A STUDY OF THE
HETEROPOLY TUNGSTATES OF SOME 2- AND 3-VALENT METALS.

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Introduction.

Tungsten, like molybdenum, and to a lesser extent like vanadium and silicon enters into complex formation with many elements, to give heteropoly acids. These may be considered to be free acids with complex anions, each consisting of two or more elements in a limited oxide lattice. More particularly, in the case of tungsten, the building unit of the anionic lattice is often the WO_6 octahedron. The role of the central atom in this anionic lattice is not restricted to the purely acid forming elements but includes, amongst others, metals of the transition groups, some amphoteric metals and some non-metals. This Thesis deals with the heteropoly acids of tungsten which contain zinc, beryllium, bismuth and 3-valent arsenic. The zinc and beryllium complexes have not previously been reported; the work on the tungstobismuthates was essentially a repeat and extension of the work of Balke and Smith[1]; several heteropoly complexes of 3-valent arsenic have been reported by Gibbs and Rosenheim[2] but this present investigation failed to reproduce these results and another complex has been identified. Attempts to prepare heteropoly acids between tungsten and cadmium, and tungsten and uranium, failed.

Historically, three main methods of investigation have been used in the study of heteropoly acids. The first and most prolific, has been the analytical approach. Although many of the compounds deduced by this method over the past hundred years have later been shown to be mixtures, the recurrence of certain ratios in the anion of central atom oxide to, in the case of tungsten, tungstic oxide, provided the basis for the early understanding and classification of these acids. In this work, the identification of stable anions recurring through a series of salts has been the criterion of heteropoly acid formation. To confirm the anionic content of the complex, solutions containing salts of the suspected heteropoly acids were passed through a cation exchange column and the effluent analysed.

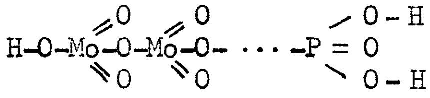
The second method of approach, again concerned with the solid state, has been the X-ray crystallographic analysis of the structures of certain of these acids. This, however, has only been applied to a few of the more commonly occurring groupings such as in the 1 : 6, 1 : 9, and 1 : 12 acids. In this work there is a description of the structure of the caesium salt of 12-tungstozincic acid.

The third method of approach deals with the specific ions existing in solution at various pH values. This has resulted in several postulated series of equilibria with however, no definite conclusions reached. No solution chemistry was attempted in this work, apart from potentiometric titrations of the free acids with standard sodium hydroxide in order to determine the equivalent weight and hence the valency of the acid.

Early History

The study of complex inorganic compounds is often confused by the inability to obtain and hence define, the purity of the speciman. From the purely analytical side, it is often very difficult to differentiate amongst solid solutions, mixed crystals and complex compounds. In particular, with heteropoly acid formation, there is the further difficulty of determining whether an atom is bound within the complex anion or not. As the analytical approach was virtually the only method used in the 19th Century, the resulting literature is highly confused. This confusion was heightened by the uncertain methods of analysis used by some workers. ~~Due~~ Owing to the large proportion of tungsten present, the % of the central atom in the salt is small and a small discrepancy in analysis can lead to an appreciable error variation in the ratio $MO : WO_3$. As much of this literature has not been sifted out, only a brief outline of the development of heteropoly acid chemistry is given.

Berzelius[3] in 1826, described the preparation and analysis of ammonium molybdophosphate. This study was further continued by Svanberg and Struve[4] who developed a method of analysis for phosphate by precipitating as ammonium molybdophosphate. In 1846, Margueritte[5] prepared metatungstic acid and in 1850, Laurent[6] claimed a ferri-alkali-tungstate which had different properties from those of its constituents. Although Marignac's[7] work in 1862 on tungstosilicic acid along with the previous work on the ammonium molybdophosphates, should have opened the field of heteropoly acid chemistry, the significance of this work was not realised and Debray,[8] in 1868, suggested that the phosphoric acid exerted only a modifying effect on the molybdenum. He compared this effect with that of carbon on steel and thus assumed that ammonium molybdophosphate was not a true compound. However Fownes[9] and later Wurtz,[10] did accept that the molybdophosphates were true compounds and suggested that they were chain molecules formed through -Mo-O-Mo- links, thus



The different properties of different acids could be due to varying chain structures with in some cases ring formation. Valency considerations, in particular by Miolati,[11] caused this theory to be abandoned. About this period several other heteropoly acids were prepared - the tungstophosphates by Von Scheibler[12] in 1872, the tungstoborates by Klein[13] in 1880, and the molybdosilicates by Parmentier[14] in 1882. From 1880 until 1910, a large number of heteropoly compounds were claimed by various workers, in particular by Gibbs,[15] Friedheim[16] and Kehrmann.[17] The importance of Kehrmann's work was that he drew attention to the similarity in chemical behaviour between compounds of similar structure.

From 1910 until 1930 this field of study was dominated by A. Rosenheim[18] who conducted a systematic study of most of the available elements with a view to heteropoly acid formation with tungsten and molybdenum. To explain these and past results, Miolati,[11] Copaux[19] and Rosenheim[18] developed successively an extension of Werner's[20] coordination theory.

Development of theory

(1) Based on analytical results

The researches of the earlier workers had shown that heteropoly acids were probably formed by the condensation of varying numbers of acid anhydride molecules, most commonly WO_3 and MoO_3, with a second acid, to form a stable anion. The acids are generally classified by the ratio of the single acid anhydride to the multiple acid anhydride e.g. a 1 : 6 or simply a 6-heteropoly tungstate would have an anion $(MO.\ 6WO_3)$. The following table shows the list of elements that can combine as the central atom in heteropoly acid formation.

Group (1) H, Cu,
(2) Be, Zn,
(3) B, Al,
(4) C, Si, Ge, Sn, Ti, Zr, Ce, Th,
(5) N, P, As, Sb, V, Nb, Ta, Bi,
(6) Cr, Mo, W, U, S, Se, Te,
(7) Mn, I,
(8) Fe, Co, Ni, Rh, Os, Ir, Pt,

Some complex heteropoly acids have been reported which contain two and three different central atoms. Some, which contain different valency states of the same element, have been prepared. However, different valency states of the same element can give rise to entirely different heteropoly compounds as is the case with 3 - and 5-valent arsenic.

The majority of the heteropoly acids which have been prepared, lie in the 1 : 6 to 1 : 12 region; the most frequently occurring being the limiting 6- and 12-acids. These two recurring values formed the basis of the Miolati, Copaux and Rosenheim theories. These theories were developed from Werner's coordination theory and though not accepted now, they provided a sufficiently accurate classification to differentiate heteropoly acids from other compounds.

The heteropoly acid formed from an element A (of valency n) as central atom, is derived from a hypothetical acid $H_{12-n}(AO_6)$. The oxygen atoms of this complex may be replaced wholly or in part, by acid radicals, WO_6, or by pyroacid radicals, W_2O_7. In this way two limiting series may be formulated -

$$H_{12-n}\left[A(WO_4)_6\right] \qquad \text{and} \qquad H_{12-n}\left[A(W_2O_7)_6\right] .$$

To explain the very high valencies required, Rosenheim postulated that most of the salts formed, were acid salts, since few gave on analysis, the required value. An exception to this was the guanidine salt of 12-molybdophosphoric acid,

$$(CN_3H_6)_7\left[P(Mo_2O_7)_6\right]\ 8H_2O.$$

This, however, was not a serious criticism, as most of the salts were heavily hydrated and tended to retain some of this water to fairly high temperatures, sometimes until obvious decomposition of the complex had taken place. Difficulty was also experienced in representing the more complex compounds and still preserving the coordination of the elements concerned e.g. the compound $K_6H_6As_2Mo_{18}O_{65}$aq. was written

$$K_6H_6\left[\begin{matrix}O\\(Mo_2O_7)_4\end{matrix}As - Mo_2O_7 - As\begin{matrix}O\\(Mo_2O_7)_4\end{matrix}\right]\ aq.$$

Paratungstate and paramolybdate salts resemble in physical and chemical properties the 6-heteropoly acid salts and metatungstate and metamolybdate salts resemble the 12-heteropoly acid salts. Chemically the similarity exists in the solubility of the free acids in hydroxylated solvents (such as ether, water, and amyl alcohol,) by the formation of ether addition compounds, by the property of coagulating albumen and by the formation of very insoluble alkaloid salts. This suggested to Copaux that the paratungstate and metatungstate ions were essentially those of 6- and 12-heteropoly acids with the central atom replaced by hydrogen. Thus the paratungstate ion would be

$\left[H_2(WO_4)_6\right]^{10-}$aq. and the metatungstate ion would be

$\left[H_2(W_2O_7)_6\right]^{10-}$aq.

This theory, although it provided a plausible explanation for much of the chemistry of heteropoly acids and also a means of classifying the vast number of salts, had no experimental basis. It postulated the existence of a W_2O_7 ion which was not otherwise known to be formed. Claims have been made for the existence of this pyrotungstate ion but none have been substantiated. There was no evidence, too, in any of the salts to separate the water present into the required amounts of constitutional water and water of hydration.

(2) Based on solution chemistry results

Although the existence of a certain ion in solution does not necessarily predict the nature of a precipitate formed in that solution, in particular with the complex equilibria obviously existing in a tungstate solution, a knowledge of the types of ion present in a solution of known pH is useful in the preparation of heteropoly acids. Several lines of investigation have been used in studying the aggregation and degradation of heteropoly acids and isopoly acids but so far no system has been completely worked out.

The isopoly acid chemistry, as it is simpler, has received most attention. Three well defined salts are obtained in the slow acidification of tungstate solutions. The normal tungstate crystallises at a pH of about 10, the paratungstate at a pH of about 6, and the metatungstate at a pH of about 3·5. The formula of the normal tungstate is $R_2O.\ WO_3.\ xH_2O$. The formula of the paratungstate is now, according to Saddington and Cahn,[21] thought to be $5R_2O.\ 12WO_3.\ xH_2O$. Previously doubt existed as to whether the formula was as above or $3R_2O.\ 7WO_3.\ xH_2O$, with the latter having preference until 1950, principally because of the analogy between paratungstate and paramolybdate, the formula of which was known to be $3R_2O.\ 7MoO_3.\ xH_2O$. The formula for the metatungstate is $3R_2O.\ 12WO_3.\ xH_2O$. Other compounds, such as ditungstates and tritungstates, have been reported in the literature but Jander and Jahr,[22] despite numerous experiments, failed to obtain from alkali tungstate solutions, crystals of intermediate composition. Souchay,[23] in a comprehensive review of the subject, has shown that the other compounds previously reported, have probably been mixed crystals of the three definite types described above.

Thus it would appear that the tungstate ions tend to aggregate as the pH falls from 10 to 3. G. Jander[24] attempted to measure the ionic weights directly by measuring the rate of diffusion of the tungstate ions, in the presence of a large excess of an inert electrolyte to provide a uniform ionic atmosphere. He applied the formula

$$D. Z.\sqrt{M} = \text{a constant}$$

where D = diffusion coefficient

Z = specific viscosity of the solution

M = ionic or molecular weight.

This work has many limitations, as shown by Souchay.[25] The diffusion coefficient has to be related to the diffusion of an ion of known atomic weight which provides possible errors, in that assumptions have to be made about the degree of hydration of the ion relative to the degree of hydration of the isopoly acid ions. Also this equation, though applicable to colloids, is not strictly accurate for ionic diffusion where the charge as well as the size must be taken into consideration. Similar disadvantages apply to the dialysis coefficient measurements of Brintzinger and Jander,[26] with the further uncertainty of irregular behaviour of the membrane. Saddington and Anderson[27] carried out experiments on the self-diffusion of ions in a tungstate solution, measured by radioactive tracer techniques. This method eliminates the uncertainty of the true concentration gradient as diffusion takes place between two identical solutions except that in one solution the ions are 'labelled' with a suitable radioactive tracer. Another advantage is the greater sensitivity of radiochemical analysis as compared with normal methods, thus allowing for the use of more dilute solutions and so cutting down inaccuracy due to electro-striction. All these experiments indicate a uniform aggregation from pH 14 to about pH 8. This changes over two pH units and achieves another constant value from about pH 6 to pH 1·5. In more concentrated solutions there is some evidence for a second transition about pH 3. This aggregation is presumably due to the progressive neutralisation of the negative ions with hydrogen ions leading to a decrease in ionic potential and hence more favourable conditions for aggregation.

Over the range of pH in which solid sodium paratungstate may be in equilibrium with the solution, calculations from the above experiments show that the predominant ionic species has an ionic weight of between 1300 and 1500 i.e. it must be a 6- or 7-fold tungsten aggregate. Jander suggested that at pH 3 an ionic species of about twice that weight was apparent. This latter result agrees with analytical evidence as sodium metatungstate, a 12-fold ion, crystallises at a pH of 3. However, the X-ray analysis of sodium paratungstate indicates a formula of $5R_2O.\ 12WO_3.\ 28H_2O$. This suggests a condensation of two ions in the formation of the solid paratungstate. Souchay[28] postulated a reaction

$$6WO_4^{2-} + 7H^+ = [HW_6O_{21}]^{5-} + 3H_2O$$

to give the paratungstate ion. This reaction may occur stepwise, according to Saddington and Anderson, thus

$$3WO_4^{2-} + 2H^+ = [W_3O_{11}]^{4-} + H_2O$$

$$2[W_3O_{11}]^{4-} + 2H^+ = [W_6O_{21}]^{6-} + H_2O$$

but the evidence for this, deduced from calculated diffusion - pH curves, is not very convincing. At higher pH values, paratungstate solutions on standing, tend to undergo a further change involving an increase in pH. This does not, however, involve, as diffusion experiments show, any appreciable change in the ionic form, and seems to be slow in occurring. Souchay[29] suggested

$$(HW_6O_{21})^{5-} + 2H^+ = (H_3W_6O_{21})^{3-}$$

and the product he called, the pseudo-metatungstate ion. This ion apparently exists in solutions down to fairly low pH values and is probably the stage before metatungstate formation. It has also been suggested as an intermediate in the formation of heteropoly acids. To explain the phenomena of ageing in paratungstate solutions Souchay[28] postulated the existence of two forms of paratungstate existing in equilibrium, the first formed in the direct acidification of a tungstate solution and the second from dissolving crystalline sodium paratungstate. The rate of conversion between the two forms is slow. It is the first form which gives rise to the metatungstate and pseudo-metatungstate ions.

