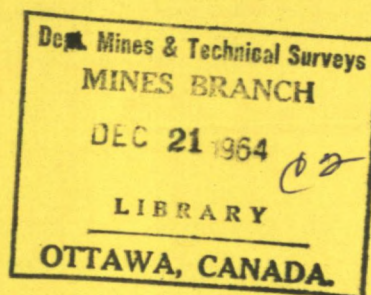




CANADA

MECHANISM OF THERMAL
DECOMPOSITION OF AMMONIUM
METAVANADATE



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MECHANISM OF THERMAL DECOMPOSITION OF AMMONIUM METAVANADATE

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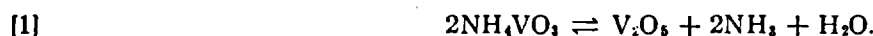
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ABSTRACT

When ammonium metavanadate is roasted at 225 °C, ammonia and water are eliminated in the ratio 2:1 and an intermediate compound identified by weight loss and chemical analysis as $(\text{NH}_4)_2 \cdot \text{O} \cdot \text{V}_2\text{O}_5$ is formed. An X-ray diffraction pattern for this material is reported. Transpiration experiments have been used to establish the free energy of this reaction. The second stage of the decomposition involves an endothermic and an exothermic process, both of which occur with the production of a gaseous product. The liberation of ammonia is not quantitative, and its oxidation on the vanadium pentoxide, in the last stage of decomposition, is suggested as a possible source of the exothermic heat.

INTRODUCTION

Ammonium metavanadate, which may be recovered from the hydrometallurgical treatment of some ores containing vanadium, is one of the major starting materials in the preparation of vanadium chemicals. Most vanadium pentoxide, for example, is produced by the roasting of ammonium metavanadate



Although there have been a number of investigations of the process of roasting ammonium metavanadate (1-5), there is no general agreement on the course of the reaction. It is agreed that a stable intermediate is formed, but it has not been positively identified. In Table I, some of the suggested intermediates are listed.

TABLE I
Weight losses accompanying formation of proposed intermediates

Proposed intermediate	% weight loss	Ratio $\text{NH}_3:\text{H}_2\text{O}$ released
$(\text{NH}_4)_2 \cdot \text{O} \cdot (\text{V}_2\text{O}_5)_2$ (1, 2)	14.84	2:1
HVO_3^* (3)	14.56	1:0
$\text{NH}_3 \cdot \text{H}_2\text{O} \cdot (\text{V}_2\text{O}_5)_2$ (4)	14.77	3:1

*Accepted by most current textbooks.

It will be apparent from Table I that since the weight losses involved in the production of the intermediate are almost identical, any technique based entirely on thermogravimetric methods would be likely to produce inconclusive results. When balanced chemical equations are written for the formation of each of these intermediates, it is evident from the wide variation in the ratio of ammonia to water, as shown in the third column of Table I, that analysis of the gaseous decomposition products should be helpful in resolving the reactions involved.

In this work chemical analyses have been made of the gaseous products of reaction.

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This information has been combined with the weight loss and chemical analysis to determine the composition of the intermediate. The transpiration method was used to estimate the free-energy change for the reaction to form the intermediate. Differential thermal analysis was used to detect the temperatures at which the most vigorous reaction was obtained, and to assess the complexity of the decomposition reactions.

EXPERIMENTAL METHODS AND RESULTS

Material

The ammonium metavanadate used in the experiments was "purified ammonium metavanadate" (14.56% NH_3 , 44.48% V) supplied by Fisher Scientific Co. A few experiments were done using British Drug House reagent grade material, but, from the development of a yellow color on roasting, it was evident that the material was contaminated with a potassium salt.

Analytical Methods

Ammonia and Water

Two methods were used for the determination of ammonia. When only ammonia was required, it was absorbed from the gaseous decomposition products in 0.1 N H_2SO_4 and the excess back-titrated with standard alkali.

When both ammonia and water were required for determining the ratio in which they were produced during the decomposition, the products were passed through a known weight of concentrated sulphuric acid. The increase in weight was equivalent to the absorption of both water and ammonia. The amount of ammonia in the acid was determined by the Kjeldahl method.

Vanadium

Vanadium was determined by a redox titration, using $N/30$ KMnO_4 , $N/30$ $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, and a diphenylamine phosphoric acid indicator.

