484. *Heteropoly-tungstic Acids and Heteropoly-tungstates. Part I. 11-Tungstoferric*(III) *Acid and its Salts.*

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The reaction between ferric salts and sodium paratungstate in boiling aqueous solution has been investigated, and 11-tungstoferric(III) acid, the first member of a new series of 11-heteropoly-tungstic acids with mainly positive central ions, has been isolated. The acid and a number of its salts have been described and analysed, and a reaction mechanism has been suggested to account for their formation. In all, three methods of preparation have been studied, one or more of which can be used to determine with reasonable certainty whether any metallic ion forms a heteropoly-tungstate and, if so, to which series it belongs. A rapid and economical method for the preparation of metatungstic acid and of sodium metatungstate has also been indicated.

Although the field of heteropoly-molybdate and heteropoly-tungstate preparation, apart from subsidiary valency states of the central ion, has been very fully investigated since the discovery by Marignac of the tungstosilicates, no clear picture of the mechanism of formation of these compounds can be derived from a study of the relevant literature. Whether a particular ion is capable of heteropoly-molybdate or -tungstate formation depends on two factors, the structural and the chemical. There is at present no means of predicting whether an ion can form part of a stable condensed anion containing between 6 and 12 MoO_3 or WO_3 residues; the question must be answered by experiment. The chemical factors are more amenable, and some indication of their nature can be obtained from consideration of the equilibrium between molybdate or tungstate ions and hydrogen ions in aqueous solution.

Acidification of alkali molybdate or tungstate solutions, provided that these are not too concentrated and that the temperature is kept near the boiling point to allow equilibrium to be more rapidly attained, leads eventually (at pH values near 3) to almost quantitative formation of alkali metamolybdate or metatungstate. On further acidification (to $pH < 1$), molybdic acid passes through its isoelectric point and forms cationic complexes with the anion of the acid used in acidification; the metatungstate ion, on the other hand, behaves as a stable ion, giving rise to metatungstic acid, $H_6[H_2W_{12}O_{40}]$,aq. This acid is the hypothetical parent of all 12-heteropoly-tungstic acids, these being derived from it by replacement of hydrogen ion by other anions, or, as the sequel shows, by cations. No comparable stable form of molybdic acid is known (apparently the $Mo_{12}O_{40}$ group is stable only in presence of co-ordinated negative ions), and to this is doubtless due the smaller number and generally lower stability of the heteropoly-molybdic acids. Heteropoly-compounds containing between 11 and 8 MoO_3 or WO_3 residues to each central atom are either derived from 12-acids by hydrolysis, or represent the upper attainable limit of saturation consistent with stability.

If another ion is present along with molybdate or tungstate during acidification, it may replace hydrogen ion in the condensed molybdate or tungstate nucleus, thus giving rise to a heteropoly-compound. Whatever the details of preparation may be, all heteropoly-acids are formed in this way. Where the central ion is negative, *e.g.*, PO_4^{3-}, preparation of the heteropoly-acid is a simple matter, stoicheiometrical relations being of minor consequence, so long as the minimum quantity of central ion demanded by the formula is present. Where the central ion is positive, excess over the stoicheiometrical proportion may lead to decomposition, through secondary precipitation reactions, of the heteropoly-compound already formed.

The rule by which the correct relative proportions of positive ion and molybdate or tungstate ion may be determined is simple, and follows from what has already been stated. With sodium paramolybdate or paratungstate as initial substance (the usual material for heteropoly-compound preparations), and complete hydrolysis of the added salt containing the required positive ion being assumed, saturation is complete when the acid derived from hydrolysis is just sufficient to convert the molybdate or tungstate from the para- into the meta-form. The process is thus an indirect acidification of paramolybdate or paratungstate solutions to an extent which, an equivalent amount of mineral acid being used for the purpose, would give the meta-form. In general, if no heteropoly-compound is formed, and if the equilibrium is not disturbed by secondary precipitation, which usually takes place in such cases, the final product is sodium metamolybdate or metatungstate. If the metatungstic acid, obtained from the latter by extraction with ether and hydrochloric or sulphuric acid, shows no trace of the originally added ion, the evidence for heteropoly-compound formation is almost certainly negative.

If the salt formed is of the higher series, with 8 or more MoO_3 or WO_3 residues, and if no secondary precipitation has taken place during saturation, the solution will have a pH similar to that of an equivalent metamolybdate or metatungstate solution, and the free heteropoly-acid may be isolated as its ether addition compound by extraction with ether and sulphuric or hydrochloric acid, or, though this is less conclusive, the solution may be used for preparation of salts by double decomposition. If the solution, however, has a pH similar to that of the original paramolybdate or paratungstate solution, only a 6-heteropoly-molybdate or -tungstate is present, again on condition that there has been no secondary precipitation during saturation. Since the alkali salts of the 6-series are usually of low solubility in water, they normally crystallise from solution on cooling. Where no heteropoly-compound is formed, precipitation of double metal–alkali metal paramolybdates or paratungstates usually takes place from an early stage of the saturation, though such precipitation must not be taken as conclusive without further trial by the alternative methods of saturation described below.

