CCLXXVII.—*Physicochemical Studies of Complex Acids. Part III. Molybdic Acid.*

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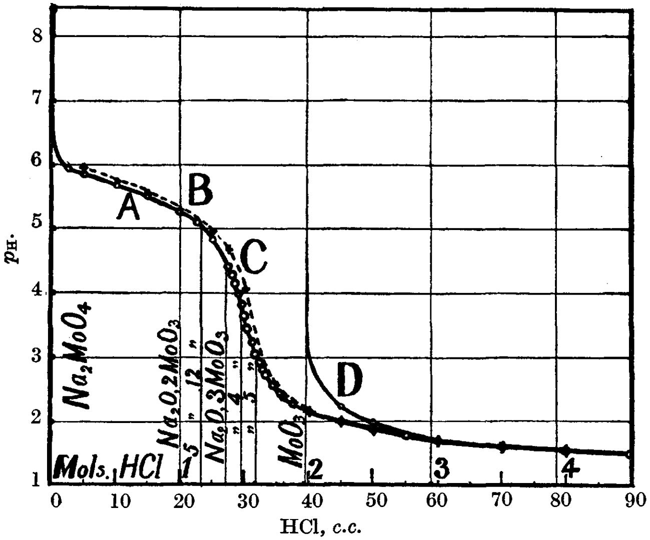
TRAVERS and MALAPRADE (*Bull. Soc. chim.*, 1926, **39**, 1406, 1543) investigated the course of neutralisation of molybdic acid with the quinhydrone and the hydrogen electrode, and Dumanski, Buntin, Dijatschovski, and Kniga (*Kolloid Z.*, 1926, **38**, 208) employed measurements of electrical conductivity and of depressions of freezing point to study the mode of displacement of molybdic acid from sodium molybdate solutions. As it appeared from their results that molybdates, though abnormal as regards their ionisation when compared with salts of normal dibasic acids, were very similar to tungstates (compare Britton and German, this vol., p. 1249), it was considered necessary to study the subject more fully.

It appears from the following work that molybdic acid exists in acidified solutions of sodium molybdate in the form of sodium polymolybdate, whose decomposition depends on the strength and the concentration of the acid used. The complex molybdate first formed in acid solutions is less stable than the corresponding tungstate and in the presence of hydrochloric acid rapidly undergoes decomposition (with the liberation of a highly ionised polymolybdic acid), after which the molybdic acid seems to pass into a pseudo-colloidal solution and is probably stabilised by the small quantities of hydrochloric acid which it adsorbs or, maybe, with which it combines.

FIG. 1.



EXPERIMENTAL.

The potentiometric titrations of sodium molybdate were carried out with the quinhydrone electrode, and the apparatus previously described (Parts I and II, this vol., pp. 1249, 1261) was used for the conductometric titrations.

Reaction between Sodium Molybdate and Hydrochloric Acid. (a) *Potentiometric Method.*—In Fig. 1 are given the quinhydrone curves indicating the change in hydrogen-ion concentration when 50 c.c. of 0·045*M*-sodium molybdate solution were titrated with 0·114*M*-hydrochloric acid. Curve A represents the values obtained when 2—3 minutes elapsed between each addition of acid, curve B represents the values obtained after solutions corresponding to various stages of the reaction had been boiled and then allowed to cool, and curve C, which is coincident with curve B, shows the values after

8 days' standing. The inflexion in curve A occurs at p_H 4·8 when the composition of the solute is that demanded by the paramolybdate $3Na_2O,7MoO_3$ (or $5Na_2O,12MoO_3$). Boiling and ageing caused a sharper inflexion to be formed when the solution had the composition corresponding to the formation of metamolybdate, $Na_2O,4MoO_3$, in solution. Curve D indicated the p_H values that would be expected were the reaction simply double decomposition according to the scheme $Na_2MoO_4 + 2HCl \longrightarrow 2NaCl + MoO_3,H_2O$, it being assumed that after 2 mols. of acid have been added the hydrogen ions arise from the excess acid and that the liberated molybdic acid has no effect.

