Tungsten(VI) Equilibria: A Potentiometric and Calorimetric Investigation

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Tungsten(VI) equilibria has been investigated in the range pH 5—7.8 (corresponding to a degree of protonation, $Z \lesssim 1.2$) by potentiometric and enthalpimetric titrations at 25 °C in 1.0 mol dm^{-3} NaCl. The potentiometric data were treated with the computer program SUPERQUAD to examine a large number of reaction models. The model that gave the best fit to the data comprises $[WO_4]^{2-}$ and the four polyions $[W_6O_{20}(OH)_2]^{6-}$, $[W_7O_{24}]^{6-}$, $[HW_7O_{24}]^{5-}$, $[H_2W_{12}O_{42}]^{10-}$ with formation constants $\log \beta_{6,6} = 49.01$, $\log \beta_{7,8} = 65.19$, $\log \beta_{7,9} = 69.96$, and $\log \beta_{12,14} = 115.38$. The enthalpy and entropy changes for the formation of the polyions were calculated from the enthalpimetric data using these constants. The enthalpy values are $\Delta H^\circ_{6,6} = -231$, $\Delta H^\circ_{7,8} = -333$, $\Delta H^\circ_{7,9} = -328$, and $\Delta H^\circ_{12,14} = -542$ kJ mol^{-1}. The energetics of condensation is discussed in terms of the thermodynamic quantities for heptatungstate and heptamolybdate.

Although the chemistry of isopolytungstates has been studied extensively for many years, only a few potentiometric investigations have been reported in which equilibrium analysis by computer methods had been done.[1–5] The results of these investigations have been interpreted mainly in terms of the formation of hexameric and dodecameric polyions in addition to monomeric tungstic acid. Aveston,[2] for example, found that a reaction scheme comprising the species $[HW_6O_{21}]^{5-}$, $[H_2W_{12}O_{42}]^{10-}$, and $[H_2W_{12}O_{40}]^{6-}$ gave a satisfactory explanation of his acidity measurements at 50 °C in 3 mol dm^{-3} LiCl medium. Tytko and Glemser[3] deduced approximate equilibrium constants for the ions $[HWO_4]^-$, $[HW_2O_8]^{3-}$, $[W_6O_{21}]^{6-}$, and $[HW_6O_{21}]^{5-}$ from equilibrium data obtained at 22 °C in 3.0 mol dm^{-3} NaNO$_3$. For Sasaki's measurements[1,4] made at 25 °C in 3.0 mol dm^{-3} NaClO$_4$ the species H_2WO_4, $[W_6O_{21}]^{6-}$, $[HW_6O_{21}]^{5-}$, and $[H_2W_{12}O_{42}]^{10-}$ were found to give the best fit of the various models tried. Recently, Wesolowski *et al.*[5] reported the results of a potentiometric investigation involving measurements at various temperatures and ionic strengths in the ranges 95—295 °C and 0.10—5.1 mol dm^{-3} NaCl respectively. These authors considered several criteria to select three reaction schemes compatible with all their data, but gave slight preference to the following scheme, mainly because of its overall goodness of fit to the data: $[HWO_4]^-$, H_2WO_4, $[HW_6O_{21}]^{5-}$, $[W_6O_{21}]^{6-}$, $[W_6O_{19}]^{2-}$, and $[H_2W_{12}O_{40}]^{6-}$. The ambiguity in the choice of schemes concerned the inclusion of hexameric or heptameric species. Numerous other investigations of the reactions occurring in acidified aqueous tungstate solutions have been carried out; the results of these studies, which have been reviewed by several authors,[6–10] clearly indicate the existence of a number of simultaneous equilibria some of which are established very slowly (from minutes to weeks) and involving hexameric, decameric, dodecameric, as well as some unidentified polyions. The occurrence of a hexameric ion $[HW_6O_{21}]^{5-}$ ('paratungstate A'), originally proposed by Jander *et al.*,[11] has been accepted as certain by nearly all authors. Recently, however, the results of both Raman[12] and n.m.r.[13] investigations have been interpreted in terms of a heptameric tungstate ion, $[W_7O_{24}]^{6-}$ rather than $[HW_6O_{21}]^{5-}$; the former ion is similar to the well established heptamolybdate ion, $[Mo_7O_{24}]^{6-}$. Reaction models including a heptatungstate ion have not been considered in previous equilibrium analysis investigations at 25 °C. A renewed potentiometric investigation of this system is therefore desirable especially because of the indispensability of equilibrium data in the interpretation of results obtained by several other experimental methods,[14–16] including calorimetry. The results of a previous calorimetric investigation[17] have been interpreted in terms of the reaction model proposed by Arnek and Sasaki.[4]