Since boiling sodium paratungstate solutions of the concentration used have a $pH > 6{\cdot}4$, it follows that all cations whose hydroxides precipitate (or begin to precipitate) at this value of pH, or below it, are potentially capable of heteropoly-tungstate formation. Comparable sodium paramolybdate solutions have a lower pH (*ca.* 4·8). Their hydrolytic capacity is thus substantially less, and so far it has not been found possible to prepare a heteropoly-molybdate of type higher than the 6-type, with a positive central ion. An approximate relation between heteropoly-molybdates and heteropoly-tungstates having the same positive central ion is that, when the heteropoly-molybdate is a 6-compound, as with Fe^{3+}, Al^{3+}, Cr^{3+}, the corresponding heteropoly-tungstate is an 11- or 12-compound, and *vice versa.* In the case of Mn^{3+}, structural factors must also be involved, since, while tungsten gives an 11-heteropoly-compound, molybdenum reacts only with quadrivalent manganese, and tungsten does not. It is obvious that with cations such as Ag^{1+}, Hg_2^{2+}, Hg^{2+} and Pb^{2+}, whose normal, para-and meta-molybdates are all of low solubility, heteropoly-molybdate or -tungstate formation is scarcely possible, because of limits set by secondary ionisation of any complex formed, and by the restricted range of methods of preparation, though the pH relations for salt hydrolysis are favourable.

In the sequel, alternative methods of preparation are described which can be applied as tests of heteropoly-compound formation in such and similar cases, and for use when a weakly basic cation, *e.g.*, Bi^{3+} or Sb^{3+}, can only be retained in solution by an excess of mineral acid, which would preferentially give rise to metamolybdate or metatungstate before the desired hydrolysis was under way. Many anomalous heteropoly-compounds, particularly of tungsten, with positive central atoms, are described in the literature, and it is intended, on the basis set out, to establish some degree of order in this field, on the purely chemical side at least.

The only 6-heteropoly-tungstates so far described are the 6-tungstoferrates (Rosenheim and Schwer, *Z. anorg. Chem.*, 1914, **89**, 234). These belong to a series which, for molybdenum, includes the 6-molybdo-ferrates, -chromates, -aluminates, and -rhodates. As Rosenheim (Gmelin, " Handbuch," Syst. Nr. 54, 396; Abegg, " Handbuch," Vol. 4, Part 1, ii, p. 1050) has given varying accounts of the preparation and properties of the 6-tungstoferrates, the matter was reinvestigated as a preliminary to the preparation of the chromium and aluminium analogues. These 6-heteropoly-compounds are of paratungstate or paramolybdate type, having a tervalent central atom; the 6-tungstoferrates derive from a hypothetical acid $H_9(FeW_6O_{24})$,aq. Since the molybdenum analogues are appreciably dissociated into their components in aqueous solution, it would seem unlikely that 6-tungstoferric acid could exist in the free state. The sodium salts of these compounds are prepared by saturation of boiling sodium paratungstate or paramolybdate solutions with the nitrate or chloride of the tervalent metal. From the solution of the sodium salt of the 6-heteropoly-compound thus obtained, the other salts are prepared by double decomposition. Although the alkali paramolybdates are correctly represented by the general formula $3R_2O,7MoO_3$,aq., the formulation of the alkali paratungstates is less certain. Analytical results favour the formula $5R_2O,12WO_3$,aq., but, on grounds of general resemblance between molybdenum and tungsten compounds, the $3R_2O,7WO_3$,aq. formulation seems preferable. Anderson's suggestion (*Nature,* 1937, **140**, 850) that the paramolybdates and paratungstates are in fact $R_6[Mo(MoO_4)_6]$,aq. and $R_6[W(WO_4)_6]$,aq., emphasises in particular the very marked differences in chemical behaviour between alkali paratungstates and metatungstates, the latter being undoubtedly dodecatungstates.

Aqueous solutions of sodium paratungstate show a marked rise in pH on boiling, the increased alkalinity persisting after cooling. It was suggested by von Knorre (*Ber.*, 1885, **18**, 2363) that this behaviour is due to hydrolytic fission of the paratungstate ion into normal tungstate and metatungstate ions, $3(3Na_2O,7WO_3) \rightleftharpoons 5Na_2WO_4 + 4(Na_2O,4WO_3)$, the rise in pH being due to the normal tungstate. Rosenheim and Wolff (*Z. anorg. Chem.*, 1930, **193**, 54) have isolated metatungstates by double decomposition from such sodium paratungstate solutions, the equilibrium in which is certainly complex. Souchay (*Ann. Chim.*, 1943, **18**, 87) has shown that metatungstate ion cannot exist at pH values similar to those prevailing in sodium paratungstate solutions. The behaviour of metatungstate ion alone in buffer solutions of pH 6·5 does not, however, invalidate von Knorre's hypothesis, since in sodium paratungstate solutions the metatungstate ion is derived from paratungstate itself, and would be regenerated at once if destroyed. Experience shows that pH alone, although distinctive for each separate species of tungstate, gives little indication of the relative proportions of each in solutions whose history is not known.

