The Hydrolysis of Metal Ions. Part 10.[1] Kinetic and Equilibrium Measurements of Molybdenum(VI)

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The potentiometric titration technique has been used to study molybdenum(VI) equilibria in 1.0 mol dm^{-3} sodium nitrate and at 25 °C. Numerical treatment of the data indicates that the 'best' model includes the species $[HMoO_4]^-$, H_2MoO_4, $[Mo_7O_{24}]^{6-}$, $[Mo_7O_{23}(OH)]^{5-}$, $[Mo_7O_{22}(OH)_2]^{4-}$ $[Mo_7O_{21}(OH)_3]^{3-}$, $[Mo_8O_{26}]^{4-}$, and $[Mo_{10}O_{34}]^{8-}$ whose formation constants, log β_{pq}, are, respectively, 3.92, 8.09, 52.49, 57.57, 61.33, 64.96, 73.18, and 79.15. Evidence is given for the existence of a high-molecular-weight species even though computational limitations preclude its identification. A 'slow' region of equilibrium has also been found and its kinetics studied. The reaction mechanism is discussed; the rate constants of the forward and backward reaction, k_1 and k_{-1}, are 642 ± 300 dm^6 mol^{-2} s^{-1} and (2.51 ± 1.00) × 10^{-5} s^{-1}, respectively. Further evidence for the co-ordination numbers of the protonated forms of the molybdate ion is given.

The chemistry of the molybdenum(VI) ion, in both solution and the solid state, is notoriously complex and, consequently, has attracted a great deal of attention over many decades.[2–10] The solution chemistry is dominated by polymerisation reactions [and is therefore often referred to as polyoxomolybdenum(VI) equilibria] in which heptameric species are usually believed to be formed.[11] However, despite many investigations of the system, its complexity has prevented a definitive description being obtained.

We are interested in the formation and properties of zirconium molybdate gels[12,13] which are being developed for the generation of technetium-99m radiopharmaceuticals. A knowledge of the molybdate(VI) equilibrium system is of fundamental importance to the understanding of the behaviour of these gels. Accordingly, using experimental and numerical methods developed by us over recent years,[1,14–18] we have investigated this system using the potentiometric technique and have obtained a definitive result. Because of the complexity of this system, the amount of experimental data and the associated computing facilities have been on an unprecedented scale. The results of this investigation are given in this paper together with a critical examination of earlier work.

Experimental

Reagents.—The source of molybdenum was molybdenum(VI) oxide (Johnson, Matthey and Co., Spec. Pure). Other reagents were of Merck Suprapur grade. The molybdenum stock solution was nominally 40 mmol dm^{-3} sodium molybdate(VI) in 1.0 mol dm^{-3} sodium nitrate. This solution was analysed using atomic absorption spectroscopy.

Procedure.—The titration equipment consisted of a Radiometer pH meter (PHM84), a Radiometer ABU80 Autoburette (2.5 cm^3 burette, tolerance ±0.0001 cm^3), and a conventional stirred–degassed–thermostatted reaction vessel. Radiometer GK2401C glass electrodes were used. They had negligible drift over extended periods[14] (*ca.* 0.002 pH unit per 24 h), an important feature since many titrations were ⩾50 h in duration. The titrant (nominally 0.10 mol dm^{-3} nitric acid) was delivered *via* a Teflon needle (Hamilton, bore 0.01 in) dipping about 1 cm below the solution surface. Measurements were carried out at 25.0 ± 0.1 °C and at a total ionic strength of 1.0 mol dm^{-3}, using sodium nitrate. The equipment was controlled by a microprocessor (Intel 8085A). Titrant was added in constant increments (for a given titration) every 5 min; the pH was recorded every minute.

In each of four kinetic experiments, the pH was adjusted to within the appropriate range and pH readings then taken every minute until equilibrium was established. The regions of slow equilibrium observed in each titration were used in the subsequent data analysis as these regions represented only a small portion of the total number of data points. The inclusion of these data points in the analysis had, at most, a small effect on the data refinement as is indicated by our criteria of model selection:[1,14–18] (*a*) the standard deviations of all species in the model are ⩽10%; and (*b*) R (the normalised agreement factor[16]) is less than 0.002. If the inclusion of these points were to have a significantly deleterious effect on the data analysis, no model would be found which met these acceptance criteria.

Experimental Design.—The computational procedure and the selection criteria for the pH range have been given previously.[1,18] In systems of cation hydrolysis the accessible pH range is limited by precipitation reactions and/or slow equilibrium. These reactions do not occur in the molybdenum system, therefore the accessible pH range is much larger. The design of two separate series of experiments was found to be necessary so that all areas of complex formation could be studied adequately. The experimental design was determined from a preliminary series of titrations and previous literature.[2–10] The two series are as follows.

First series. In this series, the initial total molybdenum(VI) concentration ranged from 0.80 to 20.0 mmol dm^{-3} and the pH range of each titration was from *ca.* 5.0 to 2.3. Data analysis of this set of experiments indicated a model which met the acceptance criteria. However, the addition of a polymer of large molecular weight (which forms at low pH) to this model refined with a standard deviation just outside the criteria. Thus, both the range of initial total molybdenum(VI) concentration and pH were increased to facilitate the detection of this latter species.

Second series. In this series of titrations, the initial total molybdenum(VI) concentration was between 1.20 and 33.59 mmol dm^{-3} and the pH range was from 5.0 to 1.3. Data analysis indicated that the extension of the pH range had a detrimental

Table 1. Summary of potentiometric tiration data for molybdenum(VI) hydrolysis at 25 °C and in 1.0 mol dm^{-3} sodium nitrate

Series	Total initial molybdenum(VI) concentration (mmol dm^{-3})	pH Range	Number of points
1	20.00	5.000—2.269	244
	16.00	4.999—2.270	273
	10.00	4.991—2.287	283
	6.00	5.000—2.507	291
	2.00	4.565—2.299	233
	0.80	4.224—2.400	201
2	33.59	5.300—1.852	311
	20.00	5.001—2.302	248
	10.00	4.897—2.302	323
	5.20	5.140—2.501	460
	2.20	4.808—2.300	346
	1.20	4.653—2.301	243

effect on the agreement factor, R.[17] However, when a similar pH range was used, as in the first series of titrations, the same model met the acceptance criteria. The data referred to in this paper are those which were used to obtain this model (see Table 1).

