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Hydrolysis of Tungsten(VI): Ultracentrifugation, Acidity Measurements, and Raman Spectra of Polytungstates[1]

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The aggregates formed on acidification of alkali tungstate solutions have been studied by equilibrium ultracentrifugation at 50°, acidity measurements at 50°, and Raman spectroscopy at *ca.* 35°. Equilibrium ultracentrifugation indicated that in a freshly prepared solution of sodium paratungstate, $Na_{10}W_{12}O_{41} \cdot 28H_2O$, the main tungstate species is the ion $W_{12}O_{41}^{10-}$, which hydrolyzes slowly to give a mixture of $HW_6O_{21}^{5-}$ and $W_{12}O_{41}^{10-}$. A similar mixture is obtained when an alkali tungstate solution is acidified to give a proton binding $\mathbf{p} = {}^7/_6$; at higher acidities $W_{12}O_{39}^{6-}$ is formed. The close correspondence of Raman spectra of $Na_{10}W_{12}O_{41} \cdot 28H_2O$, which has been shown elsewhere to contain polyanions with twelve tungsten atoms, and a concentrated solution of lithium tungstate acidified to $\mathbf{p} = {}^7/_6$ indicates that the dodecatungstate predominates at high concentration. The potentiometric acidity measurements also may be interpreted by postulating only these three polyanions. The least-squares refined equilibrium constants (3 *M* LiCl medium, 50°) are

$$7H^+ + 6WO_4^{2-} = 3H_2O + HW_6O_{21}^{5-} \qquad \log K_{7,6} = 53.98 \pm 0.02$$

$$14H^+ + 12WO_4^{2-} = 7H_2O + W_{12}O_{41}^{10-} \qquad \log K_{14,12} = 110.03 \pm 0.05$$

$$18H^+ + 12WO_4^{2-} = 9H_2O + W_{12}O_{39}^{6-} \qquad \log K_{18,12} = 132.51 \pm 0.03$$

The chemistry of the isopolytungstates has been intensively studied for several decades. Numerous experimental methods have been used and almost equally numerous hypotheses made on the species existing in acidified tungstate solutions. As Kepert[3] cites over 200 references in a recent review of tungstates, only the background of the problem along with a few papers published since Kepert's review will be discussed. The limitations of some of the methods used have been discussed in a paper on the analogous molybdate system.[4]

Marked changes in properties such as pH, conductivity, and diffusion occur on acidification of alkali tungstate solutions when $^7/_6$ and $^9/_6$ moles of acid per mole of tungstate have been added. The free acid in such solutions is usually negligible so that the average number of protons bound per tungsten atom, $\mathbf{p}$, is also $^7/_6$ or $^9/_6$. The corresponding crystalline solids are referred to as paratungstates and metatungstates, respectively. This stoichiometry has been taken to imply polyanions containing six tungsten atoms; thus Souchay[5] and Jander[6] both propose that the dominant complex between $\mathbf{p} = 0$ and $^7/_6$ is $HW_6O_{21}^{5-}$.

Souchay also proposed that $HW_6O_{21}^{5-}$ is slowly transformed in solution to an ion "paratungstate B" with the same formula but differing in some of its chemical reactions. According to Jander, in concentrated solutions $H_3W_6O_{21}^{3-}$ condenses to $W_{12}O_{39}^{6-}$.

Sasaki[7,8] interpreted his acidity measurements of tungstate solutions in 3 *M* $NaClO_4$ at 25° by assuming only the single species $HW_6O_{21}^{5-}$. In subsequent work at 80° and in 1 *M* $NaClO_4$ a series of hexatungstates $H_nW_6O_{21}^{(6-n)-}$ where $n = 1, 2, 3,$ or 4 were postulated in order to fit his data to the calculated titration curves. Glemser[9] found that the molecular weights of the tungstate species in solutions with $\mathbf{p} = {}^7/_6$ and $^9/_6$ as measured with the ultracentrifuge were more consistent with the formulations $W_{12}O_{41}^{10-}$ and $W_{12}O_{39}^{6-}$, although as apparently no supporting electrolyte was used these conclusions must be treated with caution. Schwarzenbach,[10] using flow methods, measured the acidity of polytungstate solutions within a few deciseconds of the addition of acid and base and suggested that a tetramer, a hexamer, and a series of dodecamers exist under the appropriate conditions.

Many workers have reported that equilibrium is reached slowly, and Duncan and Kepert[11] have taken advantage of this fact to separate the components using paper chromatography. The four separate bands so obtained were assigned the formulas WO_4^{2-}, $HW_6O_{21}^{5-}$, $H_3W_6O_{21}^{3-}$, and "paratungstate B" of unknown composition.