Differential Thermal Analysis and Effluent Gas Analysis Experiments

The first group of experiments on the thermal decomposition of ammonium metavanadate was done using a Robert L. Stone Co. differential thermal analysis apparatus equipped with a thermal conductivity cell for analyzing the effluent gas stream. During a run, a carrier gas was flushed through the powdered sample at the rate of 50 cc per min as the sample was heated at a rate of 3 °C per min. The carrier gases were nitrogen, oxygen, ammonia, and steam. The results of the thermal analysis and gas analysis were plotted simultaneously on a strip chart. Tracings of two typical charts are shown in Fig. 1.

It is evident, from the lines for a nitrogen carrier gas experiment shown at the bottom of Fig. 1, that the decomposition reaction is complex, involving several stages. The first stage of the reaction, which occurs in the temperature range 210–215 °C, may take place in two steps. A gaseous product is evolved, but the gas analysis trace does not differentiate the gas from each step. At the completion of the first stage of reaction, an intermediate product is formed that is stable up to a temperature of 260 °C. The material then undergoes an endothermic reaction, evolving a gaseous product at maximum rate at about 325 °C. The product from this second stage then undergoes additional reaction; an exotherm is developed at 375 °C and a gaseous product is evolved. The final product of this decomposition reaction in nitrogen was a dark-colored vanadium oxide in which the average vanadium valence was slightly less than 5.

When the same experiment was repeated using oxygen as a carrier gas, as shown at the top of Fig. 1, there was better differentiation of the doublet developed in the first

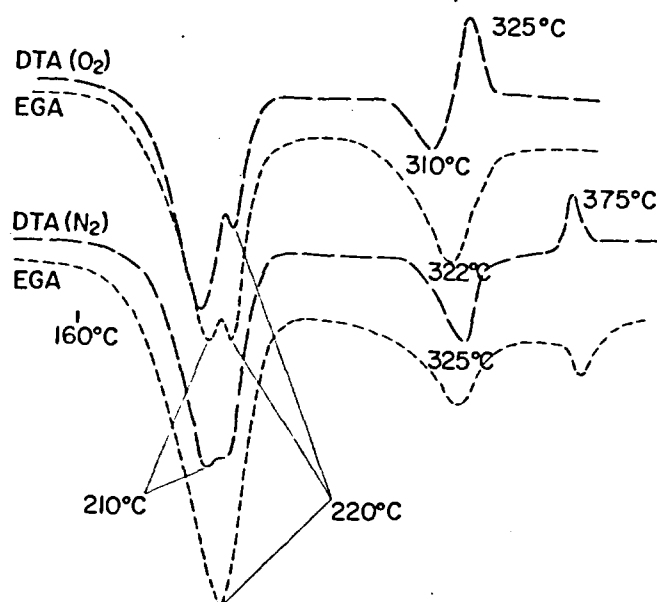


FIG. 1. Differential thermal analysis and effluent gas analysis traces of the reactions involved in the conversion of ammonium metavanadate to vanadium pentoxide, with oxygen and nitrogen sweep respectively.

stage of reaction. It was shown by both the thermal- and gas-analysis tracings. The first part of the second stage of decomposition was identical with that observed in nitrogen. However, because of the increased area under the gas analysis tracing and the occurrence of the exotherm at a temperature 50 deg less than that in the nitrogen experiment, it seems likely that both of the gases evolved in the second stage of the decomposition were released simultaneously. It also seems reasonable to expect that in an oxygen atmosphere, the intermediate is oxidized at a lower temperature than when vanadium pentoxide is the source of oxygen.

When the experiments were repeated using steam and ammonia as carrier gases, the effluent gas analysis tracings were erratic. In both instances, however, a single clearly defined peak was generated by the first stage of the reaction. The peak occurred at 225 °C in steam and at 240 °C in ammonia. The sharpness of the peaks indicated that some suppression of the reaction may have occurred.

Determination of the Composition of the Intermediate

In this group, three types of experiments were done. The first type consisted of heating a sample of ammonium metavanadate in an American Instrument Company recording thermogravimetric balance. The heating was done at a constant rate of 5 °C per min in a 50 cc per min stream of nitrogen gas. A tracing of the instrument-drawn chart is shown in Fig. 2, from which it is evident that the decomposition reaction takes place in two stages that are sufficiently well defined to warrant attempts to isolate the intermediate.

