

A New Method for the Production of Tungstic Acid from Tungstates.

By

Yoshio Nakazawa and Shinzo Okada.

ABSTRACT.

This paper deals with a characteristic property of tungstic acid and its reaction with hydrochloric acid solution.

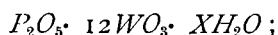
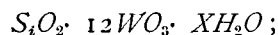
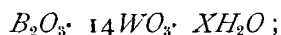
The authors' experiments prove that tungstic acid freshly formed from tungstate by decomposition with hydrochloric acid, dissolves in its concentrated acid solution forming a chemical compound, provided that the produced tungstic acid is brought into contact with concentrated hydrochloric acid immediately after its formation. It was found also that if the degree of its concentration is reduced, this chemical compound gives the insoluble tungstic acid as a precipitate in the solution.

Details are given for lixiviating the tungstic acid from tungstate and for preparing it.

INTRODUCTION.

It has been known for some time that strong acids usually form salts of comparatively simple composition, while weak acids such as chromic acid, silicic acid and stannic acid form more complex salts.

Tungstic acid, being a weak acid, has the property of forming various salts of complex composition, and also has that of forming acids having conspicuously large molecules by combining with various other acids: such salts with the oxides of silicon, boron, and phosphorous are given below:



However, very little quantitative work has been done on the formation of chemical compounds by tungstic acid and the ordinary mineral acids such as hydrochloric acid and sulphuric acid. It is only known that tungstic acid is slightly soluble in conc. hydrochloric acid.⁽¹⁾ Olson⁽²⁾ produced hydrochloric acid solution containing 4% tungstic acid by adding potassium tungstate solution, drop by drop, to conc. hydrochloric acid solution. In this article, we explain and discuss in detail the reaction between tungstic acid and hydrochloric acid, and we deal with a new method of producing tungstic acid as the result of our experiments.

Article 1. Solubility of Tungstic Acid in Concentrated Hydrochloric Acid Solution.

Tungstic acid is said to be insoluble in any inorganic acid, except hydrofluoric acid, and to be very slightly soluble in conc. hydrochloric acid. This fact is only a matter of concern in analytical manipulation, the degree of solubility not exceeding one percent.

The writers found by experiment that the solubility of tungstic acid in conc. hydrochloric acid could be greatly increased by properly modifying the degree of concentration of the solvent used and also the conditions under which the tungstic acid is produced.

When tungstic salts are decomposed by conc. hydrochloric acid and the whole is agitated frequently, the hydrochloric acid dissolves the tungstic acid immediately and leaves a solution containing as much as 12% of tungstic trioxide.

Among tungstic salts, calcium tungstate is most easily decomposed by hydrochloric acid: even at 20° C, tungstic acid is produced. So far as easiness of decomposition is concerned, ammonium salts come next to calcium tungstate. Decomposition of sodium and potassium salts takes place very slowly at normal temperatures. This is the reason why we adopted calcium tungstate in our experiments. As we explain in detail in the following chapters, a chloride such as calcium chloride, the by-product

1. Treadwell, *Analytische chemie*, 1 Bd. S. 511.

2. Olson, *Zs. anorg. chem.* **88**, 49, (1914).

of decomposition of tungstic salts, remaining in the solution, does not greatly affect the solubility of tungstic acid.

In our experiments, pure powdered calcium tungstate ($CaWO_4$) is prepared from calcium chloride and sodium tungstate (Cahlbaum C. P. reagents): this calcium tungstate is added continuously to hydrochloric acid solution, 0.5gm. at a time, while the solution is constantly agitated, until it is saturated with tungstic acid, and a turbid state is obtained. Then the saturated solution is kept undisturbed and filtered: a certain quantity of the filtrate is analysed.

