CCLVIII.—*The Structure of the Tungstic Acids.*

By Arthur Milnes Morley.

The object of this research was to determine whether the various "hydrated tungstic oxides" consist of a limited number of definite chemical compounds, or whether a continuous series of products of varying complexity and indefinite composition exists, as with the stannic acids (Collins and Wood, J., 1922, **121**, 441).

Laurent (*Ann. Chim. Phys.*, 1847, **21**, 54), from a study of the salts of tungstic acid, concluded that at least five or six different "acids" existed, whereas Riche (*ibid.*, 1857, **50**, 5) postulated only two acids, a white gelatinous product, $WO_3,2H_2O$, and a yellow, very dense substance, WO_3,H_2O. More recently, Burger (*Z. anorg. Chem.*, 1922, **121**, 240) made an *X*-ray examination of tungstic oxide and also of one white and one yellow tungstic acid, concluding that, in addition to WO_3, there exist two chemical compounds of composition H_2WO_4 (yellow) and H_4WO_5 (white). Hüttig and Kurre (*ibid.*, 1922, **122**, 44), from a study of dehydration curves, deduced that yellow tungstic acid prepared from a boiling solution is a compound, H_2WO_4, but that the white product prepared in the cold is a colloid, behaving as a "heap of tungsten trioxide particles, arranged in an irregular manner " (see also Hüttig, *Kolloid-Z.*, 1924, **35**, 337). Van Liempt (*Z. anorg. Chem.*, 1923, **127**, 215) has shown that under certain conditions, mixtures of white and yellow tungstic acids may be obtained by precipitating sodium tungstate solutions with mineral acids.

From these few references to the voluminous literature on the subject, it would appear that the existence of a yellow compound H_2WO_4 is definitely established, but that the composition of white tungstic acid is uncertain, it having been regarded as a compound H_4WO_5, and also as hydrated amorphous tungstic oxide. The composition of the mixed tungstic acids has not been determined.

Many changes in the general appearance of tungstic acids in particular circumstances are on record, but the reason for such changes is only partially understood. Particularly is this the case with the " white–yellow " change. Marignac (*Ann. Chim. Phys.*, 1863, **69**, 5) first pointed out the conditions under which the white acid changed colour, *viz.*, when it was either washed with hot water or kept in contact with cold water for a long time, or when it was boiled with a mineral acid. In most cases, the yellow substance produced was the usual type of amorphous precipitate. A product with a " silky lustre " was obtained by Lottermoser (*Chem. Z.*, 1911, 1111) and by Freundlich and Diesselhorst (*Physikal. Z.*, 1916, **17**, 117).

In the present experiments, various tungstic acids of known composition were submitted separately to the prolonged action of water, and of solutions of inorganic salts and of mineral and organic acids, and the products were separated and again analysed. All the original tungstic acids, and certain " aged " products were also examined by means of *X*-rays. The results show that two definite compounds exist of composition H_2WO_4 and H_2WO_4,H_2O, other tungstic acids being mixtures containing several constituents.

EXPERIMENTAL.

As a result of numerous preliminary experiments, four obviously different specimens of precipitated tungstic acid were chosen as the " standard " acids. The preparations were made from Kahlbaum's purest ammonium tungstate, $2(NH_4)_2O,5WO_3,3H_2O$, and A.R. hydrochloric acid. Analyses of the tungstate gave WO_3, 87·93; $(NH_4)_2O$, 7·93; H_2O, 4·05; total, 99·91%, and the tungstic oxide obtained by ignition was shown to be pure by quantitative reduction to metallic tungsten in a stream of purified hydrogen. Details are given of the preparation of one product of each standard type.

Preparation of the " Standard " Tungstic Acids.—Type A. Yellow, produced by a spontaneous change from white tungstic acid at laboratory *temperature.* A cold solution of ammonium tungstate (200 g. in 4·48 litres of distilled water) was poured with continuous stirring into 1·126*N*-hydrochloric acid (5 litres), the temperature of the mixture being 19·4°; the acidity of the filtered solution (methyl-orange) was 0·55*N*. The very pale yellow precipitate was washed by decantation with distilled water until the washing water contained only faint traces of chloride and ammonia; the liquid contained tungsten and had attained a constant p_H of 3. At this stage, a pronounced change occurred in the appearance of the tungstic acid : its volume considerably decreased, the yellow colour deepened, and the slightly opalescent supernatant liquid exhibited a silvery silky lustre when shaken. A suspension of the precipitate when shaken exhibited a very pronounced yellow silky lustre; this was presumably the effect obtained by Lottermoser, and by Freundlich and Diesselhorst (*locc. cit.*), but these investigators did not identify the particular tungstic acid involved. The yellow tungstic acid was now filtered through calico and dried in air to constant weight (40 g.; 19% of theoretical), precautions being taken to exclude dust.