These equilibria apply to the isopoly acids of tungsten. Very little is known about the method of formation of heteropoly acids. Jander and Souchay suggested that the pseudo-metatungstate ion reacted with the phosphate ion in the formation of 12-tungstophosphoric acid since dialysis and diffusion experiments showed that in dilute solutions, the anions of the 12-acids were dissociated into species containing 6 or 7 tungsten atoms. When the calculated weight of phosphoric acid is added to a solution of freshly prepared sodium paratungstate, pH about 6·4, and the solution boiled, the pH rises to a value just over 7. If to this solution is added a solution of ammonium chloride, only a slight precipitate occurs. If the solution is then acidified to a pH of about 3·5, a precipitate of ammonium 12-tungstophosphate appears. To prepare an ether addition compound of a 12-heteropoly acid, the solution must be at least 4N in terms of hydrogen ion. Almost all the central atoms in heteropoly acids have amphoteric properties. To explain these results, the following reactions have been suggested by various workers.

$$6Na_2WO_4 + 7HNO_3 = Na_5(HW_6O_{21}) + 7NaNO_3 + 3H_2O \qquad -(1)$$

$$Na_5(HW_6O_{21}) + 2H_2O = Na_3(H_3W_6O_{21}) + 2NaOH \qquad -(2)$$

$$Na_3(H_3W_6O_{21}) + H_3PO_4 = Na_3(PO_4W_6O_{18}) + 3H_2O \qquad -(3)$$

$$Na_3(PO_4W_6O_{18}) + Na_3(H_3W_6O_{21}) = Na_3(PO_4W_{12}O_{36}) + 3NaOH \qquad -(4)$$

Equation (2) explains the increase in alkalinity on boiling sodium paratungstate solution. This effect will be buffered by the solution. Equation (3) suggests a possible method of introducing the central atom as an acidic anion, displacing 3 OH groups from the tungsten anion, the pH of the solution thus increasing a little as the phosphoric acid is neutralised. Equation (4) suggests that by neutralising the NaOH, i.e. by making the solution more acid, the reaction would favour the formation of the 12-acid. This could also be the mechanism of substitution of the more metallic elements such as zinc. The time controlling factor could be the conversion of zinc cation to zincate anion.

12-heteropoly acids could be built up as in equation (4) and 6-acids could be built up as in equation (3). Intermediate complexes could either be built up by combination of the anion formed similar to equation (3), with tungstate or paratungstate ions, or by the degradation of the 12-acids by removal of tungstate, paratungstate or pseudo-metatungstate ions. These hypotheses, however, are, to a great extent, unconfirmed.

(3) Based on structural chemistry results

In 1929 Pauling[30] suggested that the building units in Heteropoly acids might be WO_4 tetrahedra and WO_6 octahedra. He accepted the formulation of the 6-acids as a central MO_6 octahedron surrounded by, and sharing corners with six WO_4 tetrahedra. For the 12-acids, Pauling proposed a structure in which a central PO_4 tetrahedron was surrounded by a polyhedral shell of composition $W_{12}O_{18}$ in which every tungsten atom was joined to three others via oxygen atoms. The octahedra round the tungsten atoms were completed by -OH groups outside the shell thus giving a formula $(PO_4W_{12}O_{18}).(OH)_{36}^{3-}$. This structure, though stable and neutral, could not explain the lower hydrates as it essentially contained a minimum of 18 water molecules, and this experimentally was not found to be the case. The valence of this anion was 8-n where n was the valency of the central ion. This agreed, in general, with the alkali salts of the acids.

Another theoretical attempt at the explanation of the structure of heteropoly compounds was proposed by Riesenfeld and Tobiank.[31] This was based on the geometrical arrangement of tetrahedral XO_4 and octahedral XO_6 groups. The results obtained offered a simple explanation of such previously unexplainable facts as the existence of compounds of two different valency states of the same acid e.g. the 4 and 8 basic salts of tungstosilicic acid.

The structure of the 12-acids was put on a more factual basis by Keggin[32] with his X-ray analysis of the pentahydrate of

12-tungstophosphoric acid. He accepted Pauling's idea of a separate anion with a typical oxide coordination structure but built up a tungsten-oxygen shell, complete in itself and thus not requiring the 36 -OH groups of Pauling's structure. The central MO_4 ion was surrounded by a closed shell of WO_6 octahedra. Each corner atom of the central MO_4 group was shared with three octahedra, each of which also shared one oxygen atom with each of its two neighbours. The four W_3O_{13} groups were joined together by sharing corners. The resulting anion $(MW_{12}O_{40})^{8-n}$ was large, and on packing, large spaces must be left, thus accounting for the high hydrates found. This structure has been confirmed in a number of salts of 12-heteropolyacids.[33]

The structure of the 29 hydrate of 12-tungstophosphoric acid has been described by Bradley and Illingworth[34] as an aggregate of units of $(PW_{12}O_{40})^{3-}$ and $(H_3.29H_2O)^{3+}$ arranged as two interpenetrating diamond lattices.

The next most common series of acids, the 6-acids, has also been structurally analysed. Evans[35] in 1948, worked out the structure of potassium molybdotellurate. The anion consisted of a central TeO_6 octahedron with six MoO_6 octahedra arranged in a hexagonal annulus so as to share two edges. The basicity of the anion so formed was 12-n where n was the valency of the central ion. No 6-acids of tungsten have been structurally analysed.

Two 9-heteropoly acids have been structurally analysed. Both of them, however, gave different results. B. Dawson studied the structure of $(P_2W_{18}O_{62})^{6-}$. This anion is composed of two identical half-units, each consisting of a central PO_4 tetrahedron surrounded by nine WO_6 octahedra linked together by sharing both corners and edges. It is similar in structure to $(PW_{12}O_{40})^{3-}$, discussed above, with three octahedra removed and the resulting group doubled up.

The other 9-acid worked out, was ammonium 9-molybdomanganate $(NH_4)_6 MnMo_9O_{32}.8H_2O$.[37] The postulated structure has only a single unit in the anion and not a condensed one as above. The central atom here, is situated in an oxygen octahedron and not, as above, in a tetrahedron. The central quadrivalent manganese ion is surrounded by nine MoO_6 octahedra. On the same level as the MnO_6 octahedron are three MoO_6 groups each sharing one of their edges with three non adjacent edges of the central octahedron. Above and below this middle layer of four octahedra are groups of three MoO_6 octahedra. In each of these groups, the three octahedra have one vertex in common, and each octahedron of the group shares two adjacent edges with the other two octahedra. The two groups of three octahedra are placed above and below the middle layer in such a way that six oxygen atoms in the next plane inwards from each unique oxygen atom on the threefold axis coincide with six oxygen atoms belonging to the middle layer of octahedra. This gives the anion $(MnMo_9O_{32})^{6-}$.

Basicities of heteropoly acids.

Keggin's structure for the 12-heteropoly acids imposes a set valency on a particular acid. In most cases so far examined this valency agrees with that of the majority of the salts, in particular the alkali metal salts. However, certain heavy metal salts, in particular silver, lead and mercury tend to give high basicities and others, in particular caesium, rubidium and thallium tend to give low basicities. The high basicities could be due to the formation of basic salts. The highly oxygenated anionic structure, in aqueous solution, must contain several W-O-H-O-H groups. The replacement of a hydrogen ion with another cation, electrical neutrality being maintained, is probable in a solution containing excess of the replacing ion, provided structural hindrance is not too great. This question of structural hindrance is probably the most important criterion in the crystallisation of heteropoly acids. The caesium salts of a number of 12-acids contain only three caesium ions per anion, irrespective of the valency of the central ion. To maintain electrical neutrality, these salts must be regarded as acid salts.

Potentiometric titration does not show, in the case of the heteropoly acids so far tried, each separate neutralisation stage, as the dissociation constants seem to lie too close to each other. However, it should show the maximum basicity. This is well defined in some acids e.g. 12-tungstoferric acid, but in some others the change in pH round the end point is either too slow or too inconsistent to give a reliable equivalent weight. There is also the difficulty that, in the titration, the alkali, as well as neutralising the acid, may be breaking down the complex anion with resulting equilibrium changes which may affect the pH. In the case of 12-tungstophosphoric acid, two equivalent points have been observed, corresponding to the addition of three and seven equivalents of alkali respectively. This second value may represent the completion of a degradation reaction although it seems unlikely as Nikitina[38] has claimed the formation of a seven basic sodium salt.

Not enough is, as yet, known about the structures of other types of heteropoly acids to deduce basicities. The only method available is the preparation and analysis of a number of salts.

Properties of heteropoly acids.

Heteropoly acids are generally soluble in oxygenated solvents. They have large molecular weights and often show isomorphism through a series of acids. They are used as precipitants for albumin and other basic organic compounds such as proteins and alkaloids. They generally exist in weakly acid solution and are decomposed in alkaline solution. Some salts e.g. potassium borotungstate, show optically active properties and can be obtained in two enantiotropic forms.

Heteropoly acids have various applications analytically. One of the standard methods of analysing for phosphate is to precipitate it as ammonium 12-molybdophosphate. An extension of this method was developed by Wadelin and Mellon[39] in their work on liquid-liquid extraction, for the estimation of phosphorus in steels. They extracted the phosphorus as molybdophosphoric acid with a 20% by volume solution of 1-butanol in chloroform and followed the concentrations using ultraviolet spectrophotometry.

12-molybdophosphoric acid forms isomorphous salts of ammonium, potassium, rubidium and caesium. F. Nydahl (unpublished) applied this property in using a column of ammonium 12-molybdophosphate as a very efficient ion exchanger of potassium, rubidium and caesium ions.

General methods of formation

In general, all heteropoly acids are obtained from aqueous solution by mixing the components under suitable conditions of pH. They are often sensitive towards hydrolysis. Weakly complexed heteropoly anions are frequently split by the hydrolytic action of water, and excess of one component or of mineral acid is necessary to resist this. All are progressively degraded by hydroxyl ions and are completely broken up by strong alkalis.

To prepare unsaturated series of heteropoly acids stricter control of the experimental conditions is necessary. They may sometimes be prepared from solutions containing the theoretical proportions of the components. More often, however, they are prepared by the controlled degradation of the saturated acid with alkali.

Each series of heteropoly acids has different chemical properties and even within each separate series there is a wide range of behaviour. Thus the separation of each heteropoly acid must be considered by itself. A particular difficulty in the separation of heteropoly acids is the range of impurity formed and the similarity of some of the impurities to the required acid e.g. metatungstic acid and the 12-heteropoly tungstic acids.

Criteria of formation of heteropoly acids.

In the formation of complexes, the early 'lock and key' analogy of Emil Fischer[40] is not strictly correct and must be considered in the light of modern views of valency. The lock is not now considered to be rigid with fixed valency angles but can be fluid to admit alteration in the directional requirements of the valence bonds to accomodate complex formation. This may result in forced configurations and thus cause a lowering of the activation energy needed to induce a specific reaction.

In general the formation of complex molecules depends on

(1) the size and shape of the complexing groups

(2) the electronic structures involved, leading to valence restrictions and ionic charge distributions.

In heteropoly acid formation, two other conditions arise.

(3) The atom to be introduced into the tungsten nucleus must not form very insoluble tungstates, otherwise all the tungsten will be removed from solution before heteropoly acid formation can take place.

(4) The atom to be introduced must have amphoteric properties.

As these acids are formed in aqueous solution, other factors such as degree of hydration, affinity for O-H-O bonds, and the relative solubilities of intermediate compounds must also play an important part.

Heteropolyacids with divalent metallic central atoms

The divalent metallic atoms known to form heteropoly acids with tungsten are nickel, cobalt, iron, copper, zinc and beryllium. Of these nickel forms a 6-acid (J.A. Mair, unpublished - Rosenheim[45] claimed a 6-acid but from the method of preparation colour and formula, it could have been a normal paratungstate), cobalt and copper form 12-acids (J.A. Mair, unpublished), and the characteristic acids of zinc and beryllium are described in this work. Ferrous iron gives a dark coloured crystalline salt of a paratungstate nature but as yet the formula has not been confirmed.

Zinc and Tungsten

There is no mention in the literature of heteropolyacid formation with zinc and tungsten. The only compounds listed are those of the various salts e.g.

$ZnWO_4$ - zinc tungstate
$ZnO.2WO_3.\ 3H_2O$ - zinc ditungstate
$5ZnO.12WO_3.\ 35H_2O$ - zinc paratungstate
$9ZnO.22WO_3.\ 66H_2O$
$4ZnO.10WO_3.\ 18H_2O$
$2ZnO.6WO_3.\ 10\ H_2O$
$ZnO.4WO_3.\ 8H_2O$ - zinc metatungstate.

Of these only the normal tungstate, paratungstate, and metatungstate may necessarily be true compounds.

When a hot paratungstate solution was saturated with a zinc nitrate solution over a period of a few hours, filtered and concentrated to small bulk, a white solid which had comparable solubility to zinc paratungstate but a different composition, separated. The solution was further concentrated, then extracted with ether and 12 N H_2SO_4, and an ether addition compound which contained an appreciable proportion of zinc, was formed. These experiments suggested that there was some form of complex formation between zinc and tungsten. Two methods of preparation were used in the investigation.