Thus although there is general agreement on the $\mathbf{p}$ value of the various species existing in solution and also that these species contain some multiple of six tungsten atoms, there is some dispute as to whether hexamers or dodecamers predominate. It therefore seemed worthwhile to apply the technique of equilibrium ultracentrifugation in an attempt to settle the degree of polymerization of the polytungstates in solution. It should be noted in the following that species such as $HW_6O_{21}^{5-}$ or $W_{12}O_{41}^{10-}$ could equally well be

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[2] National Chemical Laboratory, Teddington, England. Guest Scientist, Oak Ridge National Laboratory, during 1963.

[3] D. L. Kepert, *Progr. Inorg. Chem.*, **4**, 199 (1962).

[4] J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, **3**, 735 (1964).

[5] P. Souchay, *Ann. Chim.* (Paris), **18**, 61, 169 (1943).

[6] G. Jander and U. Kruerke, *Z. anorg. allgem. Chem.*, **265**, 244 (1951).

[7] Y. Sasaki, *Acta Chem. Scand.*, **15**, 175 (1961).

[8] Y. Sasaki, Abstracts, Proceedings of Seventh International Conference on Coordination Chemistry, Stockholm, 1962.

[9] O. Glemser and W. Holznagel, *Angew. Chem.*, **72**, 918 (1960).

[10] G. Schwarzenbach, G. Geier, and J. Littler, *Helv. Chim. Acta*, **45**, 2601 (1962).

[11] J. F. Duncan and D. L. Kepert, *J. Chem. Soc.*, 5317 (1961).

written $H_7(WO_4)_6^{5-}$ or $H_{14}(WO_4)_{12}^{10-}$ as neither the ultracentrifuge nor acidity measurements provide any information on the degree of hydration.

Experimental

(1) **Centrifugation.**—Centrifugations were carried out using a Spinco Model E ultracentrifuge with a five-cell rotor for the equilibrium experiments and a single-cell rotor for the runs using a short column of solution. Interference optics with 12-mm. cells were used, the temperature was 50°, and speeds of rotation varied between 14,390 and 20,370 r.p.m. Full details of centrifugation technique and computational procedure have been presented elsewhere.[12]

(2) **Density and Refractive Index Measurements.**—Densities at 50° were measured with a *ca.* 24-ml. pycnometer and refractive index increments at the same temperature with a Brice-Phoenix differential refractometer.

(3) **Acidity Measurements.**—The e.m.f. of the cell

$$\text{glass electrode} \mid H^+, Li^+ (3\ M), (H_pWO_4^{(2-p)-}, Cl^-) \parallel LiCl\ (3\ M), AgCl(s);\ Ag(s)$$

was measured with a Cary Model 31 vibrating reed electrometer. The response of the glass electrode (Leeds and Northrup lithium glass Type 117163) was checked with a series of HCl–LiCl mixtures 3 *M* in chloride and was found to approach the theoretical value at 50° of 64.13 mv./equiv. of H^+ at low acidities. A buffer solution (0.01 *M* lithium acetate, 0.01 *M* acetic acid, in 2.99 *M* LiCl) was used as a secondary standard to check the electrode system every hour. The acidity of the tungstate solution was taken as

$$\log c_H = \log (c_H)_{\text{buffer}} + (E_{W(VI)\text{soln}} - E_{\text{buffer}})/64.13$$

where $\log (c_H)_{\text{buffer}} = -4.546$ at 50° was found by comparison with the standard acids. The precision of measurement was better than 0.1 mv., although the accuracy of determination of $\log c_H$ is less than implied by this precision. Although steady e.m.f. values were obtained at 50° for standards and tungstate solutions, somewhat different potentials were obtained for the same solution after the electrodes had been rinsed in 3 *M* LiCl at room temperature. These differences were usually less than 0.5 mv. and could probably be eliminated by operating continuously at 50°, *e.g.*, in an air thermostat. Because uncertainties arising from activity coefficient variations and junction potentials would remain, the extra equipment and inconvenience involved in doing so did not seem warranted.

Solutions were prepared by volume at 25° using calibrated burets and, as the density of the solutions at 25 and 50° was found, for the present purpose, to be insensitive to tungstate concentration over the range studied, a constant factor was used to convert the molarities at 25° to 50°.

(4) **Raman Spectra.**—Raman spectra at *ca.* 35° were obtained with a Cary Model 81 spectrophotometer. The 4358 Å. mercury line was isolated with a filter solution of Cyasorb U.V. 24 and ethyl violet in *n*-propyl alcohol solution. The cell used for the crystalline spectrum was developed by Keller.[14] Standard Cary 7-mm. cells were used for the solutions.

(5) **Materials.**—Reagent grade sodium tungstate was recrystallized once in an atmosphere of N_2. Lithium tungstate was prepared by cation exchange of sodium tungstate using a column of Dowex 50W-X12 in the Li^+ form.

