A study of the
HETEROPOLY TUNGSTATES of some TRIVALENT METALS

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CONTENTS

1. Preface:

2. Introductory survey:

3. The free acids:

HETEROPOLY TUNGSTATES of some TRIVALENT METALS

1. PREFACE.

(i) Concise summary:

Tungsten, like molybdenum, and to a lesser extent vanadium enters into complex acid formation with nearly all of the more weakly electro-negative and amphoteric elements, any one of which may function as the central atom of the complex anion. The role of this central atom is thus not restricted to the purely acid forming elements; most of the metals of the transition groups, the amphoteric elements, some non-metals and possibly the metal beryllium may occupy this position. This work deals with the heteropoly acids of tungsten, which contain the 3-valent aluminium, chromium and manganese (also bismuth) as the central atom of the polyacid complex. The free heteropoly acids composed of the above metals in combination with tungsten have not previously been isolated nor are described in the literature. The same applies to the salts of those acids, although a few complex compounds of indefinite composition, and containing aluminium and manganese combined with tungsten are described as having been obtained by crystallisation from mother liquors containing the various components in solution.

Tungsto-aluminic, tungsto-chromic and tungsto-manganic acids have been synthesised by roughly similar means, viz. by saturating a boiling solution of alkali paratungstate with the freshly precipitated hydroxide of the corresponding metal. The principle used was to begin from an easily hydrolysable salt and to slowly add only sufficient of this salt as would produce the requisite amount of mineral acid on hydrolysis to convert all of the paratungstate present to metatungstate. The facility with which the various metals enter into heteropoly complex formation with the tungsten, and the means of ensuring that the hydroxide is precipitated in situ in the boiling paratungstate solution are quite different in each case; also the amount of insoluble material which separates during the course of the saturation. This latter is least and the best yields obtained when the saturation is allowed to take place over a fairly long period (20 - 24 hours). Aqueous solutions of the free acids have been isolated from these mother liauors, via the ether addition compounds, which form when the saturated solutions obtained as above are extracted with ether and dilute sulphuric acid. From the aqueous solutions tungsto-aluminic and tungsto-chromic acids crystallise as white andgreen micro-crystalline powders respectively. Tungsto-manganic acid is only stable in solution and could not be isolated as a crystalline product. No heteropoly compound could be extracted from paratungstate solutions saturated with bismuth oxynitrate, so it is assumed that bismuth does not enter into complex formation with tungsten. The free acids are extremely soluble compounds (they tend to be deliquescent) and their aqueous solutions are of remarkably high density (2.8 - 3.4). They are quite strongly acidic (pH 1.5 - 2.5), and very stable to excess mineral acids, but readily decomposed by alkalis.

From aqueous solutions of the free acids various salts have been prepared by double decomposition with aqueous solutions of the appropriate metallic ion. All of these salts crystallise well, usually in the form of prisms or octahedra or bipyramids, and contain large numbers of molecules of water of crystallisation. Some water is contained in the constitution of these compounds, although it has not been possible to distinguish between this water of constitution and that which is merely water of crystallisation. On dehydration there is only a continuous loss in weight as the compounds first dehydrate and then decompose,without any definite break being shown over any temperature range. In general decomposition begins at a temperature of about 160°C. All of these heteropoly salts are very soluble. The alkali and alkaline earth salts are generally most soluble, the solubility increasing in the order of decreasing atomic weight. The ammonium salts are usually more insoluble and so more easily crystallisable. Nearly all show some tendency to effloresce on standing, principally the potassium and barium salts, which then break down to micro-crystalline powders. The tungsto-aluminates are colourless, the tungsto-chromates are coloured a characteristic green, while the tungsto-manganates are of an intense red colour. The isomorphism of the barium, potassium and ammonium salts of all 3 acids is very marked, and large crystals are quite stable. The guanidine, silver and caesium salts are much more insoluble, and crystals of those seldom grow to any appreciable size.

Some of the principal physical and optical constants of the compounds prepared have been determined. These include specific gravity, refractive index, extinction directions and optical character of crystals, and pH of the aqueous salt solutions. In general the densities (4 - 5) and the refractive indices (1.7 - 2) are very high, as could be expected for such compounds containing as they do over 80% of tungsten.

The analyses of these compounds presents many difficulties. In the first instance, the ratio of the weight of the central metal atom to the weight of the tungsten is so small, and the molecular weight so large (6,000 - 6,500), that differences of a fraction of 1% in the estimation of the principal constituent of the molecule may mean a considerable difference in the resultant, calculated, empirical formula. To obtain material of sufficient homogeneity for analyses, the samples of the material used had to be recrystallised from water at least 3 times, and then dehydrated to some constant level (usually over phosphorus pentoxide). From the analytical data collected, it is concluded that these heteropoly acids containing 3-valent aluminium, chromium and manganese are 11-acids (i.e. ratio of number of atoms of the central element to the number of atoms oftungsten is 1:11), and that they are at least 1o-basic. On the basis of these analyses the complex anion may be represented as $\left[M^{+++}W_{22}O_{74}\right]^{10-}$.

Potentiometric titration of the free tungsto-aluminic acid against N/10 sodium hydroxide was used as a means of estimating its basicity. Similar titration curves for some 12-acids have also been obtained for comparison purposes. Salt formation usually takes place at pH 3 - 5, but the tungstic acid present titrates continuously, consequent on the neutralisation and decomposition of the heteropoly anion. The individual stages in the neutralisation could not be detected, presumably due to the fact that the dissociation constants of such polybasic acids are not very widely separated.

Some preliminary x'ray studies have been carried out, based on powder photographs. However, the difficulties of arriving at a complete structure determination of such complex compounds are probably quite considerable, and this has not yet been attempted.

(ii) Outline plan of thesis:

Following on this concise summary of what has been achieved, there is an introductory survey, which includes a general review of heteropoly compounds. The preparation, isolation and properties of tungsto-aluminic, tungsto-chromic and tungsto-manganic acids are then detailed. The principal salts of those acids which have been prepared, the analytical methods employed and the measurements of the physical and optical properties which have been carried out are then described. In conclusion there is a short discussion of the data which has been collected.

2. INTRODUCTORY SURVEY.

(i) Components and occurence of heteropoly compounds:

Heteropoly acids and the salts derived from them form one of the largest classes of inorganic compounds. Either tungsten, molybdenum and to a lesser extent vanadium and silicon are present as a constituent of all of those compounds. The heteropoly silicates cannot properly be included in this classification as the structures of the complex silicates follow an entirely different plan. They include also the numerous poly-acids and poly-salts containing only one acid radical, e.g. the poly-chromates and poly-vanadates. Heteropoly acids are formed by the union of varying numbers of acid anhydride molecules, most commonly WO_3, MoO_3 and V_2O_5, with a second acid which is regarded, according to present day theory, as furnishing the central atom or central ion of the whole complex anion. It is a distinctive feature of heteropoly acids that a single radical of one of the acids is combined with many, perhaps 12 radicals derived from the second acid. The power of functioning as the central atom is widely spread over the acidic and amphoteric elements, and even amongst the true metals, as is shown in the table (i) below.

Table (i).

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

Elements capable of acting as central atom in poly-acid formation

Thus all heteropoly compounds contain at least 2 different acid radicals in their anion, but others occur which contain 3 or 4 different acidic radicals, and some even contain the same radical in different states of oxidation, e.g. the following complicated type:-

$$18BaO.V_2O_5.VO_2.5P_2O_5.60WO_3.150H_2O.$$

These substances may contain solid solutions of the simple components. Many minerals, usually of non-marine origin contain compounds of this type, usually of 4 or 5-valent elements, e.g.

$10SiO_2.Nb_2O_5.3ZrO_2.10CaO.Na_2O.3NaF$	Wöhlerite
$10SiO_2.V_2O_5.5Al_2O_3.10MnO.5H_2O$	Ardenite.

Also many silicate minerals.

(ii) Early history of heteropoly compounds:

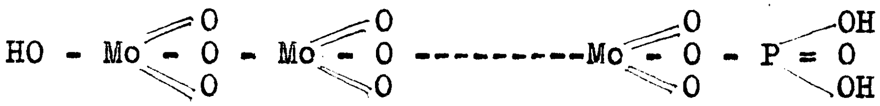
The recognition of heteropoly compounds originates from Marignac's[1] fundamental researches on tungsto-silicic acid in 1862. Berzelius[2] had previously described in 1826 the complete analysis of ammonium molybdo-phosphate. Laurent[3] had noticed that the reactions of ferri-alkali-tungstate, prepared by him (Berzelius) were different from those of the components. In 1846 metatungstic acid was discovered by Margueritte[4]. In 1848, Svanberg and Struve[5] used molybdic acid as a reagent for the analysis of phosphate, and studied ammonium molybdo-phosphate. However, it was assumed at that time by Debray[6], that phosphoric acid only exerted a modifying influence on the molybdic acid, as carbon did on steel, without recognising any definite compound. The corresponding tungsten compound was discovered by von Scheibler[7] in 1872. He represented it as $3H_2O.P_2O_5.24WO_3$ aq. Boro-tungstic acid was discovered by Klein and Mauro[8] in 1880, which was formulated by Copaux[9] as $5R_2O.B_2O_3.22WO_3$ aq. Parmentier[10] isolated molybdo-silicic acid in 1882 as $SiO_2.12MoO_3$aq. The analytical difficulties experienced by the early workers with those compounds resulted in each one having a different formulation for the same compound. Kehrman[11] first established the similarity between $5R_2O.P_2O_5.17WO_3$ and $5R_2O.As_2O_3.17WO_3$. Wolcott Gibbs[12] then greatly extended the systematisation of heteropoly compounds. Friedheim[13] worked on constitutional problems, but it was Kehrman[14] and then Copaux[15] who first produced a really systematic classification of those, by then very numerous compounds, especially of the crystallographic properties. Then came Miolati[16] and Rosenheim's[17] classifications, based on Werner's[18] co-ordination theory.

(iii) Methods of formation:

In general all heteropoly compounds are obtained from aqueous solutions by mixing the components under suitable conditions of hydrogen ion concentration. They are very sensitive towards hydrolysis. Weak complex 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 decomposed by strong alkalis. They are also obtained by heating the normal salt of the acid which supplies the central atom with the anhydride of the co-ordinated acid; e.g. 12-tungstophosphates, $3R_2O.P_2O_512WO_3$ aq. are produced when a boiling solution of alkali phosphate is saturated with WO_3. Similarly, molybdo-vanado-phosphates are produced either by the addition of phosphoric acid to a mixture of alkali vanadate and molybdate solutions, or by warming molybdo-phosphates with V_2O_5 or with vanadates; in fact by any method which allows the component salts to react with one another in acid solution. All of those compounds which are co-ordinated to a maximum may be produced by those methods. The preparation of those belonging to unsaturated series is not so easily brought about. They may sometimes be prepared from solution s containing the theoretical quantities of the components; or alternatively, by decomposition of the fully co-ordinated compounds. As the stability of such compounds is not very great, they are partly broken up in solution with the formation of equilibrium mixtures of the anhydrides. the normal hydrolytic action of water produces sufficient hydroxyl ions to decompose the polyacids, but the addition of alkali hydroxide or carbonate greatly accelerates the reaction.

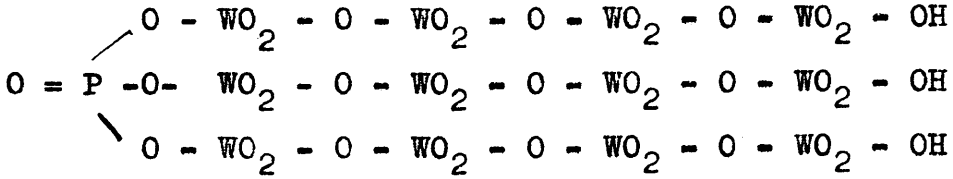
(iv) Rosenheim's theory and formulation of heteropoly compounds:

Among early workers, Fownes and Wurtz[19] assumed that the radicals of heteropoly acids were bound by oxygen atoms as below



Heteropoly acids of different degrees of saturation were simply explained as due to different lengths of Mo, W, etc. chains, and in the case of metatungstic acid by ring formation of WO_3 groups, similarly to the carbon compounds. This chain formation was also supported by the fact that the basicity of the heteropoly acids agreed with tht of their electro-negative constituents. This was later shown to be invalid by the discovery of a series of salts of composition, $5R_2O.X_2O_5.37\substack{WO_3\\ MoO_3}$ and $7R_2O.X_2O_5.22\substack{WO_3\\ MoO_3}$, where X = P or As.

By analogy with the structures of the metal ammines, it was shown that longer chains of this form, by replacement with shorter parts of chains, of number corresponding to the basicity of the metalloid acid, led to such formulations as



At the time these formulations provided quite a lucid systematisation of heteropoly compounds. Miolati then showed that, from conductivity and neutralisation curves, the acids $H_3PO_4(MoO_3)_{12}$ aq. and $H_3PO_4(WO_3)_{12}$ aq., which were at that time assumed to be 3-basic, were at least 6-basic. This provided the basis for the application by Rosenheim of Werner's co-ordination theory to the heterepoly acids.

Comparison of the constitution of numerous heteropoly compounds leads to the conclusion that in a very great number, 12 molecules of an acid anhydride such as WO_3, MoO_3, $^1/2V_2O_5$ is combined with 1 molecule of another acid (irrespective of their basicity) such as $H_3PO_4.(MoO_3)_{12}$ aq. ; $H_3AsO_4.(MoO_3)_{12}$aq. ; $4R_2O.SiO_2.12WO_3$ aq. ; $4Hg_2O.SiO_2.12 MoO_3$; $4R_2O.SnO_2.12MoO_3$aq. ; $7(NH_4)_2O.P_2O_5.12V_2O_5.26H_2O$. In many cases the number is less than 12, but it is never exceeded. As Miolati pointed out, these facts mean the existence of numerous complex ions of the type $(M^nX_6)^{6-n}$, as e.g. the halogen acids, $H_2Pt^{iv}Cl_6$ and $H_2Sn^{iv}Cl_6$; the cyanogen compounds, $H_4Fe^{ii}(CN)_6$, $H_3Fe^{iii}(CN)_6$; the hydroxy acids, $H_2Sn^{iv}(OH)_6$ etc., whose basicity changes with the valency of the central atom. On the basis of the co-ordination theory, all heteropoly acids were classified by Rosenheim as derivatives of an oxygen containing anion of constitution $(X^nO_6)^{12-n}$. These anions besided the more frequent and stable ones like $(X^{n}O_4)^{8-n}$, e.g. $(S^{vi}O_4)^{ii}$, $(P^{v}O_4)^{iii}$, are however only stable in simple acids in a few cases, and mainly in those containing weak electro-nagative and amphoteric central atoms, such as $(I^{vii}O_6)^{v}$, $(Te^{vi}O_6)^{vi}$, $(Pt^{iv}O_6)^{viii}$, $(Pb^{iv}O_6)^{viii}$ and $(Sn^{iv}O_6)^{viii}$. However, anions just as stable and containing strongly electro-negative elements like $(P^{v}O_6)^{vii}$, $(As^{v}O_6)^{vii}$, $(Si^{iv}O_6)^{viii}$, $(B^{iii}O_6)^{ix}$ are obtained if the oxygen atoms are replaced by $(MoO_4)^{ii}$, $(WO_4)^{ii}$ or $(Mo_2O_7)^{ii}$, $(W_2O_7)^{ii}$ and $(V_2O_6)^{ii}$ groups. The table (ii) below shows the heteropoly acids which can be derived from the corresponding simple oxy-acids on this basis.

Table (ii).

Element	Simple oxy-acid	Heteropoly acid
I^{vii}	H_5IO_6	$R_5[I(MoO_4)_6]$; $R_5[I(WO_4)_6]$
Te^{vi}	H_6TeO_6	$R_6[Te(MoO_4)_6]$; $R_6[Te(WO_4)_6]$
P^{v}	H_7PO_6	$R_7[P(Mo_2O_7)_6]$; $R_7[P(W_2O_7)_6]$
Si^{iv}	H_8SiO_6	$R_8[Si(Mo_2O_7)_6]$; $R_8[Si(W_2O_7)_6]$
B^{iii}	H_9BO_6	$R_9[B(W_2O_7)_6]$
Ni^{ii}	$H_{10}NiO_6$	$R_{10}[Ni(W_2O_7)_6]$

Heteropoly acids in which the central atom shows the maximum possible basicity (asabove) were termed by Rosenheim, heteropoly acids of the limiting series. Guanidine salts often show maximum basicity, also are easily crystallisable (not so soluble). This applies also to the silver and mercurous salts.

Copaux included the hypothetical aquo acids, $(H_2O)_6 =$ $H_{10}\left[(H_2O_6)\right]$, e.g. $R_6H_4\left[H_2(W_2O_7)_6\right]$, $R_3H_7\left[(Mo_2O_7)_6\right]$, $R_6H_4\left[H_2(Mo_2O_7)_6\right]$, as in the metatungstates and in the octa- and tetra-molybdates. This explained the crystallographic and chemical similarities between the metatungstates and the heteropoly acids.

For the heteropoly molybdates of 3-valent iron, chromium, aluminium, cobalt and rhodium, of molecular composition, $3R_2O.M_2^{+++}O_3.12WO_3$ aq., Rosenheim postulates 3 possible formulations

$R_3\left[M(Mo_2O_7)_3\right]xH_2O$; $R_3H_6\left[M^{+++}(MoO_4)_6\right](x-3)H_2O$ and $R_3\left[M^{+++}\begin{matrix}(H_2O)_3\\(Mo_2O_7)_3\end{matrix}\right](x-3)H_2O$. He states that estimations of water of crystallisation as well as the preparation of salts of higher basicity than 3, and also the analogy of the 6-tungsto-ferrates, $R_4H_5\left[Fe(WO_4)_6\right]$aq., support the second of those formulations and not the first or the third.A further possible representation he gives as $R_3H_6\left[M^{+++}\begin{matrix}O_3\\(Mo_2O_7)_3\end{matrix}\right](x-3)H_2O$.

Two other groups of compounds are sharply distinguished by chemical and physical properties from those of the saturated limiting series:-

(a) The group of hetero-12-tungstates and molybdates and their analogues. As representatives of this series there are the 12-tungsto-acid-aquo-acids, metatungstic acid, 12-molybdic acid aq.

and the octa- and tetra-molybdates.

(b) The group of 6-hetero-tungstates and molybdates, e.g. 6-tungstic acid aq. and 6-molybdic acid aq., which were previously regarded as paratungstates and paramolybdates. On this basis Rosenheim classified the compounds of molecular formula $5R_2O.12MoO_3.xH_2O$ and $5R_2O.12WO_3.xH_2O$ as $R_5H_5\left[H_2(WO_4)_6\right]\frac{x-7}{2}H_2O$ and $R_5H_5\left[H_2(MoO_4)_6\right]\frac{x-7}{2}H_2O$, respectively. All tungstates of the first of these groups show similar reactions to metatungstic acid. The free acids are easily prepared, stable and extremely crystallisable. The molybdenum compounds are all bright yellow coloured. Of the compounds of the second group, like the paratungstates, they are characterised by the reaction of WO_4 ions. WO_3 is precipitated with mineral acids, the free acids are not stable nor capable of being isolated. The corresponding molybdates have no colour (the MoO_4 ion is colourless).

The strongest and most stable heteropoly acids belong to the saturated limiting series, e.g.

$R_7\left[P(Mo_2O_7)_6\right]$; $R_9\left[B(W_2O_7)_6\right]$; $R_{10}\left[H_2(W_2O_7)_6\right]$; $R_8\left[Si(W_2O_7)_6\right]$

and the following belong to the second group

$R_5R_5\left[I(MoO_4)_6\right]$; $R_9\left[Co(MoO_4)_6\right]$; $R_9\left[Fe(WO_4)_6\right]$; $R_{10}\left[Ni(MoO_4)_6\right]$.

The following tri-heteropoly acids are listed by Rosenheim in which 1 or more of the W_2O_7 or Mo_2O_7 radicals are replaced by V_2O_6 radicals

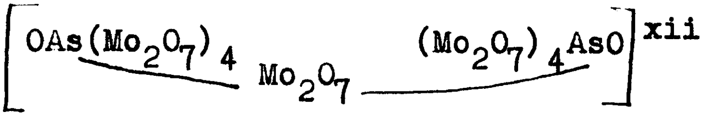
$$K_5H_2\left[\begin{matrix}P(Mo_2O_7)_5\\V_2O_6\end{matrix}\right];\quad (NH_4)_6H\left[\begin{matrix}P(Mo_2O_7)_3\\(V_2O_6)_3\end{matrix}\right];\quad (NH_4)_6H_2\left[\begin{matrix}Si(W_2O_7)_5\\V_2O_6\end{matrix}\right]$$

If the spatial octahedral formulae of the co-ordination theory are allocated to heteropoly compounds numerous isomers are to be expected, for instance there are 3 well crystallised forms of tungsto-silicic acid

$H_8\left[Si(W_2O_7)_6\right]22H_2O$; $H_8\left[Si(W_2O_7)_6\right]28H_2O$ and $H_8\left[Si(W_2O_7)_6\right]20H_2O$. The latter compound Marignac referred to distinctively as iso-12-tungsto-silicic acid.

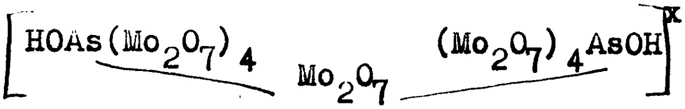
All heteropoly compounds are extremely sensitive towards hydrolysis. High concentration of hydroxyl ions destroys them completely. By careful control of the hydroxyl ion concentration new heteropoly ions can be formed from the more stable ones. Thus the 11, 10 and9 tungstophosphates may be obtained from the 12-tungsto-phosphates. Even the stable heteropoly ions are partly hydrolysed in pure aqueous solution. Those compounds in which the central atom has the highest possible basicity, but in which not all of the co-ordinated oxygen atoms have been replaced by the metal acid radical belong to the unsaturated limiting series, while those whose anion shows a lower basicity are considered unsaturated heteropoly compounds.

To include compounds of such odd series as 1:9 and 1:11 in his classification, Rosenheim had to postulate structures containing bridging groups of W_2O_7 or Mo_2O_7 radicals, such as the following representations he gives of the compound $3R_2O.As_2O_5.18MoO_3$



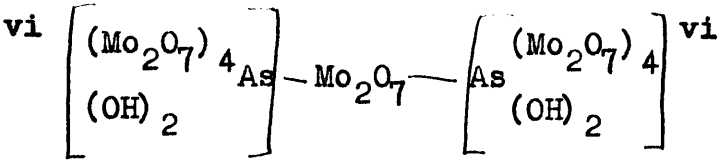
$$\left[OAs(Mo_2O_7)_4 \; Mo_2O_7 \; (Mo_2O_7)_4AsO\right]^{xii}$$

12-basic;



$$\left[HOAs(Mo_2O_7)_4 \; Mo_2O_7 \; (Mo_2O_7)_4AsOH\right]^{x}$$

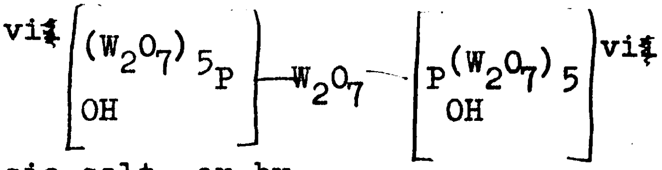
10-basic;



$$^{vi}\left[\begin{matrix}(Mo_2O_7)_4\\(OH)_2\end{matrix}As\right]-Mo_2O_7-\left[As\begin{matrix}(Mo_2O_7)_4\\(OH)_2\end{matrix}\right]^{vi}$$

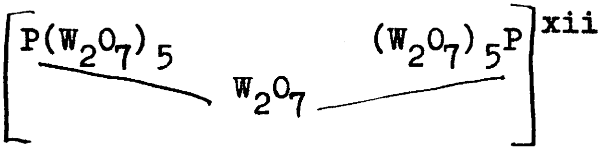
12-basic.

He represents compounds of the series $7R_2O.M^{+++}O_5.22WO_3$ either by Miolati's formula,



$$^{vii}\left[\begin{matrix}(W_2O_7)_5\\OH\end{matrix}P\right]-W_2O_7-\left[P\begin{matrix}(W_2O_7)_5\\OH\end{matrix}\right]^{vii}$$

corresponding to a 7-basic salt, or by



$$\left[P(W_2O_7)_5 \; W_2O_7 \; (W_2O_7)_5P\right]^{xii}$$

, making the salt 6-basic.

