Studies on Molybdenum and Wolfram Oxide

Phosphate Glasses

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Studies on molybdenum and wolfram oxide phosphate glasses have been performed using filter-paper chromatography and also other methods of analysis. The degree of condensation of the phosphate groups has been determined for materials of different origin. The structural significance of the results is discussed.

The first report on the formation of glasses in the system wolfram trioxide-phosphorus pentoxide seems to have been given in 1949 in a communication by Rothermel et al.[1] The existence of glasses containing molybdenum trioxide or wolfram trioxide and phosphorus pentoxide was reported by Frank,[2] Schulz,[3] and independently by Baynton et al.[4] The glasses were black or dark in colour. The latter authors concluded from conductivity measurements that the metal atoms were partly reduced. Schulz [5] observed that the formation of glass is accompanied by a loss of oxygen, and made quantitative measurements of the degree of reduction. She was also able to prepare crystalline phases in the two systems by prolonged heat treatment of the vitreous material and also from the constituent binary oxides. She characterized the crystalline compounds chemically and found them, with one exception, to contain hexavalent molybdenum or wolfram.

Extensive X-ray crystallographic studies performed at this Laboratory have given detailed knowledge of the crystal structures of most of the phases reported by Schulz and also of a few chemically related compounds prepared in the course of this work.[6-10]

The chemical and in particular structural relations between the molydenum and wolfram oxide phosphates in crystalline, vitreous and molten states are by no means obvious. Studies on such questions were considered to be of interest as they might contribute to the knowledge of the mechanism of the transitions between the various states of aggregation. Circumstances favourable in such investigations should be the detailed structural knowledge available for the crystalline phosphates and the fair proportion of heavy metal atoms

which should facilitate X-ray studies of the glasses and melts. The degree of polymerisation of the phosphate groups could be advantageously studied by filter-paper chromatographic techniques. It was realized that differences in the state of oxidation of the metal should cause some difficulty in the work. In the course of the study it was found that additional trouble arose because the preparations were apt to lose metal trioxide and phosphorus pentoxide during heat treatment. The compositions high in phosphorus pentoxide were deliberately excluded from the program as they give hygroscopic samples.

The research has been planned to be conducted along two main lines, by means of various methods of chemical analysis and by physical non-destructive techniques. Among the former are, in addition to conventional methods for determination of chemical composition, in the first place the application of filter-paper chromatography but also thermogravimetry and other techniques. X-Ray diffraction is the principal non-destructive technique to be applied but also measurements of conductivity and other physical properties are in the program.

Apparatus for registering X-ray diffractograms of vitreous material and liquids has recently been built at this Laboratory. Details of this instrument, which will be equipped with a high-temperature attachment intended to make possible the heating of the specimen to melting, will be given elsewhere.[11]

This article will report on the results obtained essentially by means of chemical analytical methods.

EXPERIMENTAL

General remarks. Due to loss of oxygen, phosphorus pentoxide and metal trioxide during the preparation of the glasses, it is not possible to obtain the composition of the glass from the proportions of the starting materials. Therefore, all the glasses prepared were analysed in order to obtain the composition. In addition, the degree of reduction of the metal atom — the occurrence of which is indicated by the dark colour — was separately determined in most of the products.

Preparative work

Molybdenum glasses. $MoO_{3-x} \cdot y\, P_2O_5$. The starting materials were in most cases molybdenum trioxide (*pro analysi*, Mallinckrodt) and phosphoric acid ($d = 1.71$, *p.a.* Merck). A mixture of these chemicals in amounts to give about 5 g of glass, was cautiously heated in a platinum crucible over a Bunsen burner until a water-free product was obtained. The crucible was thereafter heated in a furnace at $900°-1200°C$ for some minutes until a calm ("bubble-free") melt was obtained. This was rather thin for preparations with higher molybdenum contents. After cooling in dry air, the amorphous nature of the coloured cake was tested microscopically and by means of X-rays, and the composition was determined as described below. Analyses showed that the glasses so prepared were homogeneous, as the same composition was obtained for different parts of the sample. Data concerning the molybdenum glasses are given in Table 1.

