

Multicomponent Polyanions. 14. A Potentiometric and Spectrophotometric Study of Equilibria in the $\text{H}^+ - \text{MoO}_4^{2-} - \text{HAsO}_4^{2-}$ System in 3.0 M $\text{Na}(\text{ClO}_4)$ Medium Covering the Range $1.5 < -\log[\text{H}^+] < 9$

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Equilibria between H^+ , MoO_4^{2-} and HAsO_4^{2-} have been studied in 3.0 M $\text{Na}(\text{ClO}_4)$ medium at 25 °C by means of potentiometric (glass electrode) and to some extent by spectrophotometric measurements. The $-\log[\text{H}^+]$ range 1.5–9 has been covered. Data have been analysed using the least squares computer program LETAGROPVRID. All data could be explained with two types of species, the colourless $(\text{H}^+)_8(\text{MoO}_4^{2-})_6(\text{HAsO}_4^{2-})_2$, $(\text{H}^+)_{10}(\text{MoO}_4^{2-})_6(\text{HAsO}_4^{2-})_2$, $(\text{H}^+)_{11}(\text{MoO}_4^{2-})_6(\text{HAsO}_4^{2-})_2$, $(\text{H}^+)_{13}(\text{MoO}_4^{2-})_6(\text{HAsO}_4^{2-})_2$ and the “yellow” $(\text{H}^+)_{14}(\text{MoO}_4^{2-})_6(\text{HAsO}_4^{2-})_2$, $(\text{H}^+)_{15}(\text{MoO}_4^{2-})_6(\text{HAsO}_4^{2-})_2$, $(\text{H}^+)_{16}(\text{MoO}_4^{2-})_6(\text{HAsO}_4^{2-})_2$, $(\text{H}^+)_{17}(\text{MoO}_4^{2-})_6(\text{HAsO}_4^{2-})_2$ with the following formation constants: $\log \beta_{8,5,3} = 60.92 \pm 0.04$, $\log \beta_{10,5,3} = 75.25 \pm 0.04$, $\log \beta_{11,5,3} = 80.73 \pm 0.05$, $\log \beta_{12,5,3} = 84.07 \pm 0.07$, $\log \beta_{14,9,1} = 100.11 \pm 0.02$, $\log \beta_{15,9,1} = 103.81 \pm 0.05$, $\log \beta_{16,9,1} = 106.14 \pm 0.05$, $\log \beta_{17,9,1} = 107.48 \pm 0.05$. The errors given are $3\sigma(\log \beta)$.

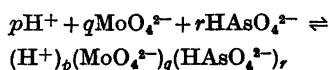
The preliminary spectrophotometric data confirm the results from the emf investigation.

Tentative structures of the proposed complexes are given.

In a current project at this department, aqueous three-component polyanion equilibria are systematically investigated using equilibrium as well as structural methods. An equilibrium analysis in the system $\text{H}^+ - \text{MoO}_4^{2-} - \text{HPO}_4^{2-}$ in the range $1.5 < -\log[\text{H}^+] < 9$ has shown that there are two series of heteropolyanions formed, one colourless with the complexes $\text{Mo}_5\text{P}_2\text{O}_{23}^{6-}$, $\text{HMo}_5\text{P}_2\text{O}_{23}^{5-}$ and $\text{H}_2\text{Mo}_5\text{P}_2\text{O}_{23}^{4-}$ and one, “yellow” with the complexes $\text{H}_3\text{Mo}_5\text{P}_2\text{O}_{23}^{3-}$, $\text{H}_4\text{Mo}_5\text{P}_2\text{O}_{23}^{2-}$, $\text{H}_5\text{Mo}_5\text{P}_2\text{O}_{23}^{1-}$, $\text{H}_6\text{Mo}_5\text{P}_2\text{O}_{23}^{0}$ and $\text{Mo}_{18}\text{P}_2\text{O}_{62}^{6-}$. The former predominates at Mo/P ratios $\lesssim 2.5$ and the latter at

Mo/P ratios $\gtrsim 9$. For a complete survey of the equilibrium results of this system together with structural and other results the reader is referred to Ref. 1.

In order to see whether the same type of complexes are found when phosphate ions are replaced with arsenate ions, we have performed a complete equilibrium analysis covering the range $1.5 < -\log[\text{H}^+] < 9$ and it is the result of this investigation that will be reported and discussed in the present paper. The equilibria that will be studied can be written in the general form.



For brevity a complex formed will in the following often be given the notation (p,q,r) .

Comments on some previous work. Complex formation between molybdate and arsenate ions in acidified solutions has long been known. As early as 1826 Berzelius² reported that arsenic acid with an excess of molybdic acid forms a yellow species. In the decades around 1900 the molybdate-arsenate system was the object of extensive research activity and a large number of crystalline molybdoarsenates were identified. The most frequently found Mo/As ratios in the compounds analysed are 9 and 3 but the ratios 12, 8, 2.5, 2, and 1 have also been proposed. This early, mainly preparative, work is extensively reviewed in Mellor³ and Gmelin.⁴

While the compositions of many solid phases are known, knowledge of the equilibrium conditions in solution is, on the other hand, incomplete, although many different experi-

mental methods have been used. The previously most thorough investigation on the system in aqueous solutions seems to have been made by Contant and other members of the Paris group.⁶⁻¹⁰ They have used spectrophotometric, polarographic, and potentiometric methods and have also prepared and analysed solid phases. They propose that the main complexes in weakly acidified solutions comprise a series of hexamolybdodiarisates $H_n Mo_6 As_2 O_{26}^{(6-n)-}$ ($n=0,1,2$). The formation constant for $Mo_6 As_2 O_{26}^{6-}$ was calculated to be 5×10^{69} and the acidity constants for the protonated species were found to be 5.9 and 2.6 respectively. For molybdenum excess they proposed an $HMo_{17} As_2 O_{34}^{11-}$ species whereas the existence of an $HMo_{11} AsO_{30}^{6-}$ complex is more questionable. In acid solutions ($pH \leq 2$) they proposed $Mo_{18} As_2 O_{32}^{6-}$ and tetrameric trimolybdoarsenate species. In strongly acidified solutions containing excess of arsenate they found indications for complexes with Mo/As ratios of 2/2 and 1/2.

Contant *et al.* have thus found indications for the existence of many molybdoarsenate species and have also given formation constants for some of them. However, it is clear that a more thorough analysis of the system is necessary. In particular, a greater data range and better data treatment must be presented before the complexes of the system can be identified with certainty.

EXPERIMENTAL

The present study has been carried out in close connection with Parts I¹¹ and II¹ in this series.

