

Multicomponent Polyanions

I. On Yellow and Colourless Molybdophosphates in 3 M Na(ClO₄).

A Determination of Formation Constants for Three Colourless Pentamolybdodiphosphates in the pH-range 3-9

LAGE PETTERSSON

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Emf data (glass electrode, 25°C, 3 M Na(ClO₄)) for the reaction between H⁺, MoO₄²⁻ and HPO₄²⁻ in the pH-range 3-9 indicated formation of two types of species, yellow and colourless. The colourless products found are (H)₈(MoO₄)₅(HPO₄)₂⁶⁻, (H)₉(MoO₄)₅(HPO₄)₂⁵⁻, and (H)₁₀(MoO₄)₅(HPO₄)₂⁴⁻ with log β_{8,5,2} = 61.97 ± 0.02, log β_{9,5,2} = 67.07 ± 0.08, and log β_{10,5,2} = 70.86 ± 0.09. The errors given are 3σ. The complexes have been found using a Letagrop-search (see Table 2 and Fig. 4). For the yellow-coloured complexes, the data range available is too limited to allow a distinct answer. Efforts to extend the data range are in progress.

Attention to molybdophosphates was first given in 1826 by Berzelius.¹ Since then, the molybdophosphates have been the object of very extensive research activity. In spite of that, the results and conclusions found in the literature give a rather diffuse and incomplete picture of the behaviour and characteristics of these ions. This is especially so for aqueous solutions. In this case, exact knowledge (verified with enough data) about the number and composition of the various species formed seems to be lacking. Also the equilibrium conditions, under which the ions are formed, are poorly defined. The molybdophosphates belong to a group of inorganic compounds, often named heteropolyanions. These ions may be regarded as composed of three components: protons (A), and two anions (B and C). Their formulas may generally be written A_pB_qC_r, where *p*, *q*, and *r* may attain values greater than or equal to unity. The formation equilibria and stability constants may be written:



$$\beta_{pqr} = [A_pB_qC_r][A]^{-p}[B]^{-q}[C]^{-r} \quad (1a)$$

The component with the lowest nuclearity is usually denoted as the heteroion, and is considered being the central group within the complex (C in the

present paper). The B-component is mostly an anion of elements in groups 5A and 6A. Examples most frequently encountered are molybdates, tungstates, vanadates, niobates, and tantalates. The ability to act as the central atom is widely spread, not only amongst the acid forming elements, but also among the metals of the transition series. Borates, silicates, germanates, phosphates, arsenates, tellurates, and periodates are common examples. Further details about the heteropolyanions may be found in reviews in Gmelin,² Mellor,³ and Emeleus-Anderson.⁴

We will now shortly consider some of the difficulties often encountered in studies of aqueous heteropolyanions. We may summarize these difficulties under the following three main points:

(i) *Firstly*, if one considers the complexity of the system, we may note that in most of the aqueous heteropolyanion systems, not only 3-component complexes $A_pB_qC_r$, but also a series of binary complexes, *e.g.* A_pB_q (isopolyanions) and A_nC (weak acids), are present. Thus it is necessary to consider binary equilibria (2), (3) in addition to equilibria (1).



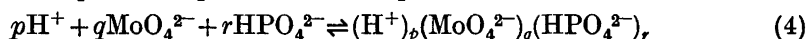
Consequently, before a successful attack can be made upon a heteropolyanion system, the binary systems A-B and A-C must be studied separately, and accurate determinations of the species formed and their formation constants made. In some situations it may also be necessary to consider complex formation between formed complexes and medium ions.

(ii) *Secondly*, considering the experimental methods. Of suitable experimental methods, one may mention: emf, spectrophotometry, conductometry, X-ray diffraction, ultracentrifugation, NMR- and Raman-spectroscopy. Among these methods, emf is without doubt the only one of sufficient accuracy to be useful in studying complicated heteropolyanion systems. It is then necessary to be able to measure at least one equilibrium concentration with highest accuracy. The concentration most readily measurable is that of H^+ . Activity coefficient variations, impurity contents, slow equilibria and liquid junction potentials must be under exact control. The accuracy of the determination would be considerably increased if it were possible to measure also some additional species, *e.g.* some of the molybdate or phosphate ions. Suitable electrodes for such measurements are, however, at present not available. In order to partly compensate for this lack of measurable quantities it is therefore necessary to extend the measurements over as wide concentration ranges as possible (without causing activity coefficient variations). An emf method alone cannot provide a complete explanation of a complicated heteropolyanion system. Complementary types of measurements are mostly necessary.

(iii) *Thirdly*, considering the data treatment. The computational problem is to determine from a great amount of experimental data, the various pqr -triplets present, and the corresponding equilibrium constants β_{pqr} . This computation is usually difficult to carry out using hand calculational methods (see eqns. (7), (8), and (9) on p. 1965). For success it seems necessary to use electronic computer methods.

Points (i), (ii), and (iii) clearly show that an equilibrium analysis of aqueous heteropolyanion systems is generally rather complicated. To obtain detailed information about such a system, very accurate and distinct experimental and calculational methods are necessary. It is no exaggeration to state that 10–15 years ago, such methods were not available or, if so, they were unsatisfactorily developed. That might be a possible reason why we know so little about the equilibria in aqueous heteropolyanion systems. However, during the last years, very accurate experimental and calculational methods have been developed. The emf and the computer methods, developed in Stockholm by Sillén and his group, seem to be especially useful.