The lemon-yellow powder so obtained appeared amorphous, but under a microscope (× 800) was seen to consist of flat leaflets, the largest being 10 μ in length and 4 μ across the broadest part. Frequent twinning occurred, suggesting that the particles should be regarded as very small crystals. Analysis gave WO_3, 85·49; H_2O, 14·39; NH_3, 0·01; Cl, nil; total, 99·89%, corresponding with the formula $WO_3,2{\cdot}17H_2O$.

Type B. Greyish-white, prepared at laboratory temperature. Acids of this type were prepared as above, but the precipitate obtained was washed by decantation with Manchester tap-water (of *ca.* 3° of hardness) instead of with distilled water. This slight variation produced a remarkable difference in the nature of the product. After precipitation, the temperature of the mixture was 16·8°, and the acidity (methyl-orange) of the filtered solution 0·55*N*. During the washing, the precipitated tungstic acid gradually assumed a bluish-white colour, and even after the most prolonged washing showed no trace of yellow. The final washing waters contained tungsten, a trace of chloride (from the tap-water), but no ammonia. The p_H value was constant at 3. The bluish-white precipitate was filtered off, and air-dried, as with type A. The final product was a greyish-white powder, which under the microscope appeared entirely amorphous and glassy. The irregularly shaped particles had a maximum breadth varying from 2 μ to 50 μ. From 200 g. of ammonium tungstate, 60 g. of tungstic acid were obtained (29% of theoretical).

All preparations of this type differed from those of type A in that, on fusion with sodium carbonate a small portion (shown to consist of calcium carbonate, with a small quantity of magnesium carbonate) was unaffected. These metals had evidently been adsorbed from the tap-water, and it was calculated that *ca.* 3% of the salts present in the washing water (calculated as $CaCO_3$) had been thus adsorbed. It is significant that Wilke-Dörfurt and Deker (*Kolloid-Z.*, 1925, **36**, Zsigmondy Festschr., 305) have shown that calcium is taken up by silicic acid during dialysis against tap-water.

The analysis of this product was: WO_3, 84·10; H_2O, 15·14; NH_3, 0·01; Cl, trace; infusible matter, 0·78; total, 100·03%, corresponding with the formula $WO_3,2{\cdot}32H_2O$.

Type C. A mixed product prepared at the boiling point. For this preparation, the concentrations of solutions were the same as for type A, but the precipitation was carried out from boiling solutions (*i.e.*, slightly above 100°), the acidity of the filtered solution being 0·59*N*. The precipitated tungstic acid was a mixture, consisting chiefly of a white product, together with a small amount of a much denser yellow product. To avoid loss by peptisation, the acid was washed by dialysis in parchment bags against distilled water. After 10 days, the washing water contained traces of ammonia and tungsten, but no chloride; the p_H was constant at 4·5. When this preparation was placed on porous tiles to dry, the white portion turned pale green, the yellow portion remaining unchanged. The colour of the final product was dependent upon the proportion of the green and yellow constituents. The ammonia content varied in a similar manner, but was always comparatively high. The water and ammonia contents of portions of the green and yellow constituents which were collected separately were as follows: Green, NH_3, 0·82; H_2O, 8·03; yellow, NH_3, 0·50; H_2O, 7·90%. The products were microscopically amorphous, and consisted of very small, almost spherical, particles, of average diameter 1 μ. (This value is identical with that given by van Liempt, *loc. cit.*, for the average diameter of the particles in a number of tungstic acids which had been precipitated at different temperatures.)

From 200 g. of ammonium tungstate, the yield of air-dried mixed tungstic acid was 62·5 g. (33% of theoretical) (WO_3, 89·69; H_2O, 9·56; NH_3, 0·77; Cl, trace; total 100·02%, corresponding with $WO_3,1{\cdot}37H_2O$).

