

THERMAL DECOMPOSITION OF AMMONIUM PARAMOLYBDATE (APM)

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The course of the thermal decomposition of APM was studied in vacuo and in air or argon atmosphere. The differences between vacuum and atmospheric pressure decompositions were pointed out. The substantial participation of redox reactions in the vacuum decomposition was observed. The course of the vacuum decomposition was described in detail as a result of sensitive continuous analysis of the gaseous products. The final product of the vacuum decomposition is a mixture of lower molybdenum oxides. In the presence of oxygen the MoO_3 obtained is only slightly reduced, mainly in the course of removal of the last of the ammonium cations from the samples.

This study has been undertaken in connection with preparative problems relating to vanadia, molybdena and vanadia-molybdena catalysts. These catalysts are normally prepared by means of the thermal decomposition of vanadates and molybdates previously deposited on the catalyst carriers. As a continuation of studies on the thermal decomposition of ammonium metavanadate [1] and $\text{NH}_4\text{VO}_3\text{--TiO}_2$ mixtures [2], we now present results on the thermal decomposition of dehydrated and hydrated ammonium paramolybdate (APM).

APM decomposition was studied previously [3–7], but the course of the decomposition was not definitely determined and the reduction taking place during this process was discussed very superficially. Mass-spectrometric analysis, which is useful for study of the redox process, was used previously only in [3, 4], but the results obtained were semi-quantitative (see discussion of APM decomposition in vacuo).

Among the intermediates, the presence of anhydrous and partially deammonated $(\text{NH}_4)_2 \cdot 4 \text{MoO}_3$ was confirmed by X-ray analysis. The other postulated intermediate $2(\text{NH}_4)_2\text{O} \cdot 5 \text{MoO}_3$ was never confirmed, although some authors [3–6] have used it to describe the results of TG measurements.

Experimental

Sample

Ammonium paramolybdate (POCh, pure), described by the formula $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$, was used without further purification. Thermal and chemical analysis showed that it was partially dehydrated; thus, the formula $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 1.62 \text{H}_2\text{O}$ adequately described the composition of the starting material.

Vacuum

Thermal decomposition of APM in vacuo was performed with continuous removal of gaseous products from the reaction chamber. Evolved gases flowed through ionization gauges and a quadrupole-mass spectrometer. More experimental details are given in [1] and [2].

Samples of about 10–15 mg were placed in a quartz reactor. After sealing, the samples were outgassed at room temperature for about 24 h. Before each thermal decomposition experiment, all the metal parts of the apparatus were heated at 300° for 2 h while the valve between the reaction chamber and the measuring system was closed. The resulting basic pressure in the measuring system was about 5×10^{-8} Torr. After re-connection the reaction chamber was heated up to 45° for about 30 min and the pressure was increased to about 1×10^{-5} Torr. During this outgassing, control mass-spectrometric analyses were carried out. The evolution of water and no evolution of NH_3 was observed.

The resulting samples were subjected to thermal decomposition with a linear increase of temperature (0.5, 1.0 and 3 deg/min) up to 600° with continuous mass-spectrometric analysis of the gaseous products.

DTA and TG analysis

DTA, TG and DTG analyses were performed with a Thermoanalyser-2 (Mettler) under the following parameters: weight of samples 60–120 mg, argon (pure), air (dehydrated with silica gel), gas flow velocity 4 l/h, heating rates 3, 6 and 10 deg/min, reference material $\alpha\text{-Al}_2\text{O}_3$, measuring thermocouple Pt/Pt-Rh.

Chemical analysis

The degree of reduction of the molybdenum ions in the decomposed product was determined by means of permanganometric titration after dissolution of samples in a small amount of H_2SO_4 (1:1). The mean oxidation number of the molybdenum ions determined by mass-spectrometric analysis in the course of the vacuum decomposition was in accordance with the results of chemical analysis. However, the sensitivity of the mass-spectrometric analysis was more than 100 times that of the chemical analysis.

Results

Thermal decomposition in vacuo

Heating of the APM samples causes their decomposition and, in consequence, increase of the pressure in the reaction chamber. In the flow system the pressure may be interpreted approximately as a measure of the decomposition velocity. Hence, the curve in Fig. 1 represents changes in velocity in the course of the thermal decomposition. Five stages can be distinguished in the decomposition of APM.