In place of the molybdenum trioxide mentioned above use was made in some syntheses of "molybdic acid" (Kebo), which was found to contain 86.4 % MoO_3 and 9.4 % NH_3, thus being an ammonium molybdate. When using this compound very viscous melts were obtained which upon cooling gave glasses. In comparison with the glasses prepared as described above the latter were considerably less soluble in hot water and diluted sodium hydroxide solution. It was also found that the metal atoms in these preparations were more reduced (*cf.* Table 1), which should be due to a partial reduction of the hexa-

Table 1. Data for molybdenum glasses: $MoO_{3-x} \cdot y\ P_2O_5$. Glasses prepared from anhydrous molybdenum trioxide (Nos. 1—16) and from ammonium molybdate (Nos. I—III).

Glass No.	Syntheses:		Composition Weight %		Degree of reduction	Composition		Density	Volume per oxygen Å³
	temp. °C	time min					Mole %	ϱ g/cm³	
			MoO_3	P_2O_5	x	$\bar{y}$*	P_2O_5		
1	1000	3	86.0	13.9	0.02(9)	0.16(5)	14.2	3.67	19.9
2	1100	10	81.5	18.7	0.05(7)	0.23(5)	19.0	3.58	19.9
3	1100	10	76.0	23.3	0.09(2)	0.32(2)	24.4	3.47	20.0
4	1120	3	71.4	28.6	0.09(8)	0.41(2)	29.2	3.29	20.4
5	1100	4	65.2	34.6	0.04(2)	0.54(2)	35.1	3.17	20.3
6	1150	7	64.2	35.9	0.07(9)	0.57(1)	36.3	3.24	19.8
7	1150	4	61.7	38.4	0.04(6)	0.63(3)	38.8	3.12	20.3
8	1150	7	55.0	45.2	0.08(4)	0.83(6)	45.5	3.01	20.3
9	1000	22	53.9	45.3	0.07(9)	0.86(2)	46.3	2.95	20.6
10	1250	15	50.7	48.5	0.13(4)	0.98(1)	49.5	3.00	20.0
11	1170	4	50.3	49.9	0.10(5)	1.00(7)	50.2	2.94	20.3
12	1150	20	50.0	50.3	0.15(5)	1.02(4)	50.6	3.01	19.9
13	1250	4	49.5	50.5	0.11(5)	1.03(9)	51.0	3.02	19.8
14	1070	7	45.8	54.3	0.09(9)	1.20(5)	54.6	2.83	20.6
15	900	15	40.1	60.0	0.08(0)	1.51(8)	60.3	2.81	20.1
16	850	20	37.1	62.9	0.07(0)	1.72(0)	63.2	2.73	20.4
I	1150	20	64.2	36.9	0.33(6)	0.59(3)	37.2	3.26	20.1
II	1120	15	56.7	44.2	0.25(8)	0.79(6)	40.3	3.18	19.6
III	1280	7	46.0	55.3	0.27(2)	1.23(8)	55.3	3.11	18.9

* From the percentages of MoO_3 and P_2O_5 it is possible to obtain two values of y respectively (y_{Mo} and y_P). The value given for $\bar{y}$ is equal to $(2\ y_{Mo} + y_P)/3$.

valent molybdenum by the ammonia. Two crystalline phases, a yellow one of the composition $MoOPO_4$ described elsewhere [8] and also a green substance $MoO_{3-x} \cdot P_2O_5$ with x close to 0.5, could also be prepared using this "molybdic acid".

Glasses were also prepared from the crystalline phases $MoOPO_4$, $MoO_{3-x} \cdot P_2O_5$, $MoO_2(PO_3)_2$, $Mo(OH)_3PO_4$, and $(MoO_2)_2P_2O_7$ prepared as described elsewhere. These compounds formed coloured glasses upon heating in a stream of oxygen to temperatures over their melting points followed by rapid cooling. With one exception, *viz.* $MoOPO_4$, the formation of a glass was accompanied by a loss in weight. The results determined are given in Table 2.

Wolfram glasses. $WO_{3-x} \cdot y\ P_2O_5$. Glasses — using wolfram trioxide (*puriss.* Kebo) as starting material for the metal oxide — were prepared, analysed and tested in the same manner as described above for molybdenum glasses. The results obtained are given in Table 3.

Data for the formation of glass from the crystalline compound [9] $W_2O_3(PO_4)_2$ are included in Table 2.