TABLE I.

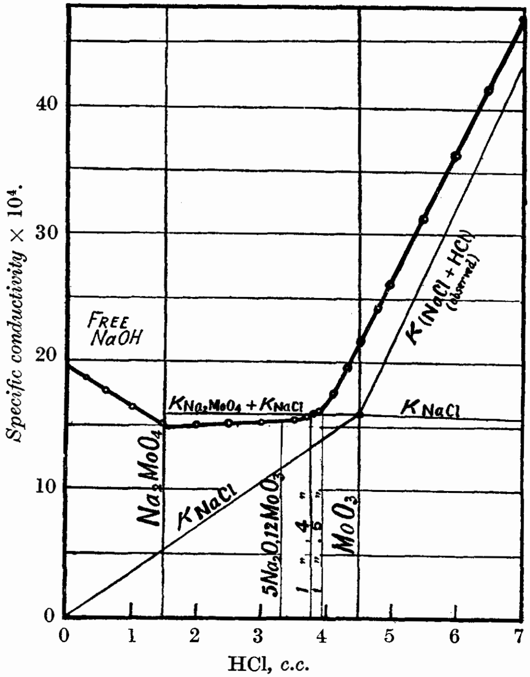
0·114*M*-HCl, c.c.	$Na_2O : MoO_3$, mols.	p_H.		
		Curve A.	Curve B.	Curve C.
0	1·0	8·47	8·47	8·47
9·9	0·75	5·68	5·77	5·72
19·7	0·5	5·28	5·30	5·35
29·6	0·25	3·68	4·00	4·09
34·5	0·125	2·47	2·61	2·60
39·5	0·0	2·14	2·19	2·23
50	Excess HCl	1·90	1·91	1·95
60	,,	1·72	1·68	1·75
70	,,	1·56	1·56	1·67

Curve D refers to the addition of 0·114*M*-hydrochloric acid to a volume of solution (89·5 c.c.) which was equal to that in the original titration when exactly 2 mols. (39·47 c.c.) of acid had been added and contained the exact weight of sodium chloride that would have been formed according to the above equation. Curve D finally merges with and just crosses curve A. It was first thought that the difference in p_H values observed between curves A and D could be explained if the sodium polymolybdate behaved as the salt of a very strong acid and therefore underwent very little decomposition on further addition of hydrochloric acid. Hence the increased hydrogen-ion concentration in curve A would be caused by the free hydrochloric acid in solution. Rosenheim and Bertheim (*Z. anorg. Chem.*, 1903, **34**, 427) and Travers and Malaprade (*Bull. Soc. chim.*, 1926, **39**, 1406) have shown, however, that molybdic acid is soluble in water, giving a solution of an acid of about the same strength as trichloroacetic acid. From determinations of the rate of hydrolysis of methyl acetate, the former workers have found a dissociation constant of $5·2 \times 10^{-2}$. Hence it appears that sodium polymolybdate, which first exists in the acid solution, eventually decomposes and liberates a highly ionised polymolybdic acid, to give rise to a hydrogen-ion concentration slightly less than would have been produced by the hydrochloric acid. Further addition of hydrochloric acid results in diminished ionisation of this poly-acid until finally only un-ionised molybdenum trioxide remains in solution. The fact that curves A and D (Fig. 1) cross may be attributed to the trioxide combining with or adsorbing small quantities of hydrochloric acid. Typical data are given in Table II.

TABLE II.

Point on curve, HCl, c.c.	Mols. HCl added.	p_H. Curve A.	p_H. Curve D.	p_H difference.
44·4	2·25	2·05	2·24	0·19
49·4	2·5	1·90	2·00	0·10
59·2	3·0	1·74	1·76	0·02
78·9	4·0	1·57	1·57	0·00
98·7	5·0	1·48	1·48	0·00
118·5	6·0	1·41	1·41	0·00
138·2	7·0	1·38	1·36	−0·02

FIG. 2.



