XCVI.—*Physicochemical Studies of Complex Acids Part V. The Precipitation of Tungstates.*

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Tungstates of the alkali metals have been reported containing 1, 2·33—2·40, and 4 molecules of WO_3 to each molecule of Na_2O and these are called tungstates, paratungstates, and metatungstates respectively. The existence of such salts is usually attributed to combination with the corresponding acids, as if they were separate chemical individuals. From this assumption the erroneous idea has arisen that similar salts of the heavy metals may be precipitated as the result of metathesis (see, *e.g.*, Abegg's "Handbuch der anorg. Chem.," 1921, IV, (1), (ii), pp. 797, 826; and Friend's "Text-book of Inorganic Chemistry," 1926, VII, 3, pp. 209, 237).

The authors have shown (Britton, J., 1927, 147; Britton and German, J., 1930, 1249) that the formation of the various tungstates corresponds to different stages in the anomalous neutralisation of tungstic acid as indicated by the changes in hydrogen-ion concentrations. It was considered, therefore, that any interaction between an alkali tungstate and a heavy-metal salt in solution would be largely governed by the hydrogen-ion concentrations that could be set up by the reactants, and these in turn would have a pronounced influence on the composition of the precipitate formed.

A series of reactions between solutions of salts of bases that are precipitated at different p_H values and each of the three tungstates has therefore been studied with regard to the changes occurring in hydrogen-ion concentration and (when possible) to the composition of the precipitates obtained.

EXPERIMENTAL.

The solutions of sodium para- and meta-tungstates were prepared by decomposing a known weight of the normal tungstate dissolved in boiling water with the required amount of hydrochloric acid. The solutions used were respectively $0{\cdot}045M\text{-}Na_2WO_4$, $0{\cdot}045M\text{-}Na_2O,(WO_3)_{2{\cdot}33}$, and $0{\cdot}045M\text{-}Na_2O,(WO_3)_4$. The changes in hydrogen-ion concentrations were followed by means of the quinhydrone electrode and, in those cases where the precipitation range lay above p_H 7, with the hydrogen electrode. Details of the metallic salts investigated are given in the first column of Table I. In this table are also recorded the p_H values at which precipitation with the various sodium tungstate solutions began; these are compared with the p_H values (col. 5) at which these solutions begin to be precipitated with sodium hydroxide (see Britton, J., 1925, **127**, 2110, *et seq.*).

The precipitates were dried at 100° and decomposed by heating for some time with concentrated hydrochloric acid. After most of the acid had been boiled off, the solutions were diluted and the tungstic oxide precipitated by means of cinchonine hydrochloride. The precipitates were filtered off, and ignited to constant weight. Other metals present were estimated in the usual ways.

TABLE I.

	p_H at which precipitation began with			
Soln. used.	Na_2WO_4.	$3Na_2O,7WO_3$.	$Na_2O,4WO_3$.	NaOH.
100 C.c. $0{\cdot}00788M\text{-}ThCl_4$	3·02	—	—	3·51
100 C.c. $0{\cdot}0095M\text{-}ThCl_4$	—	3·00	3·1	3·51
100 C.c. $0{\cdot}011M\text{-}ZrCl_4$ ...	1·77	1·77	1·76	1·86
200 C.c. $0{\cdot}1M\text{-}BeSO_4$	5·73	5·68	—	5·69
100 C.c. $0{\cdot}00667M\text{-}Al_2(SO_4)_3$	4·16	4·23	4·25	4·14
100 C.c. $0{\cdot}00667M\text{-}K_2SO_4$, $Cr_2(SO_4)_3$	3·55	3·25	—	5·34
200 C.c. $0{\cdot}01M\text{-}CuSO_4$ ...	5·09	5·04	5·2	5·2
100 C.c. $0{\cdot}02M\text{-}MgSO_4$ ...	No precipitation		—	10·49
200 C.c. $0{\cdot}01M\text{-}NiSO_4$ ...	,,	,,	—	6·66

The compositions of typical tungstate precipitates are given in Table II: the precipitates were gelatinous and consequently difficult to obtain free from adsorbed substances.

The titration curves are plotted in the figures, the scales for the thorium and zirconium curves being adjusted so that the theoretical end-point for double decomposition coincided in all cases with the

TABLE II.