Chemicals and analyses. Solutions of $NaClO_4$ and $HClO_4$ were prepared and analysed as described by Sjöberg¹² and solutions of $Na_2 MoO_4$ as described in Part I.¹¹ Arsenate stock solutions were prepared by using recrystallized $Na_2 HAsO_4 \cdot 7H_2O$ (Merck *p.a.*) and analysed by gravimetric determination as according to Vogel,¹³ these analyses were reproducible within 0.1 %.

Apparatus. The same emf equipment and arrangement as described earlier^{11,12} were used. However, in the latest part of the titration series an automat edpotentiometric titrator was used.¹⁴ The spectrophotometer used was a Heath model 721 single beam instrument with an automatic sample-reference changer combined with an automated potentiometric titrator. A detailed description of the automatic potentiometric-spectrophotometric titration system will be given in a forthcoming paper by Ginstrup and Lyhamn. A sample cell, of flow-through type, with a path length of 0.100 mm (HELLMA QS) was employed.

Methods. The emf measurements were carried out as a series of potentiometric titrations (glass electrode) in 3.0 M $Na(ClO_4)$ medium.

In every titration the total concentrations of molybdate, B , and arsenate, C , were kept constant and the free hydrogen ion concentration, h , was varied by addition of H^+ . The excess concentration of hydrogen ions, H , was calculated over the zero level MoO_4^{2-} , $HAsO_4^{2-}$, H_2O , and the titrations thus give a series of data sets $H(\log h)_{B,C}$.

The combined emf-spectrophotometric measurements were made so that for each titration point the emf was measured until equilibrium was obtained, and then the transmittance, T , was measured at 32 different wavelengths from 205 to 360 nm, mostly with increments of 5 nm. As reference a 3 M $NaClO_4$ solution was used. The spectrophotometric measurements give data $T(\lambda)_{\log h, B, C}$ or $OD(\lambda)_{\log h, B, C}$ (OD stands for absorbance).

The mathematical analysis of emf data was performed with the least squares program LETAGROPVRID¹⁵ version ETITR¹⁶ and the error squares sum $U = \sum (H_{\text{calc}} - H)^2$ has been minimized. The standard deviations are defined and calculated according to Sillén.^{17,18} The computation was performed on a CD 3300 computer in Umeå.

For some general features of the experimental and computational methods used in the present investigation the reader is referred to Ref. 19.

With regard to the binary equilibria the following assumptions on species and equilibrium constants will be made:

For the $H^+ - MoO_4^{2-}$ equilibria we will make use of the results obtained by Sasaki and Sillén,²⁰ [25 °C, 3.0 M $Na(ClO_4)$]. They report the following species and formation constants (valid for $-\log[H^+] > 2.5$): $HMoO_4^-$ ($\log \beta_{1,1} = 3.89$), H_2MoO_4 ($\log \beta_{2,1} = 7.50$), $Mo_7O_{24}^{6-}$ ($\log \beta_{8,7} = 57.74$), $HMo_7O_{24}^{5-}$ ($\log \beta_{9,7} = 62.14$), $H_2Mo_7O_{24}^{4-}$ ($\log \beta_{10,7} = 65.68$), $H_3Mo_7O_{24}^{3-}$ ($\log \beta_{11,7} = 68.21$). For $-\log[H^+] < 2.5$ a larger complex (34,19) with $\log \beta_{34,19} = 196.3$ and a cation (5,2) with $\log \beta_{5,2} \approx 19$ are proposed. This explanation of the system might not be wholly correct. In a subsequent Letagrop analysis Sillén²¹ found that some additional complexes must be present and the most likely ones seemed to be octamolybdates. We have performed some control titrations on the system (partly reported in Ref. 11) and have found that the residuals obtained when using the above mentioned complexes and formation constants are so small compared to the large effects in the molybdoarsenate system, that they will not disturb our search for three-component complexes, and will at the worst, cause some minor changes in the formation constants obtained.

For the $H^+ - HAsO_4^{2-}$ equilibria no study reporting formation constants in 3.0 M $Na(ClO_4)$ has been published and it was necessary to make a separate determination. The concentration range $5 \leq C \leq 160$ mM was covered and the system was found to be mononuclear.

There were, — however, some deviations at the highest concentrations studied which might indicate an incipient dimerisation. These deviations are, however, negligible as 40 mM is the highest arsenate concentration used in the present molybdate-arsenate investigation. In a Letagrop calculation using data with $C \leq 160$ mM we obtained the following formation constants: $\log \beta_{1,0,1} = 6.272 \pm 0.012$ and $\beta_{2,0,1} = 8.474 \pm 0.018$. The errors given are $3\sigma(\log \beta)$.

DATA, CALCULATIONS AND RESULTS

Emf measurements

Data. The data of the present investigation includes 1487 experimental points divided into 92 different titrations. The data covers the range $1.5 < -\log[H^+] < 9$ and the total concentrations have been varied within the limits $5 \text{ mM} \leq B \leq 160 \text{ mM}$ and $1.5 \text{ mM} \leq C \leq 40 \text{ mM}$. In order to check the reversibility of equilibria both backward (increasing $-\log[H^+]$) and forward (decreasing $-\log[H^+]$) titrations have been carried out and this check has been made for most B, C -combinations. Equilibria are attained rapidly except at $-\log[H^+] \approx 3$ for B/C ratios ≥ 3 . When $C \geq 20$ mM and the B/C ratio is ≥ 3 , a white precipitate, which considerably restricts the available data range, was formed. For instance in a titration with $B = 160$ and $C = 40$ mM (the highest B, C -combination studied) precipitation appeared in the range $4 \lesssim -\log[H^+] \lesssim 7$.

As was the case in our earlier molybdophosphate investigation, it was found, that the present data consists of two main groups, one with data corresponding to colourless solutions and another with data corresponding to yellow solutions. The limit between these two sets of data is rather sharp and easy to detect visually. It was found that colourless solutions were obtained for ratios $B/C \lesssim 3$ whereas for higher ratios yellow solutions were obtained at $-\log[H^+] \lesssim 6$. In order to visualize the emf "effects" arising from the ternary complexes formed, we found it convenient to construct the same type of residual plots $\Delta_0(\log[H^+])_{B,C}$ in the molybdophosphate investigation. $\Delta_0 = H_{\text{calc}} - H$, where H is the total analytical H^+ concentration over the zero level (MoO_4^{2-} , HAsO_4^{2-} , H_2O) and H_{calc} is calculated assuming that only the known

binary $H^+ - \text{MoO}_4^{2-}$ and $H^+ - \text{HAsO}_4^{2-}$ complexes are present. Examples of such residual plots for three representative concentrations are given in Fig. 1. We found for all B, C -combinations studied that there was a pit in the plots at $-\log[H^+] \approx 6$. At B/C ratios > 3 there was also another pit and this acid pit was characteristic for yellow solutions.