Ageing and boiling had no great effect on the p_H values in the acid solutions, and, unlike the case of tungstic acid, no separation of trioxide took place. These solutions, however, underwent a striking colour change, being quite yellow when first mixed, the colour disappearing on ageing, probably through a change in the size of the particles (compare vanadate solutions; Britton and Robinson, this vol., p. 1261). By using more concentrated solutions, the trioxide can be thrown out of solution on boiling.

(b) *Conductometric Method.*—Fig. 2 illustrates the results obtained when a mixture of 100 c.c. of 0·005*M*-sodium molybdate and 5 c.c. of 0·1*M*-sodium hydroxide was titrated with hydrochloric acid (0·3289*M*) at 25°. Table III gives the numerical results for the above concentrations of reagents, and the results obtained by using a higher concentration of reagents are in Table IV.

TABLE III.

(a) *Neutralisation of excess* NaOH.

HCl, c.c.	0·0	0·3	0·6	1·0	1·5
$\kappa \times 10^4$, obs.	19·5	18·36	17·60	16·24	15·06

(b) *Decomposition of sodium molybdate.*

HCl, c.c.	$\kappa \times 10^4$, obs.	$\kappa \times 10^4$, Na_2MoO_4.	$\kappa \times 10^4$, NaCl.	Total $\kappa \times 10^4$, calc.
2·0	15·09	9·0	7·4	16·4
2·5	15·30	7·0	9·2	16·2
3·0	15·31	5·4	10·9	16·3
3·5	15·60	3·7	12·6	16·3
3·7	15·77	3·0	13·3	16·3
3·9	16·24	2·4	13·9	16·3
4·1	17·63	1·7	14·6	16·3
4·3	19·61	0·95	15·35	16·2
4·5	21·58	0·2	16·0	16·2

(c) *Excess acid added.*

HCl, c.c.	$\kappa \times 10^4$, obs.	$\kappa \times 10^4$, "theoretical mixture" (obs.).	$\kappa \times 10^4$, calc. for $Na_2O,5MoO_3$.
4·1	17·63	—	17·6
5·1	27·23	20·77	29·0
6·0	36·38	32·11	39·5
7·0	46·90	43·22	49·8
8·0	57·3	54·10	60·4
9·0	67·27	64·73	70·7

TABLE IV.

100 c.c. 0·05*M*-Na_2MoO_4 + 10 c.c. 0·106*M*-NaOH titrated with 3·247*M*-HCl at 25°.

(a) *Calculations based on double decomposition.*

HCl, c.c.	0	0·5	1·0	1·5	2·0	2·5	3·0	3·5	4·0	4·5	5·0
$\kappa \times 10^3$, obs.	10·12	9·26	9·26	9·28	9·43	9·73	12·5	16·0	20·3	24·5	28·5
$\kappa \times 10^3$, calc.	—	10·12	10·36	10·4	10·5	10·5	10·3	11·4	16·7	22·0	27·0

(b) *Calculations based on formation of* $Na_2O,5MoO_3$.

HCl, c.c.	2·9	3·1	3·3	3·7	4·1	4·5	4·9
$\kappa \times 10^3$, obs.	12·2	14·3	16·35	20·6	24·7	28·7	32·5
$\kappa \times 10^3$, calc.	11·5	13·3	14·76	18·0	21·5	24·5	28·0

The curve given in Fig. 2 discloses the same behaviour of the sodium molybdate during the course of decomposition as shown by the potentiometric curve in Fig. 1. The break after 1·52 c.c. of hydrochloric acid had been added corresponds to the neutralisation of the free alkali. Thereafter little variation in specific conductivity occurred until the composition of the molybdate had become approximately that required by the paramolybdate, *viz.*, $5Na_2O,12MoO_3$. It then increased gradually until the added acid was about equal to that necessary to form $Na_2O,5MoO_3$. At this stage, a rapid and uniform increase in conductivity began, which was of the order of that which would have been established by free hydrochloric acid. This occurred before the theoretical end-point (4·56 c.c.) had been reached. The values recorded in Table IV give a similar curve.

