

PHYSICO-CHEMICAL PROPERTIES OF SOLID CATALYSTS:
STUDIES ON THERMAL ANALYSIS OF THE MOLYBDATES
OF MAGNESIUM, MANGANESE AND SILVER

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Thermal characteristics of the molybdates of magnesium ($\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$), manganese ($\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$) and silver (Ag_2MoO_4) have been studied by DTA and TG techniques. The thermal curves of $\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$ show two endothermic changes at 195° and 390° followed by an exothermic change at 420°C . The endothermic changes represent the stepwise dehydration of $\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{MgMoO}_4 \cdot \text{H}_2\text{O}$ and from $\text{MgMoO}_4 \cdot \text{H}_2\text{O}$ to MgMoO_4 . X-ray diffraction and IR studies, however, reveal that magnesium molybdate does not undergo any type of decomposition up to 900° and the exo-peak at 420° is clearly due to crystallization.

$\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ undergoes stepwise dehydration showing a flat and a sharp endothermic peak at $110\text{--}290^\circ$ and at 380° , respectively. From X-ray analysis it has been found that the course of dehydration is accompanied by a change in the crystal structure of the substance. In the DTA curve of Ag_2MoO_4 a small endothermic dent appears at 170° , followed by a base-line drift at $240\text{--}510^\circ$ and a sharp endothermic change at 580° without the appearance of any exothermic character. X-ray analysis of this process indicates that this substance is purely crystalline at 240° , with the composition, Ag_2MoO_4 .

Bhattacharyya and his co-workers have made exhaustive studies on the structural properties of a large number of solid catalysts by using thermal analysis techniques (DTA, TG and DTG) supplemented by X-ray diffraction. The results were published in various journals and the important findings have recently been summarized in two review articles [1, 2].

In the present paper, the thermal characteristics of the molybdates of magnesium, manganese and silver are presented.

Dinwiddie and Husemann [3] found magnesium molybdate to be the best catalyst for hydrocarbon aromatization at $427\text{--}704^\circ$ and Porter et al. [4] reported that magnesium molybdate was quite active for aldol condensation at $100\text{--}400^\circ\text{F}$.

Trifiro [5] found manganese molybdate a selective catalyst for the oxidation of ammonia, and Thompson [6] reported that the compound could be used as a catalyst for anodic or cathodic oxidation of ethylene in a fuel cell.

Stiles [7] used silver molybdate as a catalyst for removal of thiophene from benzene, and Annable and Jacobs [8] found it to be quite active at $450\text{--}650^\circ\text{F}$ for hydrogenation of lubricating oils and waxes.

Studies on the thermal characteristics of the above molybdates using DTA and TG techniques have not been reported so far. Nor has the characterization of the

different phases of the three molybdates treated thermally at different temperatures been studied properly by IR and X-ray diffraction techniques, except for the reports made by Wyckoeff [9] that the crystal structure of silver molybdate resembles those of spinel and magnetite, and by Abrahams and Reddy [10] that paramagnetic α -MnMoO₄, the stable phase of manganese molybdate at S. T. P., is monoclinic.

The object of undertaking this problem was to study the thermal characteristics of these molybdates by DTA and TG techniques and to identify the phase changes if any, via the IR and X-ray diffraction patterns, when the molybdates are subjected to various thermal treatment. An attempt has also been made to correlate, wherever possible, the structural properties of these molybdates with their catalytic activity.

Experimental

Preparation of the molybdates: All the reagents employed were of AnalaR quality.

A. Magnesium molybdate: Equimolar amounts of ammonium molybdate (24.89 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) and magnesium oxide (5.65 g of MgO) were dry mixed, made into a paste with distilled water and dried at 110° for 24 hours [7].

B. Manganese molybdate: 100 ml of manganese sulphate solution (10.6 g/100 ml of distilled water) saturated at room temperature was slowly added (5 ml at a time) with stirring to 100 ml of ammonium molybdate solution (12.4 g/100 ml water) followed by digestion for 45 minutes at 80–90°.