Chemical analysis

A sample of molybdenum glass (about 100 mg) was fused with sodium potassium carbonate in a platinum crucible and the cake was dissolved in boiling water. The amount of *phosphorus* was determined gravimetrically as described previously.[12] The amount of *molybdenum* was determined, using a similarly prepared solution of the glass, by adding sulphuric acid and then running the solution through a bed of amalgamated zinc in a

Table 2. Data for glasses, $MO_{3-x} \cdot y\,P_2O_5$, prepared from crystalline molybdenum or wolfram phosphates.

Ref.	Crystalline compound	Composition calc.weight %		Glass formation		Change of weight %	Glass No.
		MO_3	P_2O_5	temp. °C	time min		
7	$MoOPO_4$	69.57	34.20	950	1.5	+ 2.17	A_1
—	$MoO_{\sim 2.5} \cdot P_2O_5$	51.80 *	51.08	1140	1.5	− 0.40	A_2
26	$MoO_2(PO_3)_2$	50.35	49.65	1240	2	− 1.15	A_3
12	$Mo(OH)_3PO_4$	59.48	29.35	880	1.5	−11.20	A_4
27	$(MoO_2)_2P_2O_7$	66.98	33.02	1010	1.5	− 0.26	A_5
9	$W_2O_3(PO_4)_2$	75.56	23.44	1370	1	− 0.19	B_1

* The percentages of MoO_3 and P_2O_5 in this compound were analysed to be 51.9 and 51.3, respectively.

Table 2 (continued).

Glass No.	Composition obs.weight %		Degree of reduction	Composition		Density	Volume per oxygen
	MO_3	P_2O_5	x	$\bar{y}$	Mole % P_2O_5	ϱ g/cm³	Å³
A_1	70.5	29.5	0.23(3)	0.43(8)	30.5	3.36	20.2
A_2	52.6	47.8	0.22(3)	0.92(3)	48.1	3.01	20.2
A_3	53.6	46.7	0.08(0)	0.88(7)	46.9	2.99	20.3
A_4	67.6	32.5	0.01(0)	0.48(7)	32.8	3.28	19.9
A_5	67.7	32.6	0.00(3)	0.46(6)	32.7	3.10	20.4
B_1	77.1	23.2	0.00(4)	0.48(8)	32.8	4.76	19.3

M = Mo or W. $\bar{y}$ calculated as in Tables 1 and 3.

Jones reductor and collecting it in an excess of acidified iron alum solution, and then titrating with standard 0.02 M potassium permanganate according to Vogel.[13] The amounts of *wolfram* in the wolfram glasses were determined as described elsewhere.[9] The results obtained are given in Tables 1 — 3.

The methods of analysis were tested carefully on samples of known compositions and the errors found to be very low. The analysis of an unknown sample, made in duplicate, normally differed by less than 0.25 %. It may, however, be that the real errors are bigger. Thus, the sum of % MO_3 (M = Mo or W) and % P_2O_5 for glasses of compositions $MO_{3-x} \cdot y\ P_2O_5$ should somewhat exceed 100 % Therefore the accuracy in the figures given for the composition of the samples should be somewhat less than indicated by the agreement of the duplicate analysis.

The *densities* of the preparations were determined from the apparent loss of weight in benzene.

The *degree of reduction* of the metal atoms (molybdenum or wolfram) could not be derived from the analyses for metal and phosphorus but had to be determined separately

Table 3. Data for wolfram glasses: $WO_{3-x} \cdot y\ P_2O_5$.

Glass No.	Syntheses: temp. °C	time min	Composition Weight % WO₃	P₂O₅	Degree of reduction x	Composition $\bar{y}*$	Mole % P₂O₅	Density ϱ g/cm³	Volume per oxygen Å³
101	1200	20	87.1	12.9	0.00(3)	0.24(2)	19.5	5.58	18.8
102	1200	25	84.7	15.0	0.00(4)	0.29(3)	22.7	5.39	18.9
103	1250	8	78.0	22.0	<0.00(5)	0.46(1)	31.6	**	—
104	1250	8	75.3	24.6⎫		0.53(5)	34.9	5.04	17.9
105	1250	9	74.9	25.2⎬	0.00(5)	0.54(9)	35.4	5.30	16.9
106	1200	20	70.0	30.0⎭		0.70(1)	41.2	5.13	16.5
107	1200	20	65.5	34.9	0.00(7)	0.86(6)	44.0	4.87	16.5
108	1200	20	62.6	37.3	0.01(5)	0.97(6)	49.4	4.43	17.6
109	1100	20	57.2	42.9	0.02(4)	1.22(5)	54.4	4.11	18.0
110	1100	25	54.8	45.0	0.05(1)	1.34(6)	57.4	3.92	18.5