The aim of the present study is to apply these methods to determine the composition and formation constants of the various polyanions formed in the system $H^+ - MoO_4^{2-} - HPO_4^{2-}$. Thus the equilibria that will be studied are



EXPERIMENTAL

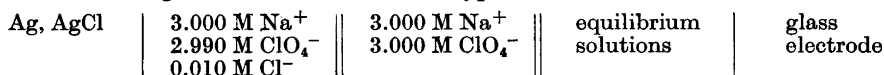
Chemicals and analysis. Stock solutions of sodium perchlorate have been prepared and analysed as described by Sjöberg.⁵ The dilute perchloric acids used were standardized against $KHCO_3$. All solutions were made using boiled distilled water.

For preparing molybdate stock solutions, crystalline sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$ (Mallinckrodt *p.a.*) recrystallized once, was used. The molybdenum content of the stocks was determined gravimetrically as $PbMoO_4$ according to Vogel.⁶ This analysis agreed within 0.1%. In order to check this method, some Mo-analyses were made by evaporating the water from a known amount of stock solution, drying the residue at 110°C and then weighing as anhydrous Na_2MoO_4 . The results from these two Mo-determinations agreed within 0.2%.

All solutions containing molybdate ions were carefully protected from contact with glass. This is necessary in order to prevent dissolution of silicate ions from the glass which contaminate the molybdate solution by forming, *e.g.*, dodecamolybdosilicate ions. Therefore, the insides of the bottles and vessels used for storing molybdate solutions were always coated with a paraffin layer. Two different qualities of paraffin were used. One of them caused "errors" in our titrations, indicating some sort of complex formation between a compound in the paraffin and the molybdate ions. The effect of this complex formation on our results will be discussed later in this paper.

Phosphate stock solutions were prepared either by using recrystallized $NaH_2PO_4 \cdot 2H_2O$ (analytical reagents of BDH quality) or $Na_2HPO_4 \cdot 12H_2O$ (Merck *p.a.*). The stock solutions were analysed for phosphate and excess H^+ (over the chosen zero level HPO_4^{2-}), using electrometrical titration methods in combination with a graphical Gran extrapolation technique. The determinations of phosphorus were checked by gravimetric determinations as magnesium ammonium phosphate according to Vogel.⁷

Apparatus. The emf measurements were carried out, using the same electrometrical equipment and arrangement described by Sjöberg.⁵ The free H^+ -concentration has been measured with a glass electrode (Beckman, type 40498) and the cell used was



The thermostating and all additional equipment are as described in Ref. 5.

The free hydrogen ion concentration, h , was calculated from the measured emf, E , using the equation

$$E = E_0 + 59.157 \log h + E_j \quad (5)$$

where E_0 is a constant determined separately in a solution with known h . For the liquid junction potential, E_j , we have used $E_j = -16.3 h$ (expressed in mV M^{-1}).

METHOD

The emf measurements. The present determination has been carried out experimentally as a series of emf titrations. In each of these titrations, the total analytical molybdenum and phosphorus concentrations, B and C , have been kept constant, and the hydrogen ion concentration has been varied by addition of H^+ (or OH^-).

The free hydrogen ion concentration has been measured electrometrically with a glass electrode (with an accuracy of ± 0.2 mV) as described in Experimental. To keep the activity factors as constant as possible during the measurements, a "constant" salt medium background consisting of 3 M $Na(ClO_4)$ has been used.

In order to check the reversibility of equilibria both backward (increasing pH) and forward (decreasing pH), titrations have been carried out, and this check has been made for each B, C -combination. From the free hydrogen ion concentration, h , calculated by using eqn. (5), and from H , the excess concentration of hydrogen ions over the zero level MoO_4^{2-} , HPO_4^{2-} and H_2O , one can calculate A , the total concentration of bound H^+ , by using the following relation:

$$A = H - h \quad (6)$$

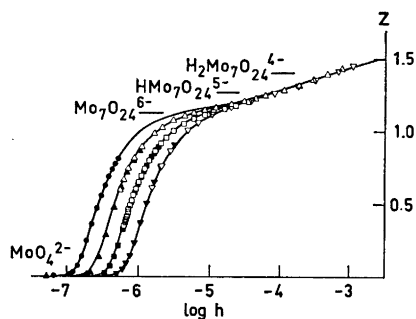
The titrations thus give a series of data sets $A(\log h)_{B,C}$ or $H(\log h)_{B,C}$. The total concentrations have been varied within the following limits: $5 \text{ mM} < B < 160 \text{ mM}$, $5 \text{ mM} < C < 80 \text{ mM}$, and $0 < H < (1.5B + 1.1C)$. This means that for the most extreme concentration cases, about 16 % of the perchlorate ions have been replaced by phosphate and molybdate ions. Biedermann and Sillén⁸ have shown that up to around 16 % of Na^+ or ClO_4^- in a 3 M $NaClO_4$ -medium may be replaced with 1- or 2-charged ions without producing any detectible changes in activity coefficients. In the present case, most of the anions formed are highly charged, and it is probable that for the highest B and C concentrations one may obtain effects due to activity coefficient variations. However, in the first instance, we will assume that we have no activity coefficient variations, and all effects will be explained by using the law of mass action. The range of $pH = -\log h$ has been kept within the limits $3 < pH < 9$. This range has a lower limit determined by experimental difficulties due to precipitation of acid polymolybdates and also partly by the lack of exact knowledge of the binary molybdate equilibria in more acid solutions. The upper limit is given by the fact that for $pH > 8$, no ternary complexes seem to be formed.

