

CXCIII.—*Physicochemical Studies of Complex Acids.*
Part VI. The Precipitation of Molybdates.

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PARTS I and III of this series (Britton and German, J., 1930, 1249, 2154) show that, despite the anomalous nature of tungstic and molybdic acids, they both ionise in a remarkably similar manner. As in the case of tungstates, three distinct forms of alkali molybdates, *viz.*, the normal molybdate, R_2O, MoO_3 , the paramolybdate, $R_2O, 2 \cdot 33 MoO_3$, and the metamolybdate, $R_2O, 4 MoO_3$, are formed, and in like manner it is often stated [compare Abegg's "Handbuch der anorganischen Chemie," 1921, IV, (1), (ii), pp. 577, 578, 636] that solutions of these salts on reacting with salts of heavy metals lead to the precipitation of the respective types of molybdate. The authors have already shown (this vol., p. 709) that this is not the case with the various tungstates, and it is now shown to be untenable with regard to the reactions undergone by the corresponding molybdates.

EXPERIMENTAL.

A series of potentiometric titrations of metallic salt solutions with the different alkali molybdate solutions was performed with the quinhydrone electrode, and wherever possible the p_H values thereby obtained were confirmed by means of the hydrogen electrode. As titrants the following solutions were employed: 0.045*M*- Na_2MoO_4 , 0.045*M*- $Na_2O, 2 \cdot 33 MoO_3$, and 0.045*M*- $Na_2O, 4 MoO_3$. They were prepared by adding the requisite amounts of hydrochloric acid to a solution of sodium molybdate at 100°, the sodium chloride formed being assumed to be without effect on the course of the reactions. Such a method of preparation is suitable, for it has been found (Part III, p. 2159) that the conductivity due to the sodium polymolybdate thus formed is the equal of that of a solution prepared by dissolving the particular molybdate at the appropriate dilution. The solutions titrated are recorded in Table I, Col. 1, and Figs. 1—3 give the variations in hydrogen-ion concentration during the reactions. The stoichiometric end-point, *i.e.*, the stage at which the reaction ends if simple double decomposition takes place, is indicated by the vertical line in each diagram corresponding to the addition of 44.4 c.c. of the alkali molybdate, and in those reactions involving the separation of precipitates the points where they first appeared are shown by arrows.

The molecular ratio of metallic base to molybdic acid present in each precipitate was ascertained either by analysis of the precipitate

itself or, in a few cases, from the amount of molybdic acid remaining in the mother-liquor after complete precipitation of the metallic base had taken place. Molybdenum was estimated either (i) by precipitating the sulphide from a concentrated hydrochloric acid solution, igniting it carefully, and weighing the oxide, or (ii) as lead molybdate with lead acetate solution. Table II gives the amounts of molybdic acid contained in the precipitates. No analyses could be made of two of the zirconium precipitates owing to the marked tendency shown by this metal to form colloidal suspensions, so much so that the amounts that could be separated in the cold were insufficient for analysis. In Table I the p_{H} values are given at which the precipitates began to separate, and these are compared with the p_{H} values at which precipitation begins when the solutions are treated with sodium hydroxide (col. 5; *vide* Britton, J., 1925, 127, 2110 *et seq.*).

TABLE I.

Solution used (100 c.c. in every case except that marked *).	p_{H} at which precipitation began with			
	Na_2MoO_4 .	$\text{Na}_2\text{O}, 2\cdot33\text{MoO}_3$.	$\text{Na}_2\text{O}, 4\text{MoO}_3$.	NaOH .
0·01M-ZrCl ₄	1·75	1·74	1·75	1·86
0·01M-ThCl ₄	3·02	3·00	2·97	3·51
0·00667M-Al ₂ (SO ₄) ₃	4·39	No precipt.		4·14
0·02M-CuSO ₄	5·28	"		5·20
0·00667M-Cr ₂ (SO ₄) ₃ , K ₂ SO ₄	4·54	"		5·34
0·02M-BeSO ₄	No precipitation			5·69
*0·01M-NiSO ₄	"	"		6·66
0·02M-MgSO ₄	"	"		10·49

* 200 C.c. of this solution were used instead of 100 c.c.