Type D. Deep yellow, prepared at the boiling point. A solution of ammonium tungstate (200 g. in 4·48 litres of distilled water) was poured into concentrated hydrochloric acid (2 litres of 35·4%), each solution being at the boiling point. The temperature of the mixture was 102°, and the acidity of the filtered solution 2·78*N*.

The deep yellow precipitate formed was immediately washed by dialysis, as with type C. After 9 days, the washing liquid was free from chloride, but contained traces of ammonia and tungsten; the p_H value was constant at 4·4. The tungstic acid was now removed from the dialysers and air-dried in the usual manner. Microscopical examination showed the visible structure of the deep yellow powder to be identical with that of preparation C. From 200 g. of ammonium tungstate, 105 g. of tungstic acid were obtained (55% of theoretical) (WO_3, 91·44; H_2O, 8·38; NH_3, 0·05; Cl, trace; total 99·87%, corresponding with $WO_3,1{\cdot}18H_2O$).

All preparations, before the final air-drying, were finely ground, so as to pass through a 90-mesh I.M.M. sieve.

Dehydration of the Tungstic Acids.—In order to gain information regarding the stability of the various preparations, specimens of each type were dried to constant weight under the conditions stated below, and the loss tabulated includes both the water and the ammonia driven off during ignition.

	Type of preparation.			
Method of drying.	A.	B.	C.	D.
Air-dried at lab. temp.	14·26%	14·56%	8·87%	8·73%
Dried at 100° in air	7·13	5·44	5·43	8·52
Dried at 220° in air	0·75	1·93	2·07	1·08
Dried in vacuum over P_2O_5 at lab. temp.	8·49	7·63	5·61	7·83
NH_3 content of air-dried product	0·01	0·02	0·82	0·045

(Calc. for WO_3,H_2O : H_2O, 7·2; for $WO_3,2H_2O$: H_2O, 13·43%.)

Ageing of the Tungstic Acids.—General method. Eight series of ageing experiments were carried out. Since, as is well known, hydroxides are much more chemically reactive in the freshly precipitated condition than when dried, the acids in four of the ageing series were used in the form of "paste," *i.e.*, they had been thoroughly washed, but not dried. In the remaining four series, air-dried acids were employed, but in such cases, much higher concentrations of the acid ageing solutions were used. For each set of experiments, one tungstic acid of each type was specially prepared. Throughout the experiments, flasks of Jena glass were used, those containing water and sodium tungstate solution being coated internally with the purest high-melting paraffin wax. Conductivity water was used for the preparation of the solutions.

All the salts used were Kahlbaum's purest products; the acids were of A.R. quality.

(a) *Series with tungstic acid as paste.* In all cases, preparations were made from 200 g. of ammonium tungstate; the washed precipitate was made up to 2 litres with distilled water, and 100 c.c. of the well-shaken suspension were placed in each of 14 flasks. 100 C.c. of the acid or salt solution of double the required concentration were then added to the appropriate flask, thus giving 200 c.c. of approximately the desired concentration.

(b) *Series with solid tungstic acid.* For these experiments, separate tungstic acid preparations were made as in (a), and in each experiment, 4·0 g. of the solid were added to 200 c.c. of the appropriate solution.

In all series, the flasks, fitted with waxed corks, were kept in a thermostat at 20° for approximately 100 days, and then transferred to a thermostat at 25° for a further 200 days, being well shaken at regular intervals. At the end of 300 days, suitable portions of each liquid were separated by centrifuge. In the paste series, the p_H values of most of the liquids were determined electrometrically, both the hydrogen and the quinhydrone electrode being used. In the solid series, the acid solutions were titrated with carbonate-free sodium hydroxide solution, with phenolphthalein as indicator. The tungstic acids were now removed from the solutions, and freed from acid or salt by dialysis in parchment bags for 90 hours, against distilled water. The purified products were then dried in air after being sieved through a 200-mesh I.M.M. sieve.

Portions of the original eight products, which had not been aged, were treated similarly, such products being regarded as standards with which the aged samples might be compared. All tungstic acids, both standard and aged products, were finally dried to constant weight in large desiccators over sulphuric acid [*d* 1·344, aqueous vapour tension 8·5 mm. at 20° (Sorel), *i.e.*, rather less than that of the atmosphere under normal conditions].