Sodium tungstate was analyzed by drying to constant weight at 150° and weighing as Na_2WO_4. The analysis was checked by anion exchange using a column of Dowex 1-X8 in the OH^- form and titrating the effluent with standard acid. The two methods agreed within 0.1%, indicating that $p = 0$ as expected for the tungstate.

Sodium paratungstate was prepared by crystallizing a solution of Na_2WO_4 to which 1.167 moles of HCl per mole of tungstate had been added. The product was recrystallized once. Analysis of the product by direct titration with base was not possible due to slowly drifting pH values and an indefinite end point. However, by boiling the paratungstate with a known amount of standard NaOH solution to convert it to Na_2WO_4 and then titrating with standard acid a sharp end point in the region of pH 9 was obtained. The solution was then evaporated and the residue dried to constant weight at 50°; subtraction of the known weight of NaCl yielded the weight of Na_2WO_4. The analysis corresponded to the formula $Na_{0.833}H_{1.167}WO_4 \cdot 1.683H_2O$ which is equivalent to $Na_{10}W_{12}O_{41} \cdot 27.2H_2O$.

(6) **Refractive Index Increments and Volumes.**—For the computation of degrees of polymerization from centrifuge data, the values of the refractive index increments dn/dc and the partial specific volumes $\bar{v}$ of the polymeric components and supporting electrolytes are needed. For the tungstate solutions, $\Delta n/c$ and the apparent molal volume ϕ_v were found not to vary significantly with concentration and the following average values were used to compute dn/dc and $\bar{v}$: $Na_{5/6}H_{7/6}WO_4$ in 1 *M* $NaClO_4$, $\Delta n/c = 0.0265$ l. monomole^{-1}, $\phi_v = 46$ ml. g.$^{-1}$; $Li_{5/6}H_{7/6}WO_4$ in 1 *M* LiCl, $\Delta n/c = 0.0270$, $\phi_v = 41$. For the supporting electrolytes the refractive index increments and partial specific volumes found at 50° were: LiCl, $dn/dc = 0.0090$ l. mole^{-1}, $\bar{v} = 0.443$ ml. g.$^{-1}$; $NaClO_4$, $dn/dc = 0.0067$, $\bar{v} = 0.392$. These values are approximate but are sufficiently accurate for the present purpose; thus, the experimental scatter about the mean of the volume and refractive index data for the tungstates was about 4% and 1%, respectively, resulting in an uncertainty of about 1% in the degree of polymerization, in each case.

Results

(1) **Ultracentrifugation.**—For a detailed discussion of the effect of uncertainty in the charge per monomer unit, z', of a polymeric solute sedimenting in a supporting electrolyte on the degree of polymerization of the solute, N_w, the reader is referred to ref. 12. Briefly the computed value of N_w for a monodisperse solute sedimenting in the presence of a supporting electrolyte with a common ion depends on z' and the concentration of the solute c_2' relative to that of the supporting electrolyte, c_3. As part of the variation of N_w with charge is concentration dependent, centrifugation at different relative concentrations of c_2' and c_3 will give, within the assumptions of the treatment, concordant results only for a single value of z', which is often less than that implied by complete dissociation of the solute. Approximations involved in treatment of data for a solute analogous to the present one (in that it was polydisperse, charged, and its various species had different refractive index increments and volumes) have been discussed earlier.[15]

(a) **Centrifugation in $NaClO_4$ Supporting Electrolyte.**—Preliminary ultracentrifugation at 25° of a 0.05 *M* W(VI) solution adjusted to $p = {}^7/_6$ in 1 *M* $NaClO_4$, *i.e.*, corresponding to p for sodium paratungstate, showed N_w to increase slowly over several days with no stable fringe pattern being obtained; eventually crystals of sodium paratungstate formed in the centrifuge cell. On increasing the rotor temperature to 50° the crystals dissolved and a stable fringe pattern was obtained within 1 week at this temperature.

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[12] J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, **63**, 787 (1959). For more recent information on the computational program (Fortran), see ref. 13.

[13] O. E. Esval, Thesis, University of North Carolina, 1962.

[14] O. L. Keller, Jr., and R. H. Busey, *J. Chem. Phys.*, in press.

[15] R. M. Rush, J. S. Johnson, and K. A. Kraus, *Inorg. Chem.*, **1**, 378 (1962).

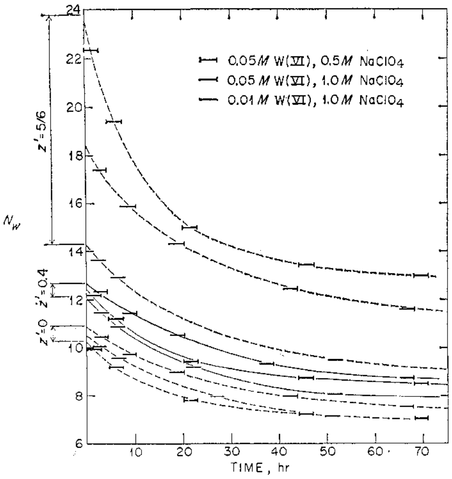

Fig. 1.—Weight average degree of polymerization of the paratungstate ion present in solutions of $Na_{10}W_{12}O_{41} \cdot 28H_2O$ as a function of time and assumed charge per monomer unit, z'; temperature 50°.

