CLXI.—*Physicochemical Studies of Complex Acids. Part I. Tungstic Acid.*

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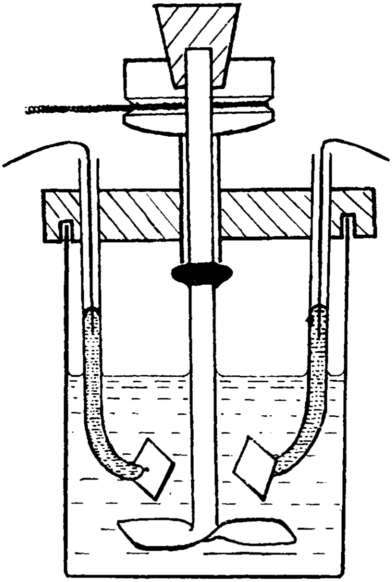
IN a previous communication (Britton, J., 1927, 147) it was shown that in solution tungstic acid reacts with sodium hydroxide as a dibasic acid, but that in all other respects its behaviour is abnormal. The present paper deals with potentiometric and conductometric experiments which have been carried out to gain some insight into its nature. For this purpose, it was possible to use the quinhydrone electrode successfully in acid solutions.

When a concentrated solution of sodium tungstate is treated with an excess of hydrochloric acid, tungstic acid is usually precipitated. If, however, dilute solutions are employed, no separation occurs, the solution remaining perfectly clear. This is a surprising fact in view of the insolubility of tungstic acid in dilute acid solutions, though the freshly precipitated oxide may often be peptised by concentrated acid solutions. It might be inferred, from the approximate p_H curve given in the earlier paper, that the comparatively high concentration of hydrogen ions set up in the solution immediately after the amount of added hydrochloric acid exceeded 1·5 mols. per mol. of sodium tungstate, was caused by the liberation of tungstic acid in an ionised form, the tungstic acid hitherto produced having combined with the undecomposed sodium tungstate in the form of polytungstates. Contrary to expectation, the following work indicates that the enhanced hydrogen-ion concentration is due to free hydrochloric acid, which, on the basis of the equation $Na_2WO_4 + 2HCl \longrightarrow 2NaCl + WO_3,H_2O$, would not be expected to exist until 2 mols. are added, unless an inert sodium polytungstate (which could resist the attack of hydrochloric acid) were produced in the course of the reaction.

FIG. 1.

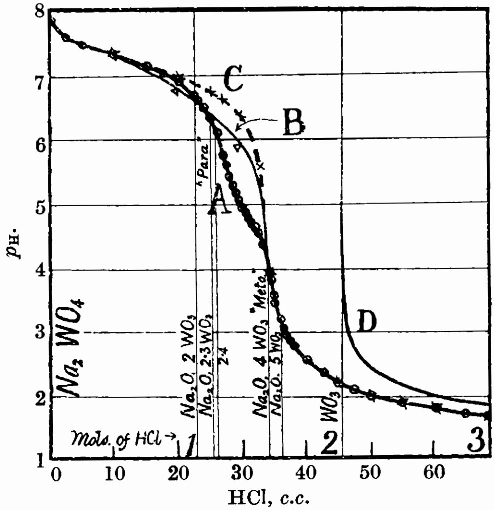


EXPERIMENTAL.

Quinhydrone yielded reproducible *E.M.F.*'s in all solutions of tungstates, the contact electrode being bright platinum foil attached to a platinum wire fused into the end of a glass tube containing mercury. The solutions undergoing examination were placed in beakers, to which about 0·05 g. of quinhydrone had been added. They were connected, through a salt bridge containing a saturated solution of potassium chloride, the ends of which were plugged loosely with filter paper, to a normal calomel electrode. Before any potentials were measured, the solution was vigorously shaken mechanically. These measurements were made at room temperature, and the p_H values were calculated by using the appropriate normal reduction potential of quinone–quinol obtained from Biilmann and Krarup's formula (J., 1924, **125**, 1954).