The loss on ignition of each product was determined, and when necessary, the ammonia and chlorine contents also. The infusible matter in certain B products was also estimated.

The results of these experiments are given in the accompanying tables, but the pronounced changes in the appearance of the tungstic acids which often occurred during ageing are not recorded. The column headed " Conc." shows the normality of the original solution unless otherwise stated, and those headed p_H give the final p_H value of the solution. In every case, S refers to the product retained as a standard.

In certain cases, peptisation of the tungstic acids occurred during the ageing, this being indicated by a definite opalescence in the solutions concerned. Sols were produced with products Nos. 1, 3, 14, 29—31, 36, 38—42, 43—45, 50, 52, 54—56, 57, 75—77, 84.

Ageing solution.	Conc.	Type A. Paste.			Type B. Paste.		
		Loss on ignition,			Loss on ignition,		
		No.	%.	p_H.	No.	%.	p_H.
		*S	14·29		*S	14·52	
Distilled water	—	1	14·39	3·80	*15	12·10	2·64
Tap water......	—	2	14·59	3·47	16	10·64	2·59
Na_2WO_4	0·0002	3	14·53	3·82	17	11·88	2·69
NaCl	0·17	*4	12·84	2·71	18	—	2·35
NH_4Cl	0·17	5	14·26	2·50	19	12·23	2·42
$CaCl_2$	0·17	6	13·22	2·36	20	13·18	2·22
HCl	1·014	7	14·34	(1·016*N*)	21	14·44	(1·000*N*)
HCl	0·01	8	14·39	1·93	22	9·04	2·07
H_2SO_4	1·008	9	14·39	(1·002*N*)	23	14·98	(1·000*N*)
H_2SO_4	0·01	10	14·39	1·97	24	12·68	2·14
$H{\cdot}CO_2H$	1·015	11	14·06	1·70	*25	8·93	1·74
$(CO_2H)_2$	0·01	12	14·42	2·24	*26	15·73	2·50
$CH_3{\cdot}CO_2H$ ...	1·020	13	14·44	2·28	27	13·95	2·35
$CH_3{\cdot}CO_2H$ ...	0·01	14	14·45	3·34	28	11·87	2·73

Type A. Paste.

Ammonia contents : S, 0·03%; No. 5, 0·085%.
Chlorine contents : S, nil; No. 5, nil; No. 7, trace.
Time of ageing : 107 days at 20°, 177 days at 25°.

Type B. Paste.

Ammonia content : S, 0·01%.
Chlorine contents : S, No. 21, trace.
Infusible matter : S, 0·87%.
Time of ageing : 108 days at 20°, 182 days at 25°.

* Products chosen for *X*-ray examination.

Ageing solution.	Conc.	Type C. Paste.				Type D. Paste.		
						Loss on ignition,		
		No.	H_2O, %.	NH_3, %.	p_H.	No.	%.	p_H.
		*S	8·61	0·60		*S	8·59	
Distilled water ...	—	*29	9·79	0·51	3·89	43	8·22	3·54
Tap water	—	30	9·43	0·54	3·61	44	8·27	3·42
Na_2WO_4 ...	0·0002	31	9·59	0·55	3·77	45	8·32	3·42
NaCl	0·17	32	8·81	0·40	2·69	46	8·21	2·85
NH_4Cl ...	0·17	33	8·28	1·02	2·45	47	8·43	2·69
$CaCl_2$	0·17	34	9·17	0·45	2·67	48	8·28	2·95
HCl	1·004	35	9·66	0·18	(1·000*N*)	*49	8·18	(1·010*N*)
HCl	0·01	36	(1) 9·01	(1) 0·35	2·03	50	8·34	2·03
H_2SO_4	1·009	37	9·64	0·24	(1·000*N*)	51	8·29	(1·009*N*)
H_2SO_4	0·01	38	(1) 8·91	(1) 0·45	2·09	52	8·38	2·07
$H{\cdot}CO_2H$ ...	1·016	39	8·93	0·42	1·76	53	8·30	1·72
$(CO_2H)_2$ ...	0·01	40	(1) 9·51 *(2) 10·12	(1) 0·37 (2) 0·59	2·38	54	8·36	2·50
$CH_3{\cdot}CO_2H$	1·022	41	(1) 9·04	(1) 0·45	2·33	55	8·28	2·33
$CH_3{\cdot}CO_2H$	0·01	42	(1) 9·63 (2) 9·71	(1) 0·36 (2) 0·65	3·53	56	8·37	3·35

(1) refers to separated yellow portion.
(2) ,, ,, green ,,

Type C. Paste.