(v) More recent theories of heteropoly compounds:

The foregoing treatment of Rosenheim's gives a convincing explanation of the structure of many heteropoly acids, but there is no proof of thee correctness of many of the formulae. The basicity of those acids is not easily determined. The well known yellow ammonium phospho-molybdate was originally given the formula, $(NH_4)_3PO_4.12MoO_3$. This salt, however, always retains some water of crystallisation, and Miolati's determinations of conductivity show that the parent acid is at least 7-basic, having the constitution, $H_7[P(Mo_2O_7)_6]$. Also ammonium phospho-molybdate is an acid salt, i.e. $(NH_4)_3H_4[P(Mo_2O_7)_6]aq$. Guanidine phospho-molybdate is also 7-basic, $(CN_3H_6)_7[P(Mo_2O_7)_6]9H_2O$, and Rosenheim prepared the 7-basic silver and mercurous salts. Salts in which the whole of the available hydrogen atoms are replaced are exceptional. The guanidine salts are regarded as anomalous ammonium salts. Rosenheim's structures agree in general with the fact that most of the heteropoly salts are acid salts.

However, the theories of Rosenheim are essentially hypothetical and with very little experimental foundation. In particular, the important 12-acids are based on the assumption of $Mo_2O_7^{--}$ and $W_2O_7^{--}$ groups, wheras there is no evidence as to the existence of such ions, apart from the analogy of the dichromates. Moreover the observed basicities of the acids, the amounts of constitutional water found and the revised formulation of the poly-vanadates and similar complexes, based on the work of Jander[20], cannot be reconciled with those structures. Most of the work done since Rosenheim's time has taken the form of studies of aggregation and degradation processes leading to poly-acid formation, and the application of stereo-chemical and structural principles, which have been derived from crystallographic data. Unfortunately, these two different approaches lead to entirely different results.

Jander's study of the aggragation and degradation processes are based on the determination of ionic weights of the species involved, by measurement of the rate of diffusion of the relevant ion in the presence of a large excess of an inert electrolyte, usually sodium nitrate. The observed diffusion co-efficient, D, is then related to the molecular or ionic weight, M, by an expression $Dz\sqrt{M}$ = constant, where z is the specific viscosity, i.e. $z = \frac{\text{viscosity of solution}}{\text{viscosity of water}}$. Brintzinger[21], by measurement of the rates of electro-dialysis of ions has determined the ionic weights of the constituents of tungstate and molybdate solutions, which agree with those of Jander. From such measurements Jander concluded that heteropoly acids are actually only molecular complexes of Mo_6, W_6 and V_8 poly-acids with the parent acid. He thus represents the 12-phosphomolybdates as $R_7\begin{bmatrix} H_3Mo_6O_{21} \\ H_2PO_4 \\ H_3Mo_6O_{21} \end{bmatrix}$ aq. This view, however, is not compatible with other evidence as to the stable and compact poly-acid anions of molybdenum and tungsten.

A different conception of poly-acids was suggested by Pfeiffer[22]. He suggested that complexes of high co-ordination number might be built about a central polyatomic ion, rather than about a central atom. Assuming the hypothetical formulation of Rosenheim, $H_{12-n}(XO_6)$, Pfeiffer conceived that WO_3

or MoO_3 radicals might be co-ordinated about the (XO_6) ion, giving for example, $H_7\left[PO_6(WO_3)_{12}\right]$. The later stereo-chemical conceptions arising from X-ray investigations have actually proceeded along those lines.

Linus Pauling[23] calculated, that from a steric point of view, a configuration is possible in which the double molecule is not introduced. In the complex compounds which contain 12 MoO_4 orWO_4 groups distorted octahedra are formed by 12 of the oxygen atoms occupying the corners. The other 36 atoms, which are not joined together either carry a negative charge or have a hydrogen atom attached to them. The neutral structures thus formed are stabilised by a central group, as RO_4^{---}, in which R may be either H_2^{++}, B^{+++}, Si^{++++}, P^{+++++} or As^{+++++}. The formulae thus arrived at are as follows

$H_6\left[H_2O_4\cdot W_{12}O_{18}\cdot(OH)_{36}\right]$; $H_5\left[BO_4\cdot W_{12}O_{18}(OH)_{36}\right]$;
$H_4\left[SiO_4\cdot W_{12}O_{18}\cdot(OH)_{36}\right]$; $H_3\left[PO_4\cdot W_{12}O_{18}\cdot(OH)_{36}\right]$. Although in some ways superior to the fotmulations of Rosenheim, in that they utilise the maximum basicity in agreemant with experimental observations, and the known high content of water, it would follow from these formulae that no acid or salt should contain less than 18 molecules of constitutional water. This is not in accordance with the experimental facts. Thus, Scroggie and Clark[24], found that 12-tungsto-silicic acid, dried

at 100°C, contained 8 molecules of water, including the 4 ionisable hydrogen atoms, so that the total formula is $H_{16}[SiW_{12}O_{46}]$. 6 of these molecules of water can be removed by dehydration without breaking up the anion giving the product, $H_4[SiW_{12}O_{40}]$, which must be regarded as the anhydrous acid. This form of anion, $RM_{12}O_{40}$, seems to be the lowest form obtainable on dehydrating the 12-acids generally. It is present in all of the 12-acids which are obtainable in the anhydrous state, e.g. $K_3[PW_{12}O_{40}]$; $K_3[PMo_{12}O_{40}]$; $(NH_4)_3H[TiMo_{12}O_{40}]$; $Tl_3H[SiW_{12}O_{40}]$ and $(NH_4)_3[AsW_{12}O_{40}]$. The existence of this form of anion invalidates the formulae of both Rosenheim and Pauling.

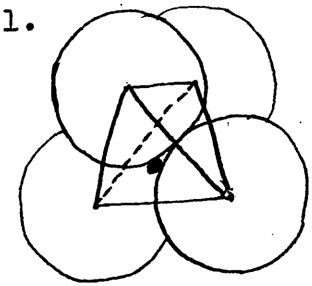
Another theoretical attempt at an explanation of the structure of heteropoly compounds was proposed by Riesenfeld and Tobiank[25]. This was based purely on the geometrical arrangement of tetrahedral and octahedral groups, XO_4 and XO_6, respectively. This classification of Riesenfeld's actually justifies Rosenheim's original formulations, at the same time offering a simple explanation of previously unexplainable facts, such as the existence of compounds of 2 different valency states of the same acid, e.g. the 4 and 8-basic salts of tungstosilicic acid. However, this paper of Riesenfeld and Tobiank's seems to have been generally ignored.

Hoard[26] and Keggin[27] have shown by X-ray analysis that the 12-heteropoly acids have structures typified by $H_3[PO_4(W_{12}O_{36})]$ and containing 5 molecules of water of crystallisation, and that the complex anion is approximately spherical, and in which the phosphorus atom is at the centre surrounded tetrahedrally by 4 oxygen atoms. Each of these 4 is common to groups of 3 octahedra. At the centre of each octahedron is a tungsten atom (i.e. 12 WO_6 groups altogether). In each WO_6 group i oxygen atom is shared with the phosphorus, 2 are shared with tungsten atoms in other groups, and 1 is unshared. A diagrammatical representation of the structure of the anion of the 12-acids, with special reference to tungsto-phosphoric acid, as determined by Keggin, is shown on page (xxiii). Signer and Gros[28] showed that this structure was also present in the hydrated forms of $H_5[BO_4(W_3O_9)_4]$; $H_4[SiO_4(W_3O_9)_4]$; and in metatungstic acid, $H_6[H_2O_4(W_3O_9)_4]$. Illingworth and Keggin[29] arrived at analogous structures for

$H_3[PMo_{12}O_{40}]$; $H_4[MnMo_{12}O_{40}]$; $H_3[AsW_{12}O_{40}]$; $H_3[AsMo_{12}O_{40}]$; $H_4[SiMo_{12}O_{40}]$; $H_4[TiMo_{12}O_{40}]$; $H_4[GeW_{12}O_{40}]$.

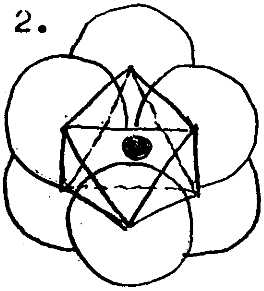
J.S.Anderson[30] has suggested a structure for 6-heteropoly acids and the related para-molybdates and para-tungstates, in which 6 MoO_6 octahedra are arranged in a hexagonal ring, Mo_6O_{24}, by each sharing 2 corners of neighbouring octahedra. The central space thus left is of the same ahape as the MoO_6 octahedra and

1.



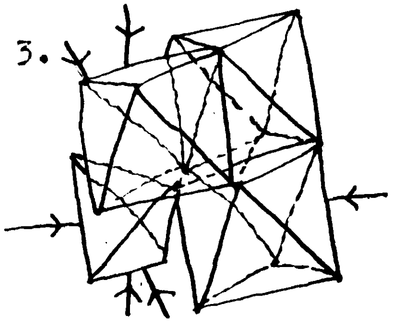
PO_4 tetrahedron.

2.



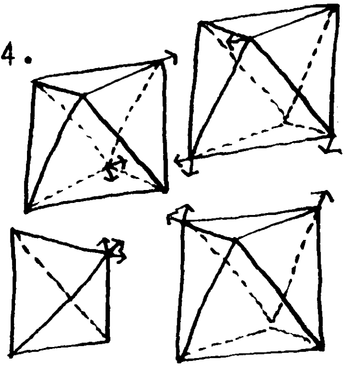
WO_6 octahedron.

3.



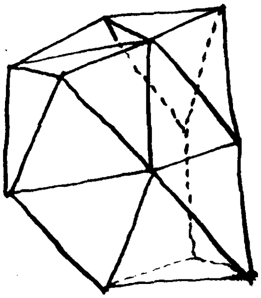
WO_6 octahedron relative to PO_4 tetrahedron.

4.



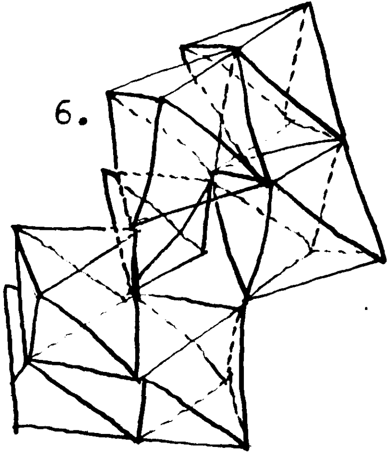
Exploded diagram of 3.

5.



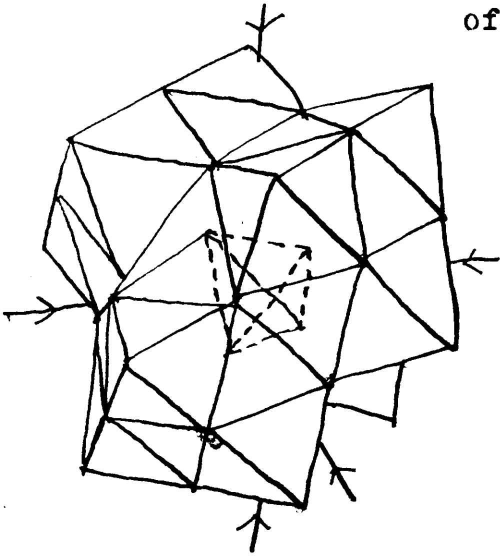
Simplified arrangement of 3.

6.



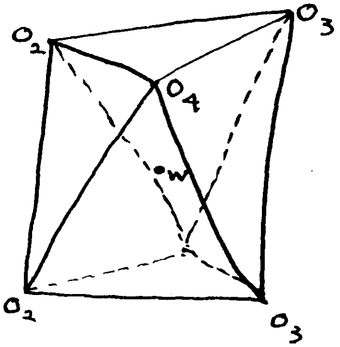
2 groups of 3 WO_6 octahedra relative to central PO_4 tetrahedron.

7.



Complete anion, $PW_{12}O_{40}^{---}$.

8.



4 types of oxygen atoms in each WO_6 octahedron:-

O_1 atoms, shared with 3 WO_6 octahedra and 1 PO_4 tetrahedron.

O_2,O_3 atoms, shared with 2 WO_6 octahedra.

O_4 atoms are unshared.

accomodates a 6-co-ordinated cation. This gives the paramolybdate structure, $R_6\left[Mo(Mo_6O_{24})\right]$, corresponding to the 6-molybdo-periodate, $R_5\left[I(Mo_6O_{24})\right]$. J.H.Sturtevant[31] has shown that ammonium paramolybdate is correctly formulated as $(NH_4)_6Mo_7O_{24}.4H_2O$.

(vi) Basicity of hateropoly acids:

In the isomorphous series of 12-acids, $H_3PW_{12}O_{40}$. $H_4SiW_{12}O_{40}$, $H_5BW_{12}O_{40}$, $H_6\left[H_2W_{12}O_{40}\right]$, there are respectively 3, 4, 5, 6, hydrogen atoms which would be expected to be replaceable by metal ions in their salts. According to recent X-ray investigations the smaller alkali metals form salts with large numbers of molecules of water of crystallisation, e.g. $Li_2H_2SiW_{12}O_{40}.26H_2O$, $Li_3HSiW_{12}O_{40}.24H_2O$, but caesium apparently forms only the salt $Cs_3HSiW_{12}O_{40}.0$ or $2H_2O$, no matter what proportions of caesium salt and acid are mixed. The other acids $H_5BW_{12}O_{40}$, $H_3PW_{12}O_{40}$ and $H_6\left[H_2W_{12}O_{40}\right]$ all give similar tricaesium salts, in spite of their different apparent basicities. It would therefore appear that the primary consideration in determining the basicity of those compounds is the packing of large complex ions, rather than the number of hydrogen atoms in the acid. The basicity of heteropoly acids is usually deduced from theoretical considerations, and from an examination of the salts of that particular acid, especially of the guanidine and silver salts, which usually show the maximum basicity.

(vii) Unsaturated heteropoly acids:

For all the other unsaturated heteropoly acids, where the ratio of the number of atoms of the central element to the number of tungsten or molybdenum atoms is 8, 8½, 9, 10, 10½ and 11 no definite information is available as to their structure. Pauling has suggested that those may result from the combination of 2 or more 12-anions, and he derived formulae such as $\left[(PO_4)_2W_{18}O_{31}(OH)_{48}\right]^{6-}$. Such formulae are however now unacceptable according to what has been decided for the 12-acids. Probably many of the unsaturated heteropoly compounds described so far are not definite compounds. They are however quite as well defined as the different series of salt hydrates. Completely or partial isomorphous mixtures of definite compounds are perhaps present. It is probable that only the maximum co-ordinated compounds are true chemical individuals, in the sense that they obey the Law of Constant Proportions, and that the free inter-atomic space of the unsaturated substance is filled up to a varying degree by MoO_3 or WO_3 groups. Thus it is only in the case of the 12-acids that any definite structure has been arrived at, and to a less certain extent for the

6-acids. For the intermediate unsaturated series very little new information has been made available in the last 25 years.

(viii) General properties of heteropoly compounds:

The specific chemical and physical properties of heteropoly compounds is due to the complex anion. They are characterised as a group by the very large molecular weight of their anions, and the high basicity of the acids. All heteropoly compounds, especially the free acids of the saturated limiting series and their salts show an extraordinary tendency to crystallise. This was early recognised as a constitutive property od such compounds. The crystallographic isomorphism was also well known. The free heteropoly acids of the limiting series crystallise in 2 isomorphous series of hydrates, which form a continuous series of mixed crystals with one another.

Some heteropoly compounds are optically active, e.g. the crystalline potassium salts of meta-tungstic, boro-tungstic, silico-tungstic and also 12-silico-molybdic acids rotate the plane of polarisation of light and crystallise in 2 enantiotropic forms, which are not distinguished so much by their solubility as by their speed of solution.

All strong complex heteropoly acids, especially those of the limiting series, and many of their salts are characterised by their high solubility. Most free acids form syrupy solutions of high specific gravity in about 1/5 of their equivalent weight of water. Exact solubility data, especially solubility curves are not recorded in the literature. They are also extremely soluble inalcohol and often more soluble than in water; in fact in any hydroxy compound. An aqueous solution of 12-tungstophosphoric acid can be completely extracted, for instance, by simply shaking with amyl alcohol. With ether, even ether vapour the acid crystals quickly melt to a heavy oil, with the developement of an appreciable amount of heat. Observation of this ability of the free acids to liquefy and dissolve so readily in ether led Drechsel[32] to propose a very convenient method of preparation of the free acids from their salts. If a dilute solution of the sodium salt of a heteropoly acid is shaken with ether and hydrochloric acid or 30 - 40% sulphuric acid, an emulsion is formed which gradually separates into 3 layers composed of the ether addition compound, water and ether.

The conditions of equilibrium in heteropoly acid solutions is exceedingly complicated. The aqueous equilibra are dependent not only on the electrolytic dissociation of the highly basic acids and salts, but also on the hydrolytic dissociation of the complex anion. There are also to be taken into account a great number of different ions and molecules in solution. Few researches on the equilibria pertaining in heteropoly acid solutions have been undertaken, as the corresponding work in the simpler cases of the poly-molybdates and poly-vanadates had shown great difficulty.

As the heteropoly compounds originate in hydrogen ion containing solutions of their components, they are stable to hydrogen ions but unstable to hydroxyl ions, which split them into their components. They are stronger acids than their constituent acids and enter into salt formation with nitrates and chlorides. They also form with nitrates characteristic double salts. The alkaline and alkaline earth salts are generally easily soluble in water, the solubility increasing in the order caesium, rubidium, potassium, sodium and lithium, from the ammonium salts, which are often very soluble. The heavy metal salts, particularly the silver and mercurous compounds are almost insoluble. They generally form at first amorphous precipitates, which on long standing in solution slowly become crystalline.

Especially characteristic of true heteropoly compounds is their ability to precipitate albumin, which reaction is used in physiological chemistry. This colloid precipitation is apparently caused by the semi-colloid nature of the heteropoly acids. This reaction is so sensitive that it can be applied to the comparison of the speed of formation of analogous heteropoly ions. In this way it has been shown that the speed of formation of heteropoly tungstates is greater than that of heteropoly molybdates and increases in the order silicon, phosphorus, arsenic and boron. As with albumin, organic nitrogen compounds like proteins, ureides, aliphatic and aromatic amines precipitate with heteropoly acids. By this method also, 1 part of quinine in 600,000 parts can be detected. Characteristic precipitates are also formed with the cobalt and chromium ammines.

(ix) Heteropoly compounds of Al^{+++}, Cr^{+++}, Mn^{+++}, Fe^{+++}, Co^{+++} and Rh^{+++}.

These 3-valent metals with amphoteric properties form a number of heteropoly compounds with both molybdates and tungstates. In order to include them in his classification, Rosenheim assumed they were salts of the hypothetical 9-basic acids $H_9\left[M^{+++}(XO_4)_6\right]$, where M may be 3-valent aluminium, chromium, mangnaese, iron, cobalt or rhodium, and X may be tungsten or molybdenum, thus corresponding to tungsto-boric acid, $H_9\left[B(W_2O_7)_6\right]$ in his scheme.

A.Struve[33] prepared molybdo-aluminates, chromates and ferrates by reacting solutions of ammonium or potassium paramolybdate with solutions of the sulphates of aluminium, iron and chromium. The amorphous precipitates which first form, gradually crystallise as rectangular plates. Rosenheim describes the aluminates and ferrates as colourless, and the chromates as bright red coloured, and from estimations of the water of constitution he concludes that they are 3-basic salts of a 9-basic acid, $R_3H_6\left[M^{+++}(MoO_4)_6\right]7H_2O$. He also prepared the 4-basic guanidine and barium salts, $(CN_3H_5)_4H_5\left[Cr(MoO_4)_6\right]6H_2O$ and $Ba_2H_5\left[Cr(MoO_4)_6\right]5H_2O$ respectively, by double decomposition between a solution of sodium 6-molybdo-chromate and guanidine hydrochloride and barium chloride. The aluminates and chromates are described as being stable against hydrolysis in aqueous solution, while the ferrates are slightly hydrolysed.

Friedheim[34] prepared 6-molybdo-cobaltates by oxidation with hydrogen peroxide or persulphate of mixed solutions of paramolybdate and cobolt salts. They are deep green coloured salts corresponding in composition to $R_3H_6\left[Co(MoO_4)_6\right]7H_2O$, where R may be ammonium or potassium. Barbieri[35] obtained the corresponding 6-molybdo-rhodates as yellow plates of composition, $R_3H_6\left[Rh(MoO_4)_6\right]7H_2O$, by double decomposition between paramolybdates and rhodium chloride.

According to Rosenheim, the existence of molybdo-manganates is very doubtful; they apparently form compounds containing 4-valent manganese only. A series of molybdo-manganates were prepared by Friedheim[36] by saturating alkali para-molybdate solutions with freshly precipitated manganese hydroxide; also by the interaction of oxidising agents like hydrogen peroxide , alkali persulphate or alkaline permenganate on mixed solutions of alkali molybdates and manganese salts; and by careful reduction of mixed solutions of alkali molybdate and alkaline permanganate with sulphur dioxide. By these means deep, purple solutions were obtained, from which very beautifully crystalline red salts separated. These included the sodium, potassium and ammonium salts and certain double salts. Friedheim assumed that only 4-valent manganese was contained in those compounds, but that a few contained manganese of a lower valency of which part functioned as a 2-valent cation. This led him to believe that the central atom in such heteropoly manganates was 4-valent, and that in the remainder the composition was variable and that the reproducable preparation os such compounds was not always possible. Compounds of the following composition were listed by Friedheim

$2R_2O.MnO_2.7MoO_3.xH_2O$; $3R_2O.MnO_2.10MoO_3.xH_2O$;
$3R_2O.MnO_2.8MoO_3.xH_2O$; $4R_2O.MnO_2.10MoO_3.xH_2O$;
3R $3R_2O.MnO_2.9MoO_3.xH_2O$; $4R_2O.MnO_2.11MoO_3.xH_2O$;

where R may be sodium, potassium or ammonium.

According to Rosenheim, the most stable of the salts of the 12-molybdo-manganates are those in the anion of which 8 or 9

MoO_4 radicals are combined with 1 manganese atom.

6-tungsto-ferrates are described as having been prepared by Laurent[37] and by Rosenheim and Schwer[38] by reacting on a boiling solution of sodium paratungstate with ferric chloride solution. The precipitate which is first formed redissolves and from the colourless solution ammonium chloride, potassium chloride and guanidine hydrochloride precipitate bright yellow, micro-crystalline material of composition represented by Rosenheim as $R_4H_5[Fe(WO_4)_6]xH_2O$, where R = NH_4, K, or CN_3H_5 (guanidine).

Rogers and Smith[39] by long boiling of ammonium paratungstate solution with freshly precipitated Mn_2O_3 obtained a red solution from which $(NH_4)_4H_5[Mn(WO_4)_6]9H_2O$ crystallised in dark red octahedra.

Rosenheim considers that any tungsto-aluminates which have been described in the literature are not definite compounds at all. Such compounds listed in Gmelin's Handbuch are $3(NH_4)_2O.Al_2O_3.9WO_3.4H_2O$; $8BaO.Al_2O_3.9WO_3.7H_2O$; $5Hg_2O.Al_2O_3.9WO_3$; $ZnO.Al_2O_3.9WO_3.20H_2O$; $CuO.Al_2O_3.9WO_3.16\frac{1}{2}H_2O$. They are variously described as semi-transparent, amorphous or micro-crystalline. All of those compounds are described by Daniels[40] as having been prepared by double decomposition from the ammonium salt above prepared by Balke and Smith[41], and solutions of the appropriate metallic ions. The formation of complex compounds between WO_3 and chromic acid was first mentioned by Klein[42] and the possibility of the existence of compounds of the type $M_2O.xM_2^{+++}O_3.yWO_3$ was assumed by Balke and Smith. Previously complex tungsto-chromates were stated to be formed by heating paratungstates with salts of 3-valent chromium, by von Knorre[43] and Kautschew[44]. However, they are all described as having been prepared from aqueous solutions of the components by crystallisation, and Rosenheim believed that the free acids containing those metals were incapable of isolation. Being thus obtained the composition of such compounds must remain doubtful, as due to the complicated conditions of equilibria which exist in such solutions, the crystallisable product will be quite variable. There cannot be such doubt about the homogeneity or chemical individuality of salts formed directly from the free acids and capable of being recrystallised from water.

DrJ.A.Mair[45] has prepared and isolated the free tungsto-ferric and tungsto-coboltic acids, and this work deals with the acids which contain 3-valent aluminium, chromium and manganese as the central atom of the complex heteropoly anions.