The three main stages (1_v , 2_v and 3_v) result in almost total thermal decomposition, amounting to more than 90%. The next two stages are less intense and demand 10 times (4_v) and 100 times more sensitive pressure scales (5_v).

The amounts of gaseous products evolved in the various decomposition stages are presented in Table 1. These data show the reproducibility of the results. For further interpretation, the mean results for each stage were taken into account.

Continuous mass-spectrometric analyses of the evolved gases are shown in Figs 2 and 3. The results were used to determine the amounts of every gaseous product liberated in each consecutive decomposition step. Thereafter, the curves were integrated and the total amounts of gas molecules were calculated. The results are shown in the diagram (Fig. 4) in Torr X min.

Thermal decomposition in air or argon streams

The curves TG1, TG2, DTG and DTA in Fig. 5 represent the thermal decomposition of APM in an air stream under atmospheric pressure. Four main stages of decomposition and the melting peak of the MoO_3 phase (the final product of the decomposition) are apparent.

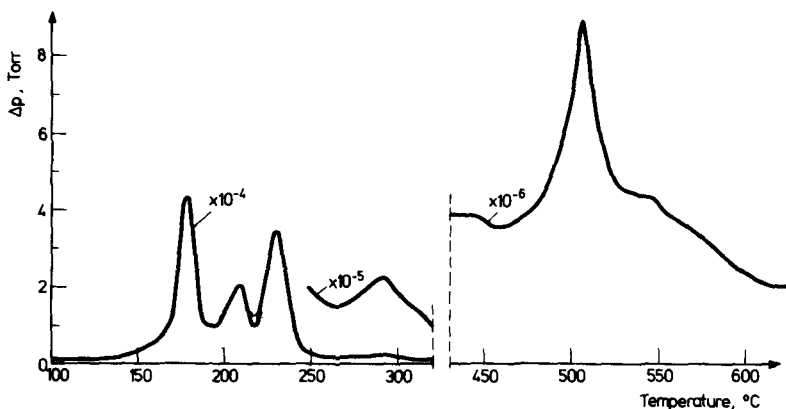


Fig. 1 Typical curve representing changes in velocity in the course of the thermal decomposition of APM in vacuo

Table 1 Amounts of gaseous products evolved in each decomposition stage in vacuo

Experiment	Decomposition stage					Sample weight, mg	Heating rate, °C/min
	1 _v	2 _v	3 _v	4 _v	5 _v		
1. Temperature range, °C Amount of evolved gases (Torr X min X 10 ⁻³)	125-200 7.20	200-225 2.15	225-270 5.90	290-360 0.95	480-560 0.48	15	0.5
2. Temperature range, °C Amount of evolved gases (Torr X min X 10 ⁻³)	120-195 6.90	195-220 2.00	220-265 5.70	275-350 0.80	470-550 0.45	15	0.5
3. Temperature range, °C Amount of evolved gases (Torr X min X 10 ⁻³)	120-195 6.95	195-220 2.05	220-270 5.60	280-350 0.77	480-560 0.45	15	0.5
4. Temperature range, °C Amount of evolved gases (Torr X min X 10 ⁻³)	120-195 7.05	195-225 2.00	225-270 5.74	285-360 0.85	470-560 0.46	15	1.0
5. Temperature range, °C Amount of evolved gases (Torr X min X 10 ⁻³)	115-190 4.75	190-220 1.40	220-270 3.80	280-350 0.58	470-550 0.33	10.	1.0
Average result for standard weight (15 mg) of APM (Torr X min X 10 ⁻³)	7.00	2.05	5.78	0.87	0.46		

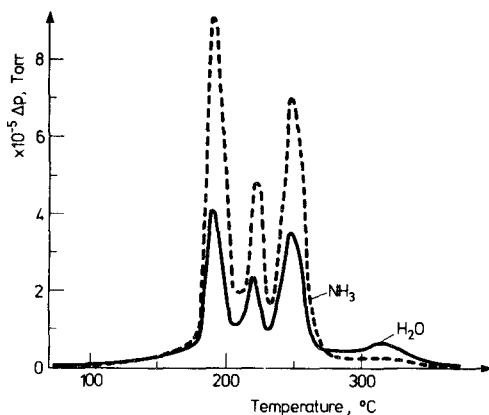


Fig. 2 Continuous mass-spectrometric analyses of the evolved gaseous products: NH_3 and H_2O molecules

