value of 1.47 Å. which has been confirmed by Abrahams and Kalnajs.[16] It is probable that the O–O distance in all these compounds is in the neighborhood of 1.49 Å.

The constancy of the O–O peroxide type bond is illustrated by several other determinations. Harr[23] obtained 1.48, 1.49 and 1.48 Å. for this distance in $CaO_2 \cdot 8H_2O$, $SrO_2 \cdot 8H_2O$ and $BaO_2 \cdot 8H_2O$, respectively. Recently, Harvey and Bauer[24] have found the O–O distance in F_5SOOSF_5 to be 1.47 ± 0.03 Å. The value found for CdO_2 is in line with all of these determinations and lends credence to the proposed structure.

One further structural relationship remains to be discussed, the effective radius of the Cd and O atoms. The well-known Pauling and Goldschmidt ionic radii for Cd are conveniently summarized in a paper by Goldschmidt[25] and in many inorganic texts. They are 0.97 and 1.03 Å., respectively, both values being for the coördination number of 6. Föppl[2] deduces that the effective radius of O in the peroxide group is between 1.23 and 1.35 depending upon whether the evaluation is made at right angles to the O–O bond or projects a distance beyond one of the O in the group. Föppl's values were found by assuming Goldschmidt's ionic radii of the Group Ia elements. As remarked before, the distance of closest approach of the Cd and O atoms is 2.30 Å. Assuming Pauling's value for Cd, the effective radius of the O is 1.33 Å. whilst if Goldschmidt's radius for Cd is assumed, the value 1.27 Å. results. Both these values appear to confirm Föppl's figures.

Acknowledgments.—The authors are indebted to G. J. Meisenhelter, J. E. Mathers and G. V. Potter for chemical analyses and density determinations and to J. E. Webster for many preparations of CdO_2.

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The Tungstic Acids

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A chemical and X-ray investigation was made of the solid phases precipitated from W(VI) solutions by strong acids at concentrations of 0.2 to 9.0 *N* and temperatures of 25, 50 and 100°. Of the four phases obtained by direct precipitation two phases, $WO_3 \cdot 2H_2O$ and $WO_3 \cdot H_2O$, were identified as hydrates by comparison with the isomorphous Mo compounds. A new phase was discovered in studying the reactions of the hydrates with Na_2WO_4 solution. This new compound, a cation exchanger, has a composition of $Na_2O \cdot (WO_3 \cdot H_2O)_n$ where *n* can vary from approximately 4 to 10. The unique phases were studied by potentiometric titration to determine acid properties and to relate their structures to those of the soluble isopoly tungstates. The tungstic acids were compared to similar compounds of Mo(VI) and U(VI) and in, particular, the relative stabilities of the oxy-anions of these elements as a function of *p*H were compared.

Introduction

Tungstic acid is the ambiguous term applied to various solids precipitated from W(VI) solutions by strong acids. Despite an extensive literature there is evident uncertainty as to the identity and chemical nature of these substances. Two compounds, H_2WO_4 and $H_2WO_4 \cdot H_2O$, have been characterized by X-ray diffraction and described as acids[1,2] while similar precipitates have been identified as WO_3 by electron diffraction.[3] A third compound, $WO_3 \cdot {}^1/_2H_2O$ or $H_2W_2O_7$, was obtained by treating H_2WO_4 with alkaline solutions.[4–6] Other compounds have been claimed.[7] Limiting conditions for the precipitation of specific compounds were not determined and the designation as acids was based only on thermal stability. Of the soluble W(VI) anions[8] only the metatungstate anion is sufficiently stable at low *p*H to be isolated as the free acid.[6,9] Acid behavior of the precipitated tungstic acids should thus be observed as a surface phenomenon, similar to silica,[10] or by cation exchange, similar to the polyuranates.[11]

This investigation was undertaken to clarify the state of knowledge of the tungstic acids. Fifty precipitations were made with HCl or HNO_3 at concentrations of 0.2 to 9.0 *N* and at temperatures of 25, 50 and 100°. The precipitates were characterized by chemical analysis, X-ray diffraction and potentiometric titration at high ionic strength. The ranges of homogeneity of the unique phases were estimated and their reactions were studied. A series of molybdic acids were prepared for comparison. The chemistry of the tungstic acids then was related to the chemistry of W(VI) compounds in aqueous solution and compared with that of Cr(VI), Mo(VI) and U(VI) compounds.

Structural Considerations.—The compounds previously written as $H_2WO_4 \cdot H_2O$ and H_2WO_4 are tungstic oxide hydrates rather than acids because they are isomorphous with the yellow $MoO_3 \cdot 2H_2O$ and $MoO_3 \cdot H_2O$ compounds which have been shown to be hydrates.[12] Also, the known structure of $MoO_3 \cdot 2H_2O$[13,14] defines that of $WO_3 \cdot 2H_2O$.