In the expression (1) the value of λ for the glass electrode was

$$[H^+] = 10^{-pH}/\lambda \quad (1)$$

found by numerical refinement[17] to be 1.357 and 1.182 for the first and second series of titrations, respectively, in the absence of a correction for the ionisation of water. This correction has a negligible effect if the pH values are below *ca.* 5. The value of λ is a correction to the observed pH values and includes the proton activity coefficient and other contributions (assumed constant) such as liquid–junction potential, asymmetry potential, and calibration errors. The data from the first and second series used in the numerical analysis are summarised in Table 1; full details are available on request.

Results

Stability Measurements.—For the reactions (2) the stoicheiometric equilibrium constants are defined as in equation (3). This

$$p[\mathrm{MoO_4}]^{2-} + q\mathrm{H}^+ \rightleftharpoons [(\mathrm{MoO_4})_p\mathrm{H}_q]^{(2p-q)-} \quad (2)$$

$$\beta_{pq} = \frac{[(\mathrm{MoO_4})_p\mathrm{H}_q{}^{(2p-q)-}]}{[\mathrm{MoO_4}{}^{2-}]^p[\mathrm{H}^+]^q} \quad (3)$$

convention is the same as that adopted, for example, by Aveston *et al.*[5] and Sasaki and Sillén,[6] except that the p and q values have been reversed to retain consistency with the program MINIQUAD.[17–20] Thus, a (p,q) species in the present work corresponds to a (q,p) species in the earlier work cited.[5,6] The description of the molybdenum(VI) system, as given by equations (2) and (3), is the simplest since the potentiometric method can yield only the p and q values, and no knowledge of the reaction products can be obtained. Chemically, however, the monomeric ion is protonated and then polymerises to produce polyanions and water. The products are often formulated with the minimum number of oxygen atoms so that, for example, the species $[(\mathrm{MoO_4})_7\mathrm{H_8}]^{6-}$ is written as $[\mathrm{Mo_7O_{24}}]^{6-}$, the reaction being given in equation (4). This convention is used here and the

$$7[\mathrm{MoO_4}]^{2-} + 8\mathrm{H}^+ \rightleftharpoons [\mathrm{Mo_7O_{24}}]^{6-} + 4\mathrm{H_2O} \quad (4)$$

products will be defined either by their formulae or as (p,q) pairs; thus, $[\mathrm{Mo_7O_{24}}]^{6-}$ is the (7,8) species.

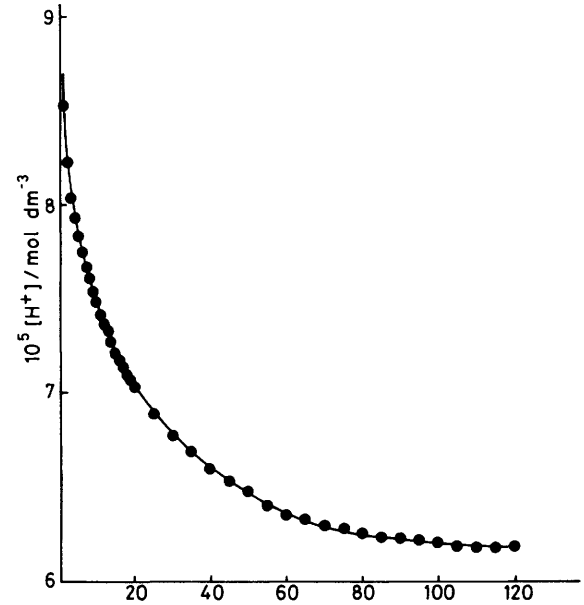

Figure 1. Plot of hydrogen-ion concentration *versus* time for a total molybdenum(VI) concentration of 23.24 mmol dm^{-3}

The view has been expressed[11] that, for systems containing as many as five species in a relatively narrow pH range, successful equilibrium analysis is not possible with potentiometric data alone. In contrast to the behaviour of cationic systems, the molybdate(VI) system has a significantly larger accessible pH range since precipitation and/or slow equilibrium reactions (which take days to months to reach equilibrium) do not occur. The number of species which are produced in this range is also larger and as many as eight species have been suggested.[4,7,21] Though the system has been investigated by a number of experimental techniques,[5] a definitive description of even the species which form in solution is unavailable. Of these techniques, by far the most generally applicable and widely used is potentiometry.[11]

Recently,[1,18,22] we have shown that the polynuclear hydrolysis species can be postulated by using the co-ordination number (in solution) of the metal ion undergoing hydrolysis. In polyoxometalate systems, however, the distinction between the metal ion and the ligand is blurred, therefore the prediction of species for these systems is not possible at the present time. Furthermore, as a result of the number of species believed to be produced in the molybdate(VI) system, there is no feasible means of systematically examining the data,[11,14] given the very large number of possible models. It was necessary, therefore, to rely on previous work for model and species selection and, subsequently, on trial and error selections. Thus, we examined a large number of models involving the species (1,1), (1,2), (2,5), (6,6), (6,7), (6,8), (6,9), (7,8), (7,9), (7,10), (7,11), (8,9), (8,10), (8,11), (8,12), (9,10), (9,11), (9,12), (9,13), (10,12), and a species of large molecularity with $p \geqslant 14$ and q/p *ca.* 1.78. Initial estimates of the formation constants were obtained from the generalised form of the Sylva–Davidson equation.[22]

Table 2 contains the results of computations for a number of models for each of the first and second series of titrations. The only model which meets the acceptance criteria for either series is model 8 which is substantial evidence of the existence of the species in this model. The agreement between the formation constants of the two series, for a given model, is very satisfactory.