As in Part I, calculations have been made of the specific conductivities at different points on the assumption that they are equal to the sum of those of the solutes present at their respective dilutions, having been formed by the reaction represented by the equation on p. 2156, and also that the liberated molybdic acid had no effect on the conductivity of the solution.

The specific conductivities of sodium molybdate were extrapolated from the data obtained by Walden (*Z. physikal. Chem.*, 1887, **1**, 529), and those for sodium chloride and hydrochloric acid from the data in Landolt–Börnstein's "Tabellen." These calculated conductivities are given in Tables III and IV. Table III shows that there is little difference in the calculated and the observed conductivities until 3·8 c.c. of acid have been added corresponding to the formation of a metamolybdate, $Na_2O,4MoO_3$, in solution. Thereafter, the observed values were much higher than those calculated on the assumption that free hydrochloric acid was present only after 4·56 c.c. had reacted. Similar results are obtained in Table IV at the higher concentration. The curves indicate that the assumption that the molybdic acid formed has no effect on the conductivity is justifiable, at any rate, until the solution has the composition $Na_2O,4MoO_3$. As stated above, molybdic acid, unlike tungstic acid, has an appreciable solubility in water, in which it has marked acidic properties. The fact that this is not reflected in an enhanced conductivity is due to its combination with the normal sodium molybdate to form a polymolybdate whose conductivity is approximately equal to that of the parent salt. This is true for polymolybdates having compositions lying between Na_2MoO_4 and $Na_2O,4MoO_3$, as may be seen from Table V, which gives the specific conductivities ($\times 10^3$) at various dilutions. The table was drawn up from the records of Walden (*loc. cit.*), Rosenheim (*Z. anorg. Chem.*, 1916, **96**, 139), and Rosenheim and Felix (*ibid.*, 1913, **79**, 292). The dilutions (in litres) refer to volumes containing 1 g.-atom of sodium, and of hydrogen in the case of the molybdic acid solutions.

TABLE V.

Dilution	32	64	128	256	512	1024
$Na_2[O(MoO_3)]$	3·14	1·66	0·87	0·45	0·23	0·12
$Na_2[O(MoO_3)_{12·5}]$	3·09	1·70	0·91	0·49	0·26	0·14
$Na_2[O(MoO_3)_4]$	3·09	1·69	0·94	0·51	0·28	0·16
$Na_2[O(MoO_3)_8]$	6·15	4·74	2·73	1·48	0·79	0·40
$\kappa_8 - \kappa_4$	3·06	3·05	1·79	0·97	0·51	0·24
$H_2[O(MoO_3)_4]$	—	2·23	1·40	0·74	0·38	0·20

The specific conductivities of sodium octamolybdate are considerably higher than those of the tetramolybdate : this, as will be shown latter, can be traced to the hydrolytic dissociation in solution of the former into the latter and free molybdic acid.

The fact that the introduction of molybdic acid into the sodium molybdate molecule results in little change in the specific conductivity suggests that the ionisation of the polymolybdate is similar to that of the normal molybdate :

