[CONTRIBUTION FROM THE REFRACTORY METALS LABORATORY, GENERAL ELECTRIC CO.]

Polymerization of Anions: The Hydrolysis of Sodium Tungstate and of Sodium Chromate[1]

BY MEYER L. FREEDMAN

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A coördination theory for the formation of isopolytungstates was developed from a study of the mode of polymerization of WO_4^{--} and of CrO_4^{--}. The pH of Na_2WO_4 and of Na_2CrO_4 solutions was measured as a function of concentration, ionic strength and time. The relation between polyion charge and polymerization number was determined from the slope of linear pH–log C plots. Structures of polynuclear species, consistent with hydrolysis equilibria, were deduced from various considerations based upon the principle that chromium retains tetracovalency while tungsten reversibly expands to octahedral coördination. The primary aggregation process of WO_4^{--} produces linear polymers of doubly linked octahedra in which one of each pair of shared oxygen atoms also binds a proton. Secondary aggregation processes involve coördination of this "ol" group to produce tetracovalent oxygen. Direct condensation of polyacids takes place in more acid solutions.

Introduction

Tungsten is one of the best known iso- and heteropolyacid forming elements, while polymerization of chromate yields only simple pyro ions.[2] The principles governing the formation of these complex anions are not known. Classical theories, such as those of Miolati and Rosenheim, have been made obsolete by the many crystal structure determinations of polyanions which have been reported.[3] Information is required concerning the aggregation processes in solution which lead to the formation of the known solid phase structures. Previous work in this area has been limited to determinations of the average composition of polyions in solution without regard to the mode of polymerization or to structural considerations.

The sulfate, chromate, molybdate and tungstate ions are all believed to be tetrahedral complexes, both in the solid state and in solution.[4] On acidification the chromate ion is converted to dichromate which is believed to retain tetrahedral coördination.[2] Acidified tungstate solutions yield paratungstate, metatungstate and tungstic acid solid phases in which octahedral coördination prevails.[5] Dissolved polynuclear species in acidified tungstate solutions have been reported as various hexatungstate ions as well as a tritungstate ion, all of unknown structure.[6] Octahedral coördination is assumed here also by analogy with the known water-derived solid polytungstates. The polytungstates obtained from fused melts are exceptions in that the coördination number of tungsten depends on the ratio of tungsten to oxygen. Thus, the ditungstate obtained by fusion has a structure containing both octahedral and tetrahedrally coördinated tungsten.[7] In water solution it is the pH rather than the tungsten to oxygen ratio which determines the coördination number of tungsten.

The hydrolysis studies of Na_2WO_4 and of Na_2CrO_4 reported here were made to determine the mode of polymerization of the anion during the initial stages of aggregation. A dilution method was used so that the normal tungstate or chromate ion, respectively, would be the predominant species at all times. Under conditions where the classical hydrolysis constant ratio may be applied, that is in dilute solution or at constant ionic strength, the slope of the dilution curve fixes the relation between polyion charge and polymerization number.[8]

$$nA^{--} + oH_2O \longleftrightarrow A_n^{z} + pOH^-$$

$z = 2n - p$ is required for electroneutrality while

$$\frac{d\,pH}{d\log C} = \frac{n}{1 + p}$$

follows from the condition of equilibrium. The composition and structure of the polyion can then be deduced for each value of n by assuming a value for the coördination number.

Dilution curves were obtained on both a one hour and a one month basis so that initial as well as final equilibria could be observed. Molar solutions of Na_2CrO_4 and of Na_2WO_4 were diluted with 3 M $NaNO_3$ and with M Na_2SO_4 to maintain an ionic strength of 3.00. Water was used as the diluent to study the hydrolysis in dilute solution. $NaNO_3$ rather than $NaClO_4$ was selected as the inert supporting electrolyte in order to retain the desirable saturated KCl salt bridge. The Na_2SO_4 was used to test for interaction between hydrolyzed and unhydrolyzed species. The SO_4^{--} is inert to hydrolysis in the pH range under consideration and might be expected to imitate the action of both CrO_4^{--} and WO_4^{--} in complex ion formation.

An electrostatic W to O bond has been postulated for the polytungstates.[9] However, the fact that the known structures violate three out of four of Pauling's rules for the linking of polyhedra in ionic crystals is evidence for covalency. The slow rate of oxygen exchange observed by Spitsyn[10] in his

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(1) Presented before the Division of Physical and Inorganic Chemistry, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 13, 1957.

(2) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, New York, N. Y., 1947.

(3) "Symposium on the Structure and Properties of Heteropoly Anions," 130th Meeting of American Chemical Society, Atlantic City, N. J., Sept. 1956.