Chlorine contents : S, No. 33, nil; No. 35, trace.
Time of ageing : 105 days at 20°, 185 days at 25°.

Type D. Paste.

Ammonia contents : S, 0·05; No. 47, 0·18%.
Chlorine contents : S, No. 49, nil; No. 47, trace.
Time of ageing : 103 days at 20°, 191 days at 25°.

		Type A. Solid.			Type B. Solid.		
Ageing solution.	Conc., g. per 100 g. soltn.	No.	Loss on ignition, %.	Final conc., g. per 100 g. soltn.	No.	Loss on ignition, %.	Final conc., g. per 100 g. soltn.
		*S	14·16		*S	14·54	
Distilled water	—	57	14·29	(p_H 4·61)	*66	13·59	(p_H 3·32)
$CH_3{\cdot}CO_2H$	23·37	58	14·19	23·38	67	14·09	23·46
,, ...	45·60	59	14·28	45·39	68	13·83	45·62
,, ...	68·1	60	14·18	67·8	69	14·47	67·93
,, (glacial)	99·7	*61	8·55	99·7	70	14·25	99·6
HCl	7·01	62	14·22	6·99	71	14·34	7·03
,, ...	13·76	63	14·25	13·75	72	14·15	13·69
,, ...	20·11	64	14·30	19·96	73	13·52	20·03
,, ...	25·86	65	14·29	25·78	*74	12·74	25·75

Type A. Solid.

Ammonia content : S, 0·01%.
Chlorine contents : S, No. 64, trace.
Time of ageing : 105 days at 20°, 188 days at 25°.

Type B. Solid.

Ammonia content : S, 0·01%.
Chlorine contents : S, nil; No. 73, trace.
Infusible matter : S, 0·86; No. 66, 0·53; No. 71, 0·43%.
Time of ageing : 105 days at 20°, 189 days at 25°.

		Type C. Solid.				Type D. Solid.		
Ageing solution.	Conc., g. per 100 g. soltn.	No.	H_2O, %.	NH_3, %.	Final conc., g. per 100 g. soltn.	No.	Loss on ignition, %.	Final conc., g. per 100 g. soltn.
		*S	8·42	0·85		*S	8·29	
Distilled water	—	*75	11·27	0·56	(p_H 3·33)	84	8·38	(p_H 3·85)
$CH_3{\cdot}CO_2H$ ...	23·37	76	9·91	0·52	23·48	85	8·54	23·42
,, ...	45·60	77	9·43	0·55	45·49	86	8·40	45·55
,, ...	68·1	78	9·28	0·67	67·9	87	8·48	67·8
,, (glacial)	99·7	*79	8·95	0·70	99·4	*88	8·56	99·5
HCl	7·01	80	10·92	0·33	6·96	89	8·27	6·97
,, ...	13·76	81	11·39	0·31	13·71	90	8·08	13·69
,, ...	20·11	*82	11·46	0·25	19·97	91	8·22	20·06
,, ...	25·86	83	11·22	0·21	25·70	92	8·23	25·74

Type C. Solid.

Chlorine contents : S, No. 82, trace.
Time of ageing : 106 days at 20°, 186 days at 25°.

Type D. Solid.

Ammonia contents : S, 0·04; No. 90, 0·008; No. 92, 0·007%.
Chlorine contents : S, No. 91, trace.
Time of ageing : 105 days at 20°, 185 days at 25°.

* *X-Ray Examination of Tungstic Acids.*—The aged products indicated in the tables, being those which had undergone the

