[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 64.]

THE AMMONIUM TUNGSTATES.[1]

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Received March 12, 1902.

THE two general classes of ammonium tungstates are designated paratungstates and metatungstates. Laurent[2] first proposed the name paratungstates, giving to these salts the formula $5M_2O.12WO_3.nH_2O$, which was confirmed by Marignac[3] who also presented numerous other types. The metatungstates were first prepared by Margueritte,[4] but their name was suggested by Laurent. Later Scheibler and Marignac studied them and arranged them under the general formula $M_2O.4WO_3.nH_2O$. From the numerous formulas proposed for the type members, these seem best established, and the salts used in the present study conformed to them.

SOLUBILITY OF AMMONIUM PARATUNGSTATE.

$$(NH_4)_{10}W_{12}O_{41}.11H_2O.$$

The solubility of the "para salt," as given by different chemists, is as follows:

Investigator.	Ratio of salt to water.	Temperature.
Anthony	1 : 25–28	"Cold"
Lotz	1 : 26.1	10.7°
Lotz	1 : 33.3	"Cold"
Lotz	1 : 5.8-9.6	100°
Marignac	1 : 22–38	15°–18°
Taylor	1 : 59.3	26°
Taylor	1 : 69.8	21°
Taylor	1 : 74	21°
Taylor	1 : 52.7	29°
SOLUBILITY OF AMMONIUM METATUNGSTATE.		
Lotz	1 : 0.84	15°
Riche	1 : 0.35	"Ordinary"

These discrepancies are irritating. When ammonia is passed into water containing tungstic acid, a white substance remains which has been called "paratungstate," but which is remarkably insoluble. It is far more insoluble than any ammonium paratungstate met with in the present investigation.

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[1] From the author's thesis presented for the Ph.D. degree, 1901.

[2] *Ann. chim. phys.* [3], **21**, 54 (1847).

[3] *Ibid.* [3], **69**, 24 (1863).

[4] *Ibid.* [3], **17**, 475 (1846).

AMMONIUM PARATUNGSTATE.

$(NH_4)_{10}W_{12}O_{41}.11H_2O$.

When a solution of "para salt" is evaporated at slightly elevated temperature, monoclinic needles crystallize out; when evaporated at a boiling temperature, flat plates appear. These needles have been described as orthorhombic prisms by Kerndt, Schabus and Marignac. Examined microscopically in polarized light they show an apparent parallel extinction, and give a biaxial interference figure, with the acute bisectrix parallel to the long axis of the crystal, and therefore appear to be orthorhombic, but give these orthorhombic reactions on account of their remarkable twinning structure, which closely resembles the wedge-shaped penetration figures seen in the hydrated zeolites,—more particularly stilbite, which is orthorhombic in form but is a complicated monoclinic twin. It is an interesting fact that these ammoniated and hydrated crystals exhibit the same internal structure as the hydrated zeolites.

Crops of crystals usually consist of mixtures of needles and plates in varying proportion; many previous analyses have undoubtedly been made with such material. Such a mixture, consisting largely of needles, was digested for three days in forty times its weight of water. The water was removed and the same amount added and allowed to stand again for three days. The needles remaining contained no admixed plates. This separation does not prove that the plates are the more soluble, for they are smaller and would therefore dissolve out first. But whatever the reason for this separation, the purpose in view was accomplished: the needles were isolated. These on analysis gave the following data:

Tungsten trioxide, determined by ignition in a porcelain crucible:

"Para needles." Grams.	WO_3. Grams.	WO_3. Per cent.
4.0016	3.4395	85.95
3.1344	2.6938	85.94

The ammonia was determined by the usual distillation and titration method.

"Para needles." Grams.	NH_3. Gram.	NH_3. Per cent.
2.9265	0.15370	5.25
2.1002	0.10983	5.23

The water was determined as follows: The salt was covered with lead oxide, and ignited in a combustion tube in a current of dry air; the water and ammonia were caught in sulphuric acid and weighed. Subtracting from this weight that of the ammonia, the weight of the water was obtained.