Methods of preparation

(1) This method is a standard method for preparing heteropolyacids. 56·2 gm. of sodium tungstate were dissolved in water and converted to paratungstate by the addition of the equivalent of 198·6 ml. of N HNO_3 and boiling for two hours. A solution of 10 gm. of $Zn(NO_3)_2 6H_2O$ in 700 ml. of water was added over a period of two days to the solution which was kept at a temperature of 80-90°C. This temperature control was necessary, as when the solution boiled a white precipitate of sodium zinc paratungstate separated. The total volume of the solution was kept about 500 ml. Throughout the saturation the solution turned progressively yellow. After all the zinc had been added, the solution was concentrated to about 150 ml. and cooled at 3°C. for a week. A product of white needle-like crystals was obtained. These on analysis gave results which were different for each saturation. However, each gave identical guanidine salts. Thus probably a mixture of sodium zinc salts of the complex was formed. The mother liquor from the saturation was kept for further investigation.

(2) 56·2 gm. of sodium tungstate were dissolved in water and converted to metatungstate by the addition of the equivalent of 255·4 ml. of N HNO_3 and boiling for four hours. 10 gm. of zinc oxide were added with

brisk stirring over a period of five days to the solution which was kept at a temperature of 80-90°C. The solution was then concentrated to about 150 ml., filtered hot, and cooled for a week at 3°C. Small white needle-like crystals separated which could be recrystallised from water. On analysis the following results were obtained-

	Na_2O	ZnO	WO_3	H_2O
Salt (1)	5·50	6·38	73·68	14·44
	5·89	6·40	73·40	14·31
Salt (2)	5·80	6·46	73·88	13·86
	5·72	6·50	74·02	13·76

The formula best fitting these results is

$3{\cdot}5Na_2O.3ZnO.12WO_3.30H_2O$. which has the % composition

5·73 6.43 73·54 14·27

A saturated aqueous solution of the salt gave a pH of 6·1 thus indicating a predominantly paratungstate character. The mother liquor was retained for further investigation.

Salts of the 12-tungsto-3-zincic acid

The valency of the sodium salt was too high for a normal paratungstate, as was also the case with the sodium zinc salts prepared by the first method. To confirm if the zinc was internally bound with the tungsten and not cationic, several salts were prepared using saturated solutions of the replacing cations.

Ammonium salt

The ammonium salt was prepared by adding a hot saturated solution of ammonium chloride to a hot, almost saturated solution of the sodium salt. White needle-like crystals were obtained which could be recrystallised from water. On analysis they gave the following results-

	$(NH_4)_2O$	ZnO	WO_3	H_2O
Salt (1)	6·06	7·26	80·70	6·00
	6·10	7·18	80·76	5·98
Salt (2)	6·22	7·28	81·10	5·72
	6·27	7·34	81·30	5·60

The formula best fitting these results is

$4(NH_4)_2O.3ZnO.12WO_3.11H_2O$ which has the % composition

6·06 7·11 81·06 5·76

Guanidine salt

The guanidine salt was prepared by adding a 5% solution of guanidine hydrochloride to a dilute solution of the sodium salt. Dilute solutions were used in this case, as, if the temperature was kept about 80°C., the precipate formed slowly. If concentrated solutions were used, the precipitate formed immediately the solutions came in contact thus preventing mixing of the solutions and the forming of a homogeneous precipitate. The white microcrystalline salt which separated was almost insoluble in water. Attempts to recrystallise the salt from water with a little hydrochloric acid resulted in a series of salts containing progressively less zinc. Without recrystallising the guanidine salts gave on analysis-

	$(CN_3H_6)_2O$	ZnO	WO_3	H_2O
Salt (1)	15·70	6·34 6·30	72·36 72·04	5·86
Salt (2)	15·92	6·38 6·42	72·46 72·44	5·62

The formula best fitting these results is

$4{\cdot}5(CN_3H_6)_2O.3ZnO.12WO_3.12{\cdot}5H_2O$ which has the % composition

15·84	6·31	72·01	5·84

Nickel salt

The nickel salt was prepared by adding a hot saturated solution of nickel nitrate to a hot saturated solution of the sodium salt and cooling at 3°C. for a week. Green crystals separated from the solution. These were recrystallised from water and analysed giving the following results-

	NiO	ZnO	WO_3	H_2O
Salt (1)	8·22	6·16	68·92	17·50
	8·41	6·01	68·54	17·44
Salt (2)	8·23	6·12	69·20	17·30
	8·28	6·18	68·98	17·42

The formula best fitting these results is

$4{\cdot}5NiO.3ZnO.12WO_3.39H_2O$ which has the % composition

8·26	6·07	68·44	17·26

Dehydration of the sodium salt

Since from its valency the sodium salt is obviously unsaturated as compared with the guanidine and nickel salts, it must be an acid salt. Thus, probably, there should be at least one water molecule bound differently from the rest of the water of crystallisation.

A sample of the sodium salt was tested on the Thermal Balance to see if there were any definite stages in the dehydration of the salt. There was a rapid loss of water until the temperature rose to about 200°C. From there to about 600°C. the loss was slow but steady and no appreciable break in the graph appeared. Thus, either all the water was similarly bound or else the oxide lattice had broken up before all the water had distilled off.

Ion exchange experiments

To ascertain whether the zinc was present wholly or in part as cation or in the anionic complex, a solution of 2 gm. of the sodium salt was passed through a cation exchange column (Amberlite Resin 1R-120H). The effluent was analysed for tungsten and zinc and the ratio was found to be $ZnO:WO_3$= 1:17·80. On washing the column through with dilute HCl and analysing for zinc, the ratio ZnO in effluent : ZnO held in column was 1:3·28. 10 gm. of the sodium salt were then passed through the column in 2 gm. lots and the bulk effluent treated with ether and 12 N H_2SO_4. An ether addition compound was formed which gave an analysis ZnO : WO_3= 1:18·42. (Some $WO_3.xH_2O$ was observed to be deposited in the column and was not removed by washing with dilute HCl or water. It was dissolved by washing with a dilute solution of ammonium acetate.)

The passage of the sodium salt through the ion exchange column was equivalent to a slow acidification (the pH of the original solution was 6·1 and that of the effluent 1·8.) To compare the column's effect with controlled acidification, 15 gm. of the salt were dissolved in water and acidified at 70-90°C. with dilute nitric acid over a period of 6 hours. The solution was then filtered and treated with ether and 12 N H_2SO_4, and the ether addition compound removed. On analysis the ratio for $ZnO:WO_3$ was found to be 1:19·76. This suggested a mixture of metatungstic acid and tungstozincic acid. The metatungstic acid was removed by repeatedly taking up in water, evaporating/

to dryness, taking up in water and filtering off the $WO_3.xH_2O$. On analysis, a ratio for $ZnO:WO_3$ of 1:12·03 was obtained. This agrees with later work, reported below, on the 12-tungstozincic acid.

Thus, on passing through the ion exchange column, the equilibrium was disturbed to give perhaps, a free para-acid, 12-tungstozincic acid and metatungstic acid. The two latter compounds were identified by their chemical behaviour. The free para-acid was doubtful and possibly did not exist for any appreciable length of time but broke up to give the higher acids, free tungstic acid and cationic zinc which was absorbed on the column.

Preparation of 12-tungstozincic acid

The mother liquors from the two saturations described above, were used. (It was shown that each method of preparation gave rise to almost the same amounts of products.) The solution was evaporated down until a considerable quantity of sodium nitrate had crystallised out with the remainder of the sodium 12-tungsto-3-zincate. The solution was treated with ether and 12 N H_2SO_4 and the ether addition compound allowed to settle. The ether addition compound was then purified by dropping it through two columns of fresh ether. The ether was removed by diluting with water and bubbling a current of hot air through the solution. The aqueous solution was then evaporated to dryness on a steam-bath, the residue extracted with water and the separated tungstic acid filtered off. The filtrate was again evaporated to dryness on a steam-bath; the process being repeated until very little tungstic acid separated. The dry residue was then baked at 120-130 °C. for two hours, extracted with water as before, and filtered. This process was repeated until separation of tungstic acid practically ceased. A point where no tungstic acid separated could not be reached as 12-tungstozincic acid itself decomposed slightly on heating. The tungstic acid residues, however, contained only traces of zinc, being derived almost entirely from the metatungstic acid. The free acid was very soluble in water and could be recrystallised from it, though there was always slight decomposition.

On analysis, the free acid gave the following results-

ZnO	WO_3	H_2O.
2·42	82·39	15·26
2·38	82·28	15·28
2·47	82·20	15·33

The formula best fitting these results is

$ZnO.12WO_3.29H_2O$ which has the % composition

2·42 82·17 15·41.

Density of the free acid

The density was found by the displacement of organic liquids from a density bottle. Some organic liquids dissolve heteropolyacids, in particular if they are hydroxylated, and so the solid was weighed before and after the liquid had been added, to ensure that no solution had taken place.

Results-

(1) Using nitrobenzene, density = 4·15 gm./ cc.

(2) Using toluene, density = 4·14 gm./ cc.

Dehydration of 12-tungstozincic acid

The valency hydrogen ions in a heteropolyacid, when the acid is decomposed by heat, will break off as water molecules. These will be bound differently from the other water molecules of crystallisation and in a controlled dehydration would be expected to come off at a different temperature. Three methods of investigating the water loss were tried.

(1) As a preliminary experiment, the free acid was left for 14 days over P_2O_5 in a vacuum desiccator and it was found that 15·81 molecules of water were lost from the initial 29 molecules.

(2) To find the rate of loss of water molecules, a weighed sample of the acid was heated for two days at a constant temperature in an air oven, left overnight in a silica gel desiccator and weighed in a closed weighing bottle.

Results -

Temp.° C.	Mols. H_2O lost	Temp.° C.	Mols. H_2O lost
20	0	220	25·67
100	18·47	230	26·01
110	18·57	240	26·30
120	18·65	250	26·55
130	18·71	260	26·75
140	18·79	270	27·03
150	19·91	280	27·38
160	20·48	290	27·50
170	21·51	300	27·70
180	22·24	320	28·00
190	23·01	350	28·21
200	24·26	500	28·70
210	24·62	1000	29·00

From the above results there does not appear to be any definite break in the rate of loss of water and nothing can be deduced about the valency of the acid. However there does seem to be a slowing down in the rate of loss of water about the 26 molecule mark. As the majority of the salts are 6-basic, this is where the break would be expected.

(3) A sample of the free acid was tested on the Thermal Balance to see if any definite stages could be detected in the dehydration. The graph of temperature v. loss in weight showed an initial rapid loss in weight over the first 100 C. degrees rise in temperature, a less rapid loss in weight up to a temperature of 200°C. and a very gradual loss in weight up to 600°C. No definite breaks appeared in the graph.

Thus the thermal dehydration of 12-tungstozincic acid does not indicate the number of constitutional water molecules present. This is probably due to the thermal decomposition of the acid before all the water molecules have been driven off.

Salts of 12-tungstozincic acid

Potassium salt

The potassium salt was prepared by adding an almost saturated solution of the free acid to a saturated solution of potassium chloride. The solution was heated at 70°C. for one hour, filtered and left to crystallise at 3°C. Long colourless hexagonal prisms were obtained which were recrystallised from water. The results of the analysis were as follows-

	K_2O	ZnO	WO_3	H_2O
Salt (1)	6·89	2·35	82·00	8·76
	6·90	2·37	82·02	8·71
Salt (2)	6·74	2·42	82·21	8·63
	6·88	2·48	82·04	8·60

The formula best fitting these results is

$2{\cdot}5K_2O.ZnO.12\,WO_3.16{\cdot}5H_2O$ which has the % composition

K_2O	ZnO	WO_3	H_2O
6·91	2·39	81·94	8·74

Zinc salt

The zinc salt was prepared by neutralising a solution of the free acid with zinc carbonate. The solution was heated at 70°C. for one hour, filtered and allowed to crystallise at 3°C. The salt which separated, was recrystallised from water, giving small white crystals. On analysis the following results were obtained -

	ZnO	WO_3	H_2O
Salt (1)	9·17 9·29	78·45 78·49	12·20 12·30
Salt (2)	9·32 9·21	78·55 78·69	12·25 12·22

The formula best fitting these results is

$4ZnO.\ 12WO_3.\ 24\ H_2O$ which has the % composition

9·19	78·59	12·20

This may be written $3ZnO.ZnO.12WO_3.24H_2O$.

Guanidine salt

The guanidine salt was prepared by adding a 5% solution of guanidine hydrochloride to a solution of the free acid, heating to 70°C. for one hour, filtering and allowing to crystallise at 3°C. Fine white crystals separated. The salt, though not very soluble, could be recrystallised using a large bulk of water. On analysis, the following results were obtained-

	$(CN_3H_6)_2O$	ZnO	WO_3	H_2O
Salt (1)	12·26	2·38 2·42	82·41 82·30	3·48
Salt (2)	11·97	2·38 2·36	82·30 82·25	3·35

The formula best fitting these results is

$3(CN_3H_6)_2O.\ ZnO.\ 12WO_3.\ 6H_2O$ which has the % composition

12·07	2.40	82·33	3·20

Ammonium salt

The ammonium salt was prepared similarly to the potassium salt but using a saturated solution of ammonium chloride. The salts gave on analysis the following results-

	$(NH_4)_2O$	ZnO	WO_3	H_2O
Salt (1)	4·54	2·47	84·76	8·28
	4·56	2·45	84·86	8·21
Salt (2)	4·62	2·51	84·71	8·04
	4·68	2·49	84·66	8·11

The formula best fitting these results is

$3(NH_4)_2O.\ ZnO.\ 12WO_3.\ 15H_2O$ which has the % composition

4·74 2·47 84·59 8·20

Barium salt

The barium salt was prepared similarly to the zinc salt but using barium carbonate. The salts gave on analysis the following results-

	BaO	ZnO	WO_3	H_2O
Salt (1)	12·08	2·18	72·90	13·14
	12·04	2·14	72·86	13·02
Salt (2)	12·11	2·17	72·85	13·06
	12·09	2·20	72·91	13·12

The formula best fitting these results is

$3BaO.\ ZnO.\ 12WO_3.\ 28H_2O$ which has the % composition

12·02 2·12 72·68 13·16

Methods of analysis

Tungsten

About 1 gm. of the heteropoly acid or salt was dissolved in water, if soluble, and boiled up with 2-3 gm. of NaOH to break up the complex. (In the case of the barium salt, the barium was removed as sulphate before the complex was treated with caustic soda.) The solution was then acidified with dilute nitric acid and evaporated almost to dryness; 10ml. of concentrated hydrochloric acid were added and again the solution evaporated almost to dryness to remove the nitric acid. About 50 ml. of water were then added. The bulk of the tungsten was precipitated as tungstic acid. To remove the remainder, the solution was heated to about 80°C. and to it was added 10 ml. of a 10% solution of cinchonine hydrochloride. The solution was kept at 80°C. until the precipitate coagulated, filtered through a No. 42 filter paper, well washed, and ignited to WO_3. The wash solution used was - 15 ml. of a 10% cinchonine hydrochloride solution + 15 ml. of conc.HCl + 500 ml. of water.

