250. *Physicochemical Studies of Complex Acids. Part XII. The Precipitation of the Normal and Complex Tungstates and Molybdates of the Alkaline Earths and of Silver.*

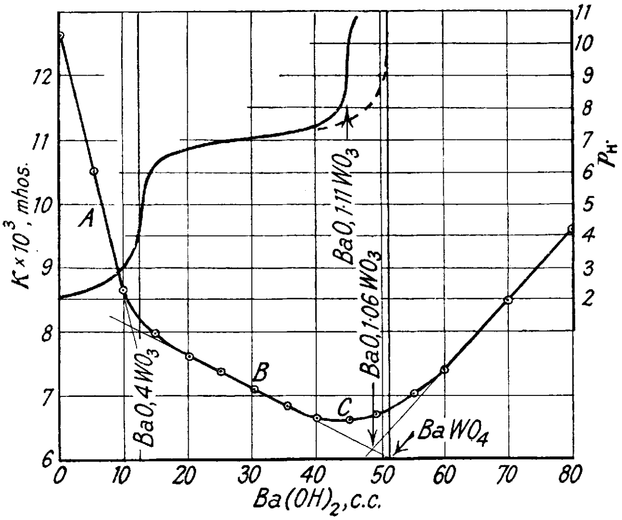
By H. T. S. Britton and William L. German.

In Parts V and VI (J., 1931, 709, 1429) we described the reactions between solutions of certain heavy-metal salts and complex alkali tungstates and molybdates. In no case was the individuality of either the paratungstate or the paramolybdate ions, or the so-called metatungstate or metamolybdate ions, established by their causing the corresponding heavy-metal salts to be precipitated. Actually, as Robinson and Sinclair (Part XI, this vol., p. 642) have shown, these polytungstate and polymolybdate ions exist in solution in a polymerised form. The electrometric curves in Parts I and III (J., 1930, 1249, 2154) reveal that, whatever the precise nature of the ions may be, the meta-salts correspond approximately with the complete neutralisation of the portions of tungstic and molybdic acids which behave as strong acids, whereas the para-salts contain in addition relatively small proportions of weak-acid stages in the neutralised state. The following work was done to ascertain (i) to what extent the precipitation processes could be correlated with the abnormal ionisation of tungstic and molybdic acids, (ii) whether any evidence could be found for the existence of the various complex ions, for many authors state that the para- and meta-salts may be precipitated by the interaction of alkali para- and meta-salts and metallic salt solutions.

Experimental.

Action of Barium, Strontium, and Calcium Hydroxides on Aqueous Solutions of Tungstic Acid.—As tungstic oxide is insoluble in water, the tungstic acid solutions were prepared by adding 2 equivs. of hydrochloric acid to a solution of sodium tungstate. The lower curve in the fig. represents the variation in specific conductivity at 25° during the addition of 0·132*N*-baryta solution to 75 c.c. of 0·045*M*-sodium tungstate to which 2·43 c.c. of 2·78*N*-hydrochloric acid had previously been added, whilst the upper curve illustrates the p_H changes. This curve is based on electrometric measurements made with both the quinhydrone and the oxygen electrode at 18°. The readings of specific conductivity and p_H were made at periods of 5 minutes after each addition of baryta with thorough stirring. Precipitation began almost immediately the baryta solution was added.

As shown in Part I (*loc. cit.*), the addition of 2 equivs. of hydrochloric acid to a solution of sodium tungstate does not liberate tungstic acid, but forms sodium polytungstate approximating to $Na_2O,4WO_3$, and the remaining 0·5 equiv. of acid is left unattacked. The initial sections of the two curves in the fig. represent largely the neutralisation of this free hydrochloric acid, but a closer study of the observed conductivities indicates that some of the barium chloride, thereby formed, must have reacted with the sodium polytungstate to give a precipitate of barium polytungstate and so produced in the solution an equivalent concentration of the less conducting sodium chloride. This is borne out by the composition of the precipitate obtained with 8 c.c. (point *A*) of baryta, *viz.*, $BaO,5{\cdot}67WO_3,3{\cdot}24H_2O$ (BaO, 10·03; WO_3, 86·15%). The inflexions in the two curves mark the end of the neutralisation of the free hydrochloric acid. The continued addition of the baryta further decomposed the unprecipitated polytungstate with increasing precipitation until the final inflexions were produced when an excess of baryta was being added. At this stage, all the tungstic acid was precipitated, and the locations of the p_H and conductivity inflexions show that the precipitates then contained $BaO,1{\cdot}11WO_3$ and $BaO,1{\cdot}06WO_3$ respectively. The course of precipitation was also followed by means of gravimetric analysis; *e.g.*, with 30 c.c. of baryta (point *B*) the precipitate was $BaO,1{\cdot}72WO_3,1{\cdot}52H_2O$ (BaO, 26·38; WO_3, 68·90%), and with 45 c.c. (point *C*) it was $BaO,1{\cdot}23WO_3,1{\cdot}05H_2O$ (BaO, 33·55; WO_3, 62·33%).