"Para needles." Grams.	$NH_3 + H_2O$. Gram.	Water. Per cent.
1.2458	0.1813	9.31
1.0636	0.1536	9.20
1.5988	0.2262	8.91

These values correspond to the formula $(NH_4)_{10}W_{12}O_{41}.11H_2O$, which requires WO_3, 85.87 per cent.; NH_3, 5.24 per cent.; H_2O, 8.88 per cent.; and are also a confirmation of Marignac's formula.

When the "para needles" are crystallized from boiling water, monoclinic plates separate (extinction parallel to diagonal of rhombic section, axial plane lying in the plane of symmetry), and to obtain these with no admixed needles, it is necessary to keep the water at the boiling-point, and to remove the plates from the boiling solution as fast as they are formed. Some plates prepared in this way, gave on ignition the following per cent. of tungsten trioxide:

"Para plates." Gram.	WO_3. Gram.	WO_3. Per cent.
0.6931	0.6170	89.02
0.2528	0.2249	88.96
0.3216	0.2816	88.93
0.5905	0.5253	88.96

The theoretical requirement of tungsten trioxide for $(NH_4)_{10}W_{12}O_{41}.5H_2O$, is 88.83 per cent. and this also confirms Marignac's formula. On comparison, these two para salts show as follows:

"Para needles." $(NH_4)_{10}W_{12}O_{41}.11H_2O$.

"Para plates." $(NH_4)_{10}W_{12}O_{41}.5H_2O$.

Thus it would appear that the "para needles" in boiling water, lose 6 molecules of water.

AMMONIUM METATUNGSTATE.

$(NH_4)_2W_4O_{13}.8H_2O$.

Margueritte[1] first prepared this salt by boiling the para salts with tungstic acid. Laurent[2] prepared it, by the continued boiling of the aqueous solution of the para salts. Scheibler[3] made it by heating the para salt to 250°, until ammonia was given off, causing

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[1] *Ann. chim. phys.* [3], **17**, 475 (1846).

[2] *Ibid.* [3], **21**. 62 (1847).

[3] *J. prakt. Chem.*, **83**, 304 (1861).

a partial separation of tungstic acid, then dissolving the residue in water and allowing it to crystallize. This method was adopted by Persoz[1] and later by Marignac[2].

Scheibler describes the salt as crystallizing in large tetragonal octahedra, which effloresce in the air. If the crystals have been scratched or bruised, they quickly lose water and become opaque. Marignac observed that the crystals lose 7 molecules of water at 100°, and the remaining molecule is not driven out below 200°. Riche noticed the same behavior. When alcohol is added to a hot solution of the "meta salt", the salt $(NH_4)_2W_4O_{13}.6H_2O$ separates, and, according to Marignac, loses 5 molecules of water at 100°.

In the present investigation the "meta salt" was prepared by boiling an aqueous solution of the "para salt" for two or three days, evaporating to small bulk and allowing the syrupy liquid thus obtained to stand. Large transparent tetragonal octahedra were obtained. After three or four recrystallizations, the crystals became almost colorless, but the yellow tint was difficult to remove. Boiled with purified bone-black the greater part of the original brown color may be removed. The crystals have a high index of refraction, which is true also of their solution. These crystals of "meta salt" were also prepared by heating the "para needles" at 150°, for four hours.

On analysis the salt gave 3.05 per cent. of ammonia.

"Meta salt." Gram.	NH_3. Gram.	NH_3. Per cent.
0.5016	0.01531	3.05

This corresponds to $(NH_4)_2W_4O_{13}.8H_2O$, which contains 3.02 per cent. of ammonia, confirming Scheibler's formula. The characteristic physical properties were in such accord with the published data that further analysis was not undertaken.

COLLOIDAL AMMONIUM TUNGSTATE.

$(NH_4)_2W_6O_{19}.4$ or $6H_2O$.

On repeating the method of Scheibler to obtain the "meta salt" (*i. e.*, heating the "para needles" to 250°), a colloidal "gum" was obtained. As many as twenty experiments failed to substantiate his claims, for the "meta salt" was produced at 150°. This "gum" would dry hard, become transparent and had a high index of re-

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[1] *Ann. chim. phys.* [4], **1**, 101 (1864).