For treatment and discussion it was found convenient to divide the data into five different sets and the following division was made:

Data I: Experimental data from $-\log[H^+] \approx 8$ to the bottom of the neutral pit. This data range corresponds to a very narrow region and includes such data that will give information of the first formed ternary complexes (colourless solutions).

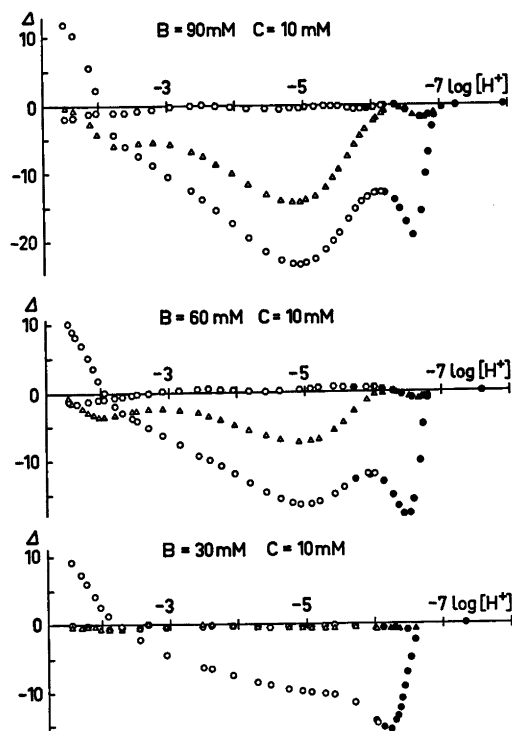


Fig. 1. Residual plots $\Delta = H_{\text{calc}} - H$ in mM for three B, C -combinations. For each combination the quantities Δ_0 , Δ_{00} , and Δ_1 are plotted with the symbols \circ , \triangle and \square , respectively. The indices refer to three different assumptions. 0: Only binary complexes. 00: Binary complexes together with (5,2) and (6,2) species. 1: Binary complexes together with (5,2), (6,2) and (9,1) species. Filled symbols are obtained in forward and unfilled in backward titrations.

Table 1. Result from Letagrop calculations performed on the Data I Region.

(p,q,r)	$U_{\min} \times 10^{-2}$	$\sigma(H)$ mM	$\log \beta_{p,q,r} \pm 3\sigma(\log \beta)$
4,2,1	29.46	4.52	28.97 ± 0.09
5,2,1	78.45	7.38	35.19 ± 0.17
4,3,1	22.74	3.97	30.37 ± 0.09
5,3,1	8.14	2.38	36.85 ± 0.05
6,3,1	42.80	5.45	43.29 ± 0.13
5,4,1	26.62	4.30	38.14 ± 0.10
6,4,1	7.60	2.30	44.70 ± 0.05
7,4,1	22.45	3.95	51.25 ± 0.10
6,5,1	33.78	4.84	45.95 ± 0.13
7,5,1	15.31	3.26	52.58 ± 0.08
7,4,2	4.98	1.86	53.35 ± 0.06
8,4,2	21.12	3.83	59.87 ± 0.11
7,5,2	14.92	3.22	54.64 ± 0.11
8,5,2	1.65	1.07	61.23 ± 0.03
9,5,2	6.24	2.08	67.77 ± 0.07
10,5,2	27.70	4.39	27.70 ± 0.16
8,6,2	16.49	3.38	62.54 ± 0.12
9,6,2	3.44	1.55	69.10 ± 0.05
10,6,2	2.79	1.39	75.68 ± 0.05
11,6,2	15.90	3.32	82.19 ± 0.12
9,7,2	20.98	3.82	70.39 ± 0.15
10,7,2	7.79	2.33	76.97 ± 0.09
11,7,2	3.78	1.62	83.57 ± 0.06
12,7,2	13.88	3.11	90.17 ± 0.12
11,8,2	13.31	3.04	84.82 ± 0.11
12,8,2	7.24	2.24	91.45 ± 0.09
10,6,3	4.77	1.82	77.79 ± 0.08
11,6,3	7.89	2.34	84.41 ± 0.10
12,6,3	18.75	3.61	90.84 ± 0.16
11,7,3	3.84	1.63	85.67 ± 0.08
12,7,3	2.21	1.24	92.25 ± 0.05
13,7,3	13.28	3.04	98.85 ± 0.14
12,8,3	4.53	1.77	93.63 ± 0.08
13,8,3	1.86	1.13	100.15 ± 0.05
14,8,3	8.34	2.41	106.78 ± 0.10
13,9,3	7.17	2.24	101.49 ± 0.09
14,9,3	3.18	1.49	108.04 ± 0.07
15,9,3	6.51	2.13	114.71 ± 0.11
14,10,3	11.88	2.87	109.30 ± 0.13
15,10,3	5.90	2.02	115.93 ± 0.10
14,8,4	4.57	1.78	108.84 ± 0.10
15,8,4	11.65	2.84	115.48 ± 0.16
14,9,4	6.45	2.12	110.13 ± 0.10
15,9,4	3.04	1.45	116.75 ± 0.08
16,9,4	7.13	2.23	123.41 ± 0.13
15,10,4	6.32	2.10	118.13 ± 0.12
16,10,4	3.20	1.49	124.64 ± 0.08
17,10,4	3.93	1.65	131.23 ± 0.09
16,11,4	8.11	2.37	126.02 ± 0.15
17,11,4	4.51	1.77	132.54 ± 0.11

Table 1. Continued.

8,5,2			61.11 ± 0.05
9,5,2	1.03	0.85	67.13 ± 0.16
8,5,2			61.22 ± 0.11
9,6,2	1.65	1.07	67.48 ± 1.03
8,5,2			61.02 ± 0.07
10,6,2	0.74	0.72	75.28 ± 0.11
12,7,3			91.56 ± 0.39
13,8,3	1.61	1.06	100.05 ± 0.18
13,8,3			100.15 ± 0.05
14,9,3	1.67	1.08	—
15,9,4			116.52 ± 0.28
16,10,4	2.93	1.43	124.23 ± 0.38
16,10,4			124.42 ± 0.16
17,10,4	2.55	1.34	130.80 ± 0.24

Data II: All colourless data with $-\log [H^+] > 2.9$. (Data in the whole neutral pit region and acid data with $B/C \leq 3$.)

Data III: Yellow data ($B/C > 3$) with $-\log [H^+] > 2.9$.

Data IV: Both colourless and yellow data with $-\log [H^+] > 2.9$. (This data set consists of a compilation of suitable data for a covariation of equilibrium constants.)

Data V: Yellow data ($B/C > 3$) with the acidity range extended to $-\log [H^+] \approx 1.5$.

Evaluation of compositions of the complexes.