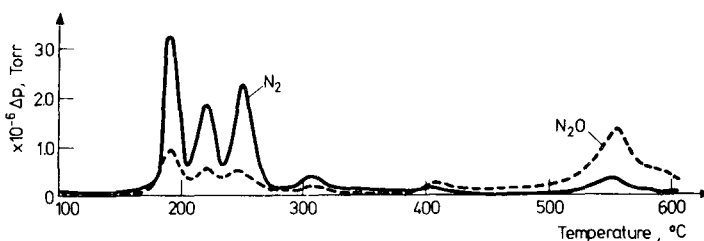


Fig. 3 Continuous mass-spectrometric analyses of the evolved gaseous products: N_2 and N_2O molecules

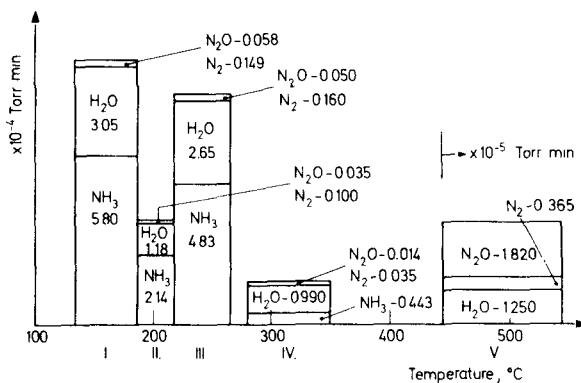


Fig. 4 Amounts of gas molecules liberated in each decomposition stage, obtained from mass-spectrometric analyses (Torr X min)

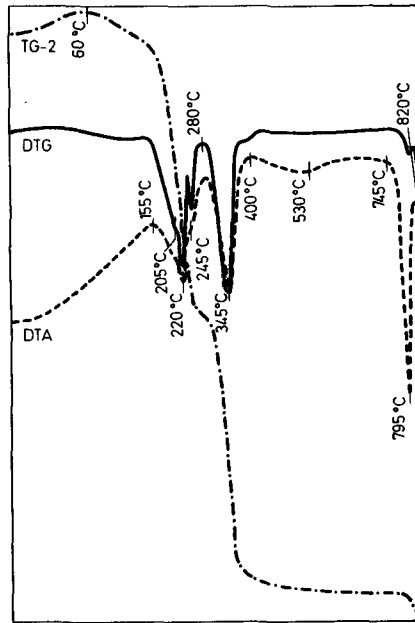


Fig. 5 TG, DTG and DTA curves of APM in air stream, with the melting peak of the final product of decomposition. Atmosphere: air, heating rate: 6 deg/min, flow velocity: 4l/h, sample weight: 0.06 g

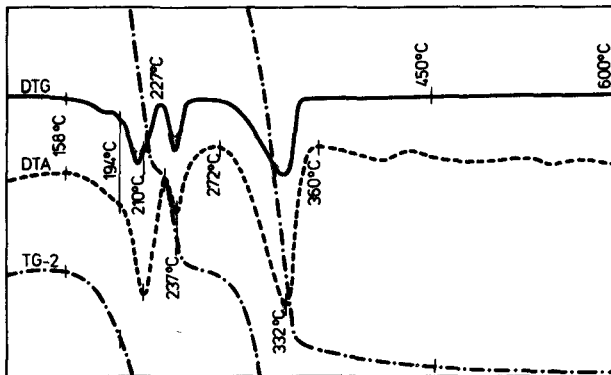


Fig. 6 Typical thermal curve of APM in air stream. Atmosphere: air, heating rate: 3 deg/min, flow velocity 4l/h, sample weight: 0.12 g

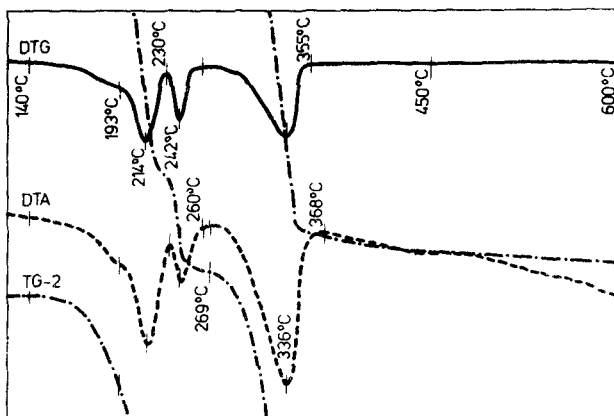


Fig. 7 Typical thermal curve of APM in argon stream

To study the details, several experiments of linearly programmed thermal decomposition in air or argon streams were carried out. Typical thermal curves are presented in Figs 6 and 7. In Tables 2 and 3 weight losses within the temperature ranges corresponding to each stage are assembled. These mean values describing all five decomposition stages will be used in the following discussion.