3. THE FREE ACIDS.

(i) General:

These 3 acids, tungsto-aluminic, tungsto-chromic and tungsto-manganic acids,eachcontaining a 3-valent central atom would be expected to be formed under fairly similar conditions, However, as only in the case of aluminium is this the normal, stable valency of the metal, the conditions under which their formation occurs are slightly different. The basis of their method of preparation is the saturation of a boiling solution of alkali paratungstate with a freshly precipitated hydroxide of the appropriate metallic ion. As the hydroxides of those metals themselves age very rapidly on standing, and soon become quite inactive, steps have to be taken to ensure that the hydroxide is actually precipitated in situ in the body of the boiling solution of alkali paratungstate. Addition of the freshly prepared hydroxides to the paratungstates solutions results merely in the precipitation of the metal paratungstates without, or at any rate with very little, heteropoly acid formation. An easily hydrolysable salt of the metal is best used, preferably the nitrate. The chlorides are to be avoided due to the possibility of extraction of the metal chlorides in the subsequent ether extraction in 6N sulphuric acid solution. As a result of e perimental observations on the preparation of tungsto-ferric acid by J.A.Mair[45] , it was decided that theoretically, probably the most complete saturation is brought about by adding only sufficient of the appropriate metallic salt, as would produce the requisite amount of mineral acid on hydrolysis to convert all of the paratungstate present to metatungstate. One of the deciding factors as to whether or not any particular element may be induced to act as the central atom in a heteropoly tungstate would appear to be the solubility of its paratungstate. This can only be a determining factor, however, where the paratungstate is so insoluble that the hydrolytic action never gets started. This hydrolytic action inturn, can only take place for metals whose hydroxides are precipitated in solutions of pH values 6 - 7, the pH of the boiling paratungstate (sodium) being about 6.4. Aqueous paratungstate solutions rise in pH on boiling and the increased alkalinity persists on cooling. It has been suggested by von Knorre[46] that this change is due to the hydrolytic fission of the paratungstate into normal tungstate and netatungstate, the increase in pH being due to the normal tungstate (pH about 10)

$$3(3Na_2O.7WO_3) = 5Na_2WO_4 + 4(Na_2O.4WO_3).$$

The hydroxides of the trivalent metals, aluminium, chromium and manganese are certainly precipitated at pH 6 - 7. The mechanism of the reaction seems to be that partial hydrolysis of the of the metal salt added gives rise to a transient precipitate of a tungstate more acid than the metal paratungstate (probably a pentatungstate). This immediately reacts with the alkali paratungstate, finally giving rise to the alkali salt of the heteropoly acid, in the same way that tungstic acid added to boiling sodium paratungstate forms sodium metatungstate.

The facility with which aluminium, chromium and manganese enter into heteropoly complex formation with the alkali paratungstate, and the means of ensuring that the hydroxides are precipitated actually within the boiling solution are rather different in each case. Also the amount of insoluble material which separates during the course of the saturation. This latter is least and the best yields of the free acids obtained when the saturation is allowed to take place over a fairly long time (20 - 24 hours). The final pH of those saturated solutions is also of some importance, and if not sufficiently acid, excess mineral acid must be added, to bring the hydrogen ion concentration down to pH 3 - 3.4. For tungsto-aluminic acid, aluminium nitrate (9-hydrate) was used as a saturating agent; for the acid containing 3-valent chromium, chromium nitrate (9-hydrate); and for tungsto-manganic acid, potassium manganicyanide, $K_3Mn(CN)_6$, or a solid mixture of manganous sulphate and potassium persulphate. The tungsto-chromic acid is especially slow to form, presumably due to the fact that chromium paratungstate is so insoluble, and probably also due to some extent to the exceptional stability of the hexa-hydrated chromium ion, $[Cr(H_2O)_6]^{---}$. In all cases a transient precipitate is first formed which subsequently redissolves on stirring. On completion of the saturation the free acids may be extracted by acidifying the solution and shaking or stirring with excess ether. The heavy, oily ether addition compound thus formed may be readily separated and further washed with more ether. This ether addition compound is colourless in the case of tungsto-aluminic acid, green in the case of tungsto-chromic acid and deep red in the acid containing manganese. The extraction with ether may only safely be carried out, provided the pH of the solution to be extracted is between 3 and 3.4. If it is attempted to extract solutions of appreciably higher pH value than this very bad emulsification is liable to occur. These emulsions are sometimes stable for periods as long as a month or more. With the chromium compound it is essential that a good excess of mineral acid is used in order to precipitate any residual tungstates as WO_3, which would otherwise be decomposed during the subsequent extraction process, to form a particularly atable emulsion. Emulsification actually occurs in all cases, but normally if the pH values are correctly adjusted at the extraction stage separation takes place rapidly. Separation of the ether addition compound from such aqueous solutions takes place only at the interface of the free ether and the aqueous layer, none separating from the body of the solution. Thus no ether addition compound will separate until some of the excess ether has layered out on top.

The initial stages of the saturation appear to be the most critical. If the metal salt solution is added too quickly, precipitation occurs and solution of this precipitated material does not readily take place. In those cases no heteropoly compound could be subsequently extracted with ether. It is essential that the first 100 ml. or so of the metal salt solution should be added very slowly to the vigorously boiling paratungstate solution with thorough and continuous stirring. Once the reaction gets started it goes quite smoothly to completion.

The free acids are obtained from the ether addition compounds by running them into excess water and removing the ether by blowing air through the solution, which is then concentrated down repeatedly to small bulk on a water bath until the separation of tungstic acid becomes slow. Any tungstic acid which separates is filtered off at intervals, and the solution finally evaporated down to dryness, before heating at 130°C for some time until any residual metatungstic acid (which is also extracted with ether) is decomposed. The thermal stability of metatungstic acid is quite low (Sobolev[47]). On redissolving the residue in water and concentrating in vacuuo overconcentrated sulphuric acid, the free acids crystallise out. Tungsto-aluminic acid and tungsto-chromic acid separate respectively as white and green micro-crystalline powders. The free tungsto-manganic acid is too easily hydrolysable to withstand this treatment and so has only been obtained in the form of its concentrated aqueous solutions.

No heteropoly compound could be extracted from sodium paratungstate solutions saturated with bismuth oxy-nitrate, so presumably 3-valent bismuth does not act as a central atom in heteropoly complex formation.

(ii) Ether addition compounds of the free acids:

Although this ability of the heteropoly acids as distinct from their salts, to form liquid addition compounds with ether has long been recognised as a specific property of such compounds, little use has previously been made of this fact in attempts to isolate the free acids. The remarkable solubility of crystals of free heteropoly acids in ether was first observed by Marignac[48], and first proposed as a convenient method of isolation of heteropoly acids by Drechsel[31]. Even with ether vapour, if crystals of the free acids are stored over ether for instance, crystals quickly melt to a heavy oil, with the developement of an appreciable amount of heat. These ether addition compounds are generally regarded as loosely bound compounds of the oxonium type, but no precise information is available as to their structure or actual constitution. They are generally dense oils of high vapour pressure and do not lose all of their ether readily by evaporation. These ether addition compounds separate more readily from their aqueous solutions the greater the stability of the acid and its resistance to hydrolysis. Crystals of the free acids reform the ether addition compounds on allowing ether to come in contact with them, and this affords probably one of the best methods of purifying heteropoly acids. This process is evidently dependent on the degree of hydration of the acid crystals. Solutions of the free acids in ether becomes successively slower as the acids are dehydrated at higher temperatures, until at about 160°C, provided the acid has suffered no decomposition before reaching this temperature, it is doubtful if the addition compound is refirmed. It is, however, difficult to decide when this stage has been reached, as the dehydrated acid may absorb sufficient moisture from the ether (which in turn absorbs moisture from the atmosphere) to a sufficient degree of hydration to allow reformation of the ether addition compound. As the process of resolution in ether becomes so slow at temperatures much above 110°C, this is quite possible.

The ether addition compounds are miscible with alcohol to the extent of about 1/2 of their volume and the free acids may be separated from their alcoholic solutions by the use of ether. They may be diluted with water in the proportion of 1:1 (by volume) without noticeably altering their homogeneity. With a larger quantity of water, the excess floats off, and then with temporary emulsification and quite a fall in temperature, separation of free ether on top of the aqueous solution of the acid results. They may similarly be diluted or thinned with more ether, or the ether drawn off by raising the temperature, until with a large amount, the excess ether forms a separate layer. The hydrolysis of heteropoly acids which is connected with an increase in the hydrogen ion concentration, is suppressed by the addition of strong mineral acid, thus leading to a corresponding increase in the amount of the ether addition compound which may be extracted from aqueous solutions of the acid. Thus, heteropoly acids do not form a simple solution in ether. This fact is supported by the unusual developement of heat with ether as a solvent, and the fact observed by Asch[49] that the osmotic pressure of the ether is lowered by the addition of acid. It has been suggested by von Baeyer[50] that it is a type of oxonium salt with ether. Vapour pressure measurements are not successful in ascertaining the true nature of this oxonium compound, whose origin is explained by the assumption of the 4-valency of the oxygen atom in ether. Only heteropoly acids containing water of crystallisation form ether addition compounds; heteropoly salts do not.

The ether addition compounds of the acids are coloured similarly to their aqueous solutions; green in the case of tungsto-chromic acid, very deep red with tungsto-manganic acid and colourless or slightly yellow with tungsto-aluminic acid. Some metatungstic acid is always extracted and present in the ether solution, so thst it is not possible to crystallise the free acids directly from solutions of their ether addition compounds. They are quite stable for long periods and lose ether very slowly by evaporation. On concentration, tungstic acid separates with more or less complete decomposition of the heteropoly acids.

(iii) Tungsto-aluminic acid, $H_{10}\left[Al_2W_{22}O_{74}\right]44H_2O$.

For the preparation of tungsto-aluminic acid, 56.12 gms. of sodium tungstate, $Na_2WO_4.2H_2O$, are dissolved in about 500 ml. of water and converted to sodium paratungstate, $3Na_2O.7WO_3$, by the addition of 194.4 ml. of N nitric acid in the cold. This solution is heated to boiling in a beaker provided with a mechanical stirrer, and while it is kept boiling, a solution containing 8 gms. of aluminium nitrate, $Al(NO_3)_3.9H_2O$ (slight excess over the theoretical amount) dissolved in 500 ml. of water is run in very slowly from a dropping funnel during the course of about 20 - 24 hours (i.e. at the rate of about 3 drops per minute), and the boiling paratungstate solution kept well stirred throughout this time. Loss by evaporation is made good by the occasional addition of water, keeping the volume constant at about 800 ml. Theoretically, to convert the sodium paratungstate ($3Na_2O.7WO_3$) obtained from 25 gms. of sodium tungstate to sodium metatungstate ($Na_2O.4WO_3$), requires 30.38 ml. of N acid, which is equivalent to 3.797 gms. of aluminium nitrate (9-hydrate). As each drop of aluminium nitrate solution falls into the paratungstate solution, a transient white precipitate is formed which almost immediately redissolves. This continues throughout the saturation, the precipitate formed taking successively longer to redissolve, the more aluminium nitrate there is added, until near the end of the saturation precipitation becomes permanent, When all of the aluminium nitrate solution has been added, the solution is evaporated down to about 150 ml., cooled and allowed to stand overnight at 4°C, to enable any residual sodium paratungstate to separate out. No adjustment in the pH of the saturated solution is necessary in this case. On filtering, the solution is cooled with ice and 400 ml. of dry ether is run in slowly from a dropping funnel with constant stirring. When this is completed, 400 ml. of 12N sulphuric acid (i.e. sufficient to give a final concentration of roughly 6N) is added during about 1/2 an hour and stirring continued for a further 15 minutes. On pouring the ether-sulphuric acid mixture into a separating funnel and allowing to settle, 3 layers form; excess ether on top of an aqueous layer and the heavy, oily ether addition compound below. If emulsification has occured and the ether addition compound does not separate out almost immediately, it may be necessary to allow the solution to satnd for a few days. Separation will take place in time, even in the case of bad emulsification, although the time required for this to happen may be excessive. The ether addition compound is usually slightly turbid on first separating, but by being further washed by running into 2 or 3 successive portions of dry ether becomes quite clear. 2 such additional washes are usually sufficient. Tungstic acid separates from the aqueous layer on standing and this may be recovered by acidifying further with sulphuric acid, concentrating down to about 1/2 bulk and filtering off. The ether addition compound is finally run into about 1/2 its own volume of water and the ether removed by evaporation on a water bath or hot plate, or by blowing a stream of air through the solution, before evaporating down to small volume. During this stage some yellow tungstic acid separates. This is filtered off and the solution evaporated down to small bulk repeatedly on a water bath until the separation of tungstic acid becomes slow. This is filtered off at intervals. On successive evaporations less tungstic acid separates each time. This indicates that most of the metatungstic acid (some of which is always extracted with the tungsto-aluminic acid) is practically all decomposed. To ensure that it is removed entirely, the residue, after being taken completely down to dryness is heated at 130°C for about 12 hours, then redissolved in water and filtered. The resulting clear solution is then carefully evaporated down in vacuuo over concentrated sulphuric acid until crystallisation takes place.

About 25 - 30 ml. of the ether addition compound are obtained using the above quantities of material. From this 50 - 70 gms. of the free acid could be recovered. It was not found practicable to use larger quantities of the starting material, as even when using twice the above amounts the yields were practically the same. It appears that in those cases more of the paratungstate is converted to metatungstate and more insoluble material precipitates during the saturation.

Free tungsto-aluminic acid is found to separate from its solutions as a white, micro-crystalline powder and from more concentrated solutions as white, silky rosettes, which when removed from their mother liquors quickly effloresce and break down to the same white powder. Large crystals of the acid can only be grown with difficulty due to its extreme solubility (about 100 gms. can be dissolved in about 5 - 8 ml. of water). From very concentrated solutions hexagonal outlines of crystals appear, but those are quickly overgrown with smaller crystals. Aqueous solutions of the acid are quite stable and of very high specific gravity (approximately 2.85) and these solutions can be greatly supersaturated without any crystallisation occuring. The specific gravity of the ether addition compound is even higher (2.92).

Being a fairly strong acid (the pH of an M/500 solution is 1.55), it decomposes bicarbonates, barium and ammonium carbonates and reacts acidic to the usual acid-base indicators. On neutralising solutions of the free acid to brom-cresol green (pH 3.6 - 5.2), the complex anion is apparently broken down and the aluminium precipitates as hydroxide, which titrates further against the strong alkali. On the basis of these titrations of approximately M/500 solutions of the acid against N/10 sodium hydroxide using brom-cresol green as indicator, and also detecting the end point of the neutralisation by potentiometric methods (cf. page (lv)), the basicity of the free acid would appear to be 10 (certainly nearer to 10 than to 9). This is in agreement with the analysis of the various tungsto-aluminates which have been prepared.

The analysis of this compound is comparatively simple as only tungsten and aluminium have to be estimated, the water being determined as the loss on heating at 130°C (cf. page (xciii)).

From the analyses carried out the empirical composition of tungsto-aluminic acid would appear to be $Al_2O_3.22WO_3.49H_2O$, which represented as a 10-basic acid gives a molecular formula of $H_{10}[Al_2W_{22}O_{74}]44H_2O$.

All of the tungsto-aluminates which have been prepared were made from aqueous solutions of the free acid, by double decomposition with aqueous solutions of the various metallic ions. Prepared in this manner it can be assumed that any crystallisable product is simply the heteropoly salt, as all of the metallic salts used are appreciably more insoluble than the heteropoly salts themselves, and excess generally separates before they begin to crystallise.

(iv) Tungsto-chromic acid:

The starting point for the praparation of this compound is, as in the case of tungsto-aluminic acid, 56.12 gms. of sodium tungstate, $Na_2WO_4.2H_2O$, which is converted to sodium paratungstate, $3Na_2O.7WO_3$, by the addition of 194.4 ml. of N nitric acid in the cold. This solution is heated to boiling, and a solution of chromium nitrate, $Cr(NO_3)_3.9H_2O$, (containing 8.5 gms. dissolved in 500 ml. of water) is run in slowly from a dropping funnel (at a rate of 2 - 3 drops per minute) while the paratungstate solution is kept at the boiling point and stirred continuously. Here, 30.38 ml. of N acid, the amount required to convert the sodium paratungstate obtained from 25 gms. of sodium tungstate to sodium metatungstate, is equivalent to 4.053 gms. of chromium nitrate (9-hydrate), and the amount used, 8.5 gms. is in slight excess of this quantity. The first few drops of chromium nitrate solution which are added colour the paratungstate solution a light yellow, which gradually changes to orange as the addition is continued. On further addition of chromium nitrate, each drop causes the temporary formation of a light green precipitate, which redissolves on stirring and the colour of the solution changes from orange to light green. The green colour becomes progressively darker throughout the saturation, becoming at one stage almost black. About this point, when nearly 3/4 of the theoretical amount of chromium nitrate have been added, precipitation begins to be permanent, and as more of this precipitated material fails to redissolve, the colour of the solution changes from a dark green back to a light green, due to the suspended precipitate. If it is attempted to extract the solution at this stage with ether and sulphuric acid, absolutely no ether addition compound separates out, due to the very stable emulsion which is formed. During this extraction much tungstic acid is precipitated, which stabilises the emulsion to such an extent that in some cases it may be more than a month before separation occurs. In order to make the ether extraction possible, it is necessary to precipitate and filter off this tungstic acid beforehand. It was found that this could be ensured by adding 100 ml. of 4N nitric acid, at the end of the saturation. By so doing any residual tungstate or paratungstate is decomposed in the hot solution and the precipitated tungstic acid may be filtered off, after allowing the solution to stand for about 12 hours at 4°C. The resulting green and sometimes purple solution may then be successfully extracted with ether and 12N sulphuric acid.

The extraction is carried out as described above for tungstoaluminic acid, i.e. by stirring in 400 ml. of ether followed by 400 ml. of 12N sulphuric acid. On being allowed to settle out in a separating funnel, the dark green ether addition compound falls out. The aqueous layer assumes the blue-purple colour of the chromium nitrate solution, while the ether layer is usually coloured light green. Emulsification in the extraction of tungstochromic acid is generally more liable to occur than with tungstoaluminic acid, and the resulting emulsions are usually much more stable.

To obtain the free acid, the ether addition compound is washed by running into 2 or 3 successive quantities of dry ether and finally into about 1/2 its own volume of water. The ether is removed by blowing a stream of air through this solution or by evaporating off on a water bath, leaving a green solution of tungsto-chromic acid in water. The acid is more unstable than tungsto-aluminic acid and more easily hydrolysed. The rate and completeness with which the ether addition compound separates from the ether-sulphuric acid solution is more or less dependent on its stability and resistance to hydrolysis. This aqueous solution of the acid is repeatedly evaporated down to small bulk, filtering off at intervals the tungstic acid which separates, and continuing this process until the separation of tungstic acid becomes slow. Much of the tungsto-chromic acid is hydrolysed and so decomposed during this operation, as is shown by the reduction in the intensity of the green colouration of the solution. This is finally evaporated down to dryness, and heated at 130°C to decompose completely any residual metatungstic acid, before redissolving in water and filtering. The resultant dark green solution, when concentrated in vacuuo over concentrated sulphuric acid, deposits the tungsto-chromic acid as a dark green, micro-crystalline powder.

Sodium paratungstate solutions saturated with potassium dichromate did not lead to any heteropoly formation.

Tungsto-chromic acid is of the same order of solubility as tungsto-aluminic acid, but it is much more easily hydrolysed in solution. It is an equally strong acid (pH of M/500 solution is 1.21), its aqueous solutions readily decompose carbonates and this is probably the most satisfactory method of obtaining the barium salts of those acids, by direct neutralisation with barium carbonate. Its solutions are decomposed by sodium hydroxide with precipitation of chromium hydroxide.

(v) Tungsto-manganic acid:

Tungsto-manganic acid has been successfully prepared by 2 different methods; firstly by saturating paratungstate solutions with a salt which already contains 3-valent manganese, viz. potassium manganicyanide, $K_3Mn(CN)_6$, and secondly by using a manganous salt as the saturating agent and oxidising it in the paratungstate solution with potassium persulphate. The first method is not as satisfactory as the second, as due to hydrolysis of the complex cyanide the solution becomes quite alkalime , which leads to the decomposition of any heteropoly compound formed and the precipitation of manganese dioxide.

The potassium manganicyanide used in the first method contains manganese in the 3-valent state. It is prepared by dissolving 50 gms. of manganous acetate in excess water and adding to this a solution containing 113 gms. of potassium cyanide dissolved in the minimum quantity of water. On blowing air through this mixed solution the colour changes from green to blue and then to a deep orange red as oxidation proceeds. The oxidative change may be accelerated by the addition of a little hydrogen peroxide. The manganicyanide crystallises out on concentration as orange red needles, and can be further recrystallised from water. For the preparation of tungsto-manganic acid using this compound, 56.12 gms. of sodium tungstate, $Na_2WO_4.2H_2O$, dissolved in 500 ml. of water are comverted as before, to sodium paratungstate, $3Na_2O.7WO_3$, by the addition of 194.4 ml. of N nitric acid in the cold. This solution is heated to boiling and while being kept well stirred, 8 gms. of solid potassium manganicyanide, $K_3Mn(CN)_6$, (which is a slight excess over the theoretical amount) are added in small quantities at a time over 24 hours, while 120 ml. of N nitric acid is slowly added to balance the solution against the alkaline hydrolysis products which are formed. Theoretically 328 gms. of potassium manganicyanide are equivalent to 3,000 ml. of N acid. More then 1/2 of the manganicyanide may be added without any permanent precipitation occuring, although with each addition a slight transient precipitate appears, which redissolves on stirring. At the same time the colour of the solution becomes more intensely red. From this point onwards hydrated manganese dioxide continues to precipitate and remains suspended in the solution. The amount of nitric acid used during the saturation to neutralise the alkaline hydrolysis products was arrived at by experimental trial, as presumably the extent to which the manganicyanide hydrolyses varies from one saturation to another. The important point is that the pH of the final solution before extraction should be at least 3 - 3.2. If this is not ensured emulsification occurs to such an extent that no heteropoly compound can be extracted. Before extraction the solution is evaporated down to 150 ml., cooled overnight at 4°C and any paratungstate together with the precipitated manganese dioxide is filtered off. The well cooled solution is then mixed with 400 ml. of dry ether followed by 400 ml. of 12N sulphuric acid with mechanical stirring, and the ether addition compound separated as before.

The second method using a manganous salt and oxidising it with potassium persulphate in the body of the boiling paratungstate solution to the 3-valent state is more satisfactory and gives much better yields of tungsto-manganic acid, Here again, 56.12 gms. of sodium tungstate are converted to sodium paratungstate by the addition of the theoretical amount of N nitric acid (194.4 ml.) in the cold. To this boiling solution which is stirred continuously is added in small quantities at a time, an intimately ground mixture composed of 7 gms. of manganous sulphate, $MnSO_4.4H_2O$, and 9 gms. of potassium persulphate, $K_2S_2O_8$, during the course of 24 hours. The deep red colour characteristic of 3-valent manganese becomes more intense throughout the saturation, without any appreciable quantity of manganese dioxide being precipitated. These quantities again are in slight excess of the theoretical equivalent of acid produced on hydrolysis, neessary to convert all of the paratungstate to metatungstate. No additional mineral acid has to be added in this case, as the potassium persulphate keeps the solution sufficiently acid to prevent any hydrolysis of the tungsto-manganic acid which is formed. On completion of the saturation the solution is evaporated down to 150 ml., cooled overnight at 4°C in a refrigerator, filtered, and extracted with 400 ml. of ether and 400 ml. of 12N sulphuric acid as before. From a saturation run using potassium permanganate as the saturating agent, no heteropoly compound could be extracted.

The heavy, oily, deep red coloured ether addition compound separates very rapidly from the ether-sulphuric acid solution, in the absence of any emulsification. The free ether layer and also the aqueous layer are red coloured, and tungstic acid separates from the aqueous layer after standing for a short time. The tungsto-manganic acid ether addition compound is quite stable by itself, but on attempting to isolate the free acid from it by running into water, removing the ether by evaporation and concentration, the tungsto-manganic acid is decomposed completely with the deposition of hydrated manganese dioxide. The intensity of the red colour of solutions of tungsto-manganic acid is dependent on the quantity of free acid present, and the colouration decreases as its solutions are concentrated. The aqueous solutions are quite stable in the cold, but heating greatly accelerates the hydrolytic decomposition. It was attempted to isolate the free acid by neutralising the barium salt with the theoretical amount of dilute sulphuric acid, and concentrating the resultant, filtered solution in vacuuo over concentrated sulphuric acid, but here again as the solution became more concentrated, tungstic acid began to separate in greater quantity; so it is assumed that the free tungstomanganic acid is incapable of being isolated in the solid, crystalline state, due to its instability against hydrolysis.