C. Silver molybdate: 100 ml of sodium molybdate dihydrate solution saturated at room temperature (47.0 g/100 ml of water) was added slowly (5 ml at a time) with stirring to about 200 ml of 0.2 M silver nitrate solution (6.8 g/200 ml water), followed by digestion (pH 6.0–7.0) for 30 minutes at 50–60°.

All the substances (except magnesium molybdate) were allowed to settle, filtered in a Buchner funnel, washed repeatedly with hot water until they were free from adsorbed soluble impurities, then dried in an air-oven at 110° for at least 24 hours.

Chemical analysis of the molybdates:

A. Molybdenum: Mo(VI) in solution was analyzed in all cases as lead molybdate, PbMoO₄, by precipitation with lead acetate at pH 3 in acetic acid.

B. Metal ions: Magnesium (Mg²⁺) in solution was determined as Mg₂P₂O₇, and manganese (Mn²⁺) as Mn₂P₂O₇ by precipitation with diammonium hydrogen phosphate and ignition at 800°. Silver (Ag⁺) in solution was analyzed as AgCl by precipitation with HCl (2 N) and drying at 110°.

C. Miscellaneous: Water was determined in all cases by absorption of water in magnesium perchlorate using a Coleman Carbon Hydrogen Analyzer. Ammonia

was estimated by digestion of a known weight of the sample in alkali, with back-titration of the excess standard acid left after the absorption of liberated ammonia.

When silver molybdate was subjected to the usual test for sodium with zinc uranyl acetate, the response was negative.

Differential thermal analysis:

Differential thermal analyses of all the molybdates were carried out in air as well as in a nitrogen atmosphere, using a manually-operated DTA apparatus [11]. The sample holder was a cylindrical nickel block with two holes of 0.86 cm diameter each. α - Al_2O_3 served as reference material. Sample weight: \sim 500 mg.

Thermogravimetry:

Thermogravimetric analyses of all the molybdates were carried out in a Stanton Mass Flow Thermobalance, Model MFH-5, with a programmed heating rate of $6.5^\circ/\text{min}$, in an air atmosphere with sample weights of 100–150 mg.

Infrared studies:

The infrared absorption spectra of samples preheated to the following different transition temperatures for at least two hours in each case were taken in nujol medium with a Perkin Elmer Spectrophotometer. The spectrum was scanned in the region $625\text{--}4000\text{ cm}^{-1}$. The temperatures were as follows:

Magnesium molybdate: $110^\circ, 280^\circ, 410^\circ, 465^\circ, 900^\circ$

Manganese molybdate: $110^\circ, 300^\circ, 400^\circ, 625^\circ$

Silver molybdate: $110^\circ, 240^\circ, 510^\circ$

X-ray diffraction studies:

The X-ray diffractograms of the above samples, except for those silver molybdate, were obtained using a Philips Diffractometer with nickel-filtered CuK_α radiation. The setting of the instrument was: 50 kV/16 ma; gain 8/0.85; beam slit 3° ; detector 0.2; EL = 0.96 V; E and E_u out; range 2000 c.p.s. (linear); time constant 2 sec; scanning speed 20/min; paper $12''/\text{hour}$.

Photographs of all the samples of silver molybdate were taken in a Guinier Camera using CuK_α radiation and an exposure of six hours.

Results and discussion

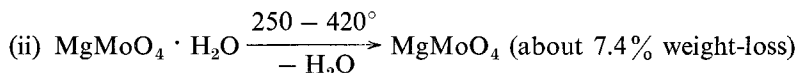
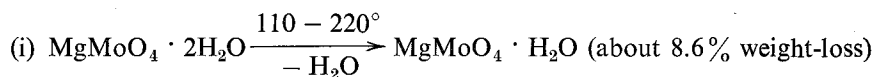
The compositions and the results of thermal analysis are shown in Table 1.