Kinetic Measurements.—The published data[2–10,21] indicate that the equilibria in the molybdate(VI) system are 'fast' in the

Table 2. Comparison of some models of molybdenum(VI) hydrolysis

Model number	Model	Series 1			Series 2		
		log β_{pq}	(%) of β_{pq}	*R*	log β_{pq}	(%) of β_{pq}	*R*
1	(1,1)	4.14	4.94	0.002 269	4.10	3.71	0.002 615
	(1,2)	8.42	2.14		8.33	3.16	
	(7,8)	52.60	7.00		52.63	2.97	
	(7,9)	58.17	2.92		57.73	4.15	
	(7,10)	62.13	3.77		61.80	4.71	
	(7,11)	66.47	4.46		65.92	6.33	
2	(1,1) (1,2) (6,6) (6,7) (6,8) (6,9)	Model rejected: (1,1) and (6,6) became negative			Model rejected: (1,1) became negative		
3	(1,1) (1,2) (8,9) (8,10) (8,11) (8,12)	Model rejected: (1,1) became negative			Model rejected: (1,1) became negative		
4	(1,1)	3.89	6.34	0.003 166	3.80	5.90	0.003 419
	(1,2)	7.96	3.46		7.97	3.24	
	(9,10)	67.26	4.81		66.66	4.67	
	(9,11)	72.06	7.23		71.51	7.22	
	(9,12)	76.11	6.76		75.46	7.50	
	(9,13)	80.21	9.88		79.67	9.79	
5	(1,1)	3.26	28.07	0.002 270	2.93	31.53	0.002 027
	(1.2)	8.12	2.72		7.89	2.87	
	(7,8)	52.91	2.59		52.48	2.78	
	(7,9)	57.69	4.71		56.80	5.68	
	(7,10)	61.24	8.51		60.89	4.63	
	(8,12)	73.19	8.39		71.68	12.71	
6	(1,1)	4.16	4.70	0.002 234	Model rejected: (14,25) became negative		
	(1,2)	8.43	2.07				
	(7,8)	52.53	8.27				
	(7,9)	58.19	2.84				
	(7,10)	62.13	3.75				
	(7,11)	66.50	4.39				
	(14,25)*	142.52	19.70				
7	(1,1)	3.79	8.82	0.002 078	2.30	132.20	0.001 979
	(1,2)	8.21	2.30		7.86	3.09	
	(7,8)	52.79	3.47		52.49	2.84	
	(7,9)	57.97	3.48		56.79	5.35	
	(7,10)	59.26	1 497.84		60.92	4.77	
	(7,11)	65.46	10.96		62.86	14.75	
	(8,12)	73.63	5.19		71.64	11.93	
8	(1,1)	4.03	5.75	0.001 981	3.78	5.03	0.001 889
	(1,2)	8.14	2.28		8.03	2.50	
	(7,8)	52.53	8.37		52.44	3.17	
	(7,9)	57.79	3.76		57.11	4.28	
	(7,10)	61.43	8.91		61.20	4.22	
	(7,11)	65.22	8.04		64.16	9.26	
	(8,12)	73.43	5.34		72.52	6.52	
	(10,12)	79.37	7.83		78.68	7.00	
9	(1,1)	4.02	5.75	0.001 948	3.81	2.92	0.001 871
	(1,2)	8.15	2.18		8.04	0.81	
	(7,8)	52.54	8.11		52.43	1.19	
	(7,9)	57.81	3.59		57.13	1.33	
	(7,10)	61.34	11.02		61.21	1.45	
	(7,11)	65.19	8.05		64.21	1.52	
	(8,12)	73.46	5.10		72.57	1.61	
	(10,12)	79.35	8.05		78.71	1.76	
	(14,25)*	140.17	16.98		138.05	13.10	
10	(1,1)	3.76	10.53	0.002 180	3.39	16.72	0.002 016
	(1,2)	8.08	3.00		7.95	3.51	
	(7,8)	52.78	3.87		52.49	2.60	
	(7,9)	57.54	6.56		56.87	6.59	
	(7,10)	61.45	5.20		60.98	5.15	

Table 2 (*continued*)

Model number	Model	Series 1 log β_{pq}	Series 1 (%) of β_{pq}	Series 1 R	Series 2 log β_{pq}	Series 2 (%) of β_{pq}	Series 2 R
10	(8,12)	73.01	11.09	0.002 180	71.93	15.69	0.002 016
	(10,12)	79.12	9.63		77.91	22.56	
11	(1,1)	3.80	9.40	0.002 130	3.45	14.38	0.002 001
	(1,2)	8.10	2.85		7.96	3.41	
	(7,8)	52.77	4.06		52.48	2.58	
	(7,9)	57.88	6.27		56.88	6.51	
	(7,10)	61.42	6.18		61.01	4.92	
	(8,12)	73.10	10.25		71.98	15.09	
	(10,12)	79.15	9.27		78.02	18.55	
	(14,25)*	139.01	22.52		136.51	30.86	

* Dummy species used to represent species with q/p ratio of *ca.* 1.78.

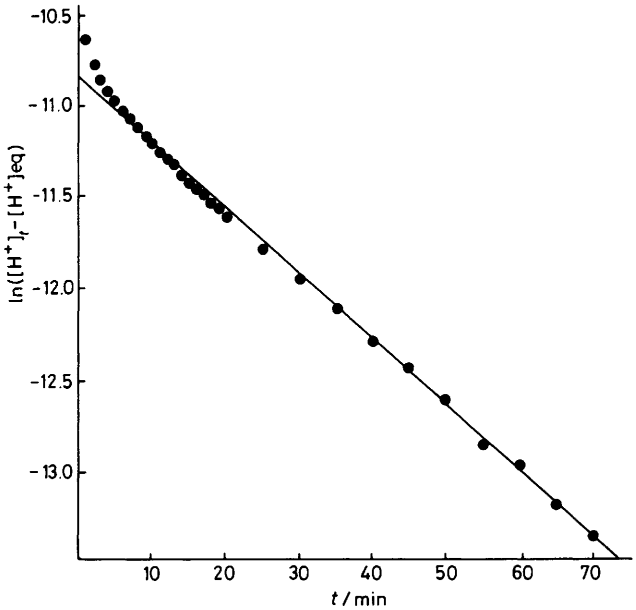

Figure 2. Plot of ln ($[H^+]_t - [H^+]_{eq}$) *versus* time, showing that the consumption of hydrogen ions is first order

sense that routine laboratory equilibrium measurements (*e.g.* titrations) can be performed without any apparent time dependence. However, the frequency and precision of the pH measurements made in this study show that there are pH regions where relatively 'slow' reactions occur. These regions are concentration dependent, reproducible, and precisely defined.