Starting from a solution of the same stoichiometry but prepared by dissolving sodium paratungstate in 1 M $NaClO_4$, N_w was found to decrease slowly to the same value.

Van Holde and Baldwin[16] have shown that, in general, the time needed to attain centrifugal equilibrium is proportional to the square of the height of solution in the centrifuge cell and inversely proportional to the diffusion coefficient of the solute. Thus by increasing the temperature and especially by using short (2-3 mm.) columns of solution the time needed to attain equilibrium is drastically reduced, although at the expense of some accuracy. This technique has been applied in the present case to follow the depolymerization of the tungstate species formed on dissolving sodium paratungstate, the object being to find the initial value of N_w and thus set a probable upper limit to the degree of aggregation in solution at equilibrium.

The results of three centrifugations in which the ratio c_2'/c_3 was varied by a factor of ten are shown in Fig. 1 where N_w is plotted as a function of time, t, for three assumed values of z'. The length of the horizontal lines represents the time found to be needed for similar solutions at chemical equilibrium to attain practical centrifugal equilibrium under the same conditions of temperature and column height; the right-hand end of each line is drawn at the point corresponding to the time the fringes were photographed. Since the centrifugation equilibrium lags somewhat behind the chemical reaction, which is moving in the direction of lower N_w, smooth curves are drawn through the center of these lines. They are anchored at the value of N_w at $t = 0$, which was found by extrapolation of the approximately linear log $(N_w - N_f)$ $vs.$ t plots, where N_f is the final value of N_w in the series. The value of N_f is not quite the equilibrium value since condensation of oil on the optical components in the centrifuge chamber terminated the experiments a little short of chemical equilibrium, but the empirical extrapolation to zero time was little affected by this.

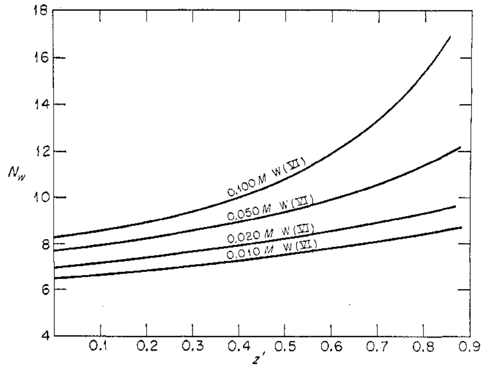

Fig. 2.—Weight average degree of polymerization of W(VI) with $\mathbf{p} = 1.167$ in 1 M $NaClO_4$ computed as a function of assumed charge z' per monomer unit; temperature 50°.

For low values of t the solutions appeared to be monodisperse by the criterion that plots of ln n^* $vs.$ x^2 were linear (n^* is the difference in refractive index between solution and background and x is the radius), although a small degree of polydispersity would be difficult to detect with such a short column of solution. If in fact the paratungstate dissolves to give initially a single species, then the curves for which z' is equal to the true value of the charge per monomer unit should coincide at $t = 0$; moreover, by the stoichiometry of the crystal, in which $\mathbf{p} = {}^7/_6$, N_w at $t = 0$ should be a multiple of six. Examination of Fig. 1 shows that the above conditions are most nearly fulfilled for z' slightly less than 0.4, which would imply that the initial product formed on dissolution of $Na_{10}W_{12}O_{41} \cdot 28H_2O$ is the ion $Na_zW_{12}O_{41}^{(10-z)-}$, which is consistent with the crystallographic formula. The natural assumption of maximum charge, with complete dissociation of counterions, is not a good one in this case; z here appears to be in the range 5-8. The implied equilibrium between the $W_{12}O_{41}^{10-}$ ion and sodium ions and thus the value of z' should depend to some extent on the concentration of sodium and polytungstate ions. However, in order to estimate the degree of polymerization it is necessary to vary at least one of these concentrations. The concordance of the result at different supporting electrolyte concentrations with the two having the same concentration indicates that the comparison is nevertheless meaningful.