Table 1
Results of thermal analysis

Substance	Composition, %	Formula	Endothermic effect		Exothermic effect		% weight-loss
			Peak temp., °C	Range of temp., °C	Peak temp., °C	Range of temp., °C	
Magnesium molybdate	Mg —10.98	$\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$	195	110–220	420	—	8.6, within 110–220°
	Mo —43.41		390	250–400			
	H ₂ O —16.74						
Manganese molybdate	Mn —22.58	$\text{MnMoO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$		110–290	—	—	7.0, within 110–290°
	Mo —39.51		380	290–400			
	H ₂ O —11.61						
Silver molybdate	Ag —57.412	Ag_2MoO_4	170	240–510	—	—	0.532, within 500–580°
	Mo —25.539		580	535–600			
	H ₂ O —Nil						

Magnesium molybdate:

A. *Thermal analysis*: DTA and TG curves of this compound are shown in Fig. 1. The DTA curve exhibits two sharp endothermic peaks at 195° and 390°, followed by an exothermic peak at 420°. The TG curve represents a gradual weight-loss, starting from 110° and ending at 400°. The total weight-loss was calculated as 16.0%, which corresponds to the removal of two molecules of water from one molecule of $\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$. The TG curve does not clearly indicate the presence of any intermediate stage, although two very clear endothermic changes are noted in the DTA curve. However, from the projection of the peaks of the DTA curve on the TG curve, the stoichiometry of each step was calculated; this indicated that the dehydration probably takes place in two stages:



The exothermic change at 420°, however, is not accompanied by a weight change in the TG curve.

B. *Infrared studies*: The results of IR studies of magnesium molybdate heated at different temperatures, are discussed below. The spectrum of the original compound exhibits significant bands at 860 and 950 cm^{-1} , attributed to the Mo—O

stretching vibration and to the partial absorption of lattice and co-ordinated water, in addition to other bands representing O–H stretching, wagging and rocking, and the H–O–H bending motion of lattice water, etc. The samples heated at 280°, 410°, 465° and 900° display in their IR spectra a number of strong bands at 940, 900, 830 cm^{-1} , etc., which are indicative of the retention of the Mo–O stretching of magnesium molybdate even at 900°. This observation clearly explains that this compound does not undergo any type of decomposition up to 900°.

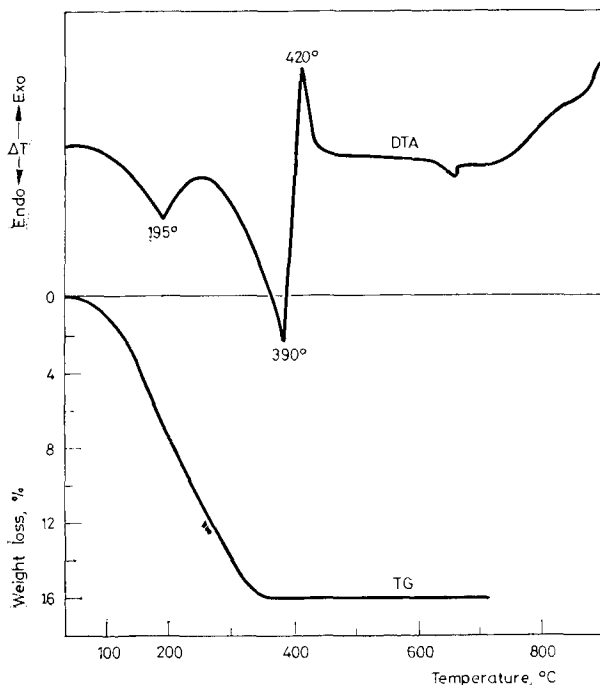


Fig. 1. DTA and TG curves of magnesium molybdate

C. X-ray diffraction studies: The results of X-ray analysis of magnesium molybdate heated at different temperatures are summarized in Table 2. In its X-ray diffraction pattern the original sample exhibits a number of lines with relevance at $d = 4.387, 3.819, 3.463 \text{ \AA}$, etc., revealing the structure of the original compound to be crystalline. X-ray diffraction patterns of the 280°-preheated sample are not similar to those obtained earlier, indicating that the structure of the compound at this stage is less crystalline than the original one. However, the patterns of the 410°-preheated samples are a little improved compared with those obtained in the preceding case, while the diffraction patterns of the sample heated at 465° are quite distinct and the intensities of the lines are markedly enhanced, indicating