Soln. used.	Na_2WO_4 ppt.	$3Na_2O,7WO_3$ ppt.	$Na_2O,4WO_3$ ppt.
$Al_2(SO_4)_3$	Al_2O_3, 1·74 WO_3, 12·5 H_2O	Al_2O_3, 2·81 WO_3, 7·30 H_2O	—
$ThCl_4$	(*a*) ThO_2, 2·05 WO_3, 15·60 H_2O (*b*) ThO_2, 2·02 WO_3, 6·73 H_2O	ThO_2, 3·57 WO_3, 4·31 H_2O	ThO_2, 3·62 WO_3, 4·76 H_2O
$CuSO_4$	CuO, 0·84 WO_3, 3·03 H_2O	CuO, 1·23 WO_3, 2·36 H_2O	— —
$Cr_2(SO_4)_3$	Cr_2O_3, 2·94 WO_3, 11·03 H_2O	Cr_2O_3, 4·70 WO_3, 9·46 H_2O	—
$ZrCl_4$	?	?	ZrO_2, 1·56 WO_3, 4·27 H_2O
$BeSO_4$	BeO, 0·54 WO_3, 3·17 H_2O	—	—

value 44·4 c.c. of reagent added, marked by the vertical line in the diagram. Incidence of precipitation is indicated by an arrow.

It was shown in Part I (J., 1930, 1249) that with a strong base, *e.g.*, sodium hydroxide, tungstic oxide is only able to enter into complete combination as a dibasic acid when the p_H value of the solution has been raised to 8. This condition must apply to the formation of all *soluble normal tungstates*, though sparingly soluble normal tungstates may conceivably be formed whilst the solution is still acid by virtue of the low concentration of WO_4'' ions that may be present being sufficient to satisfy the requirements of their respective solubility products. Should the solubility of such a tungstate be greater than that of its hydroxide, then it will be possible to bring about its precipitation only when the hydrogen-ion concentration of the solution has not been reduced to the extent necessary for the precipitation of the hydroxide. In other words, these insoluble tungstates can be obtained only from solutions of p_H values smaller than the corresponding hydroxide precipitation p_H. On subjecting them, however, to higher p_H values, it is likely, as shown by Britton (J., 1926, 125) in the case of normal phosphates, that they will suffer some decomposition, *i.e.*, become basic. If the tungstates should happen to be less soluble than their hydroxides, then it will be possible to effect their precipitation at p_H values irrespective of that required by the hydroxides. Similar considerations apply to the formation of para- and meta-tungstates. Thus, soluble paratungstates can only be formed at p_H 6—6·5 and soluble metatungstates at p_H 4—5.

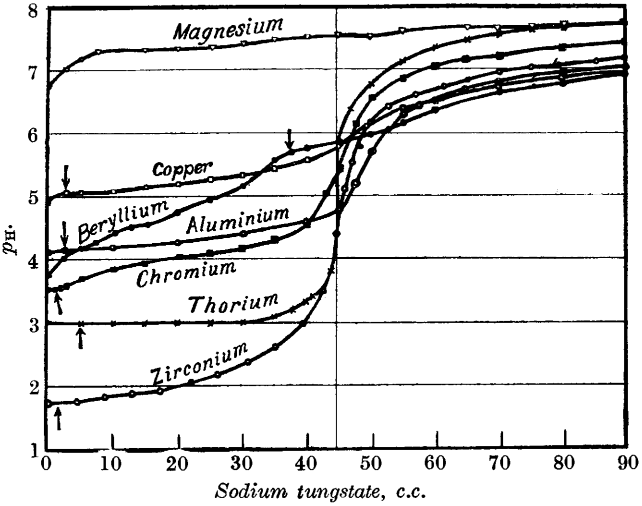
(1) *Sodium Tungstate Titrations.*—Of the metallic salt solutions that were treated with normal sodium tungstate, those whose hydroxides are precipitated in the acid zone yielded precipitates, whilst magnesium sulphate solution gave no precipitate, and incidentally it was only in this titration that the precipitant was

unable to set up the p_H value requisite for the precipitation of magnesium hydroxide, *i.e.*, p_H 10·5.

On comparing the p_H values given in cols. 2 and 5 (Table I), it will be seen that the precipitation of tungstates from the aluminium, beryllium, zirconium, and copper salt solutions began at approximately the p_H values at which their respective hydroxides also separate from solution. Table II shows that these precipitates contained considerable amounts of tungstic oxide, though not sufficient to give the ratio corresponding to the normal tungstates.