In this paper we report the results of a potentiometric and calorimetric investigation of tungsten(VI) equilibria in the pH range where equilibria are established rapidly, that is for a degree of protonation, $Z \lesssim 1.2$. A new reaction model, based on a computer treatment of the data, is proposed and values for equilibrium constants as well as enthalpy and entropy changes have been calculated for the formation of the species in question.

Experimental

Reagents and Solutions.—Analytical grade chemicals (Merck p.a.) and deionized distilled water were used for the preparation of all solutions. Sodium tungstate solution, prepared from the twice recrystallized solid $Na_2WO_4 \cdot 2H_2O$, was standardized by evaporating known volumes to dryness and heating to constant weight at 400 °C; the solution was kept in a polyethylene bottle. Sodium chloride was purified as follows: a saturated solution was prepared and allowed to stand for about a week whereupon impurities which precipitated were filtered off with a G4 sintered glass crucible. From this solution relatively large and pure sodium chloride crystals were grown by slow evaporation at 25 °C in a dust-free environment. These crystals were filtered off, washed with distilled water, and used to prepare a stock solution which was standardized by evaporating known volumes to dryness and heating to constant weight at 160 °C. Hydrochloric acid was standardized by titration with a borax solution prepared from recrystallized $Na_2B_4O_7 \cdot 10H_2O$.

Potentiometric Measurements.—The experiments were carried out as titrations at 25.0 ± 0.05 °C in 1.0 mol dm^{-3} NaCl medium. A 100-cm^3 solution, B mol dm^{-3} in sodium tungstate and $(1.0 - 2B)$ mol dm^{-3} in sodium chloride, was titrated with a hydrochloric acid solution, 1.0 mol dm^{-3} in sodium chloride. The value of B was kept constant by adding from another burette an equal volume of a solution containing $2B$ mol dm^{-3} tungstate and $(2.0 - 4B)$ mol dm^{-3} sodium chloride. Titrations were done at nine different tungstate concentrations, *i.e.* B had the values 0.0005, 0.0010, 0.0020, 0.0040, 0.0080, 0.0160, 0.0320, 0.0640, and 0.1234 mol dm^{-3}. A stream of nitrogen was passed successively through sulphuric acid, sodium hydroxide, distilled water, and 1.0 mol dm^{-3} sodium chloride and then bubbled slowly through the titration solution, which both stirred the solution and excluded carbon dioxide from the system.

The free hydrogen-ion concentration, h, of the solution was determined by measuring the potential to ±0.1 mV with a

Labion model 17 potentiometer. The cell shown below was used. The electrode system was standardized by titration of 1.0 mol dm^{-3} sodium chloride with hydrochloric acid (also 1.0 mol dm^{-3} with respect to sodium chloride) and the value of E^0 calculated from the measured potential (in mV) using equation (1) where $pH_c = -\log h$. A value for E^0 was determined before

$$E = E^0 + 59.16\,pH_c \qquad (1)$$

each titration of tungstate with acid and checked afterwards by a single E measurement of the same solution used to determine E^0. The data for a titration were accepted only if the difference between the two E^0 values was $\leqslant 0.3$ mV.