that the structure of the compound at this stage is purely crystalline. The exothermic peak at 420° is therefore clearly due to phase changes. This peak may be due to the spinel formed by the combination of MgO and ammonium molybdate according to the reaction $7\text{MgO} + \text{NH}_4\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O} \rightarrow 7\text{MgMoO}_4$. This exo-

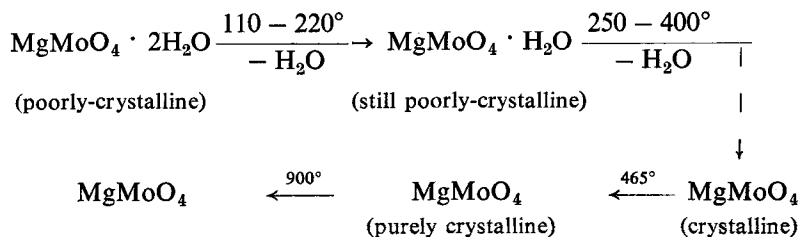
Table 2

Results of X-ray analysis of magnesium molybdate heated at different temperatures

Sample heated at 110°		Sample heated at 280°		Sample heated at 410°				Sample heated at 465°			
d, Å	I/I ₁	d, Å	I/I ₁	d, Å	I/I ₁	d, Å	I/I ₁	d, Å	I/I ₁	d, Å	I/I ₁
8.093	vw	8.241	vw	8.093	vw	2.451	vw	7.949	vw	2.464	mw
7.164	vw	7.532	vw	7.408	vw	2.293	vw	7.408	vw	2.362	mw
6.247	mw	6.627	vw	4.663	mw	2.135	vw	6.726	vw	2.282	mw
4.870	vw	6.162	vw	3.957	mw	2.069	vw	5.992	vw	2.215	mw
4.387	ms	5.405	vw	3.819	m	1.998	vw	4.663	m	2.069	mw
3.819	m	3.922	mw	3.634	m	1.949	vw	3.957	s	2.016	mw
3.575	mw	3.463	m	3.491	m	1.910	mw	3.819	ms	2.010	mw
3.463	ms	1.941	m	3.463	s	1.788	vw	3.663	m	1.918	m
2.962	w	1.888	mw	3.263	ms	1.707	mw	3.575	m	1.823	mw
2.934	w			3.024	vw			3.519	ms	1.750	m
2.387	mw			2.665	vw			3.463	vs	1.700	m
2.078	vw			2.519	vw			3.287	ms	1.639	m
1.973	vw							3.149	mw	1.596	mw
1.865	mw							2.962	mw	1.576	mw
1.756	w							2.779	mw	1.437	mw
								2.665	mw		

(I/I₁ = estimated visual intensity, vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, vvw = very very weak)

thermic peak starts at a temperature of about 410–420°, which should correspond to the temperature at which spinel formation sets in. Since the formation of spinel is detrimental to the catalytic activity, the temperature of maximum catalytic activity should be below this temperature. Thus, the thermal changes in magnesium molybdate can be expressed by the following reaction scheme:



Manganese molybdate:

A. *Thermal analysis:* The DTA and TG curves of manganese molybdate are shown in Fig. 2. The DTA curve exhibits a flat endothermic peak within the temperature range 110–290°, followed by a sharp endothermic change at 380°.