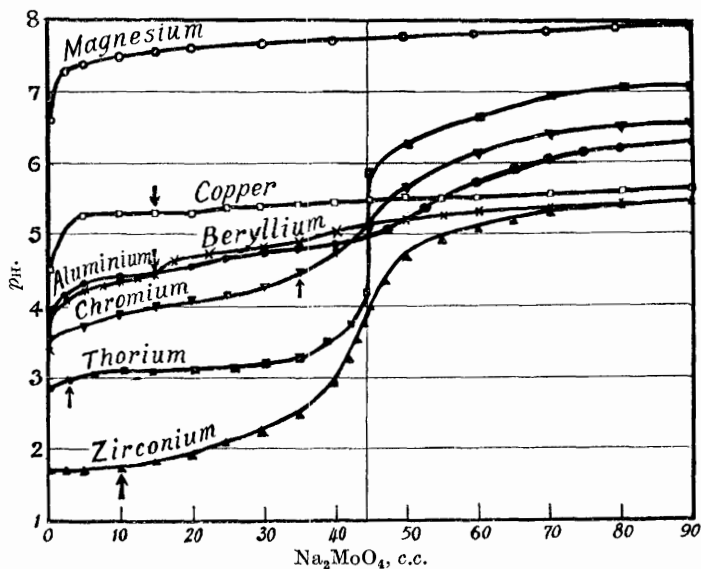
TABLE II.

Solution used.	Na_2MoO_4 .	$\text{Na}_2\text{O}, 2\cdot33\text{MoO}_3$.	$\text{Na}_2\text{O}, 4\text{MoO}_3$.
ZrCl ₄	?	ZrO ₂ , 0·86MoO ₃	?
ThCl ₄	ThO ₂ , 2·07MoO ₃	ThO ₂ , 2·21MoO ₃	ThO ₂ , 2·82MoO ₃
Al ₂ (SO ₄) ₃	Al ₂ O ₃ , 2·61MoO ₃	No ppt.	No ppt.
Cr ₂ (SO ₄) ₃	Cr ₂ O ₃ , 2·80MoO ₃	"	"
CuSO ₄	CuO, 0·70MoO ₃	"	"

Sodium Molybdate Titrations.—Although sodium molybdate solutions are very slightly alkaline, it will be seen from Part III (*loc. cit.*) that addition of a very small amount of hydrochloric acid brings the p_{H} down from about 8 to 6. Further additions set up buffer action between p_{H} 6 and 5. Fig. 1 shows that addition of sodium molybdate to a magnesium sulphate solution resulted in a gradual diminution in hydrogen-ion concentration to about p_{H} 8. This was caused by the amount of hydrolysed acid from the magnesium salt being too small to have any marked effect on the sodium molybdate. Apparently no precipitation took place from the magnesium solution because the reactant could not establish a

p_H value of 10.5, which is necessary to bring about the precipitation of magnesium hydroxide, and also because magnesium does not form an insoluble molybdate. Westphal (Diss., Berlin, 1895) has prepared a soluble molybdate, $MgMoO_4 \cdot 2H_2O$, and the curve in Fig. 1 shows that suitable conditions exist for its crystallisation from a solution of magnesium sulphate and sodium molybdate. From nickel or beryllium sulphate solution, however, no precipitate was formed. The titration curve for the latter in Fig. 1 reveals that as the sodium molybdate was added the p_H value gradually rose but did not reach the hydroxide precipitation p_H of 5.7. As pointed out

FIG. 1.



by Britton (*loc. cit.*), beryllium sulphate in its reactions behaves as if one equivalent of the acid radical were "weakly combined" and possessed much of its acid nature. In the present reaction this "weakly combined" acid has reacted with the sodium molybdate to form sodium polymolybdate whose p_H values are somewhat greater than 5 (compare Fig. 1 in Part III). Thus when 2 mols. (88.8 c.c.) of sodium molybdate were added to 1 mol. of beryllium sulphate the p_H was 5.4. The reaction might be represented thus: $2Na_2MoO_4 + BeSO_4 \longrightarrow Be(SO_4)_{0.5}(OH) + \frac{1}{2}Na_2SO_4 + \frac{1}{2}(3Na_2O, 4MoO_3)$, from which it is seen that the p_H of the solution would be largely determined by the composition of the sodium polymolybdate thereby formed. From Fig. 1 and Part III, it is found that the p_H set up by such a molybdate is 5.6, which shows

that the above equation provides a satisfactory picture of the reaction.