4. EQUIVALENCE and BASICITY MEASUREMENTS.

According to the analytical results quoted in a later section, the maximum basicity shown in any of the salts prepared is 10. Wells[51] has suggested general structures for the anions of heteropoly acids of such odd series as 8, 8½, 9, 10, 10½ and 11 and containing more than 1 central atom, e.g. the heteropoly acids containing 2 central atoms of phosphorus are represented as $\left[P_2W_pO_{3p+8}\right]^{6-}$. On this basis the heteropoly acids containing 2 trivalent central atoms would be represented as $\left[M_2^{+++}W_pO_{3p+8}\right]^{10-}$, making them 10-basic. The guanidine and silver salts of heteropoly acids usually show maximum basicity of the parent acid, and the formulae of the acids are usually deduced from such facts. As all heteropoly acids are fairly easily decomposed by alkalis, direct titration against alkali has not generally been used as a means of estimating the basicity of such compounds. However, as a matter of interest, such direct titrations have been carried out, using standard sodium hydroxide, against an approximately M/500 solution of tungsto-aluminic acid. Tungsto-chromic acid is too readily hydrolysed, even by water, for any useful information to be obtained regarding its basicity by this method. For comparison purposes, similar titrations were also carried out for some 12-acids. These included tungsto-arsenic acid, tungsto-silicic acid, molybdo-phosphoric acid and metatungstic acid. The neutralisations were followed potentiometrically.

About 1gm. of the acid dissolved in 200 ml. of water was used in each case. The potential of the solution was measured between a quinhydrone/platinum electrode as the positive terminal, and the standard saturated calomel electrode as the reference electrode. A 0.1016N solution of sodium hydroxide was run in slowly while the solution was kept well stirred, and the potential measured in millivolts, after each addition of alkali, on a Cambridge potentiometer. The figures obtained in 4 such titrations of tungsto-aluminic acid are shown in table (iii) on page (lx) , and those figures are graphed on page (lxvi) . The corresponding figures for tungsto-arsenic, tungsto-silicic and molybdo-phosphoric acids are shown in table (iv) on page (lxii) , and the graphical representation of those on page (lxvii) . Table (v) on pages (lxiii, lxiv, andlxv) shows the results of 4 titrations of metatungstic acid, carried out in a similar manner.

The titration curves of tungsto-aluminic acid are fairly typical although not very well defined curves for the neutralisation of a weak acid with a strong base. The potential falls slowly at first and then more rapidly as the heteropoly acid is neutralised, until a point is reached where the neutralisation of the acid may be regarded as complete, and the anion begins to decompose. These points are represented by arrows on page (lxvi) . The potential then remains comparatively steady while the aluminium is precipitated as aluminium hydroxide, beginning to fall rapidly again as the aluminium hydroxide redissolves in the sodium hydroxide. When the resolution of the aluminium hydroxide is complete, the potential becomes fairly steady again, in the presence of excess sodium hydroxide. If the neutralisation point is taken as the position denoted by the arrow-heads on page (lxvi) , and the equivalent of the tungsto-aluminic acid calculated, the following results are obtained. From the analysis later the molecular weight of tungsto-aluminic acid, $H_{10}[Al_2W_{22}O_{74}]44H_2O$ is 6088, which divided by the equivalent as obtained from those neutralisation curves gives values for the basicity of the acid as shown in table (vi). Thus, this indicates that tungsto-aluminic acid is most

Table (vi).

Weight of tungsto-aluminic acid	Vol. of 0.1016N NaOH for neutralisation	Equivalent	Basicity	
1.2457	19.5	629.1	9.679	(i)
1.2101	18.9	630.6	9.654	(ii)
1.3113	21	614.6	9.906	(iii)
1.2488	20.15	610.1	9.979	(iv)

probably 10-basic.

The titration curves for the 12-acids, tungsto-arsenic, tungsto-silicic and molybdo-phosphoric acids are even less well characterised; the only one which resembles a reasonably well defined weak-acid-strong-base titration curve being that of tungsto-silicic acid, $H_4SiW_{12}O_{40}.30H_2O$. If the neutralisation point be taken as shown in the curve on page (lxvii) , the basicity of tungsto-silicic acid is found to be 4.423. The other 2 curves on page (lxvii) show evidence of several ill-defined breaks, and no value can be attached to them.

The neutralisation curves of metatungstic acid shown on page (lxviii), while conforming to the general pattern of weak acid-strong base titration curves show a rather sudden rise in potential at certain points. Curve (iv) on page (lxviii) shows several of those stages. This may be due to the successive neutralisation of separate hydrogen atoms in the acid, although it would not be expected that such polybasic acids would show more than 1 well defined stage in the neutralisation. The dissociation constants of such acids are very small, in the region of 10^{-37} (Britton and Welford[52]) and in order that the successive stages in the neutralisation should be detectable, the dissociation constants of those stages should each be at least 10^{3} times its immediate successor. That this should be the case in those highly polybasic acids is very improbable.

5. HETEROPOLY SALTS of TUNGSTO-ALUMINIC, TUNGSTO-CHROMIC, and TUNGSTO-MANGANIC ACIDS.

(i) Preparation and general properties:

From aqueous solutions of the free acids, the various salts described below have been prepared, by double decomposition with saturated aqueous solutions containing the appropriate metallic ions. In the case of tungsto-manganic acid, especially, and generally, salts free from any reducing ions are preferably used for this purpose, in order to eliminate the possibility of reduction of the trivalent manganese ion. This precaution is not of so much importance in the case of the tungsto-chromates and tungsto-aluminates, as the central atom in the complex

Table (iii):

Potentiometric neutralisation of tungstoaluminic acid.

(i)						(ii)			
Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.
0	357	19.2	206	28	-64	0	365	20.5	177
1	354	19.4	205	28.5	-70	1	361	21	175
2	353	19.6	202	29	-76	2	357	21.5	171
3	352	19.8	200	29.5	-81	3	354	22	168
4	350	20	200	30	-84	4	350	22.5	163
5	348	20.2	200	30.5	-86	5	349	23	153
6	346	20.4	200	31	-90	6	346	23.5	128
7	343	20.6	198	31.5	-92	7	342	24	81
8	341	20.8	197	32	-96	8	340	24.5	24
9	338	21	195	35	-112	9	337	25	-5
10	335	21.2	194	40	-131	10	333	25.5	-24
11	332	21.4	194			11	329	26	-34
12	328	21.6	192			12	325	26.5	-45
12.5	326	21.8	192			12.5	322	27	-55
13	323	22	191			13	319	27.5	-58
14	318	22.2	190			13.5	315	28	-63
14.2	317	22.4	187			14	311	28.5	-67
14.4	315	22.6	185			14.5	306	29	-72
14.6	314	22.8	185			15	301	29.5	-76
14.8	313	23	182			15.2	298	30	-77
15	310	23.2	181			15.4	295	31	-82
15.2	309	23.4	178			15.6	291	32	-85
15.4	308	23.6	175			15.8	288	33	-90
15.6	306	23.8	170			16	284	34	-93
15.8	305	24	166			16.2	281	35	-96
16	302	24.2	158			16.4	275	36	-102
16.2	300	24.4	146			16.6	269	37	-104
16.4	298	24.6	127			16.8	262	38	-106
16.6	296	24.8	114			17	252	39	-108
16.8	292	25	98			17.2	239	40	-109
17	290	25.2	90			17.4	226	45	-124
17.2	285	25.4	58			17.6	214	50	-133
17.4	281	25.6	20			17.8	205		
17.6	276	25.8	5			18	197		
17.8	271	26	-16			18.2	193		
18	263	26.2	-26			18.4	190		
18.2	254	26.4	-33			18.6	188		
18.4	242	26.6	-38			18.8	186		
18.6	229	26.8	-44			19	185		
18.8	219	27	-48			19.5	182		
19	211	27.5	-56			20	179		

Table (iii) contd.

Potentiometric neutralisation of tungstoaluminic acid.

(iii)				(iv)			
Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.
0	355	20.5	194	0	349	18.8	216
1	352	21	189	1	348	18.9	211
2	351	21.5	184	2	344	19	206
3	350	22	182	3	342	19.1	206
4	348	23	178	4	338	19.2	204
5	346	24	171	5	338	19.3	200
6	344	25	159	6	332	19.4	200
7	340	26	118	7	330	19.5	200
8	336	27	52	8	326	19.6	200
9	331	27.5	34	9	324	19.7	200
10	334	28	12	10	322	19.8	200
10.5	332	29	-30	11	322	19.9	200
11	330	30	-48	12	316	20	200
11.5	328	31	-60	13	310	20.5	200
12	326	32	-66	14	310	21	198
12.5	325	33	-68	14.5	304	22	198
13	322	34	-76	15	300	23	190
13.5	317	35	-80	15.5	298	23.5	182
14.5	315	40	-96	16	292	24	170
15	310	50	-116	16.5	288	25	78
15.5	307			17	285	25.1	64
16	304			17.5	278	25.2	48
16.5	299			18	264	25.3	32
17	294			18.1	260	25.4	20
17.5	288			18.2	253	25.5	-16
18	281			18.3	248	25.6	-30
18.5	272			18.4	246	25.7	-40
19	256			18.5	240	25.8	-44
19.5	226			18.6	234	25.9	-36
20	207			18.7	228		

Table (iv)
Potentiometric neutralisation of

Tungstoarsenic; (i)		tungstosilicic; (ii)		and molybdophosphoric acids (iii)			
Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.
0	334	0	372	0	376	45	174
1	333	2	369	1	376	46	175
2	328	4	365	2	377	47	174
3	328	6	366	3	377	48	170
4	326	8	365	4	376	49	169
5	323	10	365	5	376	50	168
6	318	12	365	6	376	52	162
7	312	14	365	7	376	54	158
8	310	16	363	8	375	56	156
9	302	18	360	9	375	60	138
10	300	20	358	10	375	65	137
11	293	22	358	11	375	70	136
12	279	24	354	12	375		
13	270	25	354	13	374		
14	248	27	355	14	374		
15	200	30	352	15	372		
15.2	193	32	343	16	372		
15.4	184	33	340	17	370		
15.6	175	34	338	18	370		
15.8	158	35	336	19	366		
16	157	36	334	20	364		
16.2	157	37	327	21	357		
16.4	157	38	324	22	357		
17	132	40	324	23	345		
17.5	120	42	312	24	342		
18	115	43	303	25	337		
18.5	115	44	296	26	330		
19	115	45	260	27	315		
19.5	113	45.5	222	28	305		
20	109	45.6	190	29	292		
21	100	45.7	178	30	282		
22	87	46	80	31	264		
23	79	46.5	94	32	264		
24	74	47	60	33	236		
25	70	47,5	38	34	223		
26	69	48	28	35	224		
27	59	49	28	36	209		
28	59	50	28	37	200		
29	47			38	200		
30	42			39	200		
31	37			40	200		
32	34			41	190		
33	20			42	190		
34	13			43	184		
35	0			44	175		

Table (v)

Potentiometric neutralisation of metatungstic acid.

(i)

Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.
0	363	21	320	29.4	175
1	362	21.2	319	29.6	169
2	361	21.4	318	29.8	164
3	359	21.6	316	30	162
4	358	21.8	316	30.2	161
5	357	22	314	30.4	161
6	355	22.2	314	30.6	159
7	354	22.4	312	30.8	155
8	353	22.6	310	31	162
9	351	22.8	309	31.2	167
10	349	23	308	31.4	171
11	348	23.2	307	31.6	176
12	346	23.4	305	31.8	166
13	344	23.6	304	32	164
14	342	23.8	302	32.2	160
15	339	24	300	32.4	158
15.5	338	24.2	298	32.6	152
16	337	24.4	295	32.8	/
16.2	337	24.6	290	33	148
16.4	336	24.8	286	33.5	138
16.6	336	25	284	34	139
16.8	335	25.2	280	34.5	126
17	334	25.4	278	35	121
17.2	334	25.6	274	35.5	117
17.4	333	25.8	270	36	116
17.6	333	26	268	36.5	113
17.8	332	26.2	266	37	111
18	331	26.4	262	37.5	114
18.2	331	26.6	258	38	112
18.4	330	26.8	255	38.5	110
18.6	330	27	251	39	109
18.8	328	27.2	247	39.5	108
19	328	27.4	242	40	108
19.2	327	27.6	238	40.5	108
19.4	326	27.8	233	41	108
19.6	326	28	226	41.5	108
19.8	325	28.2	219	42	108
20	324	28.4	213	42.5	108
20.2	324	28.6	205	43	108
20.4	323	28.8	196	43.5	108
20.6	322	29	188	44	108
20.8	320	29.2	180	45	108

Table (v) contd.

Potentiometric neutralisation of metatungstic acid.

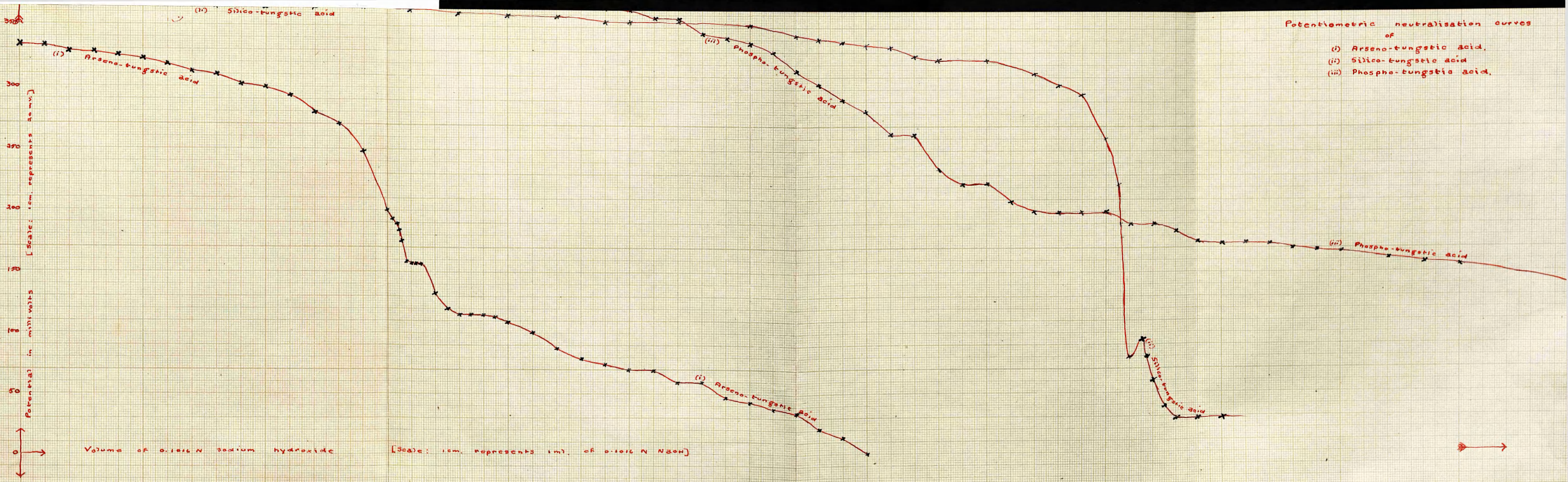
(ii)				(iii)	
Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.
0	353	16.2	107	0	361
1	351	16.4	107	1	361
2	349	16.6	106	2	360
3	346	16.8	104	3	360
4	343	17	102	4	359
5	339	17.2	103	5	358
6	336	17.4	104	6	358
7	332	17.6	104	7	348
8	327	17.8	103	7.5	348
9	321	18	102	8	347
10	314	18.2	102	9	347
10.2	312	18.4	102	10	347
10.4	310	18.6	102	11	333
10.6	308	18.8	102	12	328
10.8	305	19	102	12.5	326
11	303	19.2	102	13	325
11.2	301	19.4	102	13.5	322
11.4	298	19.6	100	14	317
11.6	294	19.8	99	14.2	315
11.8	290	20	98	14.4	314
12	286	20.5	96	14.6	312
12.2	282	21	92	14.8	309
12.4	275	21.5	90	15	308
12.6	268	22	88	15.2	/
12.8	255	22.5	86	15.4	303
13	236	23	84	15.6	299
13.2	200	23.5	84	15.8	294
13.4	148	24	84	16	292
13.6	131	24.5	84	16.2	288
13.8	123	25	83	16.4	284
14	117	26	80	16.6	279
14.2	124	27	75	16.8	272
14.4	120	28	72	17	267
14.6	118	29	70	17.2	251
14.8	116	30	70	17.4	215
15	115	31	68	17.6	162
15.2	112	32	66	17.8	137
15.4	110	35	60	18	123
15.6	110	40	51	18.2	146
15.8	109	50	40	18.4	139
16	108			18.6	134

Table (v) contd.

Potentiometric neutralisation of metatungstic acid.

(iii)		(iv)			
Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.	Vol. of 0.1016N NaOH	Potl. in mv.
18.8	132	0	355	13.8	95
19	124	1	352	14	85
19.5	114	2	350	14.2	84
20	111	3	347	14.4	84
20.5	111	4	344	14.6	92
21	106	5	340	14.8	101
21.5	105	6	337	15	93
22	104	7	333	15.2	99
22.5	104	8	328	15.4	96
23	104	9	321	15.6	95
23.5	104	10	314	15.8	92
24	104	11	302	16	91
24.5	/	11.2	300	16.5	88
25	104	11.4	297	17	84
26	101	11.6	292	17.5	87
27	100	11.8	290	18	85
28	100	12	284	18.5	82
29	100	12.2	278	19	80
30	100	12.4	270	19.5	80
35	92	12.6	259	20	78
		12.8	245	21	74
		13	195	22	70
		13.2	150	23	68
		13.4	126	24	66
		13.6	106	25	64

Potentiometric neutralisation curves of Tungsto-aluminic acid.

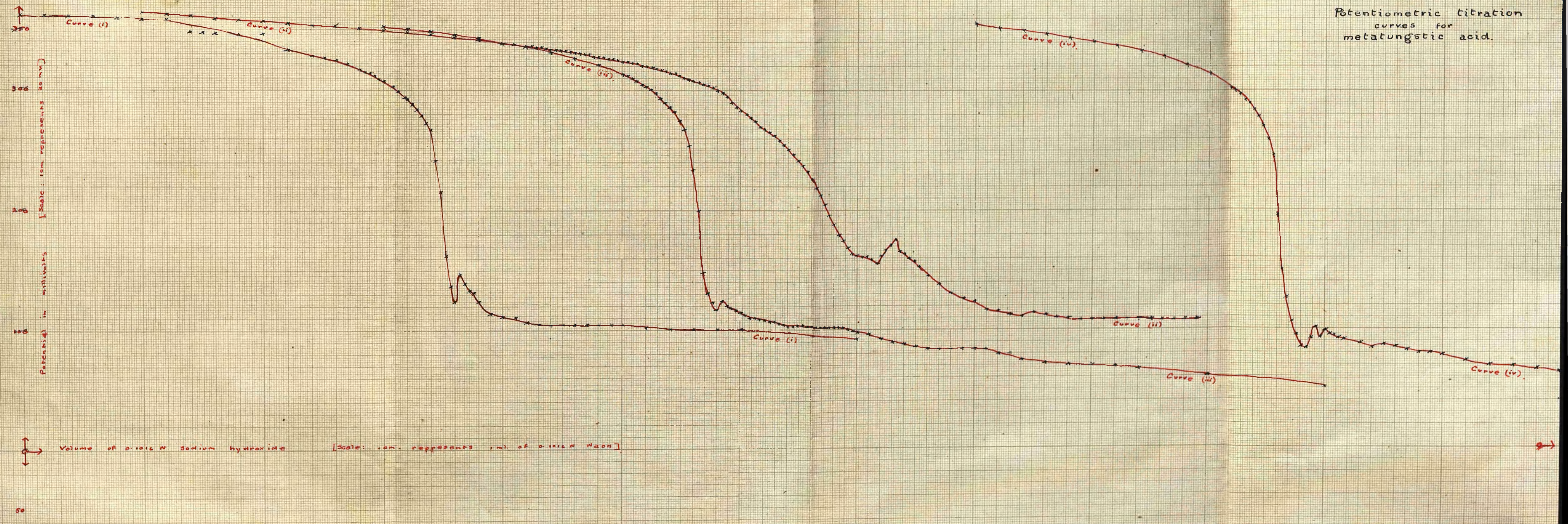


Potentiometric neutralisation curves of

(i) Arseno-tungstic acid,

(ii) Silico-tungstic acid

(iii) Phospho-tungstic acid.



Potentiometric titration
curves for
metatungstic acid.

anion in those cases is in its normal, stable, valency state; but trivalent manganese is fairly readily reduced with the resulting precipitation of hydrated manganese dioxide. Thus the nitrates are used in preference to the chlorides. The barium salts are most conveniently prepared from the acid solutions by direct neutralisation with solid barium carbonate. In addition to preventing the solutions from becoming un-necessarily dilute, this method not only removes any residual sulphuric acid as the very sparingly soluble barium sulphate, but also any paratungstates as the sparingly soluble barium paratungstate, and metatungstic acid as barium metatungstate, the much more soluble barium salts of the heteropoly acids remaining in solution. Direct neutralisation with ammonium carbonate was sometimes also used for the preparation of the ammonium salts, guanidine hydrochloride for the preparation of the guanidine salts; otherwise the corresponding nitrates. 50 gms. of each of the free acids were generally used, dissolved in about 50 ml. of water, and 1½ times the theoretical amount of the appropriate salt dissolved in the minimum volume of water stirred in. This was filtered, concentrated if necessary and put aside until crystallisation occured. In the case of the tungsto-manganates, the ether addition compound of tungsto-manganic acid was used directly, by running about 50 ml. of it into a further 25 ml. of water, removing the ether by blowing a stream of air through the solution, thus leaving an aqueous solution of the free acid together with any metatungstic acid, which had been extracted at the same time with the ether-sulphuric acid mixture. In this case quite a large amount of insoluble material separates out on saturating the acid solution with metallic salts. Concentration of aqueous solutions of those salts is preferably carried out in vacuuo over concentrated sulphuric acid, in order to reduce the rate of hydrolysis, which all of those compounds undergo to some extent in the presence of water. Concentration by evaporation of their solutions with heating greatly accelerates this hydrolytic action, and in the case of the more unstable compounds leads to more or less complete decomposition. The barium salts generally are more resistant to hydrolysis than any of the others prepared. Aqueous solutions of the tungsto-aluminates are colourless, of the tungsto-chromates green and of the tungsto-manganates red, the intensity of the colour being dependent on the concentration.

All of those heteropoly salts are very soluble and crystallise remarkably well, usually in the form of octahedra or prisms with pyramidal ends, although according to the concentration of the solution needles, leaflets or some other intermediate form in the process of crystal growth may occur. The alkali and alkaline earth salts are generally very soluble, the solubility increasing in the order of decreasing atomic weight. The amorphous precipitates which form initially become crystalline on water of crystallisation, those compounds containing the larger metallic atoms (such as caesium) being more anhydrous than those containing the smaller metallic ions. The guanidine and barium salts of all 3 acids appear to be 10-basic, while the ammonium salts are 8-basic.

(ii) Purification and crystallisation of heteropoly salts:

Heteropoly salts are most readily purified by recrystallisation from water. This recrystallisation process, however, can not be repeated too often, as hydrolytic decomposition becomes more pronounced each time such compounds are dissolved in water. Crystallisation takes place most easily, in the first instance, from the original mother liquors; and recrystallisation from water becomes more difficult and the time before any crystals form successively longer (sometimes taking as long as a period of months), even at low temperatures. Some amorphous material, probably metal paratungstate or some higher tungstate, invariably separates before the heteropoly salt crystallises out. This must be filtered off, otherwise there is the risk of it being occluded in the crystals which are subsequently formed. If solutions are made more concentrated, they simply solidify to a mass of intergrown crystals on cooling. Greatly supersaturated solutions of high specific gravity can be prepared without any crystallisation taking place from them. It is difficult to induce crystal nucleii to form in such solutions, but this can occasionally be effected by repeated cooling, seeding, shaking or otherwise disturbing the solution. In many cases solutions may be evaporated down over concentrated sulphuric acid until a thick, viscous syrup is left without separation of any solid material occuring. At other times concentrated solutions may be left, even in a refrigerator for as long as 2 or 3 months before crystallising. The exceptionally large molecular weight of such compounds is presumably responsible for the difficulty with which crystal nucleii form. Small changes in temperature cause the initially formed small crystals to redissolve, and seeding of such supersaturated solutions with larger crystals is seldom very successful. Two recrystallisations from water are usually sufficient to ensure purity of the salt concerned. Being thus prepared from the free acid and recrystallised from water there cannot be any reasonable doubt about the homogeneity or individuality of such compounds. Any similar compounds described in the literature had been prepared by crystallisation from mixed aqueous solutions of their components, where, due to the complicated conditions of equilibrium which exist in such solutions, quite variable and unreproducable material will necessarily separate, depending on conditions of concentration and temperature. It thus happens that various workers[39, 40, 41, 17] represent a compound, prepared ostensibly by the same method, by different empirical formulae. Rosenheim and Schwer[53] for those reasons believed that heteropoly aluminates previously described were simply amorphous mixtures and not definite compounds at all. He expressed similar doubt about the existence of any compounds containing 3-valent manganese and chromium.