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Experimental

Preparation of Compounds.—Analytical reagent grade materials were used throughout. Precipitations were generally made by adding a 1.0 *M* Na_2WO_4 solution to a great excess of the precipitating acid in order to avoid a large change in acid strength during the precipitation. The precipitates were washed with 0.1 *N* HCl by decantation or on a filter. Final washings were made cautiously with small portions of distilled water to avoid excessive peptization. However, in later stages of the investigation, the methods of preparation were deliberately varied over a wide range in order to obtain products with as diverse properties as possible. Each of the unique phases could be prepared either as a powder or as a glassy gel without a change in X-ray diffraction or chemical properties. Since the particle size of the precipitates is in the submicron range,[2,3,15] colloidal phenomena are very much in evidence. Typical preparations are given below. Losses were largely mechanical except for the B and C phase precipitations where considerable tungsten remained in solution.

A. Tungstic Oxide Hydrate.—Fifty ml. of 1.0 *M* Na_2WO_4 was pipetted into 450 ml. of 3.0 *N* HCl at 100°. The initial yellow solution quickly became turbid and the characteristic yellow precipitate appeared. The mixture was kept hot for 30 minutes, allowed to settle, and the precipitate washed three times by decantation with 2-l. portions of 0.1 *N* HCl at room temperature. The slurry then was filtered, washed on the filter with 25 ml. of water, and then dried at 100° for two hours to obtain 9.5 g. of orange-yellow powder (76% yield). *Anal.* Calcd. for $WO_3 \cdot H_2O$: H_2O, 7.22; WO_3, 92.78. Found: H_2O, 7.48; WO_3, 92.49; Na_2O, 0.04; total, 100.01.

B. Tungstic Oxide Dihydrate.—The procedure above was repeated at 25°. Precipitation of yellow gel particles was immediate. On aging, the precipitate formed a stiff gel which filtered well and could be washed free of HCl without becoming peptized. The washed gel was dried at room-temperature and ground to obtain 12 g. of canary yellow powder (90% yield). *Anal.* Calcd. for $WO_3 \cdot 2H_2O$: H_2O, 13.42; WO_3, 86.58. Found: H_2O, 14.32; Na_2O, 0.00; WO_3, 85.75; total, 100.07.

C. Preparation of the Hydrates in Large Amounts.—A convenient procedure was found to be the acid decomposition of solid $Na_2WO_4 \cdot 2H_2O$. Thus, 100 g. of finely powdered $Na_2WO_4 \cdot 2H_2O$ was stirred for four hours at room temperature with 500 ml. of 6.0 *N* HCl. The granular product was filtered with suction and washed on the filter with one l. of 0.1 *N* HCl followed by 500 ml. of H_2O. The filtrate at this point was nearly neutral and gave a negative test with $AgNO_3$ solution. The product was spread on a tray and dried overnight at room temperature; yield 82.5 g. (99%). *Anal.* H_2O, 15.26; Na_2O, 0.00; WO_3, 84.76; total, 100.02. This material gave the standard $WO_3 \cdot 2H_2O$ X-ray pattern and was completely converted to $WO_3 \cdot H_2O$ by baking at 100° for one hour.

D. Metatungstic Acid Anhydride (Phase B).—Ten ml. of 1.0 *M* Na_2WO_4 solution was stirred into 500 ml. of 0.25 *N* HCl at 25°. The initially yellow solution became opaque in 5 minutes and coagulated in 10 to produce a white, flocculent precipitate. This was filtered, washed with water and acetone, and then air dried to obtain 2 g. of cream colored powder (yield 75%). *Anal.* H_2O, 14.24; Na_2O, 0.14; WO_3, 85.58; total, 99.96.

E. Phase C.—One hundred ml. of boiling 1.0 *N* HCl was mixed with 100 ml. of 0.25 *M* Na_2WO_4 solution at 100° and the yellow solution boiled for 10 minutes to precipitate a white powder which was filtered, washed with 0.1 *N* HCl, and dried at 100°; yield, 2 g. of white powder (30%). *Anal.* Calcd. for $WO_3 \cdot {}^1/_2H_2O$: H_2O, 3.73; WO_3, 96.27. Found: H_2O, 4.89; Na_2O, 0.83; WO_3, 94.31; total, 100.03.

F. Phase X.—This new compound is formed by heating $WO_3 \cdot H_2O$ with a saturated Na_2WO_4 solution. The relationship to Phase C is shown in the following procedure. A tungstic acid which consisted of approximately equal portions of Phase C and $WO_3 \cdot H_2O$ as judged from X-ray patterns was prepared by boiling together equal volumes of 1.0 *M* Na_2WO_4 and 2.0 *N* HCl and then adding sufficient 12.0 *N* HCl to obtain an acid strength of 2.0 *N*. After repeated washing with hot 1.0 *N* HCl the yellow precipitate was dried to constant weight at 100°. *Anal.* H_2O, 4.12; Na_2O, 0.83. This material was ground to pass a 200 mesh screen and a 155-g. portion boiled with 66 g. of $Na_2WO_4 \cdot 2H_2O$ in 100 ml. of H_2O. The resulting granular white precipitate was filtered, washed with water, and dried to constant weight at 100° to obtain a yield of 180 g. *Anal.* H_2O, 3.83; Na_2O, 6.08. X-Ray diffraction now showed a mixture of C and X phases in equal proportion. The C phase was dissolved by boiling 20 g. of the mixture for an hour with 420 ml. of 0.1 *N* NaOH, a 10% excess over that calculated. The granular residue was filtered and water washed. After drying at 100°, a 10.8-g. yield of white powder was obtained which gave only the X phase X-ray pattern. *Anal.* H_2O, 7.24; Na_2O, 6.72; WO_3, 86.00; total, 99.96. A 5-g. portion was extracted repeatedly with 500-ml. portions of 1.0 *N* HCl over a period of several days. The Na_2O content was thus reduced to 1.08%, but X-ray diffraction showed that an approximately 50:50 mixture of C and X phases had been reformed.