The conductometric titrations were performed in a thermostat, carefully regulated to 25·0° ± 0·05°, a specially designed cell being used in which efficient mechanical stirring was possible without moving the cell or disturbing the electrodes (see Fig. 1) The cell has a capacity of 150 c c.; it is provided with a tightly fitting ebonite cap, through which pass two glass tubes supporting the square platinum electrodes and, in the centre, a short copper tube in which the rod of the glass paddle rotates. The latter, which operates below the electrodes, is prevented from coming into contact with them by means of the rubber band placed just below the copper tube. The paddle rod is supported in the aluminium pulley wheel by means of a tightly fitting rubber bung in which it is fitted. The electrodes were platinised in the usual manner. The water used in the solutions had a specific conductivity of 4 × 10^{-6} mho.

FIG. 2.



Reaction between Sodium Tungstate and Hydrochloric Acid.—(a) *Potentiometric method.* This reaction has been investigated electrometrically in solutions of various concentrations, but as the type of curve obtained in all cases is the same, reference will be made only to those relating to the more dilute solutions. In Fig. 2

are given the quinhydrone curves illustrating the course taken by the hydrogen-ion concentration when 50 c.c. of 0·05*M*-sodium tungstate were titrated with 0·1095*M*-hydrochloric acid. Curve A represents the change occurring during a titration in which about 3 minutes elapsed between each addition of acid. Curve B was constructed from p_H measurements made on solutions corresponding with various stages of the titration after they had been allowed to stand for one week. Curve C refers to data obtained from solutions corresponding with different stages of the titration after 5 minutes' boiling followed by immediate cooling to room temperature. The p_H values at different stages of the titration under these conditions are recorded in Table I. Two inflexions appear in Curve A, one of which was obscured in the curve given in the earlier paper on account of difficulties introduced by the electrodes then used. The first occurs between p_H 6·3 and 3·8, the corresponding polytungstate formed varying from about 2·3 to 4·0 mols. of WO_3 per mol. of Na_2O. These limits happen to be those associated with the so-called paratungstate and the metatungstate respectively. This inflexion disappears (as shown Curves B and C) when the solutions concerned are boiled or allowed to stand. The second inflexion indicates that after the metatungstate has been formed the solution rapidly acquires an acid reaction of a magnitude similar to that which would be caused by free hydrochloric acid. Curve D represents the course which would have been taken by the hydrogen-ion concentration if the hydrochloric acid had reacted with the sodium tungstate in accordance with the equation $Na_2WO_4 + 2HCl \longrightarrow 2NaCl + WO_3,H_2O$, on the assumptions (1) that, after the stoicheiometrical amount of acid has been added, the hydrogen ions are due only to the excess of hydrochloric acid, and (2) that the tungstic acid liberated has no effect. Such an assumption seemed justifiable in view of the observations of Kargin (*Kolloid-Z.*, 1929, **49**, 281), who found that tungstic acid sols had p_H values of 3·69—3·68.

TABLE I.

0·1095*N*-HCl, c.c.	$Na_2O : WO_3$, mols.	p_H. Curve A.	p_H. Curve B.	p_H. Curve C.
0	1	7·90	8·00	8·00
11·4	0·75	7·30	7·30	7·28
22·8	0·50	6·65	6·84	6·62
34·2	0·25	3·86	5·0	5·0
39·9	0·125	2·49	2·48	2·58
45·6	0·0	2·14	2·12	2·12
50·0	Excess HCl	2·00	2·00*	1·93*
60·0	,,	1·77	1·81*	1·74*
75·0	,,	1·61	1·61*	1·60*

* Some precipitation had taken place.

Curve D was obtained with the quinhydrone electrode, and relates to the addition of 0·1095*N*-hydrochloric acid to a volume (*viz.*, 95·6 c.c.) of solution equal to that of the solution in the original titration when exactly 2 mols. (45·6 c.c.) of hydrochloric acid had been added, and which contained the exact weight of sodium chloride that would have been formed if the reaction shown above had at that point been just completed. Typical data are given in Table II. Ageing and boiling had no great effect on the p_H values of the very acid solutions, in spite of the fact that the solutions to which more than 50 c.c. of hydrochloric acid had been added underwent partial precipitation of tungstic oxide.

TABLE II.