(4) I. Lindqnist, *Nova Acta Regiae Soc. Sci. Upsaliensis*, **15**, Sci. IV, No. 1 (1950).

(5) J. C. Bailar, Jr., Editor, "The Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956.

(6) D. J. Bettinger and S. Y. Tyree, Jr., THIS JOURNAL, **79**, 3355 (1957).

(7) I. Lindqvist, *Acta Chem. Scand.*, **4**, 1066 (1950).

(8) Kuan Pan and Tong Ming Hsen, *Bull. Chem. Soc. Japan*, **26**, 126 (1953). They obtained different results in applying a similar dilution method to Na_2CrO_4 and Na_2WO_4. However, their rate of dilution appears to have been slow. Also, they used alcohol in recrystallizing the salts. It has been shown by J. Bye, *Ann. Chim.*, **20**, 463 (1945), that alcohol can produce contamination by isopoly salts.

(9) L. Pauling, "Nature of the Chemical Bond," Cornell University Press. Ithaca, N. Y., 1940.

(10) V. I. Spitsyn, *C. A.*, **50**, 10, 494 (1956).

isotope studies further supports the covalent bond concept. It should thus be possible to derive the known polyanion structures by the rules of coordination chemistry, provided that the mode of polymerization is known.

Experimental

Reagents.—Five lots of Folin grade $Na_2WO_4 \cdot 2H_2O$ were obtained from three manufacturers. Molar solutions prepared from these salts and purified water gave *p*H values ranging from 9.4 to 10.3. Values reported in the literature range from 9.15[8] to 10.5.[11] After repeated recrystallizations a *p*H of 9.05 was obtained. The recrystallized salt analyzed 10.94 ± 0.01% H_2O (fusion) and 70.27 ± 0.01% WO_3 (precipitation and weighing WO_3).[12] Calculated values are 10.92 and 70.28%, respectively. Neither powder X-ray diffraction patterns nor chemical analyses were clearly affected by recrystallization.

Potentiometric titration of the molar solutions with 0.1 *N* HCl showed the presence of from 0.01 to 0.03% of excess alkali, calcd. as NaOH, in the salts. Extrapolation of the common, straight line portion of the neutralization curves indicated a theoretical *p*H value of 8.85 for the molar solution. Since this degree of purity could not be attained, dilutions were made with the series of salts to determine the effect of the excess alkali. Other reagents were of analytical reagent grade.

Distilled water was purified by condensing the middle portion of distillate from a Pyrex fractionating column in a quartz condenser. The purified water and all solutions were stored in polyethylene bottles under nitrogen pressure.

Apparatus.—A dilution cell was constructed from an 8 oz. polyethylene bottle by sealing on side arms capped with rubber sleeves through which electrodes were inserted. Diluents were added from a Pyrex buret which fitted into the cell. Air was excluded by passing a stream of nitrogen which had been bubbled through NaOH and H_2SO_4 solutions.

The Beckman 1190-60 glass and saturated calomel electrodes were used with the Model G potentiometer for *p*H measurement. The outer barrel of the calomel electrode was replaced by a polyethylene tube through which a small Pyrex fiber was sealed. Temperature was maintained at 25 ± 0.2° by means of an external infrared heater controlled by a mercury thermoregulator. Magnetic stirring was used. The Beckman standard buffer solutions were used for calibration.

Procedure.—In the "forward" dilutions 50 ml. of test solution was pipetted into the dilution cell and increments of diluent added from the buret. *p*H readings were taken after each addition when constancy was observed for a 1-minute period. Periodically, when the total volume reached 150 ml., 100 ml. of the solution was removed by pipet and stored in a polyethylene bottle at 25°. The *p*H of the stored solutions were measured at intervals of a week or more until constancy was observed. Salt solution diluents were adjusted to a *p*H of 6.8–7.0 with 0.05 *N* NaOH. In the "reverse" dilution 100 ml. of diluent was placed in the cell and titrated with 25 ml. of test solution.

Results and Discussion

(A) Na_2CrO_4 Hydrolysis.—The dilutions required approximately one hour. Final *p*H values were measured after one week and did not change appreciably after a second week. Similar dilution curves were obtained with freshly prepared Na_2CrO_4 solutions and with solutions which had aged for 10 days before dilution. The slope of the dilution curve defines the reaction which takes place as the equilibrium is shifted by dilution. Equilibrium concentrations of $HCrO_4^-$ or $Cr_2O_7^{--}$ present in the original solution do not interfere, since the degree of hydrolysis of the predominant CrO_4^{--} increases as dilution progresses.