* From the percentages of WO_3 and P_2O_5 it is possible to obtain two values of y respectively (y_W and y_P). The value given for y is equal to $(2\ y_W + y_P)/3$.
** The amount of sample was insufficient for the density determination.

due to the observations mentioned above. A weighed glass sample was dissolved in hot 0.5 M sodium hydroxide under an atmosphere of nitrogen purified according to Vogel (Ref.[13] p. 1080). After acidifying with sulphuric acid, 0.002 M potassium permanganate was added in excess. The solution was then titrated to decolourization with 0.0100 M sodium oxalate using a microburette. The value of x of a glass of the composition $MO_{3-x} \cdot y\ P_2O_5$ could then be easily calculated, the amounts of metal being determined as described above. All the solution used in the analysis had been made using water carefully distilled and reboiled.

The obvious difficulties associated with this determination make the data obtained for the degree of reduction given in Table 1—3 only moderately accurate ones. Other methods tried, for instance to oxidize the glasses in an oxygen atmosphere and measuring the increase of weight, were, however, inpracticable, due to the thermal instability of the glasses.

Chromatographic analysis

Filter-paper chromatography methods, which permit separation and estimation of condensed phosphates have been developed by Westman and co-workers,[14-16] and applied to studies on water-soluble alkali phosphate glasses. In this way it has been possible to analyse ring and linear phosphates containing up to four and nine phosphorus atoms, respectively. The technique has also been applied on similar systems by Thilo and co-workers,[17] Van Wazer *et al.*[18] and others.

When using the paper chromatography method on preparations containing condensed phosphates, it has been found that the separation is strongly affected by several factors. Thus, all cations other than alkali metals are disturbing [14] and ought to be removed before the analysis. This, of course, has to be done in such a way that the hydrolysis of the polyphosphates is kept to a minimum. Now, according to Van Wazer,[19] the hydrolysis process is accelerated by increasing temperature and decreasing acidity, and it is also hastened in the presence of colloidal metal oxides as well as of complexing cations.

Moreover, in order to obtain an effective separation and estimation of polyphosphates, the amount of sample, kind of filter-paper, solvent, developer, temperature and further

experimental conditions have to be considered. The experimental variables involved in the method have been extensively elucidated in the papers [14-17] quoted above.

In order to investigate the possibility of applying the method to a phosphate analysis in the preparations considered here, preliminary experiments were started, taking into consideration all the factors mentioned above. A standard solution, containing linear phosphates $P_nO_{3n+1}^{(n+2)-}$ with n up to nine, was prepared according to Thilo and Feldmann [20] and treated in the same manner as the samples to be analysed. The results showed that a qualitative analysis of the polyphosphate anions in samples containing molybdenum seemed to be possible, while big difficulties arose for the samples containing wolfram. Thus, a very pronounced hydrolysis of the phosphates occurred when an addition of wolfram was removed from the standard solution of polyphosphates. Attempts to reduce the hydrolysis by variation of acidity, temperature and concentration failed, neither was it possible to obtain a separation by running chromatograms with wolfram present. Using the last-mentioned method it was only possible to detect ortho- and diphosphate, while higher phosphates were not separated, and moreover, rather big quantities of the phosphates were retained with wolfram in the base line spot of the chromatogram (*cf.* Fig. 1).
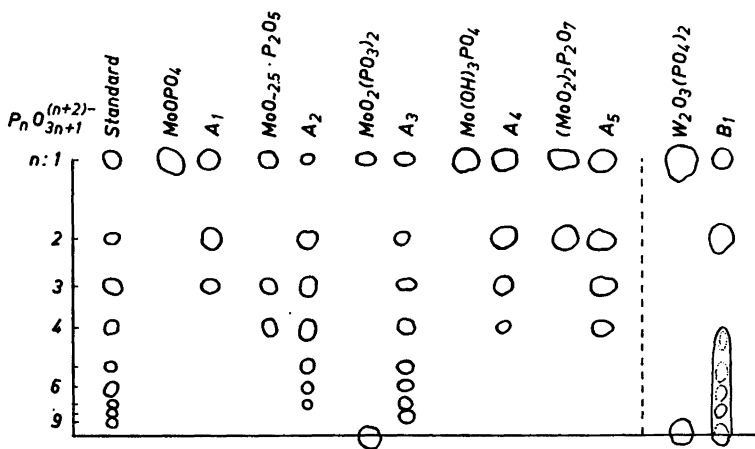