The Molybdic Acids. A. Molybdic Oxide Dihydrate.—The procedure was similar to that of Rosenheim.[16] Fifty grams of $Na_2MO_4 \cdot 2H_2O$ was dissolved in 100 ml. of H_2O and added to 300 ml. of 5 *N* HNO_3 at room temperature. Precipitation of the yellow granules began in two days and appeared complete in three weeks. The precipitate was filtered, washed with 100 ml. of 4 *N* HNO_3, then with H_2O, and air dried at room temperature; yield 27 g. yellow powder (73%). *Anal.* Calcd. for $MoO_3 \cdot 2H_2O$: H_2O, 20.01; MoO_3, 79.99. Found: H_2O, 20.07; Na_2O, 0.00; MoO_3, 79.91. Single crystals similar to those reported by Carpeni[17] were prepared as follows: 15 g. of $MoO_3 \cdot 2H_2O$ was stirred with 15 ml. of 12 *N* HCl for 30 minutes to effect nearly complete solution. The mixture was then diluted with 60 ml. of water, filtered and allowed to stand at room temperature. Crystallization of the $MoO_3 \cdot H_2O$ began in two days. After a month, approximately 2 g. of the single crystals was selected from the coarse grained product. The chemical analysis and X-ray pattern of the 1–2 mm. crystals was the same as for the previous powder preparation. The X-ray pattern agreed with that previously reported[18] and matched that of $WO_3 \cdot 2H_2O$.

B. Molybdic Oxide Hydrate (Yellow).—$MoO_3 \cdot 2H_2O$ was dried for two hours at 100°. *Anal.* Calcd. for $MoO_3 \cdot H_2O$: H_2O, 11.12; MoO_3, 88.88. Found: H_2O, 9.50; MoO_3, 90.40. The X-ray pattern matched that of $WO_3 \cdot H_2O$ as has been noted previously.[18]

C. Molybdic Oxide Hydrate (White).—Five g. of $MoO_3 \cdot 2H_2O$ was mixed with 25 ml. of 3.0 *N* HCl and heated in an oven for 5 hours at 75°. The fine white needles thus obtained were washed with water and air dried at room temperature. *Anal.* H_2O, 10.08; yield 3 g. (67%). On heating to constant weight at 100° (2 days) the water content was reduced to 10.05%. The X-ray pattern did not correspond with any of the tungsten compounds.

D. Hydrous Molybdic Oxide.—An aqueous slurry of $MoO_3 \cdot 2H_2O$ was boiled for 30 minutes. The resulting white powder was filtered and air dried at room temperature. *Anal.* H_2O, 2.90. The X-ray pattern was identical with that of sublimed MoO_3. $MoO_3(aq)$ also was formed by heating $MoO_3 \cdot 2H_2O$ at 100° in air for one day or by allowing the yellow $MoO_3 \cdot H_2O$ to stand for four months at room temperature.

Reaction of the Hydrates with Na_2WO_4 Solution.—Various proportions of Na_2WO_4 solutions were treated with $WO_3 \cdot 2H_2O$ and with $WO_3 \cdot H_2O$ on a larger scale so that the soluble products could be isolated by crystallization.

A. Sodium Paratungstate.—Twenty grams of $WO_3 \cdot 2H_2O$, 20 g. of $Na_2WO_4 \cdot 2H_2O$ and 20 ml. of H_2O were stirred together at room temperature. Solution was nearly complete in 20 minutes. After 30 minutes the solution was filtered to remove the slight turbidity and the colorless sirup was placed in a crystallizing dish in a shallow layer. The characteristic prismatic crystals of $Na_{10}W_{12}O_{41} \cdot 28H_2O$ began to form in three hours and crystallization appeared to be complete in three days. The crystals were dried between filter paper; yield 36 g. (90%). *Anal.* Calcd. for $Na_{10}W_{12}O_{41} \cdot 28H_2O$: H_2O, 14.04; Na_2O, 8.61; WO_3, 77.35. Found: H_2O, 14.03; Na_2O, 8.59; WO_3, 77.41.

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B. Sodium Metatungstate.—One hundred g. of $WO_3 \cdot H_2O$ was boiled for 2 hours with a solution of 40 g. of $Na_2WO_4 \cdot 2H_2O$ in 2.5 l. of H_2O. After filtering, washing with H_2O and dil. HCl, and drying at 100°, 9.1 g. of C phase (7.2%) was obtained. The filtrate was evaporated until a "skin" appeared on the surface when blown upon. It was then allowed to stand in a covered crystallizing dish for two weeks in a 5 mm. layer. Crystallization began in a day. The slurry of large clear crystals and mother liquor was drained on filter paper and the crystals dried by pressing between filter paper; yield 122 g. (79%). *Anal.* Calcd. for $Na_6H_2W_{12}O_{40} \cdot 29H_2O$: H_2O, 15.41; Na_2O, 5.30; WO_3, 79.29. Found: H_2O, 14.72; Na_2O, 5.46; WO_3, 79.79; total 99.97.