The results of a separate series of equilibrium ultracentrifugations of sodium tungstate adjusted to $\mathbf{p} = {}^7/_6$ in 1 M $NaClO_4$, in which the normal column height of 12-13 mm. was used, are shown in Fig. 2. The degree of polymerization computed as a function of charge per monomer unit is shown after the attainment of practical chemical equilibrium, which took about 1 week. The curve corresponding to a concentration of 0.05 M represents the results of two runs: in one the solution was prepared by neutralizing sodium tungstate with $HClO_4$ to $\mathbf{p} = {}^7/_6$ and in the second a solution of the same stoichiometry was prepared by dissolving sodium paratungstate in 1 M $NaClO_4$. The computed degrees of polymerization for the two solu-

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[16] K. E. Van Holde and R. L. Baldwin, *J. Phys. Chem.*, **62**, 734 (1958).

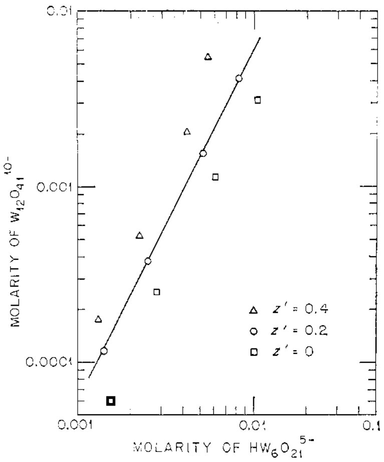

Fig. 3.—Equilibrium ultracentrifugation in 1 *M* $NaClO_4$ of W(VI) with **p** = $^7/_6$. Species concentrations computed from N_w for the scheme $2HW_6O_{21}^{5-} \rightleftarrows W_{12}O_{41}^{10-} + H_2O$. A line with slope 2 is drawn through points for z' = 0.2; temperature 50°.

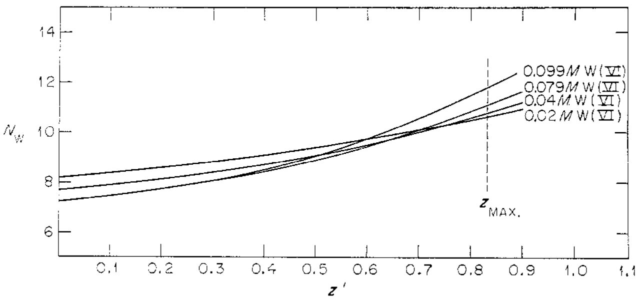

Fig. 4.—Weight average degree of polymerization of W(VI) with **p** = 1.167 in 1 *M* LiCl computed as a function of assumed charge z' per monomer unit; temperature 50°.

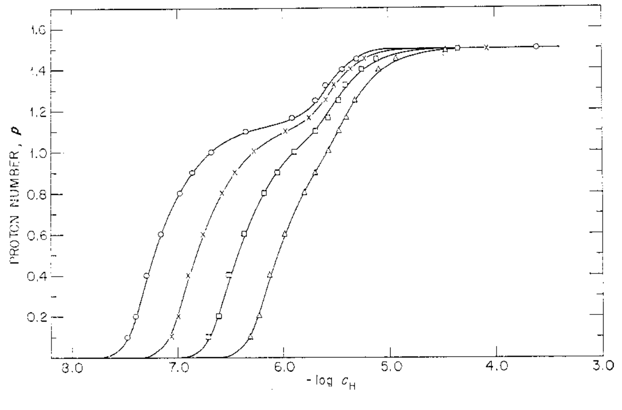

Fig. 5.—Hydrolysis of Li_2WO_4 in 3 *M* Li(Cl), 50°. Curves computed with the following formation constants: log $K_{7,6}$ = 53.98, log $K_{14,12}$ = 110.03, and log $K_{18,12}$ = 132.51. Symbols represent total molarity of W(VI) as: ○ = 0.1986, × = 0.0596, □ = 0.0179, △ = 0.00536.

tions which approached equilibrium from opposite directions were within 0.2% of each other—an agreement which is rather better than expected from the precision of the method and is no doubt to some extent fortuitous.

The strong concentration dependence of N_w even for the extreme assumption of zero charge is unusual and much greater than found with other polydisperse hydrolytic polymers, *e.g.*, U(VI),[15] Mo(VI),[4] Pb(II).[13] In these cases analysis of the results indicated that no two species of the same **p** were present in significant amounts; moreover, computation of N_w as a function of c_2' at constant **p** using the schemes and formation constants derived by independent methods for these systems indicated that over the concentration range of ultracentrifugation (c_2' *ca.* 0.01–0.1 *M*) no great change in N_w with c_2' would be expected. However, the simple assumption of two species with the same **p** enables the results of Fig. 2 to be interpreted. For low values of z', N_w appears to approach six as c_2' tends to zero which for **p** = $^7/_6$, *i.e.*, the average value for the tungstate species, would imply that $HW_6O_{21}^{5-}$ is the main species at low concentrations. At higher concentrations it is plausible that $W_{12}O_{41}^{10-}$ (which has been shown to be present on dissolving sodium paratungstate) is present in equilibrium with the hexatungstate.