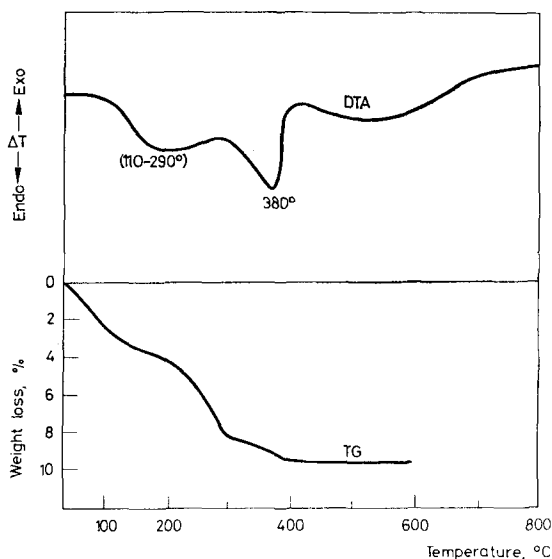
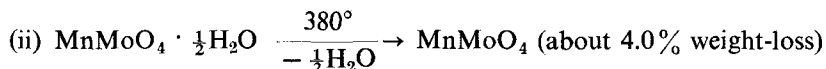


Fig. 2. DTA and TG curves of manganese molybdate

The TG curve shows a continuous weight-loss, starting from 110° and ending at 400°. The total weight-loss was calculated to be 11.0%, which corresponds to the removal of one and a half molecules of water from one molecule of $\text{MnMoO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$. The TG curve indicates the presence of two well-defined plateaus, suggesting the formation of at least two intermediate stages during the dehydration. The endothermic peaks are therefore due to the following reactions:



B. *Infrared studies:* The bands of the original compound at 940, 905, 875, 825 and 755 cm^{-1} are attributed to the Mo–O stretching vibration (as in the case of normal molybdates) and partial absorption of water. The samples heated at 300°,

400° and 625° exhibit almost similar bands as obtained in the original case, except for a small shift in the frequency region of the bands at higher temperatures, which is presumably due to the removal of adsorbed water. It is apparent from IR studies, therefore, that this manganese molybdate does not undergo any substantial change up to 625°.

C. *X-ray diffraction studies*: The results of X-ray analysis of manganese molybdate heated at different transition temperatures are shown in Table 3. The original sample exhibits a diffuse X-ray diffraction pattern of a few faint lines with relatively strong lines at $d = 3.463$ and 3.126 \AA , whereas the patterns of the 300°-preheated sample are still diffuse with the absence of the characteristic line at $d = 3.126 \text{ \AA}$; this indicates that the dehydration causes a change in the crystallinity of the sub-

Table 3

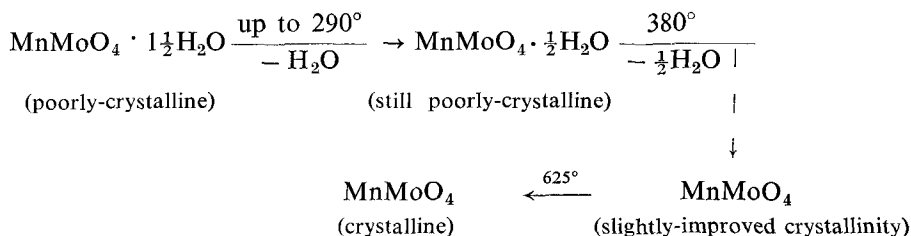
Results of X-ray analysis of manganese molybdate heated at different temperatures