In a series of studies of the neutralisation curves of Na_2MoO_4 with hydrochloric acid, Byé (*Bull. Soc. chim.*, 1942, **9**, 360; 1943, **10**, 239; *Ann. Chim.*, 1945, **20**, 463) has shown that in solutions of constant ionic strength (M. in NaCl) breaks are obtained at points corresponding to para-, tri-, and tetra(or meta)-molybdate for solutions 0·01—0·02M. in $Na_2MoO_4,2H_2O$. More concentrated solutions show extremely complex equilibria, the complexity increasing with concentration, while in very dilute solutions (0·0003M.) only the simple MoO_4^{2-} ion can be recognised. In dilute solutions, in the absence of added sodium chloride, the neutralisation curve is continuous, with a marked fall in pH only at the tetramolybdate stage, the condensation to more acidic multivalent ions masking the pH changes corresponding to para- and trimolybdate. Doucet and Carpéni (*Bull. Soc. chim.*, 1947, **14**, 496) found the isoelectric point for MoO_3,aq. to be at pH 0·9; at lower pH values molybdenum is present as a cation MoO_2^{2+} or MoO^{4+}. The change from normal molybdate to cationic complex is thus continuous in dilute solution, possibly accounting for the fact that no metamolybdic acid corresponding to metatungstic acid has yet been isolated. Byé (*Ann. Chim.*, 1945, **20**, 504) has assumed that an equilibrium of the von Knorre type is set up in paramolybdate solutions: $3Mo_7O_{24}^{6-} \rightleftharpoons 4Mo_4O_{13}^{2-} + 5MoO_4^{2-}$, moving to the left in concentrated solutions and to the right on dilution, an ion $Mo_6O_{20}^{4-}$ appearing between the para- and the tetra-molybdate stage.

Much work has been done on the neutralisation curves of $Na_2WO_4,2H_2O$, but with conflicting results. Tungstic acid, unlike molybdic acid, does not form cationic complexes, and its isoelectric point is at considerably higher pH values. On acidification of solutions of Na_2WO_4 at room temperature white hydrated tungstic acid separates, redissolving in the residual tungstate up to the point where paratungstate formation is complete: pH *ca* 6·4. Beyond this point, depending on the concentration of the solution, either the precipitate of WO_3,xH_2O becomes permanent or, in more dilute solutions, the tungstic acid remains in colloidal suspension, being precipitated only after keeping. In neither case does the whole of the tungstate ion remain to take part in the equilibrium, and neutralisation curves obtained under these conditions vary considerably, and in no case represent a true equilibrium between tungstate and hydrogen ions. If the acidification is carried out at the boiling point, however, no separation of tungstic acid occurs, and the pH of the solution can be brought below 2 without precipitation of WO_3,xH_2O. At pH values below 3·6 the solution is stable to strong acidification, and from it the ether addition compound of metatungstic acid can be obtained in quantitative yield. Acidification of alkali tungstate solutions at higher temperatures therefore finally gives metatungstate, and the equilibrium, as with molybdate solutions at ordinary temperatures, is homogeneous throughout, provided that, as emphasised by Doucet and Carpéni (*loc. cit.*, p. 486), time is allowed for equilibrium to be attained at each stage of acidification. According to Souchay (*loc. cit.*, p. 69), unless the ionic strength of the solution is kept constant (M. or 2M. in sodium chloride) during acidification, the neutralisation curve obtained shows no break corresponding exactly to paratungstate, but to metatungstate only, the change in $[H^{\cdot}]$ due to more acid salt formation being concealed or displaced by that caused by formation of polytungstate ions. Boiling of the solution after each addition of acid, although it gives higher pH values at each stage, still gives only the break at metatungstate, with nothing intermediate. Vallance and Pritchett's titration curves (*J.*, 1934, 1586) are exceptional in this respect, the formation of paratungstate being clearly shown, owing no doubt to the high concentrations of sodium tungstate and acid used. Preliminary experiments on the neutralisation of 0·022M-Na_2WO_4 with 0·1M-HCl, the tungstate solution being kept at the boiling point until, after cooling, a maximum value of pH was obtained at each stage of acidification (8—12 hours), show a well-defined break in the neutralisation curve at the paratungstate stage (pH *ca.* 6·7), a region of constant pH round the tritungstate stage (though no $Na_2O,3WO_3$ could be isolated from solution), and an abrupt break from pH *ca.* 5·8 to pH *ca.* 3·9 at the metatungstate stage. Na_2MoO_4 solution (0·022M.), similarly treated, showed no marked break in the neutralisation curve either in hot or in cold solution, even at the tetramolybdate stage. The molybdate pH values were 0·1—0·2 pH unit higher for the heated solution (after cooling) than for the corresponding stage of acidification in cold solution. Beyond $Na_2O,4{\cdot}2WO_3$ and $Na_2O,4{\cdot}2MoO_3$ the titration curves were coincident. The successive steps in the tungstate neutralisation in hot solution would doubtless be better defined in solutions of constant ionic strength, as used by Byé and Doucet and Carpéni (*locc. cit.*), but the essential point, as regards the present investigation, is the quantitative formation of metatungstate by the slow acidification of boiling normal tungstate or paratungstate solutions with an acid sufficiently strong to bring the final pH below 4, and its bearing on the interaction of paratungstate solutions and solutions of metallic salts capable of yielding hydrogen ion by hydrolysis.

The mechanism of 6-heteropoly-molybdate formation, by saturation of paramolybdate solutions with solutions of metallic salts, is obscure. The formation of ferric pentamolybdate, $Fe_2O_3,5MoO_3$,aq. (Marckwald, Diss., Basel, 1895), as a by-product of the saturation of $3Na_2O,7MoO_3$ solutions with aqueous ferric chloride suggests that hydrolysis of the ferric chloride gives rise in part to products more acid than paramolybdate.