The characteristic and usual form in which those heteropoly salts crystallise is the octahedron or prism with bipyramidal ends. Only rarely is a perfect octahedral obtained, but normally a sufficient number of faces is developed to enable this form to be recognised. It seems probable that some of those salts adopt 2 or more crystalline forms according to the conditions of concentration and on the other ions present in the solution. Ammonium tungsto-aluminate, for instance, prepared from the free acid and ammonium nitrate crystallises from this mother liquor in the form of octahedra, but on recrystallisation from water appears in the form of prismatic columns. On further recrystallisation, this same form persists. Prepared from the free acid and ammonium chloride it crystallises regularly as octahedra. Ammonium tungsto-manganate and ammonium tungsto-chromate also exist as 2 separate crystalline hydrates, one of which is cubic in each case.

The ammonium, barium and potassium salts of each of the 3 acids crystallise in beautifully, isomorphous octahedra. Crystals of those sometimes grow to an appreciable size (overall dimensions of 1 - 2 cms.) and a crystal of ammonium tungsto-manganate has been obtained which measured about 3/4 of an inch along each of its principal axial directions, and weighing several grams. The quite frequent occurence of growth of such large crystals results from anly a few crystal nucleii forming in a concentrated solution, and all of the material in solution depositing on those one or two nucleii.

The extent to which the barium and potassium salts of all 3 acids effloresce on exposure to the ordinary atmosphere (the ammonium salts do not effloresce to the same extent) is dependent on the size of the crystals; large crystals remaining quite transparent and unaffected, while smaller ones break down after only a short exposure to micro-crystalline powders. It is for these reasons that it is such a slow and difficult process to get quite homogeneous, crystalline material for analysis. The formulae of the various salts given below were arrived at empirically from analytical data, details of which are given in a later section. The figures in brackets refer to the theoretical percentage compositions, calculated to the nearest whole number of molecules.

(iii) Tungsto-aluminates:

(a) Ammonium tungsto-aluminate, $(NH_4)_8H_2[Al_2W_{22}O_{74}]35H_2O$.

Prepared from an aqueous solution of tungsto-aluminic acid by double decomposition with ammonium chloride or ammonium nitrate; or alternatively by direct neutralisation of the acid with solid barium carbonate. Crystallises from its mother liquors as perfectly transparent, colourless octahedra. It is very soluble in water and easily recrystallisable. The crystals of this salt have an unusually low specific gravity, viz. 1.848. The crystalline salt is perfectly isotropic and quite stable on exposure to the atmosphere. Plate (v) shows crystals of the salt photographed at a magnification of 250 in parallel light, while plate (vi) shows the same field between crossed Nicols. It does become opaque, however, on long standing. An approximately M/500 solution of the salt has a pH of 3.50. From analyses it contains 84.07% (84.20%) of WO_3, 1.629% (1.681%) of Al_2O_3, 3.098% (3.432%) of $(NH_4)_2O$ and 10.43% (10.69%) of water, which corresponds to an empirical formula, $4(NH_4)_2O.Al_2O_3.22WO_3.36H_2O$, thus making the salt 8-basic. As already pointed out the salt adopts 2 different crystalline habits, octahedral and prismatic, the latter crystallising from solutions containing nitrate ions.

(b) Guanidine tungsto-aluminate, $(CN_3H_5)_{10}\left[Al_2W_{22}O_{74}\right]11H_2O$.

Prepared from aqueous solutions of tungsto-aluminic acid by saturating with guanidine hydrochloride. The guanidine tungsto-

Plate (v)

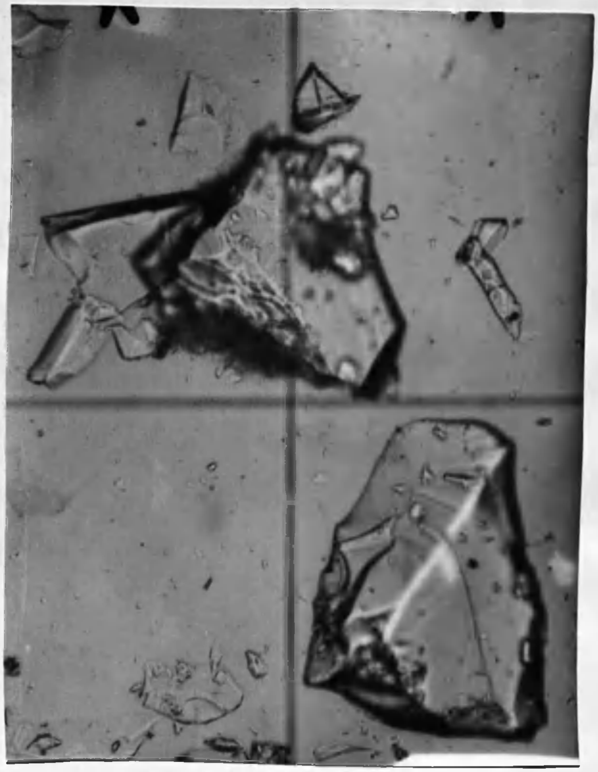


Plate (vi)

Plate (vii)

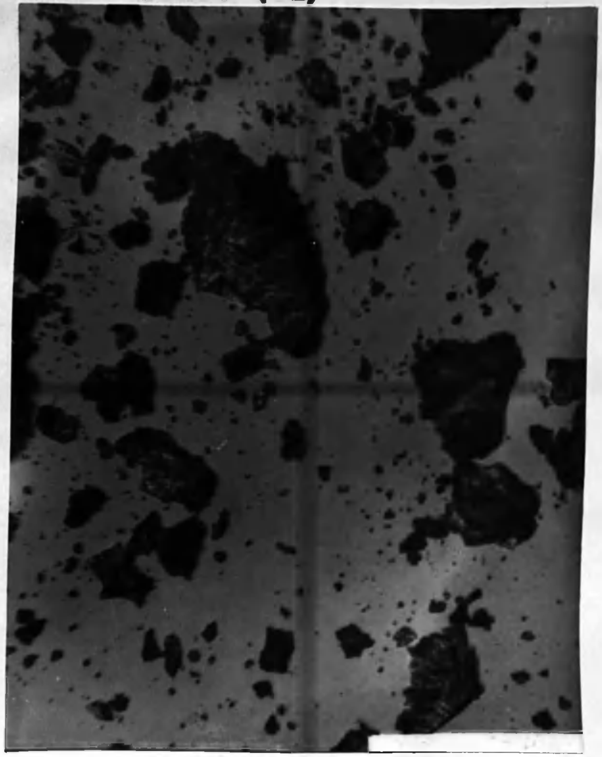


Plate (viii)

aluminate precipitates almost immediately as a white amorphous precipitate. This, on being filtered off and redissolved in a larger volume of water recrystallise as white or colourless prisms. It does not crystallise in large crystals. The specific gravity of the salt is 4.145, and an M/500 solution has a pH of 4.72. Crystals of this salt are biaxial negative andof small optic axial angle, the lowest refractive index having a value of 1.768, while the highest refractive index observed is greater than 1.78. Most of the crystallin particles show a triangular or diamond shaped outline, although frequently a rectangular outline is observed (cf. plate (xii)). Such prisms have the plane of their acute bisectrix at right angles to their principal length and parallel to the direction of view. The optic axial figures of such crystals are thus easily observed . Analysis of the salt show that it contains 1.692% (1.673%) of Al_2O_3, 84.78% (83.79%) of WO_3, 3.16% (3.546%) of water and 10.37% (11.00%) of $(CN_3H_5)_2O$, which corresponds to the empirical formula, $5(CN_3H_5)_2O.Al_2O_3.22WO_3.11H_2O$.

(c) Potassium tungsto-aluminate.

Prepared by saturating an aqueous solution of tungsto-aluminic acid with potassium nitrate or potassium chloride. On filtering and concentrating this solution over concentrated sulphuric acid, the salt crystallises as colourless octahedra.

Large crystals of this compound sometimes appear a faint yellow or violet colour. On exposure to the atmosphere potassium tungsto-aluminate crystals, which on first removing from their mother liquors are perfectly transparent, become quite opaque on the surface and gradually break down into a white powder. A complete analysis has not been obtained for this compound, but the oxide ratio $Al_2O_3:WO_3$ is found to be approximately 1:22. The salt crystals have a specific gravity of 5.449, and the pH of an M/500 solution is 4.72. It is very soluble in water although rather unstable. On boiling its aqueous solutions it is decomposed almost completely.

(d) Barium tungsto-aluminate.

Prepared by direct neutralisation of aqueous solutions of tungsto-aluminic acid with solid barium carbonate. Small quantities are added at a time until no further effervescence occurs and then a slight excess. This salt is very soluble and does not crystallise very well; it usually separates as a micro-crystalline powder. It effloresces very rapidly and is hydrolysed to some extent on boiling its aqueous solutions. This compound has a specific gravity of 3.601 and an M/500 solution has a pH of 2.60. No satisfactory complete analysis has been obtained for this compound. Also the refractive index could not be measured, due to the indefinite crystal outlines.

(e) Caesium tungsto-aluminate.

Prepared by saturating an aqueous solution of tungsto-aluminic acid with slightly more than the theoretical amount of caesium chloride. The caesium tungsto-aluminate is immediately precipitated as a white micro-crystalline deposit. It is comparatively insoluble in water but capable of being recrystallised as colourless prisms (cf. plate (xi)). Due to its low solubility crystals of this salt do not grow to any size. When dehydrated over phosphorus pentoxide it is practically anhydrous and does not decompose until temperatures abobe 170°C. An M/500 solution has a pH value of 3.05.

(f) Sodium tungsto-aluminate.

Obtained by double decomposition between an aqueous solution of tungsto-aluminic acid and sodium chloride or sodium nitrate. It crystallises as colourless, transparent octahedra, which behave similarly to the potassium salt. They effloresce quickly on exposure to the atmosphere being broken down to white powders. Its aqueous solutions are similyrly decomposed on boiling.

(g) Cadmium tungsto-aluminate.

Prepared by double decomposition between solutions of tungsto-aluminic acid and cadmium nitrate. The cadmium tungsto-aluminate crystallises on concentration as colourless or pale yellow prisms. This salt is so extremely soluble that it will only crystallise from concentrated solutions, and when this occurs the solution sets almost solid with an interlaced mass of crystals. Stable solutions of exceptionally high (greater than 4) specific gravity can be obtained with this compound.

(h) Mercurous tungsto-aluminate.

Prepared by saturating a solution of tungsto-aluminic acid with mercurous nitrate. The salt separates as colourless prisms, which are quite stable on removal from their mother liquors.

(iv) Tungsto-manganates:

(i) Ammonium tungsto-manganate, $(NH_4)_8H_2[Mn_2W_{22}O_{74}]48H_2O$.

This salt is prepared from the ether addition compound of tungsto-manganic acid by running it into a slight excess of water, removing the ether by blowing a stream of air through the solution and then saturating up with ammonium nitrate ; or alternatively by direct neutralisation of the tungsto-manganic acid solution with ammonium carbonate. In either case quite a lot of precipitation occurs. On filtering off the precipitated material, concentrating slightly by evaporation over concentrated sulphuric acid and crystallising, deep red, almost black, transparent, octahedral crystals of ammonium tungsto-manganate separate. The salt is readily soluble in water and easily re-crystallised. On exposure to the atmosphere it soon becomes opaque and a reddish brown powder appears on the surface of the crystals. There is always a little amorphous material deposited before the ammonium tungsto-manganate crystallises. When dehydrated over phosphorus pentoxide this compound is quite isotropic, but absorption of moisture from the atmosphere leads to the formation of another hydrate, which is anisotropic. Plate (viii) shows crystals of the dehydrated hydrate at magnification of 250 in parallel light, while plate (vii) shows the same field between crossed Nicols. The refractive index of the lower, cubic hydrate is 1.798 and the specific gravity 3.844. An M/500 solution has a pH of 5.02. On analysis the salt is found to contain 2.445% (2.486%) of Mn_2O_3, 80.21% (80.35%) of WO_3, 13.75% (13.89%) of water and 3.436% (3.275%) of $(NH_4)_2O$, which corresponds to an empirical formula of $4(NH_4)_2O.Mn_2O_3.22WO_3.49H_2O$. Thus it is an 8-basic salt.

(j) Barium tungsto-manganate, $Ba_5[Mn_2W_{22}O_{74}]20H_2O$.

This compound is prepared directly from the ether addition compound of tungsto-manganic acid, by running it into excess water, removing the ether by evaporation and neutralising the resultant aqueous solution of tungsto-manganic acid directly with a slight excess of barium carbonate.With each addition of barium carbonate a vigorous recation ensues which gradually subsides as a light brown precipitate is thrown down. On filtering off the precipitated material and allowing the dark red solution to crystallise dark red transparent octahedra of barium tungsto-manganate separate, which are fairly stable when removed from their mother liquor and exposed to the atmosphere. The salt has a specific gravity of 4.178, and its M/500 solution has a pH of 4.28. Thin crystal sections appear yellow to dark red in colour and are only weakly birefringent. Most sections appear isotropic. The mean refractive index is greater than 1.7. The complex anion is sufficiently stable to allow the barium to be precipitated from it as barium sulphate with dilute sulphuric acid, without decomposition, and from analysis the salt is found to contain 2.471% (2.472%) of Mn_2O_3, 79.94% (79.89%) of WO_3, 12.64% (12.00%) of BaO and 5.64% (5.635%) of water, which corresponds to the empirical formula $5BaO.Mn_2O_3.22WO_3.20H_2O$.

(k) Silver tungsto-manganate.

This salt has been obtained as a reddish brown micro-crystalline powder, by saturating an aqueous solution of tungsto-manganic acid,obtained from the ether addition compound, with silver nitrate. It is recrystallised as red coloured rectangular prisms. An M/500 solution has a pH of 2.44. This salt is almost anhydrous when dehydrated over phosphorus pentoxide, and quite stable to the atmospheric moisture. Crystals of this compound show parallel extinction and their refractive index is higher than 1.7. The oxide ratio $Mn_2O_3:WO_3$ has been determined as approximately 1:22, although a complete analysis has not been carried out.

(1) Guanidine tungsto-manganate, $(CN_3H_5)_{10}\left[Mn_2W_{22}O_{74}\right]17H_2O$.

Obtained on saturating an aqueous solution of tungsto-manganic acid with guanidine hydrochloride as a reddish brown precipitate, which may be further recrystallised from water. There is invariably an amorphous, light brown precipitate (presumably guanidine paratungstate) which separates from these solutions before the heteropoly salt crystallises out. It is probably on this account that the estimations of the guanidine content are usually slightly higher than the theoretically expected value. Guanidine tungsto-manganate is difficultly soluble in water, but recrystallises as rectangular prisms mainly, or as elongated octahedra. All of the characteristically shaped particles, which would be expected to result from crushing an octahedral shaped crystal are obtained with this compound; triangular, diamond shaped, triangular with squared corners and hexagonal. These are

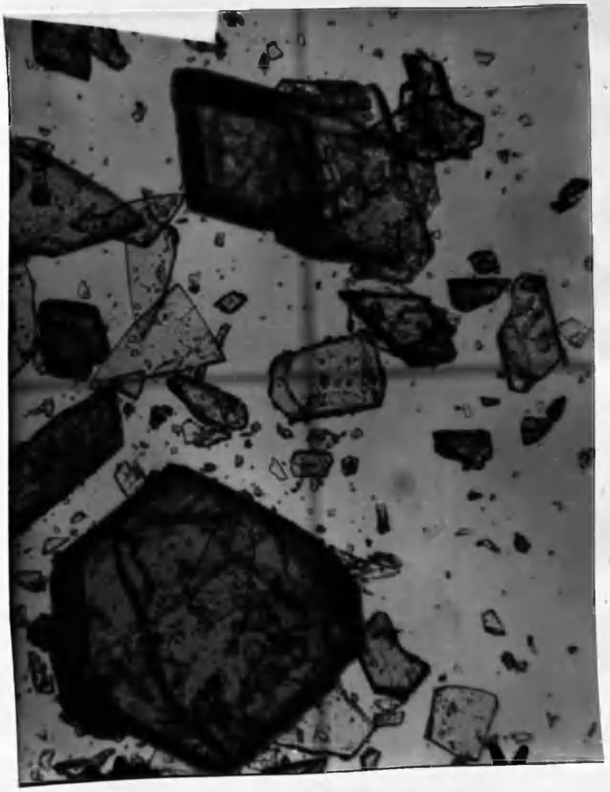


Plate (ix)

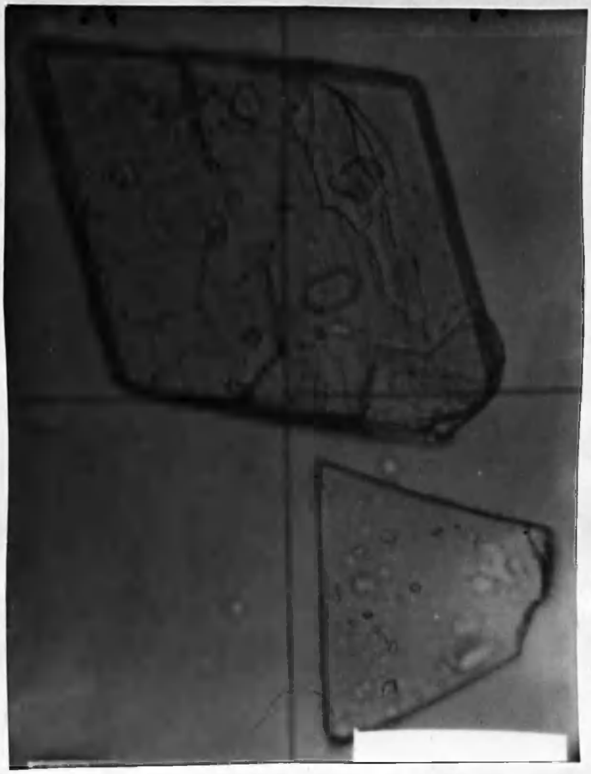


Plate (x)

Plate (xi)

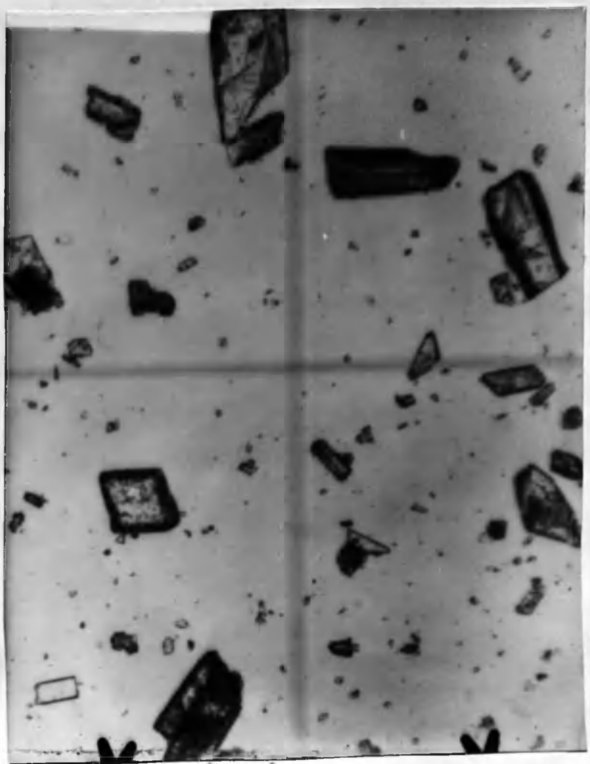


Plate (xii)

shown in plates (ix) and (x). This salt has a specific gravity of 4.322. The pH of an approximately M/500 solution is 4.49. Crystals of this compound are biaxial negative in character, and the triangular shaped particles lie on a microscope slide with the plane of their acute bisectrix parallel to the direction of view, so that their optic axial figures are quite easily observed. The lowest refractive index measured had a value of 1.728 and the highest value observed was 1.762. Analysis of the salt show that it contains 2.514% (2.531%) of Mn_2O_3, 80.87% (81.81%) of WO_3, 4.900% (4.905%) of water and 11.73% (10.74%) of $(CN_3H_5)_2O$, which approximates to the empirical formula, $5(CN_3H_5)_2O.Mn_2O_3.22WO_3.17H_2O$. The salt is thus 10-basic.

(m) Potassium tungsto-manganate.

Prepared from an aqueous solution of tungsto-manganic acid, obtained from the ether addition compound as before, by double decomposition with potassium nitrate. The deep red coloured solutions on concentration over concentrated sulphuric acid in vacuuo and on recrystallisation deposit deep red, almost black, transparent octahedra of potassium tungsto-manganate. Almost immediately on being removed from their mother liquors, wherin they are perfectly transparent, crystals of the salt become opaque and covered on the surface with a light brown deposit. On boiling an aqueous solution of the salt, complete decomposition results, with the precipitation of all of the manganese as hydrated manganese dioxide. The intensity of the colour of solutions of the tungsto-manganates provides a useful guide as to the stability of the solutions of those salts. The specific gravity of this compound is 5.094. An approximately M/500 solution of this salt has a pH of 4.47. No complete analysis has been obtained for this compound, but the oxide ratio $Mn_2O_3:WO_3$ has been determined as approximately 1:22.

(v) Tungsto-chromates:

(n) Ammonium tungsto-chromate, $(NH_4)_8H_2\left[Cr_2W_{22}O_{74}\right]42H_2O$.

Obtained on saturating an aqueous solution of tungsto-chromic acid with ammonium nitrate or ammonium chloride; or alternatively by neutralising directly the aqueous solution of the free acid obtained from the ether addition compound with ammonium carbonate. The deep green coloured solutions thus obtained on filtering, concentrating in vacuuo over concentrated sulphuric acid and being allowed to crystallise deposit large, green, transparent octahedra of ammonium tungsto-chromate. It those green solutions are concentrated by heating, the colour changes to purple, when observed in transmitted light, although in reflected light they still appear green. From such concentrated solutions violet coloured octahedra separate on being allowed to crystallise., but on redissolving these violet crystals in water a green solution is obtained, from which the green salt recrystallises. The violet hydrate is perfectly isotropic, as is shown in plates (i) and (ii), where (i) shows the crystals in parallel light and plate (ii) shows the same field between crossed Nicols. The green hydrate is uniaxial positive in character. It is shown in plate (iii) in parallel light and in plate (iv) between crossed Nicols. The ordinary refractive index of the green hydrate is 1.775 and the extraordinary refractive index is 1.736. This green salt shows parallel extinction. Its specific gravity is 4.619 and an M/500 solution has a pH of 2.83. Analysis of ammonium tungsto-chromate show that it contains 2.444% (2.436%) of Cr_2O_3, 82.10% (81.81%) of WO_3, 3.068% (3.334%) of $(NH_4)_2O$ and 12.39% (12.41%) of water, which represents an empirical formula of $4(NH_4)_2O.Cr_2O_3.22WO_3.43H_2O$. Both the green and purple hydrates are very soluble in water, the violet hydratebeing more stable on exposure to the effects of atmospheric moisture than the green variety.

(o) Barium tungsto-chromate, $Ba_5\left[Cr_2W_{22}O_{74}\right]43H_2O$.

