

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY]

THE INSTABILITY OF CERTAIN TUNGSTATES IN WATER

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During determinations of the electrical conductivity of various solutions it was noticed that certain tungstate solutions slowly increased in conductivity at ordinary temperatures. It was decided to investigate the matter further in order to throw light upon the nature of the change, and the physico-chemical study has led to a number of new observations upon the tungstates.

Salts Studied.—Several tungstates were very kindly placed at my disposal for this purpose by Professor Edgar F. Smith. The principal observations were made with ammonium paratungstate. This salt as shown by Marignac, and confirmed by Taylor¹ crystallizes with the composition $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$ in plates with $5\text{H}_2\text{O}$ on the steam bath, but in needles with $11\text{H}_2\text{O}$ at ordinary temperatures. The specimen used had been purified by the method of Exner² and was of a high degree of purity.

A number of observations were also made with a salt supposed to be sodium metatungstate, but which proved upon analysis to possess a different composition. It was analyzed by dissolving in water, repeatedly warming with hydrochloric acid, evaporating and baking. The tungstic oxide was weighed in the same dish in which decomposition took place. After complete separation of all tungstic oxide from the filtrate, the sodium was determined as chloride with the following results:

Theory $\text{Na}_6\text{W}_5\text{O}_{27}\cdot 17\text{H}_2\text{O}$		Found		
		I	II	Average
$3\text{Na}_2\text{O} =$	186.0 7.92	8.00	7.96	7.98
$8\text{WO}_3 =$	1856.0 79.04	78.78	79.03	78.91
$17\text{H}_2\text{O} =$	<u>306.2</u> <u>13.04</u>	<u>13.37</u>	<u>12.89</u>	<u>13.13</u>
	2348.2 100.00	100.15	99.88	100.02

The salt was therefore sexasodium-octatungstate, and so far as I can find, has not been described in the literature. It is very soluble in hot water, and crystallizes slowly from cold solution. It is highly efflorescent. It may be briefly designated sodium octatungstate.

Very little is known about the molecular structure of these salts. They appear to be examples of a very large number of salts containing a large proportion of tungstic oxide and water. The chief uncertainty concerns the line of demarcation between water of constitution and water of crystallization.

Effect of Temperature.—The increase of conductivity with time was so slight at 20° that it escaped notice when the conductivity was first taken at that temperature. At 25° the increase was noticeable. With a fresh

¹ Thesis, Univ. of Penn., 1901.

² Pr. Am. Phil. Soc., 43, 123.

solution N/128 equivalent-normal, of ammonium paratungstate, the equivalent conductivity increased from 95.1 to 109.0 in six days' standing in glass. Part of the same solution in a platinum bottle, under similar conditions, suffered the same change. This was a most conclusive proof that the change was not due to the action of the tungstates upon the glass. For double assurance, a number of the conductivity cells were tested with various electrolytes and the glass was found to be of excellent quality.

At 50° the rate of increase was decidedly greater.

When a cell containing the solution was immersed in a thermostat at 80°, the value of Λ rose rapidly to about 217, then more gradually to 283 in 3 hours. The concentrating of the solution by evaporation was extremely slight. The same solution cooled to 25° gave $\Lambda = 122$.

Again, solutions of both ammonium para- and sodium octatungstates were made up afresh to N/64 normal and heated in a thermostat at 80° \pm 1. Small portions were pipetted into the conductivity cell from time to time, cooled to 25° and measured. Below are given the times and equivalent conductivities.

Time from start of dissolving.	Equivalent Conductivity	
	Ammonium paratungstate.	Sodium octatungstate.
25 minutes		125
40 "	98	142
50 "	103	146
60 "	107	148
70 "	110	149
90 "	112	150
180 "	114	153

Evidently the increase under study was the same transformation which has long been known in the case of the paratungstates to occur on boiling.¹ The transformation of the octatungstate is similar. Both complete themselves in about three hours at 80°.

The initial conductivities of these salts.—Since the rate of the transformation which these salts undergo when dissolved in cold water is not a rapid one, it is obvious that the conductivity observed immediately after dissolving most nearly represents their true conductivity. Of course, owing to hydrolysis, the observed conductivity, even then, may be partly that of base or acid, but this need not be considered here. The problem was to get weighed quantities dissolved quickly in *cold* water and made up to standard volumes. It was found very difficult to effect this solution rapidly. It seems to be a general rule that the more a salt is hydrated, the more slowly it dissolves in water. But the tungstates were unusually bad in this respect. Even when the salts were reduced to a very fine powder in an agate mortar, it required nearly two hours

¹ Knorre : Ber., 18, 2362 (1885).

with constant agitation to get weighed portions completely into solution. Accordingly the results probably approach only within about one per cent. of accuracy.