[2] *Ibid.* [4], **3**, 72 (1864).

fraction. It did not cement itself to porcelain, in the way "colloidal tungstic acid" is said to do, but would shrink away from the sides of the containing vessel, and could easily be removed. Under the microscope "para needles" were found embedded in it, and were removed by dialysis. The fraction passing through the parchment paper in a few hours, crystallized in tetragonal octahedra; later fractions in "para needles," and still later fractions would not crystallize at all but consisted largely of "gum" which had passed through. This "gum" therefore, when first prepared, consists of a mixture of "para salt," "meta salt," and a "colloidal salt."

The best condition for getting a large yield of the "gum" is as follows: Pulverized "para needles" are spread out on a watch-glass, and heated in an air-bath at 220° for one hour. The air-bath must allow the escape of water and ammonia. The product is covered with water and boiled vigorously for fifteen or twenty minutes, when a clear, but dark, heavy liquid results. This is filtered away from any residue and on evaporation dries into the "gum" with an almost quantitative yield. On standing several days in water, the residue will pass into the "gum" without previous boiling. At higher temperatures considerable tungstic acid is separated and the yield is not so good. The "meta" salt free from "para" must be heated to 250°, before yielding the "gum," and the yields are nothing like so large, as when the "para salts" are taken for the starting-out material.

A marked darkening of the original white salt is noticed after heating. Different fractions of the "para salts" yield the "gum" with different degrees of readiness. These facts point to the presence of some impurity which may affect the transformations.

After dialyzing a portion of the "gum" for six days it gave the following analysis:

"Gum." Gram.	WO_3. Gram.	WO_3. Per cent.
0.6150	0.5447	88.57

"Gum." Grams.	NH_3. Gram.	NH_3. Per cent.
0.4825	0.01279	2.65
1.3776	0.03848	2.79

Another sample was dialyzed for thirteen days, through parchment paper, using ten changes of water of 2½ liters each. The dialyzer had a diameter of 15 cm. After four or five days, the increase of volume in the inner vessel ceased. The resulting colloidal salt, when dried on the water-bath and allowed to stand in the air, slowly increased in weight. When dried at the ordinary temperature and allowed to stand, it decreased in weight. A portion of the "colloidal salt," dried on the water-bath, gave the following analysis:

"Colloidal salt." Gram.	WO_3. Gram.	WO_3. Per cent.
0.4469	0.4089	91.49
0.4523	0.4143	91.60

"Colloidal salt." Gram.	NH_3. Gram.	NH_3. Per cent.
0.6334	0.01520	2.40
0.5985	0.01415	2.36

These results point to the formula $(NH_4)_2W_6O_{19}.4H_2O$, which requires ammonia 2.24 per cent. and tungsten trioxide 91.82 per cent.

In the same way another portion of "gum" was dialyzed for fourteen days, using nearly double the amount of water previously used (twelve changes of water of 3½ liters each). The resulting "colloidal salt" dried at the ordinary temperature gave the following analysis:

"Colloidal salt." Gram.	WO_3. Gram.	WO_3. Per cent.
0.1227	0.1101	89.73
0.2100	0.1885	89.76

"Colloidal salt." Grams.	NH_3. Gram.	NH_3. Per cent.
0.9243	0.01996	2.16
1.0301	0.02184	2.12

These percentages are close to the formula $(NH_4)_2W_6O_{19}.6H_2O$, which requires ammonia 2.29 per cent., and tungsten trioxide 89.69 per cent. This sample was dried at the ordinary temperature, the previous one at 100°. Since the salt loses weight on standing, it is likely that the additional water does not represent such a definite number of molecules as these analyses would indicate.

To compare the percentage of ammonia, in the different salts, the following table is given:

Salt.	NH_3. Per cent.
"Para needles"	5.24
"Para plates"	5.42
"Meta salt"	3.02
"Colloidal salt" (dialyzed six days)	2.72
" " (" thirteen days)	2.38
" " (" fourteen days)	2.14

The dialyzed salt dries hard and clear like glass, with a yellowish tint, contains no embedded crystals, and under no conditions could it be made to crystallize. It has a high index of refraction and is miscible with water in nearly all proportions. It may prove of value as a mounting medium in microscopic work, and also for the mechanical separation of minerals.