This salt is obtainedas large green, transparent octahedral crystals by crystallisation from solutions of tungsto-chromic acid neutralised directly with barium carbonate. A slight excess

Plate (i)

Plate (ii)

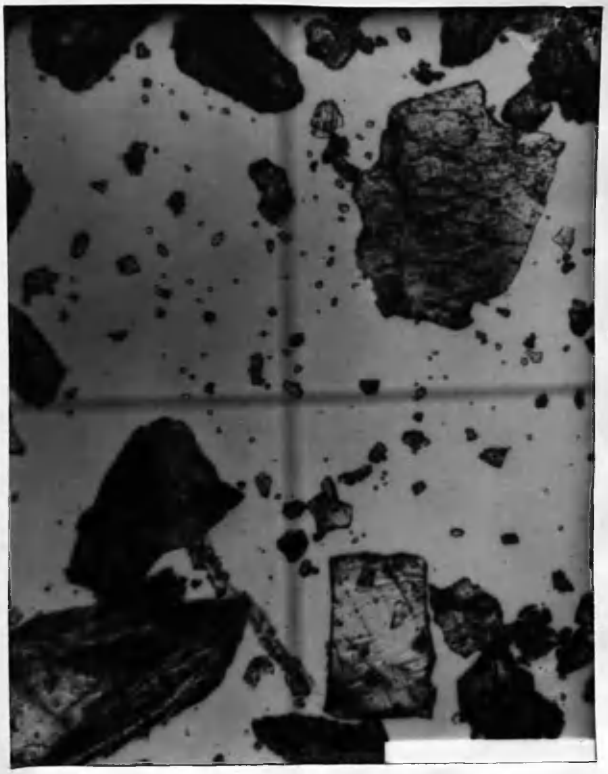


Plate (iii)

Plate (iv)

of barium carbonate is used , after the effervescence, which occurs with each addition has subsided. On filtering; a deep green coloured solution is obtained, from which the barium tungsto-chromate crystallises out on concentration over concentrated sulphuric acid and cooling. On removal from their mother liquor large crystals of the salt are fairly stable, but smaller ones quickly become coated on the surface with a light green powder and gradually fall down into a micro-crystalline mass. The salt has a specific gravity of 4.519, and an M/500 solution a pH of 2.95. As in the corresponding barium tungsto-manganate the complex anion in this salt is sufficiently stable to enable the barium to be precipitated from it as barium sulphate with dilute sulphuric acid without decomposition. From analysis the salt is found to contain 2.210% (2.236%) of Cr_2O_3, 74.98% (75.08%) of WO_3, 11.36% (11.39%) of water and 12.01% (11.28%) of BaO, and so may be represented empirically by the formula, $5BaO.Cr_2O_3.22WO_3.43H_2O$.

(p) Guanidine tungsto-chromate, $(CN_3H_5)_{10}\left[Cr_2W_{22}O_{74}\right]9H_2O$.

Prepared by saturating an aqueous solution of tungsto-chromic acid with guanidine hydrochloride. The guanidine tungsto-chromate precipitates almost at once as a light green amorphous precipitate. On filtering off, redissolving in a larger volume of water, filtering again and allowing to crystallise, the salt is obtained as a light green micro-crystalline powder. It is comparatively insoluble in water but may be recrystallised as rectangular prisms, similarly to the guanidine salts of tungsto-aluminic and tungsto-manganic acids. The refractive index of this compound is of the same order, i.e. greater than 1.7, and it is also biaxial negative and of small optic axial angle. It has a specific gravity of 4.284. An M/500 solution has a pH of 3.54. It contains 2.471% (2.497%) of Cr_2O_3, 83.24% (83.83%) of WO_3, 11.39% (11.01%) of $(CN_3H_5)_2O$ and 2.610% (2.661%) of water, corresponding to an empirical formula of $5(CN_3H_5)_2O.Cr_2O_3.22WO_3.9H_2O$. It is therefore a 10-basic salt, and comparatively anhydrous as far as such heteropoly compounds are concerned.

(q) Potassium tungsto-chromate.

Obtained on saturating an aqueous solution of tungsto-chromic acid with potassium nitrate or potassium chloride as large, green, transparent octahedral crystals, which on removal from their mother liquors quickly become coated on their surface with a light green powder. The specific gravity of the salt is 4.976, and an M/500 solution has a pH of 2.88. Like the other potassium salts described, on boiling its aqueous solutions the complex anion is decomposed. The oxide ratio, $Cr_2O_3:WO_3$ has been determined as roughly 1:22, but no complete analysis has been done.

6. ANALYSES.

(i) General methods:

The analyses of those heteropoly compounds presents many difficulties. In the first instance the ratio of the weight of the central atom to the weight of the tungsten in the molecule is so small (the central atom usually composes 1 - 3% of the total weight of the molecule, calculated as the 3-valent oxide), and the molecular weight is so large (approximately 6 - 6,500), that differences of a fraction of 1% in the estimation of the principal constituent of the compound may mean a considerable difference in the resultant, calculated, empirical formula. Very little information is contained in the literature as to the methods of analysis employed in arriving at the compositions listed. To obtain material of sufficient homogeneity for analyses, it is necessary to recrystallise from water, the specimen concerned at least twice. Even then, due to the manner in which crystals of those substances form, by depositing out almost entirely onl or 2 original crystal nucleii, variable inclusions of mother liquor (which are difficult to remove) are retained by the crystals. It is also necessary to dehydrate the sample before analysis to some constant level, as the water content may vary greatly, according to the atmospheric conditions prevalent at the time of the analysis. This is most satisfactorily brought about by storing the sample for about a week over phosphorus pentoxide, before weighing out for analysis.

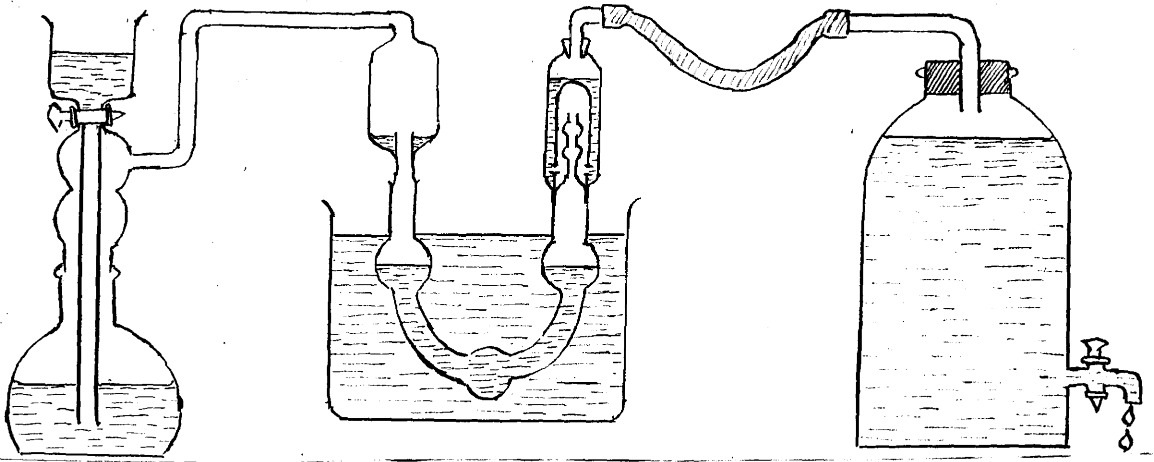
The most satisfactory basis for the solution and decomposition of those compounds is attack with concentrated alkali, which ensures complete destruction of the complex heteropoly anion However, this is not practicable in all cases; in that event, recourse has to be had to degradation of the compound with aqua regia. Another basis for the analysis is to take the ignited weight as the starting point for the estimation, e.g. in the case of the ammonium and guanidine salts, only the central metal oxide and WO_3 will be left on ignition, the ammonium or guanidine volatilising completely. Then from a separate estimation of the ammonia or guanidine, the water content will be obtained as the difference between this estimated value and the total loss on ignition, while the ratio of the central metal oxide to WO_3 may be found from the ignited residue.

The water content is usually taken as the loss in weight on drying at 130°C (Rosenheim). This is not entirely satisfactory in all cases. As will be seen later, any temperature which is selected for this purpose is purely empirical, as there is a continuous loss in weight in the case of most of those compounds as they are heated at successively higher temperatures. The dehydration on heating is continuous and is followed by decomposition without any indication of a definitely or clearly marked break between those 2 stages being indicated. Where all of the oxides involved are non-volatile, as in the sodium, potassium and barium salts, the loss on ignition at 500°C gives the total water content, since those basic oxides remain as the corresponding tungstates. The total water content includes both water of crystallisation and water of constitution, as all of those heteropoly salts decompose well below 500°C. The oxide of the central metallic atom may or may not combine with the WO_3, but it is equally retained. It is doubtful what happens to chromic oxide and manganese sesquioxide on heating with alkali tungstate but at any rate, this method gives a useful check on the analysis total.

The tungsten is usually estimated by precipitation with cinchonine hydrochloride, as cinchonine tungstate, in the presence of concentrated hydrochloric acid. The cinchonine tungstate is a beautifully, white, flocculent precipitate and is very easily filtered and washed. It was found also that quinine hydrochloride can be equally well used in place of cinchonine hydrochloride as a precipitating agent for the removal of tungsten from solutions of those compounds. The cinchonine or quinine tungstate on ignition at 900°C then gives a residue of WO_3, the alkaloid volatilising completely.

Aluminium in the tungsto-aluminates is estimated, after removal of the tungsten, by precipitating with ammonium hydroxide as the hydrated aluminium hydroxide, which on ignition at 900°C goes to alumina. It is preferable, before ignition, to redissolve the aluminium hydroxide in hydrochloric acid, filter off any precipitated WO_3, and reprecipitate with ammonium hydroxide. Normally a few milligrams of WO_3 are still in solution, and if the double precipitation is not carried out the estimation of the aluminium content will be too high. Any excess cinchonine or quinine in the solution will also be precipitated in the presence of alkali, but this volatilises on ignition without affecting the aluminiumestimation.

Manganese in the tungsto-manganates is estimated, after removal of the tungsten, by precipitation as the hydrated, manganese dioxide with a solution of sodium hydroxide in the presence of hydrogen peroxide. Here again a double precipitation is best carried out, in order to eliminate any WO_3 which may still have been in solution. On ignition of this precipitate, Mn_3O_4 is obtained as the residue, which may be recalculated as Mn_2O_3. Alternatively the ignited residue may be treated with concentrated sulphuric acid and evaporated down carefully 2 or 3 times with successive small amounts until it is completely converted to manganous sulphate and weighed as such. That the manganese was actually present in those compounds in the 3-valent form was checked by the following volumetric, oxidation method. About 1 gm. of the heteropoly manganate concerned was dissolved in about 25 ml. of water in the flask of the apparatus shown below. 2 or 3 gms. of potassium bromide were added and 15 ml.



of concentrated hydrochloric acid run in from the dropping funnel, after the apparatus had been assembled, and the absorption tube filled with a solution of potassium iodide in water The bubbler tube at the end of the U-tube was also filled with potassium iodide solution. On heating the heteropoly manganate decomposes snd liberates sufficient bromine from the potassium bromide as is equivalent to the oxidative change involved in the manganese being oxidised to the 4-valent state. The bromine in turn is driven into the U-tube containing the potassium iodide solution under the influence of gently reduced pressure provided by an aspirator connected to the end of the bubbler tube. Here an equivalent amount of iodine is liberated. This iodine in the U-tube and bubbler (if any) combined may then be estimated by titration against a standard sodium thiosulphate solution. By this means it was shown that the manganese in those compounds is actually in the 3-valent state. Had it been contained as 4-valent manganese, e.g. , twice as much iodine would have been liberated, but the values obtained by this method agreed very well with those of the manganese content obtained by the precipitation method described above.

Chromium in the tungsto-chromates is estimated, after removal of the tungsten, by first treating the solution of the tungsto-chromate with potassium bisulphite in order to reduce the chromium to the 3-valent state, or alternatively by reduction with alcohol, but the bisulphite method is preferable as it leaves the solution slightly acid for the subsequent oxidation with peroxide. The green solution thus obtained was then treated with excess sodium peroxide to oxidise the chromium to dichromate, which may then be estimated volumetrically by the addition of a known excess of ferrous ammonium sulphate and back titration against a standard permanganate or dichromate solution.

Barium in the barium salts is estimated by precipitation with dilute sulphuric acid as barium sulphate, which is filtered off and weighed as such. The complex heteropoly anion is sufficiently stable in those acids to enable this to be done without decomposition.

Ammonia in the ammonium salts was estimated on a separate sample by steam distillation with sodium hydroxide and collecting the ammonia evolved in a standard hydrochloric acid solution. Titration of this against standard alkali then gives the ammonia content, which was calculated as the percentage of $(NH_4)_2O$.

Guanidine in the guanidine salts was estimated as nitrogen on combustion by a micro-method (J.C.), the nitrogen being collected and measured at N.T.P. From the volume of this nitrogen the percentage of guanidine was calculated as $(CN_3H_5)_2O$.

In general each compound must be treated empirically, different methods of analysis being used dependent on the other elements present in the molecule and on the behaviour and properties of the particular salt concerned. Complete analyses have been carried out on tungsto-aluminic acid, and on the barium, ammonium and guanidine salts of all 3 acids. In most of the other salts where analyses have not been completed the oxide ratio, $M_2^{+++}O_3:WO_3$ has been determined, working from the basis of the ignited residue of the salt. The individual compounds analysed and the results obtained are detailed below.

(ii) Detailed analytical data:

(a) Tungsto-aluminic acid, $H_{10}[Al_2W_{22}O_{74}]44H_2O$.

About 1.5 gm . of the free acid are used for each estimation. The total water is determined on a separate sample by taking it to be the loss in weight on ignition at 900°C. The aluminium and tungsten remain as their respective oxides. These are separated and estimated as follows. 1.5 gm. of the free acid is dissolved in water and the solution diluted to 200 ml.. On being heated to 60°C, 5 ml. of concentrated hydrochloric acid are added and the tungsten precipitated as cinchonine tungstate or quinine tungstate by the addition of 2 - 3 ml. of a 10% solution of cinchonine or quinine hydrochloride in 1:3 hydrochloric acid. The precipitate is allowed to settle at 60°C for about 20 mins. before filtering off. It is then washed with a hot dilute solution containing 5 ml. of conc. HCl and 5 ml. of 10% cinchonine or quinine hydrochloride in 100 ml. of water. It is redissolved in hot dilute (1:1) NH_4OH and any precipitated aluminium hydroxide filtered off and added to the subsequent precipitate. From the ammoniacal solution the tungsten is reprecipitated with conc. HCl and an additional 1 ml. of cinchonine or quinine hydrochloride. The cinchonine or quinine tungstate is filtered off. washed with the cinchonine or quinine wash solution, dried and ignited at 850°C to WO_3. A minimum temperature of 750°C is necessary to dehydrate the tungstic acid, and WO_3 begins to volatilise at temperatures above 800°C (although this process is very slow below 950°C), so that 850°C is quite a suitable temperature. The filtrate from the tungsten precipitation is concentrated if necessary to 200 ml., 10 ml. of a 10% NH_4CL solution and 5 ml. of conc. HNO_3 added. This solution is heated to boiling and the aluminium precipitated from it by running in slowly with stirring carbonate free NH_4OH solution (1:1) until a faint permanent precipitate forms and then a slight excess. It is essential that a large excess of NH_4OH be avoided, as the aluminium hydroxide begins to redissolve at a pH greater than 8.5. Phenol red is a suitable indicator to use (Ph 6.4, yellow to 8, red) in this connection. After precipitation the solution is boiled for 2 - 3 mins., the aluminium hydroxide filtered off, washed with a dilute solution (2%) of NH_4Cl made alkaline with NH_4OH and then redissolved in dilute HCl. Any WO_3 which separates is filtered off and added to the main tungsten precipitate. The aluminium hydroxide is then reprecipitated as before with NH_4OH, filtered off, washed, dried and ignited at 900°C to Al_2O_3 Results of those analyses are shown in table (vii) below.

(b) Ammonium tungsto-aluminate, $(NH_4)_8H_2\left[Al_2W_{22}O_{74}\right]35H_2O$.

For the estimation of ammonia in this salt, 1.5 gm. are dissolved in about 100 ml. of water, 100 ml. of a solution containing 20 gms. of sodium hydroxide is added and this steam

Table (vii).

% WO_3	% Al_2O_3	% H_2O
84.92	1.703	14.37
84.78	1.665	14.30
84.59	1.638	14.19
84.41	1.717	14.39
84.78	1.650	14.28
84.40	1.596	14.33
84.82	1.712	
84.90	1.623	

84.70 : 1.663 : 14.31 mean %age composition.
(83.83): (1.673 : (14.49)
232 : 101.9 : 18 molecular weights.
22.21 : 1 : 48.69 molecular ratios.

The corresponding theoretical calculated figures are shown in brackets. From these figures it is seen that the oxide ratio, Al_2O_3:WO_3 is approximately 1:22 and that the free tungsto-aluminic acid may be represented empirically as $Al_2O_3.WO_3.49H_2O$, or represented as a 10-basic acid by the formulation

$$H_{10}\left[Al_2W_{22}O_{74}\right]44H_2O.$$

distilled into a standard N/10 solution of HCl. The ammonium salt is thus completely decomposed and the ammonia evolved on decomposition collected in the standard HCl, which may then be titrated against standard NaOH and the ammonia content calculated as the percentage $(NH_4)_2O$. The water content is determined as the loss on weight on heating the salt at 130°C, or alternatively by igniting a sample of the compound at 900°C and finding the total loss in weight. This total loss represents the water content plus the ammonia content, from which if the ammonia content as determined above is subtracted, the percentage water in the salt may be found. For the estimation of the aluminium and tungsten the following procedure is adopted. 1.5 gms. of the salt is weighed out into a pyrex glass basin and evaporated down to dryness 2 or 3 times with aqua regia in order to destroy the ammonia. The residue is then fused with about 5 gms. of Na_2CO_3 and the melt taken up in water. The solution is filtered and diluted to 200 ml. . 5 ml. of conc. HCl are added and the solution heated to 60°C, when 2 to 3 ml. of a 10% solution of cinchonine or quinine hydrochloride is added, to precipitate the W as cinchonine or quinine tungstate. The precipitate is allowed to settle at 60°C for about 20 mins. and then filtered off, washed with a dilute solution containing 5 ml. of conc. HCl and 5 ml. of 10% cinchonine or quinine hydrochloride in 100 ml. of water. It is redissolved in dilute (1:1) NH_4OH, any aluminium hydroxide filtered off and added to the subsequent aluminium hydroxide precipitate, and reprecipitated with conc. HCl and an additional 1 ml. of cinchonine or quinine hydrochloride. This second cinchonine or quinine tungstate precipitate is filtered off, washedwith the cinchonine or quinine wash solution, dried and ignited at 850°C to WO_3. The filtrate from the W precipitation is concentrated if necessary to 200 ml., heated to boiling, 4 - 5 gms. of NH_4Cl added and 0.5 ml. of a 0.1% solution of methyl red added as indicator.

A 1:1 solution of carbonate free NH_4OH is run in slowly with stirring to the end point of the indicator, and boiling continued for a further 2 to 3 mins. The precipitated aluminium hydroxide is filtered off, washed with a hot, dilute (2%) solution of NH_4Cl made alkaline with NH_4OH, redissolved in dilute HCl and any residual W filtered off and added to the main precipitate. The aluminium hydroxide is then reprecipitated as before, filtered off, washed, dried and ignited at 900°C to Al_2O_3. The table (viii) below contains the analytical data which have been obtained for this salt . The theoretical calculated values are shown in brackets.

Table (viii).

% $(NH_4)_2O$	% WO_3	% Al_2O_3	% H_2O
3.055	84.03	1.589	10.38
3.349	84.12	1.636	10.42
3.096	83.82	1.676	10.51
3.455	84.15	1.612	10.41
2.916	83.99	1.683	
3.035	84.76	1.581	
2.940	84.01		
	83.98		
	83.77		

3.121 : 84.07 : 1.629 : 10.43 mean % composition.
(3.432) (84.20) (1.681) (10.69)
52 : 232 : 101.9 : 18 molecular weights.
3.753 : 22.67 : 1 : 36.22 molecular ratio.

From those figures the salt may be represented empirically as $4(NH_4)_2O.Al_2O_3.22WO_3.36H_2O$, or as a salt of a 10-basic acid as $(NH_4)_8H_2\left[Al_2W_{22}O_{74}\right]35H_2O$, making it 8-basic.

(c) Barium tungsto-aluminate.

The method employed in the analysis of this compound is to dissolve about 1.5 gms. of the salt in 200 ml. of water, add 1 ml. of conc. HCl, heat to boiling and precipitate the barium as $BaSO_4$ by the addition of a hot solution of dilute H_2SO_4 (4N). The precipitated $BaSO_4$ is allowed to digest for about 30 mons. before filtering off, washed with a dilute solution of H_2SO_4 (0.5%), dried and ignited at 600°C. The filtrate is concentrated to 200 ml., 5 ml. of conc. HCl added and the W precipitated as cinchonine or quinine tungstate by the addition of 2 -3 ml. of a 10% solution of cinchonine or quinine hydrochloride in 1:3 HCl. The precipitate is filtered off, washed with the cinchonine or quinine wash solution and redissolved in diluteNH_4OH (1:1). Any aluminium hydroxide which separates is filtered off and the W reprecipitated with conc. HCl and a drop of cinchonine or quinine solution. This second precipitate is filtered off, washed, dried and ignited to WO_3. The filtrate from the W precipitation is concentrated to about 200 ml. 4 - 5 gms. of NH_4Cl added and 0.5 ml. of a 0.1% solution of phenol red added as indicator. On heating to boiling, carbonate free NH_4OH is slowly run in with stirring until the red end point is reached. Boiling is continued for 2 - 3 mins. before filtering off the aluminium hydroxide. This is washed with an alkaline solution of NH_4Cl (2%) redissolved in dilute HCl and any WO_3 which separates filtered off. The aluminium is then reprecipitated with NH_4OH, filtered off, washed, dried and ignited at 900°C to Al_2O_3. The results obtained are shown in the table (ix) below.

Table (ix).

% BaO	% WO_3	% Al_2O_3	% H_2O
17.81	68.53	0.5698	14.26
17.25	65.10	0.3462	14.68
16.30	67.79	0.2023	14.53
17.73	64.86	0.3736	14.47
15.01	63.48	0.331	14.26
17.32			

These figures are obviously quite unsatisfactory and valueless for thepurpose of calculating an empirical formula, the aluminium content being apparently very low. However as pointed out previously (cf.page (lxxix)) this salt has never been obtained in a definitely crystalline form and the micro-crystalline material used for this analysis may not have been quite homogeneous, or it may have been contaminated with paratungstate.

(d) Guanidine tungsto-aluminate, $(CN_3H_5)_{10}\left[Al_2W_{22}O_{74}\right]11H_2O$.

The guanidine in this salt is estimated by a micro-combustion method (J.C.) as nitrogen which is collected and measured at N.T.P. From the volume of nitrogen obtained the guanidine content is calculated as the %age $(CN_3H_5)_2O$. The water is estimated as the loss in weight on heating at 130°C or alternatively by igniting the salt at 900°C and finding the total loss in weight. This total loss includes the water content plus the guanidine content, the aluminium and tungsten being left as the corresponding oxides;and the difference between this and the guanidine value as found above gives the %age of water in the salt. In order to estimate the proportionsof W and Al, 1.5 gm. of the salt are weighed into a pyrex glass basin, and evaporated down to dryness 2 or 3 times with aqua regia to destroy the guanidine, and then with conc. HNO_3 to destroy the last traces of organic matter. The residue is then fused with 5 gm. of Na_2CO_3 and the fused mass on cooling extracted with water. The aqueous extract is filtered, diluted to 200 ml., 5 ml. of conc. HCl added and heated to 60°C. 2 - 3 ml. of a 10% solution of cinchonine or quinine hydrochloride in 1:3 HCl are added to precipitate the W. On settling for a few minutes the cinchonine or quinine tungstate is filtered off, washed with a solution containing 5 ml. of conc. HCl and 5 ml. of cinchonine or quinine hydrochloride in 100 ml. of water and then redissolved in dilute NH_4OH (1:1). Any aluminium hydroxide which separates is filtered off and added to the subsequent aluminium precipitate. Thw W is reprecipitated from the ammoniacal solution with conc. HCl and an additional few drops of the cinchonine or quinine solution, filtered off, washed with the wash solution, dried and ignited at 850°C to WO_3.

The filtrate is concentrated if necessary to 200 ml., 5 gms. of NH_4Cl added and 0.5 ml. of a 0.1% solution of phenol red used as indicator. This solution is heated to boiling and the Al precipitated from it by running in slowly with stirring carbonate free NH_4OH (1:1) until the indicator reaches its red end point. Boiling is continued for 2 - 3 mins. before filtering off the aluminium hydroxide, which is washed with a 2% solution of NH_4Cl made alkaline with NH_4OH. The precipitate is redissolved in dilute HCl and any WO_3 which separates is added to the main W precipitate. The aluminium is reprecipitated with NH_4OH, filtered off, washed, dried and ignited at 900°C to Al_2O_3. The analyses obtained are shown in table (x) below, the corresponding, theoretical, calculated values being shown in brackets.

Table (x).

% $(CN_3H_5)_2O$	% WO_3	% Al_2O_3	% H_2O
10.37	84.86	1.709	3.168
	84.79	1.699	3.159
	84.91	1.641	3.155
	84.77	1.698	3.158
	84.82	1.711	
	84.71	1.694	
	84.70		

10.37 : 84.78 : 1.692 : 3.160 mean % composition.
(11.00) (83.79) (1.673) (3.546)
134 : 232 : 101.9 : 18 molecular weights.
4.660 : 22.01 : 1 : 10.57 molecular ratios.