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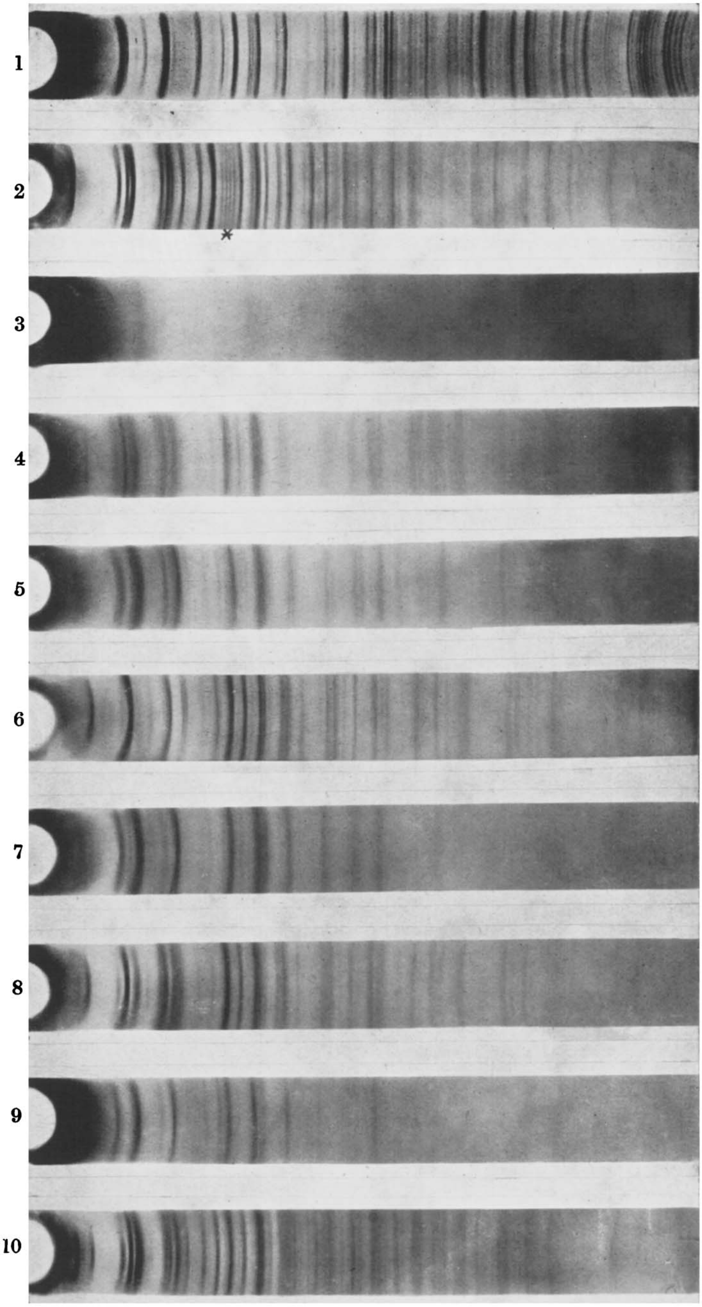
* The *X*-ray examination was undertaken in collaboration with Dr. A. J. Bradley in Prof. W. L. Bragg's laboratories. The author wishes to express his appreciation of the help rendered by Dr. Bradley, without which the photographing of the specimens would have been impossible.



[*To face page* 1995.]

greatest change in external appearance or composition, were submitted to X-ray examination, together with the eight standard tungstic acids and the following additional products.

(a) Anhydrous tungstic oxide, a primrose-yellow oxide prepared by heating a preparation of type A in an electric muffle furnace for 3 hours at *ca.* 800°.

(b) The separated green and yellow components of tungstic acid, type C.

(c) *Solids from solubility experiments.* It was shown during a series of solubility experiments (to be described in a subsequent publication) that green products of type C usually turned white when subjected to the prolonged action of a solution of sodium hydroxide. In certain cases a similar effect was observed with yellow products of type D. The following white products were selected for X-ray examination : (i) Solid extracted after 226 days from a solution of a tungstic acid C in 0·06N-sodium hydroxide at 25°; (ii) solid extracted after 60 days from a solution of tungstic acid D in 0·06N-sodium hydroxide at 25°.

(d) Tungstic acid, type E, a special preparation made as follows : A solution of ammonium tungstate (100 g. in 2·24 l. of distilled water) was poured into hydrochloric acid (1 l. of 4·9N) at the boiling point, and the bright yellow precipitate obtained washed in exactly the same manner as tungstic acids of type D; yield 43 g. (44% of theoretical) [Found : H_2O, 9·19; NH_3, 0·22; Cl, trace; WO_3 (by diff.), 90·59%].