Its solution has an acid reaction and absorbs ammonia with avidity. One long series of dialyzations was spoiled, by working with ammonia in the same room, the "colloidal salt" changing to the "meta" and "para" salts. By treating the solution of the "colloidal salt" with tenth-normal ammonia, till the acidity is barely neutralized, it passes into the "meta salt". Unless care is used considerable amounts of the "para salts" will be formed.

Under certain conditions the "colloidal salt" passed into a white modification, which on microscopical examination proved to be an emulsion, the globules closely resembling fat globules. On drying, the white emulsion gradually passed into the transparent variety. The emulsion can be produced by cooling a clear concentrated solution with ice-water. Frequently a more dilute solution, would be filled with spurious clouds, floating in suspension, which appeared to be some foreign matter. This could not be filtered out and was a source of annoyance, until it was examined microscopically, and found to be the emulsion. Emulsions are common enough among organic substances, but are rarely observed with inorganic salts.

At first it was thought that this "colloidal salt" might be "colloidal tungstic acid," but since after prolonged dialysis, the ammonia could not be removed, it was taken to be a colloidal ammonium tungstate.

The history of "colloidal tungstic acid" is of some interest. Graham,[1] in 1864, reported the existence of "colloidal tungstic acid," which he prepared by treating a 5 per cent. sodium paratungstate solution with dilute hydrochloric acid and dialyzing the mixture. The resulting heavy liquid had such a high specific gravity, that glass would float on it. Sabanejeff[2] made a molecular weight-determination using cryoscopic methods, and reported the formula $3WO_3.H_2O$. Later[3] he retracted his determinations,

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[1] *Proc. Roy. Soc.*, London, **13**. 340 (1864).

[2] *J. Russ. Chem. Soc.*, **21**, 1 (1889).

[3] *Ztschr. anorg. Chem.*, **14**, 354 (1897).

and published an article on the "Non-Existence of Colloidal Tungstic Acid," saying that he had previously taken Graham's word for the composition of the "gum." On examination he found it was impossible to dialyze out the sodium, and concluded that it was amorphous sodium metatungstate. His proof of this is open to criticism, for: he states that the salt had a marked acid reaction; his analyses do not conform closely to the theoretical for sodium metatungstate; and the periods of dialysis used were not long enough to thoroughly separate the material. The conversion of one form into the other was rather violent. Sabanejeff changed the amorphous salt into the crystallized variety, by heating to 130°-150°, in a sealed tube with an excess of water. This temperature is about the same as that which changes the ammonium "para salt" to the "meta salt" and seems altogether too high to prove the dimorphism, of the two sodium salts. Had the acidity of his colloidal salt been gradually neutralized with sodium bicarbonate or carbonate, the salt might have reverted to the crystallized form, and its dimorphism thus been disproved. It seems probable that his dimorphous colloidal sodium metatungstate may prove to be a colloidal sodium tungstate analogous to the colloidal ammonium tungstate prepared in the present investigation.

TEMPERATURE AT WHICH THE AMMONIUM SALTS BEGIN TO LOSE AMMONIA.

Some "para needles" were placed in a glass U-tube immersed in an oil-bath and dry air was rapidly passed over them into Nessler's solution. It was found that if the glass tube leading into the solution, was etched on the inner surface, a brown ring would form on the roughened surface, several minutes before the solution showed any traces of color. The moment of formation of this brown ring, was taken as the signal for the first appearance of ammonia, and the temperature of the bath noted. In this manner the "para needles" began to lose ammonia at 60°. The "para plates" at the same temperature, and the "meta salt" at 120°.

It is significant that the "meta salt" should begin to lose ammonia at 120° as it was prepared at 150°. It seems improbable that a salt which begins to lose ammonia at 120° could be made at 250°, as recorded by Scheibler.