In the table below the dilution, v , represents the number of liters containing the indicated equivalent weight of salt and $A = 1000 Kv$ the, *equivalent conductivity*, where K is the specific conductivity. The apparatus employed was essentially that described by Ostwald¹. The cell factors were determined by pure $N/50$ KCl, using Kohlrausch's values for the specific conductivity of that salt. The bridge wire, flasks, pipettes and thermometer were calibrated and standardized with somewhat greater care than the best results warranted. The difficulties were chiefly of a chemical nature. The water used had a specific conductivity of less than 2.0×10^{-6} . It was preserved in a Jena flask with glass stopper through which passed a siphon and connection to a soda-lime tube. Its conductivity was subtracted from all observed conductivities.

V	INITIAL EQUIVALENT CONDUCTIVITY, Λ , AT 25°.	
	$1.10 (NH_4)_{11}W_{12}O_{41} \cdot 5H_2O = 513.4$	$1.6 Na_6W_8O_{27} \cdot 17H_2O = 391.4$
32	62.0	86.0
64	71.7	101.8
128	83.7	118.0
256	93.3	135.7
512	103.9	155.
1024	120.2	177.
2048	...	199.

Since ammonium paratungstate is not very soluble, the conductivity of its saturated solution was also determined, to aid in getting at its true solubility. A special cell was used, similar to one described by Böttger². It could be closed by a well fitting glass stopper carrying the electrodes, and could be rotated in a thermostat at any desired temperature. An excess of the finely powdered salt was introduced into conductivity water and agitated at 25°. Small portions were added every few minutes for about 15 minutes, when the conductivity became fairly steady. The specific conductivity of the saturated solution of ammonium paratungstate at 25° was 0.0051, 0.0054, and 0.0053, the average being 0.0053. By extrapolation this yields a solubility of about 3.5 grams in 100 grams of water, which is much less than Taylor obtained. It is true that the conductivity would have increased a little upon further agitation, but the increase would also have continued indefinitely on account of the transformation of some salt in solution and the dissolving of more to maintain a constant solubility of the body in excess. The fairly steady value above, therefore, seems most nearly accurate.

¹ Ostwald-Luther's Physik. chem. Messungen, p. 395.

² Z. physik. Chem. 46, 189.

Final values of the conductivity.—Ammonium para- and sodium octatungstates were again investigated to establish with certainty the maximum that would be reached with each salt when equilibrium had been established. The trials made to find out how long the solutions must be heated to attain this maximum had shown that over 3 hours heating at 80° caused no further increase in conductivity. The solutions were accordingly heated 3 hours in a platinum bottle, thus avoiding contamination with silica. The conductivity, however, was taken at 25°.

MAXIMUM VALUES OF EQUIVALENT CONDUCTIVITY.

V	Ammonium para-tungstate.	Sodium octatungstate.
16	139
32	(102)	149
64	112	160
128	121	172
256	131	184
512	139	197
1024	148	210

Although these values do not represent the conductivities of the original salts, it is an open question whether all, or if not, how much of the salts is transformed. The fact that these salts may be recrystallized does not necessarily prove incomplete transformation, because previous workers may not have heated them long enough to completely decompose them. Still, all evidence favors the view that the decomposition is incomplete. Probably an equilibrium is established in the solution between salts of various degrees of complexity. The salt which crystallizes out, therefore, will depend not only upon the solubility but also upon the concentration of the individual constituents in the solution. Knorre has in fact shown that from a mixture of meta- and normal sodium tungstates in solution the intermediate para-salt will separate. There was no evidence, after 3 hours' heating, of any further shifting of the equilibrium at ordinary temperatures. The conductivity of previously heated solutions showed in one case 0.2 per cent. increase, in another case 0.4 per cent. decrease in 5 days.

After the above considerations with two tungstates, some other experiments may be described which bear upon the topic under discussion.

Sodium paratungstate.—A preparation of Schuchardt was dissolved. Its conductivity increased even more rapidly than in the case of the ammonium salt at 25°. A solution which was slightly warmed for 2 hours increased in conductivity by 16 per cent. Upon passing carbon dioxide into the solution a decrease resulted, as one would expect.