These figures imply an empirical formula $5(CN_3H_5)_2O.Al_2O_3.22WO_3.11H_2O$, or otherwise written $(CN_3H_5)_{10}[Al_2W_{22}O_{74}]11H_2O$.

(e) Ammonium tungsto-chromate, $(NH_4)_8H_2[Cr_2W_{22}O_{74}]42H_2O$.

The ammonia content is estimated on a separate sample of about 1 gm. by dissolving it in 100 ml. of water, adding 100 ml. of a solution containing 10 gms, of NaOH and steam distilling. The ammonia evolved on decomposition is collected in a standard solution of HCl, which on titrating against standard N/10 NaOH gives the amount of ammonia present in the original salt. This is calculated as the %age of $(NH_4)_2O$. The water is taken as the loss in weight on heating at 130°C, or alternatively by igniting a sample of the salt at 900°C, wherby the ammonia an water are completely volatilised. The difference between this total loss and the ammonia content as determined above gives the %age of water in the salt. The Cr and W are estimated as follows. 1.5 gms. of the salt are weighed into a pyrex glass basin and evaporated down to dryness 2 or 3 times with aqua regia to decompose the salt and destroy the ammonia present. The residue on cooling is fused with 5 gms. of Na_2CO_3, the melt extracted with water, filtered and the solution diluted to 200 ml. This is heated at 60°C, 5 ml. of conc. HCl added and the W precipitated from it as cinchonine or quinine tungstate by the addition of 2 - 3 ml. of a 10% solution of cinchonine or quinine hydrochloride in 1:3 HCl. The precipitate on settling for 2 - 3 mins. is filtered off, washed with a solution containing 5 ml. of cinchonine or quinine hydrochloride and 5 ml.

of conc. HCl in 100 ml. of water, and then redissolved in dilute (1:1) NH_4OH. Any chromium hydroxide which separates out is filtered off, redissolved in HCl and added to the subsequent Cr solution. The W is reprecipitated from the ammoniacal solution with conc. HCl and a few drops of cinchonine or quinine hydrochloride. It is filtered off, washed with the wash solution, dried and ignited at 850°C to WO_3. The filtrate from the W estimation, which contains the Cr, is boiled for a few mins. with 20 ml. of H_2SO_4, before adding 1 ml. of a 10% solution of $AgNO_3$, followed by 20 ml. of a 10%^{2} solution of potassium persulphste. Boiling is continued for a further 20 mins. to oxidise the Cr completely to chromate and decompose any excess persulphate. On cooling a weighed excess of ferrous ammonium sulphate is added and the solution titrated against N/10 $KMnO_4$ (which has been standardised against $Na_2C_2O_4$). From this titre the % age of Cr_2O_3 is calculated. Some Cr estimations were also carried out by precipitating as chromium hydroxide and igniting to Cr_2O_3, but the volumetric method is preferred. This is done by boiling the filtrate from the W precipitation with 1 - 2 gms. of potassium bisulphite ($K_2S_2O_4$) to reduce all the Cr to the 3-valent state. Carbonate free NH_4OH (1:1) is then run in slowly with stirring to the yellow end point of methyl red. The precipitated chromium hydroxide is filtered off, washed with a dilute (2%) solution of NH_4Cl, redissolved in dilute HCl, filtered and reprecipitated with NH_4OH

The chromium hydroxide precipitate is finally ignited at 900°C to Cr_2O_3. Results are shown in table (xi) below, where the figures in brackets represent the calculated values. From these the salt may be represented empirically as $4(NH_4)_2O.Cr_2O_3.22WO_3.43H_2O$ or $(NH_4)_8H_2[Cr_2W_{22}O_{74}]42H_2O$, where the ammonium tungsto-chromate is 8-basic.

Table (xi).

% $(NH_4)_2O$	% Cr_2O_3	% WO_3	% H_2O
3.094	2.471	81.80	12.40
3.053	2.394	82.32	12.48
3.072	2.486	82.12	12.31
3.053	2.410	82.09	12.37
	2.459	82.27	
		82.16	
		82.21	
		81.83	

3.068 : 2.444 : 82.10 : 12.39 mean % age composition.
(3.334) (2.436) (81.81) (12.41)
52 : 152 : 232 : 18 molecular weights.
3.668 : 1 : 22.01 : 42.8 molecular ratio.

(f) Barium tungsto-chromate, $Ba_5[Cr_2W_{22}O_{74}]42H_2O$.

The water in this compound is estimated as the loss on ignition at 900°C, as all of the other constituents are non-volatile. The other components are determined as follows. 1.5 gms. of the salt are dissolved in water and the solution diluted to 200 ml. This is heated to boiling and 3 ml. of conc. HCl added. A boiling solution of 4N H_2SO_4 is slowly added until no further precipitation takes place on adding 1 drop more.

The precipitated $BaSO_4$ is allowed to digest for 1/2 an hour and then filtered off. It is washed with a dilute solution of $(NH_4)_2SO_4$ and finally with a very dilute NH_4OH solution (1 ml. of conc. ammonia in 250 ml. of water). On drying the precipitate is heated to constant weight at $600^{\circ}C$ and the barium content calculated as % age BaO. The filtrate from the Ba precipitation is concentrated to 200 ml. , 5 ml. of conc. HCl added and the W precipitated at $60^{\circ}C$ as cinchonine or quinine tungstate with a 10% solution of cinchonine or quinine hydrochloride, in 1:3 HCl. On settling the cinchonine or quinine tungstate is filtered off, washed with the cinchonine or quinine wash solution (5 ml. of cinchonine or quinine hydrochloride and 5 ml. of conc. HCl in 100 ml. of water), and redissolved in dilute NH_4OH (1:1). Any chromium hydroxide which separates is filtered off, redissolved in HCl and added to the subsequent Cr solution. From the ammoniacal solution the W is reprecipitated with conc. HCl and a few drops of cinchonine or quinine hydrochloride, filtered off, washed with the wash solution, dried and ignited at $850^{\circ}C$ to WO_3. The filtrate from the W precipitate is boiled for 5 mins. with 20 ml. of H_2SO_4, before adding 1 ml. of a 2.5% solution of $AgNO_3$, followed by 20 ml. of a 10% solution of potassium persulphate. Boiling is continued for a further 15 mins. to ensure that the Cr is completely oxidised to chromate and that the excess persulphate is all decomposed. The solution is allowed to cool and excess ferrous ammonium sulphate added and the excess titrated against N/10 $KMnO_4$ (standardised against $Na_2C_2O_4$). From the titre the Cr in the original salt is calculated as Cr_2O_3. Some Cr estimations were also carried out by reducing the Cr solution to the 3-valent state with potassium bisulphite ($K_2S_2O_4$), precipitation with NH_4OH as chromium hydroxide and ignition to Cr_2O_3. The analytical data are shown in table (xii) below, and the theoretical, calculated results in brackets for comparison. From these figures the barium tungsto-chromate may be represented empirically as $5BaO.Cr_2O_3.22WO_3.43H_2O$ or $Ba_5\ Cr_2W_{22}O_{74}\ 43H_2O$.

Table (xii).

% BaO	% Cr_2O_3	% WO_3	% H_2O
12.19	2.224	74.92	11.39
12.04	2.231	75.03	11.32
11.98	2.206	74.98	11.41
11.83	2.208	74.81	11.32
	2.192	75.11	
	2.199	75.15	
		74.86	

12.01 : 2.210 : 74.98 : 11.36 mean % age composition.
(11.28) (2.236) (75.08) (11.39)
153.4 : 152 : 232 : 18 molecular weights.
5.384 : 1 : 22.23 : 43.4 molecular ratio.

(g) Guanidine tungsto-chromate, $(CN_3H_5)_{10}\left[Cr_2W_{22}O_{74}\right]9H_2O$.

The guanidine content of this compound is estimated by a micro-combustion method (J.C.) as nitrogen, which is collected and measured at N.T.P. From this corrected volume the guanidine is calculated as the % age $(CN_3H_5)_2O$. For the determination of the other components, 1.5 gms. of the salt is ignited at 900°C. The total loss in weight represents the proportion of water plus the guanidine content, and the difference between this value and the guanidine content as found above gives the % age of water in the salt. The ignited residue consisting of the Cr and W as oxides is fused with 5 gms. of Na_2CO_3 and a little Na_2O_2 and the melt extracted with water. On filtering the aqueous solution is diluted to 200 ml., heated to 60°C, 5 ml. of conc. HCl added and the W precipitated with 2 - 3 ml. of a 10% solution of cinchonine or quinine hydrochloride in 1:3 HCl. On settling the cinchonine or quinine tungstate is filtered off, washed with the cinchonine or quinine wash solution (5 ml. of the above solution and 5 ml. of conc. HCl in 100 ml. of water) and redissolved in dilute NH_4OH (1:1). Any chromium hydroxide which separates is filtered off and redissolved in dilute HCl to be added to the subsequent Cr solution. The W is reprecipitated from the ammoniacal solution with conc. HCl and a few drops of cinchonine or quinine hydrochloride, filtered off, washed with the wash solution, dried and ignited at 850°C to WO_3. The filtrate containing the Cr is boiled with 20 ml. of H_2SO_4 for 15 mins. and concentrated down to 200 ml. 1 ml. of a 2.5% solution of $AgNO_3$ followed by 20 ml. of a 10% solution of potassium persulphate is added and boiling continued for a further 20 mins. until the Cr is completely oxidised to chromate and the excess persulphate is decomposed. On cooling excess ferrous ammonium sulphate is added and the solution titrated against N/10 $KMnO_4$. From the titre obtained the % age Cr in the salt is calculated as Cr_2O_3. Table (xiii) below shows the results obtained from the analyses of this compound, wherethe figures in brackets are the theoretical, calculated values. These corresponmd to the empirical formula

$5(CN_3H_5)_2O.Cr_2O_3.22WO_3.9H_2O$ or otherwise expressed to

$(CN_3H_5)_{10}[Cr_2W_{22}O_{74}]9H_2O$.

Table (xiii).

% $(CN_3H_5)_2O$	% Cr_2O_3	% WO_3	% H_2O
11.39	2.486 2.399 2.452 2.547	82.32 82.98 83.67 82.86 83.49 83.12	2.53 2.67 2.60 2.64

11.39 : 2.471 : 83.24 : 2.610 mean % age composition.

(11.01) (2.497) (83.83) (2.661)

134 : 152 : 232 : 18 molecular weights.

5.228 : 1 : 22.07 : 8.967 molecular ratios.

(h) Ammonium tungsto-manganate, $(NH_4)_8H_2[Mn_2W_{22}O_{74}]48H_2O$.

The ammonia in this salt is estimated on a separate sample of about 1 gm. by dissolving in 100 ml. of water, adding 100 ml. of a solution containing 10 gms. of NaOH and steam distilling. The ammonia evolved on decomposition is absorbed in

N/10 HCl, which is then titrated against standard N/10 NaOH. From the titre obtained the ammonia content of the salt is calculated as the % age of $(NH_4)_2O$. The amount of water present is obtained by igniting about 1.5 gm. of the compound at 900°C and measuring the total loss in weight. This total loss includes the water content plus the ammonia content, and by subtracting from it the ammonia value as determined above, the % age of water in the salt may be found. The W and Mn which are left as the corresponding oxides on ignition are determined as follows. 1.5 gms. of the salt are weighed out and dissolved in 200 ml. of water. This solution is heated to boiling and conc. NH_4OH added until a slight precipitate appears, and then 10 ml. of '20 volumes' H_2O_2, in order to oxidise the manganese to the 4-valent state. A 20% solution of NaOH is then added dropwise until no further precipitation occurs. The liquid is allowed to stand for a further 10 mins. without heating, and the precipitated H_2MnO_3 filtered off rapidly and washed with a hot 1% solution of NH_4Cl. The filtrate is tested for complete precipitation of Mn. The precipitated, hydrated manganese dioxide is redissolved in 1:1 HCl and any WO_3 which separates is filtered off, redissolved in NH_4OH and added to the original filtrate containing the W. From the HCl solution the Mn is reprecipitated as before with NaOH and H_2O_2, the hydrated manganese dioxide filtered off, washed with a 1% NH_4Cl solution, dried, the paper charred at a low temperature and the precipitate then ignited at 900°C to Mn_3O_4 and weighed as such. The ignited residue is afterwards converted to $MnSO_4$ by evaporating down to dryness 2 or 3 times with conc. H_2SO_4. It is preferable to redissolve the $MnSO_4$ in 1:1 HCl as there are sometimes still a few milligrams of WO_3 carried down with the hydrated manganese dioxide even on the second precipitation; this is filtered off (if any) and the Mn in the filtrate evaporated down again with conc. H_2SO_4 and finally weighed as $MnSO_4$. From this weight the Mn content of the original salt is calculated as Mn_2O_3. The filtrate from the Mn precipitation is neutralised with conc. HCl and 5 ml. in excess added. This solution is concentrated down to 200 ml. and 2 - 3 ml. of a 10% solution of cinchonine or quinine hydrochloride in 1:3 HCl added. The precipitated cinchonine or quinine tungstate is allowed to settle for 10 mins. , filtered off, washed with a solution containing 5 ml. of the cinchonine or quinine hydrochloride and 5 ml. of conc. HCl in 100 ml. of water, and then redissolved in 1:1 NH_4OH. The solution is filtered, the W reprecipitated as before, filtered off, washed, dried and ignited at 900°C to WO_3. The results obtained are shown in table (xiv) where the figures in brackets are the calculated values. From those figures it is seen that the ammonium tungsto-manganate may be represented by the empirical formula $6(NH_4)_2O.Mn_2O_3.22WO_3.49H_2O$. The manganese content was also checked by the volumetric oxidation method described on page (xcvi), and the values obtained by this means are also included in table (xiv) in the left hand column under the % Mn_2O_3.

Table (xiv).

% $(NH_4)_2O$	% Mn_2O_3		% WO_3	% H_2O
3.291	2.440	2.471	80.23	13.50
3.601	2.438	2.489	80.01	13.47
3.415	2.457	2.412	80.00	13.92
		2.408	80.60	14.12

3.436 : 2.445 : 80.21 : 13.75 mean % composition.
(3.275) (2.486) (80.35) (13.89)
52 : 157.9 : 232 : 18 molecular weights.
4.286 : 1 : 22.33 : 49.33 molecular ratios.

(i) Barium tungsto-manganate, $Ba_5[Mn_2W_{22}O_{74}]20H_2O$.

The water is estimated by taking it to be the loss in weight on ignition at 900°C as all of the other constituents are non-volatile. The Ba content is arrived at by dissolving 1.5 gms. of the salt in 200 ml. of water, adding 1 ml. of conc. HCl and heating this solution to boiling. On slowly adding a boiling dilute (4N) solution of H_2SO_4, the Ba is precipitated as $BaSO_4$, without decomposition of the complex anion. This is allowed to digest for 1/2 an hour, after it is founf that 1 drop more of H_2SO_4 produces no further precipitation, whilst avoiding a large excess of acid. The $BaSO_4$ is filtered off, washed with a dilute solution of $(NH_4)_2SO_4$ (5ml. of 6N H_2SO_4 and 5 ml. of ammonia in 250 ml. of water), and then with a very dilute solution of NH_4OH (2ml. of ammonia in 250 ml. of water) to redissolve any WO_3 which may precipitate in the acid solution. $BaSO_4$ is almost completely insoluble in dilute NH_4OH. The $BaSO_4$ is heated at 600°C and weighed as such, the barium being calculated as the % age of BaO. The filtrate from the Ba precipiation is concentrated to 200 ml. and conc. ammonia added until a faint precipitate appears and then 10 ml. of '20 vols.' H_2O_2, to oxidise the Mn to the 4-valent state. A 10% solution of NaOH is added dropwise until no further precipitation of hydrated manganese dioxide occurs. The H_2MnO_3 is allowed to settle for 20 mins., filtered and washed with a 1% solution of NH_4Cl, before being redissolved in 1:1 HCl. Any WO_3 which separates is filtered off, redissolved in NH_4OH and added to the main W solution. The Mn is reprecipitated with NaOH and H_2O_2 as before, filtered off, washed with 1% NH_4Cl solution, dried, the paper charred at a low temperature and the precipitate ignited at 900°C to Mn_3O_4, which is weighed. The ignited residue is afterwards converted to $MnSO_4$ by evaporating down 2 or 3 times with conc. H_2SO_4, the $MnSO_4$ redissolved in 1:1 HCl, the solution filtered, and again evaporated down with conc. H_2SO_4, before finally weighing as $MnSO_4$. The Mn in the salt is calculated from this weight as the % age of Mn_2O_3. The Mn was also estimated by oxidation with KBr in HCl solution, the Br_2 liberated in this process being collected in a KI solution and the I_2 liberated here titrated against standard $Na_2S_2O_3$, as described on page (xcvi). The filtrate from the Mn preis neutralised with conc. HCl, 5 ml. in excess added and the solution concentrated to 200 ml. before precipitating the W as cinchonine or quinine tungstate by the addition of 2 - 3 ml. of a 10% solution of cinchonine or quinine hydrochloride in 1:3 HCl. The precipitated W is filtered off, washed with the wash solution (composed of 5 ml. of the cinchonine or quinine hydrochloride solution and 5 ml. of conc. HCl in 100 ml. of water), redissolved in 1:1 NH_4OH, filtered and reprecipitated as before. The cinchonine or quinine tungstate precipitate is finally ignited at 900°C to WO_3. Some estimations were also carried out by evaporating a solution of 1.5 gms. of the salt in 200 ml. of water with a solution of an 80:20 mixture of Na_2CO_3 and NaOH, wherby the Ba and Mn were co-precipitated as $BaCO_3$ and H_2MnO_3 respectively. The W in the filtrate is estimated as before. The mixed precipitate is dissolved in dilute HCl and filtered, and the Ba then precipitated as $BaSO_4$, filtered off and the Mn in the filtrate estimated as before. The analytical results obtained for this salt are shown in table (xv) below. The theoretical values are in brackets and the Mn estimations obtained by the volumetric, oxidation method are in the left hand column under % Mn_2O_3. These figures imply an empirical formula for barium tungsto-manganate of

$5BaO.Mn_2O_3.22WO_3.20H_2O$.

Table (xv).

% BaO	% Mn_2O_3		% WO_3	% H_2O
12.20	2.520	2.453		5.636
12.53	2.489	2.370	80.74	5.664
12.90		2.382	80.72	5.612
12.77		2.612	80.83	5.648
12.86			77.85	
12.58			79.93	
12.64				

12.64 : 2.471 : 79.94 : 5.640 mean % composition.
(12.00) (2.472) (79.89) (5.635)
153.4 : 157.9 : 232 : 18 molecular weights.
5.266 : 1 : 22.02 : 20.02 molecular ratios.

(j) Guanidine tungsto-manganate, $(CN_3H_5)_{10}\left[Mn_2W_{22}O_{74}\right]17H_2O$.

The guanidine in this compound, as in the other guanidine salts is estimated by a micro-combustion method (J.C.), and from the volume of N_2 obtained, collected and measured at N.T.P. the amount of guanidine in the original salt is calculated as the % age of $(CN_3H_5)_2O$. Another sample of about 1 gm. is ignited at 900°C and the total loss in weight measured. This total loss includes both the water and guanidine contents, the Mn and W remaining as their respective oxides; and the difference between this value and the guanidine content as obtained above gives the % age of water in the salt. The Mn and W are determined on another sample of 1.5 gms. by evaporating down 2 or 3 times with aqua regia to decompose the anion and destroy the guanidine; finally with conc. HNO_3 to destroy the last traces of organic matter. The residue is boiled up with 10 gms. of NaOH and 2 gms. of Na_2O_2 in about 150 ml. of water. This solution is filtered and any residue remaining is treated in the same way. The filtrate is put aside for the W estimation. The precipitate which has been filtered off contains the Mn as H_2MnO_3. It is redissolved in 1:3 HCl, and any WO_3 which separates is filtered off, redissolved in NH_4OH and added to the main W solution. The Mn is reprecipitated from the HCl solution with NaOH and Na_2O_2, allowed to settle, filtered off, washed with 1% NH_4Cl solution, the paper charred at a low temperature and the precipitate finally ignited at 900°C to Mn_3O_4 and weighed. The residue after ignition is evaporated down with conc. H_2SO_4 2 or 3 times to convert it to $MnSO_4$, which is redissolved in 1:1 HCl, filtered and evaporated down again with conc. H_2SO_4 before weighing as $MnSO_4$. A separate estimation of the Mn content was also obtained using the volumetric oxidation method described on page (xcvi). The filtrate containing the W is evaporated down to 200 ml. after neutralising with conc. HCl, and adding 5 ml. in excess. The W is precipitated as cinchonine or quinine tungstate with a 10% solution of cinchonine or quinine hydrochloride in 1:3 HCl. On settling, the precipitate is filtered off, washed with the wash solution (containing 5 ml. of cinchonine or quinine hydrochloride and 5 ml. of conc. HCl in 100 ml. of water), redissolved in 1:1 NH_4OH, filtered and reprecipitated with conc. HCl and a few drops of the cinchonine or quinine hydrochloride solution.

The tungsten precipitate is filtered off, washed, dried and finally ignited at 900°C to WO_3. Table (xvi) contains the values obtained on analyses of this salt, the theoretical figures being in brackets, and the Mn estimations obtained by the volumetric , oxidation method are shown in the left hand column under % Mn_2O_3. These figures imply an empirical formula of $5(CN_3H_5)_2O.Mn_2O_3.22WO_3.17H_2O$.

Table (xvi).

% $(CN_3H_5)_2O$	% Mn_2O_3		% WO_3	% H_2O
11.73	2.507	2.516	81.46	4.914
	2.521	2.495	81.04	4.921
		2.518	80.98	4.878
		2.527	80.91	4.887
			80.05	
			80.89	
			80.76	

11.73	2.514	80.87	4.900	mean % age
(10.74)	(2.531)	(81.81)	(4.905)	composition.
134	157.9	232	18	mol. wts.
5.498	1	21.90	17 .10	mol. ratios.

(iii) Summary of analyses:

Thus, a complete analysis has been carried out on 10 different heteropoly compounds, viz. free tungsto-manganic acid, and the ammonium, barium and guanidine salts each of tungsto-aluminic, tungsto-chromic and tungsto-manganic acids. The analysis of barium tungsto-aluminate is inconclusive, but the other compounds are shown to be either 8 or 10-basic salts of

11-heteropoly acids. At least 6 different analyses were carried out for each compound, and the mean value selected in order to calculate the empirical formulation. In the case of the potassium salts of each acid, the oxide ratio $M_2^{+++}O_3:WO_3$ has been determined and found to be approximately 1:22 also. This has also been done for silver tungsto-manganate. Probably the determination of the central atom is most certain in the case of manganese, as 3 different methods of arriving at the manganese content were used, viz. gravimetric precipitation as the hydrated manganese dioxide starting from an aqueous solution of the tungsto-manganate, similar precipitation after Na_2CO_3 fusion of the ignited residue, and the volumetric, oxidation m thod with KBr. Each of those 3 different attacks give agreeable values for the Mn contents. The tungsten estimation will be of the same order of accuracy as the water determination (0.2 - 0.5%), while the estimations of the other constituents will be within the range ± 0.5 - 1.0%. Probably the greatest inaccuracy in those analyses is due to the different degrees of hydration of the salts used.

All of those analyses are summarised in the table (xiii) on page (cxxiv), while table (xiv) on the same page summarises the oxide ratio values, the basicities and the stable hydrates of the same compounds. The abbreviations usedto denote the various salts in those tables indicate the principal components.

Table (xiii).

Compound	Percentage						Composition.			
	$\% M_2^{+++}O_3$		$\% WO_3$		$\% H_2O$		% BaO		$\% (Gu)_2O$ or $(NH_4)_2O$	
	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.
H-Al-W	1.673	1.663	83.83	84.70	14.49	14.31				
NH_4-Al-W	1.681	1.629	84.20	84.07	10.69	10.43			3.432	3.121
NH_4-Cr-W	2.436	2.444	81.81	82.10	12.41	12.39			3.334	3.086
NH_4-Mn-W	2.486	2.445	80.35	80.21	13.89	13.75			3.275	3.436
Ba-Cr-W	2.236	2.210	75.08	74.98	11.39	11.36	11.28	12.01		
Ba-Mn-W	2.472	2.471	79.89	79.94	5.635	5.640	12.00	12.64		
Gu-Al-W	1.673	1.692	83.79	84.78	3.546	3.160			11.00	10.37
Gu-Cr-W	2.497	2.471	83.83	83.24	2.661	2.610			11.01	11.39
Gu-Mn-W	2.531	2.514	81.81	80.87	4.905	4.900			10.74	11.73

probably contains some paratungstate.