Marignac and others dry the "para salts" at 100° and attribute the loss to expulsion of water, but a part of that loss is ammonia.

However, the ammonia that escapes below 100° is but a trace.

ACTION OF DRY AMMONIA GAS ON "PARA NEEDLES."

The effect of ammonia on "para needles" was determined as follows: A boat, filled with needles, was placed in a bent tube immersed in paraffin. Ammonia gas (dried by lime and caustic potash) was passed over it, and escaped through 0.75 cm. mercury and 9.00 cm. of water, so that the gas was under a pressure of about 14 mm. of mercury, in excess of the atmospheric pressure. After heating for one and a half hours the boat was placed in a capsule and weighed. The percentage of ammonia was then determined. The loss in weight, together with the percentage of ammonia furnish data, from which the changes in the salt may be calculated.

ACTION OF DRY AMMONIA GAS ON AMMONIUM PARATUNGSTATE.

Temperature.	"Para needles." Grams.	Weight after treatment.	NH_3. Gram.	Molecules of NH_3 added.	Molecules of water lost.	Approximate formula.
		Original "para needles."				$10NH_3.12WO_3.16H_2O$
100°	0.7193	0.6904	0.04276	+1.3	− 8.5	$11NH_3.12WO_3.\ 7H_2O$
110°	1.0012	0.9632	0.06295	+2.0	− 8.7	$12NH_3.12WO_3.\ 7H_2O$
120°	1.1203	1.0796	0.07268	+2.4	− 8.8	$12NH_3.12WO_3.\ 7H_2O$
130°	0.9936	0.9619	0.06901	+3.2	− 8.8	$13NH_3.12WO_3.\ 7H_2O$
140°	0.8391	0.8101	0.05563	+2.7	− 8.7	$13NH_3.12WO_3.\ 7H_2O$
150°	1.2278	1.1768	0.07514	+1.7	− 9.1	$12NH_3.12WO_3.\ 7H_2O$
160°	1.2204	1.1696	0.06530	+0.2	− 7.7	$10NH_3.12WO_3.\ 8H_2O$
200°	0.9730	0.9251	0.04797	−0.6	− 8.3	$9NH_3.12WO_3.\ 8H_2O$
250°	1.3238	1.2286	0.05872	−1.6	−11.5	$8NH_3.12WO_3.\ 4H_2O$

Attention is directed to the nearly constant loss of water; and that at 130° the maximum amount of ammonia is absorbed. Tungsten trioxide was separated at 250°.

These ammonia-addition salts are quite unstable; when dissolved in water, the water is made alkaline and "para needles" crystallize out; when allowed to stand in the air they revert to their original weight, and percentage of ammonia, as evidenced in the following experiments: Two boats containing "para needles" placed side by side in the same U-tube were heated together in dry ammonia gas at 130° for one and a half hours. The ammonia in one was determined at once; the companion boat was allowed to stand over night, before determining the ammonia.

	"Para needles." Gram.	NH_3. Gram.	NH_3. Per cent.
Boat A.	0.8754	0.06242	7.13
Companion Boat A.	0.9718	0.05034	5.18
Boat B.	0.8744	0.05859	6.70
Companion Boat B.	0.9321	0.04866	5.22

Companion Boat B, after standing over night, weighed 0.9319 gram. It appears therefore that the salt has lost its added ammonia, and absorbed its lost water.

ACTION OF MOIST AMMONIA GAS ON THE "META SALT" AT THE ORDINARY TEMPERATURE.

A boat containing 0.9874 gram of "meta salt" was placed in a vacuum desiccator, over ammonium hydroxide. After standing several hours, the transparent crystals were found to be replaced by a white salt covered with water. This water was removed by spontaneous evaporation in the air, and the residue weighed 0.9327 gram and contained 0.04803 gram ammonia, equivalent to 5.15 per cent., or 3.83 molecules of ammonia added. Hence the "meta salt" has been changed by moist ammonia gas, at the ordinary temperature into the "para needles," and the conversion has been practically quantitative.