Glass electrode (Schott)	Test solution	Bridge solution	Reference electrode
	H^+, 1.0 mol dm^{-3} Na^+ B mol dm^{-3} WO_4^{2-} $(1.0 - 2B)$ mol dm^{-3} Cl^-	0.1 mol dm^{-3} KCl 0.9 mol dm^{-3} NaCl	Hg(l) Hg_2Cl_2(s)

Calorimetric Measurements.—An isothermal titration calorimeter, Tronac model 550, described elsewhere[18,19] was used for the measurements. Sodium tungstate solution (20.0 cm^3) was titrated with hydrochloric acid from a 2.5-cm^3 Gilmont precision microburette and the data collected as described previously.[20,21]

The concentrations of the sodium tungstate solutions used in the titrations were 0.1, 0.05, and 0.01 mol dm^{-3} and those of the hydrochloric acid solutions were 1.0, 0.5, and 0.1 mol dm^{-3} respectively. All solutions were made 1.0 mol dm^{-3} with respect to sodium ions by addition of sodium chloride. Blank titrations were done to correct for the heat of dilution; for the titration with 0.01 mol dm^{-3} hydrochloric acid no correction was necessary and for the higher acid concentrations the correction amounted to $\leqslant 1\%$ of the total heat measured.

Results and Discussion

Potentiometric Measurements.—The results of a number of potentiometric titrations are shown in Figure 1 as plots of Z against pH_c; Z represents the degree of protonation and is given by equation (2) where H is the total acid concentration. The pH_c

$$Z = (H - h)/B \qquad (2)$$

measurements for this investigation correspond to $Z \lesssim 1.14$ for which stable potentials were obtained practically immediately after addition of acid to the tungstate solution. From $Z \gtrsim 1.14$ the potential started to drift towards higher pH_c so that constant values could not be obtained within a reasonable period of time. At these Z values slow equilibria occur and the change in pH_c of a series of solutions was monitored for several weeks. The results of these measurements will be reported elsewhere.

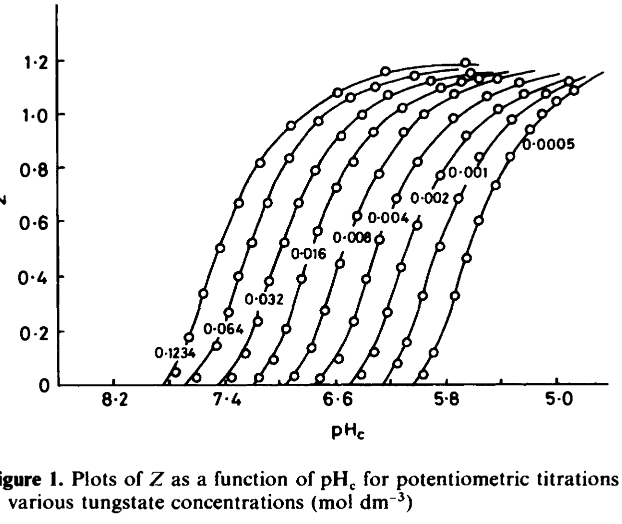

Figure 1. Plots of Z as a function of pH_c for potentiometric titrations at various tungstate concentrations (mol dm^{-3})

Equilibrium data at $Z < 1.10$ were treated with different computer programs to find a reaction model that would give the 'best' and presumably the correct description of the system. Species previously suggested on the grounds of equilibrium analysis and for which equilibrium constants pertaining to different ionic media (at 25 °C) have been reported are[1-5] $[HWO_4]^-$ (1,1), H_2WO_4 (1,2), $[HW_2O_8]^{3-}$ (2,1), $[W_6O_{21}]^{6-}$ (6,6), $[HW_6O_{21}]^{5-}$ (6,7), and $[H_2W_{12}O_{42}]^{10-}$ (12,14). Except for the $[H_2W_{12}O_{42}]^{10-}$ polyion of known structure,[9,22] the other species are formulated with as few H_2O molecules as possible; the numbers in parentheses refer to the stoicheiometric coefficients p and q in the general equation (3).