Although precipitation ended with slightly less than the stoicheiometric amount of baryta, yet on standing in contact with an excess of baryta the precipitate changed from a flocculent to a microcrystalline form, and analysis showed it had become $BaWO_4,H_2O$ (cf. Péchard, *Compt. rend.*, 1889, **108**, 1167). On adding the baryta to a boiling tungstate solution, the liquid did not become alkaline to phenolphthalein (p_H change indicated by broken line) until the amount required to form the normal tungstate had been added.

The electrometric curves representing the attack of both strontia and lime water were similar to those in the fig. The first inflexions occurred when the added reactant bore to the tungstic acid the same ratio, *viz.*, $RO : 4WO_3$. At this stage in the strontium titration, the p_H being 4·2, an amorphous precipitate appeared, but with calcium hydroxide precipitation was delayed until the ratio of $CaO : WO_3$ in the solution was 1 : 1·9 and the p_H was 6·77. Strontia was in all respects similar to baryta. At about p_H 7 the amorphous precipitate reacts with the excess of strontia to form the normal crystalline strontium tungstate, but the reaction is so slow that the inflexion corresponding to the end of the reaction is produced prematurely. Boiling in presence of excess of strontia readily converts the strontium polytungstate into the normal tungstate, $SrWO_4$. With lime water, the calcium polytungstate is much more soluble, but, as the p_H rises, it undergoes precipitation. The change into the normal tungstate is slow at ordinary temperatures but the crystalline precipitate of the normal tungstate, $CaWO_4$, may be produced by boiling with lime water.

It is interesting to compare the solubility of the sulphates and chromates of barium, strontium, and calcium with that of their tungstates (or polytungstates) as exemplified by the p_H values at which the precipitations begin.

Double-decomposition Reactions.—Quinhydrone-electrode titrations at 18° of 0·05*M*-barium chloride with either sodium tungstate or molybdate showed that the p_H remained at about 7 during precipitation. Small inflexions were produced when the stoicheiometric amounts of the reagents were added. On addition of excess of the alkali tungstate or molybdate, the p_H gradually rose to about 8. The precipitate obtained on adding an excess of sodium tungstate was $BaWO_4,0{\cdot}71H_2O$ (BaO, 38·38; WO_3, 58·25%); whilst with sodium molybdate in excess it was $BaMoO_4$ (BaO, 51·40; MoO_3, 48·31%). Solutions of 0·05*M*-barium chloride were also titrated with the quinhydrone electrode with 0·05*M*-sodium paratungstate, paramolybdate, metatungstate, and metamolybdate. The para-salts, which corresponded with the formula $Na_2O,2{\cdot}33XO_3$, and the meta-salts with $Na_2O,4XO_3$, were prepared by adding suitable quantities of hydrochloric acid to either sodium tungstate or sodium molybdate.

On addition of sodium paratungstate to the barium chloride solution, the p_H rapidly fell from 7·0 to 4·65 when half the amount of reactant to form barium paratungstate had been added. It then gradually increased, being 5·09 with the stoicheiometrical amount, to a little over p_H 6 when a large excess had been added. Such a p_H value indicated that the solution must have then contained a polytungstate approximating in composition to that of the paratungstate. Precipitates given with 0·25, 0·67, and 1·5 times the theoretical amount of sodium paratungstate contained BaO, WO_3, and H_2O in the following respective ratios : 1 : 1·75 : 5·40, 1 : 2·28 : 4·20, 1 : 2·33 : 5·36. The final precipitate thus corresponded with barium paratungstate.