$$Na_2[O(MoO_3)_x] \rightleftharpoons 2Na^{\bullet\bullet} + [O(MoO_3)_x]''.$$

From the potentiometric and conductometric curves it appears that soon after $x = 4$, corresponding to the formation of the metamolybdate, a polymolybdate is formed which, since it is not decomposed by weak acids (*vide infra*), behaves as the salt of a strong polymolybdic acid. The work of Travers and Malaprade and of Rosenheim and Bertheim (*locc. cit.*) shows that molybdic acid in a polymerised form is not quite as strong as hydrochloric acid. Therefore a strong acid like hydrochloric would slowly decompose the polymolybdate, liberating the somewhat weaker polymolybdic acid in an amount depending on the excess added. Hence the large increase in conductivity observed in Fig. 2 on addition of hydrochloric acid in excess of 4 c.c. of acid (less than 2 mols.) is due, in the first place, to the free hydrochloric acid, and subsequently to some polymolybdic acid, similarly dissociated and having much the same specific conductivity as hydrochloric acid. Table III (c) was compiled on the assumption that the sodium polymolybdate was not attacked by hydrochloric acid and that the conductivity after the addition of 3·95 c.c. of acid was due to free hydrochloric acid. The column headed " theoretical mixture " gives the observed specific conductivities of solutions containing sodium chloride and hydrochloric acid in quantities which would have been present had no molybdate been present in the solution. Addition of increasing amounts of hydrochloric acid represses the ionisation of the liberated polymolybdic acid until a stage is reached at which the conductivity of the solution equals that of the "theoretical mixture." Afterwards only un-ionised molybdenum trioxide remains (Table IV). Finally, the conductivity of the solution is lower than that of the "theoretical mixture" by a fairly constant amount, showing that the trioxide has removed hydrogen ions, probably in functioning as a sexavalent base in combining with a little hydrochloric acid.

TABLE VI.

0·3289M-HCl, c.c.	$\kappa \times 10^4$, obs.	$\kappa \times 10^4$, "theoretical mixture."	$\kappa \times 10^4$, difference.
10	77·20	75·05	2·15
15	124·55	124·55	0
20	168·80	169·30	−0·50
25	212·30	213·7	−1·40
30	250·40	251·2	−0·80
35	285·10	287·40	−2·30
40	320·20	322·20	−2·00

The values in the third column were obtained in exactly the same way as for curve D in the potentiometric method.

If a complex, $Na_2O,5MoO_3$, were formed in the potentiometric titration, as suggested by the curve, then amounts of hydrochloric acid added in excess of 31·6 c.c. should determine the hydrogen-ion concentration by forming equivalent amounts of a polymolybdic acid. Were this acid completely dissociated, the following p_H values would be obtained :

HCl, c.c.	35·0	40·0	45·0	50·0	55·0	60·0	80·0
p_H, obs.	2·47	2·14	2·00	1·90	1·79	1·72	1·56
p_H, calc.	2·34	1·97	1·80	1·68	1·60	1·53	1·37

The higher observed p_H values might possibly be due, at least in part, to the smaller dissociation of the liberated polymolybdic acid.

Reaction between Sodium Molybdate and Weak Acids.

In Fig. 3 are given the quinhydrone curves obtained on titrating 50 c.c. of 0·045M-sodium molybdate solutions with 0·0936M-acetic and 0·0667M-phenylacetic acids. As before, the upper curves represent the p_H values which would have been obtained if simple double decomposition had occurred and the liberated molybdic acid had no effect on the hydrogen-ion concentration of the solution. At first, there is a sharp increase in the hydrogen-ion concentration, followed by a buffering action in the same zone as when hydrochloric acid was used. The positions of the inflexions of the curves (Fig. 3), together with the discrepancies between the p_H values observed and those calculated on the above assumption, seem to indicate that a stable polymolybdate, $Na_2O,3MoO_3$, is formed in solution, which resists further attack by the weak acid. This hypothesis accounts for the hydrogen-ion concentration observed, as Tables VII and VIII show.

TABLE VII.

Phenylacetic acid, $K_a = 5{\cdot}4 \times 10^{-5}$.