Saturation of boiling sodium paratungstate solutions with aqueous ferric nitrate gives a precipitate varying in composition between $Fe_2O_3,3{\cdot}3WO_3$,aq. and $Fe_2O_3,4{\cdot}3WO_3$,aq., dissolving readily in the residual paratungstate solution up to a fairly definite point, at which it becomes permanent. If sodium paratungstate, derived by acidification from 6 moles of $Na_2WO_4,2H_2O$ is used, precipitation becomes permanent when about 0·75 mole of ferric nitrate nonahydrate has been added. Saturations carried beyond this point give a mother-liquor much poorer in iron, as is to be expected from the composition of the precipitate. There is thus a fairly definite optimum point in the saturation. The precipitate dissolves readily and almost completely in boiling sodium paratungstate solutions to give a solution of similar properties to that from which it originally separated, the process resembling the conversion of sodium paratungstate into metatungstate by saturation of a boiling solution of the former with WO_3,xH_2O, the pH of the solution falling from above 6·4 to between 3 and 4. At the point in the saturation of sodium paratungstate with ferric nitrate where precipitation becomes permanent, the pH of the solution has also fallen to between 3 and 4, and acidification no longer precipitates WO_3,xH_2O. To convert 6 moles of $Na_2WO_4,2H_2O$ from $3Na_2O,7WO_3$,aq.(para-) into $Na_2O,4WO_3$,aq.(meta-) without loss of tungsten, requires 2·14 equivs. of acid. Complete hydrolysis of the added ferric nitrate being assumed, 2·14 equivs. of acid would be given by 0·71 mole, approximately the amount required for optimum saturation of the sodium paratungstate used. In the saturation of sodium paratungstate with ferric salt it appears that the maximum iron content of the solution is attained when, complete hydrolysis of the ferric salt being assumed, the hydrogen ion set free is just enough to convert the whole of the paratungstate into metatungstate. This stoicheiometric relation has been found to apply generally to saturations of sodium paratungstate solutions with solutions of metallic salts, provided no secondary precipitation takes place. The solutions then have a pH value similar to that of an equivalent sodium metatungstate solution, and are similarly stable to strong acidification. It may be that, in the boiling paratungstate solution (a hydrolytic equilibrium of the von Knorre type being assumed) the normal tungstate acts both as hydrolytic agent and as precipitant for the ferric salt, and that the ferric ion in part replaces hydrogen ion in the spontaneous change of paratungstate ion $[W(W_6O_{24})]^{6-}$ to metatungstate ion $[H_2W_{12}O_{40}]^{6-}$, the paratungstate merely providing the material for these reactions. Saturation is complete when insufficient paratungstate remains to carry either reaction further. There is some indication that sodium metatungstate, on saturation with ferric hydroxide, gives identical products, but whether this is due to direct replacement of hydrogen ion by ferric ion in the metatungstate ion, or whether reversion to paratungstate forms an intermediate stage, is not certain.

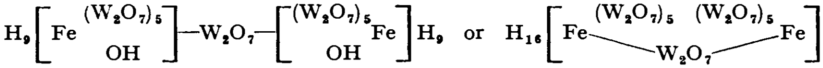
Acidification of boiling sodium tungstate or paratungstate solutions, with an acid sufficiently strong to give a final pH between 3 and 4, gives quantitative conversion into metatungstate (von Knorre, *loc. cit.*). Here again it is possible that the acid merely converts the normal tungstate (the most alkaline component) into paratungstate, which again undergoes hydrolytic fission to normal tungstate and metatungstate, the cycle being repeated till finally only metatungstate remains. The reaction is thus not a simple displacement of the weak " tungstic acid " by a stronger acid, but represents the driving to virtual completion of a complex hydrolytic equilibrium present from the first. Preparation of heteropoly-tungstates by saturation of sodium paratungstate solutions must therefore be carried out slowly to keep pace with the hydrolytic displacement, and neglect of this precaution, especially in saturations with metallic salts, may lead to failure in the isolation of these compounds. Absence of paratungstate, corresponding to complete saturation, cannot be safely assumed even at pH values below 4, unless saturation has been extended over several hours. Even in acidified molybdate solutions equilibrium is only slowly reached, though stable values of pH may be obtained almost at once (Doucet and Carpéni, *loc. cit.*, p. 486).

Almost all methods for the preparation of heteropoly-tungstates depend on saturation of boiling sodium paratungstate solutions with a compound containing the ion which is to form the central ion in the heteropoly-tungstate anion, and, if the von Knorre hypothesis is accepted, all such preparations must contain more or less sodium metatungstate, the amount varying inversely with rapidity of formation of the heteropoly-tungstate. This applies even more to the use of ammonium paratungstate for such preparations, since it passes spontaneously into metatungstate when its solutions are boiled. Heteropoly-tungstic acids derived from such saturations will therefore be accompanied by more or less metatungstic acid.

The potassium and ammonium 6-tungstoferrates described by Rosenheim and Schwer (*loc. cit.*) could not be reproduced, no definite compounds separating when the product of saturation was treated with concentrated potassium chloride or ammonium chloride solution. Guanidine hydrochloride gave yellow microcrystalline products of variable composition, all containing more tungsten than required by the 6-formulation. The pH of the saturation products and their stability to strong acidification showed that compounds of paratungstate type could only be present in small amount, if at all.

Treatment of the products of saturation with ether and 6M-sulphuric acid (Drechsel, *Ber.*, 1887, **20**, 1452) gave a typical heteropoly-acid–ether addition compound. Analyses of specimens from identical saturations showed a widely variable iron content. From the relative proportions of sodium paratungstate and ferric nitrate used in the saturations, Fe : W could have a maximum value of 8·5. Values obtained ranged from 14 to 21 and above. It was assumed, for the reasons already given, that the high proportion of tungsten was due to the presence of metatungstic acid, derived from sodium metatungstate formed furing the saturation with ferric nitrate.