$$p WO_4^{2-} + q H^+ \rightleftharpoons (WO_4^{2-})_p H^+_q \qquad (3)$$

Only a few species are expected to occur at $Z < 1.10$. The first model examined in the computations, using the program MINIQUAD,[23] was the one proposed by Arnek and Sasaki[4] comprising the species (1,2), (6,6), (6,7), and (12,14). The (1,2) species was rejected (log β negative), but a good fit was obtained and the standard deviations of the constants of the remaining species were low enough to be acceptable (4.6, 5.1, and 6.8% respectively, *cf.* Table 1). By substituting the (7,8) species for the (6,7) the fit could be improved considerably; the sum of squares was reduced by 14%. Although the (1,2) species was not rejected the standard deviation of its formation constant had an unacceptably high value (> 80%). Addition of the (7,9) species to the previous model brought about a further significant improvement in the fit and also resulted in the rejection of the (1,2) species. This model comprising $[WO_4]^{2-}$ and the four polyions (6,6), (7,8), (7,9), and (12,14), was the 'best' model although many other models, including species with $p = 2$, 8, and 9, have been examined to improve the fit. Calculations with models containing both the (6,7) and the (7,8) species always resulted in rejection of the (6,7) species, see for example model 4.

Some time after these calculations had been finished[24] a new improved computer program, SUPERQUAD,[25] developed by the authors of MINIQUAD, became available. An important feature of this program is that the equilibrium constants are determined by a minimization of an error square sum based on measured potentials. In MINIQUAD the total concentrations of the reactants are minimized so that for the data of the present investigation (when treated together) more weight is given to the titrations pertaining to the highest concentrations. The possibility therefore exists that species with small p values, which have their greatest relative concentrations at low total tungsten(VI) concentrations, could be overlooked. In view of this and SUPERQUAD's excellent model-selection facilities we considered it worthwhile to recalculate our data using this program. Models that include species with ill defined formation constants (*i.e.* calculated standard deviation > 33% of the value, or log β has a negative value) are rejected automatically by the program; the species with the 'worst' constant is removed and the refinement is then continued with this new model.

Table 1. Results of model testing with the computer programs MINIQUAD and SUPERQUAD. Formation constants, log (β_{pq} ± 3σ), for species $(WO_4^{2-})_pH^+_q$

MINIQUAD Model	$W(OH)_6$ log $\beta_{1,2}$	$[W_6O_{21}]^{6-}$ log $\beta_{6,6}$	$[HW_6O_{21}]^{5-}$ log $\beta_{6,7}$	$[W_7O_{24}]^{6-}$ log $\beta_{7,8}$	$[HW_7O_{24}]^{5-}$ log $\beta_{7,9}$	$[H_2W_{12}O_{42}]^{10-}$ log $\beta_{12,14}$	Error square sum × 10^6	
1	Negative	49.07 ± 0.06	56.48 ± 0.06			115.20 ± 0.09	11.32	
2	10.2 ± 1.1	48.81 ± 0.13		65.37 ± 0.04		115.00 ± 0.14	9.69	
3	Negative	48.7 ± 0.15		65.46 ± 0.01	70.74 ± 0.16	114.77 ± 0.21	7.25	
4	Negative		Negative	65.46 ± 0.01	70.82 ± 0.13	Negative	10.25	
SUPERQUAD							*s*	χ^2
1	9.39 ± 0.08	49.30 ± 0.06	56.09 ± 0.05			115.60 ± 0.05	3.41	40.3
3		49.01 ± 0.12		65.19 ± 0.04	69.96 ± 0.06	115.38 ± 0.08	2.98	11.7

In addition to models 1 and 2, listed in Table 1, a large number of models were examined with SUPERQUAD by introducing practically all possible species with *p* values ranging from 1 to 17. The best fit to the experimental data was again obtained with model 3 which includes the heptatungstate species and this fit was also distinctly better than that of model 1, containing the hexatungstate ion, $[HW_6O_{21}]^{5-}$, instead of heptamers. The very good fit, as indicated by the relatively small value of the *s* statistic, the sample deviation,[25] is noteworthy keeping in mind that nine titration curves are involved while the errors in the measured potential and added volume have been estimated as 0.1 mV and 0.02 cm^3 (0.01 cm^3 for each burette) respectively.