Zinc

About 1 gm. of the heteropoly acid or salt was dissolved in water, if soluble, and boiled up with 2-3 gm. of NaOH to break up the complex. (Nickel and barium were both removed before the caustic soda was added.) The solution was then acidified to phenolphthalein with dilute hydrochloric acid, 5 gm. of tartaric acid added, and the solution neutralised back to the red of phenolphthalein with caustic soda. 1·2 gm. of solid caustic soda were then added and the solution diluted to 100 ml. A 15% oxine solution in alcohol was made up and an excess of it was poured gently into the zinc solution which had been heated to about 60°C. After heating on the steam-bath for one hour, the solution was filtered, while hot, through a No.3 sinter crucible. The precipitate was washed with hot water until the washings were free from caustic soda, dried at 130-140°C. and weighed as $(C_9H_6ON)_2$ Zn.

Guanidine

The nitrogen present in it was estimated by the micro-analyst and the guanidine content calculated.

Ammonia.

The ammonium content was found by taking about 2 gm. of the salt, adding excess NaOH to displace the ammonia, and steam distilling the liberated ammonia into excess of a standard acid solution which was then back-titrated with standard caustic soda.

Barium

About 1 gm. of the barium salt was dissolved in water and to it was added sufficient dilute sulphuric acid to give complete precipitation of the barium as barium sulphate. The solution was left to stand for 15 minutes, filtered through a No.42 filter paper, washed and ignited to $BaSO_4$.

Nickel

About 1 gm. of the nickel salt was dissolved in water with a few drops of dilute hydrochloric acid. Excess of a 1% solution of dimethylglyoxime in alcohol was added and the solution heated to 80°C. 5 gm. of sodium acetate were dissolved in the solution which was then cooled and filtered through a sinter crucible. The precipitate was washed with hot water, dried at 120°C., and weighed as $(C_4H_7N_2O_2)_2Ni$.

Water

This was found by ignition loss of the salt or acid. In the case of the ammonium or guanidine salts, the ignition loss was water + ammonia or guanidine.

Potassium and sodium

These were not analysed for directly but values were found by difference.

Potentiometric titration of 12-tungstozincic acid

A standard solution of 12-tungstozincic acid was titrated potentiometrically against a standard sodium hydroxide solution using a Cambridge Meter and standard Calomel-Platinum (quinhydrone) electrodes.

Results -

Titre(NaOH)	Millivolt	Titre(NaOH)	Millivolt
0	382	37	353
1	380	38	351
2	379	39	350
3	378	40	347
4	378	41	345
5	377	42	343
6	377	43	341
7	377	44	339
8	377	45	337
9	377	46	334
10	376	47	332
11	375	48	328
12	374	49	324
13	374	50	319
14	373	51	312
15	372	52	300
16	372	53	276
17	371	53·5	256
18	370	53·6	241
19	370	53·7	225
20	370	53·8	209
21	369	53·9	193
22	368	54·0	176
23	367	54·1	158
24	367	54·2	138
25	366	54·3	122
26	365	54·4	106
27	365	54·5	90
28	363	54·6	82
29	362	54·7	75
30	361	54·8	68
31	361	54·9	62
32	360	55·0	56
33	360	55·1	50
34	358	55·2	45
35	357	55·5	31
36	355	56·0	10

The weight of $ZnO. 12WO_3. 29H_2O$ used = 3·6431 gm.

Equivalence point taken =54·20 ml.

Normality of caustic soda = 0·1176

Therefore, equivalent weight = 571·6

The equivalence point was found by taking the 'double differential' of the millivolt readings around the point of maximum change. (The 'double differential' was the figure obtained by subtracting each reading from the previous reading and then subtracting these differences in turn. Where the 'double differential' passed through zero was taken as the equivalence point.)

From other titrations the results obtained for the equivalent weight were (to the nearest whole number) - 572,574,575,570,578,580,572. From the molecular weight, assuming a 6-basic acid, the equivalent weight is 565. These results are sufficiently close to suggest that a 6-basic state is the maximum valency of the acid. (A 5-basic state gives an equivalent weight of 677.)

Structure of 12-tungstozincic acid.

12-tungstozincic acid and its salts resemble closely in chemical behaviour 12-tungstophosphoric acid and its salts. This is not to be expected, due to the cationic behaviour of zinc in the acid solution used in the preparation of the heteropoly compounds as compared with the anionic behaviour of phosphorus. However, if the tungsten structure is similar, chemical properties may be controlled by that rather than by the central atom. Keggin[32] and Santos[33] had analysed the structures of 12-tungstophosphoric acid and caesium 12-tungstophosphate. 12-tungstozincic acid is difficult to obtain in a pure state since on standing in solution there always seems to be some decomposition with subsequent precipitation of tungstic acid. Thus the caesium salt was used for comparison purposes. It was prepared by adding an almost saturated solution of caesium chloride to a solution of 12-tungstozincic acid and recrystallising the precipitate from water. On analysis, it gave the formula

$$Cs_3H_3ZnW_{12}O_{40}\cdot 12H_2O$$

Powder photographs were used with copper $K\alpha$ radiation. The salt was ground up in an agate mortar and left standing open to the atmosphere, for three days to allow the water of hydration content to reach equilibrium. Two methods of mounting the powder were tried -

(1) with acetone collodion on a glass fibre

(2) in a fine Lindemann glass tube.

Care had to be taken with the first method that the collodion was almost dry before applying it to the powder, as the complex was soluble in acetone.

The distance of the lines on the powder photograph from the respective knife edges (x_1 and x_2) were measured as was also the distance between the knife edges (2d). The mean (x + d) was found and substituted in the formula

$$\theta = \frac{x+d}{2R} \text{ radians. } (R = \text{radius of film in camera})$$

Also $(d^*)^2 = \frac{4\sin^2\theta}{\lambda^2} = \left(\frac{1}{a}\right)^2 (h^2 + k^2 + l^2)$.

where (h,k,l,) are the plane indices and 'a' is the unit cell length. The structure was found to be cubic with symmetry O_h^4. The unit cell length was found, using Bradley and Jay's[41] extrapolation method, to be 11·86 A units. This value is very close to those of caesium 12-tungstophosphate (11·83), and caesium 12-tungstosilicate (11·78).

The intensities of the lines were found by the 'multiple film' method and compared with the calculated intensity values from

$$I \propto K\left(\frac{1+\cos^2 2\theta}{\sin^2\theta \cdot \cos\theta}\right) F^2 . p . A.$$

where F is the structure factor

p is the multiplicity

A is the absorption factor.

The structure was assumed to be similar to the caesium salts analysed by Santos[33]. The six caesium atoms were placed at

$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$0,0,\frac{1}{2}$
$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$

The tungsten atoms were arranged as 12 WO_6 octahedra in four groups each group consisting of three WO_6 octahedra round a trigonal axis so that the three tungsten atoms had two coordinates equal and one different when referred to the rectangular axis of cubic symmetry with origin at the centre of the shell. This centre was a tetrahedral hole occupied by a zinc atom.

There were four types of oxygen atoms present-

O_1 - shared between three WO_6 octahedra and the ZnO_4 tetahedron

O_2 - shared between two WO_6 octahedra

O_3 - shared between two WO_6 octahedra

O_4 - unshared.

The four O_1 atoms had coordinates of the type (a,a,a,) where a = 0·99 A.

The twelve O_2 atoms had coordinates of the type (b,b,c,) where b = 0·97 A. and c = 2·84 A.

The twelve O_3 atoms had coordinates of the type (d,d,e,) where d = 1·49 A. and e = 3·54 A.

The twelve O_4 atoms had coordinates of the type (f,g,g,) where f = 0·1 A. and g = 3·79 A.

The twelve W. atoms had coordinates of the type (h,k,k,) where h = 0·157 A. and k = 2·50 A.

The effect of the water of crystallisation was not taken into consideration.

Results

X_1	X_2	$2d$	Σ	$\frac{\Sigma}{2}$	θ rad.	θ°	$\sin^2\theta$	Σh^2
1·35	1·55	3·20	6·10	3·05	·1605	9°12'	·02557	6·024
1·70	2·02	3·20	6·92	3·46	·1821	10°26'	·03279	7·729
2·25	2·44	3·20	7·89	3·95	·2076	11°54'	·04252	10·02
2·62	2·80	3·20	8·62	4·31	·2269	13°0'	·05060	11·93
3·32	3·50	3·20	10·02	5·01	·2636	15°6'	·06785	15·99
3·62	3·82	3·20	10·64	5·32	·2800	16°2'	·07628	17·98
4·20	4·40	3·20	11·80	5·90	·3106	17°48'	·09346	22·02
4·58	4·70	3·20	12·48	6·24	·3284	18°49'	·1040	24·47
4·75	4·94	3·20	12·89	6·45	·3391	19°26'	·1107	26·08
4·85	5·00	3·20	13·05	6·53	·3434	19°41'	·1129	26·70
5·25	5·42	3·20	13·87	6·94	·3650	20°55'	·1292	30·01
5·48	5·68	3·20	14·36	7·18	·3779	21°39'	·1361	32·08
5·62	5·80	3·20	14·62	7·31	·3847	22°2'	·1407	33·14
5·80	5·91	3·20	14·91	7·46	·3926	22°30'	·1464	34·44
5·97	6·05	3·20	15·22	7·61	·4005	22°57'	·1521	35·84
6·15	6·35	3·20	15·70	7·85	·4131	23°40'	·1612	37·98
6·47	6·65	3·20	16·32	8·16	·4294	24°36'	·1734	40·84
6·61	6·80	3·20	16·61	8·31	·4371	25°3'	·1793	42·19
6·80	7·00	3·20	17·00	8·50	·4473	25°38'	·1873	44·11
7·24	7·42	3·20	17·86	8·93	·4689	26°52'	·2043	48·14
7·40	7·60	3·20	18·20	9·10	·4788	27°26'	·2122	50·01
7·58	7·80	3·20	18·58	9·29	·4889	28°1'	·2206	51·99
7·78	7·98	3·20	18·96	9·48	·4989	28°35'	·2290	53·96
8·18	8·42	3·20	19·80	9·90	·5210	29°51'	·2477	58·38
8·55	8·72	3·20	20·47	10·24	·5389	30°52'	·2632	62·04
8·88	9·08	3·20	21·16	10·58	·5567	31°54'	·2793	65·82
9·05	9·26	3·20	21·51	10·76	·5662	32°26'	·2876	67·78
9·22	9·42	3·20	21·84	10·92	·5746	32°55'	·2952	69·58
9·42	9·62	3·20	22·24	11·12	·5852	33°32'	·3052	71·93
9·60	9·80	3·20	22·60	11·30	·5947	34°4'	·3137	73·94
9·95	10·15	3·20	23·30	11·65	·6131	35°8'	·3313	78·07
10·25	10·45	3·20	23·90	11·95	·6288	36°2'	·3459	81·53
10·60	10·80	3·20	24·60	12·30	·6473	37°5'	·3636	85·69
10·95	11·15	3·20	25·30	12·65	·6658	38°9'	·3816	89·93
11·28	11·48	3·20	25·96	12·98	·6831	39°8'	·3983	93·87
11·58	11·80	3·20	26·58	13·29	·6993	40°4'	·4140	97·57
11·94	12·12	3·20	27·26	13·63	·7173	41°6'	·4323	101·9
12·28	12·45	3·20	27·93	13·97	·7352	42°7'	·4498	105·9

Σh^2	Observed intensity	Calculated intensity
6	14·40	13·67
8	5·85	5·85
10	25·20	25·65
12	148·8	150·0
14	Absent	0·87
16	76·50	79·91
18	16·60	17·60
20	Absent	0·21
22	91·50	94·48
24	11·50	11·79
26	77·50	79·69
27	7·80	8·84
30	50·40	46·68
32	90·00	86·56
33	8·70	10·20
34	9·60	9·11
36	15·30	15·13
38	90·00	92·12
40	Absent	2·09
41	24·00	28·92
42	42·00	47·50
44	79·00	78·96
46	Absent	2·69
48	30·60	29·49
50	209·0	206·3
52	34·80	35·81
54	37·20	37·55
56	Absent	1·48
58	25·90	26·38
62	230·0	222·3
64	Absent	2·69
65	Absent	1·90
66	130·2	130·6
68	20·00	20·40

These figures confirm the assumed structure. Thus, 12-tungstozincic acid and 12-tungstophosphoric acid owe their resemblance in chemical behaviour to their similarity in structure. This suggests that an important criterion in the formation of a 12-heteropolyacid is the ability of the central atom to fit into the tetrahedral hole in the middle of the tungsten lattice.