The thermal stability of metatungstic acid is low (cf. Sobolew, *Z. anorg. Chem.*, 1896, **12**, 30), and by making use of this property it was found possible to eliminate this acid, leaving tungstoferric acid as final product. This substance, recrystallised from water, and air-dried, has a composition agreeing with the empirical formula $Fe_2O_3,22WO_3,50H_2O$. From its stability it might be expected to belong to the limiting series and be an analogue of 12-tungstoboric acid, $B_2O_3,24WO_3,53H_2O$, but the results of analysis of the free acid and its salts, as also of those of its homologues (see Part II), agree better with the 11-formulation. It is thus the first member of a new series of 11-heteropoly-tungstic acids with positive or mainly positive central ions, and may be described as 11-tungstoferric(III) acid. It retains $5H_2O$ at temperatures up to 240°, and gives a series of salts of which the ammonium and barium salts are 10- or 9-basic, the cæsium and silver salts 9-basic, and the sodium, potassium, and guanidine salts, 8-basic. As with many other heteropoly-acids, the mercurous salt is anomalous, being approximately 16-basic, but its insolubility as compared with the other salts suggests that it is a basic salt (cf. Souchay, *Bull. Soc. chim.*, 1942, **9**, 289), and does not indicate a true basicity. Potentiometric neutralisation with sodium hydroxide shows a basicity of *ca.* 9·2, as does also neutralisation with barium carbonate, and conductometric titration with potassium or ammonium hydroxide gives a value of *ca.* 10·1. The acid appears therefore to be 10-basic, and may be formulated as, $5H_2O,Fe_2O_3,22WO_3,45H_2O$. Its formula on the Rosenheim–Miolati basis would be either



$$\mathrm{H_9}\left[\mathrm{Fe}\begin{matrix}(\mathrm{W_2O_7})_5\\ \mathrm{OH}\end{matrix}\right]\text{—}\mathrm{W_2O_7}\text{—}\left[\begin{matrix}(\mathrm{W_2O_7})_5\\ \mathrm{OH}\end{matrix}\mathrm{Fe}\right]\mathrm{H_9} \quad \text{or} \quad \mathrm{H_{16}}\left[\mathrm{Fe}\overset{(\mathrm{W_2O_7})_5\qquad(\mathrm{W_2O_7})_5}{\diagdown\!\!-\!\mathrm{W_2O_7}\!-\!\!\diagup}\mathrm{Fe}\right]$$

neither of which agrees with its basicity as found experimentally. Wells (" Structural Inorganic Chemistry," p. 345) has suggested (following Pauling) alternative binuclear formulæ for the tungstophosphoric acids containing less than 12 tungsten atoms to each PO_4^{3-}. These formulæ assume the presence of two central ions in a structure based possibly on the cubo-octahedron, and give the general anionic form as $[P_2W_pO_{3p+8}]^{6-}$. By analogy the ion of 11-tungstoferric(III) acid would be $[Fe_2W_{22}O_{74}]^{10-}$, in agreement with the basicity as experimentally determined; the anhydrous acid would be $H_{10}[Fe_2W_{22}O_{74}]$. The Rosenheim–Miolati formulations imply that 11-tungstoferric acid is the hydrolysis product of a higher acid, presumably 12-tungstoferric acid, but its stability is much higher than that of 10(or 11)-tungstosilicic acid or 11-tungstophosphoric acid, and the preparation of the acid and of its salts has been carried out, as far as possible, under conditions unfavourable to hydrolysis. No evidence has been obtained, for either 11-tungstoferric acid or its homologues, of the presence of salts derived from a 12-acid, apart from the uncertainties of analysis. 11-Tungstoferric(III) acid appears to resist reduction by sulphurous acid to an 11-tungstoferric(II) acid, possibly because ferrous iron gives only a 6-heteropoly-tungstate, which oxidises rapidly in air to give indefinite products resembling the by-products in the tungstoferrate preparation. 11-Tungstoferric acid is stable in the solid state, only a trace of water-insoluble material separating on long keeping. Aqueous solutions are equally stable.

EXPERIMENTAL.

$Na_2WO_4,2H_2O$ (56·2 g.), dissolved in water (300 ml.) was converted into $3Na_2O,7WO_3$ by addition of N-nitric acid (194·4 ml.). The boiling, mechanically stirred solution was saturated dropwise during 20—24 hours with aqueous ferric nitrate solution (8·6 g. of nonahydrate in 400 ml.). This is 5% in excess of the amount required to give 60·8 ml. of N-nitric acid on complete hydrolysis, being the volume of N-nitric acid necessary to convert the paratungstate present into metatungstate. This excess was found to be desirable, owing to slight precipitation losses during saturation. Ferric chloride was not used because of the risk of its extraction by ether in the subsequent stages of preparation. Ferric sulphate was found to be unsatisfactory because of loss of iron as basic sulphate through incomplete hydrolysis. The yellow solution (described as " colourless " by Rosenheim, Abegg, " Handbuch," *loc. cit.*, p. 1050) was concentrated to 200 ml. and kept overnight at 6° to allow unchanged paratungstate to separate. After filtration, ether extraction by Drechsel's method (*loc. cit.*) gave the golden-yellow ether addition compound of 11-tungstoferric acid, mixed with that of metatungstic acid; 6M-sulphuric acid was used for acidification in this process, no cooling being necessary.