Discussion

Vacuum conditions

Preliminary outgassing of the APM samples at room temperature causes dehydration, i.e. the nominal $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_2 \cdot 4\text{H}_2\text{O}$ loses all its hydration water. In consequence, the temperature-programmed thermal decomposition concerns anhydrous $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$. This was confirmed by two experimental results. Firstly, in the course of the preliminary outgassing only water molecules evolve from the APM samples. Secondly, the mass-balance of all evolved gas molecules shows that no water other than constitutional water is liberated from $3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3$.

In the course of the thermal decomposition (Fig. 1) five stages were found but more strictly we should additionally distinguish the preliminary outgassing, the dehydration stage (0_V).

Further discussion is based on the mass-spectrometer analysis results. In the gaseous products there are NH_3 , H_2O , N_2 and N_2O molecules. In consequence, two reaction types take place: the "pure" thermal decomposition (1a-c) and redox reactions (2 and 3).

Table 2 Decomposition of APM in air stream

Experiment	Decomposition stage					Total decomposition
	I	II	III	IV	V	
1. * Temperature range, °C	170-210	210-244	244-283	283-400	400-600	170-600
Weight loss, %	2.35	3.89	1.65	7.80	0.49	16.18
2. * Temperature range, °C	160-192	192-227	227-275	275-380	380-600	160-600
Weight loss, %	2.07	4.14	1.82	7.80	0.74	16.57
3. * Temperature range, °C	160-198	198-228	228-272	272-360	360-600	160-600
Weight loss, %	2.65	3.81	1.57	7.78	0.58	16.39
4. ** Temperature range, °C	155-192	192-227	227-257	257-363	363-600	155-600
Weight loss, %	2.33	3.98	1.75	7.66	0.49	16.21
5. ** Temperature range, °C	160-196	196-226	226-272	272-360	360-600	160-600
Weight loss, %	1.88	3.98	1.65	7.70	0.51	15.72
6. ** Temperature range, °C	150-192	192-224	224-252	252-365	365-600	150-600
Weight loss, %	2.25	3.96	1.67	7.78	0.57	16.23
Average weight loss, %	2.23	3.98	1.67	7.75	0.55	16.18

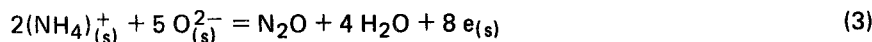
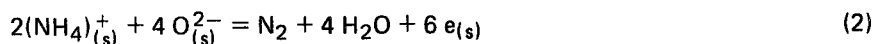
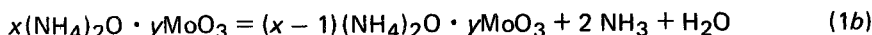
* Heating rate 3 deg/min

** Heating rate 6 deg/min

Table 3 Decomposition of APM in argon stream

Experimental*	Decomposition stage					Total decomposition
	I	II	III	IV	V	
1. Temperature range, °C	130-195	195-226	226-260	260-361	361-600	130-600
Weight loss, %	2.55	4.06	1.68	7.61	0.60	16.50
2. Temperature range, °C	158-194	194-226	226-270	270-363	363-600	158-600
Weight loss, %	2.05	4.22	1.74	7.79	0.60	16.40
3. Temperature range, °C	160-194	194-227	227-272	272-370	370-600	160-600
Weight loss, %	1.60	4.21	1.74	7.71	0.41	15.67
4. Temperature range, °C	140-190	190-226	226-266	266-370	370-600	140-600
Weight loss, %	1.97	4.08	1.68	7.54	0.41	15.58
Average weight loss, %	2.04	4.14	1.70	7.66	0.50	16.04

* Heating rate 3 deg/min



Equation (1a) used in the previous papers [3–7], suggests that the starting material (APM) would decompose directly to MoO_3 . In fact, the thermal decomposition consists of a progressive deammonation of the oxy salt, which, step by step, approaches the oxide composition. The removal of the remainder of the NH_4^+ ions demands a severe calcination, much stronger than that ordinarily used in metal oxide catalyst preparation, at least in the cases of molybdena and vanadia catalysts [1, 2].