$$2HW_6O_{21}^{5-} \rightleftharpoons W_{12}O_{41}^{10-} + H_2O$$

$$K_d = \frac{[W_{12}O_{41}^{10-}]}{[HW_6O_{21}^{5-}]^2}$$

$$\log\,[W_{12}O_{41}^{10-}] = 2\log\,[HW_6O_{21}^{5-}] + \log K_d$$

On this assumption the concentrations of the two species were computed from N_w and c_2' using the data in Fig. 2 for z' = 0, 0.2, and 0.4. The results shown in Fig. 3 indicate that for z' = 0.2 the centrifuge results are consistent with this scheme, whereas for z' = 0 and 0.4 the points depart from the predicted line with slope 2. At higher values of z' the curvature increases and at $z' = z_{\max}$, $N_w > 12$ and the scheme becomes inapplicable. The agreement at low charge is gratifying, but the actual value, z' = 0.2, should not be taken too seriously as it will be shown later that at the lower concentration a third species could be present in a significant amount.

A single ultracentrifugation of a 0.05 *M* W(VI) solution with **p** = 1.5 indicated that the solution was essentially monodisperse. Computation of N_w (the refractive index increment used was 0.027 l. monomole^{-1}; it is somewhat less certain than the values listed for **p** = $^7/_6$.) by the approximate method outlined by Johnson, *et al.*,[12] gave a value of 10 for z' = 0 and 12 for z' = 0.5, which implies that $W_{12}O_{41}^{10-}$ protonates further to $W_{12}O_{39}^{6-}$ at **p** = 1.5.

(b) Centrifugations in LiCl Supporting Electrolyte.—It has been shown elsewhere[4] that, although the extent of counterion binding in polymolybdates is lower in LiCl medium than in the corresponding NaCl supporting electrolyte, there is no evidence that the polyanions formed are different in the two media. As it was found necessary to make the potentiometric acidity measurements of W(VI) in LiCl medium, it was desirable to show a similar correspondence for the polytungstates. In addition, the variation of computed N_w, as a function of assumed z', decreases with decrease in molecular weight of the supporting electrolyte so that the uncertainty of z' in a polydisperse system becomes less serious.

The results for lithium tungstate with **p** = $^7/_6$ in

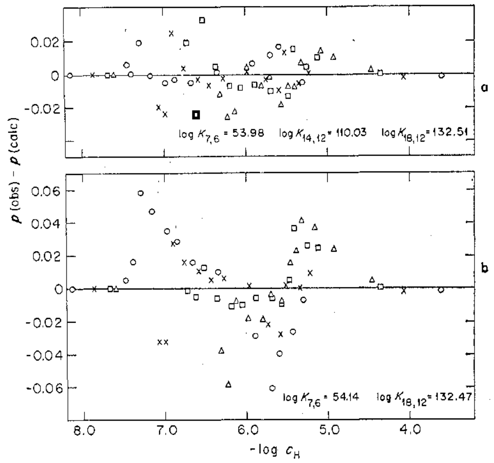

Fig. 6.—Test of hydrolysis schemes for W(VI) in 3 *M* LiCl at 50°. Deviation of observed proton number, p (obsd.), from values computed with constants obtained from least-squares fit, p (calcd.), of all data points. Symbols represent total molarity of W(VI) as: ○ = 0.1986, × = 0.0596, □ = 0.0179, △ = 0.00536. All solutions 3 *M* total lithium.

1 *M* LiCl are shown in Fig. 4. All the solutes were clearly polydisperse by the criterion that plots of ln n^* *vs.* x^2 were concave upward; computation of N_w at three points in the centrifuge cell also showed that in each solution N_w increased with x^2 and hence with c_2' for all values of z'. This sets a lower limit to z' of about 0.6, below which the computed curves in Fig. 3 show a decrease in N_w with c_2'. Above z' = 0.6 the results are consistent with the scheme proposed for the centrifugations in 1 *M* $NaClO_4$, although as with the analogous polymolybdates it appears that the lithium compounds are more completely dissociated.

(2) **Acidity Measurements at 50°.**—The slow equilibria implied by the centrifugations showed that the usual type of e.m.f. titration could not yield equilibrium data and that the method of "point titration" must be used. Initial experiments in 3 *M* NaCl showed that even at 50° the solubility of the tungstate species between **p** = 0.5 and 1.25 precluded making the wide variations in concentration which are necessary for the study of aggregation by this method. Acidity measurements were therefore made in 3 *M* LiCl medium where the solubility at **p** = $^7/_6$ is some 40-fold greater than in the corresponding NaCl medium. All solutions were aged for 10 days at 50°, before measurement, which has been shown in section 1 to be ample for equilibration.