The kinetics of the slow reactions were observed at the total molybdenum(VI) concentrations, 8.42, 14.66, and 23.24 mmol dm^{-3}, two being at the highest metal-ion concentration. The time dependence of the 23.24 mmol dm^{-3} molybdate(VI) concentration is shown in Figure 1. Plots of ln ($[H^+]_t - [H^+]_{eq}$), where $[H^+]_t$ is the hydrogen-ion concentration at time t and $[H^+]_{eq}$ is the equilibrium hydrogen-ion concentration, against time, are linear. This demonstrates that the reaction(s) is reversible and first order with respect to the disappearance of protons.[23] These plots are illustrated, for the 23.24 mmol dm^{-3} total molybdate(VI) concentration, by Figure 2.

The rate expression for the disappearance of protons can then be represented by equation (5), where k^* is the observed

$$-d[H^+]/dt = k^*([H^+]_t - [H^+]_{eq}) \quad (5)$$

Table 3. Calculated value of k^* determined from the function $k^* = \frac{1}{t}\ln\{[H^+]_{eq}/([H^+]_t - [H^+]_{eq})\}$

Kinetic run	Total molybdenum(VI) concentration (mmol dm^{-3})	$10^4\ k^*$/s^{-1}
1	23.24	5.967
2	14.66	7.000
3	8.42	6.850
4	23.24	6.083
		Mean = 6.483 ± 0.45

rate constant calculated from the plots in Figure 2. The value determined for the constant for each of the kinetic experiments is given in Table 3. The values are independent of total molybdenum(VI) concentrations and equal to $(6.5 \pm 0.5) \times 10^{-4}$ s^{-1}.

Discussion

Stability Measurements.—Previous potentiometric investigations[5,6,9,24] of polyoxomolybdenum(VI) equilibria at 25 °C have been surveyed and are shown for comparative purposes in Table 4. The agreement between the values of the estimated formation constants is satisfactory given the differences in ionic strength. However, the agreement between proposed models is poorer.

Earlier techniques[25–29] (*e.g.* inflexions in titration curves) provided data that were so limited that several interpretations were equally supported. More recently, potentiometric techniques were utilised[5,6,9,24] in an attempt to obtain a more reliable description of the system. Of these studies, the work of Sasaki and Sillén[6] is the most detailed. Although Aveston *et al.*[5] supplemented potentiometric with ultracentrifuge and Raman spectroscopic measurements, conjecture still remains as to the species which are actually produced.

The results of these potentiometric studies, however, indicate that the dominant polymeric species contain either seven or eight molybdenum atoms. Indeed, Sasaki and Sillén chose to interpret their data with the heptameric species (7,8), (7.9), (7,10), and (7,11) together with the monomeric species (1,1) and (1,2). Conversely, Aveston *et al.*[5] chose (8,12) in preference to the (7,11) species because the Raman spectra of $[Mo_8O_{26}]^{4-}$ in the solid state and of a solution with Z of *ca.* 1.5 (Z is the ligand number, the amount of bound acid per metal ion) were similar. The uncertainty in the two studies is whether (7,8) or (8,12) is the predominant polynuclear species or both occur simultane-

Table 4. Survey of potentiometric investigations of the hydrolysis of molybdenum(VI) at 25 °C

Medium	Total molybdenum(VI) concentration (mmol dm^{-3})	log β_{pq} (1,1)	(1,2)	(7,8)	(7,9)	(7,10)	(7,11)	(8,12)	(10,12)	Ref.
1 mol dm^{-3} $Mg(ClO_4)_2$	3.088—13.35		7.80	51.91	56.17	59.78				9
1 mol dm^{-3} NaCl	1.25—80	3.55	7.20	52.81	57.39	61.02	63.40			5
1 mol dm^{-3} NaCl	1.25—80	3.53	7.26	52.80	57.42	60.84		71.56		5
3 mol dm^{-3} $NaClO_4$ [a]	0.3125—160.98	3.89	7.50	57.74	62.14	65.68	68.21			6
1 mol dm^{-3} NaCl	0.5—100.0	3.56	7.33	52.60	57.52	60.82		71.57		24
1.0 mol dm^{-3} $NaNO_3$ [b]	0.80—33.59	3.92	8.09	52.49	57.57	61.33	64.96	73.18	79.15	This work

[a] $\log \beta_{25} = 19$, $\log \beta_{19\ 34} = 196.30$. [b] The average value of the formation constants, β_{pq}, given in model 8 of Table 2, for the two series of titrations, is quoted.

ously. It is thought[9,30] that the relative presence of the two species is significantly dependent upon the ionic strength; the (7,8) species is favoured by high and the (8,12) species by low ionic strength. Schwing and co-workers[10,31] proposed the three species (6,8), (6,9), and (7,8). However, a recalculation of these data by Sillén[21] showed that the fit was significantly improved if the model of Sasaki and Sillén[6] was used. The work of Cruywagen[24] is in good agreement with the earlier work of Aveston *et al.*[5]

The uncertainty associated with the interpretation of previous potentiometric data is based on several factors.

(*a*) None of the previous workers[5,6,9,10] defined their method of model selection. The choice of model appears to be based solely on the goodness-of-fit parameter $\sigma(Z)$ (estimated standard deviation based on Z), whereas our present and earlier work[1,14–18] conclusively demonstrates that this parameter alone does not provide even an approximately satisfactory criterion of acceptability. Indeed, the lack of suitable selection criteria belies the precision of the measurements taken.