The evaluation was carried out using the same procedure as described earlier.¹⁹ This procedure includes a trial and error search for complexes using the computer program LETAGROPVRID. In the present search we started with a *pqr*-analysis based on the data set denoted Data I. The result of this analysis is given in Table 1 and visualized in Fig. 2. It is seen that the lowest error squares sums are obtained for the complexes (8,5,2) and (13,8,3) with a somewhat lower error squares sum for the (8,5,2) complex. An inspection of the residuals obtained for these best complexes indicated, however, rather large systematic deviations and it was concluded that none of the complexes tested could alone satisfactorily explain the data range in question. We therefore extended our analysis and on the basis of the results obtained we then tested some pairs of complexes. The results of these calculations are collected in Table 1. Apparently, the pair of complexes giving the lowest error squares sum is (8,5,2) + (10,6,2). However, other pairs also give comparable error squares sums. In spite of this we will initially assume

Table 2. Results from Letagrop calculations. In all the calculations the binary complexes and constants given under "EXPERIMENTAL" were used. When no 3σ is given, the constant has not been varied.

Data range	No. of titr./No. of points	$U \times 10^{-3} \sigma(H)$ mM	$\log \beta_{p,q,r} \pm 3\sigma(\log \beta)$									
			(8,5,2)	(10,6,2)	(11,6,2)	(12,6,2)	(14,9,1)	(15,9,1)	(16,9,1)	(17,9,1)		
I	16/145	0.74	61.02 ± 0.07	75.28 ± 0.11	80.73 ± 0.05	84.23 ± 0.06						
II	24/319	0.43	60.92 ± 0.04	75.25 ± 0.04	80.73	84.23	100.07 ± 0.03	103.81 ± 0.06	106.12 ± 0.12			
III	18/319	1.66	60.92	75.25	80.73 ± 0.06	84.07 ± 0.07	100.11 ± 0.02	103.81 ± 0.05	106.11 ± 0.09			
IV ^a	25/360	0.71	60.92	75.25	80.73 ± 0.07	84.05 ± 0.06	100.10 ± 0.02	103.81 ± 0.03	106.11 ± 0.07			
V	19/369	1.73	60.92	75.25	80.68 ± 0.07	84.07	100.11	103.81	106.14 ± 0.05	107.48 ± 0.05		

^a Alter E_0 var.

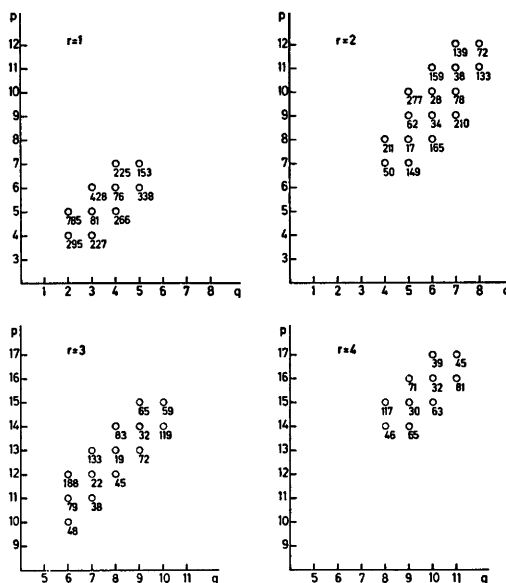


Fig. 2. Results of a pqr -analysis in the Data I region. Lowest error squares sums ($10^{-1} \times U_{\min}$) are plotted as a function of various pq -sets for $r = 1, 2, 3,$ and 4 .

that the complexes (8,5,2)+(10,6,2) are the main complexes in the Data I region and then continue and test these complexes in the Data II region as well. The analysis of the Data II region resulted in a model containing the complexes (8,5,2), (10,6,2), (11,6,2), and (12,6,2). This model gave a good fit to the data and the residuals showed no systematic deviations and seemed to lie within the experimental errors. Formation constants with corresponding standard deviations are given in Table 2. Attempts to explain this data range solely with a (5,2) or a (6,2) series of complexes were not successful.

In the next step of our search for complexes we analysed the data set denoted Data III and assumed that the colourless complexes found were exactly known. Concerning the remaining residuals, the neutral pit had practically disappeared, but a distinct acid pit still remained (exemplified in Fig. 1, the residuals are denoted Δ_{00}). Inspection of the $\Delta_{00}(\log [H^+])_{B,C}$ plots pointed to an Mo/As ratio in the formed complexes of about nine and Letagrop calculations also confirmed that a model

including the complexes (14,9,1), (15,9,1) and (16,9,1) could best explain our experimental data. Formation constants with corresponding standard deviations are given in Table 2. It might be mentioned that yellow solutions in the previous studied molybdophosphate system also could be explained with an analogous (9,1) series.¹

Our analysis of experimental data with $-\log[\text{H}^+] > 2.9$ thus resulted in a model consisting of two series of complexes, one series of colourless and one series of yellow complexes. In order to confirm these two series further and also to obtain a final set of "best" equilibrium constants and standard deviations we have carried out a calculation on the Data IV set and made a covariation of equilibrium constants of both yellow and colourless species (except (8,5,2) and (10,6,2)). The result of this covariation is given in Table 2. As seen, the equilibrium constants of the complexes came out as much the same as in the separate determinations and the standard deviations obtained were also of satisfactory magnitude. The residuals obtained after this calculation are collected in Table 3 and denoted Δ_1 .

In order to test for the influence of an error in E_0 (a constant in the expression for the measured emf) a calculation was carried out where the E_0 -values were setwise adjusted and then the ternary constants (except (8,5,2) and (10,6,2)) were varied. This calculation lowered the error squares sum and the standard deviations, but the values of the formation constants were, as expected, approximately unchanged (See Table 2). The remaining residuals (denoted Δ_2) are given in Table 3.

In order to obtain better confirmation of the (16,9,1) complex and also in order to find additional more acidic complexes, the data range was extended to $-\log[\text{H}^+] = 1.5$ for B/C ratios greater than three. Some titrations with B/C ratios less than three were also performed in this extended $-\log[\text{H}^+]$ -range, but the residuals obtained were so small that we found it meaningless to try to find additional more acidic low B/C ratio species using solely emf data.

Calculations on data with $B/C > 3$ (Data V) strongly confirmed the (16,9,1) complex. However, inspection of the residuals obtained indicated that some additional complex must

be present. We assumed that this complex was (17,9,1) and when (16,9,1) and (17,9,1) were varied together we obtained a good fit to the experimental data. Formation constants with corresponding standard deviations are given in Table 2.

In the molybdophosphate system previously studied we found indications of a dimerization of (17,9,1) to (34,18,2),¹ but when, in the present molybdoarsenate system, the monomer was replaced by the dimer in the calculations, the error squares sum was increased from 173 to 205 and when they were allowed to compete against each other the dimer was not accepted at all. However, when concentrated (16,9,1) and (17,9,1) solutions are stored for some days the colour changes from faint-yellow to bright-yellow and in the Raman spectra of such solutions a new peak with high intensity appears indicating the formation of a new species, probably the dimer.