The results are plotted in Fig. 5 as **p** *vs.* log c_H where c_H is the hydrogen ion concentration. Formation quotients

$$K_{p,q} = \frac{[H_p(WO_4)_q{}^{(2q-p)-}]}{[WO_4{}^{2-}]^q[H^+]^p}$$

were calculated and refined using the O.R. G.L.S. Fortran least-squares program[17] to give the least-square deviation in **p** from the experimental points for the species $W_{12}O_{41}{}^{10-}$, $W_{12}O_{39}{}^{6-}$, and $HW_6O_{21}{}^{5-}$ suggested by the centrifugations. The experimental points together with the titration curves calculated using the converged values of the formation quotients are shown in Fig. 5. The deviations in **p** from the computed values for this scheme, shown in Fig. 6a, appear to be random at all concentrations, and the standard deviation σ_p = 0.0124 is considered acceptable for such a wide range of **p**. Addition of the intermediate species $W_{12}O_{40}{}^{8-}$ also gave σ_p = 0.0124 but the high standard error associated with its formation quotient did not warrant the inclusion of this species. A scheme with $H_3W_6O_{21}{}^{3-}$, which has frequently been proposed,[5,6,8] added to $HW_6O_{21}{}^{5-}$, $W_{12}O_{41}{}^{10-}$, and $HW_6O_{21}{}^{5-}$ did not converge; a zero diagonal element corresponding to its formation quotient was finally obtained. Scheme b in Fig. 6, which is that advanced by Sasaki[7] but with the addition of $W_{12}O_{39}{}^{6-}$ (which is only important for **p** > $^7/_6$) to fit the curves between **p** = $^7/_6$ and 1.5 is also unacceptable; not only is the standard deviation in **p** of 0.025 twice that of our preferred scheme but inspection of the deviation plot, Fig. 6b, shows substantial systematic deviations. Species fraction curves computed for 0.2 and 0.002 *M* W(VI) using scheme a are given in Fig. 7.

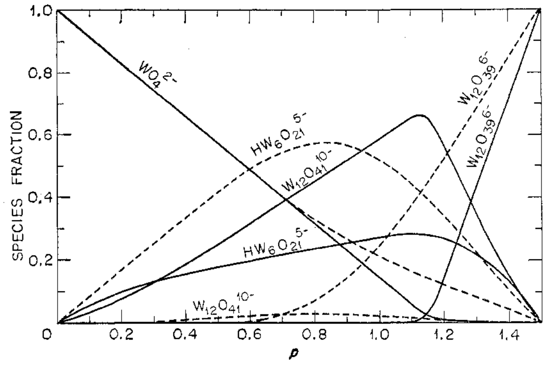

Fig. 7.—Fractions of total W(VI) as $WO_4{}^{2-}$, $HW_6O_{21}{}^{5-}$, $W_{12}O_{41}{}^{10-}$, and $W_{12}O_{39}{}^{6-}$ in 3 *M* LiCl at 50° computed using the scheme in Fig. 6a for 0.2 *M* W(VI) (solid lines) and 0.002 *M* W(VI) (broken lines).

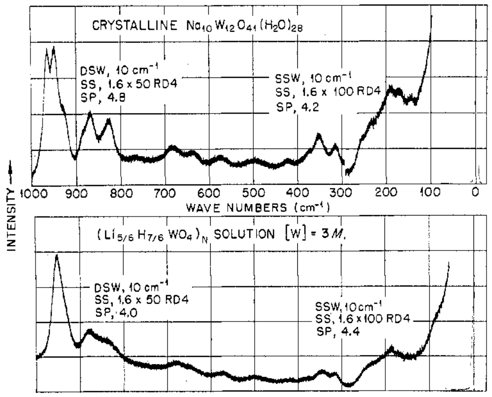

Fig. 8.—Comparison of Raman spectra of crystalline sodium paratungstage with lithium tungstate solution acidified to p = $^7/_6$. Cary Model 81; lamp current 13.5 amp.; scan speed 0.25 cm./sec.; period control setting 0.5. Abbreviations: SS = sensitivity setting, SP = suppression setting, SSW = single slit width, DSW = double slit width.

(3) **Raman Spectra.**—It has recently proved possible in the case of the polymolybdates[4] to gain some

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[17] W. R. Busing and H. A. Levy, Oak Ridge National Laboratory Report TM-271 (1962).

information on the state of aggregation in solution by comparing solutions of appropriate acidity with crystals having a corresponding value of **p** and a known structure determined by X-ray diffraction. The tungstates are analogous in that a structural study has been made of crystalline sodium paratungstate.[18] The results indicated the existence of discrete anions containing twelve tungsten atoms which in conjunction with the chemical analysis implied the formula $Na_{10}W_{12}O_{41} \cdot 28H_2O$.