Isolation of 11-*Tungstoferric*(III) *Acid.*—The ether addition compound was freed from entrained mother-liquor by dropping it through two or three portions of fresh ether. On dilution with water the ether separated, and was removed by an air current. The aqueous solution was evaporated to dryness on the steam-bath, the residue was extracted with water, and the separated tungstic acid filtered off. The filtrate was again evaporated to dryness on the steam-bath, the process being repeated till separation of tungstic acid became slow. The dry residue was then baked at 120—130° for 4 hours, the residue being extracted with water, as before, and filtered. This process was repeated until separation of tungstic acid practically ceased. The tungstic acid residues contained only traces of iron, being derived almost entirely from the metatungstic acid. The final aqueous extract was partly concentrated on the steam-bath, then *in vacuo* over sulphuric acid. 11-*Tungstoferric acid* separated as a yellow crystalline mass, which was drained on a sintered filter and dried between filter-papers (yield variable, but averaging 30%) (Found: Fe_2O_3, 2·53; WO_3, 82·89; H_2O, 14·58. $Fe_2O_3,22WO_3,50H_2O$ requires Fe_2O_3, 2·59; WO_3, 82·80; H_2O, 14·62%). On dehydration, constant weight was attained between 180° and 240°, $35H_2O$ being lost at 110° and a further $10H_2O$ between 110° and 180° (Found: loss at 180°, 13·12. $Fe_2O_3,22WO_3,50H_2O$ requires $45H_2O$, 13·16%). The residue of anhydrous 11-tungstoferric acid was almost completely soluble in water, indicating little decomposition (less than 2% insoluble after 100 hours at 240°), and rapidly regained weight on exposure to moist air. For comparison the composition of the possible 12-acid, $Fe_2O_3,24WO_3,54H_2O$, would be: Fe_2O_3, 2·38; WO_3, 83·16; H_2O, 14·52%; and loss of 13·12% at 180° would leave $5{\cdot}5H_2O$.

Properties. The acid is very soluble in water (408 g. of 50-hydrate per 100 g. of water at 19°, density of solution 2·76) and crystallises only in aggregates, with occasional octahedral outlines; pH of 0·0014M-solution, 1·82 (cf. Rosenheim and Breuer, *Z. anorg. Chem.*, 1915, **93**, 284, for pH values for other heteropoly-acids); the acid has *d* 4·28, m. p. *ca.* 43°. It is stable to strong acids or bases in cold solution, and is decomposed on heating with separation of tungstic acid or ferric hydroxide, and therefore does not cause interference in the analytical separation of iron from tungsten by digestion with hydrochloric acid and cinchonine. Potentiometric titration with sodium hydroxide gave an equivalent weight *ca.* 670, the basicity of the acid being 9·2 on the assumed M.W. of 6162·74, the maximum value of dE/dV occurring near pH 5·7.

Further Methods of Preparation.—Two other methods of preparation of 11-tungstoferric acid were used for exploratory purposes.

(1) *Ferric hydroxide method.* To a sodium paratungstate solution, prepared as described above from 56·2 g. of $Na_2WO_4,2H_2O$ by addition of 194·4 ml. of N-nitric acid, was added well-washed ferric hydroxide, prepared from 10 g. of hydrated nitrate by precipitation with aqueous ammonia. The boiling, mechanically stirred mixture was acidified during 20—24 hours with an approx. 0·1N-nitric acid solution containing 64 ml. of N-acid (5% excess: cf. p. 2369). On completion of saturation, the solution was concentrated to 200 ml., filtered, and kept overnight at 6°. After separation of any unchanged paratungstate which had been deposited, the filtrate was extracted as before with ether and 6M-sulphuric acid. The tendency to emulsification, due to traces of WO_3,xH_2O derived from residual paratungstate, was more marked with these preparations, direct saturation with ferric nitrate being preferable, but an identical ether addition compound of 11-tungstoferric acid, mixed with metatungstic acid, was obtained. This method of saturation is of value, however, in those cases where, as with Bi^{3+} or Mn^{3+} salts, the metal ion can only be retained in solution by a substantial excess of acid, which would tend to give metatungstate as main product, or where the metal paratungstate is so sparingly soluble that addition of the salt gives double decomposition only.

The residue of ferric hydroxide contained substantial amounts of tungsten, and dissolved almost completely in water to give a dark red solution which, after sedimentation or centrifuging, was only perceptibly turbid, and remained unchanged for long periods. Evaporation to dryness on the steam-bath gave a dark red vitreous residue which again dissolved completely in water, and the process could be repeated many times. Addition of sodium chloride to the solution caused immediate and almost complete precipitation of a reddish-brown solid resembling ferric hydroxide. Air-dried specimens had an average composition represented by $3Na_2O,7WO_3,4{\cdot}3Fe_2O_3,31H_2O$, the pH of a 2·25% aqueous solution being 6·56. Other oxides and hydroxides have been found to behave similarly. Saturation of ammonium paratungstate solutions with metallic hydroxides has been used by various workers to prepare heteropoly-tungstates, and there can be little doubt that, electrolytes being virtually absent in such cases, the products isolated were contaminated with peptized hydroxides, as described above, and showed an excessively high metal oxide content.