Fig. 1. Schematic drawings showing the chromatograms obtained for the standard solution and the crystalline compounds and corresponding glasses (*cf.* Table 2).

It was also observed from the presence of varying amounts of orthophosphate always observed in the chromatograms that a prolonged treatment with sodium hydroxide increased the extent of hydrolysis of the standard solution. Such a treatment was, however, necessary to dissolve the highly reduced samples prepared using ammonium molybdate.

The method applied in this study was as follows. Two parallel samples, *viz.* the one to be analysed and a standard phosphate solution with an addition of molybdenum or wolfram, were treated with hot 0.5 M sodium hydroxide solution for 10 min (or about 1 h for the more reduced preparations) during which time the samples were completely dissolved. During this process oxygen was bubbled through the solution. The colourless solutions were saturated with hydrogen sulfide and thereby turned orange-red. After cooling, sulphuric acid was added until colourless solutions were formed, while molybdenum was quantitatively precipitated as MoS_3. After filtration and adjustment of pH to 7.5 − 8 by means of sodium hydroxide, the solutions were analysed by paper chromatography at 4°C using Schleicher and Schüll filter paper No. 589 ("green ribbon") and applying the technique as described by Smith[21] and Berg.[22]

The following reagents were used:
$NaH_2PO_4 \cdot 2H_2O$, p.a. (B.D.H.)
$Na_4P_2O_7 \cdot 10H_2O$, p.a. (Merck)
Ammonium molybdate, p.a. (Merck)
$Na_2WO_4 \cdot 2H_2O$, p.a. (Merck)
The solvent used had the composition: 5 g trichloroacetic acid (p.a. Merck),
70 ml isopropyl alcohol (p.a. Mallinckrodt),
30 ml of water, and 0.3 ml of ammonia (25 %).
The visualization of spots was made according to Feigl [23] using a benzidine-sodium acetate developer.
Schematic drawings showing the results obtained are given in Figs. 1—2.

RESULTS AND DISCUSSION

From the results obtained from the syntheses and the analyses, it is found that coloured glasses of the composition $MO_{3-x} \cdot y\ P_2O_5$ (M = Mo or W), with $MO_3 \leq 87$ % by weight, exist in the systems Mo—P—O or W—P—O.

This corresponds to values of y of 0.17 for molybdenum and 0.29 for wolfram (cf. Tables 1 and 3). It is certainly possible to synthetize glasses containing up to 100 mole % P_2O_5, but due to the difficulties in handling the hygroscopic material with more than about 60 mole % P_2O_5, this investigation was accordingly restricted. With reference to the molybdenum glasses the value of x, although certainly being subject to experimental errors, seems to have a minimum for glasses with $y \approx 1$, i.e. about 50 mole % P_2O_5 (cf. Table 1). Now, according to Schulz [5] the solubility in hot water of the molybdenum glasses and also of the wolfram glasses shows a minimum at a composition of about 50 mole % P_2O_5. The reason for this might be the higher degree of reduction of the metal atoms. This assumption seems to be supported by the very low solubility observed for the highly reduced molybdenum glasses made from ammonium molybdate. The very low values of x for the wolfram glasses prevent any discussion of the correlation between the degree of reduction and the solubility curve of these materials.

The densities determined for the glasses have values decreasing with a decreasing metal content. The volume (in $Å^3$) per oxygen atom thus calculated is given in Tables 1—3. The values of about 20 $Å^3$ for the molybdenum glasses are close to those reported [24-25] for some reduced molybdenum oxides such as Mo_4O_{11}. The oxygen atoms in the wolfram glasses are somewhat more closely packed. This observation may be related to structural details such as the degree of distortion of the metal-oxygen arrangements present in the glasses.