HCl, c.c.	Corresponding vol. of HCl for Curve A, c.c.	p_H. NaCl + HCl.	p_H. Curve A.	Difference, 100 [H˙].
4·4	50	2·44	2·00	0·64
14·4	60	2·00	1·77	0·70
24·4	70	1·77	1·67	0·44
34·4	80	1·67	1·58	0·49

Increasing the concentrations of the reactants had little effect on the reaction as indicated by p_H data. One significant difference, however, occurred in the appearance of solutions containing more than 1·5 mols. of hydrochloric acid on boiling or ageing. Thus, when 0·55*N*-hydrochloric acid and 0·250*M*-sodium tungstate were used, the solution became opalescent with 1·5 mols. and increased with more acid until coagulation ensued at p_H 1·9 on ageing and at p_H 1·3 after boiling. The tungstic acid formed in these experiments, therefore, first exists in a perfectly clear solution, but on being boiled or kept, it undergoes very gradual precipitation. The surprising facts are that this precipitation has very little influence on the hydrogen-ion concentration, and further, that this concentration is greater than that which can be attributed to the excess of hydrochloric acid. It was suggested in the previous paper that the tungstic acid might possibly exist in the clear acid solution in a sub-colloidal form peptised by the hydrochloric acid. Were this the case, it would appear that a little hydrochloric acid would be either adsorbed by or chemically combined with the tungstic acid, and consequently the hydrogen-ion concentration of the acid solution would be slightly reduced. This is contrary to the facts. Nevertheless, the precipitation of the tungstic acid on standing suggests that it is colloidal; so also does the fact that if an electrolyte, such as potassium chloride, be included in the sodium tungstate solution, precipitation occurs much more readily on addition of hydrochloric acid.

A series of electrometric titrations was made of solutions to which 25 c.c. of N-potassium chloride had been added. The curves obtained were identical with A in Fig. 2, but the solutions began to become cloudy at the stage corresponding approximately with the formation of sodium metatungstate. Table III (col. 2) shows the p_H values relating to various additions of 0·535N-hydrochloric acid to a mixture of 50 c.c. of 0·1M-sodium tungstate and 25 c.c. of N-potassium chloride : since the amount of acid required for double decomposition is 18·7 c.c., the acid is in excess in every case. The third column, referring to the p_H values of solutions containing the same amounts of potassium chloride, sodium chloride, and hydrochloric acid, again shows that the tungstic acid solutions possessed enhanced hydrogen-ion concentrations. It should be emphasised that any possible influence caused by the potassium chloride was eliminated by the inclusion of this salt in all these solutions.

TABLE III.

HCl, c.c.	p_H, obs.	p_H, obs. for NaCl + HCl + KCl.	p_H, calc. for $Na_2O,5WO_3$ formation.
20	1·58	2·25	1·56
30	1·23	1·37	1·12
40	1·00	1·14	0·94
50	0·79	0·98	0·83

(b) *Conductometric method.* The two conductometric titrations detailed in Tables IV and V illustrate the nature of the reaction taking place between sodium tungstate and hydrochloric acid in solutions of different concentrations.

TABLE IV.

100 C.c. of 0·005M-Na_2WO_4 + 5 c.c. of 0·125M-NaOH titrated by 0·3247M-HCl.

HCl, c.c.	$\kappa \times 10^4$ (obs.), mhos.	Specific conductivities ($\times$ 10^4) of solutes.			$\kappa \times 10^4$ (calc.), mhos.
		Na_2WO_4.	NaCl.	HCl.	
0	24·4	10·0	0	—	—
0·5	22·5	9·9	1·9	—	—
1·0	20·5	9·8	3·8	—	—
1·5	18·7	9·7	5·5	—	—
2·0	17·3	9·6	7·3	—	16·9
2·5	17·3	8·0	7·4	—	15·4
3·0	17·3	6·3	10·8	—	17·1
3·5	17·3	4·9	12·4	—	17·3
4·0	17·7	3·0	14·1	—	17·1
4·5	19·6	1·7	15·7	—	17·4
5·0	25·1	0·04	17·3	—	17·3
5·5	30·8	—	17·2	5·4	22·6
6·0	36·1	—	17·1	10·8	27·8
6·5	42·2	—	17·1	16·0	33·1

TABLE V.