Zinc and molybdenum

By analogy with, amongst others, iron and aluminium, zinc, which forms a 12-heteropoly acid with tungsten, might be expected to form a 6-heteropoly acid with molybdenum. Several zinc molybdates have been recorded, but there is no reference to any heteropoly acid formation between zinc and molybdenum. The methods used in the investigation were the same as those used in the preparation of the tungstozincates, with sodium molybdate in place of sodium tungstate.

(1) Zinc nitrate solution added to sodium paramolybdate solution.

During the saturation, a slight precipitate formed which was filtered off, dried and analysed. The formula obtained was

$ZnO.\ MoO_3.\ 8H_2O.$ i.e. zinc molybdate.

The solution was evaporated down to 50 ml. and cooled at 3°C. for a week. A further precipitate was obtained. This, on analysis gave the formula

$2Na_2O.\ ZnO.\ 7MoO_3.\ 15H_2O.$ i.e. sodium zinc paramolybdate.

The solution was then diluted to 100 ml. and to it was added a saturated solution of barium chloride in water. The resulting precipitate was recrystallised from water and analysed to give the following formula-

$3BaO.\ 7MoO_3.\ 12H_2O.$ i.e. barium paramolybdate.

These precipitates accounted for all the molybdenum originally added.

(2) Zinc oxide added to a solution of sodium metamolybdate.

After all the zinc oxide had been added, the solution was filtered and allowed to cool at 3°C. for a week. No precipitate formed. The solution was evaporated down to 100 ml. and to it was added a saturated solution of barium chloride in water. The resulting precipitate was recrystallised from water and analysed to give the following formula-

$3BaO.\ 7MoO_3.\ 14H_2O$ i.e. barium paramolybdate.

Thus there does not seem to be any heteropoly acid formation between zinc and molybdenum.

Cadmium and tungsten

Zinc, cadmium and mercury form group 2b of the Periodic Table. Zinc forms heteropoly tungstates, as has been shown; mercury tends to form very insoluble tungstates and is thus unlikely to form any heteropoly complex; cadmium, however, does not form very insoluble tungstates and is weakly amphoteric, thus permitting, if structural conditions are satisfied, heteropoly acid formation. The only recorded compounds in the literature between tungsten and cadmium are the various cadmium tungstates-

$Cd\ WO_4 . 4H_2O$ - cadmium tungstate
$CdO. 2WO_3 . 3H_2O$ - cadmium ditungstate
$3CdO. 7WO_3 . 16H_2O$ - cadmium paratungstate
$CdO. 3WO_3 . 4H_2O$ - cadmium tritungstate
$CdO. 4WO_3 . 10H_2O$ - cadmium metatungstate

The following methods were used in the attempt to prepare a heteropoly acid of cadmium with tungsten.

(1) 28·1 gm. of sodium tungstate were converted to the paratungstate by the addition of 99·3 ml. of N HNO_3 and boiling for two hours. The solution was diluted to 600 ml. and to it, while boiling, was added, over a period of three days, 15 gm. of $Cd(NO_3)_2\ 4H_2O$ dissolved in 500 ml. of water. The solution turned progressively cloudy. After all the cadmium nitrate had been added, the solution was filtered while hot. The filtrate, on testing, contained only a little tungsten and cadmium. It was then evaporated down to 100 ml. and left to cool at

3°C. for a week. A small precipitate settled out but not enough to analyse. Successive evaporation and cooling produced similar results until at about a volume of 5 ml. no tungsten remained in solution. The initial precipitate, on analysis, accounted for most of the tungsten added. The experiment was repeated, with similar results and again the first precipitate was analysed. The figures obtained for the CdO : WO_3 ratio were

(1) 1 : 1·94

(2) 1 : 1·83

Attempts to recrystallise these precipitates failed as they were fairly insoluble in water. As the existence of ditungstates is doubtful, these precipitates were probably mixtures of cadmium tungstate and cadmium paratungstate. Most internally substituted para-acids give appreciably more soluble salts than the corresponding paratungstates but in this case no differently soluble salts were observed.

The second saturation was not evaporated down as the first one was, but was extracted with ether and 12 N H_2SO_4. On standing for almost a week, a trace of ether addition compound was obtained but this contained no cadmium.

(2) The above method was repeated, but this time the temperature was kept below 70° C. in case the heteropoly acid, if one was formed, was unstable to heat. Again most of the tungsten was removed from the solution in the initial precipitate which on analysis gave for the CdO : WO_3 ratio

(1) 1 : 2·2

(2) 1 : 2·0

As before one saturation was evaporated down gradually and the other extracted with 12 N H_2SO_4 and ether. The results were similar to those in the first experiment.

(3) 28·1 gm. of sodium tungstate were converted to the metatungstate by the addition of the equivalent of 127·7 ml. of N HNO_3 and boiling for four hours. To the boiling solution was added freshly prepared cadmium hydroxide over a period of five days. (The cadmium hydroxide was prepared by dissolving 15 gm. of $Cd(NO_3)_2 4H_2O$ in water, precipitating with sodium hydroxide and washing with water until free from alkali.) The solution was filtered hot and tested for tungsten and cadmium. Tungsten was found to be present but only a trace of cadmium. The solution was extracted with ether and 12 N H_2SO_4 and the ether addition compound formed, tested for cadmium. There was none present.

(4) The third method was repeated but this time the temperature was kept below 70°C. The results were similar.

Thus it seems unlikely that there are any heteropoly acids of cadmium and tungsten.

Methods of analysis.

Cadmium.

The cadmium was estimated by the precipitation of cadmium oxinate from a solution buffered with sodium acetate. About 1 gm. of the salt was taken and decomposed by heating with a concentrated sodium hydroxide solution. 3 gm. of tartaric acid were added to complex the tungsten and the solution neutralised with dilute HCl. 4 gm. of sodium acetate were added and an excess of a 2% oxine solution in alcohol. The solution was heated almost to boiling for five minutes then filtered through a sinter crucible, dried at 130-140°C. and weighed as $Cd(C_9H_6ON)_2$.

Tungsten

The tungsten was estimated by the method described before in the analysis of the tungstozincates.

Uranium and tungsten.

Uranium is amphoteric and exists in cationic form in aqueous solution as a divalent uranyl ion. In the literature there is no reference to heteropoly acid formation between tungsten and uranium and only a few uranyl tungstates are described e.g.

$UO_3.WO_3.2H_2O$ uranyl tungstate

$UO_3.3WO_3.5H_2O$ uranyl tritungstate

In the methods used here to examine the possibility of heteropoly acid formation between tungsten and uranium, uranium was added as uranyl nitrate and ammonium diuranate. Six valent uranium hydroxide is a doubtful compound and an attempt to prepare it resulted in a semi-colloidal solution of unknown composition.

Method (1).

28·1 gm. of sodium tungstate were dissolved in water and converted to paratungstate by the addition of the equivalent of 99·3 ml. of HNO_3 and boiling for two hours. To this solution was added, over a period of five days, a solution of 15 gm. of uranyl nitrate in 700 ml. of water. A yellow precipitate gradually formed. After the uranyl nitrate had all been added, the solution was filtered and the precipitate dried and analysed. The ratio of UO_3 : WO_3 was found to be 1 : 1·10. The filtrate contained both tungsten and uranium. On cooling at 3°C. for five days, a precipitate formed which after filtering, drying and analysing, gave for the ratio UO_3 : WO_3 a value of 1 : 1·95. These salts were almost insoluble in water. The solution was then evaporated down to about 20 ml. and left to cool at 3°C. for a further five days. A small precipitate separated which removed most of the remaining tungsten from the solution. This last precipitate gave on analysis $UO_3 : WO_3 = 1 : 2{\cdot}32$.

On extracting some of the original solution with ether and 12 N H_2SO_4 a trace of ether addition compound was obtained, which contained no uranium.

Method (2)

The above method was repeated but this time the temperature was controlled between 60-70°C. The results obtained were similar.

First precipitate, $UO_3 : WO_3 = 1 : 1{\cdot}05$

Second precipitate, $UO_3 : WO_3 = 1 : 1{\cdot}75$

Third precipitate, $UO_3 : WO_3 = 1 : 3{\cdot}11$

Method (3)

28·1 gm. of sodium tungstate were dissolved in water and converted to the metatungstate by the addition of 127·7 ml. of N HNO_3 and boiling for four hours. 10 gm. of freshly prepared ammonium diuranate were added and the solution boiled for three days. It was then filtered, and on testing the filtrate for uranium, only a trace was found to be present.

Method (4)

The above method was repeated but this time the temperature was kept between 60-70°C. The results obtained were similar.

From the above results, it seems unlikely that tungsten and uranium form a heteropoly acid.

Methods of analysis

Uranium

About 1 gm. of the salt was dissolved in dilute nitric acid and the solution filtered to remove any tungstic acid precipitated. Dilute ammonia was added, to the yellow of methyl red. The solution was warmed for five minutes, then filtered through a No. 42 filter paper, and washed with a hot 2% solution of ammonium nitrate. The filter paper was dried, ignited over a very low flame until all the carbon had been burned off, and then ignited strongly to U_3O_8.

Tungsten

After the uranium had been removed, the solution was acidified with dilute HCl and the tungsten precipitated with cinchonine hydrochloride. It was then filtered through a No. 42 filter paper, washed, dried and ignited to WO_3. The tungstic acid precipitated in the solution of the salt in nitric acid, was also ignited to WO_3.

Beryllium and tungsten

Although Rosenheim in his chapter on heteropoly acids in Abegg's 'Handbuch der Anorganischen Chemie' includes beryllium in the list of elements forming the central atom in heteropoly acids, and this list is repeated in Emeleus and Anderson's 'Modern Aspects of Inorganic Chemistry', no references could be found to any actual compounds prepared. Rosenheim refers to the formation of beryllium minerals and beryllium tartrates but to no other source for his information.

Beryllium is amphoteric and its hydroxide, according to A. Hantzsch,[42] resembles that of zinc, both being weak acids. Beryllium is also a very strong complexing agent and its poisonous effect is due to this property. In the human body beryllium tends to complex with the alkaline phosph~~o~~tase and so inhibit its natural action. The complexing is thought to take place through the -OH groups present and it can be countered by using stronger organic complexing agents. These properties suggest that beryllium might be capable of complexing with tungsten to form a heteropoly acid. Few beryllium-tungsten compounds are listed in the literature-

$BeWO_4$ - beryllium tungstate
$BeO.4WO_3$ - beryllium metatungstate
$xBeWO_4 . yBe(NO_3)_2 . zBeO$
$xBeWO_4 . yBeCl_2 . zBeO.$

Preliminary experiments showed that there must be some form of complex formation, as on acidifying a solution containing beryllium and tungsten from pH 7 to pH 3, little metatungstic acid was formed and no subsidiary precipitates were obtained. A more thorough investigation was carried out as follows.

Preparation of Beryllium-Tungsten Complex

28·1 gm. of sodium tungstate were acidified to the paratungstate stage with the equivalent of 99·3 ml. of N HNO_3, and boiled for two hours. The solution was heated to about 90°C. and to it was added a solution of 10 gm. of beryllium nitrate in 700 ml. of water, over a period of two days. The solution was halved. One half was extracted with ether and 12 N H_2SO_4. There was only a trace of ether addition compound formed. Thus there was little metatungstate present. Only a slight trace of a tungstic acid precipitate appeared in the acid layer. Thus there was little paratungstate present. The other half of the solution was acidified slowly on boiling to a pH of 3 with dilute nitric acid. This solution was extracted with ether and 12 N H_2SO_4, but again only a small amount of ether addition compound was formed. Both ether addition compounds were diluted with water and the ether removed in a stream of hot air. The resulting aqueous solutions were tested for beryllium using the quinalizarin test. A very faint positive result was observed in both but due to the very sensitive nature of the test and to subsequent attempts at analysis giving no beryllium content, the tests were considered negative.

To isolate the tungsten-beryllium complex, part of the acid layer, which was approximately 8 N, was evaporated down, but this caused decomposition of the complex and precipitation of tungstic acid. As this was probably due to heating in a strongly acid solution, part of the acid layer was neutralised with dilute ammonia to a pH of 5 and then evaporated down gradually. The tungsten fraction did not precipitate in bulk until the solution was almost evaporated to dryness. The solid obtained, contained tungsten, beryllium, nitrate and ammonium ions. The experiment was repeated with beryllium sulphate instead of beryllium nitrate, and dilute sulphuric acid instead of dilute nitric acid. This was tried because

(1) beryllium sulphate and sodium sulphate are less soluble than beryllium nitrate and sodium nitrate respectively and thus perhaps would crystallise out before the tungsten complex, and

(2) there is generally a greater tendency for nitrate ion to complex with tungstates than for sulphate ion.

However again no effective separation was achieved.

Thus, since the free acid was so very soluble, separation would have to be carried out by precipitation of a salt. However the solution was too strongly acid, after extracting the metatungstic acid as the ether addition compound, to allow heating without decomposing the complex. Attempts at neutralising the solution with ammonia and barium carbonate were not satisfactory. In the case of the ammonia there was appreciable decomposition, either due, probably, to local alkalinity or to the heat developed in the still strongly acid solution. In the case of the barium carbonate there was decomposition, again probably due to heat, and also the difficulty in dealing with the large quantity of sludge obtained.

Most heteropoly acids are soluble in hydroxylated organic solvents and if the solvent is immiscible with water a separation can be effected. In this case the most satisfactory solvent was amyl alcohol.

After shaking up the acid solution with three fresh lots of amyl alcohol, separating the amyl alcohol, shaking up the amyl alcohol with three lots of water and separating the water, about an 80% extraction of the tungsten content of the solution was achieved. The resulting solution was still slightly acid due to some sulphuric acid being carried through the extraction but it could be neutralised with only slight decomposition using barium carbonate. Barium carbonate was used as it precipitated the sulphate as barium sulphate and as it was itself almost insoluble, it left the solution free from interfering ions. This solution was used in the preparation of the salts.

Salts of 10-tungstoberyllic acid.