For the X-ray examinations, the powder method was used. The radiation employed was copper K_α, the β radiation being filtered out by a nickel screen. In each case, the powder was exposed to the radiation for 8 hours, the tube current being about 8 milliamps. The photographs reproduced were made from diapositives screened to show up the centre lines; the relative intensities of the lines near the centre holes are therefore not exactly true to the originals, on which they are almost obscured by fog.

The photographs are numbered as follows :—

(1) Anhydrous tungsten trioxide.
(2) Standard tungstic acid, type A, solid. (In place of the 4 lines marked with a star, standard, type A paste shows only 3 faint lines. This difference is discussed below.)
(3) Standard tungstic acid, type B.
(4) Standard tungstic acid, type C, paste.
(5) Standard tungstic acid, type C, solid.
(6) Standard tungstic acid, type D.
(7) Green component of C preparation.

(8) Yellow component of C preparation.
(9) White solid, obtained as described under (c) (ii), above.
(10) Aged product No. 29.

Results of X-Ray Examination.—A visual examination of all the twenty-eight *X*-radiograms taken shows that in addition to the crystal structure of anhydrous tungstic oxide there are only three other types of structure, each of the standard preparations A, C, and D corresponding to a unique type. Standard type C preparations are variable in character, the genuine C type of structure being found mixed with various proportions of the A structure (in standard C, solid) or the D structure (in standard C, paste). Products of type B may be regarded as amorphous. A slight variation in the structure of type A tungstic acids has been indicated in the key to the photographs. A possible explanation of this is that a group of atoms inside the crystal is capable of replacement by another group of identical size; for example, occasional H_2WO_4 molecules might be replaced by a group of four molecules of water. Standard tungstic acids D (paste and solid series) gave identical photographs.

The two white solids from solubility experiments showed identical lines with the "nuclear C" structure (*i.e.*, C without superimposed A and D lines), see photograph 9.

Tungstic acid E (photograph not shown) exhibited a crystal structure identical with that of product D.

The green and yellow portions of the mixed product C showed different structures (photographs 7 and 8); in (7) the green portion shows the nuclear C structure with two of the strong D lines superimposed; in (8) the yellow portion shows a pronounced D structure, with some of the broader C lines as a background.

The aged products possessed the following structures:

Type A. Paste, No. 4, structure A, with some D.
Solid, No. 61, complete D structure.
Type B. Paste, No. 15, mixture of A and D; No. 25, complete D structure; No. 26, complete A structure.
Solid, No. 66, complete A structure; No. 74, mixture of A and D.
Type C. Paste, No. 29, mixture of A and D, with possibly the original C; No. 40 (2), mixture of A, D, and nuclear C.
Solid, No. 75, mixture of A and C; No. 79, identical with standard; No. 82, A structure with a little nuclear C.
Type D. Paste, No. 49, and Solid, No. 88, identical with standard.

(It should be realised that in all cases there is the possibility of the presence of several units % of amorphous products and also of small quantities of other crystalline substances, which would scarcely be noticeable in the X-ray examination.)

It can be seen from the above analysis of the X-radiograms that in all cases where a change of structure occurred as a result of ageing, the new structure was identical with that of one of the original standard tungstic acids, or was a mixture of two or more of such structures. The complete evidence from all the X-radiograms shows that the following tungstic acids exist (the statements regarding stability are deduced from the general ageing results given in the tables) : (1) Greyish-white amorphous products (type B, very unstable). (2) White tungstic acids with a definite structure (one component of type C, unstable). (3) Two yellow tungstic acids, differing in shade, one microscopically crystalline (type A, comparatively stable), and one microscopically amorphous, but crystalline to X-rays (type D, very stable).

Discussion.

Deduction of the Structure of the Various Tungstic Acids.—Structure D. This structure is shown by tungstic acids of types D and E, and by the yellow portion of tungstic acid C. The water content of the air-dried product is rather higher than the value demanded by the formula WO_3,H_2O.

The following possible structures may be considered : (1) WO_3,H_2O ; (2) a mixture of an amorphous product of high water content with a crystalline substance of low water content ; (3) H_2WO_4. The great firmness with which the water is held during attempted dehydration, and the stability exhibited during ageing, suggest strongly that tungstic acid D is a compound H_2WO_4, containing a little adsorbed water. (There is also evidence, from the solubility experiments previously referred to, which indicates that a small proportion of the nuclear C tungstic acid is present in type D products.)