(2) *Metatungstate method.* A solution of $Na_2O,4WO_3$,aq. was prepared by following the same procedure as described above, but omitting the ferric hydroxide and shortening the time of addition of the second portion of nitric acid to 4—5 hours. To this solution, heated to boiling and mechanically stirred, was added, as before, freshly precipitated ferric hydroxide prepared from 10 g. of hydrated nitrate. The reaction is very slow and saturation was continued for about 50 hours. The solution was concentrated to 200 ml., filtered, and extracted with ether and 6M-sulphuric acid. Analysis of the ether addition compound showed that about 10% of tungstoferric acid was present. The yield could probably be improved by using successive portions of fresh ferric hydroxide, since this ages rapidly in boiling solution. The residue of ferric hydroxide was again almost completely soluble in water, and gave on sedimentation and evaporation a dark red solid similar to that described above, and containing substantial amounts of tungsten.

According to Souchay (*loc. cit.*, p. 84) only sodium paratungstate solutions, freshly prepared by acidifying alkali tungstate, are active in heteropoly-acid formation, losing activity in a few hours, while paratungstate or metatungstate solutions prepared from the crystalline salts are almost inactive. There may thus be a decrease in reactivity of the metatungstate solution as well as of the ferric hydroxide during the saturation, accounting for the relatively poor yield of heteropoly-acid.

Metatungstic Acid.—The solution of sodium metatungstate described above, on extraction with ether and 6M-sulphuric acid, gives a quantitative yield of the ether addition compound of metatungstic acid, and from this sodium metatungstate can be obtained by neutralisation with sodium hydroxide to pH 3·6 and concentration to crystallisation. This method of preparation is superior to the tedious and wasteful process of saturating solutions of sodium tungstate or paratungstate with freshly precipitated tungstic oxide, much of the added tungsten being lost as insoluble alkali polytungstate. The low stability of metatungstic acid in aqueous solutions leads to considerable loss in isolation in solid form, no matter from what source it is derived.

On addition of aqueous barium chloride to a solution of sodium metatungstate, a small amount of barium tritungstate, $BaO,3WO_3,6H_2O$ (Scheibler, *J. pr. Chem.*, 1860, **80**, 204) separates in microcrystalline form before the barium metatungstate. This happens with sodium metatungstate, whether prepared by saturation of paratungstate with WO_3,xH_2O or by neutralisation of aqueous metatungstic acid with sodium hydroxide. If the formation of tritungstate were due to disproportionation, hydrogen ions should be set free. Potentiometric and conductometric titration of sodium metatungstate solutions from both sources with aqueous barium chloride shows no apparent fall in pH, or rise in conductivity. It seems probable that the tritungstate (averaging 2—3% of the total) is constantly present in sodium metatungstate, representing the not quite complete conversion of paratungstate into metatungstate by the hydrolytic displacement assumed by von Knorre.

Salts of 11-*Tungstoferric*(III) *Acid.—Sodium salt.* This *salt* was obtained by neutralising 11-tungstoferric acid with sodium hydroxide to pH 4·0 (checked potentiometrically on aliquot portion of solution) and concentrating the solution; it was a pale yellow, slightly efflorescent solid, melting below 50°, very soluble in water and crystallising only in aggregates (Found: Na_2O, 3·82; Fe_2O_3, 2·52; WO_3, 79·52; H_2O, 14·15. $4Na_2O,Fe_2O_3,22WO_3,50H_2O$ * requires Na_2O, 3·87; Fe_2O_3, 2·49; WO_3, 79·59; H_2O, 14·05%). It retains *ca.* $2H_2O$ at 200°; the pH of a 0·0014M-solution is 5·28.

Ammonium salt. This *salt* can be prepared either by neutralising the free acid with aqueous ammonia (potentiometrically checked as for the sodium salt) or by saturating aqueous solutions of the acid with ammonium chloride; recrystallised from water, it forms pale yellow hexagonal prisms, usually in rosettes, but sometimes with long axes parallel in bundles [Found: $(NH_4)_2O$, 4·33; Fe_2O_3, 2·73; WO_3, 88·36; H_2O, 4·58. $5(NH_4)_2O,Fe_2O_3,22WO_3,15H_2O$ requires $(NH_4)_2O$, 4·49; Fe_2O_3, 2·76; WO_3, 88·09; H_2O, 4·66%]; *d* 4·714. The salt is anhydrous at 160° and decomposes from 170°; it is easily soluble in water and a 0·0014M-solution has pH 4·78.

The salt prepared by neutralisation is not homogeneous. On recrystallisation from water it gives a first fraction of yellow crusts, with higher ammonia content [Found: $(NH_4)_2O$, 7·28; Fe_2O_3, 2·80; WO_3, 81·89; H_2O, 8·03. $8(NH_4)_2O,Fe_2O_3,20WO_3,25H_2O$ requires $(NH_4)_2O$, 7·36; Fe_2O_3, 2·82; WO_3, 81·87; H_2O, 7·95%]. This may be a hydrolysis *product.* The later fractions are identical with the 10-basic salt, crystallising in the same form, but occasionally, from concentrated solutions, as deliquescent octahedra.

Potassium salt. This *salt* was prepared by saturating an aqueous solution of the acid with potassium chloride; it is isomorphous with the ammonium salt, but rather less soluble in water; pH of 0·0014M-solution, 4·67 (Found: K_2O, 5·96; Fe_2O_3, 2·61; WO_3, 82·27; H_2O, 9·1. $4K_2O,Fe_2O_3,22WO_3,31H_2O$ requires K_2O, 6·08; Fe_2O_3, 2·58; WO_3, 82·34; H_2O, 9·01%).