By tempering glasses prepared from anhydrous molybdenum trioxide the crystalline compounds $MoO_2(PO_3)_2$ and $(MoO_2)_2P_2O_7$ have been obtained. Using commercial "molybdic acid" (ammonium molybdate) as the starting material the crystalline phases $MoOPO_4$ and $MoO_{3-x} \cdot P_2O_5$ resulted. More detailed information about the preparation of the three first-mentioned compounds have been published [8,26-27] in connection with accounts of the crystal structure determinations. A structure study is now in progress for the green compound $MoO_{3-x} \cdot P_2O_5$ and accounts of data on this matter will be published later on. It may be remarked, that it has not been possible to obtain $MoO_2(PO_3)_2$ by a prolonged heating of $MoO_{3-x} \cdot P_2O_5$ at about 450°C.

This observation seems to be contrary to a statement by Schulz [3] concerning a reduced green compound $MoO_{3-x} \cdot P_2O_5$, with x probably $0.2-0.3$, obtained from molybdenum glasses. By tempering, this material transformed into $MoO_2(PO_3)_2$, some phosphorus pentoxide being lost. The divergence observed in these investigations may be due to the fact that Schulz seems to have used a hydrate of molybdenum trioxide in the preparations, and possibly because a higher temperature was used for tempering.

The chromatogram of the compound $MoO_{3-x} \cdot P_2O_5$ reported here shows the presence to tetra-, tri-, and orthophosphate, while no diphosphate could be detected. The value of x was determined to be within the range $0.4-0.5$. Assuming $x = 0.5$, an idealized formula of the material could be written $(MoO)_2P_4O_{13}$ corresponding to a tetraphosphate. Now, it has been found by Crowther and Westman [16] that tetraphosphate anions hydrolyse to give triphosphate and orthophosphate but no diphosphate. Therefore the result from the chromatographic analysis seems to support the formula proposed for the green compound. This hypothesis, however, requires further examination by the structural study now in progress.

Using wolfram trioxide and phosphoric acid as starting materials it has been possible to prepare only one compound, $W_2O_3(PO_4)_2$, within the W—P—O system.

From the various crystalline compounds mentioned above glasses were prepared by heating in a stream of oxygen above the melting points (cf. Table 2) and subsequent cooling. The formation of the glasses was accompanied by a loss in weight with one exception, viz. $MoOPO_4$, which transformed to a glass with an increase of weight. Analyses of the compositions of the vitreous materials showed that this change of weight was due not exclusively to a difference in oxygen content, but also to a loss of phosphorus pentoxide occurring during the preparation of the glasses. The results of the analyses are given in Table 2. The loss of phosphorus pentoxide — also found to be somewhat dependent on the heating time — will be associated with considerable structural changes. Thus, when the crystalline compounds described here are transformed into the glassy state this process should cause rearrangements of the phosphate group.

The results of the paper chromatography method applied on the crystalline compounds and on the corresponding glasses show (cf. Fig. 1) that the latter always contain three or more phosphate anions of different degree of polymerisation, while the chromatograms of the former show the particular phosphate group found in the crystal structure determination. (The presence of small amounts of orthophosphate caused by hydrolysis and thus invariably present in all chromatograms has been mentioned above).

In a previous article [6] possible atomic arrangements in the glasses obtained from the crystals were discussed assuming no difference in the contents of phosphorus pentoxide to occur at this reaction. The observations reported in this investigations, however, show a decrease of the phosphate contents and also give evidence of a partial condensation of the phosphate groups to occur during the transformation from crystal to glass. As to the arrangement of the metal atoms in the glasses, further experimental data are needed before any definite conclusion can be drawn. X-Ray diffraction studies at room tempera-
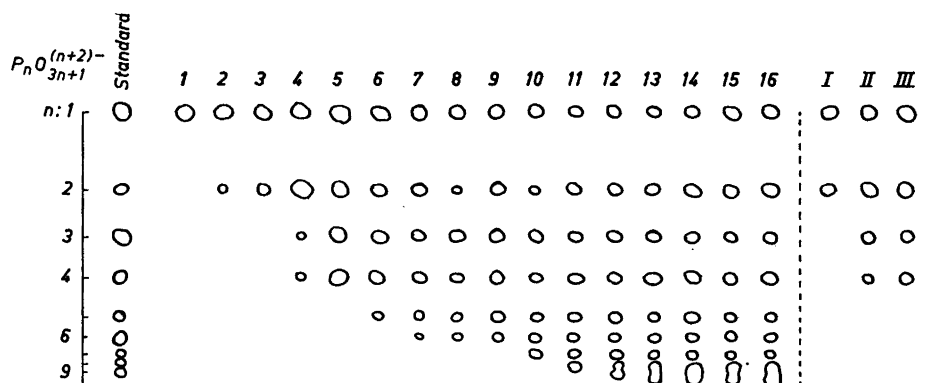
Fig. 2. Schematic drawings showing the chromatograms obtained for a standard solution and the molybdenum glasses listed in Table 1.