Dilution curves are shown in Fig. 1, while the indicated reactions are summarized in Table I. The dilution curve with water is considered only at low concentrations where the activity coefficient ratio can be assumed to be constant. Similarly, the dilution curve with Na_2SO_4 is considered only at low Na_2CrO_4 concentrations where the SO_4^{--} concentration is approximately constant.

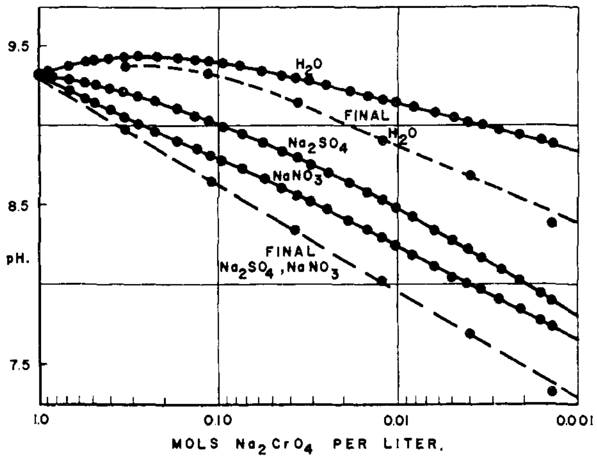

Fig. 1.—Dilution curves for Na_2CrO_4. Final values were taken after 1 week.

The initial hydrolysis reaction at low ionic strength appears to be the binding of two protons by a hydrated CrO_4^{--} to produce a labile neutral molecule. This initial product rearranges slowly at low ionic strength to chromic acid, which is largely ionized to $HCrO_4^-$. The rearrangement may involve the transfer of protons from bound water of hydration to the central CrO_4^{--}. This rearrangement is more rapid at high ionic strength, since $HCrO_4^-$ is the initial product observed in the dilution with $NaNO_3$ solution. The near linearity of the $NaNO_3$ curve shows that NO_3^- and CrO_4^{--} interact only to a minor extent. However, SO_4^{--} reacts to produce a sulfato-chromate complex ion as an initial product. Both $HCrO_4^-$ and $Cr_2O_7^{--}$ are unstable at high ionic strength. The final dilution curves with both $NaNO_3$ and Na_2SO_4 solutions coincide and show $Cr_2O_7^{--}$ to be the final hydrolysis product in both cases.

Since the final equilibrium is at a lower *p*H than that producing $HCrO_4^-$, the latter ion does not appear to be an intermediate in $Cr_2O_7^{--}$ formation. Direct condensation of $HCrO_4^-$ to $Cr_2O_7^{--}$ has been postulated by Neuss and Rieman.[13] They assumed a mechanism

$$CrO_4^{--} \overset{K_1}{\longleftrightarrow} HCrO_4^- \overset{K_2}{\longleftrightarrow} Cr_2O_7^{--}$$

and calculated the constants from *p*H measurements of mixed K_2CrO_4 and $K_2Cr_2O_7$ solutions. Since all three ions were present in their test solutions, the *p*H measurements fixed the over-all constants without defining the equilibria involved. The data of Neuss and Rieman fit an alternate mechanism equally well

$$HCrO_4^- \text{ (unstable) } \overset{K_1}{\longleftrightarrow} CrO_4^{--} \overset{K_1^2K_2}{\longleftrightarrow} Cr_2O_7^{--} \text{ (slow)}$$

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[11] K. Saddington and R. Cahn, *J. Chem. Soc.*, 3526 (1950).

[12] "Scott's Standard Methods of Chemical Analysis," 5th Ed., D. Van Nostrand Co., New York, N. Y., 1939.

[13] J. Neuss and W. Rieman III, THIS JOURNAL, **56**, 2238 (1934).

The observed slow rate of $Cr_2O_7^{--}$ formation suggests a molecular rather than an ionic reaction. A bimolecular condensation of H_2CrO_4 followed by ionization to $Cr_2O_7^{--}$ would be in agreement with the experimental observations and is suggested as a possible mechanism.

Classical hydrolysis constants were used here because activity coefficients of the ions could not be estimated for the high ionic strength solutions and were not needed at the low ionic strengths.