Sample heated at 110°		Sample heated at 300°		Sample heated at 400°		Sample heated at 625°			
d, Å	I/I ₁	d, Å	I/I ₁	d, Å	I/I ₁	d, Å	I/I ₁	d, Å	I/I ₁
6.829	vw	7.949	vvw	6.829	vvw	7.949	vvw	2.375	m
3.547	vvw	5.405	vvw	4.615	vvw	5.032	vvw	2.315	m
3.491	m	4.259	vvw	4.387	vvw	4.342	mw	2.060	mw
3.463	m	4.027	vvw	3.922	vvw	4.299	mw	1.982	m
3.126	vw	3.465	vs	3.491	vs	3.971	mw	1.769	vvw
2.779	vw	2.850	vvw	3.126	vvw	3.650	vw	1.744	vvw
2.259	vw	2.698	vvw	2.905	vvw	3.465	vs	1.725	vvw
1.684		1.973	vvw	2.730	vw	3.334	ms	1.707	vvw
		1.769	vvw	2.665	vvw	3.216	m	1.592	vvw
				2.400	vvw	2.934	ms	1.505	vvw
				2.315	mw	2.779	m	1.491	vvw
				2.016	vvw	2.730	ms	1.455	vvw
				1.990	mw	2.620	mw		
				1.769	mw	2.519	m		

(I/I₁ = estimated visual intensity, vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, vvw = very very weak)

stance. However, the diffraction patterns of the 400°-preheated sample are a little improved, with the presence of a new strong line at $d = 3.491 \text{ \AA}$, revealing the fact that the endothermic peak at 380° is due to dehydration with subsequent crystallization. The X-ray diffraction patterns of the sample heated at 625° appear to be relatively well-defined, with the presence of a number of strong lines, indicating that the structure of manganese molybdate at this stage is reasonably crystalline. The decomposition of this substance into its component oxides, however, is not indicated by X-ray diffraction studies at any stage of thermal treatment.

Thus, the thermal changes in manganese molybdate can be summarized as follows:



Silver molybdate:

A. *Thermal analysis:* DTA and TG curves of silver molybdate are presented in Fig. 3. The DTA curve shows a small endothermic depression at 170°, followed by a base-line drift within the temperature range 240–510°, and a sharp endothermic peak at 580°, without the appearance of any exothermic character.

The TG curve does not register a weight-change within the temperature range 110–480°. A negligible weight-loss, amounting to 0.532%, however, is recorded in the TG curve at 500–580°.

B. *Infrared studies:* The characteristic band of the original compound at 800 cm^{-1} is assigned to the Mo–O stretching vibration. The bands corresponding to water are extremely weak, indicating the presence of water of crystallization in the silver molybdate to be almost insignificant. The 240°-preheated sample exhibits almost the same spectrum, with the retention of the strong band at 775

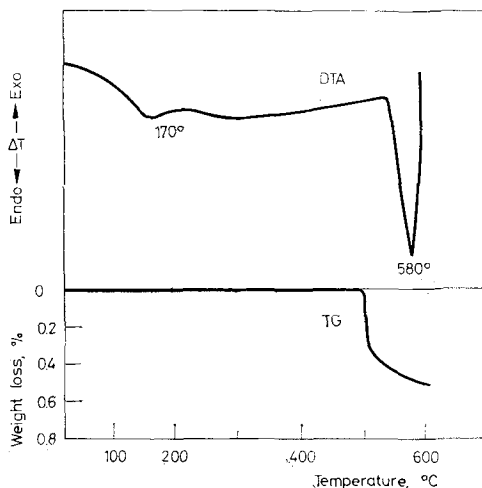


Fig. 3. DTA and TG curves of silver molybdate

cm^{-1} , although the intensity and sharpness of this band are enhanced at this stage. However, the characteristic band observed in the earlier cases is conspicuously absent from the spectrum of the 510° -preheated sample, indicating that a considerable structural change takes place in the range $240-510^\circ$.