No precipitation in the beryllium titrations occurred until a relatively large quantity of the titrant had been added and the p_H value of the solutions had attained that at which the hydroxide separates.

FIG. 1.

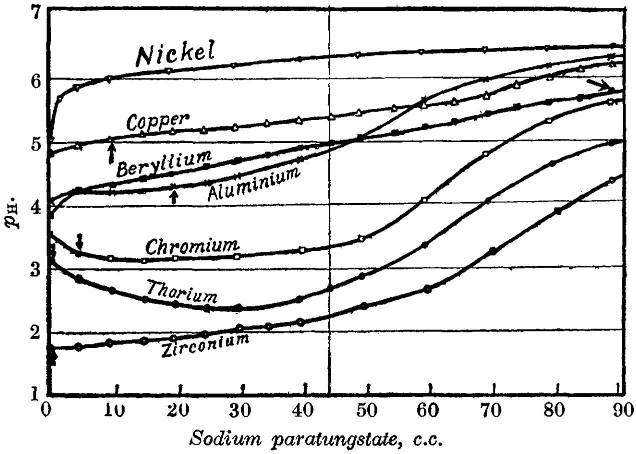


A similar behaviour has been noted by Britton (*loc. cit.*) in the case of the hydroxides, carbonates, borates, and chromates. Fig. 1 shows that in each of these titrations, the p_H values attained after the addition of an excess of alkali tungstate solution were below 7. As shown by the composition of the precipitates, some tungstic oxide escaped precipitation and subsequently combined with the excess sodium tungstate solution as a polytungstate $Na_2[O(WO_3)_x]$.

Chromium tungstate was precipitated at a p_H much lower than that required for the precipitation of chromium hydroxide, *viz.*, 5·34. Fig. 1 shows that p_H 7·5 was reached on adding an excess of sodium tungstate, a value which is only slightly lower than that attained when the molecular ratio of $Na_2O : WO_3$ in the solution is 1 : 1 (compare Fig. 1, Part I). Hence it might be inferred that the chromium tungstate precipitate was that of a definite normal salt, which appears to be confirmed by the composition given in Table II.

Thorium chloride gave a heavy white gelatinous precipitate at p_H 3 and there was little change in p_H until the stoicheiometric quantity of tungstate had been added. Since basic compounds of thorium are precipitated at p_H 3·5, it would appear that the gelatinous precipitate is a normal tungstate, especially as the final p_H values of the solution after addition of an excess of the precipitant were very near that of sodium tungstate itself. The compositions given in Table II support this, though it is not possible to state the exact extent of the hydration. Unlike the other precipitates referred to in Table II, these precipitates were dried at room temperature. The compositions of the precipitates refer to two distinct precipitations.

FIG. 2.



(2) *Sodium Paratungstate Titrations.*—Fig. 2 shows the changes in hydrion concentration which occurred when solutions of metallic salts were treated with sodium paratungstate solution. In the copper, aluminium, and zirconium reactions, precipitation did not take place until the p_H values of the solutions were very near those at which the respective hydroxides are precipitated. Table II shows that the precipitates contained less tungstic oxide than that required to form the respective paratungstates. The p_H values prevailing during the precipitation of the aluminium and copper tungstates were just those at which the respective hydroxides undergo precipitation. This points to the basic nature of the tungstate precipitates, though it is, of course, possible that they are composed of a mixture

of the normal and basic tungstates. The zirconium solution produced a heavy opalescence on addition of sodium paratungstate solution, but insufficient material separated (at these dilutions) for analysis. Precipitation of the beryllium solution was again delayed until the p_H value had been attained at which basic beryllium compounds are precipitated, *i. e.*, 5·69, whereat the solution just became opalescent. That this opalescence was caused by the formation of a basic substance was evident from the fact that the p_H value of the solution after excess of the paratungstate had been added was about 1 p_H unit lower than the value which would have been expected had the solution contained nothing but sodium paratungstate, *i.e.*, p_H 6·4. Tungstic oxide was therefore liberated in the reaction, and this formed a polytungstate with the excess paratungstate solution. The depressions of the final p_H values noted in the above cases of aluminium, zirconium, and copper are due to the same cause.