100 C.c. of 0·05M-Na_2WO_4 titrated by 3·247M-HCl.

HCl, c.c.	0	0·4	0·8	1·2	1·6	2·0	2·5	3·0	3·2	3·4	3·6	3·8	4·0	4·4
$\kappa \times 10^3$, obs.	8·77	8·77	8·76	8·75	8·75	9·13	10·0	13·66	15·82	20·00	22·42	24·34	26·52	31·15
$\kappa \times 10^3$, calc.	8·60	9·96	9·50	9·80	9·10	9·10	8·9	8·95	9·60	12·00	14·30	16·60	18·90	23·3

The curve illustrating Table IV is given in Fig. 3, and is seen to be in harmony with the potentiometric curves given in the previous paper and in Fig. 2 of the present paper. The sharp break at 1·93 c.c. corresponds with the neutralisation of the free alkali. Afterwards the conductivity does not begin to change appreciably until sufficient acid has been added to form the paratungstate in solution, whereupon a somewhat gradual increase occurs until 4·35 c.c. of acid have been added. At this point a sharp rectilinear increase in conductivity begins, and passes through the theoretical end-point at 5·01 c.c., *i.e.*, when the additional 3·08 c.c. calculated for the conversion of the sodium tungstate into sodium chloride have been added. The data in Table V give a similar curve.

An attempt has been made to analyse these conductometric-titration curves on the assumption that the observed specific conductivity of a solution at any point in a titration is equal to the sum of the specific conductivities of the solutes at the dilutions in which they are present. For the purpose of calculation, the reaction between sodium tungstate and hydrochloric acid was regarded as taking place according to the equation on p. 1250, and the liberated tungstic oxide was assumed to contribute no conductivity to the solution. The data for sodium tungstate were extrapolated from the records of Walden (*Z. physikal. Chem.*, 1887, **1**, 529), and those for sodium chloride and hydrochloric acid from the data given in Landolt–Bornstein's "Tabellen." Tables IV and V give the calculated values of the specific conductivities so obtained. Table IV shows a satisfactory agreement between the calculated and observed values over the range of 2—4 c.c. of added acid; thereafter the observed values are considerably higher than those calculated on the assumption that free hydrochloric acid was present in the solution only after 5·01 c.c. had reacted. The character of the curve in Fig. 3 indicates that the free acid must have existed before that point, actually from 4·35 c.c. If this were so, it would appear that the sodium polytungstate formed at this stage behaved as if it were the salt of a strong acid and therefore was not decomposed by hydrochloric acid. Such a possibility is not easily reconciled with the p_H values of tungstic acid sols. Similar conclusions may be drawn from

Table V, although it will be observed that, corresponding with additions of acid up to 2·0 c.c., the differences between the observed and calculated specific conductivities of these more concentrated solutions are somewhat greater than in Table IV. Although the theoretical end-point in this case is at 3·08 c.c., the considerable discrepancies appeared at 2·5 c.c.

It may be argued, that, in the first stages of these titrations, the tungstic acid immediately combines with the undecomposed sodium tungstate to form a polytungstate. This appears to be the case, at any rate until the solute has acquired the composition of sodium metatungstate ($Na_2O,4WO_3$), as may be seen from Table VI. This table gives the specific conductivities ($\kappa \times 10^3$) of solutions of sodium tungstate, paratungstate, and metatungstate at various dilutions as calculated from the data of Walden (*loc. cit.*), Rosenheim (*Z. anorg. Chem.*, 1916, **96**, 139), and Soboleff (*ibid.*, 1896, **12**, 16) respectively. The dilutions refer to the volumes in litres containing 1 g.-atom of sodium.

FIG. 3.

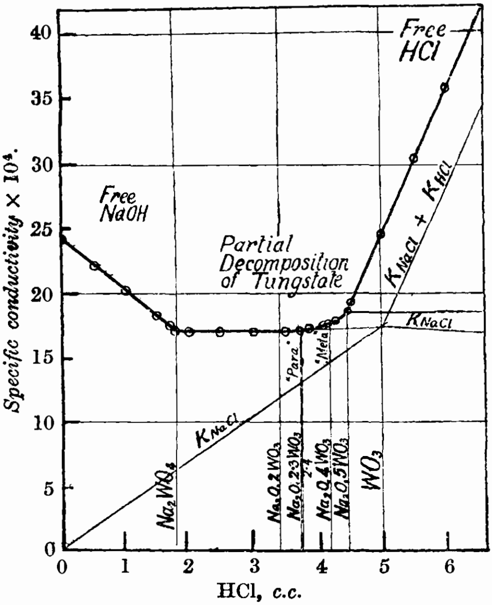


TABLE VI.