C. *X-ray diffraction studies*: The results of X-ray analysis of silver molybdate heated at different temperatures are shown in Table 4. The original compound exhibits a well-defined X-ray diffraction pattern, suggesting the structure of the substance to be crystalline. The characteristic strong lines at $d = 3.287, 2.8, 2.67, 2.32, 1.79, 1.642 \text{ \AA}$, etc. compare reasonably with those reported for standard

Table 4

Results of X-ray analysis of silver molybdate heated at different temperatures

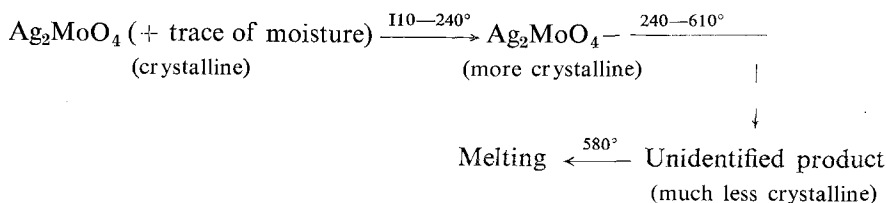
Sample heated at 110°C				Sample heated at 240°C				Sample heated at 510°C	
d, \AA	I/I ₁	d, \AA	I/I ₁	d, \AA	I/I ₁	d, \AA	I/I ₁	d, \AA	I/I ₁
6.431	vw	2.477	vw	6.726	vw	2.339	s	4.027	vw
5.405	vw	2.413	vw	5.755	vw	2.216	vw	3.604	vw
5.094	vw	2.32	s	5.470	vw	2.165	vw	3.519	m
4.565	vw	2.216	w	3.787	vw	2.145	vw	3.412	ms
4.342	vw	2.135	m	3.663	vw	1.973	w	3.000	mw
3.957	vw	2.011	m	3.491	vw	1.939	ms	2.81	vs
3.359	m	1.79	s	3.412	vw	1.858	w	2.69	ms
3.287	s	1.642	m	3.334	s	1.788	s	2.33	ms
3.177	vw	1.586	w	3.126	w	1.64	s	2.124	mw
3.000	vw	1.462	w	3.086	w	1.501	w	1.806	w
2.8	vs	1.409	m	2.905	mw	1.470	w		
2.67	s	1.391	m	2.81	vs	1.418	ms		
2.575	vw	1.338	m	2.69	s	1.398	ms		
		1.314	w	2.533	mw				
		1.30	vw						
		1.243	w						
		1.21	w						
		1.163	w						

(I/I₁ = estimated visual intensity, vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, vvw = very very weak.

patterns of silver molybdate (A. S. T. M. Card 1-1002). The small shift in the d -values in the case of the prepared sample is due to the presence of traces of moisture. X-ray diffraction patterns of the 240° -preheated sample are similar to the earlier ones, except that the lines at $d = 2.80, 1.78$ and 1.64 \AA are found to be predominantly strong in this case. The characteristic d -values compare excellently with those reported for standard patterns of Ag_2MoO_4 ($2.80, 1.78, 1.64$, A. S. T. M. Card 1-1002), and it is quite certain that the substance at 240° is purely Ag_2MoO_4 . However, the structure of the compound appears to be more crystalline at this stage.

The X-ray analysis of the 510°-preheated sample exhibits an entirely different diffraction pattern from that observed in the earlier cases, with a single strong line at $d = 2.81 \text{ \AA}$. The structure of the substance seems to be highly disordered at this stage and the compound is no longer Ag_2MoO_4 . The product obtained at 240–510° could not be identified as the characteristic d -values do not match with the results of any of the decomposition product of silver molybdate reported so far in the A. S. T. M. chart.

Thus, the thermal changes in silver molybdate can be expressed as follows:



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ZUSAMMENFASSUNG — Die thermischen Charakteristika der Molybdate von Magnesium ($\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$), Mangan ($\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$) und Silber (Ag_2MoO_4) wurden unter Anwendung der TG- und DTA-Methoden ermittelt. Die DTA-Kurven von $\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$ zeigen zwei endotherme Veränderungen bei 195° und 390°, welchen eine exotherme bei 420°C folgt. Die endothermen Veränderungen entsprechen der stufenweisen Dehydratisierung von $\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$ zu $\text{MgMoO}_4 \cdot \text{H}_2\text{O}$ und von $\text{MgMoO}_4 \cdot \text{H}_2\text{O}$ zu MgMoO_4 . Röntgendiffraktions- und IR-Untersuchungen zeigen jedoch, daß im Falle von Magnesiummolybdat bis zu 900° keinerlei Veränderung auftritt und daß der Exo-Peak bei 420° eindeutig der Kristallisation zuzuschreiben ist.