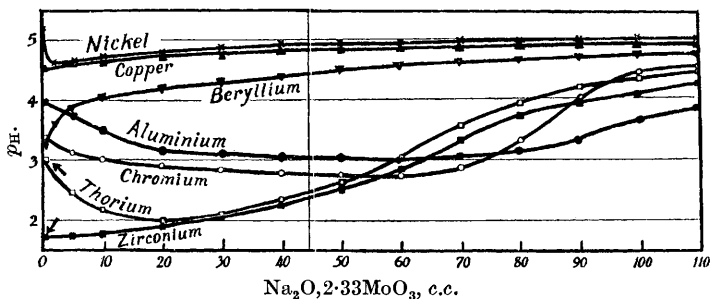
In the case of the interaction of sodium molybdate with copper sulphate solution, the p_H (*viz.*, 5.2) at which basic copper precipitates ordinarily begin to form was only just exceeded. As a result, a somewhat basic copper molybdate, $CuO, 0.70MoO_3$, began to be precipitated, and as the addition of an excess of the reactant only caused a small increase in p_H the precipitation of copper was far from complete. Although sodium molybdate caused aluminium to begin to be precipitated at p_H 4.4, a value slightly higher than that at which aluminium hydroxide begins to separate, both analysis of the precipitate and the p_H values produced on adding excess of the reagent indicate that 2.6 mols. of molybdenum trioxide were removed from the solution by each mol. of alumina. Whether this fact can be attributed to the precipitate containing a definite aluminium molybdate, $Al_2(MoO_4)_3$, is not certain, although it is unlikely that aluminium hydroxide would have adsorbed such a relatively large proportion of molybdic acid. An important factor, however, in the process of precipitation is the prevailing hydrogen-ion concentration.

Thorium and chromium differed from the others in that precipitation took place at p_H values below those at which basic compounds of these elements become precipitable. In the former case, precipitation began immediately at p_H 3, there being little subsequent p_H change until almost the stoichiometric quantity of alkali molybdate had been added. Thereafter, a large inflexion was produced, the p_H rising just above 7. That the normal compound was precipitated is suggested by (i) the fact that precipitation takes place at a p_H value lower than that at which the hydroxide separates, (ii) the sharp inflexion produced when 44.4 c.c. of the titrant had been added, and (iii) the final p_H value of the solution. This was supported by analysis of the precipitate dried at 100° (Found : MoO_3 , 44.78; ThO_2 , 39.71%; $MoO_3 : ThO_2 = 2.07 : 1$). In the case of chromium, precipitation began at a p_H value lower than that at which the hydroxide is precipitated. As in the reactions with sodium phosphate, borate, carbonate, and hydroxide, precipitation was considerably delayed, but in these reactions the delay was until a p_H value of 5.34 was attained, whereas in the present case it began at p_H 4.54. After the addition of an excess of the precipitant, the p_H value of the solution was 6.7, showing that a small amount of molybdic oxide had passed into the mother-liquor in consequence of the formation of a slightly basic molybdate (Table II). Since precipitation began at a p_H value lower than 5.34, it seems that a normal chromium molybdate first begins to separate, which is later followed by the precipitation of a little basic chromium molybdate.

On comparison with Fig. 1 (Part III), the final section of the zirconium curve reveals that much molybdic acid escaped precipitation with the zirconium hydroxide. The p_H values prevailing during the actual precipitation are very similar to those obtained during the precipitation with sodium hydroxide (Britton, *loc. cit.*).

Sodium Paramolybdate Titrations.—Fig. 2 represents the changes in hydron concentration which occurred on adding sodium paramolybdate solution to the various salt solutions. Since the p_H value of a sodium paramolybdate solution is 5.1 (Part III), it would be expected that this solution would be incapable of precipitating solutions of metallic salts whose hydroxides are precipitated at p_H values above 5, unless insoluble normal molybdates are formed. It is not surprising, therefore, that no precipitates were obtained

FIG. 2.



with solutions of the salts of beryllium, copper, nickel, and chromium. Addition of excess of sodium paramolybdate to the salt solutions of the first three metals tended to set up hydrogen-ion concentrations that were not very much removed from that of the reactant itself.

Unlike the reaction with sodium paratungstate (see this vol., p. 713), the addition of sodium paramolybdate solution to one of aluminium sulphate caused an increase in hydron concentration, followed by a decrease after addition of a large excess of the titrant. This increase could be caused by the liberation of molybdic acid due to basic compound formation, but no precipitation of this substance took place because the requisite p_H value (4.14) was not realised. Thorium and chromium showed a somewhat similar behaviour. Addition of the first amounts of reagent caused a fall in p_H value, this being especially marked in the case of thorium. No precipitate was obtained with the chromium salt, but after the addition of 60 c.c. of reagent the green solution turned violet, and the p_H gradually rose to 4.8. With thorium chloride a precipitate was obtained immediately at p_H 3. This is below the p_H value at which the