Spectrophotometric measurements

The spectrophotometric measurements are in progress and the main purpose of the study is to confirm the results obtained from the emf investigation. The final results, including calculated molar absorption coefficients of the proposed species at the different wave lengths, will be published in a forthcoming paper by Lyhamn and Pettersson. Here only some preliminary observations will be stated.

Fig. 3 shows some representative curves in a titration where the total molybdenum concentration was kept constant and where the B/C ratio was continuously changed. In addition the free hydrogen ion concentration was kept almost constant in the course of the titration. Curve 1 represents a pure polymolybdate solution and when the B/C ratio is decreased to about nine by the addition of arsenate (curves 2,3 and 4) the absorbance increases over the whole wavelength range studied due to the formation of molybdoarsenate complexes. The binary $\text{H}^+ - \text{HAsO}_4^{2-}$ system does not absorb in the wavelength range chosen. Further addition of arsenate (curves 5, 6 and 7) causes the curves to intersect at two so-called isosbestic points (at $\lambda \approx 235$ and 274 nm). The B/C ratio in curve 7 is three and

Table 3. Experimental data $H(\log h)_{B,C}$ in the data IV region. For each point the quantities $\log h$, H , Δ_0 , Δ_1 , and Δ_2 are given (in mM). The quantity Δ is the residual $H_{\text{calc}} - \bar{H}$. The indices 0, 1, and 2 refer to three different assumptions.

- 0. Only binary $\text{H}^+ - \text{MoO}_4^{2-}$ and $\text{H}^+ - \text{HAsO}_4^{2-}$ complexes with constants given under "EXPERIMENTAL".
- 1. Binary complexes and constants as in 0 together with proposed ternary complexes with constants given in Table 2.
- 2. The same complexes as in 1, but with constants obtained after an E_0 -variation; see Table 2.

SATS 1. B=0.160 C=0.040					SATS 10. B=0.110 C=0.010				
log h	H	Δ_0	Δ_1	Δ_2	log h	H	Δ_0	Δ_1	Δ_2
-2.916	296.57	-18.22	0.43	-0.63	-2.965	180.69	-9.23	-0.15	0.42
-3.072	294.00	-21.12	0.64	0.20	-3.044	179.02	-10.33	-0.16	0.05
-3.216	291.47	-23.27	0.95	0.52	-3.263	176.57	-12.08	-0.09	0.07
-3.375	288.98	-25.08	0.97	0.55	-3.417	174.96	-13.36	-0.16	0.00
-3.542	286.54	-28.15	0.89	0.47	-3.576	173.41	-14.73	-0.29	-0.12
-3.725	284.13	-30.96	0.68	0.27	-3.739	171.87	-16.18	-0.45	-0.29
-3.926	281.77	-36.16	0.49	0.09	-3.910	170.36	-17.73	-0.62	-0.47
-4.148	279.45	-37.53	0.43	0.02	-4.090	168.87	-19.36	-0.75	-0.62
-4.381	277.16	-40.42	0.57	0.10	-4.283	167.41	-21.08	-0.82	-0.71
					-4.487	165.98	-22.73	-0.78	-0.69
					-4.687	164.56	-24.06	-0.41	-0.32
					-4.884	163.18	-24.92	-0.63	-0.59
					-4.982	161.81	-25.16	-0.25	-0.13
					-5.218	157.66	-24.24	-0.06	0.14
					-5.401	152.87	-22.33	-0.10	0.17
					-5.580	145.98	-19.58	-0.32	-0.01
					-5.748	137.65	-16.75	-0.62	-0.25
					-5.894	129.37	-14.84	-0.79	-0.35
					-6.010	126.51	-13.63	-0.73	-0.18
					-6.157	107.47	-12.86	-0.41	0.36

SATS 2. B=0.080 C=0.040					SATS 6. B=0.060 C=0.020				
log h	H	Δ_0	Δ_1	Δ_2	log h	H	Δ_0	Δ_1	Δ_2
-2.956	173.00	-11.67	-0.53	-0.16	-3.111	117.77	-9.89	-0.63	-0.05
-3.092	171.22	-12.47	-0.44	-0.05	-3.517	114.86	-12.25	-0.74	-0.00
-3.366	167.98	-14.74	-0.33	0.06	-4.026	111.98	-15.07	-0.73	-0.25
-3.678	164.79	-16.88	-0.19	0.13	-4.606	109.30	-17.92	-0.44	-0.13
-3.869	163.24	-18.26	-0.16	0.09	-4.974	106.74	-18.75	-0.05	0.39
-4.199	160.97	-20.67	-0.01	0.19					
-4.430	158.49	-22.20	0.15	0.17					
-4.623	156.03	-23.12	0.40	0.36					
-4.786	156.61	-23.68	0.62	0.52					

SATS 3. B=0.040 C=0.040					SATS 7. B=0.020 C=0.020				
log h	H	Δ_0	Δ_1	Δ_2	log h	H	Δ_0	Δ_1	Δ_2
-2.986	110.00	-6.12	-0.69	-0.41	-2.930	56.00	-2.91	-0.38	-0.25
-3.165	107.85	-7.02	-0.66	-0.40	-3.001	55.45	-3.13	-0.39	-0.27
-3.375	105.78	-7.83	-0.60	-0.36	-3.153	54.37	-3.50	-0.36	-0.24
-3.561	104.28	-8.46	-0.54	-0.33	-3.330	53.34	-3.84	-0.32	-0.21
-3.787	102.83	-9.24	-0.47	-0.32	-3.547	52.35	-4.23	-0.29	-0.19
-3.971	101.88	-9.90	-0.43	-0.31	-3.833	51.39	-4.74	-0.26	-0.19
-4.182	100.94	-10.69	-0.36	-0.29	-4.213	50.47	-5.21	-0.21	-0.19
-4.386	100.03	-11.36	-0.25	-0.20	-4.595	49.58	-5.66	-0.12	-0.13
-4.567	99.13	-11.85	-0.08	-0.08	-4.945	48.72	-6.66	-0.03	-0.06
-4.729	98.27	-12.22	0.03	0.01	-5.225	47.89	-7.02	0.04	-0.00
-4.902	96.95	-12.55	0.20	0.16	-5.180	47.09	-7.38	0.07	0.03
-5.042	95.69	-12.80	0.32	0.27	-5.398	45.46	-8.07	0.07	0.05
-5.189	94.06	-13.14	0.45	0.40	-5.607	44.13	-9.08	0.06	0.06
-5.409	90.96	-14.14	0.56	0.55	-5.867	42.78	-9.98	0.02	0.06
					-6.171	39.76	-12.04	-0.08	0.04
					-6.476	37.63	-13.30	-0.12	0.05
					-6.724	35.18	-15.11	-0.22	0.06
					-6.924	49.16	-13.90	-0.64	-0.19