Table (xiv).

Compound	Ratio $M_2O_3:WO_3$	Basicity	Hydrate
H-Al-W	1:22.21	10	44
NH_4-Al-W	1:22.67	8	35
NH_4-Cr-W	1:22.04	8	42
NH_4-Mn-W	1:22.33	8	48
Ba-Cr-W	1:22.33	10	43
Ba-Mn-W	1:22.02	10	20
Gu-Al-W	1:22.21	10	12
Gu-Cr-W	1:21.89	10	9
Gu-Mn-W	1:21.90	10	17

7. THERMAL DEHYDRATION EXPERIMENTS.

This series of experiments was undertaken in an attempt to distinguish between the quantity of the total water, in those heteropoly compounds, which is combined as water of constitution and that which is merely held as water of crystallisation. For this purpose, weighed samples of about 1 gm. each of the various salts were retained for 18 hours at a time at temperatures between $100^{\circ}C$ and $300^{\circ}C$ at intervals of $10 - 20\ C^{\circ}$, and the % age loss in weight calculated at each of those stages. After heating to each of those temperatures the samples were allowed to cool for 6 hours in an empty dessiccator before weighing, in order to ensure that a steady equilibrium state had been arrived at. The precaution of keeping the specimens out of contact with the atmosphere during the process of cooling and weighing was taken by having them in silica crucibles inside stoppered glass weighing bottles.

Rosenheim assumes that at $130^{\circ}C$ all of the water of crystallisation is driven off, and that heating at this temperature has the same effect as dehydration over P_2O_5 for a sufficiently long period. It was found, however, that even after dehydrating samples of those salts over P_2O_5 for a fortnight, there was still a further loss in weighton heating at $130^{\circ}C$. It is realised that P_2O_5 will only dehydrate crystals of any size on the surface, but that heating will disintegrate crystals and so ensure a more uniform dehydration. This no doubt will account for the greater loss on heating at 130°C, over that on dehydration at room temperatures.

It would be expected that if any definite hydrates were formed that there would be a discontinuous loss in weight, with evidence of definite breaks at some temperatures between 100°C and 300°C. However, only a gradual and continuous loss in weight was shown as the salt molecules first dehydrated and then decomposed. Signs of decomposition usually first appear about a temperature of 160°C, although this also seems to be only a gradual process. The powder photograph method of Illingworth[29] would probably be very useful here, as any sign of decomposition or change in the structure due to the removal of water, would be very evident from changes in position or intensity of the diffraction lines on such photographs, wheras chemical evidence of decomposition is very indefinite.

The facility with which crystals of tungsto-aluminic acid reform an ether addition compound is very dependent on their state of hydration. If the crystals have been stored under ordinary atmospheric conditions they melt quite readily when mixed with dry ether to form a heavy oil. The viscosity of this oil decreases greatly at first on warming, until as the ether gradually evaporates, the mass becomes more and more viscous, and finally the acid is left in the free condition. It cannot be very easily crystallised from ether, the ether addition compound being quite stable and having a very high vapour pressure. After dehydration at 10 C° intervals between 100°C and 160°C, at which temperature the acid first shows signs of decomposition, the facility with which an ether addition compound is reformed becomes less, and the process much slower to take place. Here again, however, no definite stage could be detected at which it could be said that an ether addition compound was formed, or at which this did not take place. The process becomes so slow at temperatures above 130°C that it is possible that the partially dehydrated acid first absorbs water from the atmosphere before liquefying with the ether. It would appear that the free tungsto-aluminic acid does not only form the ether addition compound most easily when fully hydrated, but that this process takes place right up to the temperatue at which it first shows signs of decomposition, if sufficient time is allowed.

In table (xvii) are listed the % age loss in weight of the various salts which were subjected to this dehydration treatment. The samples of ammonium tungsto-aluminate and guanidine tungsto- manganate were stored over P_2O_5 for 3 days before being thus treated; all of the others had been stored at

Table (xvii).

Temp. °C.	Percentage loss in weight of					
	H-Al-W	Ba-Al-W	NH_4-Al-W	Ba-Mn-W	NH_4-Mn-W	Gu-Mn-W
100			1.787	8.653	8.693	
110	9.183					
120	9.589	6.636	3.353	8.974	8.965	
130	10.23	7.298	3.455	9.835	9.238	
140	11.06	8.005	3.468	10.67		
150	11.62	8.521	3.536	10.82	9.371	0.8354
160	12.93		3.704	10.90		1.299
170		8.837	3.747		9.763	
180					9.993	1.507
190	13.44					
200	13.99		3.841			
210		9.253			10.65	2.342
220	14.46					
230						
240	14.57	9.260	4.545		12.76	
250	14.98					
260				11.55		11.94
270					13.94	
280						
290						
300	15.25	9.723	4.910	11.72	14.07	13.92

ordinary room temperatures. From these figures it will be seen how gradual is the loss in weight during dehydration, and how indefinite is the position where decomposition begins. It will be noted that guanidine tungsto-manganate is apparently almost anhydrous after storing over P_2O_5, and that the decomposition does not become apparent much below 210°C. Caesium tungsto-aluminate also, after the initial loss, which takes place on heating up to 130°C, suffers very little subsequent loss in weight on heating to higher temperatures. In view of the inconclusive evidence derived from those thermal dehydrations, all of the compounds prepared were not subjected to this treatment.

8. MEASUREMENT of some PHYSICAL CONSTANTS.

Some of the principal physical constants of the heteropoly compounds which have been prepared, have been measured. These include specific gravity determinations, estimations of the hydrogen ion concentrations of aqueous solutions, and some of the optical properties such as colour, extinction directions, optical character and refractive indices. For the pH measurements, solutions of approximately M/500 concentration have been chosen. The study of the optical properties has been limited to the more easily crystallisable and stable salts; the easily efflorescent and micro-crystalline materials, such as the potassium salts, being excluded.

(i) Specific gravity:

The specific gravity measurements have been carried out using the specific gravity bottle method, and a liquid in which the heteropoly compounds are insoluble. Any organic liquid which does not contain hydroxyl groupings is suitable for the purpose, preferably one which boils under slightly reduced pressure. Benzene and dioxan were found to be quite suitable. About 2 - 3 gms. of the crystalline salt concerned is used for each determination, in the form of crystals of a size sufficiently small to enter the neck of a 25 ml. specific gravity bottle. The specific gravity of the benzene or dioxan used in those determinations was estimated at the same time. The specific gravity bottle is weighed empty (w_1), and then containing 2 - 3 gms. of the compound whose specific gravity is required, (w_2). The bottle is then approximately 1/2 filled with benzene or dioxan and placed in a vacuum dessiccator, which is evacuated. After about 15 mins. when all of the air bubbles occluded by the sample have been expelled by the gentle boiling of the liquid, the bottle is removed from the dessiccator and filled up to the fiducial mark with benzene or dioxan and reweighed, (w_3). The bottle is also weighed when filled with the liquid, benzene or dioxan, alone, (w_4), and when filled with distilled water, (w_5). From those 5 weighings the specific gravity of the specimen is calculated by

$$\text{specific gravity} = \frac{(w_2-w_1)(w_4-w_1)}{(w_5-w_1)(w_4-w_1) - (w_3-w_2)(w_5-w_1)}$$

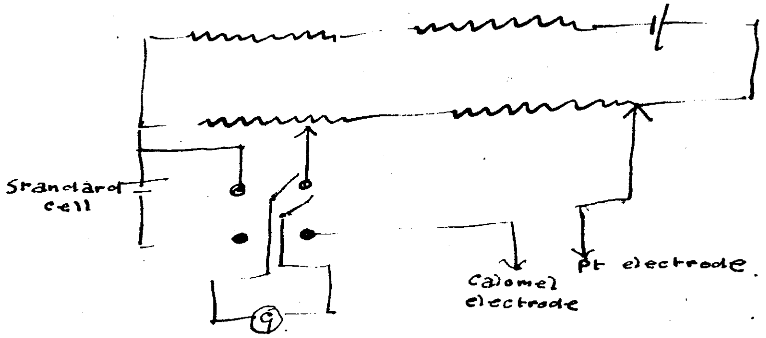
The values obtained are shown in table (xviii) below.

Table (xviii).

Compound	Specific gravity.
Tungsto-aluminic acid	5.624
Ammonium tungsto-aluminate	1.848
Ammonium tungstochromate	4.619
Ammonium tungsto-manganate	3.844
Barium tungsto-aluminate	3.401
Barium tungsto-chromate	4.519
Barium tungsto-manganate	4.178
Potassium tungsto-aluminate	5.511
Potassium tungsto-chromate	4.967
Potassium tungsto-manganate	5.094
Guanidine tungsto-aluminate	4.145
Guanidine tungsto-chromate	4.284
Guanidine tungsto-manganate	4.322
Silver tungsto-manganate	5.828

(ii) Hydrogen ion concentration:

The hydrogen ion concentration of approximately M/500 solutions of the various heteropoly salts prepared have been measured against the standard quinhydrone electrode and the saturated calomel electrode, using the equipment shown in the diagram below.



The potential developed in the aqueous solution was measured using both a gold and platinum electrode as the positive terminal of the system, and the mean value selected. The various compounds are weighed out into a small electrode vessel in sufficient amount to give an approximately M/500 solution when dissolved in 25 ml. of water. The solution is saturated with quinhydrone (about ½ - 1 gm.) and the 2 electrodes inserted into the solution. The saturated calomel or negative terminal is connected through a salt bridge, containing saturated potassium chloride solution, to the appropriate terminal of a Cambridge potentiometer and the gold or platinum electrode (the positive terminal) is connected directly to the potentiometer. On allowing a minute or so to allow the electrode system to come to a steady equilibrium state and depressing the galvanometer key the resistors in the circuit are then altered until no current is shown to be flowing through the galvanometer. When the currentflowing through the circuit is thus balanced the potential is read off in millivolts, and the pH calculated from the relationship

$$pH = \frac{E - E_0}{0.057} = \frac{454 - E}{0.057}$$ at 15°C. where E is the potential

observed. The electrode system may be checked by using a standard buffer solution of potassium hydrogen phthalate in the electrode vessel. The values measured are corrected by adding or subtracting the difference between this figure and the value as actually measured at the time of the determination. To ensure that the metal electrodes are completely discharged at the time of each determination, it is advisable to heat them in an alcohol flame for a few seconds before inserting them into the solution, whose pH is to be determined. The values obtained are shown in table (xix). It will be noticed that the potential as measured against the platinum electrode is usually slightly higher than that measured against the gold electrode.

Table (xix)

Compound	Potential in millivolts		pH
	Au	Pt	
Tungsto-aluminic acid	365	366	1.55
Tungsto-chromib acid	385	385	1.21
Ammonium tungsto-aluminate	254	255	3.50
Ammonium tungsto-chromate	292	293	2.83
Ammonium tungsto-manganate	167	169	5.02
Barium tungsto-aluminate	306	306	2.60
Barium tungsto-chromate	286	286	2.95
Barium tungsto-manganate	209	211	4.28
Potassium tungsto-aluminate	185	185	4.72
Potassium tungsto-chromate	289	291	2.88
Potassium tungsto-manganate	198	200	4.47
Guanidine tungsto-aluminate	185	185	4.72
Guanidine tungsto-chromate	251	253	3.54
Guanidine tungsto-manganate	198	198	4.49
Silver tungsto-manganate	315	317	2.44
Caesium tungsto-aluminate	280	280	3.05

In the case of solutions of the tungsto-manganates reduction takes place on addition of quinhydrone with the precipitation of hydrated manganesedioxide. Generally it will be seen from those figures that the guanidine and potassium salts are more basic than the ammonium salts, which in turn are more basic than the barium salts. All are definitely acid salts.

(iii) Microscopic examination:

This microscopic study of some of the compounds prepared was undertaken to determine some of their principal optical constants, and has been limited to a few of the better crystalline and stable salts. It is proposed later to make a more complete optical and X-ray diffraction study of those heteropoly compounds.

The colour of thin sections of the tungsto-manganates is dependent on the thickness of the crystalline specimen, varying from a light yellow brownin thin layers to a deep red for thicker sections which are almost opaque. The tungsto-chromates similarly are coloured a light yellow green to dark green depending on the thickness of the specimen observed; while the tungsto-aluminates are uniformly colourless. Typically octahedral cleavage is shown by nearly all crystal fragments of those compounds. Silhouette views are usually triangular or triangular with squared corners. Most of the salts appear as prisms or slightly elongated or stunted octahedra; square or rectangular silhouettes are also common. The more elongated crystals show fine traces of cleavage planes on their surfaces. The ammonium salts of all 3 acids, tungsto-aluminic, tungsto-chromic and tungsto-manganic acids, appear to exist each as a cubic, perfectly isotropic hydrate. In the case of ammonium tungsto-aluminate this is the normal form. Ammonium tungsto-manganate when first removed from its mother liquors is anisotropic, but when dehydrated over P_2O_5 becomes isotropic.

On exposure to the atmosphere again it develops weak polarisation colours when observed between crossed Nicols. This more hydrated form is only weakly birefringent of of lower refractive index than the dehydrated specimen. With ammonium tungsto chromate the lower cubic hydrate is coloured violet, while the higher hydrate is green and uniaxial positive. The guanidine salts of all 3 acids are biaxial negative in optical character and of small optic axial angle. It would appear from the manner in which crystals of those guanidine salts orient themselves preferably on one or other of 2 faces each inclined at only a smallangle to the plane of their acute bisectrix that they are most probably monoclinic. Silver tungsto-manganate and caesium tungsto-aluminate crystallise in long prisms which extinguish parallel to their principal length. These prisms are often observed with pyramidal ends. No evidence as to the optical character of the potassium salts could be obtained, due to their very marked tendency to effloresce, especially when crushed. Crushed crystal fragments were used in all cases, except the guanidine salts, which were of a convenient size for microscopic examination as obtained directly from their mother liquors.

The refractivity of those heteropoly salts is very high; only in the case of ammonium tungsto-aluminate was the value og the refractive index found to be below 1.7 Their measurement thus necessitated the use of special media of high refractive index. A saturated solution of the heavy metal iodides (Sn,Sb,As, Bi) in methylene iodide was used for this purpose, as this solution could be further diluted with methylene iodide as required. It was prepared by dissolving 20 gms. of iodoform, 10 gms. of sulphur, 8 gms. of arsenious iodide, 5 gms. of bismuth iodide, and 4 gms. each of arsenious sulphide and antimony sulphide in 50 gms. of methylene iodide. This solution on filtering is very dark red coloured but quite transparent in thin layers. The iodides of Sn, Sb and Bi were prepared directly from their elements by mixing them in CCl_4 and subsequently evaporating off the solvent. As all of the refractive indices measured, with the exception of that of ammonium tungsto-aluminate, were outside the range of the Abbe refractometer (1.3 - 1.7), they had to be measured indirectly by diluting with a miscible liquid of lower refractive index (C_6H_6 or CCl_4) to give a liquid of refractive index lower than 1.7, and so measurable on the Abbe refractometer. From this measured value the original refractive index could then be calculated according to the mixture rule. This measurement was further checked by direct determination of the refractive index, using a hollow cell made from a microscope slide with a hole cut from it of ½ inch diameter, and a cover slip cemented to one side. This was found to give a suitable depth of liquid which was within the working distance of the high power objective of the microscope used. The refractive indices were measured using the Becke line method. A small fragment of the crystal of the salt concerned is placed on a microscope slide, immersed in 1 of the refractive index media, covered with a thin cover slip and using a high power objective (35x), medium eyepiece (6x) and central illumination note taken as to whether or not the refractive indices of the crystals are higher or lower than those of the liquid. The liquid is then altered until one is found in which the crystals are barely visible, and the refractive index of this liquid measured. The refractive indices of the uni-and bi-axial crystals are usually fairly close together and the polarisation colours of a low order. Crystal sections of those compounds which show optic axial interference figures are quite easily recognised as pale grey, usually triangular shaped sections, which do not extinguish completely on rotating the microscope stage between crossed Nicols. On inserting the converging lens and Bertrand lens in the body tube (using a 45 X objective) the interference figures could be observed. Only in the case of ammonium tungsto-chromate (the green hydrate) was a positive uniaxial figure seen; all the other compounds examined were either cubic or biaxial negative. The sign of the interference figure is quite easily distinguished using a 1/4 wave retardation plate and a unit retardation gypsum plate. The principal data obtained are shown in table (xx) below.

Table (xx).

Salt	Colour	Extinction	Optical character	Refractive indices
NH_4-Al-W	colourless		isotropic	1.4599
NH_4-Cr-W (i)	violet		isotropic	
NH_4.Cr-W (ii)	light green	straight	uniaxial positive	$\omega = 1.775$ $\varepsilon = 1.736$
NH_4-Mn-W (i)	yellow to dark red		isotropic	1.798
NH_4-Mn-W (ii)	yellow to dark red	straight	anisotropic	>1.7
Ba-Mn-W	yellow to dark red		isotropic	>1.7
Gu-Al-W	colourless	symmetrical	biaxial negative	all $3 > 1.7$
Gu-Cr-W	light green	symmetrical	biaxial negative	all $3 > 1.7$
Gu-Mn-W	yellow to red	symmetrical	biaxial negative	$\alpha \doteqdot 1.728$ $\gamma \doteqdot 1.762$
*Gu-Fe-W	pale yellow	symmetrical	biaxial negative	$\alpha \doteqdot 1.853$ $\gamma \doteqdot 1.898$
Ag-Mn-W	yellow to dark red	parallel	anisotropic	>1.7
Cs-Al-W	colourless		isotropic	

* Dr Mair's sample.

9. DISCUSSION.

According to Rosenheim[17] the semi-transparent masses obtained on saturating ammonium paratungstate with aluminium hydroxide are not definite compounds, and the free acid cannot be isolated. He also expresses doubt about the existence of the various heteropoly compounds described by Balke and Smith[41], Daniels[40] and Rogers and Smith[39] as containing 3-valent Mn and Cr. Of the corresponding Mo compounds only 6-molybdo-aluminates are known; no compounds of a higher series being formed. 3-

valent manganese does not appear to form molybdate complexes, but 4-valent manganese does, giving apparently a series of 9-molybdo-manganates[36]. Compounds listed in Gmelin's Handbuch such as $3(NH_4)_2O.Al_2O_3.9WO_3.4H_2O$; $8BaO.Al_2O_3.9WO_3.7H_2O$; $5Hg_2O.Al_2O_3.9WO_3.nH_2O$ and $ZnO.Al_2O_3.9WO_3.20H_2O$ are variously described as semi-transparent, amorphous or micro-crystalline. The only salt of 3-valent manganese contained in the literature is $(NH_4)_4H_5\left[Mn^{+++}(WO_4)_6\right]9H_2O$ (Rosenheim's formulation) or $4(NH_4)_2O.Mn_2O_3.12WO_3.23H_2O$. Although thus formulated the composition of those salts must remain doubtful, as being prepared from solutions in which very complicated conditions of equilibrium exist, the crystallisable product will be quite variable. There cannot be the same doubt about the homogeneity of salts prepared directly from the free acids and capable of being recrystallised from water.

As has been shown the sodium salts of tungsto-aluminic, tungsto-chromic and tungsto-manganic acids are obtained on saturating boiling solutions of sodium paratungstate with the respective salts of the 3-valent metals. Solutions of sodium paratungstate show a rise in pH on boiling and this increased alkalinity persists on cooling. It has been suggested vy von Knorre[46] that this is due to the hydrolytic fission of the para~~normal~~ tungstate to normal tungstate and metatungstate, the increase in pH being due to the normal tungstate (cf. page xxxv).

The precipitate which is initially formed on adding the metal salt to the paratungstate solution redissolves readily up to a certain point, where it becomes permanent. It is probable that in the boiling paratungstate solution, the normal tungstate acts as both hydrolytic agent and precipitant for the salt of the 3-valent metal, and that the 3-valent metal ion in part replaces the hydrogen ion in the spontaneous change of paratungstate ion, $\left[W(W_6O_{21})\right]^{6-}$, to metatungstate ion, $\left[H_2W_{12}O_{40}\right]^{6-}$, and that the paratungstate merely provides the material for these reactions. There is some indication that sodium paratungstate on saturation with the activated hydroxides of the 3-valent metals gives similar products, but whether paratungstate is an intermediate in this process is not certain. Acidification of boiling sodium tungstate or paratungstate gives quantitative conversion to metatungstate[46]. But it is possible that the added acid merely converts the normal tungstate (the most alkaline component) to paratungstate, which again undergoes hydrolytic fission into the normal tungstate and metatungstate, this cycle being repeated until finally only metatungstate remains. The reaction is thus not merely the displacement of a weak acid (the tungstic acid) by a stronger acid but represents a complex hydrolytic equilibrium being driven to completion, and this hydrolytic equilibrium exists from the beginning in the paratungstate solution. Therefore the preparation of heteropoly tungstates by saturation of sodium paratungstate solutions must be carried out to keep pace with this hydrolytic displacement. Therefore all preparations carried out in this way are accompanied by some metatungstate. It would appear also that one of the deciding factors as to whether or not a particular element may be induced to act as the central atom in a heteropoly tungstate is not so much dependent on the atomic radius or stability of the atoms of that element, but on the solubility of its paratungstate. This will only be a determining factor, however, where the paratungstate is so insoluble that the hydrolytic conversion of the metal salt to the hydroxide never gets started. This hydrolytic action in turn can only take place for metals whose hydroxides are precipitated in solutions of pH values 6 - 7, the pH of the boiling paratungstate being about 6.4. This list certainly includes 3-valent aluminium, manganese and chromium. The reaction mechanism seems to be then, that partial hydrolysis of the metal salt added gives a transient precipitate of a tungstate more acid than the metal paratungstate (probably the pentatungstate). This immediately reacts with the alkali paratungstate, finally giving rise to the alkali salt of the heteropoly acid, in the same way as tungstic acid added to boiling sodium paratungstate solutions forms sodium metatungstate. It may also be related to the capacity of the elements concerned to form co-ordination compounds with aggregates of weakly negative groups (parallel with the corresponding complex cyanides), but why in one or two cases only compounds of the 6-type are formed , nor why the heteropoly molybdates should (with the exception of 4-valent manganese, which does not form a heteropoly tungstate) all be of the 6-type, it is not clear. Yet the reaction mechanism seems to be similar , since in the preparation of sodium-6-molybdoferrate, ferric pentamolybdate is also formed in small amount. A further factor which may be of importance in the case of chromium is the stability of the hexa-hydrated chromium ion, $\left[Cr(H_2O)_6\right]^{+++}$.

From the analytical results described above, it seems that the 3-valent metals aluminium, chromium and manganese form 11-heteropoly acids with tungsten, and that the anion may be represented by $\left[M_2^{+++}W_{22}O_{74}\right]^{10-}$. Up to the present time the structure of only 3 of such complex ions has been elucidated, viz. tungsto-phosphoric acid[27], tungsto-silicic acid[29,53] and tungsto-boric acid[53]. Metatungstic acid has a similar structure. Actually only the structure of tungsto-phosphoric acid was deduced from original powder photographs, the others being assumed similar from identity of diffraction photographs All of these are 12-acids. It has been suggested[23] that 11-acids and in general unsaturated acids of such add series as 10, 10½ and 11 may have a structure composed of a combination of 2 or more of such anions, and based on a larger polyhedra of the same type , such as the cubo-octahedron, but containing

2 central atoms. According to this structure, whatever the detailed arrangement within the molecule may be, the maximum basicity of such acids containing 3-valent central atoms would be 10, as appears to be so with the above compounds. Riesenfeld and Tobiank[25] have attempted theoretically, to formulate structures for all heteropoly compounds, based purely on the geometrical arrangement of WO_4 and WO_6 groups, tetrahedral and octahedral respectively. Indeed, this system serves to substantiate Rosenheim's original methods of formulation involving WO_4 and W_2O_7 groups, at the same time giving a simple explanation for previously unexplained facts, such as the existence of 2 different valency states of the same acid (e.g. the 4 and 8 basic salts of tungsto-silicic acid). According to more recent structural considerations, arising fromthe work of Santos[53], Illingworth[29] and Signer and Gros[28] the number of hydrogen atoms external to the acidic anion is of very little importance in determining the basicity of such compounds. The principal consideration appears to be the packing of the constituent atoms, the number of hydrogen atoms replaced by any metal in salt formation being determined primarily by the size of that atom and the space available for it in the molecule. Thus the larger caesium atoms form less basic salts than the smaller lithium atoms, although the alkali metals are normally uniformly monovalent. Also it would be expected that in a compound containing a smaller central atom, more space would be available for the

packing of additional water molecules than in a compound containing a larger central atom. Also a normal salt should have a lower water content than an acid salt due to the same considerations.

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