TABLE I

Na_2CrO_4 HYDROLYSIS EQUILIBRIA

Diluent	Ionic strength	CrO_4^{--} concn.	Slope		Hydrolysis product	pK_h	
			Obsd.	Calcd.		Obsd.	Calcd.[a]
			Initial Hydrolysis				
Water	<0.15	<0.05	0.30	0.33	$(CrO_4{\cdot}2H_2O)$	12.9	..
$NaNO_3$	3.00	> .001	.55	.50	$HCrO_4^-$	9.5	..
Na_2SO_4	3.00	< .02	.65	.66	$CrSO_7^{--}$	14.9	..
			Final Equilibrium				
Water	< .30	<0.10	0.50	0.50	$HCrO_4^-$	8.2	7.5
$NaNO_3$	3.00	> .001	.66	.66	$Cr_2O_7^{--}$	14.1	13.4
Na_2SO_4	3.00	> .001	.66	.66	$Cr_2O_7^{--}$	14.1	13.4

[a] Data of Neuss and Rieman.[13]

(B) **Na_2WO_4 Hydrolysis.**—Dilution curves for the recrystallized $Na_2WO_4{\cdot}2H_2O$ are shown in Fig. 2. The *p*H values of aged solutions made with all three diluents coincided within a range of 0.05 *p*H unit after a month, as shown by the dotted line in Fig. 2. There was no further change in *p*H after an additional two weeks storage. The same phenomenon was observed with the stored solutions from 60 dilution experiments made with the various molar Na_2WO_4 solutions having initial *p*H values of 9.05 to 10.3.

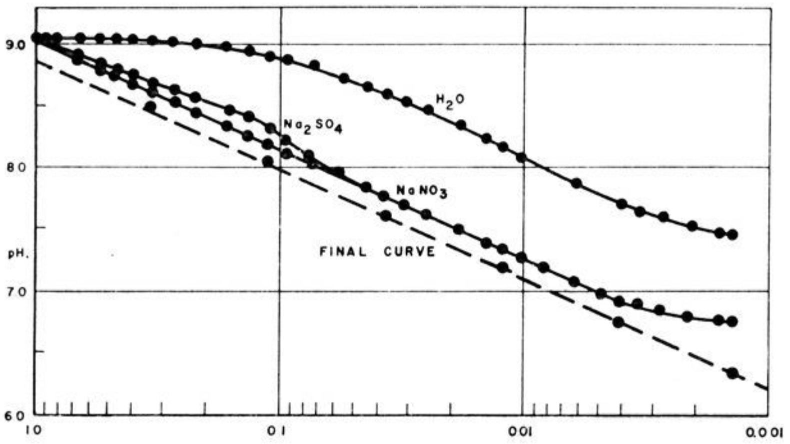

Fig. 2.—Dilution curves for Na_2WO_4. Final values were taken after 4 weeks.

The shape of the dilution curves was independent of the initial *p*H value in this range. Dilutions with water produced a family of parallel curves having a slope of 1 over the 0.05 to 0.004 *M* range. Dilutions with 3 *M* $NaNO_3$ produced linear curves with a slope close to 1 (0.90–0.95) over the 1.0 to 0.004 *M* range. Erratic results were obtained with the *M* Na_2SO_4 diluent, although these tended to coincide with the $NaNO_3$ curves. Below 0.004 *M* the curves for all three diluents approximate a slope of 0.3.

Similar dilution curves were obtained for Na_2WO_4 solutions made up directly in the dilution cell as for solutions which had aged several weeks. Forward and reverse dilution curves agreed closely provided the dilution time was below 1.5 hr. At a slower rate of dilution the inflection at 0.004 *M* disappeared. When the dilution time with water was prolonged beyond 2 hr. an "S" shaped curve was obtained. The *p*H in this case dropped sharply near the 0.1 *M* concn. point and then followed the $NaNO_3$ dilution curve to lower concentrations.

A dilution curve with water having a slope of 0.3 over the 0.1 to 0.01 *M* range was obtained by eliminating most of the points so that the dilution time was decreased to 20 minutes. The slope of this curve was nearly zero below 0.01 *M*. Both the inflection near 0.01 *M* observed in this rapid dilution and the inflections at 0.004 *M* previously discussed are electrode effects probably due to adsorption by the glass electrode. The point of inflection can be raised to higher concentrations by reducing the volume of solution as well as by shortening the dilution time.