Tungstic oxide.—According to Dammer's handbook, a white hydrate $\text{WO}_3 \cdot 2\text{H}_2\text{O}$, is precipitated from tungstates by acids in the cold and said to possess an acid reaction towards litmus. It could not be shown and

seems doubtful whether the well washed hydrate would be soluble enough to affect litmus and the acid reaction was more likely due to acid adsorbed during the precipitation. This adsorption effect was easily shown in a quantitative way. Some hydrate in a nitric acid solution after thorough shaking was allowed to settle. The clear solution above was titrated with alkali and 1 gram found equivalent to 0.62 cc. of alkali. The remaining solution around the hydrate, with the latter present, was titrated, the tungstic oxide determined and subtracted from the weight of the mixture, and it appeared that 1 gram of the solution bathing the precipitate required 0.70 cc. of alkali.

The hydrated oxide repeatedly washed with conductivity water became yellow. That its conductivity is very small was shown by the conductivity of its solution, as follows :

Some oxide was prepared both from the sodium and the ammonium salts by precipitation with nitric acid, and washed many times. It was finally introduced into the special solubility cell in a thermostat at 25°. Washing was continued until a constant value was obtained. The water had a specific conductivity of 1.7×10^{-6} , which was subtracted as before.

SPECIFIC CONDUCTIVITY OF HYDRATED TUNGSTIC OXIDE SOLUTION AT 25°.

Oxide from sodium octatungstate	$K = 9.4 \times 10^{-6}$	
	10.6	“
	10.7	“
“ “ ammonium para salt	10.7	“
	10.3	“
Average		

The above values were obtained after about 15 minutes shaking with fresh water. The increase after 15 minutes shaking was very little, but, it must be admitted, persistent. There appeared to be no limit to their increase, but in such a small conductivity the part due to the water seemed too uncertain to ascribe the increase wholly to the tungstic oxide. It is possible, but improbable, that the hydrate was passing into a more stable and soluble form. The increase in some of the solution which was preserved for 6 months in a clean glass vessel was almost exactly the same as that of conductivity water under the same circumstances, viz. both rose to $K = 4 \times 10^{-5}$. This was sufficient to show that no very large amount of a soluble acid, like metatungstic acid, is formed by any transposition on long standing. It would be interesting to try the action of hot water in a sealed tube.

Normal Sodium Tungstate. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. This salt showed no tendency whatever towards a transformation. It was tested like the other salts by standing and heating, but its conductivity remained unchanged.

The mixed potassium-sodium, sodium-ammonium and similar salts will probably behave like the simple salts from which they are derived. It is

hoped that the colloidal tungstic acid can be prepared in the near future and its stability studied.

Conclusions. The electrical conductivity appeared to be the best property to use in studying the stability or instability of these salts. Knorre followed the transformation of a paratungstate by titration. But this changes the composition of the mixtures and may lead to doubtful results. The refractometer was not applicable because of the great dilution of the solutions. The results so far obtained are chiefly valuable in indicating the *rate* of change of the tungstates in question. Assuming that the transformation products may be new salts or mixtures of several known salts, it is obvious that these solutions will only possess properties characteristic of the salts taken when freshly made up, and certainly not after prolonged boiling. The effect of a transformation has been overlooked especially in solubility determinations. For example, Marignac stated that the solubility of ammonium paratungstate was still slowly increasing even at the end of a year. His final result is obviously too high as are also probably those in the case of the other paratungstates.¹

The conductivity data so far obtained are insufficient to decide whether the transformation consists in the addition or rearrangement of water, a hydrolytic dissociation, or a decomposition of one salt into a mixture of two others, as suggested by Knorre. The data at hand are submitted for the benefit of others at work upon similar problems; and as rapidly as possible further conductivity data will be collected upon metatungstic acid and its salts. The possibility of these salts being partly hydrogen or acid salts is being considered, and it is hoped that before long the tungstates can be classified as simply as the phosphates.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]
**DENSITIES OF LITHIUM, SODIUM, POTASSIUM, RUBIDIUM AND
CAESIUM**

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The densities of the alkali metals are of especial interest for several reasons. In the first place, they include the lowest of all the metallic densities; in the next place, the highest members of this series of elements have the largest atomic volumes of all solid substances, each of the metals forming a cusp in the atomic volume curve. Again, these are the most compressible of metals, and have the largest coefficients of expansion; two properties which are closely concerned with volume, and, therefore, with density.

¹ Cf. Taylor, loc. cit.