Nickel hydroxide is precipitated at p_H 6·66, and as sodium paratungstate solution can only set up a p_H value of 6·4 no precipitate would be expected on adding it to nickel sulphate solution unless an insoluble nickel paratungstate were formed. Actually no precipitation took place.

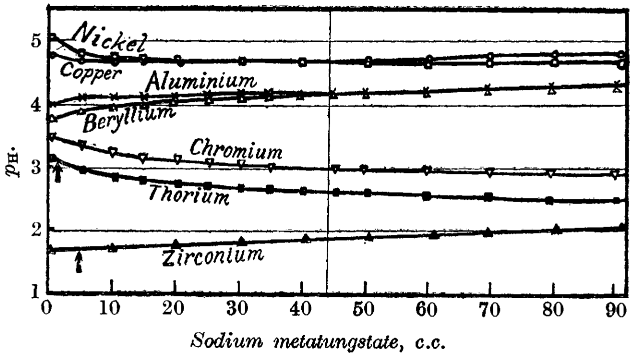
The reactions between sodium paratungstate and the solutions of salts of chromium and thorium differ from the other reactions in two respects: (1) precipitates containing large proportions of tungstic oxide were formed in solutions whose p_H values were considerably lower than those at which their respective hydroxides become precipitable; (2) simultaneously with the separation of these precipitates there occurred a remarkable increase in hydrogen-ion concentration. In neither reaction was the heavy metal completely precipitated on adding the stoicheiometric amount of the sodium salt. Both contained less tungstic oxide than required by the paratungstates of the two metals. This oxide remained in solution in combination with some undecomposed sodium paratungstate as a soluble polytungstate, $Na_2O,(WO_3)_x$, in which x tended to become increasingly great. As the precipitation reactions continued, some of this polytungstate probably became converted into free tungstic acid.

Although tungstic acid does not dissolve in water, it is highly probable that it can exist in solution as a comparatively strong acid, thus: $H_2[O,(WO_3)_x] \rightleftharpoons 2H^{\cdot} + [O,(WO_3)_x]''$, in which $x =$ or >4. Such an acid might be formed by decomposing a polytungstate with a strong acid. This view is substantiated by cryoscopic and conductometric measurements of solutions obtained by decomposing barium metatungstate with sulphuric acid (Soboleff, *Z. anorg.*

Chem., 1896, **12**, 16; see also Rosenheim and Kohn, *ibid.*, 1911, **69**, 251). On addition of either an excess of a strong acid or a neutral salt, *e.g.*, alkali chloride, these solutions readily decompose and deposit tungstic oxide. Thus it would appear, from the composition of the precipitates obtained and the p_H at which they were precipitated, that they were mixtures of the normal tungstate, $Cr_2(WO_4)_3$ or $Th(WO_4)_2$, with varying amounts of tungstic oxide.

(3) *Sodium Metatungstate Titrations.*—The changes in hydrogen-ion concentration that occurred during the reactions of various salt solutions with sodium metatungstate are represented in Fig. 3. The p_H of the sodium metatungstate solution prepared by boiling the normal tungstate with the correct amount of acid was 5, but, as will be understood from Fig. 1 in Part I (*loc. cit.*), the introduction of the slightest amount of acid will cause a rapid decrease to just below p_H 4. It would be expected, therefore, that this reagent would be unable to precipitate any basic substances which depended on the attainment of p_H values higher than about p_H 4. No precipitates could be obtained from salt solutions of nickel, copper, beryllium, and chromium. In the aluminium titration, the p_H at which aluminium hydroxide normally separates was only very slowly exceeded on adding an increasing excess of sodium metatungstate. The precipitation then became incipient, as indicated by a slight turbidity. The inability of sodium metatungstate to form a precipitate from copper sulphate solution is thus seen to be directly connected with the non-attainment of the hydroxide precipitation p_H of 5·2. Incidentally, it emphasises why precipitation occurred in the previous copper titrations, though it does not offer an adequate explanation why the copper precipitates there obtained contained relatively large proportions of tungstic acid. It may be that the precipitates contained some normal copper tungstate besides an

FIG. 3.



indefinite basic salt. If this was the case, then non-precipitation in the present titration must have been caused by an insufficiency of WO_4'' ions.