Dilution.	32.	64.	128.	256.	512.	1024.
Normal tungstate	2·80	1·49	0·78	0·40	0·21	0·11
Paratungstate	2·14	1·25	0·70	0·39	0·21	0·12
Metatungstate	2·80	1·54	0·84	0·46	0·24	0·13

These figures reveal that the introduction of tungstic acid into a solution of sodium tungstate results in a comparatively small change in conductivity, probably owing to the ionisation of the polytungstates being similar to that of the normal tungstate, thus : $Na_2[O(WO_3)_x] \rightleftharpoons 2Na^{\cdot} + [O(WO_3)_x]''$. It appears probable, in view of inflexions in the potentiometric and conductometric curves occurring when approximately 1·5 mols. of hydrochloric acid have been added to 1 mol. of sodium tungstate, in which case $x = 4$, that a polytungstate is formed very soon afterwards which behaves as a salt of a strong acid, and therefore resists reaction with further hydrochloric acid and thus remains in solution as such, imparting increased hydrogen-ion concentration and specific conductivity to the solution. Such a view seems feasible when it is remembered that tungstic acid sols, prepared by the prolonged dialysis of solutions of sodium tungstate to which an excess of hydrochloric acid has been added, contain an appreciable amount of sodium oxide (compare Graham, *Proc. Roy. Soc.*, 1864, **13**, 340; Sabanéeff, *Z. anorg. Chem.*, 1897, **14**, 354; Biltz and Vegesack, *Z. physikal. Chem.*, 1910, **68**, 376). If it be assumed that such a sodium polytungstate is formed in these conductometric titrations at the points at which the sudden increases in conductivity begin, *viz.*, at 4·35 c.c. in the first titration and 2·42 c.c. in the second, and that the conductivities then prevailing remain constant as far as the complex tungstate and sodium chloride in the solution are concerned, then the increases in conductivity caused by subsequent additions of hydrochloric acid will be due entirely to the added acid. It happens that in both cases the complex tungstate formed at this stage corresponds with $Na_2O,5WO_3$. It will be seen from Fig. 3 that the specific conductivity due to it and the sodium chloride is $17{\cdot}4 \times 10^{-4}$ mho. To test this view, the specific conductivities of the supposed excesses of hydrochloric acid in the various dilutions were calculated and added to the observed conductivity at the point when the limiting complex tungstate was considered to be formed. Table VII, giving

TABLE VII.

Titration.	HCl, c.c.	Dilution of HCl (litres).	Specific conductivity × 10^3, obs.	calc.
I	5·0	521	2·51	2·61
	5·5	296	3·07	3·20
	6·0	207	3·61	3·78
	6·5	160	4·22	4·35
	7·5	110	5·09	5·48
II	3·4	35·4	20·0	20·5
	3·8	24·6	24·3	25·0
	4·2	18·9	28·6	29·4
	4·4	16·9	31·2	31·5

the observed and calculated conductivities of the acid solutions in the two titrations, supports this hypothesis.

It was decided to test whether this idea would account for the increased acidity of solutions of sodium tungstate to which an excess of hydrochloric acid had been added. If the complex $Na_2O,5WO_3$ were formed in the course of the potentiometric titration (Fig. 2), then the amount of acid added in excess of 36·5 c.c. would determine the hydrogen-ion concentration. The following table has been compiled on this basis, it being assumed that the hydrochloric was completely ionised.

HCl, c.c.	40·0	50·0	60·0	70·0	80·0
p_H, obs.	2·49	2·00	1·77	1·67	1·58
p_H, calc.	2·37	1·83	1·63	1·51	1·44

The agreement is not entirely satisfactory, although comparison with the data given in the third column of Table II shows that the hypothesis accounts for much of the increased hydrogen-ion concentration. It also explains the difference in p_H found in the potassium chloride experiments (see Table III).

Boiling and ageing of acid tungstate solutions had no effect on their specific conductivity, but had slight effects on those solutions in which insufficient acid had been added to form the complex. This is in accordance with the p_H observations.