(*b*) Although Aveston *et al.*[5] supplemented potentiometric with ultracentrifuge and Raman spectroscopic measurements, the species proposed by their study are ill defined since, (*i*) only 68 potentiometric measurements were taken which, considering the complexity of the system, is hardly sufficient to define the species properly (3 456 data points were taken in the present study), (*ii*) the ultracentrifuge measurements indicate that the *most probable* species contain between six and nine molybdenum atoms, and (*iii*) the Raman spectroscopic data are used to make the very tenuous[15] comparison between aqueous and solid-state samples.

(*c*) It is difficult to determine the data set used, or the actual model proposed, by Sasaki and Sillén.[6] Although a number of titrations were performed at each molybdenum(VI) concentration, only one is presented in the publication and it is not possible to determine whether all of the data were used in the subsequent numerical analysis. Furthermore, even though it is claimed on a number of occasions[4,6,9] that a detailed account of the numerical analysis would be given, it was never published. These aspects mean that any re-examination of their work is of questionable value.

(*d*) The absence of stated or established acceptance criteria has caused some authors[9,12] to propose species which cannot be supported by their relative contribution to the data. The usefulness and necessity of back calculations, *i.e.*, speciation calculations, must be stressed; it is essential that each species in the proposed model is in sufficient detectable concentrations, and that their refinement is not merely a numerical artifact of the model.

A satisfactory interpretation of the present data and those of previous studies[5,6,9] requires the inclusion of the monomers (1,1) and (1,2). Indeed, the present results suggest that the formation of these two momeric species is more significant than had previously been thought.[5,11]

The present data indicate (in addition to the monomeric species) all the heptameric species suggested by Sasaki and Sillén[6] and the (8,12) species of Aveston *et al.*[5] Furthermore, the (10,12) species, not previously thought to be present in solution, is also indicated. Although this latter species has been identified in the solid state[32] it was believed that its structure is destroyed when dissolved in water. The potentiometric technique, however, gives no information on the structure of a postulated complex. The results shown in Table 2 clearly indicate the formation of the (10,12) species (compare model 7 with model 8). In reference to earlier work,[2–10,21] the table also indicates the following: (*a*) the formation of both the (7,8) and (8,12) species in 1.0 mol dm^{-3} $NaNO_3$; and (*b*) the first polynuclear species is the heptamer (7,8) which is then successively protonated until the formation of the (7,11) species. The hexameric, octameric, and nonameric series give a much poorer fit to the data (compare models 1—5).

In the concentration ranges studied in the present work, the monomers (1,1) and (1,2) are important at low molybdenum(VI) concentrations; the (1,2) species becomes significantly more important with decreasing pH. At higher molybdenum(VI) concentrations, all the polymers are significant, their relative percentage depending on the pH. The speciation of molybdenum(VI) for 6.0 mmol dm^{-3} is illustrated in Figure 3.

At Z values greater than *ca.* 1.5—1.6 Sasaki and Sillén[4] chose the single species (19,34), a polymer of high molecular weight, to explain their previous data[6] in this region. The ultracentrifuge data of Aveston *et al.*[5] also indicate the presence of a species of high molecular weight in these regions; however, they did not take potentiometric measurements in this region. A subsequent recalculation[7] of the data of Sasaki and Sillén[6] has shown that $[Mo_{36}O_{112}]^{8-}$ (postulated because it had been identified in the solid state by X-ray studies[33–35]) also fits the data in the region, giving only a slightly poorer fit. Studies at this laboratory on zirconium molybdate gels[12,13] showed that the efficiency of eluting technetium-99m is significantly lower when the gels are prepared from a pH region where a high-molecular-weight species would form than from pH regions where heptameric or octameric species form. Such a fall in elution efficiency is inconsistent with the continued formation of these latter species in the region of $Z \geqslant 1.6$. Thus, we believe that a high-molecular-weight polymer forms in this region with $q/p \approx 1.78$.

In attempting to analyse the data for a species of high molecular weight, computational limitations of the IBM mainframe computer precluded the use of the (19,34) or (36,64) species and necessitated the use of a dummy species; the largest stoicheiometry which could be used was the (14,25) species

Table 5. Some properties of the oxometalate ions, $[MO_4]^{z-}$

Metal	Charge	Ionic radius[a] (Å)	Stepwise formation constant[b] log K_1	log K_2	log K_3	No. of metal ions per polymer unit
V	3	0.59	14.26	8.55	4.6	2, 3, 4, 10
Nb	3	0.69			8.3	6
Ta	3	0.68			10.5	6
Cr	2	0.52	6.51	−0.20		2, (3), (4)
Mo	2	0.62	3.9[c]	3.6[c]		7, 8, 10[c]
W	2	0.62	3.5	4.6		6, 12
Mn	1	0.46	−1.6			
Tc	1	0.56				
Re	1	0.56	−1.25[d]			

[a] Value given is Ahrens ionic radius of the central metal ion as quoted in R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 1969, **25**, 925. The radius of the $[MO_4]^{z-}$ moiety will be a function of the value given for M. [b] Values given are at zero ionic strength and 25 °C, from Baes and Mesmer[11] unless otherwise stated. log β_{1q} = log K_1 + log K_2 + ... + log K_q. [c] Present work. [d] Value given in N. Bailey, A. Carrington, K. A. K. Lott, and M. C. R. Symons, *J. Chem. Soc.*, 1960, 290.