The binary equilibria – assumptions and comments. In order to obtain composition and concentration of the various ternary species as accurately as possible, the binary complexes must first be determined in separate experiments. However, in the present work, no separate study of the system $H^+ - MoO_4^{2-}$ was made. Accurate data for this system has already been presented by Sasaki and Sillén⁹ (25°C and 3 M $Na(ClO_4)$). They report the following species and formation constants:

$HMoO_4^-$ ($\log \beta_{1,1} = 3.89$); H_2MoO_4 ($\log \beta_{2,1} = 7.50$); $Mo_7O_{24}^{6-}$ ($\log \beta_{8,7} = 57.74$); $HMo_7O_{24}^{5-}$ ($\log \beta_{9,7} = 62.14$); $H_2Mo_7O_{24}^{4-}$ ($\log \beta_{10,7} = 65.68$); $H_3Mo_7O_{24}^{3-}$ ($\log \beta_{11,7} = 68.21$).

Curves $Z(\log h)_B$ calculated using their proposals are given in Fig. 1. The points given are those obtained in some control titrations, and we see that our experimental points fit the calculated curves satisfactorily. However,

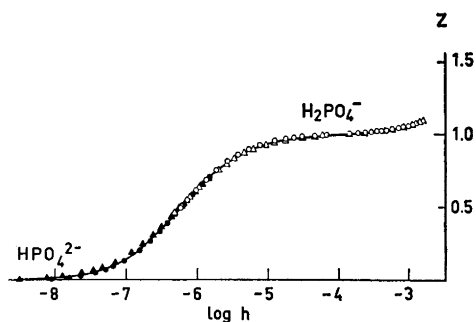
Fig. 1. Curves $Z(\log h)_B$ for the binary system $H^+ - MoO_4^{2-}$. The full curves have been calculated using the complexes and formation constants proposed by Sasaki and Sillén.⁹ The points are experimentally obtained from some control titrations. The symbols stand for the following total molybdenum concentrations B (in mM): ∇ 20; \square 40; \triangle 80; \circ 160. Filled symbols are obtained in forward titrations (decreasing pH), and unfilled in reverse titrations.



a more careful analysis shows small systematic deviations in H , which increase when the molybdenum concentration increases. Initially, it was difficult to decide whether this effect depended on the formation of additional polymolybdate complexes or on some impurity. As the investigation proceeded, we found that the deviations were probably caused by an impurity in the paraffin used. The effects can be found in most of our titrations and are more pronounced when a molybdate excess is used. However, to a good approximation the impurity effects can be neglected compared with the effects due to formation of the molybdophosphates.

For the "mononuclear" phosphate equilibria we have made a separate determination. We found that different phosphate concentrations gave small systematic changes in the equilibrium constants. However, the difference could be neglected in the pH-range studied. In a Letagrop calculation, using

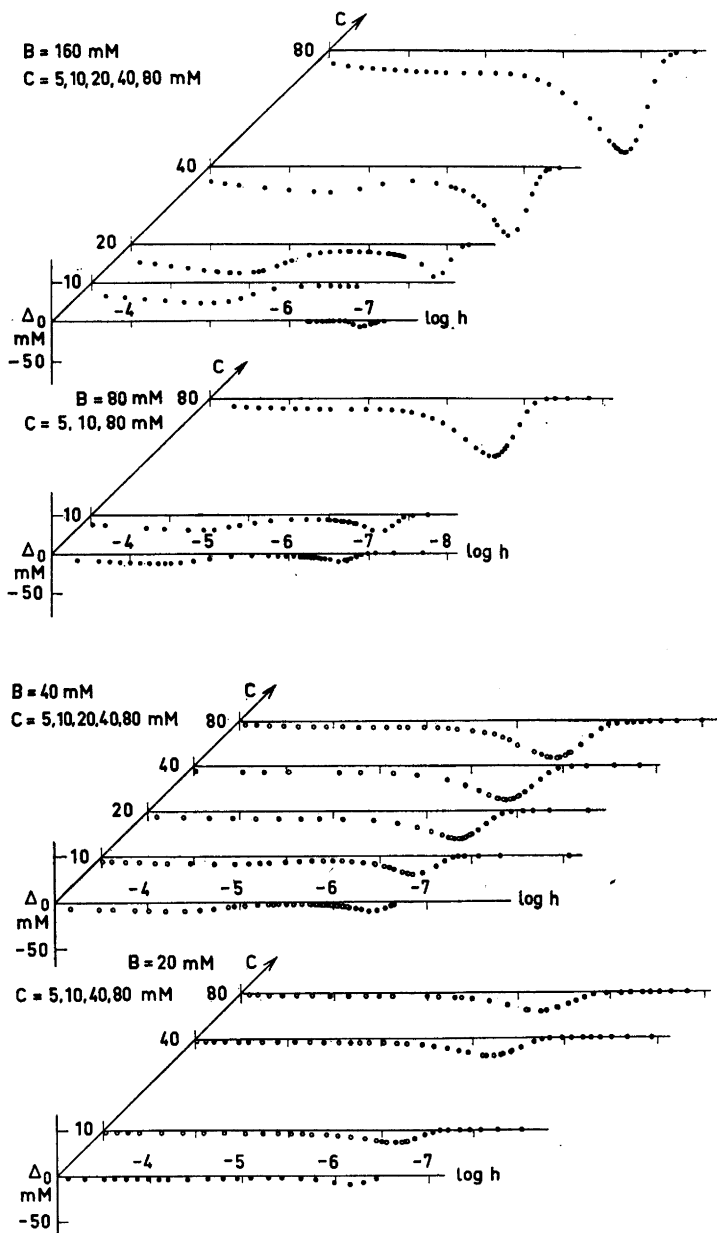
Fig. 2. Curves $Z(\log h)_C$ for the binary system $H^+ - HPO_4^{2-}$. The full curve has been calculated, using the complexes and formation constants given in the text. The symbols stand for the following total phosphorus concentrations C (in mM): \circ 10; \triangle 80. Filled symbols are obtained in forward titrations (decreasing pH), and unfilled in reverse titrations.