The Raman spectra of this solid and also of a concentrated (*ca.* 3 *M*) lithium tungstate solution containing $^7/_6$ equivalent of HCl per mole of WO_4^{2-} are shown in Fig. 8 and Table I. All fourteen lines found in the solution spectrum have their counterpart in that of the crystal within about 5 cm.$^{-1}$. The greatest shift between the solution and solid spectra of 8 cm.$^{-1}$ for the 878 cm.$^{-1}$ line of the solution probably arises from the nonresolution in solution of the shoulder occuring at 885 cm.$^{-1}$ in the crystal. With the rather naïve assumption that the formation constants given in Fig. 5 are applicable in the absence of supporting electrolyte, then at a W(VI) concentration of 3 *M*, 8% of the W(VI) should be present as $HW_6O_{21}^{5-}$ and the remainder as $W_{12}O_{41}^{10-}$. As no lines are observed in solution which, by comparison with the solid, cannot be ascribed to $W_{12}O_{41}^{10-}$, it appears that this assumption may be unjustified, although at the predicted $HW_6O_{21}^{5-}$ concentration only an intense Raman line would be visible. The observed replacement of two lines in the crystal (at 948 and 964 cm.$^{-1}$) by a single line in solution is not unexpected; a vibration in a complex ion which is degenerate in solution often has this degeneracy removed in a regular crystal lattice with the appearance of two closely spaced lines in place of the single line found in solution.

TABLE I

$Na_{10}W_{12}O_{41} \cdot 28H_2O$	$Li_{5/6}H_{7/6}WO_4$
143[a]	
170[a]	
190	187
ca. 250 (sh)	*ca.* 250 (sh)
315	315
352	346
ca. 375 (sh)	*ca.* 375 (sh)
422	420
500	500
575	575
635	*ca.* 640
681	*ca.* 680
828	835
870	878
ca. 885 (sh)	
ca. 930 (sh)	*ca.* 930 (sh)
948	952
964	

[a] These lines are not considered to correspond to genuine vibrations; spurious lines at these wave lengths have often been observed with crystalline spectra using the O.R.N.L. Cary Model 81 spectrophotometer.

Discussion

The conclusion is that in a freshly prepared solution of sodium paratungstate, $Na_{10}W_{12}O_{41} \cdot 28H_2O$, the main species (ignoring sodium complexing) is the ion $W_{12}O_{41}^{10-}$. This ion hydrolyzes slowly to yield a mixture of $W_{12}O_{41}^{10-}$ and $HW_6O_{21}^{5-}$; at higher acidities $W_{12}O_{39}^{6-}$ is formed. These polytungstates are also present in equilibrated solutions of acidified Li_2WO_4 and Na_2WO_4. This scheme differs from those of Sasaki,[7,8] Jander,[6] and Souchay,[5] in that an appreciable fraction of the total W(VI) exists as a dodecamer at moderate concentrations. Reference to the species fraction curves in Fig. 7 shows that the composition of the solution up to $\mathbf{p} = {}^7/_6$ is markedly dependent on the total W(VI) concentration, with $HW_6O_{21}^{5-}$ being the predominant polymeric species only at high dilution. Our conclusions further conflict with Sasaki[8] in that we can find no evidence for $H_3W_6O_{21}^{3-}$ and in this respect our findings are more consistent with the earlier work of Jander,[6] who first proposed the existence of $W_{12}O_{39}^{6-}$. The failure of Sasaki to detect the $W_{12}O_{41}^{10-}$ ion probably stems from the difficulty of establishing equilibrium with the usual titration experiment. Thus at a W(VI) concentration of 0.2 *M* and $\mathbf{p} = 0.6$ the total change in e.m.f. between the schemes of Fig. 6a and 6b (which at this value of **p** is equivalent to that of Sasaki) amounts only to *ca.* 3 mv. The corresponding change in N_w is from 4.2 to 7.1, which corresponds to as much as 30 fringes (depending on the speed of rotation) in the interference picture obtained from the centrifuge. As the fringe positions may be determined to within 0.1 fringe, and as the readings are normally taken only every 24 hr., quite slow changes in N_w can be detected.

The counterion binding observed with the polytungstates has also been indicated in ultracentrifugation studies of Mo(VI)[4] and Ta(V).[19] Moreover, the light scattering studies of Ta(V) by Nelson and Tobias[20] imply substantial complexing of potassium ions by the hexatantalate. This rather unexpected behavior by what are usually regarded as strong electrolytes appears worthy of further study. With some independent method of determining such complexing, the apparent formation constants of the polyanions as determined by e.m.f. methods would become more meaningful and independent of ionic medium within the usual assumptions regarding constancy of activity coefficient quotients, junction potentials, etc. Interpretation of centrifuge patterns for polydisperse ionic solutions would also be greatly facilitated.

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(18) I. Lindqvist, *Acta Cryst.*, **5**, 667 (1952).

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(20) W. H. Nelson and R. S. Tobias, *ibid.*, **2**, 985 (1963).