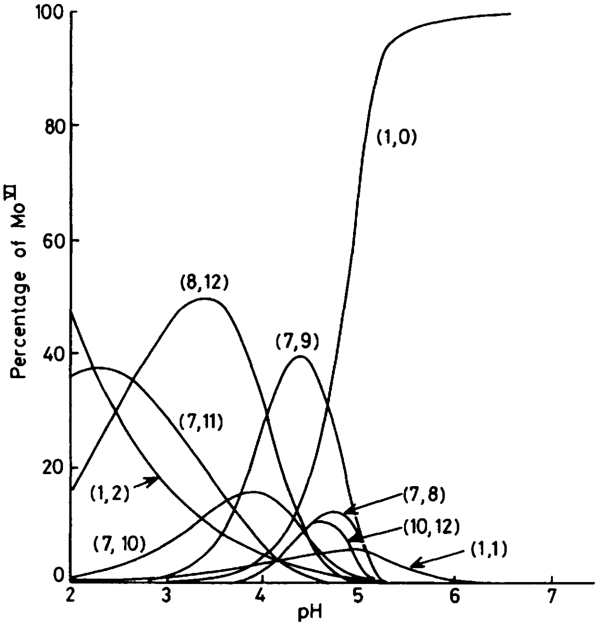

Figure 3. Percentage distribution of molybdenum(VI) in various hydrolytic species for a total concentration of 6.0 mmol dm^{-3}

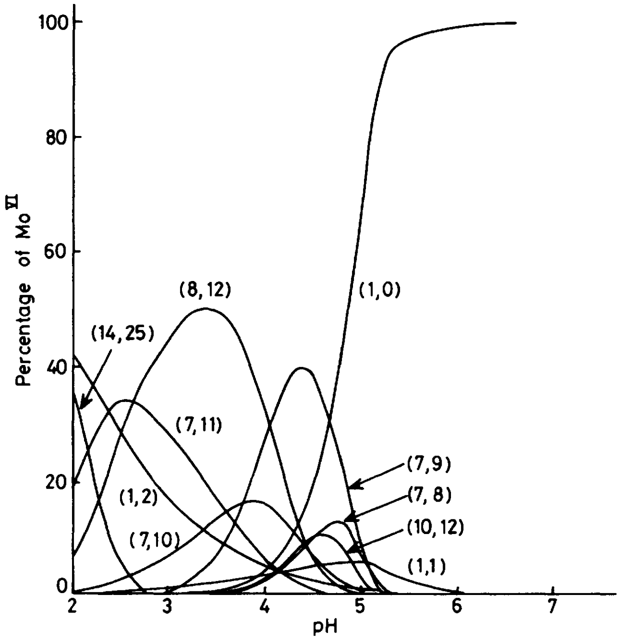

Figure 4. Percentage distribution of molybdenum(VI) in various hydrolytic species for a total concentration of 6.0 mmol dm^{-3}, with the inclusion of a high-molecular-weight polymer

(q/p = 1.786). The addition of this in model 8 of Table 2 giving model 9 (for the first series of titrations, range pH *ca.* 5.0—2.3), improved the fit, the standard deviation of the species being slightly higher than 10%. Thus, a second series of experiments was designed in which the molybdenum(VI) concentration range was increased and pH measurements as low as 1.3 were recorded; these concentration ranges would facilitate the detection of a high-molecular-weight species. Unfortunately, the data accumulated in the low pH region were not useful in the data analysis because of the combined effect of, first, the reduced *accuracy* of the measurement of $[H^+]$ at these acidities,[5] and thus the systematic errors associated with its potentiometric determination are larger.[7] This does not mean, however, that such measurements are not *precise*. Secondly, at these acidities the free molybdenum concentration is almost negligible which means that the relative errors associated with the analytical data refinement are larger. Thus, any associated errors for these data points are relatively much larger. Indeed, these results can be likened to previous results[23] concerning negligible amounts of total hydrolysis.

These effects cause the error-square sum to increase (and hence the agreement factor, R) when these data points are included. Successful interpretation of the second series of titrations can be made, however, by assuming an identical model to that which fitted the first series and using similar pH ranges. Therefore, although the available data indicate the formation of a species of high molecular weight, it was not possible to design an experiment in which the species could be sufficiently defined. Its existence must therefore be verified by other techniques. Figure 4 illustrates the percentage speciation of molybdenum(VI) at 6.0 mmol dm^{-3} with the inclusion of a high-molecular-weight species; the formation constant is taken from the average value of the formation constants of the dummy species, (14,25), given in model 9 of Table 2.

A comparison of the two sets of data given in Table 2 shows

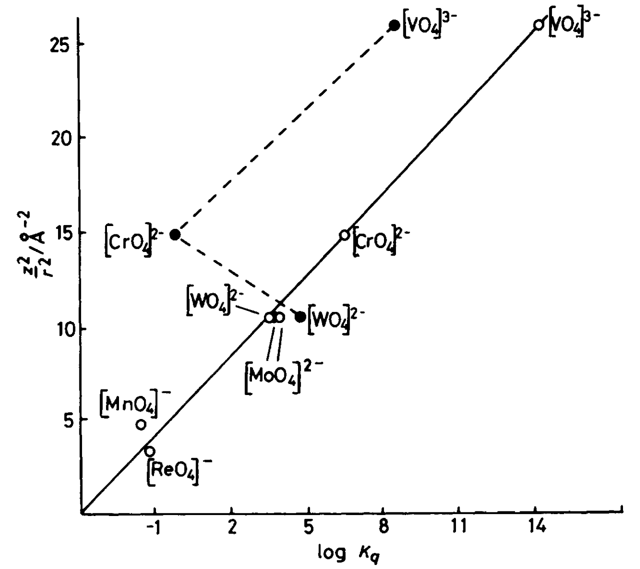

Figure 5. Electrostatic dependence of the first (○) and second (●) protonation reactions of the Group 5, 6, and 7 oxometal ions

that good agreement is obtained between the model from each set which meets the acceptance criteria (model 8). However, the differences between the formation constant calculated for any species is always much larger than the estimated standard deviation (of the formation constant) thus demonstrating the differences between accuracy and precision.

The elements vanadium, niobium, and tantalum, and chromium, molybdenum, and tungsten, in their Group valencies (maximum oxidation states) exhibit a marked tendency to form polyoxoanions in both aqueous solution and the solid state. The elements on either side, *i.e.* titanium, zirconium, and hafnium and manganese, technetium, and rhenium, show no such tendency.