Other ratios of Na_2WO_4 and the hydrates reacted and the soluble salts were recovered by fractional crystallization. Sodium paratungstate 28 hydrate was obtained in the crystal habit of cubes and as a microcrystalline powder as well as in the form of prisms and opaque aggregates. While their analyses varied slightly, all of these preparations gave the same X-ray powder diffraction pattern which duplicated that of a standard sample prepared by the method of Saddington and Cahn.[19]

Analysis.—The H_2O content of the tungsten compounds was determined as the loss in weight on heating at 700°. This temperature was reduced to 500° for the molybdic acids to avoid volatilization of MoO_3. Na_2O was determined by chlorination, the WO_3 being volatilized as WO_2Cl_2 to leave a residue of NaCl. The weighed sample in a platinum boat was covered with 12 *N* HCl and slowly evaporated to dryness. Chlorination then was carried out at 550° in a stream of air saturated with CCl_4. Similar analytical chlorinations have been made with gaseous HCl[19] and with $CHCl_3$.[20] In the absence of Na_2O, both WO_3 and MoO_3 were determined as metal by reduction in H_2 at 900°. Otherwise, the sample was dissolved in NaOH and $WO_3 \cdot H_2O$ precipitated and ignited to WO_3.[21] These procedures were tested with $Na_2WO_4 \cdot 2H_2O$ and WO_3 of known purity and were found to give accurate results.

Phase Identification.—X-Ray powder diffraction patterns were obtained with the GE XRD-5F unit using a 14.32-cm. camera and nickel filtered Cu K α-radiation. The photographs obtained in the present work duplicated those of Morley, Kerr and Young for $WO_3 \cdot 2H_2O$ and $WO_3 \cdot H_2O$.[1,2] Morley's "nucleic acid C" pattern was also identical with the present phase C.

Phase Composition.—Large variations in composition were observed without apparent change in the X-ray patterns. Ranges of phase homogeneity were observed in dehydration experiments and in preparations of the acid phases.

Hydrate phases	Composition range
Tungstic oxide hydrate, $WO_3 \cdot H_2O$	$WO_3 \cdot 0.6\text{–}1.1H_2O$
Tungstic oxide dihydrate, $WO_3 \cdot 2H_2O$	$WO_3 \cdot 1.2\text{–}2.2H_2O$
Acid phases	Compositon range
Phase B, metatungstic acid anhydride	$WO_3 \cdot \sim 2H_2O$
Phase C, sodium octatungstate	$Na_2O\ (WO_3 \cdot {}^1/_2H_2O)_{8-40}$
Phase X, sodium tetratungstate	$Na_2O\ (WO_3 \cdot H_2O)_{4-10}$

The composition ranges observed for the hydrates are in agreement with the dehydration curves of Prof. Moses.[2]

Potentiometric Titrations.—The potentiometric titrations were carried out at 25° in a magnetically-stirred polyethylene cell under a purified nitrogen atmosphere. The Beckman 1190-60 glass electrode and model G potentiometer were used. Half-gram samples of the tungstic acids were dispersed in 50 ml. of neutral 3.0 *M* $NaNO_3$ solution and titrated with a 3.0 *M* $NaNO_3$ solution which was 0.1 *N* in NaOH or 0.05 *M* in Na_2WO_4. Duplicate titrations of each phase were made with samples prepared under different conditions and the data were plotted on the same curve. Readings were taken when the *p*H remained constant to 0.02 *p*H after one minute of vigorous stirring. The curves are the resultant of solution and precipitation reactions, molecular changes and ionic reactions in solution. These kinetic processes were not studied separately. The titrations were made at high ionic strength to intensify acid action of the solid phases and to accelerate ionic reactions in solution.

The results of the titrations are shown graphically in Figs. 1–6. The initial portion of the C phase titration curve shows the neutralization of a strong acid by 0.14 mmole of Na_2O. Since this sample originally contained 2.05 mmole of WO_3 and 0.12 mmole of Na_2O, the composition at the inflection point corresponded to $Na_2O \cdot 7.8WO_3$.

In contrast to the other phases, 90% of the $WO_3 \cdot H_2O$ phase dissolved below a *p*H of 5. In the titrations with both NaOH and with Na_2WO_4 these slurries became translucent at a *p*H of 5 and white at a *p*H of 6. A new solid phase amounting to 10–11% of the starting material was obtained at a *p*H of 6 with both NaOH and Na_2WO_4. X-Ray diffraction patterns of these residues showed only C phase.

A pronounced acid action is shown by the X phase in Fig. 4. The sharp inflection in the lower curve follows the neutralization of 0.65 mmole of NaOH. Since this sample originally contained 0.18 mmole of Na_2O and 1.94 mmole of WO_3 the salt composition at the inflection point corresponded to $Na_2O \cdot 3.9WO_3$. While the X phase can be considered nominally as a tetratungstate, only part of the Na_2O content of the salt form is replaceable by H^+.