The salts of this acid, like the free acid itself, were very soluble. The sodium, potassium and ammonium salts did not give any precipitate until the solution was almost dry and only the heavier metallic ions such as lead gave precipitates from solution. To overcome this difficulty and also for ease of analysis, as shown later, organic precipitants, in particular alkaloids were used. Attempts to prepare the barium salt by evaporating down the above solution after neutralising with barium carbonate, failed, as on analysis of several preparations, varying results were obtained. This was also the case in attempting to prepare the lead salt by this method, using lead carbonate instead of barium carbonate, although reproducible results could be obtained from the lead salt prepared by adding a solution of lead nitrate to the above solution.

The quinine, brucine, cinchonine, pyridine and guanidine salts were prepared by dissolving the respective hydrochlorides in water and adding each slowly to a hot neutral solution of the complex. The nitron salt was prepared by dissolving the nitron in dilute sulphuric acid and adding it to a slightly acid solution of the complex. The lead salt was prepared by adding a solution of lead nitrate to a neutral solution of the complex.

Results of analyses

Guanidine salt

	$(CN_3H_6)_2O$	BeO	WO_3	H_2O
Salt (1)	14·35	0·96	81·86	2·83
		0·93	81·70	
Salt (2)	14·40	0·98	81·63	3·08
		0·95	81·77	

The formula best fitting these results is

$3(CN_3H_6)_2O.\ BeO.\ 10WO_3.\ 5H_2O$ which has the % composition

14·35 0·88 81·60 3·17

Nitron Salt

	$(C_{20}H_{16}N_4)_2O$	BeO	WO_3	H_2O
Salt (1)	31·93	0·72	62·24	5·11
		0·70	62·40	
Salt (2)	32·57	0·76	62·65	4·02
		0·71	62·52	

The formula best fitting these results is

$2(C_{20}H_{16}N_4)_2O.\ BeO.\ 10WO_3.\ 8H_2O$ which has the % composition

33·96 0·66 61·56 3·82

Lead Salt

	PbO	BeO	WO_3	H_2O
Salt (1)	18·34	0·70	61·93	19·03
	18·62	0·69	62·11	18·58

The formula best fitting these results is

$3PbO.\ BeO.\ 10WO_3.\ 40H_2O$ which has the % composition

	PbO	BeO	WO_3	H_2O
	17·92	0·67	62·13	19·28
Salt (2)	21·50	0·79	72·85	4·86
	21·67	0·81	72·64	4·88

The formula best fitting these results is

$3PbO.\ BeO.\ 10WO_3.\ 10H_2O$ which has the % composition

	PbO	BeO	WO_3	H_2O
	20·94	0·78	72·63	5·64

Pyridine salt

	$(C_5H_6N)_2O$	BeO	WO_3	H_2O
Salt (1)	15·08	0·86	80·46	3·60
	15·11	0·88	80·70	3·31
Salt (2)	15·20	0·89	80·84	3·07
	15·16	0·88	80·68	3·28

The formula best fitting these results is

$2{\cdot}5(C_5H_6N)_2O.\ BeO.\ 10WO_3.\ 6H_2O$ which has the % composition

	$(C_5H_6N)_2O$	BeO	WO_3	H_2O
	15·22	0·86	80·19	3·73

The following organic salts were analysed to find the $BeO:WO_3$ ratio. The carbon and nitrogen contents of the cations were too low for micro-analysis.

Cinchonine salt

	BeO	WO_3	$BeO : WO_3$
Salt (1)	0·68	66·47	1 : 10·52
	0·70	66·56	1 : 10.24
Salt (2)	0·75	69·81	1 : 10·03
	0·74	69·95	1 : 10·19

Quinine salt

Salt (1)	0·76	72·38	1 : 10.26
	0·74	72·14	1 : 10·50
Salt (2)	0·74	71·83	1 : 10·47
	0·75	71·96	1 : 10·34

Brucine salt

Salt (1)	0·55	53·15	1 : 10·41
	0·57	53·22	1 : 10·06
Salt (2)	0·60	58·14	1 : 10·43
	0·59	57·89	1 : 10·57

Methods of analysis

Tungsten

About 1 gm. of the salt was boiled with a concentrated sodium hydroxide solution for at least 30 minutes to decompose the complex. (In the case of the lead salt, the lead was removed as lead sulphate before the alkali was added.) The solution was then acidified to methyl red and 15 ml. of a 10% solution of cinchonine hydrochloride added. The solution was heated on a steam-bath for about thirty minutes to coagulate the precipitate, filtered through a No.42 filter paper, thoroughly washed with the cinchonine wash solution (prepared as before in the tungstozincate analysis,) dried and ignited to WO_3.

Guanidine and Nitron

The nitrogen content of the guanidine and nitron salts was estimated by the micro-analyst and the % of guanidine and nitron oxides calculated.

Pyridine.

About 1·5 gm. of the pyridine salt was taken. 30 ml. of a concentrated sodium hydroxide solution were added and the solution steam-distilled until all the pyridine had been carried over. The pyridine/water solution was then titrated with a standard hydrochloric acid solution using as indicator a few drops of a solution of 0·1% dimethyl yellow and 0·1% methylene blue. Each time a blank run was carried out i.e. the experiment was repeated exactly but with no pyridine salt. The blank titre was subtracted from the experimental titre. This was to make allowance for any sodium hydroxide carried over in the distillation.

Lead

About 1 gm. of the lead salt was dissolved in water. The solution was buffered with ammonium acetate and acetic acid, and sufficient of a potassium dichromate solution added to precipitate all the lead. The solution was filtered through a No.4 sinter crucible, washed, heated to 140°C. until at constant weight and weighed as lead chromate.

In the analysis of the lead salt, the lead was removed by precipitating it as lead sulphate with dilute sulphuric acid, and the tungsten was estimated as above. To find the beryllium another weighed sample of the salt was taken, the lead removed as sulphate, the beryllium-tungsten complex precipitated as the cinchonine salt and the $BeO : WO_3$ ratio found.

Beryllium

The standard methods of beryllium analysis involve the precipitation of beryllium hydroxide with ammonium chloride and ammonium hydroxide. Beryllium hydroxide is a bulky precipitate and occludes other ions very readily. These ions are difficult to remove by washing. This disadvantage was accentuated in the case of the alkaloid salts, by the precipitation, on making alkaline, of the free base, which also was a rather bulky precipitate and also tended to occlude ions. Since the beryllium present accounted for only about 1% of the salt this adsorbtion rendered the results relatively inaccurate, particularly as one of the main coprecipitated impurities was tungsten. However, satisfactory results were obtained by developing a method used by Saddington and Cahn[21] to remove the tungsten and thus find the beryllium by a dry method.

The salts used were all organic-base salts. In the case of the lead salt, the lead was removed as the sulphate and the beryllium-tungsten complex precipitated as the cinchonine salt. A quantity of the salt was weighed out in a porcelain boat and placed in an ignition tube. The tube was heated to 500°C. and a stream of dry HCl was passed through for about six hours. The tungsten was removed as the volatile oxychloride and condensed in a cold receiving tube. The dry HCl was then turned off and dry air passed through the heated tube to ignite off the carbon from the organic base. These two processes were repeated until the material in the boat was pure white. Finally the boat was heated in dry air for two hours to convert any $BeCl_2$ formed to BeO.

As the beryllium oxide formed was in a finely divided state, it had to be handled out of draughts and it had to be cooled out of contact with moist air due to its high absorbing quality. This was done by sliding the boat from the ignition tube into a pyrex quick-fit test-tube and allowing it to cool there, sealed off from the air. Another boat was heated, sealed in a similar test-tube and used as a counterpoise in weighing. The process was repeated until constant weighings were obtained.

Potentiometric titrations

To determine the equivalent weight of the acid, a solution of the free acid was titrated potentiometrically against a standard sodium hydroxide solution. The solution of the free acid was prepared by neutralising the aqueous washings of the amyl alcohol extraction, with barium carbonate, filtering off the precipitate formed and passing the resulting solution through a cation exchange column. (The sulphate ion, which was the main impurity, was removed as barium sulphate.)

Results-first titration

Titre	Millivolts	Titre	Millivolts
0	342	18	300
1	338	19	295
2	336	20	288
3	334	21	280
4	333	22	268
5	332	22·5	258
6	331	22·7	252
7	329	22·9	244
8	327	23·0	240
9	325	23·1	236
10	323	23·3	224
11	321	23·5	200
12	318	23·6	170
13	316	23·7	130
14	314	23·8	74
15	312	23·9	46
16	308	24·0	22
17	304		

Equivalence point = 23·80 ml.

Results-second titration

Titre	Millivolts	Titre	Millivolts
0	320	20	271
1	319	20·5	267
2	317	21·0	262
3	316	21·5	256
4	315	22·0	250
5	314	22·2	246
6	313	22·4	241
7	311	22·6	237
8	309	22·8	230
9	307	23·0	223
10	305	23·2	212
11	303	23·3	201
12	302	23·4	186
13	299	23·5	161
14	297	23·6	132
15	294	23·7	109
16	290	23·8	90
17	285	23·9	74
18	282	24·0	59
19	278	24·1	50

Equivalence point = 23·60 ml.

The potentiometric titrations were carried out using a Cambridge Meter and standard Calomel-Platinum (quinhydrone) electrodes.

Normality of sodium hydroxide solution = 0·08580

In the first titration, equivalence point = 23·80 ml.

Weight of BeO + WO_3 = 0·8080 gm.

Therefore, equivalent weight = 395·7

In the second titration, equivalence point= 23·60 ml.

Weight of BeO + WO_3 = 0·7983 gm.

Therefore, equivalent weight = 394·3

The maximum basicity found in the salts was six. Assuming the formula $3H_2O$. BeO. $10WO_3$, a molecular weight of 2399 and an equivalent weight of 399·8 are obtained. Allowing for the $3H_2O$ as constitutional water, and recalculating the above results, equivalent weights of 404·8 and 403·4 are found.

<u>Introduction</u> - three valent central atoms.

The literature of heteropoly acid chemistry describes a few well defined acids with three valent central atoms, and many doubtful ones. Rosenheim and Schwer[46] prepared a series of salts corresponding to the formula $H_2(MoO_4)_6$, in which the central hydrogen atoms could be replaced by, amongst others, three valent aluminium, iron, chromium, cobalt and rhodium to give rise to complex metallo-paramolybdate anions. The existence was also known of a paratungstate ion which might have been expected to give rise to a similar series of metallo-paratungstate anions. However only a ferric paratungstate of type $4R_2O.Fe_2O_3.12WO_3.xH_2O$[6] was prepared and this is now considered to be doubtful. J. A. Mair[43] attempted to reproduce the ammonium and potassium 6-tungstoferrates but did not obtain any definite compound when the saturation product was treated with concentrated potassium or ammonium chloride solution. The pH of the saturation products and their stability to strong acidification showed that compounds of the paratungstate type could only be present in small amount, if at all.

The other heteropoly acids of tungsten reported before 1950 contained three valent non-metallic central atoms. Of these the most definite was 12-tungstoboric acid, first characterised by Klein[13] in 1880. The structure of the caesium salt of this acid has been worked out by J. A. Santos[33] and the formula thus confirmed. In 1885, W. Gibbs[2] had attempted to prepare complex tungstoarsenites by saturating a solution of sodium tungstate with arsenious oxide. On evaporating down the solution an oil was obtained from which long colourless crystals eventually separated. By saturating solutions of these crystals with solutions of ammonium chloride and barium chloride he obtained further salts. He suggested as possible formulae

$$9Na_2O.8As_2O_3.16WO_3.55H_2O$$

$$7(NH_4)_2O.2As_2O_3.18WO_3.18H_2O$$

$$4BaO.2As_2O_3.9WO_3.18H_2O$$

The variation in analysis could be due either to mixtures of salts being present or to the increased solubility of arsenious oxide in solutions of alkali salts as compared with water, leading to incomplete purification on recrystallising. A further investigation was then carried out by Rosenheim and Wolff[2] along the lines of the paramolybdate experiments. This time a new series of compounds involving as the central atom three valent arsenic, antimony and phosphorus were prepared. The free acids could not be isolated due to their extreme solubility in water but the anions were characterised by their sodium, ammonium, potassium and guanidine salts. Typical formulae obtained from these analyses were

$$7R_2O.As_2O_3.18WO_3.xH_2O \qquad 6R_2O.Sb_2O_3.18WO_3.xH_2O$$

$$4R_2O.P_2O_3.12WO_3.xH_2O \qquad 3R_2O.2Sb_2O_3.18WO_3.xH_2O$$

The method used by Rosenheim in obtaining these results for arsenic, was to saturate a boiling solution of sodium paratungstate with arsenious oxide until no further precipitation of tungstic acid was given with hydrochloric acid.

On cooling this solution no crystals were obtained, but eventually a syrupy mass formed. A concentrated solution of this syrup in water was mixed slowly with a concentrated solution of potassium chloride and cooled in ice. This yielded on prolonged standing, a colourless oil, which eventually solidified to needle-shaped crystals. These were very soluble in water and gave only a metatungstate reaction i.e. no tungstic acid was precipitated on the addition of hydrochloric acid.

In 1950, J. A. Mair[43] showed that the series of metallo-tungstic anions corresponding to the metallo-molybdates of Rosenheim and Schwer were 11- or 12-acids and not 6-acids, as far as three valent aluminium, chromium, manganese and iron were concerned. Recent work by J. A. Mair on crystal habits of the potassium and barium salts of these acids compared with the similar salts of other 12-acids, and by myself on the structure of the caesium salt of the tungstoferric acid, have shown that they are almost certainly 12-acids. They were prepared, using the tungstoferric acid as an example, by saturating a boiling solution of sodium paratungstate with a solution of ferric nitrate (8·6 gm. of the nonahydrate in 400 ml. of water) during a period of 20-24 hours. The yellow solution obtained was concentrated to 200 ml. and kept overnight at 6°C. to allow any unchanged paratungstate to separate. After filtration, ether extraction by Drechsel's[44] method gave the golden yellow ether addition compound of 12-tungstoferric acid mixed with that of metatungstic acid. The ether addition compound was purified by dropping it through two columns of dry ether then broken up by the addition of water and the evaporation off of the ether. The 12-tungstoferric acid is more stable to heat than is metatungstic acid and this property was used to separate them. The aqueous solution was evaporated to dryness and then baked at 120-130° C. for 4 hours. The residue was extracted with water and filtered. This process was repeated until separation of tungstic acid practically ceased. The final aqueous extract was concentrated on the steam-bath, then in vacuo over sulphuric acid. The 12-tungstoferric acid separated as a yellow crystalline mass.