Of the polyanions of the Group 5 and 6 elements, some are of low and limited molecularity (*e.g.* chromium) and others are poorly documented (*e.g.* niobium and tantalum) and/or form slowly in solution at room temperature taking hours or days to reach equilibrium (*e.g.* tungsten and some species of vanadium). Those of molybdenum are of 'high' molecularity (heptamers, octamers, decamers, and higher polymers) and are produced rapidly (minutes or less); thus the molybdenum(VI) system provides the most experimentally accessible system for the investigation of such polyanion equilibria.

How these oxometalates polymerise to form species of certain stoicheiometry is poorly understood;[36] for example, the first detectable polymeric species of molybdenum are heptamers, whereas those of tungsten are hexamers, and those of chromium are dimers. However, a number of aspects are expected to be important in this behaviour, namely: (*a*) the size of the metal ion, since it affects not only the co-ordination number but also the π-bonding ability;[36] (*b*) the charge of the metal ion; (*c*) the stability of the various monomeric species, hence the basicity of the oxygen atoms of the MO_4 moiety; and (*d*) the ability of these monomeric species to expand their co-ordination sphere by the co-ordination of water molecules.[36] The values of some of these parameters, together with the number of metal ions per discrete polymer unit, are given in Table 5 for Group 5, 6, and 7 elements.

Of immediate interest are the values, given in Table 5, of the formation constants, log K_1 and log K_2, for molybdenum(VI) which are approximately equal, when it would be expected that log $K_1 \gg$ log K_2, as is the case with chromium(VI); *i.e.* H_2CrO_4 is a much stronger acid than $[HCrO_4]^-$. It has recently been shown,[37] from consideration of the enthalpy changes of reaction, that $[HMoO_4]^-$ is tetrahedral (as is the parent ion, $[MoO_4]^{2-}$) whereas H_2MoO_4 is octahedral, and is more correctly written as $Mo(OH)_6$. Further evidence for this can be obtained by considering the protonation constants of the oxometal ions given in Table 5 as a function of z^2/r^2 (z is the charge of the monomeric anion, MO_4, and r is the Ahrens ionic radius quoted in Table 5).

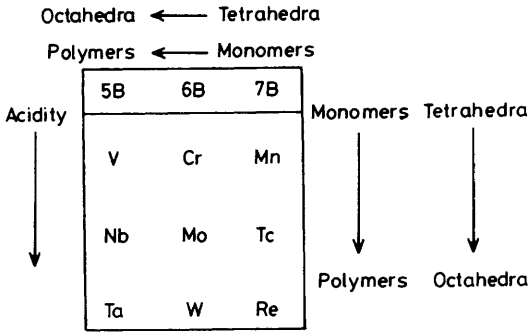

Figure 6. Some features of the Group 5, 6, and 7 oxometal ions

When the value of log K_1 for each of the oxometal ions is plotted against the function z^2/r^2, as is illustrated in Figure 5, the linearity of the plot (slope = 0.71 ± 0.03, intercept = -4.00 ± 0.32, correlation coefficient = 0.9969) suggests that the first protonation step of these ions ***does not*** involve an expansion from tetrahedral to octahedral stereochemistry. The second plot (broken line) in Figure 5, log K_2 *versus* z^2/r^2 (which is incomplete because of the lack of data), is not linear, and a marked departure occurs for molybdenum and tungsten. This behaviour therefore suggests that $[VO_4]^{3-}$, $[HVO_4]^{2-}$, $[H_2VO_4]^-$ (and $[V_2O_7]^{4-}$), $[CrO_4]^{2-}$, $[HCrO_4]^-$, H_2CrO_4 (and $[Cr_2O_7]^{2-}$), $[MoO_4]^{2-}$, $[HMoO_4]^-$, $[WO_4]^{2-}$, $[HWO_4]^-$, and of course $[MnO_4]^-$, $HMnO_4$, $[ReO_4]^-$, and $HReO_4$, are all tetrahedral whereas H_2MoO_4 and H_2WO_4 (and their polymeric species) are all octahedral. The linear plot allows the prediction of the log K_1 values (protonation of MO_4 ion) for Nb, Ta, and Tc, these being 9.42, 9.82, and -1.73, respectively.

An examination of the tendency of the monomeric ions of these elements to polymerise, and the stoicheiometry of the polymeric products, indicates two features. (*a*) The tendency to polymerise decreases along a Period and increases down a Group. (*b*) There are two polymerisation reaction types, the first preserving the tetrahedral chemistry and thus involves corner sharing of oxygen atoms, the second involving expansion to octahedral co-ordination and thus edge sharing of oxygen atoms. In the former process, the stoicheiometry is stepwise (monomers to dimers to trimers, *etc.*), whereas in the latter there are 'large jumps' of stoicheiometry (monomers to hexamers or monomers to heptamers). The occurrence of one or other of these processes for a given metal ion corresponds to the tendency of the doubly protonated monomer to become octahedral.

Collectively, considering both monomeric and polymeric species (where they occur), the tendency to expand from tetrahedral to octahedral stereochemistry parallels the tendency to polymerise; these features decrease along a Period and increase down a Group. Some of the features of the Group 5, 6, and 7 oxometalate ions are shown in Figure 6.

Kinetic Measurements.—The 'slow' equilibrium regions observed in this work are dependent upon the total molybdenum(VI) concentration. There is a tendency for the effect to be more marked and extend to higher pH values as the metal concentration increases. The compositional plots, as illustrated by Figure 4 for the total molybdenum(VI) concentration of 6.0 mmol dm^{-3}, reveal that the regions have the following features. (*a*) The regions commence at a pH where the (7,10), (7,11), and (8,12) species begin to form (> 5%). (*b*) At the same pH, the (7,9) species concentration maximises and throughout the regions continues to decline. (*c*) As the pH continues to decrease the (8,12) species concentration continues to rise and peaks at the conclusion of each region. The concentration of the (7,10) species peaks and then begins to fall within the regions. The concentrations of the (7,11) and (1,2) species continue to increase within the regions, maximising at lower pH (outside each region). These are the only species of significant concentration present within the regions.