Equation (1b) can better serve the description of such a thermal decomposition but its notation is too complicated. If redox reactions take place in a decomposition process, as in our case, a notation of this type cannot be practically applied to calculate their contribution to the total process.

Therefore, we decided to employ the notation used in Eq. (1c). This notation is considerably simpler and, at the same time, detailed enough to describe the total process of APM thermal decomposition and also to calculate each partial reaction contribution.

The extent of the thermal decomposition of APM can be conveniently expressed as the degree of removal of ammonium ions from the samples being decomposed. Necessary data can be obtained by the integration of the p_i vs. t curves, which represent the dependence of the evolution velocity of particular gas molecules. p_i vs. t curves were recorded simultaneously with p_i vs. T curves. As mentioned above, the temperature increased linearly with time and both curves had similar shapes.

In Table 4 the numbers of NH_3 , N_2 and N_2O moles evolved in each particular step of the thermal decomposition of APM are presented. These data relate to the numbers of moles of a hypothetical $(\text{NH}_4)_2\text{O}$ undergoing decomposition. However, considering Eqs (1c–3) it should be remembered that one mole of $(\text{NH}_4)_2\text{O}$ yield two moles of NH_3 and one mole of N_2 and N_2O . For direct comparison, in Table 4 the numbers of half the evolved NH_3 molecules are presented.

From the amounts of $(\text{NH}_4)_2\text{O}$ decomposed, the degree of APM decomposition in each stage can be estimated. Similarly, considering the amounts of NH_3 , N_2 and N_2O evolved, the percentage contributions of reactions (1c–3) in each stage of the thermal decomposition can be calculated.

All results in Table 5 refer to an amount of the starting material APM containing 100 moles of $(\text{NH}_4)_2\text{O}$. In this way these numbers represent the percentage contributions of the given reactions in the total process of thermal decomposition.

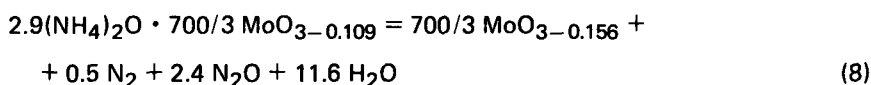
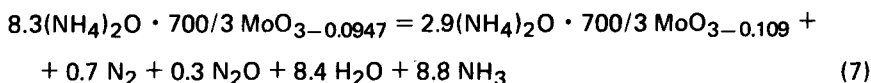
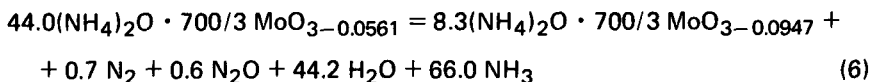
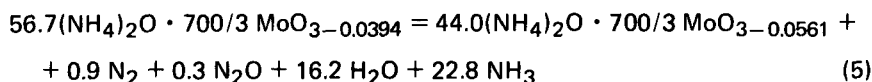
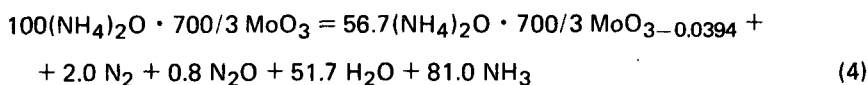
Finally, the course of vacuum thermal decomposition of APM can be described as a sequence of consecutive balance equations:

Table 4

Decomposition stage	Mole amounts of reagents (Torr X min X 10 ⁻³) expressed for the standard weight of APM (15 mg)			
	1/2 NH ₃	N ₂	N ₂ O	(NH ₄) ₂ O
1 _v	6.54	0.33	0.13	7.00
2 _v	1.85	0.15	0.05	2.05
3 _v	5.33	0.35	0.11	5.78
4 _v	0.72	0.11	0.04	0.87
5 _v	0.02	0.10	0.44	0.46