data with $C \leq 80$ mM, we obtained the following "best" $\log \beta_n \pm 3\sigma$: $\log \beta_2 = 8.067 \pm 0.019$; $\log \beta_1 = 6.240 \pm 0.008$; and $\log \beta_{-1} = -10.72 \pm 0.03$.

Calculated curve and experimental points ($C = 10$ and 80 mM) are shown in Fig. 2.

Data treatment (pqr-analysis). The equilibria that must be taken into account have been discussed earlier in this paper and are defined by eqns. (1), (2), and (3). Applying the law of mass action to these equations, the conditions for the concentrations give:



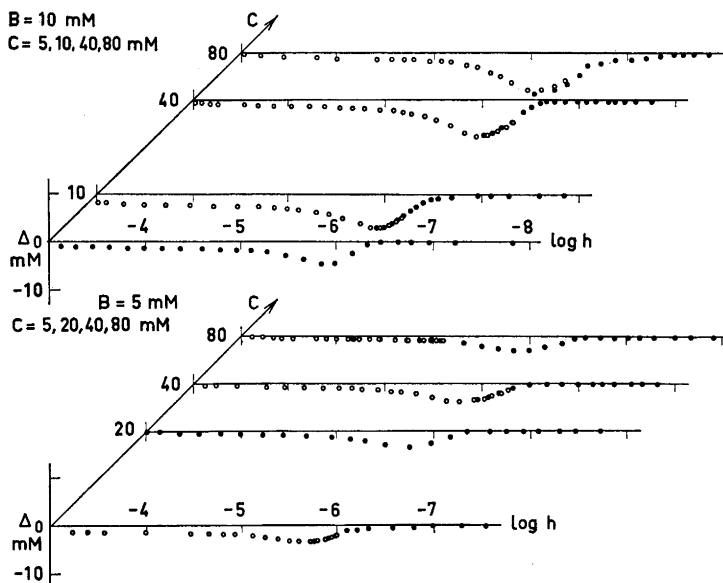


Fig. 3. Residual diagrams $\Delta_0(\log h)_{B,C}$. The residuals $\Delta_0 = 1000(H_{\text{calc}} - H)$ have been calculated assuming that only binary phosphates and molybdates are formed. The constants used are those given in Table I. Filled symbols are obtained in forward titrations (decreasing pH), and unfilled in reverse titrations.

$$B = b + B_1 + \sum_{p=1}^p \sum_{q=1}^q \sum_{r=1}^r q \beta_{pqr} h^p b^q c^r \quad (7)$$

$$C = c + C_1 + \sum_{p=1}^p \sum_{q=1}^q \sum_{r=1}^r r \beta_{pqr} h^p b^q c^r \quad (8)$$

$$H = h + B_1 Z_1 + C_1 Z_2 + \sum_{p=1}^p \sum_{q=1}^q \sum_{r=1}^r p \beta_{pqr} h^p b^q c^r \quad (9)$$

where $b = [\text{MoO}_4^{2-}]$, $c = [\text{HPO}_4^{2-}]$, $h = [\text{H}^+]$, $\beta_{pqr} = [\text{A}_p \text{B}_q \text{C}_r] h^{-p} b^{-q} c^{-r}$, and B_1 , C_1 , $B_1 Z_1$ and $C_1 Z_2$ are the "known" quantities for the binary equilibria:

$$\begin{aligned} B_1 = & [\text{AB}] + [\text{A}_2\text{B}] + 7[\text{A}_8\text{B}_7] + 7[\text{A}_9\text{B}_7] + 7[\text{A}_{10}\text{B}_7] + \\ & 7[\text{A}_{11}\text{B}_7] = \beta_{1,1} h b + \beta_{2,1} h^2 b + 7\beta_{8,7} h^8 b^7 + 7\beta_{9,7} h^9 b^7 + \\ & 7\beta_{10,7} h^{10} b^7 + 7\beta_{11,7} h^{11} b^7 \end{aligned} \quad (10)$$