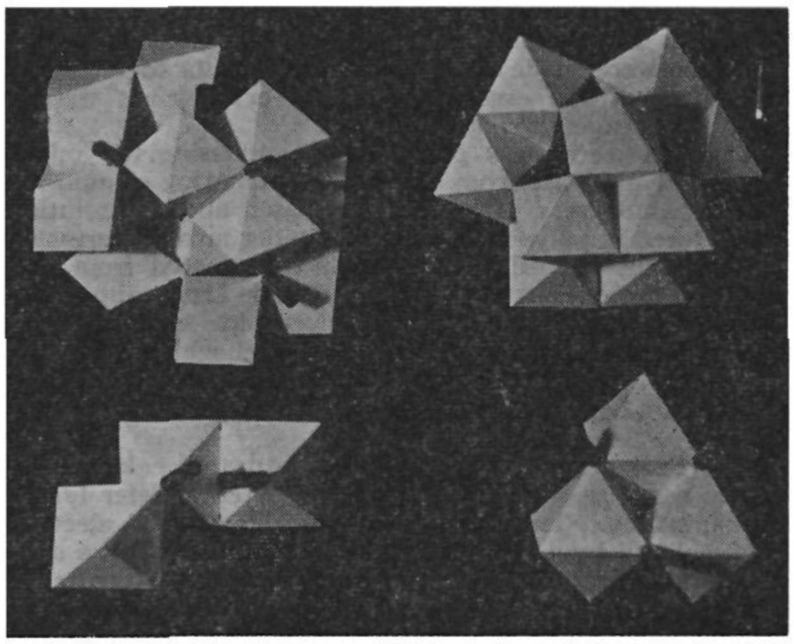

Fig. 3.—Octahedral models showing bound hydrogen atoms: top row, paratungstate $H_{10}W_{12}O_{46}^{-10}$, metatungstate $H_2W_{12}O_{40}^{-6}$; bottom row, linear $H_2W_3O_{12}.2H_2O^{-4}$ and limiting $H_4W_3O_{13}^{-4}$ tritungstate ions.

A mononuclear hydrolysis product, presumably a labile dihydrotungstate molecule, appears only at rapid dilution rates. While a sulfato-tungstate complex ion appears to form, it is too unstable for definite characterization. At the slower dilution rates both the unstable polynuclear species produced in dilute solution and those formed at higher ionic strength are characterized by a dilution curve slope of 1. As was observed previously with Na_2CrO_4, the effect of high ionic strength is to accelerate attainment of the final equilibrium state.

The Na_2WO_4 solutions exhibit a very strong but slow acting buffering effect. The NaOH present in the original solutions is gradually neutralized so that all solutions having the same Na_2WO_4 concn. finally reach the same *p*H. These solutions were stored in tightly closed polyethylene bottles. Since it has been shown that polyethylene is permeable to gases,[14,15] an experiment was made to determine the magnitude of atmospheric CO_2 absorption. A clear solution of $Ba(OH)_2$ was stored in a polyethylene bottle and observed

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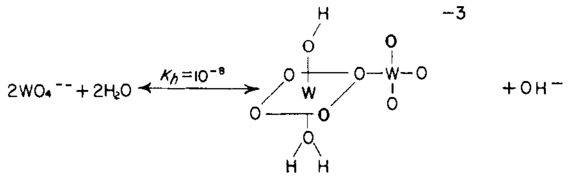
(14) R. G. Bates, "Electrometric *p*H Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954.

(15) A. W. Myers, *et al.*, "Modern Plastics," May, 1957.

periodically. Since a month was required to develop the first traces of turbidity, it is considered that the absorption of CO_2 was not a factor in effecting the *p*H changes of the aged Na_2WO_4 solutions.

(C) **Polymerization of WO_4^{--}.**—An equilibrium between four and six coördinated tungsten is postulated as the basic mechanism in the formation of iso- and heteropolytungstates. This mechanism applies also to the molybdates and presumably to the vanadates as well. Evans has noted the tendency of vanadium to increase coördination under acid conditions.[16]

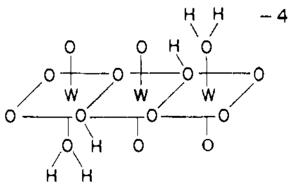
Binding of protons by a hydrated WO_4^{--} ion is presumed to weaken the tetrahedral complex so that expansion of covalency takes place with the coördination of two water molecules to complete the octahedral structure. Displacement of a coördinated water molecule by a tetrahedral WO_4^{--} group would produce an unstable ditungstate ion which is suggested as the initial hydrolysis product observed in dilute solution. The coördinated WO_4^{--} group may itself add a proton and expand to octahedral covalency. The resulting complex ion contains coördinated water molecules which may be further replaced by donor ions such as WO_4^{--}. A series of linear complexes may thus form by the successive additions and expansions of covalency of tetrahedral WO_4^{--} ions.



Since stable, polynuclear tungstates are octahedral, the structure and mode of formation of these linear complexes can be estimated from the observed dilution curves. In the past, researches on acidified tungstate solutions have been based upon the assumption of single predominant polyionic species. However, as Sillén has pointed out, "One may doubt whether it is ··· at all likely that Nature would select, out of all possible polynuclear complexes, exactly the one or two proposed by a certain chemist."[17]

The ionic charges of the stable linear polytungstate ions produced by hydrolysis of WO_4^{--} must be numerically one greater than their polymerization numbers (n) to fit the observed slope of 1. The number of bound hydrogen atoms must be one less than n, and two molecules of coördinated water are required per polyion to complete the octahedral structure. The structure consists of octahedra sharing edges, one oxygen of each bonding pair being olated. A linear tritungstate structure is shown as