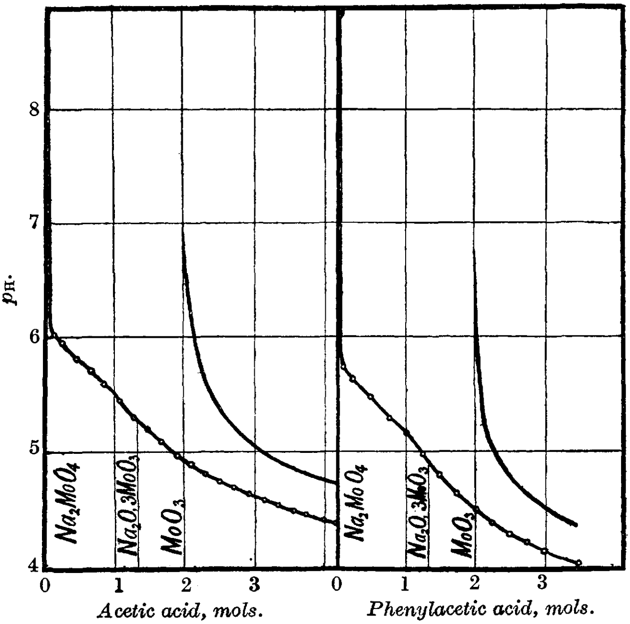
Acid, c.c.	p_H (1).	p_H (2).	p_H (3).
70·0	4·46	5·73	4·56
80·0	4·34	5·03	4·41
90·0	4·26	4·78	4·30
100·0	4·15	4·62	4·22
110·0	4·08	4·50	4·14
120·0	4·01	4·41	4·08

TABLE VIII.

Acetic acid, $K_a = 1{\cdot}8 \times 10^{-5}$.

Acid, c.c.	p_H (1).	p_H (2).	p_H (3).
40·0	5·10	—	5·30
50·0	4·88	6·10	4·96
60·0	4·74	5·30	4·76
70·0	4·64	5·04	4·63
80·0	4·55	4·88	4·53
90·0	4·48	4·76	4·45
100·0	4·41	4·67	4·38

FIG. 3.



The values indicate (1) the p_H values of the acid solutions in the two titrations, (2) those which would have been set up if the sodium molybdate had been completely decomposed, liberating molybdic oxide, and (3) those calculated on the assumption that the polymolybdate formed which resisted the attack of these acids was $Na_2O,3MoO_3$.

In both tables the agreement between the values given in the second and the fourth columns is good. Hence molybdic oxide exists in dilute solutions of weak acids in the form of a polymolybdate, probably as a colloidal electrolyte, *e.g.*, $2Na^{\cdot\cdot} + [O(MoO_3)_x]''$.

As might be expected, these weak acids decompose the normal molybdate to a smaller extent than hydrochloric acid, the complex in the former case being $Na_2O,3MoO_3$, and in the latter $Na_2O,5MoO_3$. Further addition of strong acids causes total decomposition of the complex, liberating molybdic oxide in solution.

In view of this, it was thought that a titration of sodium molybdate solution with a moderately strong acid like monochloroacetic acid would be of interest. The dissociation constant of this acid is $1 \cdot 55 \times 10^{-3}$ (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 170), a value lying between those of acetic and phenylacetic acids and hydrochloric acid. As this value was derived from conductivity data, it has been redetermined by the potentiometric method. For this purpose, quantities of $0 \cdot 106M$-monochloroacetic acid were added to 41·8 c.c. of $0 \cdot 108M$-sodium hydroxide, and the p_H values determined with the quinhydrone electrode. The values of K were then derived from the formula

$$p_H = p_K + \log \frac{[\text{salt}] + [\text{H}^{\cdot}]}{[\text{acid}] - [\text{H}^{\cdot}]}$$

(compare Britton, " Hydrogen Ions," 1929, p. 129) and are tabulated below.

C.c. of $CH_2Cl \cdot CO_2H$	45·0	50·0	80·0	90·0	100·0
p_H	4·07	3·60	2·90	2·80	2·72
$K \times 10^3$	1·45	1·46	1·53	1·75	1·56

Mean $K_a = 1 \cdot 55 \times 10^{-3}$.

The mean value is in good agreement with that obtained by Ostwald. The titration of sodium molybdate solution with monochloroacetic acid gives the same type of curve as before, but owing to the fact that this acid is much stronger than acetic or phenylacetic acid, it has been found by calculation that much more decomposition occurs, in fact the p_H values obtained indicate that the polymolybdate formed has a composition intermediate between $Na_2O,3MoO_3$ and $Na_2O,5MoO_3$.