Treatment of barium chloride with sodium paramolybdate immediately brought about a rapid diminution in p_H. With one-tenth of the theoretical amount it had fallen to 5·04, and with twice the theoretical amount it had only increased to 5·21. Although such a p_H is approximately that of a solution of alkali paramolybdate, analysis showed the final precipitate to be $BaO,1{\cdot}93MoO_3,0{\cdot}21H_2O$. The additional molybdic acid required to form barium paramolybdate had remained in solution.

The addition of sodium metatungstate to barium chloride again caused a diminution in p_H to 3·15 when half the theoretical quantity was added. A gradual increase then began to p_H 3·41, when the theoretical amount was added, but even with a large excess the p_H never reached 4·0, the p_H value of alkali metatungstate. At no stage of the reaction was barium metatungstate precipitated, as will be seen from the molecular ratios of the precipitates, *viz.*, $BaO : WO_3 : H_2O = 1 : 3{\cdot}14 : 6{\cdot}80$, $1 : 3{\cdot}23 : 5{\cdot}30$, $1 : 3{\cdot}33 : 5{\cdot}80$ formed on adding 0·125, 0·56, 1·27 mols. respectively of sodium metatungstate.

In a similar way, sodium metamolybdate does not yield barium metamolybdate, $BaO,4MoO_3$, by metathesis. Addition of 0·05*M*-sodium molybdate to 0·05*M*-barium chloride results in an immediate increase in hydrogen-ion concentration. With equimolar proportions, the p_H is 2·75, whilst with 2 mols. of alkali metamolybdate it is 2·88. The p_H of alkali metamolybdate solutions is approximately 4·0. It appears, therefore, that the barium precipitate must have contained less than 4 mols. of MoO_3 per mol. of BaO. The precipitate obtained with excess of sodium metamolybdate was $BaO,2{\cdot}40MoO_3,4{\cdot}12H_2O$.

The Action of Alkali Tungstates and Molybdates on Silver Nitrate.—The precipitation of the silver salts was studied by potentiometric titrations at 18° of 100 c.c. of 0·01*M*-silver nitrate solutions with 0·045*M*-sodium salts. The following combination was used

$$Ag|0{\cdot}1M\text{-}AgNO_3|\text{Satd. }KNO_3|100\text{ c.c. }0{\cdot}01M\text{-}AgNO_3|Ag + x\text{ c.c. of }0{\cdot}045M\text{-Na Salts}$$

The table records the *E.M.F.*'s observed when the volumes (col. 1) of either sodium tungstate or molybdate (col. 2), sodium paratungstate or paramolybdate (col. 6), or sodium metatungstate or metamolybdate (col. 8) had been added. The respective silver-ion concentrations (cols. 3, 7, and 9) were calculated by means of the expression : $E.M.F. = -0{\cdot}063-0{\cdot}058\log[Ag^{\cdot}]$ (see Britton, J., 1925, **127**, 2956). On comparing the concentrations of silver ions in equilibrium with the precipitates formed in the titrations with the normal, para- and meta-tungstates and molybdates in the presence of equal concentrations of the precipitants, it is seen that they are least in the case of the normal salt, and greatest in that of the meta-salt titrations. The failure of both the para- and meta-salts to bring about complete precipitation is also apparent from the high silver-ion concentrations when compared with that of the original silver nitrate solution.

Silver electro-titration of 100 c.c. of 0·01*M*-$AgNO_3$ with (i) 0·045*M*-Na_2WO_4, (ii) 0·045*M*-$Na_2O,2{\cdot}33WO_3$, (iii) 0·045*M*-$Na_2O,4WO_3$.

	(i)				(ii)		(iii)	
Tungstate, c.c.	*E.M.F.*, mv.	$[Ag^{\cdot}]$ $\times 10^4$.	$[WO_4'']$ $\times 10^3$.	$L_{Ag_2WO_4}$ $\times 10^{10}$.	*E.M.F.*, mv.	$[Ag^{\cdot}]$ $\times 10^4$	*E.M.F.*, mv.	$[Ag^{\cdot}]$ $\times 10^4$.
15	125	5·73	1·52	5·0	100	15·49	73	45·6
20	134	4·01	3·33	5·4	109	10·81	77	38·6
25	138	3·43	5·00	5·9	114	8·87	82	31·6
30	144	2·71	6·54	4·8				
40	148	2·30	9·29	4·9				

Mean $L_{Ag_2WO_4} = 5{\cdot}2 \times 10^{-10}$.