In the titrations of the freshly prepared, amorphous B phase samples, shown as the lower curve in Fig. 5, the inflection at *p*H of 4 coincided with complete solution of the samples. The middle curve is for one of the samples which had aged for one week in a closed bottle. In this case an insoluble residue remained during the course of the titration. The top curve is for B phase samples which had been dried to constant weight at 100° (4.76% H_2O). This curve is very similar to that obtained with the C phase.

The slope of the titration curves in the 3 to 6 *p*H range shows the neutralization of surface acidity. The magnitude of this action is in agreement with the cation-exchange capacity of 0.34 me./g. reported.[22] This polyelectrolyte action is evidenced by the effect of ionic strength on the *p*H of aqueous slurries. Thus, slurries containing 0.5 g. of the $WO_3 \cdot 2H_2O$, C phase, and $WO_3 \cdot H_2O$ samples in 50 ml. of water had *p*H values of 3.50, 2.37 and 3.46, respectively. With 3.0 *M* $NaNO_3$ the *p*H values were 3.05, 1.86 and 2.80.

Titrations of the "Molybdic Acids" are shown in Fig. 6. The $MoO_3 \cdot 2H_2O$ and MoO_3 (aq.) samples were entirely dissolved below a *p*H of 3. Both $MoO_3 \cdot H_2O$ samples had dissolved by a *p*H of 5. In contrast to the tungsten compounds, titrations of these molybdenum oxide and oxide hydrate samples were rapid and complete. They all gave sharp quantitative end-points.

Figure 7 is included for reference purposes.[17,23,24] Since the shape of such curves is dependent upon time, concentration and ionic strength, these titrations were made under similar conditions to those of the tungstic and molybdic acids. Since available alkali provided by the hydrolysis of Na_2WO_4 is a function of *p*H, comparison with the curves in Figs. 1–3 indicates that the dissolution of the solid phase is accomplished by reaction with hydroxyl ion, except at the high WO_4^{--} concentrations where the X phase is formed. The titration curves also show that $WO_3 \cdot H_2O$ dissolves over a *p*H range where meta- and paratungstate ionic species are in equilibrium. $WO_3 \cdot 2H_2O$ and the C phase dissolve in a *p*H region where WO_4^{--} and paratungstate ions are in equilibrium while the solution which dissolves the X phase produces only WO_4^{--}. With the molybdenum compounds, both the hydrous oxide and the dihydrate produce solutions at the point of complete dissolution having the composition of the metamolybdate, $Mo_8O_{26}^{4-}$. Dissolution of the $MoO_3 \cdot H_2O$ compounds extends into the paramolybdate, $Mo_7O_{24}^{6-}$, range.

The Na_2WO_4 neutralization curve of Fig. 7 shows two inflections. These serve as "markers" for the Na_2MoO_4 curve also. The compositions of the solutions at the first inflection point correspond to $Na_{10}W_{12}O_{41}$ (11.9 ml.) or $Na_6Mo_7O_{24}$ (11.7 ml.). At the second inflection point the compositions of the solutions correspond to $Na_6H_2W_{12}O_{40}$ (15.4 ml.) or to $Na_4Mo_8O_{26}$ (15.4 ml.). These compositions are the averages of all the solute species which may be present in the solutions.

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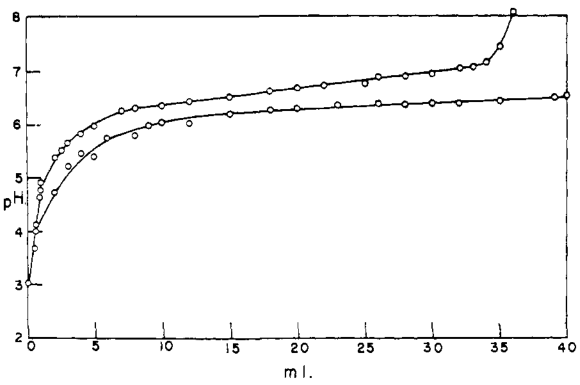

Fig. 1.—Titration of 0.500-g. sample of $WO_3 \cdot 2H_2O$ with 0.095 *N* NaOH (upper curve) and with 0.050 *M* Na_2WO_4 (lower curve) in 3 *M* $NaNO_3$ medium.

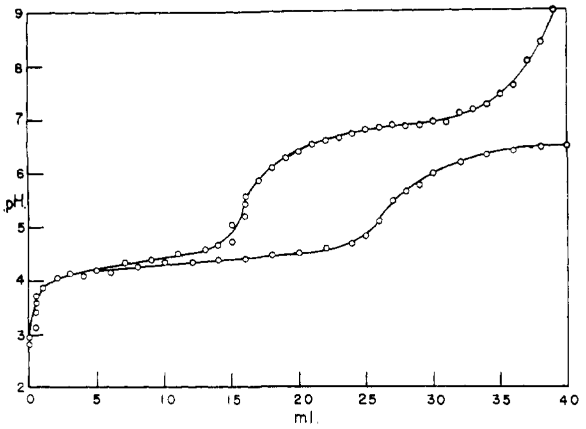

Fig. 2.—Titration of 0.500-g. samples of $WO_3 \cdot H_2O$ with 0.095 *N* NaOH (upper curve) and with 0.050 *M* Na_2WO_4 (lower curve) in 3 *M* $NaNO_3$ medium.