SATS 4. B=0.160 C=0.020					SATS 8. B=0.160 C=0.010				
log h	H	Δ_0	Δ_1	Δ_2	log h	H	Δ_0	Δ_1	Δ_2
-2.893	272.84	-16.96	-0.82	-0.60	-2.936	273.00	-20.62	0.14	-0.05
-3.133	268.94	-20.10	-0.50	-0.07	-3.157	271.36	-18.56	0.21	-0.01
-3.303	266.40	-22.31	-0.06	0.19	-3.404	274.49	-16.78	0.29	0.06
-3.522	263.41	-25.31	0.01	0.27	-3.618	270.11	-15.89	0.40	0.17
-3.793	260.25	-29.37	0.27	-0.03	-3.836	270.71	-14.44	0.47	0.23
-4.044	257.87	-33.47	-0.71	-0.51	-3.971	269.14	-13.14	0.50	0.25
-4.334	255.54	-38.02	-1.01	-0.86	-3.972	264.99	-12.09	0.38	0.13
-4.560	253.70	-40.99	-0.99	-0.87	-3.981	267.72	-11.12	0.22	-0.03
-4.727	252.11	-42.58	-0.87	-0.75	-7.405	252.51	-10.02	0.06	-0.21
-4.904	249.88	-43.44	-0.67	-0.54					
-5.077	246.60	-43.12	-0.38	-0.21					
-5.287	240.30	-40.72	0.12	0.35					
-5.572	226.77	-34.48	0.15	0.46					

SATS 5. B=0.120 C=0.020					SATS 9. B=0.120 C=0.010				
log h	H	Δ_0	Δ_1	Δ_2	log h	H	Δ_0	Δ_1	Δ_2
-2.955	210.16	-13.59	-0.18	-0.19	-3.020	192.59	-8.90	1.14	1.16
-3.117	204.06	-15.33	0.08	0.00	-3.163	190.79	-10.07	1.13	1.16
-3.293	206.30	-17.20	0.21	0.23	-3.307	189.03	-11.26	1.16	1.14
-3.478	203.99	-19.15	0.24	0.26	-3.454	187.30	-12.47	1.08	1.08
-3.664	202.01	-21.40	0.13	0.10	-3.604	185.60	-13.77	0.91	0.96
					-3.761	183.93	-15.21	0.72	0.76
					-3.924	182.20	-16.74	0.51	0.55
					-4.095	180.67	-18.33	0.36	0.37
					-4.274	179.09	-19.96	0.25	0.27
					-4.464	177.53	-21.55	0.25	0.27
					-4.658	176.01	-22.94	0.37	0.38
					-4.836	174.50	-24.88	0.58	0.59
					-5.088	171.57	-24.29	0.98	0.97
					-5.239	168.74	-23.66	1.13	1.09
					-5.428	163.35	-21.67	1.05	0.94

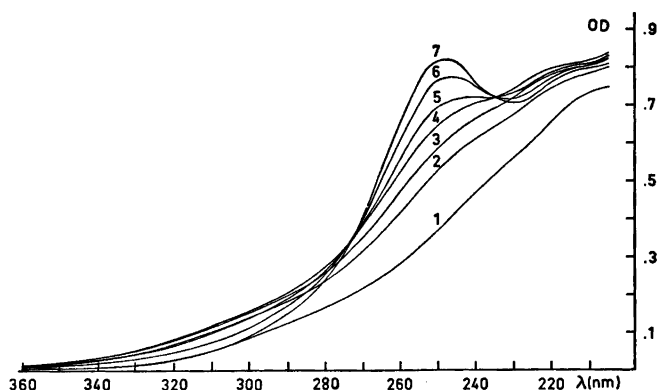


Fig. 3. Absorbance curves $OD(\lambda)_{B,C}$ for solutions with $B = 12.01$ mM at some chosen B/C -ratios. Curve No., B/C , $-\log[H^+]$; 1, ∞ , 2.24; 2, 15.3, 2.30; 3, 11.3, 2.32; 4, 8.9, 2.35; 5, 6.0, 2.36; 6, 4.0, 2.39; 7; 3.0, 2.42.

when further decreasing the B/C ratio to one (the last point in the titration) the curves practically coincide. However, they are omitted in the figure for the sake of clarity.

In the hope of obtaining a more accurate estimate of the B/C ratios in predominant complexes, we have plotted the measured absorbance as a function of the B/C ratio at different wavelengths. Two such plots are illustrated in Fig. 4. In Fig. 4a ($\lambda = 235$ nm, one of the two isosbestic points) there is an evident break in the absorbance at $B/C \approx 9$ and in Fig. 4b ($\lambda = 300$, where the "yellow" complexes are the major contributors to the absorbance) there is an equally evident break at $B/C \approx 3$.

In some other titrations both B and C were kept constant and the H^+ concentration was changed. It was found that for B/C ratios where, according to the emf results, the colourless series of complexes should be predominant, absorbance curves almost identical to 7 in Fig. 3, with absorbance peaks at $\lambda \approx 250$ nm, were obtained and the position of this peak changed very little when the H^+ concentration was changed. In titrations where the "yellow" complexes should be predominant, no characteristic peak was obtained (see curve 4 in Fig. 3). However, the shape of the absorbance curve changes very little with the H^+ concentration, an indication for a series of complexes with the same nuclearity.

The spectral behaviour of titrations hitherto performed thus seems to be consistent with the emf result. Some preliminary Letagrop calculations on spectrophotometric data have also confirmed that all data hitherto collected (five titrations) can be completely explained with the complexes and formation constants proposed from the emf measurements.