Bei $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ tritt eine stufenweise Dehydratisierung auf, welche einen flachen und einen scharfen Peak bei 110–290°, bzw. bei 380° aufweist. Mittels Röntgen-Analyse wurde gefunden, daß der Dehydratisierungsprozeß von einer Veränderung in der Kristallstruktur der Substanz begleitet wird. In der DTA-Kurve von Ag_2MoO_4 erscheint bei 170° ein kleiner endothermer Peak, dem eine Verschiebung der Grundlinie bei 240–510° und eine scharfe endotherme Veränderung bei 580° ohne irgendeinen exothermen Charakter folgt. Die Röntgen-Analyse dieses Prozesses deutet an, daß diese Substanz der Zusammensetzung Ag_2MoO_4 bei 240° kristallin vorliegt.

RÉSUMÉ — On a étudié par TG et ATD les caractéristiques thermiques des molybdates de magnésium ($\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$), de manganèse ($\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$) et d'argent (Ag_2MoO_4). Les courbes ATD de $\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$ montrent deux pics endothermiques à 195 et à 390° suivis d'un pic exothermique à 420°C. Les pics endothermiques correspondent à la déshydratation en deux étapes de $\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$ d'abord en $\text{MgMoO}_4 \cdot \text{H}_2\text{O}$ puis en MgMoO_4 . Des études par diffraction des rayons X et par absorption infrarouge indiquent cependant que le molybdate de magnésium ne subit plus de décomposition jusqu'à 900° et que le pic exothermique à 420° est dû avec certitude à la cristallisation.

Dans le cas de $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$, la déshydratation s'effectue en deux étapes révélées par un pic aplati et un autre aigu à 110—290° et 380° respectivement. L'analyse par rayons X montre que le processus de déshydratation s'accompagne d'un changement de structure cristalline. La courbe ATD de Ag_2MoO_4 montre à 170° un petit pic endothermique suivi par une dérive de la ligne de base entre 240 et 510° puis un pic endothermique net à 580° sans apparition d'effet exothermique. L'analyse aux rayons X indique qu'à 240° la substance de formule Ag_2MoO_4 est bien cristallisée.

Резюме — Изучены с помощью ДТА и ТГ термические характеристики молибдатов магния ($\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$), марганца ($\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$) и серебра ($\text{Ag}_2 \cdot \text{MoO}_4$). Термические кривые $\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$ показывают два эндотермических изменения при 195° и 390° с последующим экзотермическим изменением при 420°. Эти эндотермические изменения характеризуют ступенчатую дегидратацию $\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$ до $\text{MgMoO}_4 \cdot \text{H}_2\text{O}$ и MgMoO_4 . Однако, исследования, проведенные с помощью ИК-спектроскопии и дифракции рентгеновых лучей показывают, что молибдат магния не подвергается какому-либо разложению до температуры 900°, а имеющийся экзопик при 420° целиком обусловлен кристаллизацией. $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ подвергается ступенчатой дегидратации, показывая плоский и резкий эндотермический пик соответственно при 110—290° и 380°C. Из данных рентгеноструктурного анализа найдено, что процесс дегидратации сопровождается изменением кристаллической структуры этого вещества. На кривой ДТА Ag_2MoO_4 при 170° появляется небольшой эндотермический выступ, за которым следует дрейфованной линии при 240—510° и резкое эндотермическое изменение при 580°, при отсутствии какого-либо экзотермического изменения. Рентгеноструктурный анализ этого процесса показывает, что это вещество состава Ag_2MoO_4 кристаллизуется в чистом виде при 240°.