Reaction between Sodium Tungstate and Weak Acids.—As typical acids, phenylacetic and acetic were chosen, but since the published values of the dissociation constant of the former acid had been obtained from conductivity data, it was considered advisable to redetermine its value at 18° by means of the hydrogen electrode.

NaOH, c.c.	7·5	12·5	15·0	20·0	23·0	25·0	27·5
p_H	3·73	4·04	4·18	4·45	4·68	4·78	4·95
$K_a \times 10^5$	5·51	5·48	5·44	5·34	5·38	5·54	5·30

Mean $K_a = 5{\cdot}4 \times 10^{-5}$.

The following p_H values of various points on the titration curve of 50 c.c. of 0·0667*N*-phenylacetic acid with 0·0980*N*-sodium hydroxide were confirmed by the *E.M.F.* obtained with the quinhydrone electrode. Previous values at 25° range from $5{\cdot}0$—$5{\cdot}45 \times 10^{-5}$ (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 369; Dittrich, *J. pr. Chem.*, 1896, **53**, 368; White and Jones, *J. Amer. Chem. Soc.*, 1910, **44**, 197).

Fig. 4 gives the titration curves of 50 c.c. of 0·05*M*-sodium tungstate solution with 0·0667*N*-phenylacetic acid and with 0·0936*N*-acetic acid solution. The upper curves represent the p_H values which would have been established if the sodium tungstate had been entirely converted into the sodium salts of the weak acids when the stoicheiometric amount of the respective acids had been added, and if, thereafter, the curves represented the p_H values of weak acid solutions buffered by the sodium salts, it being assumed as before that the tungstic acid set free had no effect on their hydrogen-ion concentrations. It is seen that the initial parts of the curves indicate a buffered action in the same p_H zone as when hydrochloric acid was used. The lower p_H values assumed by the two solutions soon after 1 equiv. of acid had reacted prove that, some time before the 2 mols. of weak acid had been added, a sodium polytungstate must have been formed which behaved as the salt of strong acid and was in consequence undecomposable by weak acids. If it be considered that this particular sodium polytungstate is formed very soon after the inflexions have occurred, say at 50 c.c. ($\equiv$ 1·33 equivs.) of phenylacetic acid, and 35·6 c.c. ($\equiv$ 1·33 equivs.) of acetic acid, then it is easy to calculate what p_H values would be set up by the added acids in the presence of the amounts of salts of the respective weak acids formed in the production of the complex tungstate. Tables VIII and IX give (1) the p_H values of the acid solutions in the two titrations, (2) those which would have been set up if the sodium tungstate had been completely decomposed, liberating tungstic oxide, and (3) those calculated on the basis that the polytungstate formed which resisted the attack of these acids was $Na_2O,3WO_3$.

FIG. 4.

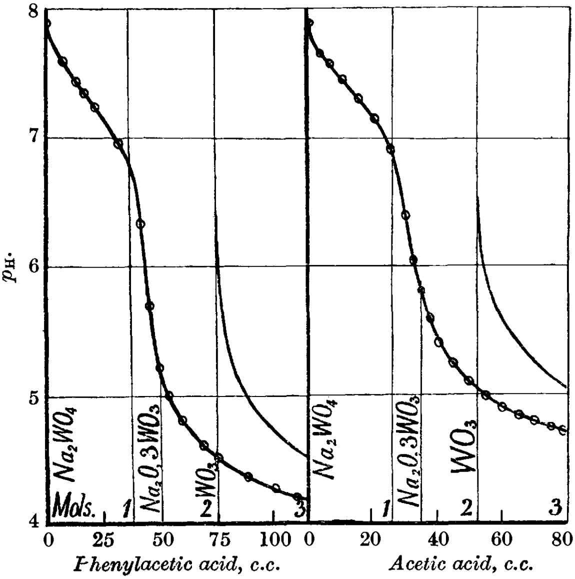


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TABLE VIII.

Phenylacetic acid; $K_a=5{\cdot}4\times10^{-5}$.

Acid, c.c.	p_H (1).	p_H (2).	p_H (3).
60	4·81	—	4·97
70	4·59	—	4·67
80	4·46	5·49	4·49
90	4·35	4·97	4·36
100	4·26	4·74	4·27
110	4·20	4·59	4·19
120	4·11	4·48	4·12

TABLE IX.