ture, as well as at elevated temperatures, should here constitute suitable methods.

The results of the chromatographic analyses of the molybdenum glasses prepared from anhydrous molybdenum trioxide are given in Fig. 2. The degree of maximum condensation of the phosphate tetrahedra observed, *i.e.* the highest value of n in $P_nO_{3n+1}^{(n+2)-}$ increases, roughly linearly with increasing content of phosphorus pentoxide. Thus, in the glasses highest in molybdenum (1—4) only few different phosphate groups — ortho (*cf.* above), di-, tri-, and tetra-phosphates — are observed, which seems to be consistent with the low viscosity observed for the melts during the synthesis. The extensive degree of condensation observed for the glasses low in molybdenum is likewise in accordance with the low fluidity of the corresponding melts.

On the other hand the molybdenum glasses prepared from ammonium molybdate were always formed from very viscous melts. The chromatograms of these sparingly soluble materials just show few spots corresponding to low degrees of condensation of the phosphate groups. Such observations seem to accentuate the need for further investigations of the relations between the structural conditions in the molten and glassy states.

Owing to the experimental difficulties mentioned above it was not possible to perform a corresponding chromatographic analysis of the wolfram phosphate glasses.

A general observation of interest is concerned with the valency state of the metal atoms in the molybdenum and wolfram oxide phosphates. The values obtained for the degree of reduction accompanying the formation of glasses show that the average valency of the metal atoms is always below 6 and actually can assume values down to about 5.5 for molybdenum glasses prepared from the oxide. The degree of reduction of the wolfram glasses corresponds to valencies somewhat lower than 6. Most of the crystalline phases, however, contain hexavalent metal atoms. The only crystalline phosphates containing reduced molybdenum are $MoOPO_4$ and $MoO_{3-x} \cdot P_2O_5$, with x likely to be equal to 0.5.

The valency of molybdenum is five in the former and probably so, also in the latter compound. It thus seems as if molybdenum oxide phosphates do not easily form in a crystalline state with mixed oxidation states of the metal atoms. On the other hand, average fractional values of the metal atom valency seem to be characteristic of the glasses. The existence [24-25] of a large number of crystalline molybdenum and wolfram oxides of average valency states in the region $MO_{2.92}-MO_{2.72}$ does not seem to have a counterpart in the crystalline phosphates. However, the vitreous phases show an average valency state between 5 and 6 and it may be that these observations have some relation to structural conditions, but this requires further studies.

The colours of the various materials should also be relevant in this connection, *viz.* being light green or yellowish for the Mo(V) crystals, colourless for the Mo(VI) compounds and black or very dark blue for the glasses, thus parallelling the colour of the reduced molybdenum and wolfram oxides. Measurements of the electrical conductivity might provide further information about the valency states and interaction of the metal atoms.

The results obtained in this investigation and also in previous crystal structure studies on molybdenum and wolfram phosphates suggest that the glasses contain aggregates formed by PO_4 tetrahedra linked in various degrees of condensation and MO_z polyhedra with $z \leq 6$. The aggregates are of different size and are likely to exist also in the melts from which they cannot, or only with difficulty, arrange themselves into a crystal lattice. This should be due to an irregular shape and a fairly rigid character of the aggregates. This picture of the atomic arrangement, making a melt disposed to supercool and form a glass, which was first suggested by Hägg [28] and is also closely related to the reorganisation theory advanced by Van Wazer,[29-30] is also in concordance with the results obtained by Westman and co-workers [14-16] on alkali phosphates.

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