.9992	0.9872	0.9462	0.9774
	k	0.3589	0.7024	0.1530	0.1154	0.2395	0.2139
D ₃	$-r$	0.9649	0.9589	0.9909	0.9818	0.9791	0.9608
	k	0.0178	0.0221	6.4 · 10 ⁻³	5.7 · 10 ⁻³	0.0109	0.0105
R ₃	$-r$	0.9995	0.9625	0.9531	0.9502	0.9758	0.9955
	k	0.0531	0.0456	0.0169	0.0176	0.0236	0.0345
623 K							
F ₁	$-r$	0.9754	0.9909	0.9851	0.9650	0.9611	0.9851
	k	0.3602	0.4527	0.2362	0.0916	0.1584	0.1743
SO	$-r$	0.9105	0.9510	0.9465	0.9967	0.9877	0.9872
	k	0.8077	2.1913	1.2785	0.3402	0.3781	0.6281
D ₃	$-r$	0.9174	0.9624	0.9836	0.9923	0.9861	9.9975
	k	0.0378	0.0691	0.0323	0.0121	0.0135	0.0226
R ₃	$-r$	0.9878	0.9986	0.9612	0.9310	0.9291	0.9622
	k	0.0947	0.1005	0.0507	0.0210	0.0464	0.0406

$$\ln [\ln (1/(1-x))] = n \ln t + \ln k . \quad (I)$$

Application of this equation to our data showed that for the reaction at 453 K $n = 0.6 - 1.0$ in most cases whereas for the other three temperatures (503, 573, 623 K) it was 1.15 - 1.95. The evaluated activation energies decreased in the following order: O₂, 2.07 kPa H₂O, air, N₂, 0.60 kPa H₂O, vacuum. The respective values are 58.6, 52.4, 43.5, 38.2, 32.2 and 29.5 kJ mol⁻¹.

As the data for 453 K showed very low decomposition rates (Tables I and II), the corresponding k values were omitted and E_a values were evaluated from the reaction rate constants at 503, 573 and 623 K (Table V). More satisfactory linear relationships were thus obtained. The decreasing order of the activation energy becomes: O₂, 2.07 kPa H₂O, N₂, air, vacuum, 0.60 kPa H₂O. The value in air is identical to that calculated by deWaal et al.¹³ (48.6 kJ mol⁻¹) using Raman spectroscopy for the reaction at 423 and 443 K.

TABLE IV
Activation energy, E_a (kJ mol⁻¹), associated with decomposition of AMV under various atmospheres at 453 - 623 K

Model	Parameter	Air	Oxygen	Vacuum	Nitrogen	0.60 kPa H ₂ O	2.07 kPa H ₂ O
F ₁	$-r$	0.9335	0.9361	0.9785	0.9925	0.9093	0.9976
	E_a	89.3	103.1	55.1	45.6	57.0	57.9
	log A	7.35	8.61	4.04	2.82	4.14	4.16
SO	$-r$	0.9437	0.9551	0.9546	0.9967	0.9627	0.9968
	E_a	89.4	122.3	69.8	58.4	66.8	66.8
	log A	7.66	10.93	5.87	4.37	5.38	5.39
D ₃	$-r$	0.9431	0.9936	0.9417	0.9992	0.9482	0.9959
	E_a	89.0	128.7	61.8	56.9	63.8	63.8
	log A	6.31	9.86	3.67	2.87	3.72	3.75
R ₃	$-r$	0.9331	0.9304	0.9787	0.9866	0.8574	0.9959
	E_a	89.4	98.4	53.3	42.1	54.4	55.6
	log A	6.78	7.58	3.13	1.91	3.31	3.35
Mean values	$-r$	0.9384	0.9538	0.9633	0.9937	0.9195	0.9965
	E_a	89.3	113.1	60.1	50.8	60.5	61.1

The frequency factor A shows an identical trend of the change as that indicated above for E_a (Tables IV and V). Both parameters are exactly parallel. The oxidizing atmospheres give the highest E_a and $\log A$, whereas the low humidity and N_2 or vacuum exhibit the lowest E_a and $\log A$.

CONCLUSIONS

Isothermal gravimetry of ammonium vanadate exhibited three well established stages of decomposition shown by definite limiting values. These correspond fairly to the formation of ammonium tetravanadate at 453 K (50% conversion), ammonium hexavanadate at 503 K (67% conversion), and vanadium pentoxide at 623 K (100% decomposition). The extent of conversion to any of the intermediate or final products largely depends on the reaction environment and the temperature of reaction. At a low temperature (453 K) oxygen and N_2 have a retarding effect whereas at 573 – 623 K oxygen and vacuum accelerate decomposition considerably.

Although the reaction is favoured in the presence of oxygen, it is associated with the highest activation energy, 70 kJ mol^{-1} , whereas decomposition in low humidity and vacuum shows the lowest values of $35 - 37 \text{ kJ mol}^{-1}$.

TABLE V

Activation energy, E_a (kJ mol^{-1}), associated with decomposition of AMV under various atmospheres at 503 – 623 K

Model	Parameter	Air	Oxygen	Vacuum	Nitrogen	0.60 kPa H_2O	2.07 kPa H_2O
F_1	$-r$	0.9997	0.9996	0.9908	0.9997	0.9991	0.9993
	E_a	43.5	50.4	29.5	38.2	32.3	52.4
	$\log A$	3.23	3.89	1.57	2.15	1.93	3.67
SO	$-r$	0.9993	0.9996	0.9994	0.9884	0.9905	0.9936
	E_a	46.9	70.7	56.3	57.5	41.5	61.1
	$\log A$	3.84	6.28	4.85	4.29	3.10	4.87
D_3	$-r$	0.9989	0.9875	0.9788	0.9978	0.9781	0.9983
	E_a	45.8	113.4	41.2	53.3	35.7	55.4
	$\log A$	2.42	8.48	1.95	2.54	1.19	2.98
R_3	$-r$	0.9962	0.9993	0.9967	0.9919	0.9936	0.9981
	E_a	42.5	45.5	23.7	50.6	31.3	32.5
	$\log A$	2.57	2.82	0.69	2.85	1.30	1.04
Mean values	$-r$	0.9985	0.9965	0.9914	0.9944	0.9903	0.9973
	E_a	44.7	70.0	37.7	49.8	35.2	50.4

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