Barium salts. There appear to be two *barium* salts. (i) That prepared by neutralising the acid with the carbonate and concentrating the solution crystallises in pale yellow, slightly deliquescent octahedra, *d* 4·452, readily soluble in water (Found: BaO, 10·41; Fe_2O_3, 2·36; WO_3, 75·99; H_2O, 11·48. $4{\cdot}5BaO,Fe_2O_3,22WO_3,43H_2O$ requires BaO, 10·26; Fe_2O_3, 2·37; WO_3, 75·85; H_2O, 11·52%); it retains *ca.* $2H_2O$ at 180°. (ii) Saturation of aqueous solutions of the acid with barium chloride gives a distinctive tetragonal form, pale yellow, usually twinned, *d* 4·734, and stable in air (Found: BaO, 11·69; Fe_2O_3, 2·46; WO_3, 76·71; H_2O, 9·24. $5BaO,Fe_2O_3,22WO_3,34H_2O$ requires BaO, 11·55; Fe_2O_3, 2·41; WO_3, 76·83; H_2O, 9·22%). This salt is apparently 10-basic and would be formulated as $Ba_5[Fe_2W_{22}O_{74}],34H_2O$. Since barium chloride is tenaciously held by barium salts of heteropoly-acids, the higher barium content may be due to this cause, the two salts being 9-basic, but different hydrates.

Cæsium salt. Prepared from aqueous solutions of the free acid and cæsium chloride, this very sparingly soluble *salt* crystallised from hot water in pale yellow slender prisms, isomorphous with the ammonium salt (Found: Cs_2O, 18·5; Fe_2O_3, 2·36; WO_3, 75·60; H_2O, 3·64. $4{\cdot}5Cs_2O,Fe_2O_3,22WO_3,14H_2O$ requires Cs_2O, 18·70; Fe_2O_3, 2·35; WO_3, 75·23; H_2O, 3·72%); it retained *ca.* $1H_2O$ at 180°. Recrystallisation apparently causes some hydrolysis, and it is difficult to obtain well-defined crystals.

Guanidine salt. Prepared from aqueous solutions of the acid and guanidine hydrochloride, this *salt* formed pale yellow leaflets, sparingly soluble in water [Found: $(CN_3H_6)_2O$, 9·14; Fe_2O_3, 2·54; WO_3, 84·72; H_2O, 3·61. $4(CN_3H_6)_2O,Fe_2O_3,22WO_3,12H_2O$ requires $(CN_3H_6)_2O$, 9·04; Fe_2O_3, 2·65; WO_3, 84·72; H_2O, 3·59%]; it retains $5H_2O$ at 200°.

Silver salt. The *silver* salt, prepared from aqueous solutions of the acid and silver nitrate, formed pale yellow prisms, isomorphous with the cæsium and potassium salts (Found: Ag_2O, 15·76; Fe_2O_3, 2·33; WO_3, 76·47; H_2O, 5·58. $4{\cdot}5Ag_2O,Fe_2O_3,22WO_3,21H_2O$ requires Ag_2O, 15·60; Fe_2O_3, 2·39; WO_3, 76·36; H_2O, 5·66%). It is sparingly soluble in water, but crystallises out only slowly; it dissolves completely in dilute nitric acid without separation of tungstic oxide.

Mercurous salt. Prepared from aqueous solutions of the acid and the nitrate, the *mercurous* salt formed a pale yellow microcrystalline solid, insoluble in water, completely soluble in dilute nitric acid (Found: Hg_2O, 38·52; Fe_2O_3, 1·84; WO_3, 56·73; H_2O, 2·91. $8Hg_2O,Fe_2O_3,22WO_3,14H_2O$ requires Hg_2O, 37·71; Fe_2O_3, 1·83; WO_3, 58·48; H_2O, 2·85%); it rapidly darkens on exposure to light, becoming almost black, and is probably a basic salt.

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* This salt can be formulated as $Na_8H_2[Fe_2W_{22}O_{74}],49H_2O$, and the other salts described can be based on the same complex ion.

Analysis.—This has been based, wherever possible, on ignition followed by fusion with sodium carbonate, the residue of ferric oxide being freed from tungstic oxide by double precipitation from hydrochloric acid solution with aqueous ammonia, followed by solution of the ignited and weighed ferric oxide in hydrochloric acid and precipitation of the remaining trace of tungstic oxide with cinchonine. Most of the ferric oxide residues showed a trace of silica when heated with sulphuric and hydrofluoric acids. Tungsten was determined as trioxide after precipitation with cinchonine hydrochloride; barium as sulphate, usually on a separate sample, the anion of tungstoferric acid being stable to dilute sulphuric acid. Potassium and cæsium were determined as chloroplatinates, sodium as triple salt with zinc uranyl acetate, ammonia by distillation into standard acid, and guanidine by micro-combustion (J. C.). Silver and mercury were determined by thiocyanate titration after decomposition of the salts with nitric acid. The average value of $Fe_2O_3 : WO_3$ obtained is more nearly 1 : 23 than the 1 : 22 assumed in the formulæ already given, but no values exceeding 1 : 24 were obtained. Since traces of metatungstic acid might be expected to persist in spite of the drastic treatment of tungstoferric acid during isolation, and since small amounts of paratungstate separate in the double decompositions used to prepare the salts, the absence of values of $Fe_2O_3 : WO_3$ corresponding to a 12-tungstoferric acid suggests that the 11-formulation is the more probable. A final decision is, however, scarcely possible on analytical grounds alone.

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