In the chromium titration with sodium metatungstate, an appreciable increase (similar to the changes previously observed) in hydrogen-ion concentration occurred. No precipitate was formed, however, which apparently was due to the lack of WO_4'' ions in the metatungstate solution. The action of sodium metatungstate on thorium chloride also caused a lowering of the p_H value, but unlike the chromium titration, precipitation of a thorium tungstate, $ThO_2,3{\cdot}6WO_3$, took place. This precipitate separated much below p_H 3·5, the hydroxide precipitation value, and can only be assumed to be a mixture of $Th(WO_4)_2$ and some entrained tungstic oxide.

When sodium metatungstate reacted with zirconium chloride, the solution became opalescent after the addition of 5 c.c. of metatungstate solution, the p_H then being near that at which the hydroxide is precipitated. Even with excess of reagent, the p_H value never rose much above 2, indicating the presence of a polytungstate in solution. Precipitation was partial. The acid reaction of the solution even after an excess of sodium metatungstate had been added was, as may be seen from Fig. 1 in Part I, due to hydrolysed acid from the zirconium chloride solution reacting with the sodium metatungstate to form a polytungstate and at the same time to maintain a low p_H.

Discussion.

It will be apparent from these experiments that the para- and meta-tungstates of the various metals are not formed by double decomposition. Except where definite normal tungstates were formed, as in the case of thorium and chromium, the p_H values established when precipitation began were those necessary for the beginning of precipitation of the respective hydroxides. The composition of the tungstate precipitates was indefinite, and their precipitation appears to be directly connected with that of their respective bases.

The precipitation of basic substances involves the use of salts of weak acids, or of acids which are weak in their final stage of ionisation. On referring to Part I (*loc. cit.*), it is seen that if tungstic acid be expressed as $H_2[O,(WO_3)_x]$, it reacts as a weak acid when x lies between 1 and 2·33; when $x = 2{\cdot}3$—4 it still behaves as a weak acid, although the extent is somewhat dependent on the treatment accorded to its salts, boiling and ageing tending to make it weaker; and when $x =$ or >4 it assumes the character of a strong acid. Alkali tungstates, $Na_2[O,(WO_3)_x]$, in which $x = 1$—4, are, in effect, salts of a weak acid and possess the characteristics necessary to set up the p_H conditions requisite for the precipitation of basic tungstates. On the other hand, solutions of sodium metatungstate, $Na_2[O(WO_3)_4]$, contain the salt of a strong acid and may scarcely be expected to cause the precipitation of basic tungstates; in fact, they were unable to precipitate either nickel, copper, beryllium, or chromium salt solutions and only just able to render the aluminium sulphate solution faintly turbid.

The aluminium tungstates obtained in this work contained 1·73 and 2·81 mols. of WO_3 to 1 mol. of Al_2O_3, which amounts are very much lower than those, *viz.*, 3—7 mols., recorded by Lefort (*Compt. rend.*, 1878, **87**, 748; *Ann. Chim. Phys.*, 1878, **15**, 321) and Bernoulli (*Pogg. Ann.*, 1860, **111**, 576). In regard to beryllium tungstates, Tanatar and Kurovski (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 813) prepared substances that were indefinite and basic. Copper tungstates are described containing 1, 2, 2·33, and 4 mols. of WO_3 per mol. of CuO, and Anthon (*J. pr. Chem.*, 1836, **9**, 341) stated that the normal tungstate was prepared by adding a cupric salt solution to one of normal sodium tungstate. The above work, however, discloses that these conditions were more conducive to the production of a basic tungstate. Lefort (*Compt. rend.*, 1879, **88**, 798) claimed to have prepared normal chromium tungstate from sodium ditungstate, $Na_2[O(WO_3)_2]$, and chrome alum solutions, but Kantshew (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 729) maintained that it was the paratungstate, $Cr_2O_3,7WO_3,9H_2O$. No precipitates have been obtained in this work having such high tungsten contents, and it is likely that those found by Kantschew were the result of using higher concentrations and the consequent entrainment by the precipitate of large amounts of tungstic oxide.

In regard to the inability of sodium tungstate solution to form a basic magnesium tungstate, as indicated in Fig. 1, and also to the fact that the p_H conditions obtain for the formation of a soluble normal magnesium tungstate, it is of interest to note that Lefort (*loc. cit.*) has prepared a soluble crystalline magnesium tungstate, $MgWO_4,3H_2O$.

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