It is interesting to compare the values for the equilibrium constants of the heptatungstate ions, namely log $\beta_{7,8} = 65.19$ and log $\beta_{7,9} = 69.96$, with those of the heptamolybdate ions, log $\beta_{7,8} = 52.79$ and log $\beta_{7,9} = 57.43$, which also apply to 1.0 mol dm^{-3} NaCl.[26,27] Although the value for the protonation constant of heptatungstate (log $K = 4.77$) is almost the same as that of heptamolybdate (log $K = 4.64$) the formation constant of heptatungstate is much greater than that of heptamolybdate which reflects the greater tendency towards condensation of tungsten(VI). It is because of these large values of the stability constants of the tungsten(VI) polyions that the (1,1) and (1,2) species occur in such low concentrations as to impair characterization of their equilibria by potentiometry. The (6,6) species is the least stable of the tungsten(VI) polyions and is merely a minor species attaining a maximum share of only 11% of the total tungsten(VI) even at the highest concentration (0.1234 mol dm^{-3}) used in this investigation (Figures 2 and 3). Its stability constant is calculated with a rather low standard deviation (10%) and on statistical grounds it appears quite acceptable, but less so from a structural point of view. If this ion is formulated as $[W_6O_{21}]^{6-}$, it is not possible to build a structure consisting of edge-sharing WO_6 octahedra which satisfies Lipscomb's principle,[28] *i.e.* that no octahedron should have more than two unshared vertices. However, if one is willing to accept a structure in which terminal oxygen atoms are protonated,[9] the (6,6) species can be formulated as $[W_6O_{20}(OH)_2]^{6-}$. A structure can then be constructed in which none of the six octahedra would have more than two terminal oxygens, two oxygens being 'non-terminal' because they are protonated. This structure can be considered as a fragment of $[W_7O_{24}]^{6-}$ (or $[Mo_7O_{24}]^{6-}$ which has the same structure[9,13]) as it can be obtained by removing any octahedron from the $[W_7O_{24}]^{6-}$ structure except the central one which has no terminal oxygens.

It is seen that the values calculated for the equilibrium constants employing SUPERQUAD are slightly different from those calculated with MINIQUAD. Because of the former program's superior refinement algorithm, its values for the constants are regarded as being the closest to the 'true values' and were therefore used in treating the data of the calorimetric investigation described in the following section.

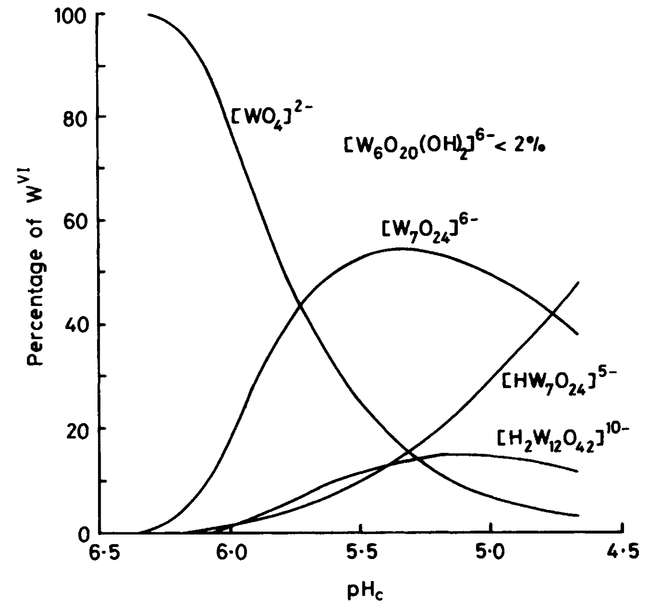

Figure 2. Concentration of polytungstates, expressed as a percentage of the total tungsten(VI) concentration (0.001 mol dm^{-3}) as a function of pH_c

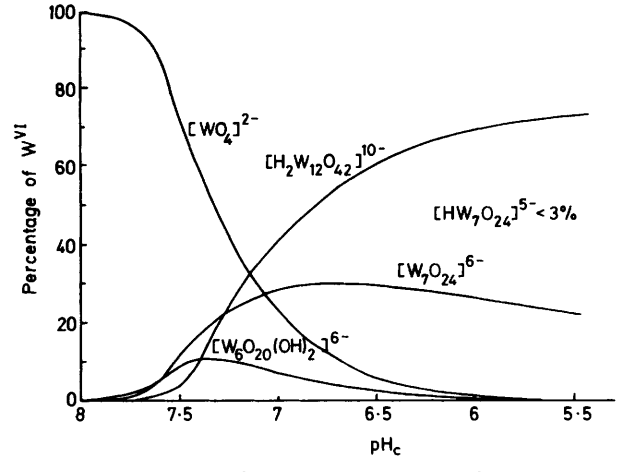

Figure 3. Concentration of polytungstates, expressed as a percentage of the total tungsten(VI) concentration (0.1 mol dm^{-3}), as a function of pH_c