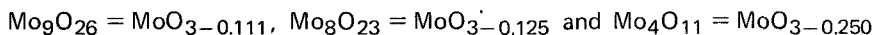
Table 5

Stage	Degree of decomposition %	% participation of particular reaction in each stage			Mole amounts of (NH ₄) ₂ O decomposing in particular way, expressed for amounts of APM corresponding to 100 moles of (NH ₄) ₂ O		
		1/2 NH ₃	N ₂	N ₂ O	1/2 NH ₃	N ₂	N ₂ O
1 _v	43.3	93.4	4.7	1.9	40.5	2.0	0.8
2 _v	12.7	90.2	7.3	2.5	11.4	0.9	0.3
3 _v	35.7	92.2	6.1	1.7	33.0	2.2	0.6
4 _v	5.4	82.8	12.6	4.6	4.4	0.7	0.3
5 _v	2.9	—	16.7	83.3	—	0.5	2.4
total:	100.0				89.3	6.3	4.4



It should be added that the products on the right side of the equations (4)–(8), cannot be interpreted as really existing chemical compounds. The formulas describe the compositions of intermediates of a more complex nature (amorphous mixtures of crystallites which are not well defined). The only exception is $0.243(\text{NH}_4)_2\text{O} \cdot \text{MoO}_3_{-0.039}$, which is oxidized from $(\text{NH}_4)_2\text{O} \cdot 4 \text{MoO}_3$ was postulated as an intermediate by [3–5], and the presence of which in the intermediates was confirmed by X-ray analysis. The other postulated intermediate, $2(\text{NH}_4)_2\text{O} \cdot 5 \text{MoO}_3$, should be excluded in the vacuum decomposition of APM.

The composition of the final product of APM decomposition in vacuum, $\text{MoO}_3_{-0.156}$, corresponds to none of the known lower molybdenum oxides:



Hence, we may conclude that the final product is a mixture of these oxides.

This is in accordance with the studies by Ma on APM decomposition [3, 4]. Ma observed the X-ray diffraction patterns of all three oxides in the decomposition product. However, the experimental conditions used by Ma (about 200 mg of APM, periodic injections of small portions of the gaseous products, no controlled change of pressure in the reaction chamber) did not enable him to describe quantitatively the course of APM vacuum decomposition.

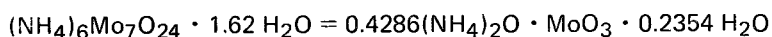
Atmospheric pressure

The results obtained in air and argon streams are similar. In both cases the final products were slightly reduced: $\text{MoO}_3_{-0.07}$ (in air) and $\text{MoO}_3_{-0.05}$ (in argon). Taking into account the accuracy of the chemical analysis ($x = \pm 0.01$ in the formula MoO_3_{-x}), the observed differences between air and argon streams are not significant.

The argon used in the TG and DTA measurements contained about 0.5% of oxygen, i.e. the partial pressure of oxygen was equal to about 15 Torr. Such an oxygen pressure therefore limits the reduction to the same degree as 1 atm of oxygen. On the other hand, the thermal decomposition of APM is connected with the redox reactions, even in oxygen atmosphere although the contribution of these reactions is inconsiderable in comparison with the vacuum decomposition.

The total losses of weight were not sufficient to accept the formula $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$. We should assume partial degradation of the hydrate before the experiments, and the formula $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 1.62 \text{H}_2\text{O}$ was in accordance with the results of thermogravimetric and chemical analyses.

In the thermal analysis curves (Figs 6 and 7) five stages can be distinguished in the thermal decomposition of APM. The starting material,



gradually loses water and ammonia. The compositions of the products after each stage of the decomposition are presented in Table 6.

Table 6 Composition of the products after each decomposition stage under atmospheric pressure