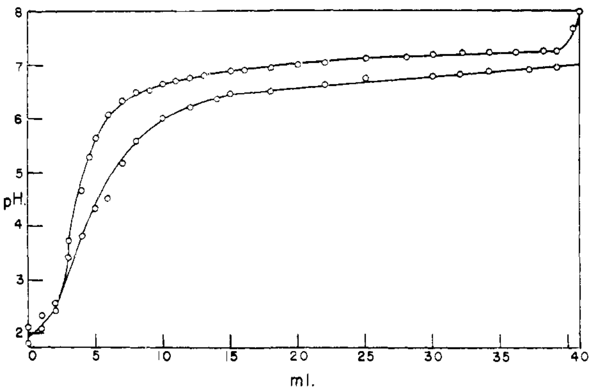

Fig. 3.—Titration of 0.500-g. samples of phase C with 0.095 *N* NaOH (upper curve) and with 0.050 *M* Na_2WO_4 (lower curve) in 3 *M* $NaNO_3$ medium.

The sodium polyuranate suspension (Fig. 7) was prepared by mixing 25 ml. of 0.050 *M* $UO_2(NO_3)_2$ with 25 ml. of 0.100 *N* NaOH and aging for one hour before titration. Both solutions were 3.0 *M* in $NaNO_3$. Under these conditions the U(VI) is precipitated as the "Structure A" compound.[11] This was confirmed by X-ray examination of the yellow precipitate. The extreme buffering effect shown in the titration is due to the amphoteric ion exchange properties of the precipitate and to the polyanion equilibria in solution. The inflection point coincided with complete dissolution of the solid phase.

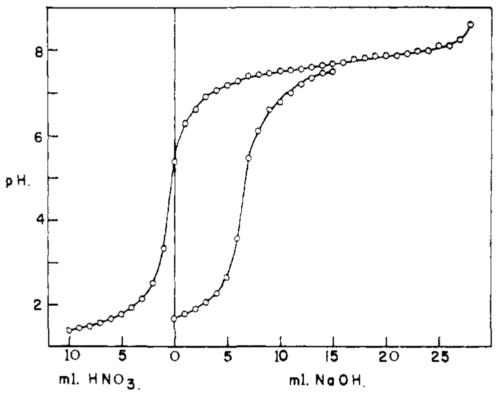

Fig. 4.—Titration of 0.500-g. phase X samples with 0.101 *N* NaOH and with 0.102 *N* HNO_3 in 3 *M* $NaNO_3$ medium.

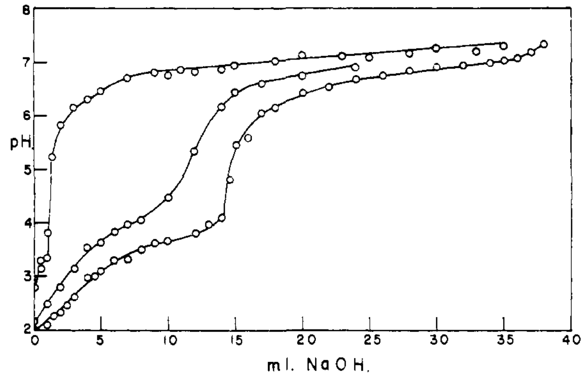

Fig. 5.—Titration of 0.500-g. portions of B phase tungstic acids with 0.092 *N* NaOH in 3 *M* $NaNO_3$ medium: lower curve, freshly prepared; middle curve, aged; upper curve, dried at 100°.

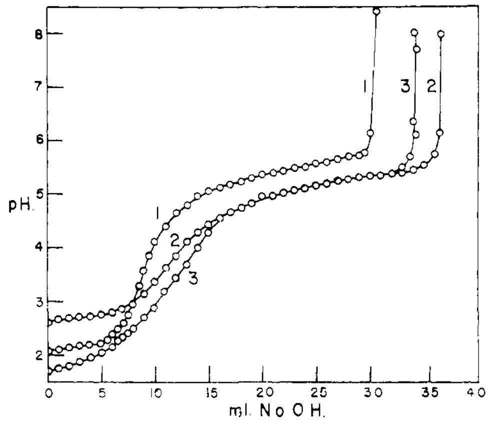

Fig. 6.—Titration of 0.250-g. portions of molybdic acids with 0.092 *N* NaOH in 3 *M* $NaNO_3$ medium: curve 1, $MoO_3 \cdot 2H_2O$; curve 2, MoO_3 (aq.); curve 3, $MoO_3 \cdot H_2O$ (white) and $MoO_3 \cdot H_2O$ (yellow).