$$\begin{aligned} B_1 Z_1 = & [\text{AB}] + 2[\text{A}_2\text{B}] + 8[\text{A}_8\text{B}_7] + 9[\text{A}_9\text{B}_7] + 10[\text{A}_{10}\text{B}_7] + \\ & 11[\text{A}_{11}\text{B}_7] = \beta_{1,1} h b + 2\beta_{2,1} h^2 b + 8\beta_{8,7} h^8 b^7 + \\ & 9\beta_{9,7} h^9 b^7 + 10\beta_{10,7} h^{10} b^7 + 11\beta_{11,7} h^{11} b^7 \end{aligned} \quad (11)$$

$$C_1 = [\text{A}^{-1}\text{C}] + [\text{AC}] + [\text{A}_2\text{C}] = \beta_{-1} h^{-1} c + \beta_1 h c + \beta_2 h^2 c \quad (12)$$

$$C_1 Z_2 = -[\text{A}^{-1}\text{C}] + [\text{AC}] + 2[\text{A}_2\text{C}] = -\beta_{-1} h^{-1} c + \beta_1 h c + 2\beta_2 h^2 c \quad (13)$$

The main problem of the present data treatment is to try to find out which equilibrium model (set of pqr -triplets) and corresponding equilibrium constants (β_{pqr}) can "best" explain the experimental data, $H(\log h)_{B,C}$. For this search a trial and error method was used based on the least squares program LETA-GROPVRID¹⁰ (mainly using version ETITR¹¹). Assuming that only one pqr -complex is present, different values of p , q , and r were tested. That pqr -set giving the lowest error squares sum was considered being the "best" one. When proved necessary, additional pqr -complexes will be added and tested. However, the main aims of the search will be to explain the data with as few complexes as possible.

In the Letagrop calculations we have assumed that the emf E is without error and that all errors are in H . The quantity $(H_{\text{calc}} - H)^2$ is calculated on all experimental points giving the error squares sum:

$$U = \sum (H_{\text{calc}} - H)^2 \quad (14)$$

As "best" β_{pqr} -values we consider those giving the lowest error squares sum, U_{min} . The standard deviations $\sigma(H)$ and $\sigma(\beta_{pqr})$ given are defined and calculated according to Sillén.^{12,13} The computer calculations have been carried out by using both the CD 3600 (Uppsala) and the CD 3200 (Umeå).

DESCRIPTION OF DATA

It is difficult from the data, $H(\log h)_{B,C}$ or $A(\log h)_{B,C}$, to decide directly whether ternary complexes are formed or not. In order to make this decision easier, we have made use of plots $\Delta_0(\log h)_{B,C}$, where $\Delta_0 = H_{\text{calc}} - H$. H_{calc} have been calculated assuming that only binary phosphates and molybdates are formed (species and constants given above). These plots, including all our experimental points, are given in Fig. 3. By inspecting the plots we see that over the pH-range studied there are marked "effects", which in some cases rise up to over 100 mM. We will consider that these effects are caused by formation of ternary complexes. One may note particularly that for most sets of BC there are two characteristic pits, a sharp one at around pH 6 and a broader one between pH 3 and 5. The two pits are changed systematically through all the B and C concentrations studied. They will, in the following, be denoted as the alkaline and the acid pit respectively. The plots $\Delta_0(\log h)_{B,C}$ in Fig. 3 seem to indicate formation of at least two types of complexes. Both are strongly dependent on the total molybdenum concentration. The type that corresponds to the alkaline pit seems, however, to be more dependent on the total phosphorus concentration than the type corresponding to the acid pit. Furthermore, the residual plots show that there is good reversibility between forward and backward titrations (filled and unfilled symbols in Fig. 3).

In order to simplify the data treatment and also to obtain a more detailed data description, it was found convenient to divide data into five different groups:

Data I. Experimental points from $\text{pH} \approx 7.5$ to the bottom of the alkaline pit. Uncoloured solutions.

Data II. The remaining part of the alkaline pit (from the bottom to $\text{pH} \approx 6 - 5$). Uncoloured solutions.

Data III. Data between the two pits. Uncoloured solutions.

Data IV. Points in the acid pit region and with $B/C \geq 4$. Yellow coloured solutions. The Δ_0 -changes indicate the existence of complexes with B/C ratio between 8 and 12.

Data V. Data from the same pH-range as data IV but with $B/C \leq 2$. Uncoloured solutions. For this case, one can find no typical pit, but there are still Δ_0 residuals. In this region, the existence of uncoloured complexes with $B/C < 4$ seems probable.

The data of the present work consist of over 1200 experimental points, and in order to simplify the data treatment (and save computer time) only a restricted number of the total number of points in each of the groups will be used in the calculations. These points have been arbitrarily chosen so that they are evenly distributed over the B and C concentrations. However, in the final calculations, most of the data have been used.

LETAGROP SEARCH FOR COMPLEXES

The Letagrop-search was started in the data I region. The results of the calculations of main interest are given in Table 2 and Fig. 4. The lowest error squares sum was obtained for the complex $A_8B_5C_2$. By extending the calculations to include data II and then testing successively additional complexes we found that a model with $A_8B_5C_2$ and $A_9B_5C_2$ gave the best explanation of the alkaline pit.