Thus (1) by analogy with three valent boron, aluminium, chromium, manganese and iron

(2) by the addition of sufficient arsenious oxide to a boiling solution of sodium paratungstate, according to Rosenheim and Wolff, a solution is obtained which contains no free paratungstate.

(3) by the amphoteric nature of three valent arsenic, the formation of a 12-heteropoly-tungstoarsenite(111) could be expected. This, however, was not the case, and an acid was obtained which gave salts of the form

$$3R_2O.As_2O_3.10WO_3.xH_2O$$

Preparation of an aqueous solution of tungstoarsenic(111) acid

56·2 gm. of sodium tungstate were dissolved in water and converted to paratungstate by the addition of 198·6 ml. of N H_2SO_4 and boiling for two hours. (Originally HNO_3 was used, but this was stopped when it was realised that the HNO_3 liberated in the Drechsel[44] extraction was oxidising a little of the arsenite to arsenate). To the boiling solution, of volume approximately 500 ml. and pH 6·2-6·4, were added 8 gm. of pure arsenious oxide, and the solution boiled with continuous stirring for five hours, during which time the arsenious oxide dissolved almost completely. The volume was controlled to give at the end of the five hours boiling about 100 ml. of solution. The pH was 7·2-7·4. The solution was then cooled, filtered and extracted with ether and 12 N H_2SO_4 according to the Drechsel method. If the solution was too concentrated before extraction, then on the addition of the ether and sulphuric acid an emulsion formed which often took several days to settle out. If on the other hand, the solution was too dilute, 18 N H_2SO_4 had to be added to extract all the arsenious complex. To purify the ether addition compound it was dropped through two columns of fresh ether. It was then broken up by diluting with water and evaporating off the ether. A yellow, fairly dense aqueous solution was obtained. Almost all the tungsten added originally could be accounted for at this stage. This agreed with the fact that the solution was stable to strong acidification i.e. as there was little precipitation of tungstic acid, there can have been only a little free paratungstate ion present in solution. The proportion of arsenious oxide in the ether addition compound varied with the amount of arsenic added to the solution, but in general using 8 gm. of arsenious oxide, the ratio of As_2O_3: WO_3 was of the order of 1:6 to 1:10. If too much arsenious oxide was added, the solution, on extraction, tended to emulsify. The ether addition compound appeared to absorb a little free arsenious oxide, as on dropping through the fresh ether a scum containing arsenious oxide formed on the surface of the complex and on the sides of the glass container. If the ether from a purified specimen of the ether addition compound was slowly evaporated off, sometimes a dark yellow viscous oil was obtained. This oil on prolonged standing gave a glass. Other times decomposition took place. This is different from the normal behaviour of ether addition compounds where on standing, either the compound breaks up to deposit yellow tungstic acid or else crystals of the heteropoly acid are formed.

The aqueous solution of the free acid was evaporated down to small bulk and left at 0°C. for two months. No crystals of the free acid appeared though there was evident decomposition with some semi-colloidal tungstic acid settling out. On further evaporation a yellow glass was obtained. If the glass was heated to drive off the water, a solid was left which was only partially soluble in water. The insoluble portion contained both arsenic and tungsten. By analogy with subsequent experiments it might have been due to polymerisation.

The main impurity expected in the aqueous extract from the ether addition compound was metatungstic acid. On attempting to utilise its thermal instability to destroy it and thus purify the tungstoarsenic(111) acid, several difficulties were met with. Firstly, after evaporating to dryness and baking at 140°C., on extracting with even the minimum amount of water the tungstic acid peptised. Secondly, the tungstoarsenic(111) acid itself gradually decomposed, partly to tungstic acid and arsenious oxide, and partly to the insoluble polymeric form. On repeating the process, but this time only heating to 110°C. for five minutes, the decomposition was considerably decreased but the peptisation of the tungstic acid still prevented clear solutions being obtained. This method of removing the metatungstic acid was rejected in favour of fractional crystallisation of the salts.

Samples of the aqueous extract from the ether addition compound were run through a cation exchange column and the effluent analysed for arsenite and tungsten. The following results were obtained for the ratio $As_2O_3 : WO_3$

1 : 9·96

1 : 10·22

1 : 11·02

Preparation and purification of salts

Potassium salt

An attempt was made to prepare the potassium salt by adding a saturated solution of potassium chloride to a fairly concentrated aqueous extract from the ether addition compound and leaving at 0°C. for one week. An oil first separated which later partly gave a white crystalline solid. This solid was extremely soluble in water and very difficult to recrystallise as in the small bulk of mother liquor required, it tended to form an oil on cooling. Though qualitatively it always contained potassium, arsenic and tungsten, quantitatively no reproducible results were obtained. The values for the ratio As_2O_3: WO_3 ranged from 1:8·5 to 1:11·3.

Ammonium salt

The ammonium salt was also anomalous in behaviour. Two methods of preparation were used.

(1) A saturated solution of ammonium chloride was added to a fairly concentrated solution of the aqueous extract from the ether addition compound and the mixture was allowed to stand at 0°C. for three days. An oily solid separated which like the potassium salt was difficult to recrystallise. However solid matter could be obtained which gave on successive recrystallisation colourless crystals of progressively decreasing arsenic content. The first crystals gave for the ratio As_2O_3: WO_3 a value of 1:7·2 (approximately that of the ether addition compound) and after four recrystallisations the ratio rose to 1:10·8. Since the salt was very

soluble in water, the solutions were fairly concentrated. Thus the solubility of the arsenious oxide would be increased, and with the repeated heating some decomposition of the tungstoarsenic(111) acid would occur. To eliminate free arsenious oxide by working in dilute solution and to prevent as far as possible, thermal decomposition, the second method was tried.

(2) Ammonia vapour was bubbled through an aqueous extract from the ether addition compound until the solution reached a pH of 6·5. However, although a porcelain diffuser was used, local alkalinity seemed to decompose some of the complex as a sludge formed. The solution was concentrated to about 20 ml. and filtered. On cooling an oil formed from which colourless crystals eventually separated. This was repeated several times and the crystals analysed, but no consistent results were obtained.

Since the nature and purity of these oils were unknown, it was decided to attempt to prepare salts which did not form oils, and which were only moderately soluble in water. Thus the solutions required would be dilute and the concentration of free arsenious oxide would be small. The salts, fitting these conditions, which were prepared, were the silver, barium and guanidine salts. Attempts to prepare a pyridine salt were unsuccessful, as on heating the salt, which was solid when precipitated, it became plastic about 60-70°C., and formed a viscous oil, which was immiscible with water, about 90°C. This oil again solidified on cooling below 60°C.

Silver salt.

This was prepared by adding a solution of silver nitrate to an aqueous extract from the ether addition compound, both about 90°C., filtering hot and cooling at 0°C. for 12 hours. The mother liquor was decanted off and the salt recrystallised from water and a little perchloric acid.

Barium salt.

This was prepared as above but using a solution of barium chloride. It was recrystallised from water and a few drops of dil. HCl.

Guanidine salt.

This was prepared as above but using a dilute solution of guanidine hydrochloride. It was recrystallised from water.

Methods of analysis.

Silver. About 1·5 gm. of the silver salt were dissolved up in the minimum of hot 5% perchloric acid and the silver precipitated as AgCl by the addition of dilute hydrochloric acid. The precipitate was filtered through a No.4 sinter glass crucible, dried at 130°C. and weighed. The tungstoarsenite anion was broken up by heating with caustic soda solution and the tungsten and arsenic estimated in separate samples, the silver being first removed.

Barium. About 1·5 gm. of the barium salt were dissolved in hot water with a few drops of dilute HCl, and the barium was precipitated as barium sulphate by the addition of dilute sulphuric acid. The solution was filtered through a No.42 filter paper which was then washed and ignited. The anion was broken up as before and the tungsten and arsenic estimated in separate samples, the barium being first removed.

Guanidine. The nitrogen content was obtained by the micro-analyst and the guanidine content calculated from it. The guanidine did not interfere with the analysis (volumetric) for arsenic. In the analysis for tungsten, it helped the cinchonine hydrochloride as a preciptant for the tungsten in acid solution.

Arsenic. (a) Volumetrically

About 1·5 gm. of the salt were taken and, in the case of barium and silver the cations were removed. The solution was made alkaline with caustic soda solution and heated at 80°C. for over thirty minutes to break up the anionic complex. 3 gm. of Na_2HPO_4 were added to complex the tungstate present and the solution neutralised with dil. HCl to the red end-point of methyl orange. To the cold solution were then added 20 ml. of a saturated sodium bicarbonate solution and the arsenite present titrated with standard iodine solution, using starch as indicator.

(b) Gravimetrically

This method was used to confirm if there was any five-valent arsenic present by comparing the results obtained, with those from the volumetric method. The cations were removed and the anionic complex broken up as before. The arsenite was oxidised to arsenate by adding 100 volume hydrogen peroxide to the boiling alkaline solution. The boiling was continued until all the excess hydrogen peroxide was destroyed. The solution was cooled and neutralised with dilute HCl to phenolphthalein. 25 ml. of Magnesia Mixture were added slowly with stirring, then one third of the total volume of ·880 ammonia, and the solution left for twenty four hours. The precipitate was filtered off through a No. 4 Sinter Glass crucible, washed first with 2 N NH_4OH, then with acetone and finally with a little ether. The precipitate was dried in a desiccator and weighed as $MgNH_4AsO_4.6H_2O$.

Tungsten. About 1 gm. of the salt was taken and, in the case of barium and silver, the cations were removed. The anionic complex was broken up as before and then the solution was made just acid to phenolphthalein with dilute HCl. Sufficient cinchonine hydrochloride solution was added to completely precipitate the tungsten present and the solution heated on a steam-bath for about thirty minutes to coagulate the precipitate, which was then filtered through a No.42 filter paper, washed repeatedly with a prepared wash solution (30 ml. of a 10% cinchonine hydrochloride solution and 30 ml. of conc. HCl to 1 litre of water), dried and ignited at 900°C. to WO_3.

Water. This was found by difference after the arsenic, tungsten and cationic weights had been obtained.

Results of analyses

Barium salts. (The figures given are % oxide.)

	BaO	As_2O_3	WO_3	H_2O	$As_2O_3 : WO_3$
Salt (1)	13·17	5·76	68·60	12·47	1 : 10·1
	13·30	5·71	68·20	12·79	1 : 10·2
Salt (2)	12·94	5·57	67·03	14·46	1 : 10·2
	13·07	5·51	67·22	14·20	1 : 10·4
Salt (3)	13·37	5·48	66·00	15·15	1 : 10·3
	13·40	5·48	66·26	14·86	1 : 10·3

The formula best fitting these results is-

$3BaO.As_2O_3.10WO_3.27H_2O$ with % composition

13·40 5·71 66·97 14·03

Silver salts

	Ag_2O	As_2O_3	WO_3	H_2O	$As_2O_3 : WO_3$
Salt (1)	21·71	5·88	65·86	6·55	1 : 9·6
	21·77	5·90	65·99	6·34	1 : 9·5
Salt (2)	21·42	5·80	66·62	6·16	1 : 9·8
	21·34	5·89	66·55	6·22	1 : 9·6
Salt (3)	21·00	5·71	66·30	6·99	1 : 9·9
	21·20	5·75	66·32	6·73	1 : 9·8

The formula best fitting these results is-

$3Ag_2O.As_2O_3.10WO_3.12H_2O$ with % composition

20·28 5·76 67·67 6·30

Guanidine salts

	$(CN_3H_6)_2O$	As_2O_3	WO_3	H_2O	$As_2O_3 : WO_3$
Salt (1)	12·39	5·99	75·02	6·60	1 : 10·6
		6·06	75·18		1 : 10·5
Salt (2)	12·66	5·93	74·72	6·69	1 : 10·7
		5·90	74·90		1 : 10·8

The formula best fitting these results is-

$3(CN_3H_6)_2O.As_2O_3.10WO_3.12H_2O.$ with % composition

12·98 6·30 73·84 6·88

	$(CN_3H_6)_2O$	As_2O_3	WO_3	H_2O	$As_2O_3 : WO_3$
Salt (3)	10·98	5·54	63·96	19·52	1 : 9·8
		5·58	64·27		1 : 9·8
Salt (4)	10·75	5·50	63·90	19·85	1 : 9·9
		5·44	64·31		1 : 10·1

The formula best fitting these results is-

$3(CN_3H_6)_2O.As_2O_3.10WO_3.38H_2O.$ with % composition

11·31 5·48 64·27 18·95

Cation exchange column effluent

	$As_2O_3 : WO_3$
(1)	1 : 10·22
(2)	1 : 9·96
(3)	1 : 11·02

Discussion of analysis

(a) The silver salt was fairly insoluble and had to be heated for almost thirty minutes in dilute perchloric acid to dissolve it. The solution, however, never became quite clear due to an almost colloidal suspension, probably of tungstic acid. This could account for the high values for silver chloride (which on precipitation cleared the solution) and the low values for tungsten.

(b) The first two guanidine salts prepared, were in a larger crystalline form than the second two, and crystallised more slowly from solution. This increased time in solution would have allowed more decomposition to take place with the possible coprecipitation of impurities.