It was suggested on p. 2160 that sodium polymolybdates are formed in solution which are slowly decomposed by strong acid with the liberation of a highly ionised polymolybdic acid. Travers and Malaprade (*loc. cit.*) observed an inflexion corresponding to the formation of $Na_2O,4MoO_3$ on titrating molybdic acid with sodium hydroxide. They assumed, therefore, that molybdic acid was present in solution, not as H_2MoO_4, but as tetramolybdic acid, $H_2[O(MoO_3)_4]$. Cryoscopic determinations and rates of catalytic decomposition of esters have been found by them, and by Rosenheim and Bertheim, to point to this mode of ionisation. Travers and Malaprade carried out determinations of the hydrogen-ion concentration of molybdic acid solutions with the quinhydrone electrode, and found that not more than two hydrogen ions were set free from 4 mols. of molybdic acid. The work of Dumanski and his collaborators shows that after 1·6 mols. of hydrochloric acid have been added to 1 mol. of sodium molybdate, there is a sudden increase in the difference between the freezing-point depressions of the actual reaction mixture and of a theoretical mixture made up on the assumption of simple double decomposition. This may be attributed to the decomposition of the $Na_2O,5MoO_3$ formed with the liberation of a highly ionised polymolybdic acid in solution. Similar conclusions may be drawn from the conductivity results of these authors.

Rosenheim and Bertheim's conductivity data on molybdic acid solutions can best be explained on the view that the molybdic acid is present in solution in a polymerised form, approximating to $H_2[O(MoO_3)_4]$. Extrapolation of $\Lambda_{\frac{1}{2}Na_2[O(MoO_3)_4]}$ to infinite dilution by Kohlrausch's "square-root method" gives a value of 100 approximately, and if 51 be taken as the ionic mobility of the sodium ion at 25°, it follows that the ionic mobility of $\frac{1}{2}[O(MoO_3)_4]''$ is 49. On plotting the molecular conductivities of molybdic acid, it is found that Λ_∞ of H_2MoO_4 is also about 100 mhos. If it be assumed that the acid in solution is $H_2[O(MoO_3)_4]$ instead of H_2MoO_4, then Λ_∞ becomes 400 approximately. This is in qualitative agreement with the conductivity obtained by adding the ionic mobilities, *viz.*, $l_{H^\cdot} = 319$, and $l_{[O(MoO_3)_4]''} = 49$, whence $\Lambda_\infty = 368$. Whilst, owing to the errors inherent in the extrapolations, no great confidence is attached to these figures, it is considered that they definitely indicate that in solution molybdic acid dissociates in a manner similar to $H_2[O(MoO_3)_x] \rightleftharpoons 2H^\cdot + [O(MoO_3)_x]''$, where x is about 4.

It appears from these experiments that the polymolybdate which is able to exist in the undecomposed condition in solution corresponds to the acid $H_2[O(MoO_3)_x]$, where x may vary from 1 to 4, and possibly to 5, in view of the results here recorded. Rosenheim and Felix isolated the salt $Na_2[O(MoO_3)_8]$ from an acidified solution of sodium molybdate, and determined the conductivity of its solutions (see Table V). On referring to Fig. 1, it will be seen that on the addition of the 34·5 c.c. of hydrochloric acid requisite to form this salt, the solution had become distinctly acidic, and Fig. 2 shows that at 4·19 c.c. of acid the conductivity was of such a magnitude as would be produced by the presence of some free strong acid. It was therefore considered that the greater specific conductivities of the salt indicated in Table V, compared with the other molybdates, was due to the production of free molybdic acid in the solution according to the following equation :

$$Na_2[O(MoO_3)_8] \rightleftharpoons H_2[O(MoO_3)_4] + Na_2[O(MoO_3)_4].$$

If this were the case, then κ_8, the specific conductivity of the octamolybdate, minus κ_4, the specific conductivity of the tetramolybdate, should be equal to the specific conductivity of $H_2[O(MoO_3)_4]$ in the dilution at which it happens to be present. The values of $\kappa_8 - \kappa_4$ are given in Table V, together with the values of κ for tetramolybdic acid which were calculated from the observed data of Rosenheim. Though the agreement between the two sets of figures is not very good, it is sufficiently close to justify the conclusion that hydrolytic dissociation of the octamolybdate does actually occur.