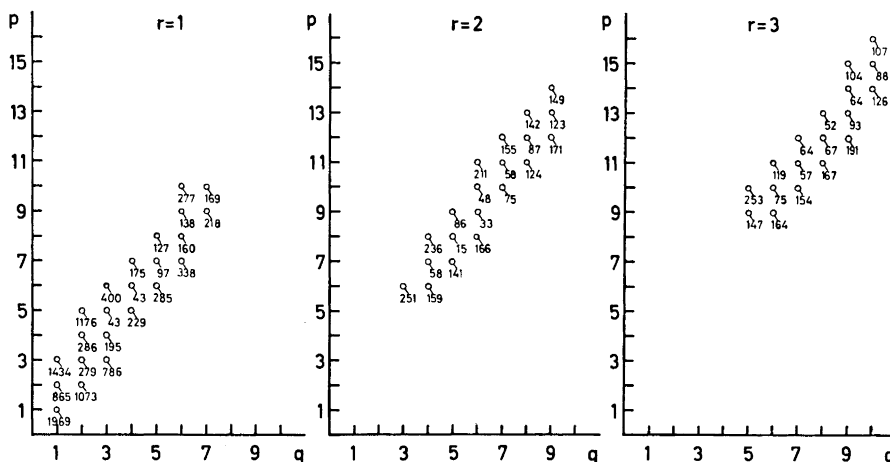


Fig. 4. Letagrop-search. Results of the calculations using Data I. Error squares sums $10^5 U_{\min}$ as a function of various (p, q, r) -sets. All details of the calculations are given in Table 2.

An analysis of the remaining data with uncoloured solutions (data III and V) gave evidence for an additional complex $A_{10}B_5C_2$. A refinement of data III and V together with data I and II, assuming formation of $A_8B_5C_2$, $A_9B_5C_2$, and $A_{10}B_5C_2$, gave the following "best" log $(\beta_{pqr} \pm 3\sigma)$ values:

$$\begin{aligned} \log (\beta_{8,5,2} \pm 3\sigma) &= 61.97 \pm 0.02 \\ \log (\beta_{9,5,2} \pm 3\sigma) &= 67.07 \pm 0.08 \\ \log (\beta_{10,5,2} \pm 3\sigma) &= 70.86 \pm 0.09 \end{aligned}$$

although the lowest error squares sum is obtained for the complex $A_{19}B_{12}C$, equally valid explanations with other pqr -values cannot be ruled out.

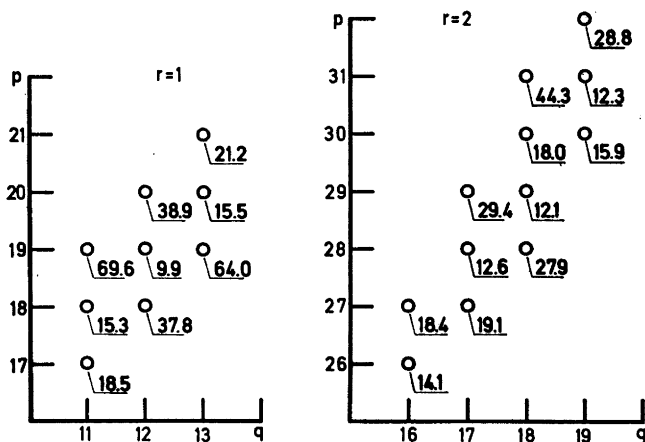


Fig. 5. Letagrop-search. Results of the calculations using Data IV. Error squares sums $10^4 U_{\min}$ as a function of various (p, q, r) -sets.

A relatively good fit was obtained by assuming $A_{18}B_{12}C$, $A_{19}B_{12}C$, and $A_{20}B_{12}C$ ($\log \beta_{18,12,1} = 125.15 \pm 0.16$, $\log \beta_{19,12,1} = 129.34 \pm 0.24$, $\log \beta_{20,12,1} = 132.92 \pm 0.21$, $U_{\min} = 1.9 \times 10^{-4}$). However, attempts to connect this result with the result from the calculation on uncoloured solution data failed completely. Before we can analyse the data for the yellow coloured solutions successfully, it is necessary to extend the pH-range to more acid solutions and also to complement the emf data with, for instance, spectrophotometric data. Investigations in this direction are in progress.*

CONCLUSIONS

The present equilibrium analysis has given clear indications for the existence of two types of complexes, one yellow and one colourless. Moreover, through the present work, composition and equilibrium constants for main complexes of the colourless type have been well established. A good criterium for that is the low standard deviations of the determined equilibrium constants (Table 2). Strengths and concentrations of these complexes are well illustrated by the distribution diagrams given in Fig. 6.