These features led to the conclusion that the 'slow' reaction is that of the formation of the (8,12) species. The most conceivable reaction mehanism is therefore the formation of the octameric species from a heptameric and monomeric species. As already shown, the reaction is first order and reversible with respect to the uptake of hydrogen ions and may be represented by equation (6) (charges are ignored); where $x = 9$, 10, or 11,

$$[(MoO_4)_7H_x] + [(MoO_4)H_y] + H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(MoO_4)_8H_{12}] \quad (6)$$

$y = 0$, 1, or 2, $x + y = 11$, and k_1 and k_{-1} are the forward and backward rate constants, respectively. Of the three reaction mechanisms represented by equation (6) (*i.e.* $x = 9$, 10, or 11) all are possible, and indeed likely to occur since the only species which forms slowly is (8,12), the other species rapidly reaching equilibrium. The most consistent reaction mechanism with the features listed above, however, is the formation of the (8,12) from the (7,9) and (1,2) species and a proton. If we consider this reaction, the formation of the (8,12) species (or the disappearance of protons) can be determined from the rate equation (7). In solving this equation it is necessary to make two assumptions. First, the concentration of (8,12) species at $t = 0$ is zero; this assumption is reasonable since the kinetic experiments were designed so that its concentration before the addition of acid was nil (or negligible). Secondly, the rate of formation of the (8,12) species is first order and reversible; this would seem a valid assumption when considering the most likely reaction mechanism [equation (6)]. Thus, we may express the rate of formation of the (8,12) species as in equation (8),

$$\begin{aligned} &d[Mo_8O_{26}{}^{4-}]/dt \\ &= k_1[Mo_7O_{23}(OH)^{5-}][H_2MoO_4][H^+] - \\ &\qquad k_{-1}[Mo_8O_{26}{}^{4-}] = -d[H^+]/dt \quad (7) \end{aligned}$$

$$\begin{aligned} d[Mo_8O_{26}{}^{4-}]/dt &= k^o([Mo_8O_{26}{}^{4-}]_{eq} - [Mo_8O_{26}{}^{4-}]_t) = \\ -d[H^+]/dt &= k^*([H^+]_t - [H^+]_{eq}) \quad (8) \end{aligned}$$

where k^o is the rate constant of the first-order and reversible formation of $[Mo_8O_{26}]^{4-}$. The values of k^o and $[Mo_8O_{26}{}^{4-}]_t$ can be determined from equation (8); the concentrations of the other species can then be determined by subtracting the concentration of $[Mo_8O_{26}{}^{4-}]_t$ from the total molybdenum(VI) concentration, using speciation calculations since the other species are in equilibrium at each point. Substitution of equation (8) into (7), with rearrangement, leads to equation (9), which may be solved by

$$[Mo_7O_{23}(OH)^{5-}]_t[H_2MoO_4]_t[H^+]_t = \frac{k^o[Mo_8O_{26}{}^{4-}]_{eq}}{k_1} + \frac{k_{-1} - k^o}{k_1}[Mo_8O_{26}{}^{4-}]_t \quad (9)$$

linear least-squares analysis; the intercept is $k^o[Mo_8O_{26}{}^{4-}]_{eq}/k_1$ and the slope is $(k_{-1} - k^o)/k_1$. This solution produces values of 642 ± 300 dm^6 mol^{-2} s^{-1} and $(2.51 \pm 1.00) \times 10^{-5}$ s^{-1}, for k_1 and k_{-1}, respectively. The ratio of the two rate constants, k_1/k_{-1}, is the formation constant of the reaction and equals (log *K*) 7.41; the value for the same reaction from the stability measurements is 7.52, so very satisfactory agreement has been obtained from the two methods.

The kinetics of the reaction of a heptamer and monomer to produce an octamer have been studied by Honig and Kustin[38] using temperature-jump techniques. It is unfortunate that the pH range studied in their work was 6.75—5.50 and, therefore, their results cannot be compared more directly with those of the present work; all reactions in this pH range are relatively 'fast.' Even so, there is reasonable agreement between the results of the two studies. The earlier paper[38] also discusses a probable structural reaction mechanism in which the heptamer is attacked by an octahedral monomer and both polymers have six octahedral units in common. This supports the postulate that the heptameric species is $[Mo_7O_{23}(OH)]^{5-}$ since, as indicated above, the only octahedral monomeric species is H_2MoO_4.

Conclusions

An extensive potentiometric study has clarified the solution equilibria of molybdenum(VI). Although the heptameric species are dominant the octameric species, (8,12), is also significant. Differences in the interpretation between this and earlier work[5,6] can be partly attributed to the marked ionic strength dependence of the reactions,[9,30] but deficiencies in the earlier work preclude a more fruitful comparison. Our results are consistent with the presence of a high-molecular-weight species, proposed by previous workers,[6,7] in the low pH region. However, limitations of the potentiometric method prevent any detailed study in this region.

Although all reactions in the molybdate(VI) system have been assumed[2,5] to be 'fast,' a region of relatively 'slow' reactions has been identified. This region is concentration dependent, extending to higher pH values as the concentration of molybdenum increased. A study of the concentrations of the species present in, and the kinetics of, the 'slow' region indicates that this reaction is the formation of the (8,12) species.

By comparing two series of data we were able to demonstrate the difference between accuracy and precision. Indeed, the inaccuracy inherent in such measurements indicates that the differences between formation constants measured experimentally and those predicted theoretically[22,39] may be relatively large (especially for polymeric species) because of the systematic errors inherent in the experimentally determined value. Furthermore, the first protonation reaction of the oxometal ions of Groups 5, 6, and 7 may be predicted by equations based on purely electrostatic arguments. The deviation from linearity of the second protonation reaction based on the same arguments can be used (among other properties) to indicate those oxometal ions which will change the stereochemistry from tetrahedral to octahedral by co-ordination of water molecules.

Acknowledgements

The authors would like to thank Drs. J. V. Evans, T. D. Waite, and G. R. Erickson of the Environmental Chemistry Section, Australian Nuclear Science and Technology Organisation, for many useful suggestions.

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Received 25th September 1986; *Paper* 6/1906