Results

Only the four phases described by Morley[1] were found in these precipitations. The nearly amorphous B phase was obtained at 0.2 *N* with both HCl and HNO_3 at 25°. At 100° both acids produced a C phase precipitate at 0.2 and 0.5 *N*, while at 1.0 *N* mixtures of C phase and $WO_3 \cdot H_2O$ were obtained. $WO_3 \cdot 2H_2O$ was the only product at 25° over a range of 0.5 to 9.0 *N*. The B phase

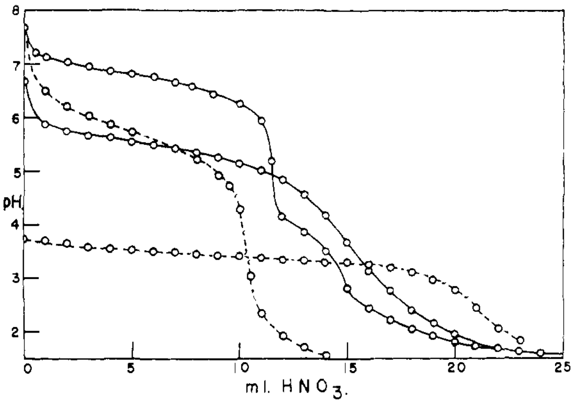

Fig. 7.—Titration of Group VI-B salt solutions with 0.122 N HNO_3. All solutions were 3.0 M in $NaNO_3$: upper solid curve, 50 ml. of 0.025 M Na_2WO_4; lower solid curve, 50 ml. of 0.025 M Na_2MoO_4; upper dotted curve, 50 ml. of 0.025 M Na_2CrO_4; lower dotted curve, 50 ml. of 0.025 M sodium polyuranate suspension.

was also converted to $WO_3 \cdot 2H_2O$ by contact with 0.2 N HCl for several hours or with distilled water for several days. Because of his lengthy washing procedures Morley obtained the B phase only when contaminated with Ca and Mg salts. These cations apparently inhibit the conversion to $WO_3 \cdot 2H_2O$. The B phase appeared to form first at 0.5 N also but was recovered as $WO_3 \cdot 2H_2O$. With acid concentrations of 2 to 9 N pure $WO_3 \cdot H_2O$ was obtained at 100° while mixtures of $WO_3 \cdot H_2O$ and $WO_3 \cdot 2H_2O$ formed at 50°. $WO_3 \cdot 2H_2O$ dehydrated to $WO_3 \cdot H_2O$ when heated at temperatures over 50° and this phase conversion took place both in the dry state and in aqueous suspension. This conversion was also effected at room temperature by drying over P_2O_5.

The B phase is not colloidal WO_3 as has previously been supposed on the basis of dehydration curves.[25] While diffuse, the X-ray pattern of the B phase matches the principal line in the C phase pattern. On aging or heating at 100° the B phase acquires the properties of the C phase and is thus an intermediate stage in the formation of the C phase by condensation or of $WO_3 \cdot 2H_2O$ by hydrolysis. The C and X phases are both white solids which are peptized easily by water. However, such colloidal solutions are coagulated readily by acids or high salt concentrations. The X phase, of composition $Na_2O \cdot (WO_3 \cdot H_2O)_{4-10}$, compares directly with the sodium polyuranate, $Na_2O \cdot (UO_3 \cdot H_2O)_{3-16}$.[11] A solid sodium polymolybdate having cation exchange properties also has been reported.[18]

The reactions of $WO_3 \cdot H_2O$ with Na_2WO_4 solutions produced either sodium metatungstate or sodium paratungstate depending upon the relative proportions of the reactants. Only sodium paratungstate was obtained from $WO_3 \cdot 2H_2O$. The crystalline $Na_{10}W_{12}O_{41} \cdot 28H_2O$ and $Na_6H_2W_{12}O_{40} \cdot 29H_2O$ phases obtained in these reactions were found to have homogeneous ranges of composition. They appear to be the only soluble isopoly tungstate phases. The slow rate of crystallization observed with these compounds is in agreement with the view that these polyions are in equilibrium with other solute species in solution. Thus, the solution of sodium paratungstate prepared by dissolving $WO_3 \cdot 2H_2O$ in Na_2WO_4 solution contained ten times as much solute as the equilibrium value. However, crystallization began only after several hours and required days for completion. The degree of supersaturation with respect to the paratungstate phase was thus very low throughout the crystallization process. However, the known structural features of the paratungstate ion[26] should characterize other polytungstate ions which may exist in the 4 to 7 pH range. Similarly, the structural characteristics of the metatungstate ion should prevail in the 1 to 4 pH range.

While only the five "tungstic acid" phases were found a larger number of "molybdic acids" appear to exist. The isomorphous hydrates of WO_3 and of MoO_3 differ greatly in stability and in their modes of formation. The very slow crystallization of $MoO_3 \cdot 2H_2O$ contrasts with the immediate precipitation of $WO_3 \cdot 2H_2O$. The yellow $MoO_3 \cdot H_2O$ is produced as an unstable intermediate by the loss of H_2O from $MoO_3 \cdot 2H_2O$. If dehydration is prevented decomposition to MoO_3 occurs on heating.

Discussion

The considerable variations in compositions which are observed without change of phase indicate that these compounds are all polynuclear complexes of infinite size. The designation of the $WO_3 \cdot H_2O$ and $WO_3 \cdot 2H_2O$ compounds as hydrates follows also from chemical considerations. None of the soluble iso- or heteropoly tungstates is stable in acid concentrations greater than 2 or 3 N. Since such structures are based upon edge sharing between WO_6 octahedra, the octahedra must be joined by sharing only corners in the oxide hydrates. Hydroxyl groups, if present, should condense under the strongly acid conditions. Condensation of the weak octahedral acid, $H_2WO_4 \cdot 2H_2O$, would produce chains of singly linked octahedra, $(WO_3 \cdot 2H_2O)_x$. These chains could crystallize by hydrogen bonding in two directions. On loss of water cross linking between the chains could produce a layer lattice, $(WO_3 \cdot H_2O)_x$, in which the layers are held together by hydrogen bonding. The known structure for $MoO_3 \cdot 2H_2O$ appears to eliminate the possibility of the linear polymer, although the disposition of the hydrate water in $MoO_3 \cdot 2H_2O$ is not known. A perfect cleavage has been noted for $WO_3 \cdot H_2O$[2] in agreement with the layer lattice hypothesis.