Calorimetric Investigation.—The results of the enthalpimetric titrations are shown in Figure 4 where the amount of heat measured, *Q*, is plotted against the molar ratio of acid to tungstate. A practically linear relationship between *Q* and the

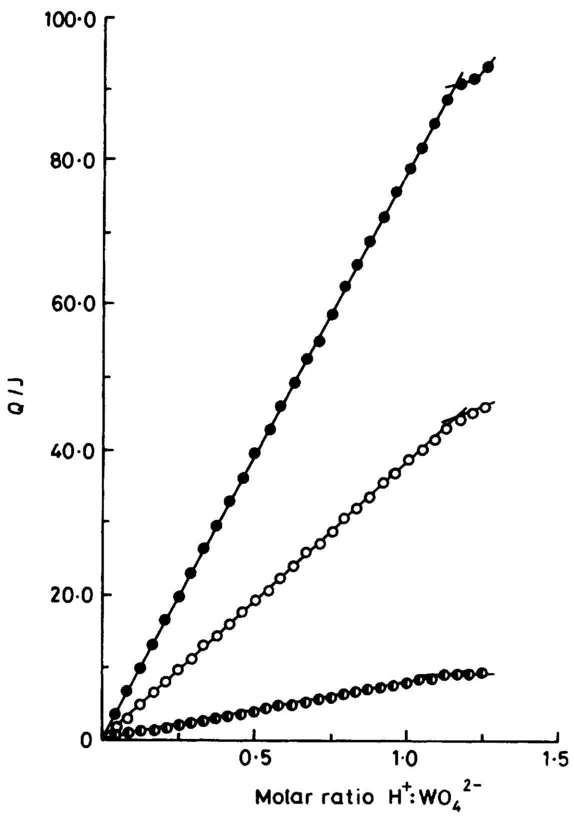

Figure 4. Measured heat, Q, as a function of the molar ratio of acid to tungstate for the titration of (◐) 0.01 mol dm^{-3} $[WO_4]^{2-}$ with 0.1 mol dm^{-3} HCl, (○) 0.05 mol dm^{-3} $[WO_4]^{2-}$ with 0.5 mol dm^{-3} HCl, and (●) 0.1 mol dm^{-3} $[WO_4]^{2-}$ with 1.0 mol dm^{-3} HCl

amount of acid added is observed which indicates that the enthalpy change involved per mol of acid consumed in the formation of the different polynuclear tungstate species is about the same. The enthalpy change involved per mol of tungstate reacted also appears to be very similar for the different polyanions, as reflected by the nearly linear increase in Q with increasing tungstate concentration (at any particular molar ratio) in spite of the different species distribution at the different concentrations. These preliminary observations were borne out by the results of the quantitative treatment of the data. The break observed in each of the curves indicates that the formation of a major species has been completed at a molar ratio of about 1.15. An endothermic reaction which was only just measurable at the break was immediately followed by some slow exothermic reaction(s). Because of overlapping of equilibria and experimental uncertainties the molar ratio at which the break in the curve occurs cannot be taken as a measure to distinguish between a (6,7) or a (7,8) species which have Z values of 1.17 and 1.14 respectively. Breaks in conductivity, pH$_c$, and other titration curves have often been presented in the past as evidence for the existence of a (6,7) species.[9]