Silver electro-titration of 100 c.c. of 0·01*M*-$AgNO_3$ with (i) 0·045*M*-Na_2MoO_4, (ii) 0·045*M*-$Na_2O,2{\cdot}33MoO_3$, (iii) 0·045*M*-$Na_2O,4MoO_3$.

	(i)				(ii)		(iii)	
Molybdate, c.c.	*E.M.F.*, mv.	$[Ag^{\cdot}]$ $\times 10^4$.	$[MoO_4'']$ $\times 10^3$.	$L_{Ag_2MoO_4}$ $\times 10^{11}$.	*E.M.F.*, mv.	$[Ag^{\cdot}]$ $\times 10^4$.	*E.M.F.*, mv.	$[Ag^{\cdot}]$ $\times 10^4$.
15	160	1·43	1·52	3·1	127	5·30	107	117
20	170	0·96	3·33	3·1	135	3·86	112	96
25	175	0 79	5·00	3·1	139	3·29	116	82

Mean $L_{Ag_2MoO_4} = 3{\cdot}1 \times 10^{-11}$.

Precipitation with sodium tungstate gave the normal anhydrous silver tungstate, Ag_2WO_4, whereas the dry silver molybdate, obtained by precipitation with sodium molybdate, was so insoluble in acids that an analysis of the wet precipitate, which could be dissolved in nitric acid, was made. It contained $Ag_2O,1{\cdot}02MoO_3$ and was thus the normal silver molybdate. Col. 4 gives the concentrations of tungstate and molybdate ions in equilibrium with the respective precipitates (the ionisation of the alkali salts in excess being assumed complete), and col. 5 gives the values of the two solubility products $[Ag^{\cdot}]^2[XO_4'']$. Considering the sluggish tendency of the silver electrode to reach equilibrium in alkaline solutions, the agreement is satisfactory. It is interesting to compare the above solubility products with that of silver chromate, *viz.*, 1×10^{-12}, whence it is observed that the solubility increases in the order chromate < molybdate < tungstate, and is thus in harmony with the sequence of the three metals in the periodic classification.

The precipitate obtained with excess of (*a*) sodium paratungstate was $Ag_2O,1{\cdot}87WO_3,1{\cdot}31H_2O$; (*b*) sodium metatungstate was $Ag_2O,2{\cdot}07WO_3,0{\cdot}93H_2O$; (*c*) sodium paramolybdate was $Ag_2O,1{\cdot}40MoO_3,xH_2O$; (*d*) sodium metamolybdate was $Ag_2O,2{\cdot}26MoO_3,xH_2O$. In every instance the silver precipitate contained less acidic oxide than was present in the precipitant actually employed.

CONCLUSION.

The foregoing work shows that the normal tungstates and molybdates, particularly those of silver, are more insoluble than the precipitates which contain larger amounts of either tungstic or molybdic acid. Excepting the single instance of the precipitate formed by the addition of excess of sodium paratungstate to barium chloride, no tungstate or molybdate precipitate was obtained which contained the metallic base and the acidic oxide in the proportions required for either the para- or the meta-salts. Even in the instance cited, in which the composition of the precipitate corresponded with that of barium paratungstate, the precipitates formed when the precipitant was not in excess contained somewhat smaller amounts of tungstic oxide. Unlike the precipitation of the normal tungstates and molybdates, the precipitates obtained with alkali para- and meta-salts vary in composition with the amount of precipitant employed. Despite the fact that alkali para- and meta-tungstates and molybdates may be prepared in crystalline form, these precipitation reactions, in common with the previous work described in Parts I, III, V, and VI, provide no evidence of the individuality of the complex para- and meta-ions as such. It seems that in the dilute solutions here studied, the stability of sodium meta-tungstate and -molybdate, which are in effect salts of strong acids, may be responsible for the resulting precipitates being appreciably soluble. During reaction with both the para- and the meta-salts there is a definite tendency for some of the tungstic or molybdic acid to escape precipitation and, at the same time, for the alkali polytungstate or polymolybdate in the solution to become enriched in its corresponding acidic oxide. In the process, appreciably large acidic micelles are formed in solution. It is probable that they ionise slightly to give some normal tungstate or molybdate ions, and in consequence cause the normal salt to be precipitated in the first place. Such precipitation then brings about the partial disruption of the micellar anions, resulting in the co-precipitation of some acidic oxide with the normal salts.

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