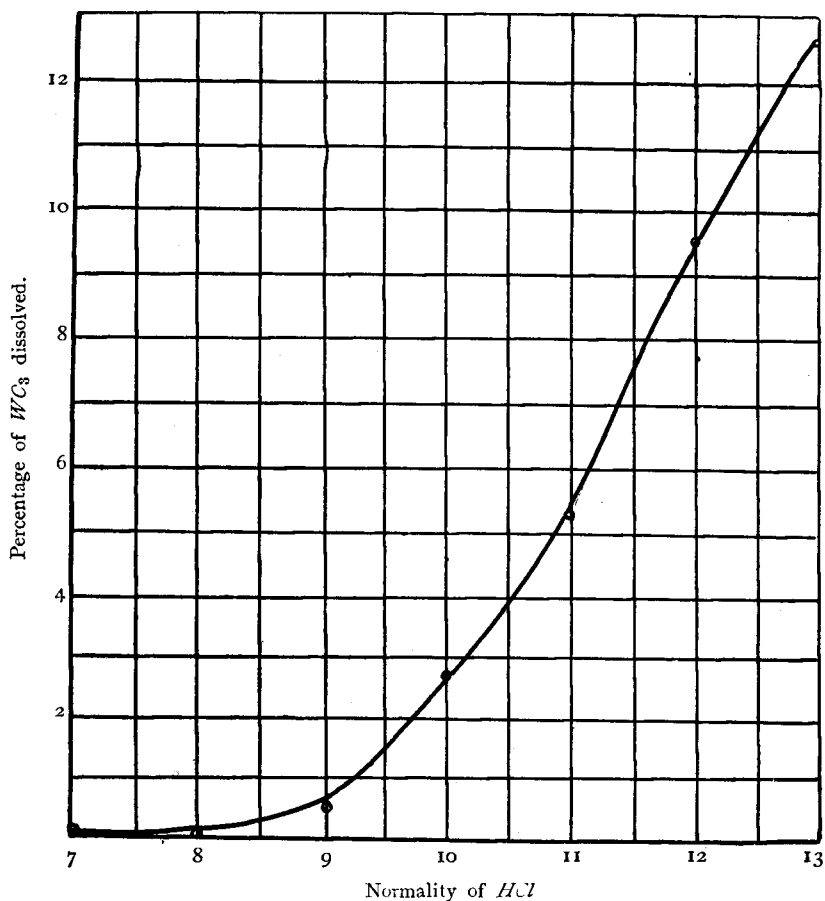
The results obtained in the above mentioned experiments: the relation between the solubility of tungstic acid and the degree of concentration of the solvent may be tabulated as follows:—

Table No 1.

Solubility of tungstic acid in hydrochloric acid solution at 20°C under ordinary pressure		
Normality of <i>HCl</i> solution used	Sp. gr. of hydrochloric acid sol. of tungstic acid	Percentage of WO_3 in the solution
13 <i>N</i>	1.37	12.67 %
12 <i>N</i>	1.32	9.61 %
11 <i>N</i>	1.24	5.29 %
10 <i>N</i>	1.17	2.74 %
9 <i>N</i>	1.15	0.50 %
8 <i>N</i>	1.14	0.05 %
7 <i>N</i>	1.12	—

As clearly described above, we obtain a solution containing as much as 12% of tungsten trioxide by using hydrochloric acid solution of 13 normality, when the tungstic acid produced by virtue of decomposition

Fig. 1. Solubility curve of tungstic acid
at 20° C.



of calcium tungstate in hydrochloric acid is treated with concentrated hydrochloric acid immediately after its formation. However, the newly formed tungstic acid does not dissolve in the solvent even when treated as mentioned above, if the solvent has the lower concentration than seven normal. It is evident that the solubility of tungstic acid depends greatly upon and is influenced by the concentration of the hydrochloric acid solution; when the normality becomes below 10, the percentage of solubility decreases a great deal. By taking advantage of the property of the newly formed tungstic acid to dissolve in concentrated hydrochloric acid, by

adjusting the degree of concentration of the solvent used, and also by employing agitation in order to prevent any sudden decrease in the concentration of the solvent on account of the local chemical reaction occurring between the solute and the solvent, we succeeded in making the solubility of tungstic acid as much as 12% tungstic trioxide, while it had been said to be almost insoluble in ordinary mineral acids.

Article 2. Properties of Hydrochloric Acid Solution of Tungstic Acid.

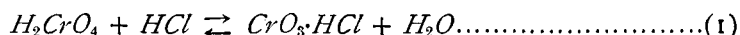
Olson⁽²⁾ obtained hydrochloric acid solution containing 4% WO_3 by adding, drop by drop, a solution of potassium tungstate and a small quantity of potassium carbonate to concentrated hydrochloric acid, while the solution was agitated. In discussing the properties of the solution, he stated that tungstic acid simply dissolved in the solvent. According to Gmelins' inorganic chemistry, tungstic acid dissolves in conc. hydrochloric acid slightly: "by the addition of water to this solution, a creamy sediment is obtained, and the sediment may be a chemical compound of tungstic acid and hydrochloric acid" [Bd III, p 761]. Recently Collenberg and Guthe⁽³⁾ have produced a crystalline precipitate by adding chinoline hydrochloric solution to concentrated hydrochloric acid solution of tungstic acid: after analysing the precipitate, they asserted that WO_2Cl_2 or anion $WO_2Cl_3^-$ might exist in the solution.