CONCLUSION AND DISCUSSION

The present investigation has by means of emf, but also by spectrophotometric methods, greatly clarified the equilibrium conditions in molybdoarsenate solutions and has given compositions and equilibrium constants for the main complexes formed in the system. Two series of complexes exist, one colourless with the species (8,5,2), (10,6,2), (11,6,2), (12,6,2) and one "yellow" with the species (14,9,1), (15,9,1), (16,9,1), (17,9,1). The molybdoarsenate system thus shows great similarities with the molybdophosphate system previously studied.¹

The main "yellow" species in both systems belong to an analogous monomeric (9,1)-series. The emf data in the molybdoarsenate system do not indicate any dimerization to (18,2)-species as is the case in the molybdophosphate system. However, Raman spectra from concentrated (16,9,1) and (17,9,1) solutions showed that a new species was formed and comparison with a solid phase isomorphous to Na_6Mo_{18} -

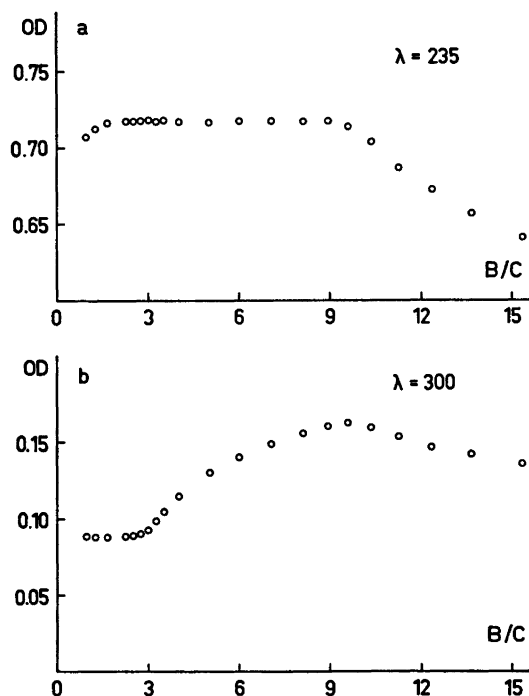


Fig. 4. Absorbance values plotted as a function of B/C -ratio for two different wave lengths.

$P_2O_5(H_2O)_{24}$ indicated that this species probably is a (34,18,2) species.

The colourless complexes in the molybdophosphate data could be completely explained with a series of the three pentamolybdodiphosphates (8,5,2), (9,5,2), (10,5,2), whereas in the present system the data could not be explained solely with one series homonuclear in B and C. In addition to the three hexamolybdodiarsenates (10,6,2), (11,6,2), (12,6,2), an (8,5,2) complex also seems to be formed.

Comparisons of the strength of analogous complexes in the two systems are given in Table 4. Apparently (8,5,2) is stronger in the molybdophosphate system, while the (9,1) complexes and especially (14,9,1) are stronger in the molybdoarsenate system.

In order to visualize the equilibrium conditions in the present system we have calculated the concentrations of different species as a function of $\log[H^+]$. The calculations have been performed by using a version of the computer program SOLGAS,²² valid for equilibria in solution and equipped with a plotting pro-

cedure (Gunnar Eriksson, to be published). The results, for some representative total concentrations, are illustrated as diagrams in Fig. 5, a-e.

In solutions with an excess of arsenate, for instance at $B/C=1$ (Fig. 5a), all the molybdenum is bound in the colourless (5,2) and (6,2) complexes. At $B/C=3$, the same ratio as in the hexamolybdodiarsenate complexes, these are predominating, but there are also small amounts of the (9,1) complexes present (Fig. 5b). At $B/C=6$ (Fig. 5c) both the colourless and the "yellow" series of complexes are present and as the (9,1) series is built up at higher acidities than the colourless series, there is a space in the $\log[H^+]$ range where binary $H^+ - MoO_4^{2-}$ species are formed. At $B/C=9$ (Fig. 5d), the same ratio as in the enneamolybdoarsenate complexes, the (9,1) complexes predominate in the acid range and before they are formed, the first members of the colourless molybdoarsenate series together with binary $H^+ - MoO_4^{2-}$ species are present. Finally, in solutions with molybdenum excess, for instance

Table 4. Formation constants of analogous complexes in the molybdoarsenate and molybdophosphate systems.

(p,q,r)	Proposed formula	$\log \beta_{p,q,r} \pm 3\sigma(\log \beta)$		pK_a	
		X = P	X = As	X = P	X = As
(8,5,2)	$\text{Mo}_5\text{X}_2\text{O}_{32}^{6-}$	61.97 ± 0.02	60.92 ± 0.04	—	—
(14,9,1)	$\text{H}_3\text{Mo}_9\text{XO}_{34}^{6-}$	98.40 ± 0.06	100.11 ± 0.02	—	—
(15,9,1)	$\text{H}_4\text{Mo}_9\text{XO}_{34}^{5-}$	102.81 ± 0.06	103.81 ± 0.05	4.41	3.70
(16,9,1)	$\text{H}_5\text{Mo}_9\text{XO}_{34}^{4-}$	105.84 ± 0.07	106.14 ± 0.05	3.04	2.33
(17,9,1)	$\text{H}_6\text{Mo}_9\text{XO}_{34}^{3-}$	106.85 ± 0.18	107.47 ± 0.06	1.01	1.33