The enthalpy changes for the formation of the various polyanions were calculated from the measured heat at $Z \leqslant 1.1$ (corrected for dilution effects) using equation (4) where n is the

$$Q = \Sigma n_{pq} \Delta H^{\circ}_{pq} \qquad (4)$$

number of moles formed and ΔH°_{pq} the molar enthalpy change for the formation of a given polyion at 25 °C in 1 mol dm^{-3} NaCl medium. Values for n_{pq} at each titration point were calculated from the concentrations of the species obtained by simultaneous solution (using Newton's method[29]) of the two mass-balance equations (5) and (6). The set of linear equations

$$B = b + \Sigma p \beta_{pq} b^p h^q \qquad (5)$$

$$H = h + \Sigma q \beta_{pq} b^p h^q \qquad (6)$$

thus obtained from corresponding Q and n values were solved for the unknown ΔH°_{pq} parameters following a least-squares procedure.[30]

Table 2. Thermodynamic quantities for formation of the polytungstate ions in 1 mol dm^{-3} NaCl medium (298 K)

		ΔG°	ΔH°	$T\Delta S^{\circ}$	$\Delta H^{\circ}/p$
Polyion	log β_{pq}	kJ mol^{-1}			
$[W_6O_{20}(OH)_2]^{6-}$	49.01	−279.8	−231 ± 3	49	−38.5
$[W_7O_{24}]^{6-}$	65.19	−372.1	−333 ± 2	39	−47.6
$[HW_7O_{24}]^{5-}$	69.96	−399.3	−328 ± 3	71	−46.9
$[H_2W_{12}O_{42}]^{10-}$	115.38	−658.6	−542 ± 4	117	−45.2

The thermodynamic quantities for the formation of the four proposed polyanions $[W_6O_{20}(OH)_2]^{6-}$, $[W_7O_{24}]^{6-}$, $[HW_7O_{24}]^{5-}$, and $[H_2W_{12}O_{42}]^{10-}$ are listed in Table 2. Two of these species, *i.e.* $[W_6O_{20}(OH)_2]^{6-}$ and $[H_2W_{12}O_{42}]^{10-}$, were included in the model accepted by Arnek[17] for the interpretation of his calorimetric data. The ΔH° values for $[W_6O_{20}(OH)_2]^{6-}$ and $[H_2W_{12}O_{42}]^{10-}$ determined in the present investigation, namely −231 and −542 kJ mol^{-1}, can therefore be compared with those reported by Arnek[17] for 3.0 mol dm^{-3} NaClO$_4$ medium, *i.e.* −239 ± 4 and −531 ± 8 kJ mol^{-1} respectively. The agreement between the two sets of values indicates that the enthalpy changes for the formation of these tungsten polyions are little affected by changes in ionic strength. This finding also agrees with the observation by Arnek[17] that the heat effects for titrations in 3.0 mol dm^{-3} NaClO$_4$ are about the same as those for titrations without NaClO$_4$. The formation constants and ΔG° values, however, are significantly different in the two media. For example, log $\beta_{7,8}$ increases from 49.01 to 52.46 and log $\beta_{12,14}$ from 115.38 to 123.24 when the medium is changed from 1 mol dm^{-3} NaCl to 3 mol dm^{-3} NaClO$_4$. A substantial amount of this increase in log β values must therefore be entropy related.

Since the model now proposed for the tungsten(VI) system at $Z \leqslant 1.14$ includes heptanuclear ions, similar to those generally accepted for the molybdenum(VI) systems, it is useful to compare the corresponding thermodynamic parameters for the two systems. From the values of the constants listed in Tables 2 and 3 it is seen that the protonation constants for $[W_7O_{24}]^{6-}$ and $[Mo_7O_{24}]^{6-}$ in 1 mol dm^{-3} NaCl are practically identical. The formation constant for $[W_7O_{24}]^{6-}$ (log $\beta_{7,8}$ = 65.19) is, however, much greater than that for $[Mo_7O_{24}]^{6-}$ (log $\beta_{7,8}$ = 52.79).[27] Enthalpy and entropy values for the formation of heptamolybdates in 1 mol dm^{-3} NaCl are not available, but have been reported for 3.0 mol dm^{-3} NaClO$_4$.[14] Assuming that ΔH° values are not much affected by the difference in ionic medium, a comparison of the enthalpy changes for the formation of $[W_7O_{24}]^{6-}$ (−333 kJ mol^{-1}) and $[Mo_7O_{24}]^{6-}$ (−234 kJ mol^{-1}) shows that the enthalpy factor is the reason for the much greater stability of the tungsten polyion. The enthalpy change for the condensation process is favourable because of the bond energy gained when the tetrahedral tungsten or molybdenum atoms expand their co-ordination spheres from four to six. Expansion of co-ordination is therefore more favourable for tungsten than for molybdenum. Part of this effect can be rationalized in terms of stronger σ and especially π