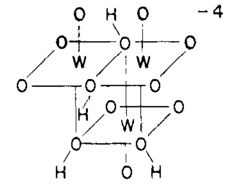
$$nWO_4^{--} + (n+1)H_2O \xrightleftharpoons{K_h = 10^{-15}} H(n-1)(WO_4)_n\,{}_2H_2O^{-(n+1)} + (n-1)\,OH^-$$



The linear polytungstate ions derived above are considered to be the anions of moderately strong acids. Baker has reported acid dissociation constants for a heteropoly anion in the 10^{-3} range.[18] Ionization of the bound hydrogen (oxolation) would generate acid equivalent only to the base produced by formation of the polyion. An additional source of hydrogen ion is needed to account for the neutralization of excess alkali and the extension of the dilution curves into the acid region.

A limiting tritungstate ion having acid properties is derived from geometric considerations. The linear ditungstate ion, which consists of 2 octahedra with one edge in common, has 22 available edges to share with a third octahedron. Eight of these edges lie between the two linked octahedra so that a third WO_4^{--}, after coördination with one octahedron and expansion of covalency, could form an olated bond to the second octahedron and coördinate with the originally doubly linked oxygen. The resulting structure would contain no coördinated water. It should be more stable than the linear polymers since each tungsten atom is now linked to its neighbors by three bonds.

The limiting tritungstate ion must contain four bound hydrogen atoms in agreement with the slope of the dilution curve. These are assigned to the four multiply linked oxygen atoms to give the structure



The reversible oxolation of this ion as a function of *p*H and concentration provides the acid buffering action shown by the dilution curves.

$$(H_4W_3O_{13})^{-4} \longleftrightarrow (W_3O_{13})^{-8} + 4H^+$$

Additional evidence for the limiting tritungstate ion is obtained from the aqueous and crystal chemistry of the isopolytungstates. The paratungstate ion has an analytical formula of $(W_{12}O_{41})^{-10}$,[11] while the crystal structure is $(W_{12}O_{46})^{-20}$.[19] It is necessary for the present work to locate the hydrogen atoms in the paratungstate structure. Published dehydration studies are not in agreement.[11,20] Due to the high atomic weight of tungsten, even a limited degree of polyionic structure should provide an X-ray diffraction pattern. Accordingly, finely powdered samples of $Na_{10}W_{12}O_{41}\cdot{}_{28}H_2O$ and $Na_6H_2W_{12}O_{40}\cdot{}_{29}H_2O$ were dehydrated over P_2O_5 at room temperature and 10μ pressure for

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(16) H. T. Evans, Jr., paper presented at the 130th National Meeting of American Chemical Society, Atlantic City, N. J., Sept., 1956.

(17) L. Sillén, *Acta Chem. Scand.*, **8**, 299 (1954).

(18) L. C. W. Baker, *et al.*, THIS JOURNAL, **75**, 2493 (1953).

(19) I. Lindquist, *Acta Cryst.*, **5**, 667–670 (1952).

(20) V. I. Spitsyn, *C. A.*, **51**, 925 (1957).

two days. The apparatus was arranged so that the dehydrated salts could be sealed into micro glass capillaries without exposure to moisture. The dehydrated metatungstate produced a powder X-ray diffraction pattern of a few diffuse lines, while that of the dehydrated paratungstate was completely blank. The bound hydrogen in the paratungstate anion structure thus appears to be uniformly distributed, since the structure was so completely disrupted by dehydration. Shott and Harzdorf have reviewed the Keggin structure for the metatungstate anion and show that two hydrogen atoms are bound within the anion.[21] The metatungstate anion contains four oxygen atoms which are each bound to three tungsten atoms. These oxygen atoms are located in the interior of the structure where only two bound hydrogen atoms can be accommodated. The paratungstate structure of Lindquist contains 10 triply linked oxygen atoms. These are located over the exterior of the structure. Accordingly, a hydrogen atom is assigned to each triply linked oxygen and the paratungstate ion is then written as $H_{10}W_{12}O_{46}^{-10}$.

The metatungstate anion structure is composed of four limiting tritungstate ions which have condensed by sharing corners. All of the doubly linked oxygen atoms are oxolated, while the triply linked oxygen retains bound hydrogen. The metatungstate structure is derived in acid solution by condensation of four molecular limiting tritungstate acids with elimination of water. Two additional bonds per tritungstate unit are produced by anion exchange as dictated by geometrical considerations.