Isolation of the intermediate was done by heating 2 g samples of ammonium metavanadate in an open boat within a tube furnace in a slow stream of dry oxygen. Oxygen was used because the experiments shown in Fig. 1 indicated that the steps in the decomposition occur more sharply in it than in nitrogen. At a selected temperature, the boat was heated and then periodically cooled and weighed. It was found that at 225 °C a constant weight was attained after 2.5 h. The weight loss was 14.85%. At a temperature of 200 °C, equilibrium was not obtained after 4 h. At a temperature of 245 °C, there was no observable plateau in the weight loss curve.

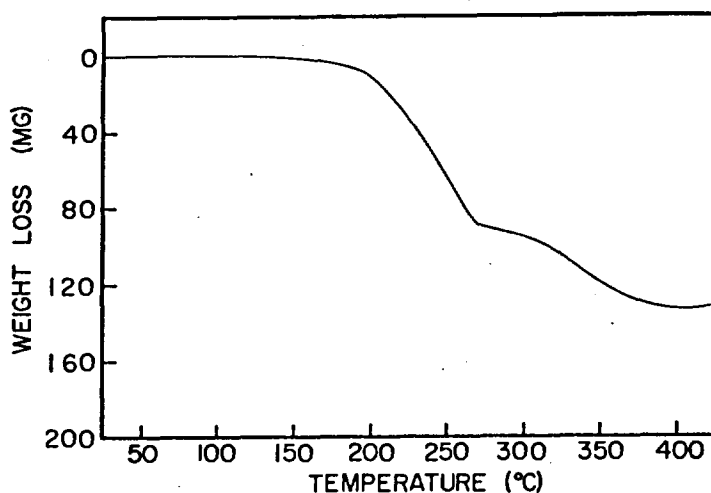


FIG. 2. Thermogravimetric analysis curve of the conversion of ammonium metavanadate to vanadium pentoxide - oxygen sweep at 3 deg per min increase in temperature.

When the conditions for achieving a constant composition had been established, the experiment was repeated and the product gases analyzed for ammonia and water. It was found that the weight loss was entirely accounted for by the combined loss of ammonia and water, and it was established that they are released in the ratio of 2.00 ± 0.02 ammonia to 1.00 water. Chemical analyses were done on the intermediate. The results are shown in Table II.

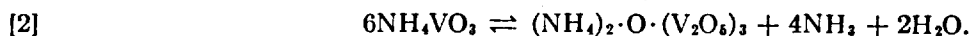
TABLE II
Percentage composition of intermediate

	NH ₃	H ₂ O	V	O*	NH ₃ /V
Found	5.69	2.97	52.19	39.15	0.109
Calc'd.†	5.69	3.01	51.10	40.20	0.111

*By difference.

†Calculation was made on the assumption that the intermediate is of formula $(\text{NH}_4)_2\text{O} \cdot (\text{V}_2\text{O}_5)_2$.

The weight loss, gas composition, and chemical analysis are in agreement with the following equation representing the first stage in the thermal decomposition of ammonium metavanadate:



X-ray powder diffraction patterns were made of the intermediate compound, and the results shown in Table III were obtained.

Transpiration Experiments

The object of the transpiration experiments (6) was to establish the free-energy function for the formation of the intermediate compound from ammonium metavanadate. These experiments were done using the pyrex vessel shown schematically in Fig. 3. Preheated oxygen at a known flow rate was passed through a loosely fitted plug of pyrex glass wool into the saturation zone. This zone was about 7 cm in length in a 2.5 cm diameter pyrex glass tube. The ammonium metavanadate powder was piled in ridges to a depth of about 1 cm. The product-saturated oxygen stream was discharged through another plug of pyrex wool and a 2 cm length of 0.05 cm capillary. The exit gases were passed to

TABLE III
X-ray powder diffraction data for $(\text{NH}_4)_2\text{O} \cdot (\text{V}_2\text{O}_5)_2$
(Cu K radiation, Ni filter)

$d(\text{\AA})$	I^*	$d(\text{\AA})$	I^*
8.2	vs	2.33	vw
6.2	vw	2.21	m
5.7	vw	2.04†	mw-b
4.1	m-b	1.93	vw
3.46	m	1.86	vw
3.34	m	1.80	s
3.17	s	1.76	mw
2.88†	vw-b	1.58	mw-b
2.71	w	1.54	mw-b
2.61	m	1.48	vw-b
2.42	mw	1.45	vw-b
		1.40	w-b

Plus additional weak lines

*Abbreviations: vs(very strong), s(strong), m(medium), mw(medium weak), w(weak), vw(very weak), b(broad).
†Probably two unresolved lines.

absorbers for analysis. The gas saturation vessel was arranged in a fixed position and a movable 12×1 in. cylindrical tube furnace was used to heat the vessel. The temperature of the furnace was controlled to $\pm 2^\circ\text{C}$ with a Kelvin and Hughes controller. Sample temperature was determined by a chromel-alumel thermocouple fitted in the central thermocouple well shown in Fig. 3.