These experiments, in demonstrating that sodium polymolybdates exist in acidified solutions, supply an explanation of the methods that have been adopted to prepare the various polymolybdates; thus Ullik (*Sitzungsber. Wien Akad.*, 1867, **55**; *Annalen*, 1867, **144**, 204, 320) prepared $Na_2O,3MoO_3$ by adding an excess of acetic acid to sodium paramolybdate, and $Na_2O,8MoO_3,17H_2O$ by adding 1·75 mols. of hydrochloric acid to 1 mol. of normal molybdate. Rosenheim and Felix (*Z. anorg. Chem.*, 1913, **79**, 292) and Wempe (*ibid.*, 1912, **78**, 298) adopted the same method. Using larger quantities of hydrochloric or nitric acid, Ullik (*Annalen*, 1870, **153**, 373) and Rosenheim and Felix (*loc. cit.*) prepared a decamolybdate, $Na_2O,10MoO_3$, with 6, 12, or 21 mols. of water of crystallisation. On boiling a fairly concentrated solution of sodium molybdate with nitric acid (*d* 1·5) for some time, Ullik (*loc. cit.*) obtained $Na_2O,16MoO_3,9H_2O$. This compound was apparently only stable in the presence of acid. The same author (*Annalen*, 1867, **144**, 325) obtained a tetramolybdate by treating the normal compound with the calculated amount of hydrochloric acid. Travers and Malaprade (*loc. cit.*), however, on repeating this preparation always got the trimolybdate, $Na_2O,3MoO_3$, or mixtures of the tetramolybdate and the trimolybdate.

The last two authors confirmed the observations of Ullik (*Annalen*, 1867, **144**, 204, 320) that polymolybdates gave characteristic colour reactions with potassium ferrocyanide solutions that were not given by the normal molybdate. They therefore considered this test to be specific for certain polymolybdates. It is an interesting fact that if a few drops of a solution of potassium ferrocyanide be added to a solution of sodium molybdate, and this is then titrated with hydrochloric acid, reduction of the sexavalent molybdenum just begins to occur, as shown by the appearance of a brown colour, and eventually of a reddish-brown precipitate containing ferrocyanide, when the composition of the solute is approximately $Na_2O,4MoO_3$. On further addition of acid the colour becomes more intense, so much so that after the stoicheiometrical amount to decompose the sodium molybdate has been added, the variation in the colour change is slight. It will be seen from Fig. 1 that the incidence of reduction occurs at the stage when a considerable increase in the hydrogen-ion concentration of the solution is about to take place. As the hydrogen-ion concentration increased, so did the extent of the reduction of the solution. Similar observations were made with a solution of ferrous sulphate. Unfortunately, it was not possible to ascertain whether any reduction occurred in molybdate solutions having a p_H value between 7 and 4 on account of the precipitation of ferrous molybdate. It is significant, however, that the blue colour of quinquevalent molybdenum did not become apparent until 1·5 mols. of acid had been added to 1·0 mol. of the normal molybdate, after which the blue coloration became increasingly intense.

These two sets of observations seem to suggest that the reducibility of sexavalent molybdenum is a function of the prevailing hydrogen-ion concentration of the solution, as might be expected from the ionic reaction, *e.g.*, $MoO_4'' + 8H^{\cdot} \rightleftharpoons Mo^{\cdot\cdot\cdot\cdot\cdot} + 4H_2O$, and that the colour changes produced are the outcome of the different reduction potentials of the sexavalent molybdenum in solutions of different hydrogen-ion concentrations.

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