The paratungstate ion is derived in neutral or weakly acid solution by coördination of limiting and linear tritungstate ions. The coördinated water molecules of the linear ions are displaced by the limiting tritungstate ions. Additional bonds are then produced by the exchange of a singly linked oxygen from the limiting ion for an olated oxygen of the linear ion. The combination of two limiting ions with two linear ions to generate paratungstate results in the conversion of eight olated oxygen atoms to triply linked ones. Since these oxygen atoms which bind together three tungsten atoms also bind a hydrogen atom, the coördination of the oxygen is tetrahedral. The driving force for the aggregation of the polyions in weakly acid solutions is thus the tendency for an olated oxygen atom to expand to tetrahedral coördination.

Sodium paratungstate is not stable in solution but disproportionates to tungstate and metatungstate.[22] The rate both of disproportionation and of formation is slow at room temperature. A molar solution of Na_2WO_4 which had been acidified with nitric acid to a *p*H of 5 was allowed to stand in a polyethylene bottle at room temperature. Crystals of $Na_{10}W_{12}O_{41}\cdot 28H_2O$ began to form in a few days and continued to deposit for a period of a month. Further crystallization did not take place after that time. The total yield was approximately 40%. When a freshly acidified solution was concentrated to half its original volume by boiling, an 80% yield of $Na_{10}W_{12}O_{41}\cdot 28H_2O$ was obtained. It thus appears that the limiting tritungstate ion is produced by hydrolysis of WO_4^{--} at a rate about the same as that of the linear tritungstate ions. However, the latter ions are unstable with respect to rearrangement to the limiting ion structure. Because of its symmetrical structure the paratungstate ion can crystallize readily. This particular combination of linear and limiting tritungstate ions is thus removed from solution at the expense of other less symmetrical polynuclear species which may be present in equilibrium.

Linear and limiting polytungstate ions would not be expected to combine in the diluted Na_2WO_4 solutions because of their very low concentrations. A large number of polynuclear species should form in acidified tungstate solutions by secondary aggregation processes involving anion exchange and formation of tetrahedral oxygen linkages. Further acidification results in hydrolysis of olated bonds so that only those aggregates remain stable in which the tungsten atoms are bound by a tetrahedral oxygen atom. These simple polyacids, however, can condense to larger aggregates by elimination of water. At higher acid strengths the tetrahedral oxygen linkages are hydrolyzed and the resulting mononuclear H_6WO_6 octahedra link together by elimination of water to form the infinite ion tungstic acid structure.[23]

(D) Heteropoly Anions.—The principles observed in the polymerization of the tungstates should apply also to heteropoly complexes. It appears that the hetero atom is always linked through tetrahedrally coördinated oxygen atoms. The basicity of polyanions of unknown structure might be estimated on this basis.

Evans has determined the structure of the 6-molybdotellurate anion.[24] The central tellurium atom is bound to six doubly linked oxygen atoms of a linear hexapolymolybdate ion so that six tetrahedral oxygen atoms are produced. A molecular $H_6TeMo_6O_{24}$ composition is obtained by assigning 6 hydrogen atoms to complete the tetrahedral oxygen array. Due to the electronegativity of tellurium the complex has acid character and is ionized to $TeMo_6O_{24}^{-6}$.

Baker has found that trivalent aluminum, chromium, iron and cobalt are octahedrally coördinated in their 6-molybdoheteropoly anions.[25] The structure of these anions should then duplicate the Evans model. However, due to the positive nature of these hetero atoms, the six tetrahedral oxygen atoms would now be expected to bind protons firmly. The composition can then be written as $H_6AlMo_6O_{24}^{-3}$. Baker has suggested a dimeric structure without bound hydrogen.[25] An X-ray diffraction study of one of the salts showed the simplest crystallographic unit cell to contain two empirical formulas.[26] However, this was not considered either to prove or to disprove dimerization.

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(21) G. Shott and C. Harzdorf, *Z. anorg. Chem.*, **288**, 15 (1956).

(22) K. C. Li and C. V. Wang, "Tungsten," Reinhold Publ. Corp., New York, N. Y., 1955.

(23) I. Lindquist, *Acta Chem. Scand.*, **4**, 650 (1950).

(24) H. T. Evans, Jr., THIS JOURNAL, **70**, 1291 (1948).

(25) L. C. W. Baker, *et al.*, *ibid.*, **77**, 2136 (1955).