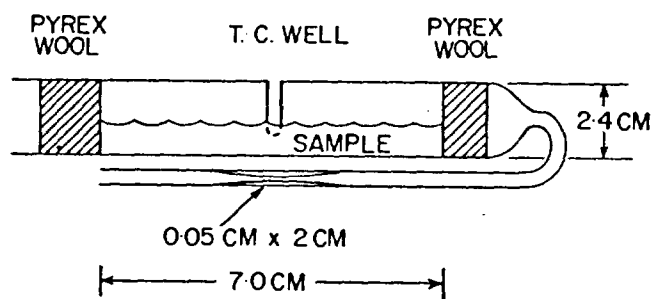


FIG. 3. Pyrex sample vessel used in transpiration experiments.

At a given temperature, experiments were done at a variety of flow rates with the object of establishing a gas composition over the sample such that the composition would be independent of changes in the gas flow rate and in which the partial pressures of ammonia and water would be identical with the decomposition pressures that the two gases would establish over the sample in an evacuated vessel at the same temperature. The results of this series of experiments are shown graphically in Fig. 4, from which it will be apparent that, for at least three of the experimental temperatures, there is a relatively wide range of gas flows for which the sample is in equilibrium with the gas flow.

From a chemical analysis of the ammonia in the oxygen stream, the partial pressure of ammonia in the equilibrium gas was calculated for each of the experimental temperatures. The calculations are shown in Table IV.

Regression analysis of the results in Table IV and Fig. 5 yielded the following equation for 1 mole of ammonium metavanadate