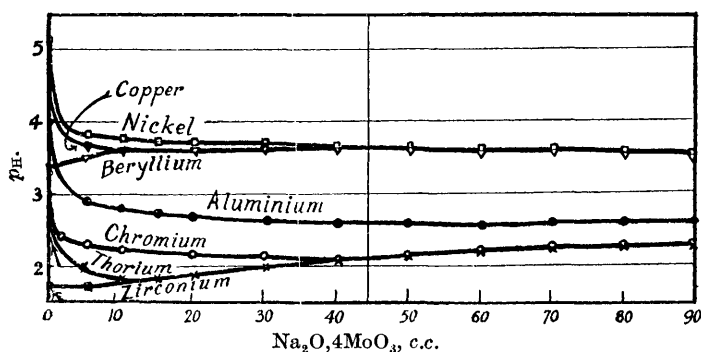
hydroxide is precipitated, but the large initial increase in hydron concentration, together with the final depression in p_H value, showed that the normal paramolybdate, $\text{ThO}_2 \cdot 4 \cdot 66\text{MoO}_3$, is not formed. The molybdic acid content of the white precipitate is given by $\text{ThO}_2 : \text{MoO}_3 = 1 : 2 \cdot 21$, suggesting that the precipitate was a mixture of the normal thorium molybdate $\text{Th}(\text{MoO}_4)_2$, and some molybdic oxide. If the normal molybdate were less soluble than the hydroxide, then it would be precipitated irrespective of the composition of the molybdate used as a precipitant, liberating molybdic oxide in solution. This would account for the initial increase in hydron concentration observed, whilst, since the molybdic oxide liberated would eventually combine with the excess sodium paramolybdate to form a polymolybdate of lower p_H value (Part III), the final p_H values are explained. At these p_H values, too, it is possible that the thorium molybdate would carry down quantities of molybdic oxide. A similar explanation holds in the case of aluminium and chromium, with the exception that metallic molybdate is not precipitated.

On adding the alkali paramolybdate solution to one of zirconium chloride, immediate precipitation began at a p_H value near that at which the same solution is precipitated by sodium hydroxide. The final p_H value of the solution was depressed below 5, showing that a polymolybdate had been formed in solution through the liberation of molybdic oxide in the reaction. That basic compound formation had taken place was confirmed by analysis, the ratio of metallic oxide to molybdic oxide in the white precipitate being $\text{ZrO}_2 : \text{MoO}_3 = 1 : 0 \cdot 86$. In view of this, it appears extremely improbable that the substance obtained by Kulka (Diss., Berne, 1902), *viz.*, $\text{Zr}(\text{MoO}_4)_2 \cdot 20\text{H}_2\text{O}$, by precipitation with ammonium paramolybdate, is actually a normal compound. It is more likely to be a mixture of free molybdic acid and basic zirconium molybdate, the analyses on which the formula was based being fortuitous.

Sodium Metamolybdate Titrations.—The changes in hydron concentration occurring during the reactions between the various metallic salts and sodium metamolybdate solution are indicated in Fig. 3. Fig. 1 (Part III) shows that the p_H of a sodium metamolybdate solution is 4, but that addition of the slightest amount of acid to such a solution brings about a great change in hydron concentration. Consequently, precipitation of basic compounds would not be expected from those solutions which are precipitated by sodium hydroxide at p_H values above 4. In the light of these observations, the non-precipitation of solutions of nickel, copper, beryllium, aluminium, and chromium salts under these conditions finds a ready explanation, for the hydroxide precipitation p_H value is never

attained. From Fig. 3, it appears that relatively large amounts of sodium polymolybdate were present in solution in the reactions with aluminium, chromium, and thorium salts due to the liberation of molybdic oxide. Thorium and zirconium salts gave immediate white precipitates on titration with sodium metamolybdate solution. In the former case, precipitation began at a p_H value lower than that required to precipitate the hydroxide, and was accompanied by a large increase in hydron concentration, the final p_H being 2.5. Hence large amounts of molybdic oxide had not entered into combination, but had formed a sodium polymolybdate of lower p_H with the excess sodium metamolybdate solution. In agreement with this,

FIG. 3.



analysis of the precipitate gave the ratio $\text{ThO}_2 : \text{MoO}_3 = 1 : 2.82$, which showed that it was probably the insoluble thorium normal molybdate together with co-precipitated molybdic oxide. Precipitation of the zirconium solution began at a p_H not far removed from that necessary to precipitate the hydroxide from the same solution. As in the previous case, a large depression of the p_H value of the solution showed that all the molybdic oxide had not entered into combination owing to basic compound formation.

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