Concerning the yellow complexes it may be said that the range studied is too limited to allow a distinct conclusion. What can be said at present is that the B/C ratio of the complexes probably lies between 8 and 12. Attempts

* Note added in proof. Some recent results on yellow coloured solutions are presented elsewhere.¹⁴

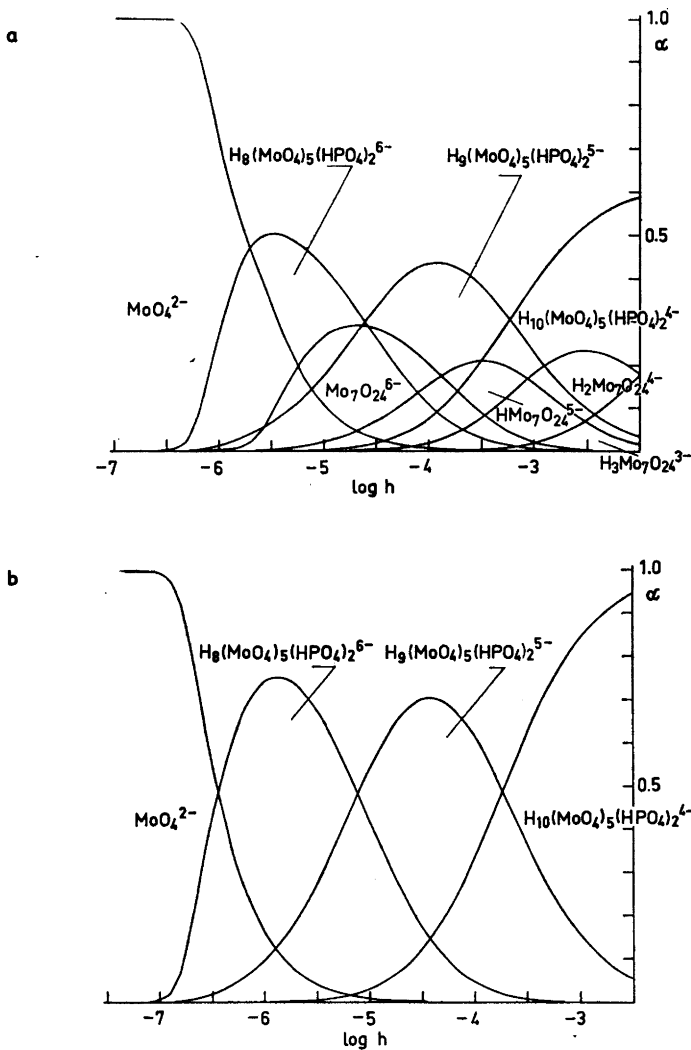
Table 2. Results of *pqr*-analysis for colourless solutions, using LETAGROP. The binary constants used are those under 0 in Table 1.

	Species tested (<i>p,q,r</i>)	U_{\min} $\times 10^3$	$\sigma(H)$ mM	$\log(\beta_{pqr} \pm 3\sigma)$
Data I (79 points)	(1,1,1)	19.69	15.89	8.42 ± 0.48
	(2,1,1)	8.65	10.53	14.85 ± 0.15
	(3,1,1)	14.34	13.56	21.37 ± 0.18
	(2,2,1)	10.73	11.73	16.13 ± 0.22
	(3,2,1)	2.79	5.98	22.79 ± 0.09
	(4,2,1)	2.86	6.06	29.47 ± 0.09
	(5,2,1)	11.76	12.28	36.08 ± 0.21
	(3,2,1) (4,2,1)	2.11	5.24	$22.52 \pm 0.27, 29.14 \pm 0.30$
	(3,3,1)	7.86	10.04	24.02 ± 0.21
	(4,3,1)	1.95	5.00	30.73 ± 0.09
	(5,3,1)	0.43	2.35	37.47 ± 0.05
	(6,3,1)	4.00	7.16	44.17 ± 0.14
	(5,4,1)	2.29	5.42	38.71 ± 0.12
	(6,4,1)	0.43	2.33	45.47 ± 0.05
	(7,4,1)	1.75	4.74	52.20 ± 0.09
	(6,5,1)	2.85	6.04	46.71 ± 0.15
	(7,5,1)	0.97	3.53	53.48 ± 0.09
	(8,5,1)	1.27	4.04	60.24 ± 0.09
	(7,6,1)	3.38	6.58	54.73 ± 0.21
	(8,6,1)	1.60	4.53	61.51 ± 0.12
	(9,6,1)	1.38	4.21	68.28 ± 0.12
	(6,3,2)	2.51	5.68	45.81 ± 0.12
	(6,4,2)	1.59	4.52	47.08 ± 0.12
	(7,4,2)	0.58	2.73	53.83 ± 0.07
	(8,4,2)	2.36	5.50	60.56 ± 0.17
	(7,5,2)	1.41	4.26	55.08 ± 0.13
	(8,5,2)	0.15	1.36	61.85 ± 0.04
	(9,5,2)	0.86	3.33	68.60 ± 0.09
	(8,6,2)	1.66	4.62	63.09 ± 0.15
	(9,6,2)	0.33	2.06	69.87 ± 0.06
(10,6,2)	0.48	2.47	76.64 ± 0.07	
(10,7,2)	0.75	3.11	77.90 ± 0.10	
(11,7,2)	0.58	2.72	84.68 ± 0.09	
(10,6,3)	0.75	3.10	78.28 ± 0.11	
(11,6,3)	1.19	3.91	85.04 ± 0.17	
(10,7,3)	1.54	4.44	79.52 ± 0.18	
(11,7,3)	0.57	2.70	86.31 ± 0.09	
(12,7,3)	0.64	2.86	93.08 ± 0.10	
(11,8,3)	1.67	4.62	87.54 ± 0.19	
(12,8,3)	0.67	2.94	94.34 ± 0.12	
Data I + II (94 points)	(3,2,1)	10.94	10.85	22.95 ± 0.17
	(4,2,1)	9.82	10.27	29.31 ± 0.16
	(3,2,1) (4,2,1)	3.82	6.31	$22.71 \pm 0.20, 28.82 \pm 0.15$
	(8,5,2)	0.25		61.85
	(8,5,2) (9,5,2)	0.12	1.14	$61.79 \pm 0.04, 66.93 \pm 0.16$
Data I + II + III + V (359 points)	(8,5,2) (9,5,2) (10,5,2)	0.12	0.58	$61.97 \pm 0.02, 67.07 \pm 0.08, 70.86 \pm 0.09$