The "para needles" being a hundred times more insoluble than the "meta salt," have crystallized out from the water of crystallization of the latter. In other words the water of the old salt has been pushed out by the new salt, and the new salt is found "swimming" in the water of crystallization of the old salt. After standing several days the amount of water in the boat gradually increased, so that water evidently slowly distils into the boat.

ACTION OF MOIST AMMONIA GAS ON THE "META SALT" AT 100°.

"Meta salt" treated with ammonia passes to the "para needles;" the latter in solution change at 100° to the "para plates" so that the action of moist ammonia on the "meta salt" at 100° can almost be predicted. A boat containing 0.4408 gram of "meta salt" (placed in the same apparatus used for determining the action of dry ammonia on the "para needles") was treated with moist ammonia gas at 100°, for one hour. After treatment, the salt weighed 0.4189 gram; after standing sixty hours in the air it weighed 0.4186 gram. This contained 0.02276 gram of ammonia equivalent to 5.44 per cent., or 4.04 molecules of added ammonia.

Hence at 100° moist ammonia gas transforms the "meta salt" into the "para plates." Dry ammonia gas would probably form the ammonia-addition product produced at that temperature.

THEORETICAL CONSIDERATIONS.

NORMAL AMMONIUM TUNGSTATE.

The normal sulpho-salt $(NH)_2WS_4$ exists and one might expect the existence of the corresponding oxygen salt. However, normal ammonium tungstate has never been prepared. Marignac,[1] by the spontaneous evaporation of a solution of "para salt," in a bell-jar over lime (which would absorb water and not ammonia), obtained a salt of the composition $2(NH_4)_2O.3WO_3.3H_2O$. This salt was soluble in cold water but soon changed to the "para salt." In the air it gave off ammonia reverting to the "para salt."

The ratio between the ammonia and tungsten trioxide, in the different salts is tabulated as follows:

Salt.	NH_3.	:	WO_3.
Theoretical normal salt	1.0	:	0.5
Marignac salt (unstable)	1.0	:	0.75
"Meta salt"	1.0	:	2.0
"Para salt"	1.0	:	1.2

It is seen from these ratios that Marignac's salt approaches more closely to the normal ratio than any salt which has yet been prepared, but it was not stable at the ordinary temperature. Of the other salts, the "para salt" follows next in order.

The para ammonio-addition salts prepared in this investigation are unstable, easily losing their excess of ammonia. It seems therefore that at the ordinary temperature, tungsten can not hold any more ammonia than that expressed by the para ratio. It is believed that the formation and preservation of the normal salt is simply a question of temperature.

WATER OF CRYSTALLIZATION.

In boiling water the "para needles" lose exactly 6 molecules of water and crystallize out as "para plates." Five molecules of water remain in the salt, and it is significant that 5 ammonium oxide molecules remain also. Possibly 5 ammonium oxide molecules influence 5 water molecules in such a manner, that the latter are more firmly bound or linked than the others. Whatever ex-

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[1] *Ann. chim. phys.* [3]. **69**, 22 (1863).

planation may be advanced, the fact remains that 6 molecules of water are driven out at 100°, and 5 are not.

The "meta salt" $(NH_4)_2W_4O_{13}.8H_2O$ at 100° loses 7 molecules of water. The remaining molecule can not be driven out below 200°. The "meta salt" from alcohol, $(NH_4)_2W_4O_{13}.6H_2O$, loses at 100° 5 molecules of water, and the remaining molecule behaves as before. In these salts 1 molecule of water must be very differently combined from the others, for one requires 200° of temperature to remove it, while the others leave the salt quite rapidly even at the ordinary temperature. The number of water molecules remaining again correspond to the number of ammonium oxide molecules, and the probability increases that 1 ammonium oxide molecule influences 1 hydrogen oxide molecule.

These two salts may be written:

$$[2NH_4OH.4WO_3].[7H_2O]$$
$$[2NH_4OH.4WO_3].[5H_2O]$$

At 100° in the air the water is split off from both salts, and the common residue or nucleus $[2NH_4OH.4WO_3]$ remains, which is stable at 200°.

AMMONIA CONTENT.