Decomposition stage	Argon stream	Air stream
starting model	0.4286 $(\text{NH}_4)_2 \cdot \text{MoO}_3 \cdot 0.2354 \text{H}_2\text{O}$	0.4286 $(\text{NH}_4)_2 \cdot \text{MoO}_3 \cdot 0.2354 \text{H}_2\text{O}$
I	0.4286 $(\text{NH}_4)_2 \cdot \text{MoO}_3 \cdot 0.038 \text{H}_2\text{O}$	0.4286 $(\text{NH}_4)_2 \cdot \text{MoO}_3 \cdot 0.021 \text{H}_2\text{O}$
II	0.3065 $(\text{NH}_4)_2 \cdot \text{MoO}_3$	0.3055 $(\text{NH}_4)_2 \cdot \text{MoO}_3$
III	0.2509 $(\text{NH}_4)_2 \cdot \text{MoO}_3$	0.2509 $(\text{NH}_4)_2 \cdot \text{MoO}_3$
IV	0.0092 $(\text{NH}_4)_2 \cdot \text{MoO}_3-0.03$	0.0130 $(\text{NH}_4)_2 \cdot \text{MoO}_3-0.05$
V	$\text{MoO}_3-0.05$	$\text{MoO}_3-0.07$

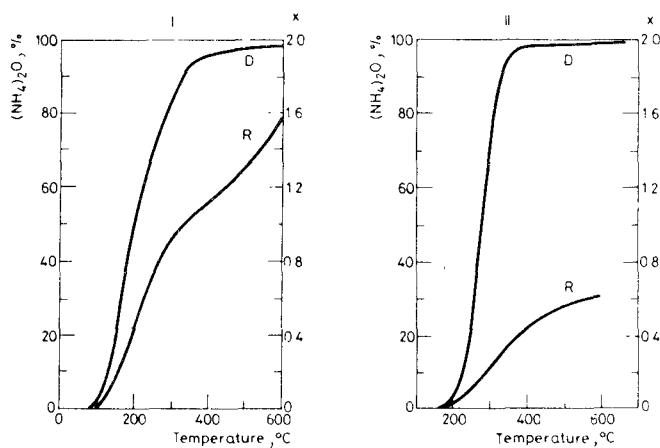


Fig. 8 D – degree of decomposition, expressed as a percentage of the moles of the hypothetical $(\text{NH}_4)_2\text{O}$ undergoing decomposition; R – reduction degree (x) of the MoO_3-x system formed; I – decomposition of APM in vacuo, II – decomposition of APM under atmospheric pressure

The decomposition products in argon and air streams are practically the same. The product after three main stages, $0.2509(\text{NH}_4)_2\text{O} \cdot \text{MoO}_3 = (\text{NH}_4)_2\text{O} \cdot 4 \text{MoO}_3$, was discussed above as an intermediate of APM decomposition. After the fourth stage the product can be treated as a solid solution of NH_4^+ cations in partially reduced MoO_3 . Removal of the remainder of the NH_4^+ ions demands a high-temperature calcination.

The courses of the thermal decomposition of APM under atmospheric pressure and in vacuo are different. For convenient comparison they are presented side by side in Fig. 8. There are curves which represent the removal of ammonium cations (the degree of decomposition) and the mean value of the reduction degree of molybdenum cations in the decomposed material.

The final products of APM thermal decomposition can be reoxidized but the process is not easy. Effective reoxidation was observed at about 600°.

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Zusammenfassung — Es wurde der Verlauf der thermischen Zersetzung von Ammoniumparamolybdat im Vakuum und in Luft- und Argonatmosphäre untersucht. Auf Unterschiede in der Zersetzung unter Vakuum und atmosphärischem Druck wird hingewiesen. Bei der Zersetzung im Vakuum spielen Redox-Reaktionen eine Rolle. Der Verlauf der Zersetzung im Vakuum wurde detailliert durch empfindliche kontinuierliche Analyse der gasförmigen Reaktionsprodukte verfolgt. Als Endprodukt der Zersetzung im Vakuum wird ein Gemisch von niederen Molybdänoxiden erhalten. In Gegenwart von Sauerstoff wird das erhaltene MoO₃ nur geringfügig reduziert, und zwar in der letzten Phase des Abbaus der Ammoniumkationen in den Proben.

Резюме — Изучен процесс термического разложения парамолибдата аммония в вакууме и в атмосфере воздуха и аргона. Установлены различия между разложением в вакууме и атмосферном давлении. Наблюдалось, что при разложении в вакууме, значительный вклад принадлежит реакции окисления-восстановления. На основе результатов непрерывного анализа газообразных продуктов, представлено детальное описание процесса разложения в вакууме. Конечным продуктом разложения в вакууме является смесь низших окислов молибдена. Полученная в присутствии кислорода трехокись молибдена только незначительно восстановлена, а главным в процессе разложения является удаление неподвижных катионов аммония из вещества.