The recent electron diffraction studies do not necessarily contradict these conclusions.[3] The conditions of sample preparation in this case were such as to produce $WO_3 \cdot 2H_2O$ and the description of the plate-like crystals is in agreement with other observations of this phase.[2] Due to the preferred orientation the period of only the basal plane could be determined. While the data were found to correspond with WO_3 it should fit $MoO_3 \cdot 2H_2O$ equally well. The Mo–Mo distances in the layer

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(25) J. W. Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green & Co., 1931, Vol. XI, p. 762.

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

are given as 3.71 and 3.77 Å.[13] while in one WO_3 plane the W–W distances are 3.71 and 3.79 Å.[27]

The nearly amorphous B phase is the polymerization product of acidified WO_4^{--} solution which has reached a sufficiently high molecular weight to become insoluble in water. This increase in molecular weight preceding precipitation has been observed most recently by light scattering.[8] The B phase also slowly precipitates from solutions of metatungstic acid. The titration of the freshly prepared B phase resembles that of metatungstic acid although an inflection due to the neutralization of free acid does not appear. The composition of the solution at the inflection point is that of sodium paratungstate. The metatungstate ion structure consists of four "Keggin" tritungstate groups which have condensed to form a spherical ion.[28] If alternate groups were turned through 180° an infinite ion would be formed by sharing of the same oxygen atoms as in the metatungstate ion. Further condensation, by cross linking, would produce the relatively inert C phase. Similarly, the X phase structure might be formed by a two-dimensional polymerization of the same groups which form the spherical paratungstate ion. The cation-exchange capacity of these polyanion phases may be limited by geometrical considerations as well as by the solubility of the phases at higher *p*H values.

Dissolution of the tungstic acids requires the breaking of bonds and the ultimate conversion to monomeric WO_4^{--}. With $WO_3 \cdot 2H_2O$ and $WO_3 \cdot H_2O$ the breaking of a single linkage by the addition of a hydroxyl ion might be followed by the formation of two new linkages. After the solvolysis of one bond the adjacent octahedra are still held in their lattice positions. The coördinated water molecules of each octahedron might then be replaced through the formation of hydroxo bridges. The $WO_3 \cdot 2H_2O$ structure presumably contains 2 molecules of water per octahedron so that continued attack by hydroxyl ion might convert the crystal surface to chains of doubly linked octahedra. These would resist depolymerization by the chelate effect. In the $WO_3 \cdot H_2O$ structure, since there is probably only one coördinated H_2O per octahedron, the double linkage formed by hydroxyl attack would alternate with single linkages. Continuous dissolution of the $WO_3 \cdot H_2O$ phase should then occur at lower hydroxyl concentrations than required to dissolve $WO_3 \cdot 2H_2O$.

Mo imitates the WO_3 structure in forming the $MoO_3 \cdot 2H_2O$ and yellow $MoO_3 \cdot H_2O$ compounds. The stable, white $MoO_3 \cdot H_2O$ may be a hydrate with a structure based on that of MoO_3. The structural differences between MoO_3 and WO_3 and the resulting relationship between the W and Mo bonding systems in non-aqueous phases have recently been reviewed.[29] In aqueous systems Mo can imitate W and possibly also U as well as form its own unique structures. The species of Mo(VI) in acid solutions (*p*H less than 1) have been reported as MoO_2^{++} complexes,[30,31,32] either monomeric or polynuclear depending on the anion. At higher *p*H values anionic complexes based on polymers of $(MoO_3)_4OH_2$ have been described.[33] In contrast, WO_3 is appreciably soluble only at acid concentrations greater than 10 normal[24] so that a WO_2^{++} complex is not stable at lower acidities. The UO_2^{++} complex is predominate in the aqueous and crystal chemistry of U(VI).[34] For Cr(VI) the CrO_4^{--} complex predominates.

Lindqvist has suggested that the isomorphous SO_4^{--}, CrO_4^{--}, MoO_4^{--} and WO_4^{--} anions are all tetrahedral complexes.[18] The equilibria between monomeric tetrahedral and polymeric octahedral species as a function of *p*H is described for W(VI) and Mo(VI) by the upper portions of the curves in Fig. 7. The MoO_4^{--} ion can be quantitatively precipitated as $PbMoO_4$ at a *p*H of 3 while a *p*H greater than 6.5 is required to precipitate stoichiometric $CoWO_4$.[35] The fact that polymolybdate compounds similar to sodium paratungstate are not known may thus be due to the greater stability of MoO_4^{--} in weakly acid solutions where olation phenomena may come into prominence.[36] Thus, the paratungstate ion structure[26] contains bound hydrogen while the paramolybdate ion structure[37] does not.

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