The "para needles" and "plates" begin to lose ammonia at 60°; the "meta salt" at 120°. If the ammonia in these salts is combined in the same manner, it ought to be given off at the same temperature. Such is not the case, and consequently it looks as though part of the ammonia was combined or linked differently from the rest. At 150° the "para salts" lose 4 molecules of ammonia, and revert to the "meta salt." The "meta salt" on the addition of 4 molecules of ammonia advances to the "para salt." The commonest double salt of sodium with ammonium paratungstate, has the composition $Na_4(NH_4)_6W_{12}O_{41}.15H_2O$ (Knorre, Marignac, Hallopeau). Four molecules of ammonia have been replaced by 4 molecules of sodium. The fact that all the ammonia has not been displaced by sodium, indicates that 4 molecules are differently combined than the others, and probably these are the same 4 which are lost at 150° (or on long standing in water, even at the ordinary temperature).

TRANSFORMATIONS.

The transformations in this series of salts are of interest. The entire series may be prepared from the first member or the entire series may be prepared from the last member. In fact, the whole series may be prepared from any member.

Temperature of formation.	Series.		
(Below 100°)	"Para needles"	$(NH_4)_{10}W_{12}O_{41}$.	$11H_2O$
(100°)	"Para plates"	$(NH_4)_{10}W_{12}O_{41}$.	$5H_2O$
(150°)	"Meta salt"	$(NH_4)_2W_4O_{13}$.	$8H_2O$
(220°)	"Colloidal salt"	$(NH_4)_2W_6O_{19}$.	4 or $6H_2O$

Before taking up the transformations, attention may be called to the difference between the last two salts. This difference is $2WO_3.2$ or $4H_2O$. Gibbs[1], in his classic work on the complex inorganic acids, pointed out the existence of a "homologous series" of metatungstates having a common difference $2WO_3.RO$. The difference noticed here, while not exactly the common difference discovered by him, is equivalent to it, as far as the tungsten trioxide is concerned.

The two "para salts" (in the series) on long standing in solution, at the ordinary temperature revert to the "meta salt." The "colloidal salt," on absorbing ammonia, reverts to the "meta salt." The "meta salt" on standing reverts to the residue [$2NH_4OH.4WO_3$]. This residue, therefore, may be considered a decomposition product or nucleus of the whole series. It is the most stable portion in the entire series; when it is attacked, the structure of the salt is broken down, and tungstic acid separates. It is well known that the "meta salts" are broken down by acids or alkalies only with difficulty.

Beginning with the first member, we may go down the series by physical means: "Para needles" heated to 100° (in water) go into the "para plates." The "plates" at 150° (in air) pass into the "meta salt." The latter heated to 250° changes to the "colloidal salt."

Again we may proceed down the series by chemical means. "Para needles" treated with acetic acid go to the "para plates."[2] The "para plates" boiled with tungstic acid or dilute mineral acids pass into the "meta salt." The "meta salt" as yet has not been changed into the "colloidal salt" by chemical means; boiling with tungstic acid did not produce it.

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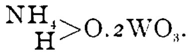
[1] *Proc. A. A. A. S.*, **47**, 1 (1898), and previous papers.

[2] Gibbs: *Am. Chem. J.*, **1**. 229 (1879). Gibbs states that the salt formed with acetic acid has the composition $(NH_4)_{10}W_{12}O_{41}.6H_2O$, and adds that it appears to be the same salt, to which Marignac attributed $5H_2O$. The temperature of crystallization may clear up the discrepancy.

To reverse the transformations: Beginning with the last member we may proceed up the series by chemical means. The acidity of the "colloidal salt" neutralized with ammonia, produces the "meta salt." The "meta salt" on the addition of 4 molecules of ammonia at 100° advances to the "para plates." The "para plates" on the addition of water at the ordinary temperature proceed to the "para needles."

From these considerations it appears probable that a common nucleus runs through the whole series, and that the nucleus is $[2NH_4OH.4WO_3]$. The molecular weight of this nucleus is as yet unknown; it may be a polymer, or it may be one-half, which would correspond to Gibbs' difference $[RO.2WO_3]$, and might be written



$$\overset{NH_4}{\underset{H}{}}{>}O.2WO_3.$$

The simplest view of the matter would favor the nucleus $[NH_4OH.2WO_3]$, and until molecular weight determinations have been made, the salts may be written with this in mind.