(c) The variation in composition of the cation exchange column effluent could be due to slight decomposition of the anion in the acidic media. Identical conditions of flow could not be achieved, as the column after each run was washed with dilute HCl and distilled water, which tended to "pack" it. The rates of flow into and out of the column could be controlled but the nature of the contact of the solution with the resin varied.

Potentiometric titration results

Some of the aqueous extract from the ether addition compound was passed through the cation exchange column and the effluent titrated against 0·1176 N NaOH using a Cambridge Meter and standard Calomel-Platinum (Quinhydrone) electrodes.

Titre (NaOH)	Millivolt
0	349
1	348
2	347
3	344
4	341
5	337
6	335
7	335
8	335
9	329
10	324
11	320
12	316
13	313
14	310
15	306
16	298
16·5	294
17·0	288
17·5	282
18·0	279
18·5	275
19·0	271
19·5	266
20·0	262
20·5	258
21·0	244
21·5	235
22·0	224
22·5	213
22·7	210
22·9	205
23·0	200
23·2	194
23·4	188
23·6	182
23·8	176
24·0	168
24·2	161
24·4	158
24·6	154
24·8	148
25·0	144
25·5	136
26·0	127
26·5	118
27·0	112
27·5	107
28·0	102

On analysis, the weight of $As_2O_3 + WO_3 = 1{\cdot}2179$ gm.

Equivalence point taken = 24·0 ml.

Allowing for three water molecules as constitutional water, the equivalent weight works out to be 440·7.

Titre (NaOH)	Millivolt	Titre (NaOH)	Millivolt
0	368	19·2	256
1	366	19·4	252
2	362	19·6	240
3	361	19·8	237
4	357	20·0	234
5	355	20·2	233
6	352	20·4	228
7	350	20·6	222
8	347	20·8	214
9	344	21·0	206
10	342	21·2	198
11	339	21·4	189
12	333	21·6	180
13	328	21·8	169
14	324	22·0	164
15	314	22·2	160
16	308	22·4	156
17	297	22·6	153
18	284	22·8	150
19	264	23·0	147

On analysis, the weight of As_2O_3 + WO_3 = 1·1192 gm.

Equivalence point taken = 21·8 ml.

Allowing for three water molecules as constitutional water, the equivalent weight works out to be 445·7.

For $3H_2O.As_2O_3 10WO_3$ the molecular weight is 2572 and assuming it to be six valent, the equivalent weight is 428·7.

The results of these potentiometric titrations do not show a substantial fall in the millivolt reading (i.e. in pH) over a small titre difference and resemble the results of a very weak acid-strong base titration. If the double differential of these figures is taken (by subtracting each reading from the previous reading and then subtracting these differences in turn) several 'turning-points' are obtained. The 'turning-point' taken in the above calculations was the one which occurred in the region of greatest change in the millivolt reading.

Bismuth and tungsten

A tungstobismuthate has been claimed by Balke and Smith of formula $3K_2O.\ 2Bi_2O_3.\ 11WO_3.\ 15H_2O.$ with corresponding salts of ammonia and strontium. Also the mercurous salt has been prepared by Sweeney. The method used was to boil bismuth metahydroxide with ammonium paratungstate for two days, filter and cool. The salt separated as an oil which on dehydration gave a glass. This method would involve self-acidification as some ammonia would boil off. Thus the resulting solution would probably contain some ammonium metatungstate, some ammonium paratungstate, a small amount of bismuth in solution and any heteropoly complex formed. (The preceding statement is not correct for the ions present but is probably correct for the precipitates which could be obtained.) The salts described above do not fit into any known series. It is not unusual for heteropoly acid salts to form oils especially with hydroxylated solvents. The salts of heteropoly acids precipitated from aqueous solution, are often highly hydrated and in conditions where the formation of -O-H-O- bonds between the anionic oxygen and the -O-H of the solvent, is favoured, the 'padding effect' of the water molecules could so weaken the interionic forces that a rigid lattice would not be stable and a viscous liquid would result. The above experiment with ammonium paratungstate was repeated and similar results were obtained. Three other methods were also tried.

(1) 28·1 gm. of sodium tungstate were converted to the paratungstate by the addition of the equivalent of 99·3 ml. of N HNO_3 and

boiling for two hours. Some hydrated bismuth oxide was added and the solution was boiled for two days. (The hydrated bismuth oxide was prepared by dissolving 10 gm. of bismuth carbonate in nitric acid, precipitating with ammonia and washing with water until the precipitate was free from alkali.) The solution was filtered, concentrated to about 30 ml. and cooled for a week at 3°C. A small quantity of an oil separated, which on analysis gave

$$3Na_2O.\ 2Bi_2O_3.\ 11WO_3.\ 16H_2O.$$

(2) The above method was repeated but this time after the hydrated bismuth oxide had been added the solution was acidified to pH 3 with dilute nitric acid. More oil separated, but on analysis the same formula was obtained.

(3) 28·1 gm. of sodium tungstate were boiled up with hydrated bismuth oxide and the solution slowly acidified, over a period of two days, with dilute nitric acid to a pH of 3. After filtering and cooling, an oil separated, though in smaller bulk than in the previous method. On analysis the same formula was obtained.

If the solution was acidified below a pH of 2 and boiled, a much smaller yield of oil was obtained. Prolonged boiling caused decomposition of most of the complex.

Properties of the bismuth-tungsten complex

The properties of the sodium salt were similar to those found by Balke and Smith for the potassium and ammonium salts.

(1) Dilute acids had no effect.

(2) Hot concentrated acids caused decomposition.

(3) Cold ammonia solution had no effect, except on long standing.

(4) Hot ammonia solution caused decomposition.

It was further shown

(5) that the complex did not form an ether addition compound with ether and 12 N H_2SO_4, and

(6) that bismuth and tungsten existed in the effluent after passing through a cation exchange column. This last experiment could not be carried out quantitatively as there was a large amount of decomposition in the column. However it did show that some of the bismuth was bound in the anion.

The sodium salt, on attempts at recrystallisation, gave either the oil again or a white emulsion. However on drying at 80° C. for a week, a brittle glass was obtained which could be ground up for analysis.

Results:-	Na_2O	Bi_2O_3	WO_3	H_2O
Method (1)	4·70	23·35	64·30	7·65
Method (2)	4·81	23·48	64·63	7·08
Method (3)	4·78	23·20	64·61	7·41

The formula best fitting these results is

$3Na_2O.\ 2Bi_2O_3.\ 11WO_3.\ 16H_2O$ which has the % composition

4·70 23·55 64·45 7·28

The aqueous layers above the oils were extracted with ether and 12N H_2SO_4 and the ether addition compound which was formed, separated. To purify the compound, it was filtered through a No. 4 sinter crucible into ether and then dropped through two columns of fresh ether. It was then tested and found to contain bismuth. On analysis, the $\frac{1}{2}(Bi_2O_3) : WO_3$ ratio was of the order of 1:30 to 1:35 over various samples. As heteropoly acids of this order are unknown, this relatively high ratio could be due to either,

(1) metatungstic acid with some occluded bismuth, or

(2) a mixture of metatungstic acid and a heteropoly tungsto-bismuthate.

To get rid of the metatungstic acid present, the ether addition compound was diluted with water and the ether removed in a stream of hot air. The solution was evaporated to dryness, extracted with water and the extract filtered. This was repeated several times. The residues, on testing, were found to contain bismuth as well as tungsten, as did the filtrate. Thus the method was not resulting in any separation. However it did suggest that the bismuth was bound in some complex with the tungsten and that this complex was, like metatungstic acid, unstable to heat. Various salts were then prepared in an endeavour to separate the components of the ether addition compound by fractional crystallisation of the salts.

The first salt tried was the guanidine salt, prepared by adding a 5% solution of guanidine hydrochloride in water to a hot aqueous solution of the acids. Fine white crystals were obtained which gave on analysis a ratio of $\frac{1}{2}(Bi_2O_3) : WO_3 = 1:30{\cdot}1$

Four successive fractional recrystallisations only succeeded in lowering the $\frac{1}{2}(Bi_2O_3)$: WO_3 ratio to 1:28·33.

The barium salt was tried next. It was prepared by neutralising the solution of the free acids with barium carbonate, filtering hot, cooling at 3°C. for a few days and filtering off the salt. After four successive recrystallisations the ratio of $\frac{1}{2}(Bi_2O_3)$: WO_3 was found to be 1 :23·10.

Since both the guanidine and barium salts were fairly insoluble and provided no evident separation, the more soluble ammonium and potassium salts were then prepared by adding respectively solutions of ammonium and potassium chloride to hot solutions of the free acids, cooling, and filtering off the fine white crystals. After numerous fractional recrystallisations the lowest ratio obtained for the ammonium salt was $\frac{1}{2}(Bi_2O_3)$: WO_3 = 1 : 14·79, and for the potassium salt = 1 : 14·84. Whether these results have any significance is doubtful as the $\frac{1}{2}(Bi_2O_3)$: WO_3 ratio did not decrease regularly on fractional recrystallisation, but varied irregularly, possibly due to conditions favouring a particular decomposition.

The presence of bismuth in the ether addition compound does seem to indicate the formation of a tungstobismuthate as it is unlikely that occluded bismuth could be carried through at least four recrystallisations. It is possible, however, that some of the $3Na_2O.\ 2Bi_2O_3.\ 11WO_3.\ 16H_2O$ which was not removed as the oil, on extraction with ether and sulphuric acid, formed a free acid which in the presence of excess metatungstic acid could be carried through in the ether addition compound, though by itself it could not form one. No definite conclusions were reached.

Methods of analysis

Bismuth

The analysis of bismuth in the presence of tungsten provided some difficulty. Most standard methods of bismuth analysis are carried out from acid solution; this, however, would result in the precipitation of tungstic acid. Precipitation of bismuth as an oxinate is carried out in an almost neutral solution which is too near the precipitation range for tungsten as an oxinate. The direct method of precipitating bismuth as the hydroxide by the addition of ammonium chloride and ammonium hydroxide resulted in the coprecipitation of relatively large quantities of tungsten. However this method could be used by first precipitating the bismuth with ammonium chloride and ammonium hydroxide, filtering through a No. 42 filter paper then dissolving the bismuth with dilute nitric acid, thus leaving the coprecipitated tungsten. The bismuth was reprecipitated with ammonium chloride and ammonium hydroxide, filtered and ignited to Bi_2O_3. The most satisfactory method was to fuse the complex with sodium carbonate in a platinum crucible, take up in water, filter off the precipitated bismuth carbonates and ignite them to Bi_2O_3.

Tungsten

After the bismuth had been removed, the tungsten was estimated as described in the analysis of the tungstozincates.

Sodium

This was found by difference.

Water

The water content was found by ignition loss after heating to 600°C for 4 hours.

Conclusions

(1) Zinc and tungsten

Zinc forms two heteropoly acids with tungsten, a 3 : 12 acid and a 1 : 12 acid. The salts of the 3 : 12 acid resemble in solubility the corresponding paratungstate salts. The free acid is unstable, does not form an ether addition compound, and can be converted partially to the 1 : 12 acid by heating in a solution of pH about 3. This suggests that the 3 : 12 acid is

(a) in direct equilibrium with the 1 : 12 acid, or

(b) along with the 1 : 12 acid, in equilibrium with a common intermediate ion. As it is doubtful if a 12-fold ion exists in solution, the latter seems most likely. Assuming heteropoly acid formation takes place through the zincate ion, a possible method of formation would be -

$$(H_3W_6O_{21})^{3-} + ZnO_2^{2-} = (HZnO_2W_6O_{19})^{3-} + 2OH^{-} \quad --- (1)$$

$$(HZnO_2W_6O_{19})^{3-} + (H_3W_6O_{21})^{3-} = (ZnW_{12}O_{40})^{6-} + 2H_2O \quad --- (2)$$

$$2(HZnO_2W_6O_{19})^{3-} + ZnO_2^{2-} = (Zn_3W_{12}O_{44})^{10-} + 2H^{+} \quad --- (3)$$

This gives an anion of maximum valency 10. The highest valency found in the salts analysed was 9. This 3 : 12 acid has no parallel, as yet reported, in other heteropoly acids.

The 1 : 12 acid, formed probably as in equation (2) above, is a typical 12-acid resembling 12-tungstophosphoric acid and 12-tungstoferric acid in structure and in general chemical properties. Potentiometric titrations indicate a maximum valency of 6, which agrees with that deduced from the structure.

(2) Zinc and molybdenum

No evidence of heteropoly acid formation with zinc and molybdenum was found.

(3) Cadmium and tungsten

No evidence of heteropoly acid formation with cadmium and tungsten was found.

(4) Uranium and tungsten

No evidence of heteropoly acid formation with uranium and tungsten was found.

(5) Beryllium and tungsten

Beryllium forms a 1 : 10 heteropoly acid with tungsten. The free acid is very soluble and cannot be isolated. It does not form an ether addition compound. The metal salts are in general, also very soluble. Potentiometric titrations indicate a maximum valency of 6 for each beryllium atom present in the anion.

(6) Arsenic(111) and tungsten

Three valent arsenic forms a heteropoly acid with tungsten, probably a 1:5 acid. The free acid is very soluble and cannot be isolated except as a glass. It forms an ether addition compound. The salts are anomalous in behaviour and some form oils. There is a tendency with the free acid and also with some of the salts to polymerise. This could be due to the unsaturated valency of the arsenic. Potentiometric titrations indicate a valency of 3 for each arsenic atom in the anion. The analyses of the salts were not very precise, but over a number of preparations the ratio As_2O_3 : WO_3 agreed best with the value 1:10.

(7) Bismuth and tungsten

Bismuth forms a heteropoly anion with tungsten of formula $(2Bi_2O_3.11WO_3)^{6-}$. The free acid is unstable and does not form an ether addition compound. The metal salts in general form oils. The complex is anomalous in behaviour and has no parallel, as yet reported, in other heteropoly acids.

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