(26) L. C. W. Baker, *et al.*, *ibid.*, **77**, 2200 (1955)

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Cleveland 17, Ohio

[Contribution from the Oak Ridge National Laboratory, Chemistry Division]

The Electrical Conductivity of Solutions of Alkali Metals in their Molten Halides[1]

By H. R. Bronstein and M. A. Bredig

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The electrical conductivity of alkali metal solutions in their molten halides has been measured by means of a synthetic sapphire conductance cell. The *specific* conductance *increases* with increasing metal concentration. The *equivalent* conductance of K, Λ_K, in both KCl and KBr also *increases*, namely, from 2800 ohm^{-1} cm.^{2} (K–KCl, 820°), 6100 (K–KBr, 760°) and 6500 (K–KBr, 870°) at infinite dilution, to 38,000, 83,000 and 71,000 ohm^{-1} cm.^{2} at 19, 23 and 20 mole % K, respectively, the maximum concentrations measured. However, Λ_{Na}, for Na in NaBr at 895° *decreases* from 12,500 to a minimum of 7300 ohm^{-1} cm.^{2} at *ca.* 9 mole % metal. At 805° Λ_{Na} in NaBr decreases from *ca.* 12,000 at infinite dilution, *i.e.*, approximately the same value as at 895°, to less than 5000, and in NaCl at both 845 and 890° from *ca.* 6000 to less than 3000 ohm^{-1} cm.^{2}. These values are the equivalent conductances at 5, 4 and 3 mole % Na, respectively, representing the metal solubility limits which are too low to permit the equivalent conductance minima to be realized. The different behavior of sodium and potassium may be related to the liquid phase equilibria and to the dissociation energies known for the diatomic gaseous metal molecules, both of which reflect a greater tendency to associate for Na than for K at the test temperatures. Such association, which increases with metal concentration, decreases the number of metal particles per equivalent of metal on which the electronic fraction of the conductance is thought to depend. The effect of the association, not strong enough in the K systems to produce a minimum in equivalent conductance, is, in the Na systems, surpassed, at the minimum, by the effect of the gradual establishment of the metallic conductance band through overlap of the orbitals of the metal polymers. The differences in equivalent conductance at infinite dilution for the various systems may be taken to reflect the influence of the different degrees of polarization of the anions by the cations on electron mobility.

Introduction

Concurrent with the determination of the phase equilibria in the sodium–sodium halide,[2] cesium–cesium halide,[3] potassium–potassium halide[4] and rubidium–rubidium halide[5] systems, a study of some of the more significant physical properties of these solutions was undertaken. Of various measurements, which should help elucidate the state of the electron introduced by the metal atom, such as those of electrical conductance and transport, viscosity, Hall effect, magnetic susceptibility and optical or infrared absorption, the determination of the electrical conductance, as a function of composition and temperature, was chosen as most readily attainable experimentally at the present time.

The literature shows examples of a decrease rather than an increase in electrical conductance on addition of metal to salt in the systems $CdCl_2$–Cd,[6] $BiCl_3$–Bi[7] and $CaCl_2$–Ca.[8] In $CdCl_2$–Cd, this effect was attributed to the formation of $(Cd{:}Cd)^{2+}$ analogous to the complex cation Hg_2^{++}. The existence of similar ions, *e.g.*, K_2^+, in the case of the alkali metal solutions also would lead to a decrease in specific conductance. If, however, the M_2^+ ion is a shallow trap for the electron, an increase in the specific conductivity could be expected. Other models for electron traps from which electrons similarly as in solid semi-conductors would be raised by thermal energy into the conduction band might stress similarity with color centers in halide crystals. However, such similarity has been disputed in the past, and undissociated metal atoms were assumed to be present in the molten state of F-center-colored halides,[9] In any case, additive behavior with respect to electrical conductance, which would correspond to an increase by a factor of little less than 100 of the specific conductivity of the pure salt for every mole per cent. of alkali metal added, is not anticipated. Rather, a pronounced negative deviation from additivity is expected, as the environmental forces acting on the electron in the solution, irrespective of the special model accepted, differ greatly from that in the pure metal.

Experimental

Apparatus.—The reactivity and volatility of the alkali metals at high temperatures necessitated the rather complicated apparatus to be described (Fig. 1). Quartz was not used for the dip cell as it is strongly attacked by alkali metals at high temperatures. Hot pressed beryllium oxide, though resistant to attack by alkali metals, was slightly porous. Single crystals of magnesium oxide, also resistant to alkali metal attack, were subject to easy fracture. Finally, a cell constructed from a large, single crystal of synthetic sapphire, Al_2O_3, was found excellent for use in these solutions. It cannot, of course, be used in fluoride salt melts.

The rotatable turret and entry ports were necessary for introducing the liquid alkali metal as well as the cell and sampler assemblies. The closure pads were incorporated in the apparatus to eliminate as much as possible the loss of alkali metal from the solution by vaporization and diffusion to the cold portion of the apparatus. The auxiliary heaters around the shield tubes permitted the cell and sampler to be heated to the solution temperature, so that their entry into the solution would not cause localized change in concentration by partial solidification of the salts.

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