AMMONIUM "PARA" AND "META" TUNGSTATES.

Temperature of formation.		
(Below 100°)	"Para needles"	$6[NH_4OH.2WO_3].4[NH_4OH].6[H_2O]$
(100°)	"Para plates"	$6[NH_4OH.2WO_3].4[NH_4OH]$
(150°)	"Meta salt"	$2[NH_4OH.2WO_3].7[H_2O]$
(220°)	"Colloidal salt"	$2[NH_4OH.2WO_3].2[WO_3].3 \text{ or } 5[H_2O]$

PARA-AMMONIO-ADDITION-PRODUCTS.

In ammonia gas.	
(100°)	$6[NH_4OH.2WO_3].\ [NH_4OH].4[NH_3]$
(110°)	$6[NH_4OH.2WO_3].\ [NH_4OH].5[NH_3]$
(120°)	$6[NH_4OH.2WO_3].\ [NH_4OH].5[NH_3]$
(130°)	$6[NH_4OH.2WO_3].\ [NH_4OH].6[NH_3]$
(140°)	$6[NH_4OH.2WO_3].\ [NH_4OH].6[NH_3]$
(150°)	$6[NH_4OH.2WO_3].\ [NH_4OH].5[NH_3]$
(160°)	$6[NH_4OH.2WO_3].2[NH_4OH].2[NH_3]$
(200°)	$6[NH_4OH.2WO_3].2[NH_4OH].\ [NH_3]$
(250°)	$4[NH_4OH.2WO_3].4[WO_3]\ .4[NH_3]$

PARA-AMMONIO-SUBSTITUTION SALT.

(Below 100°)	$6[NH_4OH.2WO_3].4[NaOH].10[H_2O]$

These tables suggest the presence of "nuclei" and "side-chains," The "para salts" appear to be polymers of the "meta salts," linked together by, or to which are added, the "side-chains." The "side-chains" may be split off by physical or chemical means, and substitutions appear to take place in them. Where transformations require the splitting off of part of the structure, both physical and chemical means may be employed to accomplish the desired end. But where transformations demand the addition of these parts, then chemical means only can accomplish the purpose.

Smith[1] and Hardin have demonstrated the tendency of tungsten trioxide itself to polymerize. And after such polymerization the material is insoluble in sulphur monochloride, whereas before, it is soluble. The polymerized ammonium salts in this series are over a hundred times more insoluble than the unpolymerized.

It is significant that the temperature which breaks down the "para salt" into the "meta salt" (*i. e.*, 150°) is not far from that temperature (130°) at which the "para salt" in ammonia gas is able to take on the maximum amount of ammonia. In other words, the polymer absorbs the most ammonia at a temperature near its rupture temperature. It looks as though the polymer when "opened up" was enabled to add more ammonia.

There is no reason why the compounds of carbon should have a monopoly over "homologous series," "polymerizations," "ring formations," "side-chains," "substitution products" or "gums."

Organic "gums" are supposed to be high polymers of some simple form, and the polymerization is usually accompanied with insolubility and non-crystalline character. The "gum" in the present investigation appears to be an ammonium salt, but no surprise will be expressed if it proves to be an acid salt of "colloidal tungstic acid" and ammonium metatungstate. If "colloidal tungstic acid" exists, it would probably be a polymer of tungsten trioxide and its affinity for ammonia would be so great that only with difficulty could the two be separated. In one experiment, a long process of dialyzation was ruined by the presence of ammonia in the atmosphere of the room, and who knows how much ammonia the other experiments absorbed? Traces of ammonia would neutralize the work performed by days of dialyzation. The subject needs to be further investigated.

It is hoped that benzylamine tungstate will form a similar series of salts, and, yielding more readily to organic methods, facts concerning their molecular magnitude and constitution may be developed.

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[1] This Journal, **21**, 1007 (1899).