Structure A. Tungstic acids of type A are microscopically crystalline, show a definite crystal structure to X-rays, and contain rather more water than is required for the formula $WO_3,2H_2O$. It would appear, therefore, that the substance is a definite chemical compound. The following possibilities may be considered : (1) $WO_3,2H_2O$; (2) H_2WO_4,H_2O ; (3) H_2WO_5 ; (4) a mixture, as with (2) described under structure D. The dehydration experiments and ageing results (No. 61) strongly suggest that *one* mol. of water is lost during the dehydration process. The X-radiogram of No. 61 shows that the product produced by ageing was tungstic acid D.

If, therefore, this type is H_2WO_4, the evidence suggests that A is H_2WO_4,H_2O. On theoretical grounds, the formula H_4WO_5 is discredited, since this would apparently require the very improbable fivefold co-ordination. Also (4) is most unlikely, since microscopical examination of the substance immediately after preparation showed that the greater part was composed of twin leaflets.

The evidence therefore clearly points to the formula H_2WO_4,H_2O for tungstic acid A. This compound either adsorbs water or takes water into solid solution, as has been suggested.

Structure C. Tungstic acids of type C are mixtures of yellow tungstic acid D (H_2WO_4), and a pale green substance having the " nuclear C " structure. This latter structure was also shown by the two white solids from the solubility experiments, but was never produced by an ageing change. The structure as a whole is unstable, tending to change into structure A.

The evidence at present available is insufficient for the satisfactory elucidation of this structure, but the following alternative explanations are suggested :

(1) The nuclear C structure may be that of an imperfectly crystallised tungstic acid—the tendency is to form crystalline H_2WO_4 at the boiling point—crystallisation being inhibited by the presence of ammonia (see tables). This impurity may thus give rise to a metastable (a kind of distorted D) structure. On the removal of ammonia (*e.g.*, by ageing), the " normal " form might then develop.

(2) The structure may be that of a condensed tungstic acid produced by the intramolecular condensation of 2 or more mols. of H_2WO_4, possibly accompanied by the splitting off of water, producing a salt-like condensation product with a higher degree of co-ordination of the oxygen atoms round the tungsten atoms. The presence of amorphous tungstic acid must also be assumed, to account for the presence of the ammonia and for the production of A structure during ageing (product No. 75).

Theory (2) would indicate that tungstic acid C is ordinarily a mixture of at least three constituents, *viz.*, (*a*) H_2WO_4, (*b*) a condensed acid, and (*c*) amorphous tungstic acid.

Structure B. Tungstic acids of this type are amorphous, but in the ageing process may be converted into crystalline H_2WO_4 or H_2WO_4,H_2O, or into a mixture of these components. In this process, the infusible matter is considerably reduced (see Nos. 66, 71). A plausible explanation of these facts is that tungstic acid B consists essentially of particles containing irregularly arranged groups of H_2WO_4, or H_2WO_4,H_2O, which are prevented from crystallising by the presence of calcium and magnesium. If, during the ageing process, the calcium content is in some way reduced, crystalline H_2WO_4 or H_2WO_4,H_2O may be produced.

Product B, therefore, may be regarded as a hydrated, amorphous tungstic acid, although the evidence is not conclusive on this point.

Summary.

(1) The preparation of four types of tungstic acid is described. The products differed in appearance and in composition.

(2) The loss on ignition of each product has been determined after drying under various conditions.

(3) With each type of tungstic acid, two series of ageing experiments have been carried out: (*a*) with the products immediately after precipitation and washing, but before drying, and (*b*) with the solid air-dried product. Tables of analytical results are given.

(4) Twenty-eight selected tungstic acid products have been submitted to *X*-ray examination by the powder method.

(5) From the combined study of the results of analytical and *X*-ray examination of the various products, the existence of the following tungstic acids has been deduced: (*a*) A crystalline yellow product, H_2WO_4, whose crystalline nature is not revealed microscopically. (*b*) A paler yellow microscopically crystalline tungstic acid of composition H_2WO_4,H_2O. (*c*) An amorphous greyish-white substance, probably a hydrated amorphous variety of either H_2WO_4 or H_2WO_4,H_2O. (*d*) A mixed product, containing at least three constituents, *viz.*, (1) H_2WO_4, (2) amorphous tungstic acid, (3) a condensed, or imperfectly crystallised tungstic acid.

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