to explain these data with *e.g.* dodecamolybdophosphates — a proposal often found in the literature — were however not successful. Complimentary works on the yellow solutions (emf and spectrophotometry) are in progress.

The present paper contains no review or comparison with earlier studies. We suggest that such a survey may be worth-while when the information concerning the yellow complexes becomes clearer.

From present studies, using other experimental methods, we hope, in the near future, to collect complementary and confirmatory information about proposed complexes. At present, the following studies are in progress:



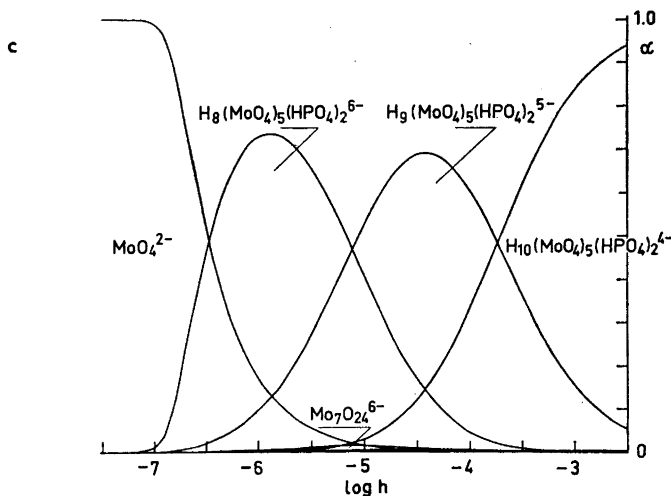


Fig. 6. Complex distribution diagrams, $\alpha(\log h)_{B,C}$ for a) $B=40$ mM, $C=10$ mM (The curves have been calculated neglecting the existence of yellow coloured species); b) $B=50$ mM, $C=20$ mM; c) $B=40$ mM, $C=20$ mM. α is defined as the ratio between molybdenum in a species and total molybdenum. Species with $\alpha < 0.008$ have been omitted.

- i. Molecular weight determinations using ultra-centrifugation.
- ii. "Structure" determination of the aqueous species by X-ray solution studies.
- iii. Structure determinations of molybdophosphates crystallized from aqueous solutions, using X-ray diffraction.
- iv. Spectrophotometric measurements in UV.

Acknowledgements. I wish to 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. Ingegård Andersson for valuable help. The English of the paper has been corrected by Dr. Michael Sharp. The work forms part of a program supported by *Statens Naturvetenskapliga Forskningsråd*.

REFERENCES

1. Berzelius, J. J. *Pogg. Ann.* **6** (1826) 369.
2. *Gmelins Handbuch der anorganischen Chemie*, 8. Auflage, Systemnummer 53, 1935, p. 312.
3. Mellor, J. W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green and Co., London 1931, Vol. XI, p. 659.
4. Emeleus, H. J. and Anderson, J. S. *Modern Aspects of Inorganic Chemistry*, 3rd Ed., Routledge and Kegan Paul, London 1960, p. 325.
5. Sjöberg, S. *Acta Chem. Scand.* **25** (1971) 2149; Ingri, N. *Svensk Kem. Tidskr.* **75** (1963) 199.
6. Vogel, A. I. *Quantitative Inorganic Analysis*, 3rd Ed., Longmans, Green and Co., London 1961, p. 507.
7. Vogel, A. I. *Quantitative Inorganic Analysis*, 3rd Ed., Longmans, Green and Co., London 1961, p. 575.
8. Biedermann, G. and Sillén, L. G. *Arkiv Kemi* **5** (1953) 425.

11. Sillen, L. G. *Acta Chem. Scand.* 18 (1964) 1015.
12. Sillen, L. G. and Sillen, L. G. *Acta Chem. Scand.* 18 (1964) 97.
13. Sillen, L. G., Sillen, L. G. and Jansson, O. *Acta Chem. Scand.* 21 (1967) 353; Brauner, P., Sillen, L. G. and Whiteker, B. *Acta Chem. Scand.* 21 (1967) 365.
14. Sillen, L. G. *Acta Chem. Scand.* 16 (1962) 159.
15. Sillen, L. G. and Warnqvist, B. *Acta Chem. Scand.* 21 (1967) 341.
16. Jansson, L., Andersson, I., Lyhammar, L. and Ingri, N. *Trans. Roy. Inst. Technol., Stockholm*, 1971. In press; An article in *Contributions to Coordination Chemistry in Memory of L. G. Sillen*, Allmänna förlaget, Stockholm 1972.

Received October 16, 1970.

KEMISK BIBLIOTEK
Den kgl. Veterinær- og Landbohøjskole