Table 3. Some thermodynamic quantities for formation of heptamolybdate ions in 1 mol dm^{-3} NaCl[30] and 3.0 mol dm^{-3} NaClO$_4$[14] (298 K)

Polyion	log β_{pq}	ΔH°/kJ mol^{-1}	$T\Delta S^\circ$/kJ mol^{-1}	Medium
$[Mo_7O_{24}]^{6-}$	52.79	—	—	1.0 mol dm^{-3} NaCl
$[HMo_7O_{24}]^{5-}$	57.43	—	—	1.0 mol dm^{-3} NaCl
$[Mo_7O_{24}]^{6-}$	57.74	-234 ± 1	95	3.0 mol dm^{-3} NaClO$_4$
$[HMo_7O_{24}]^{5-}$	62.14	-223 ± 1	131	3.0 mol dm^{-3} NaClO$_4$

metal–oxygen bonding in molybdate than in tungstate because of the smaller size of molybdenum. In octahedral co-ordination, bond distances are greater and π bonding should make a smaller contribution to the total bond energy. The gain in bond energy when the co-ordination number is increased from four to six will therefore be smaller for molybdenum than for tungsten. In the case of the much smaller chromium(VI), this effect should be much greater and together[10] with the less favourable cation-to-anion radius ratio for six-co-ordination could explain the absence of chromium(VI) polyanions consisting of edge- and corner-sharing octahedra. In dichromate and some other chromium(VI) condensed species the tetrahedral configuration is retained.[31]

The greater tendency of tungsten(VI) than molybdenum(VI) to increase its co-ordination number with respect to oxygen implies a significantly greater protonation constant for $[HWO_4]^-$ to form $W(OH)_6$ than for $[HMoO_4]^-$ to form $Mo(OH)_6$; there is reason to believe that the octahedrally co-ordinated acids are better formulated as $MO_2(OH)_2(H_2O)_2$.[32] Values of the protonation constant for $[HWO_4]^-$ (log $K = 4.6$)[33] and $[HMoO_4]^-$ (log $K = 3.8$)[34] which apply to the same ionic strength and temperature (0.1 mol dm^{-3} Na$^+$ and 20 °C) are in agreement with such a prediction; the protonation constants of $[WO_4]^{2-}$ (log $K = 3.5$) and $[MoO_4]^{2-}$ (log $K = 3.7$) have about the same values.

Finally, if the ΔH° values for the formation of the different tungsten polyions in 1 mol dm^{-3} NaCl medium are compared in terms of the number of tungsten(VI) atoms involved, it is seen that the enthalpy change per tungsten atom ($\Delta H^\circ/p = -38.5$ kJ mol^{-1}) is significantly smaller for the (6,6) species than for the other three polyions ($\Delta H^\circ/p = -45$ to -47 kJ mol^{-1}). From this it may be concluded that the (6,6) species has a relatively less stable structure than those of the other polytungstates. This conclusion is in accordance with the fact that a polyanion structure, which satisfies the Lipscomb principle,[28] cannot be constructed for the (6,6) ion, as has been discussed in the previous section.

Conclusions

The reaction model that emerged from a computer treatment of potentiometric data of $Z \leqslant 1.1$ comprises $[WO_4]^{2-}$ and the polyions $[W_6O_{20}(OH)_2]^{6-}$, $[W_7O_{24}]^{6-}$, $[HW_7O_{24}]^{5-}$, and $[H_2W_{12}O_{42}]^{10-}$. This model differs from models previously proposed in that heptameric species are included. Calorimetric data have been interpreted in terms of this model and values obtained for the formation constants were used to calculate enthalpy and entropy changes for the formation of the various polyions. Some insight into the energetics of condensation could be gained by a comparison of the enthalpy change for the formation of heptatungstate and heptamolybdate.

Acknowledgements

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