$$\log K = 10.148 - 5.052 \times 10^3/T$$

or

$$\Delta G^\circ = 23\,115 - 46.4T.$$

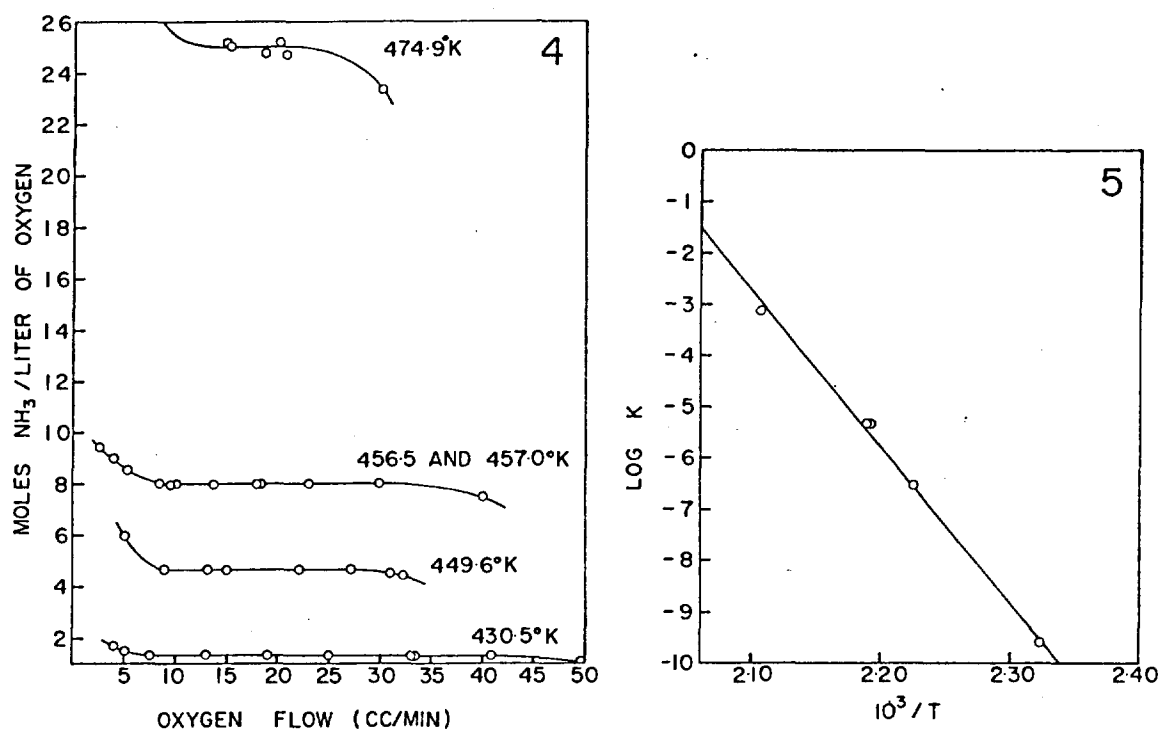


FIG. 4. Graph used to establish equilibrium ammonia pressure in transpiration experiments at 430.5, 449.6, 456.5, 457.0, and 474.9 °K.

FIG. 5. Log equilibrium constant vs. reciprocal temperature relation for the reaction to form $(\text{NH}_4)_2\text{O} \cdot (\text{V}_2\text{O}_5)_2$ from NH_4VO_3 .

TABLE IV

Decomposition pressures over ammonium metavanadate, calculated from a dynamic experiment
($p_{\text{NH}_3} + p_{\text{H}_2\text{O}} = 1.5 p_{\text{NH}_3}$)

T (°K)	$10^3/T$	Moles NH ₃ per l O ₂ at 25 °C	$p_{\text{NH}_3}^4$	$p_{\text{NH}_3}^4 \cdot p_{\text{H}_2\text{O}}^2$	Log K
430.5	2.323	13.18×10^{-4}	9.512×10^{-7}	2.319×10^{-10}	-9.634
449.6	2.225	4.66×10^{-3}	1.095×10^{-4}	2.865×10^{-7}	-6.543
456.5	2.191	8.02×10^{-3}	7.216×10^{-4}	4.846×10^{-6}	-5.315
457.0	2.188	7.77×10^{-3}	6.871×10^{-4}	4.503×10^{-6}	-5.346
474.9	2.106	25.1×10^{-3}	2.092×10^{-2}	7.564×10^{-4}	-3.121

Because a linear equation was used to fit the results in Table IV, the assumed ΔC_p for the reaction is 0; hence, $\Delta H_{298}^0 = 23.1$ kcal/mole and $\Delta S_{298}^0 = 46.4$ entropy units (e.u.). Because the heat of formation of ammonium metavanadate is not known, it is not possible to estimate the heat of formation of the intermediate compound. It is possible, however, to check the reasonableness of the entropy change. The principal change in entropy in reaction [2] is the evolution of 4 moles of ammonia and 2 moles of water for each 6 moles of ammonium metavanadate. Since the entropy of formation per mole of water at 298 °K is 45.11 e.u. and the entropy of formation of ammonia is 45.96 e.u., the combined entropy change per mole of ammonium metavanadate would be 45.7 e.u., which is in reasonable agreement with the experimental value of 46.4 e.u.

When both the transpiration technique and the analysis of the gas stream for the ratio of ammonia to water were applied to the reaction for the formation of vanadium pentoxide from the intermediate, the results were inconclusive. The ratio of ammonia to water in the decomposition gases was erratic, but always indicated that some of the ammonia was

being decomposed. In the experiments using a nitrogen carrier gas, the vanadium oxide product showed evidence of reduction. The vanadium oxide was its normal color only when oxygen was used. From these observations and from the evidence of differential thermal analysis and effluent gas analysis, it seems likely that the final stage of the decomposition reaction consists of the catalytic decomposition of ammonia on the surface of freshly formed vanadium pentoxide.

CONCLUSIONS

The production of vanadium pentoxide from ammonium metavanadate involves a series of chemical reactions. The first stage of the reaction is the almost simultaneous elimination of ammonia and water, in the molar ratio of 2:1, to produce an intermediate compound having the chemical composition $(\text{NH}_4)_2 \cdot \text{O} \cdot (\text{V}_2\text{O}_5)_3$. The second stage of the decomposition involves both an exothermic and an endothermic reaction. The endothermic reaction may be the liberation of water, and the exothermic reaction is consistent with the degradation of ammonia on the vanadium pentoxide surface.

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