Acetic acid; $K_a=1{\cdot}8\times10^{-5}$.

Acid, c.c.	p_H (1).	p_H (2).	p_H (3).
50	5·11	—	5·14
60	4·91	5·65	4·91
70	4·79	5·25	4·76
80	4·68	5·05	4·65
90	4·65	4·91	4·56
100	4·56	4·80	4·49

In both tables the figures given in the second and fourth columns are in remarkably good agreement. It is fairly certain, therefore, that the cause of the non-precipitation of tungstic oxide from dilute acid solutions is to be traced to the existence of sodium polytungstate, probably in the form of a colloidal electrolyte, *e.g.*, $2Na^{\cdot} + [O(WO_3)_x]''$, in which the anion contains much tungstic oxide that is perhaps in a molecularly polymerised form, or, more probably, in a negatively charged colloidal micelle. One difference between the action of a strong and a weak acid lies in the extent to which the normal tungstate is decomposed before it can exist in a solution containing an excess of an acid. When hydrochloric acid was used, the polytungstate shown to be present in acid solution had approximately the composition $Na_2O,5WO_3$, whereas that present in solutions of the weak acids corresponded to $Na_2O,3WO_3$. Much less decomposition had thus occurred.

These observations throw much light on the methods which have been adopted to prepare various polytungstates. Thus, Lefort (*Compt. rend.*, 1876, **82**, 1182; *Ann. Chim. Phys.*, 1876, **9**, 98) prepared $Na_2O,3WO_3,4H_2O$ by crystallising an aqueous solution of the precipitate obtained by pouring a solution of sodium tungstate into one of boiling acetic acid. Wells (*J. Amer. Chem. Soc.*, 1907, **29**, 112) and Gibbs (*Proc. Amer. Acad.*, 1880, **15**, 1) both obtained $Na_2O,2{\cdot}5WO_3$ from cold acetic acid solutions of sodium tungstate. By the use of solutions of strong acids (hydrochloric and nitric), substances considerably richer in tungstic oxide have been prepared. According to Ullik (*Sitzungsber. Wien Akad.*, 1867, **56**, 157; *J. pr. Chem.*, 1868, **103**, 147) and Leontowitsch (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 130) respectively, $Na_2O,8WO_3,12H_2O$ and $Na_2O,6WO_3,15H_2O$ may thus be prepared. The fact that these polytungstates may be obtained from acid solutions furnishes remarkable support to the conclusions drawn from the foregoing experiments.

It was suggested on p. 1257 that the sodium polytungstates containing more tungstic oxide than the metatungstate behaved as if they were the salts of a strong acid, in that they were not easily decomposed by hydrochloric acid. The mode of ionisation of such an acid cannot be confirmed by direct experiment on account of the insolubility of tungstic oxide. Dumanski, Buntin, Dijatschkovski, and Kniga (*Kolloid-Z.*, 1926, **38**, 208) studied the reaction between sodium tungstate and hydrochloric acid by means of conductivity and cryoscopic measurements. They considered that the rapid increase in conductivity and the abnormal depression of the freezing points (greater than would have been expected if colloidal tungstic acid had been liberated), which occurred after approximately 1·4 equivs. of hydrochloric acid had been added, indicated that tungstic acid was being set free as an ionised semicolloid. Although this interpretation at first sight may appear to be convincing, it is felt that the hypothesis now advanced is the true one, especially as it affords an explanation of the methods adopted to prepare various polytungstates having high acid content.

The p_H values of Kargin's (*loc. cit.*) tungstic acid hydrosols do not give any indication of dissociation of the order that would be necessary to impart to the solution the conductivity observed. It appears probable, on the basis of observations described in this paper, coupled with those of Sabanéeff (*loc. cit.*) and Biltz and Vegesack (*loc. cit.*), that dialysis, even when prolonged, does not cause all the sodium to be removed from the colloidal solution, that Kargin's tungstic acid hydrosols contained a little sodium, and that this sodium was positively charged and the tungstic acid was present as a negatively charged micelle. If the structure and stability of tungstic acid sols, prepared by dialysis of acidified solutions of sodium tungstate, can thus be accounted for, then it appears that the p_H values of such sols are caused by the hydrogen-ion concentration of the sodium polytungstate they contain.

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