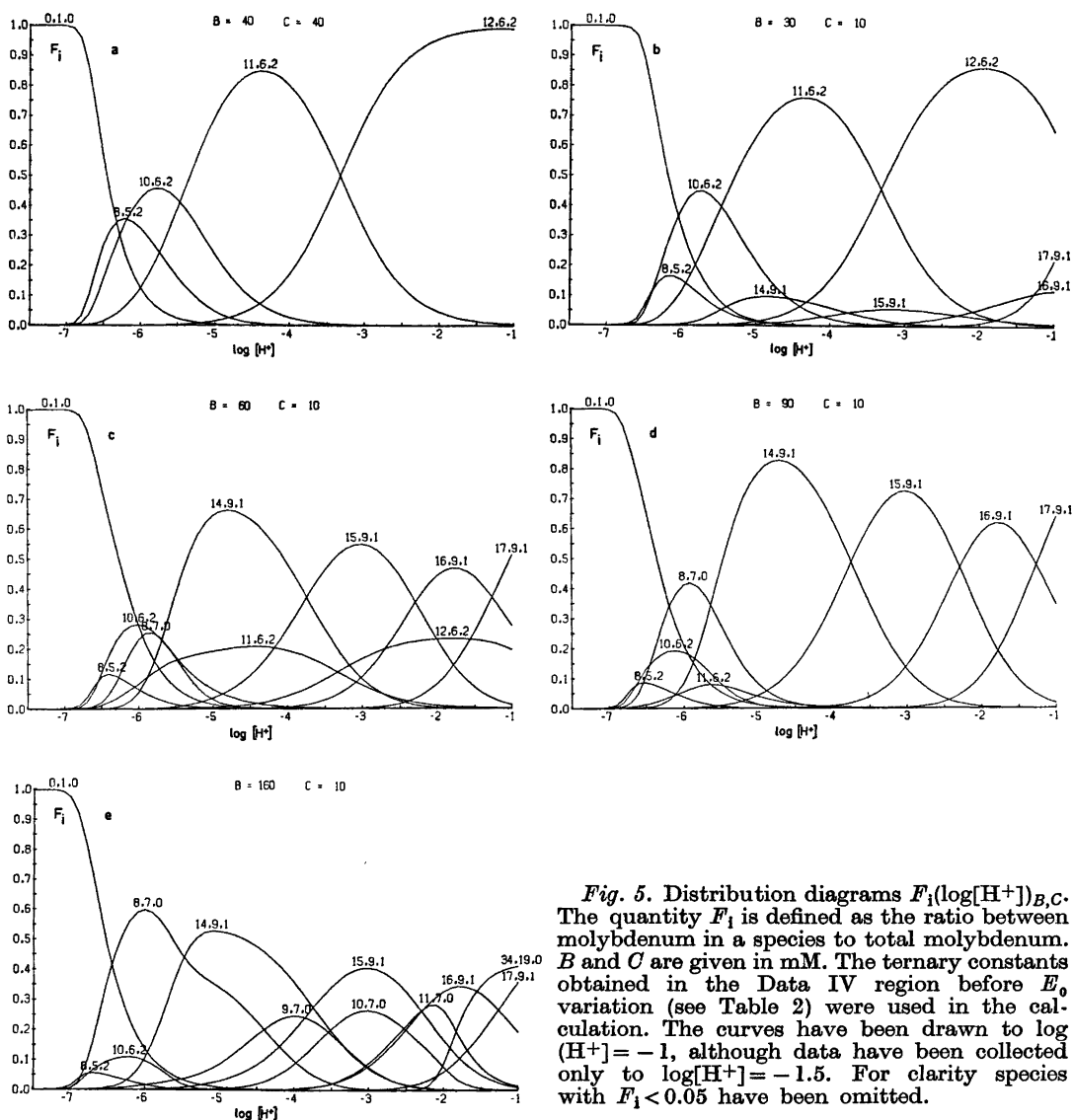


Fig. 5. Distribution diagrams $F_1(\log[\text{H}^+])_{B,C}$. The quantity F_1 is defined as the ratio between molybdenum in a species to total molybdenum. B and C are given in mM. The ternary constants obtained in the Data IV region before E_0 variation (see Table 2) were used in the calculation. The curves have been drawn to $\log(\text{H}^+) = -1$, although data have been collected only to $\log[\text{H}^+] = -1.5$. For clarity species with $F_1 < 0.05$ have been omitted.

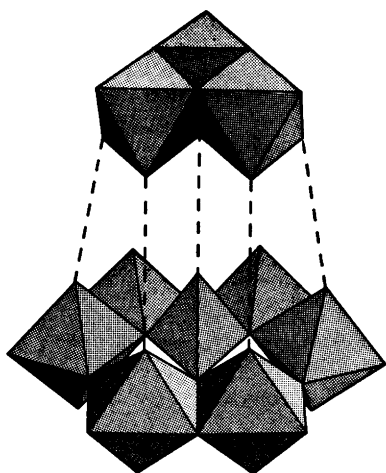


Fig. 6. Proposed structure of the (9,1) unit.

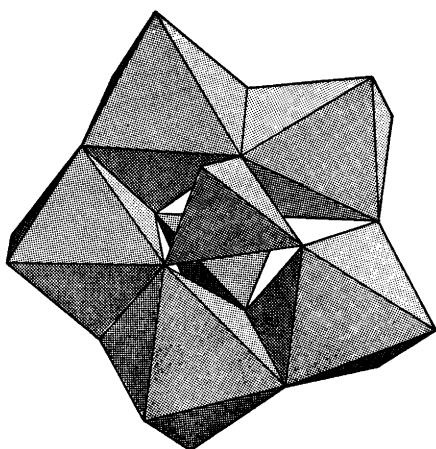


Fig. 7. Proposed structure of the (5,2) unit.

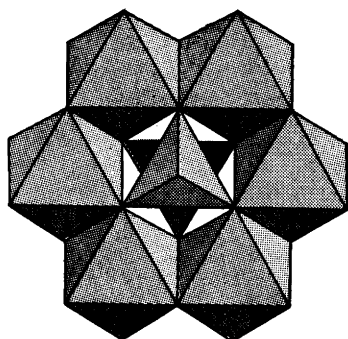


Fig. 8. Proposed structure of the (6,2) unit.

$B/C=16$ (Fig. 5e), the (9,1) complexes are quite predominant and the molybdenum excess (over the 9/1 ratio) is bound in binary $H^+ - MoO_4^{2-}$ complexes.

Solid phases and possible structures. Through slow evaporation of equilibrium solutions we have tried to obtain crystalline phases of the different complexes proposed. From colourless solutions we have not yet succeeded in preparing crystals large enough for single crystal X-ray work. White microcrystalline powders have been obtained from (8,5,2), (10,6,2) and (11,6,2) solutions and X-ray powder films have shown the powders to be of the same phase. However, from very acid (6,2) solutions (faint yellow), we have obtained two other colourless phases which are under X-ray investigation. The compositions of these colourless phases are not yet known. From (16, 9,1) and (17,9,1) solutions crystals isomorphous to the molybdophosphate phases $Na_3H_6Mo_9PO_{34}(H_2O)_{12}$, corresponding to a (17,9,1) complex, and $Na_6Mo_{18}P_2O_{62}(H_2O)_{24}$, corresponding to a (34,18,2) complex, have been obtained and are under X-ray investigation.

Because of the isomorphism it seems reasonable to assume that the series of (9,1) complexes have the same (9,1) structure unit as has been found in the phosphate case,²³ see Fig. 6. With regard to the structures of the colourless complexes, there is no reason to suspect that the (8,5,2) species would have a structure different from the (5,2) unit (see Fig. 7) found in the molybdophosphate phases $Na_6Mo_6P_2O_{23}(H_2O)_{12}$, corresponding to a (8,5,2) complex, and $Na_4H_4Mo_6P_2O_{23}(H_2O)_{10}$, corresponding to a (10,5,2) complex, that have been completely structurally determined.^{24,25} A plausible structure for the (6,2) structure unit in the three hexamolybdodiararsenate species proposed is given in Fig. 8. Support for this tentative structure can be found from the analogy with the three pentamolybdodiphosphates. The first member of the series $(H^+)_{10} - (MoO_4^{2+})_6(HAsO_4^{2-})_2$ should then be given the formula $Mo_6As_2O_{26}^{6-}$ and with the structure proposed the protons in the protonated species (11,6,2) and (12,6,2) can then easily be explained by being attached to the free arsenate oxygens. The reason that the molybdate octahedra in the main colourless molybdoarsenate complexes form a six-ring and not a five-ring

as in the molybdophosphate case may be due to the fact that the arsenate tetrahedron is somewhat larger than the phosphate tetrahedron. (The mean distances P—O and As—O are 1.53 and 1.75 Å, respectively.²⁶)

Acknowledgements. I thank Professor Nils Ingri for much valuable advice, for his great interest and for all the facilities placed at my disposal. Thanks are also due to Lab.ing. Agneta Nordin for valuable help with the experimental part of the potentiometric measurements. The English of the present paper has been corrected by Dr. Michael Sharp. The work forms part of a program financially supported by the Swedish Natural Science Research Council.

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