It should be noted that there are two kinds of soluble tungstic acids, metatungstic acid and colloidal tungstic acid. When sulphuric acid is added to metatungstic acid solution and there-by the water is removed, a precipitate appears which disappears again if water is added. But if the hydrochloric acid solution of tungstic acid mentioned previously is used, an entirely different reaction takes place: tungstic acid is immediately precipitated. This shows that the above mentioned hydrochloric acid solution of tungstic acid contains no metatungstic acid. Our observation of this solution with an ultra-microscope also confirms that it is not of colloidal constitution. There remains the problem whether this solution is

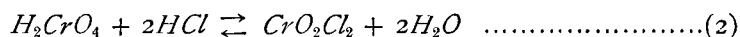
(3) Collenberg and Gütche, Zs. Anorg. chem. **134**, 317 (1924).

a simple tungstic acid solution, or whether tungstic acid exists in the solution forming another chemical compound with hydrochloric acid.

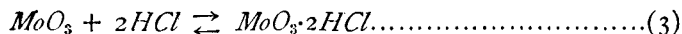
We compare the reaction between hydrochloric acid and chromic acid or molybdic acid etc, which have nearly the same properties as tungstic acid. The following formula gives the chemical reaction between hydrochloric acid and chromic acid:—



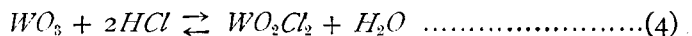
by adding H_2SO_4 to the above reaction, the reaction proceeds,



Thus chromylchloride is formed, which is a stable compound, being also produced from chromic oxide and hydrochloric acid gas. Chlorochromic acid is so unstable that it can not exist isolated. It is a well-known fact that $MoO_3 \cdot 2HCl$ is formed from hydrochloric acid gas and molybdenum trioxide.



When hydrochloric acid gas acts on tungsten trioxide at red heat, the analogous reaction takes place:



The writers produced a solution containing 8% of tungstic acid by introducing calcium tungstate into conc. hydrochloric acid (1.2). To this solution, the calculated amount of conc. sulphuric acid is added in order to separate from the solution, the calcium chloride, which is precipitated as calcium sulphate: the remaining clear solution is almost pure concentrated hydrochloric acid solution of tungstic acid. Then the same volume of conc. sulphuric acid (1.84) is gradually added to this solution, and by leaving it overnight undisturbed, small crystalline precipitates of needle shape are obtained in the solution.

These transparent needle-shaped crystals (see Fig 2) decompose easily with water and even moisture in air reacts on the crystals, setting free hydrochloric acid gas. They are soluble in concentrated hydrochloric

acid and anhydrous alcohol, and insoluble in concentrated sulphuric acid. The colour becomes blue in the sunlight, and is very unstable against heat; complete decomposition takes place even in hydrochloric acid gas at 300°C, hydrochloric acid gas and tungsten trioxide being the products of the decomposition.

This property is quite different from that of WO_2Cl_2 , which begins to sublime at red heat.

After carefully washing off the hydrochloric acid adhering to the crystals with concentrated sulphuric acid, we estimated the ratios of the weights of tungstic oxide (WO_3) and hydrochloric acid in the crystals.

Fig. 2.



Table No. 2

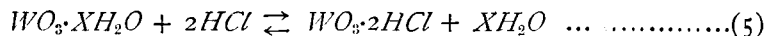
	WO_3	HCl	$WO_3 : HCl$
No. 1	0.2560	0.0651	1 : 1.92
No. 2	0.4911	0.1249	1 : 1.99
No. 3	0.5015	0.1276	1 : 1.97

In order to remove sulphuric acid from the crystals, they are washed with anhydrous ether and kept in a vacuum for drying. The ratios of WO_3 and HCl by weights in the samples are given in Table No 3.

Table No. 3

	Sample No. 1	Sample No. 2	Sample No. 3	Calculated value as $WO_3 \cdot 2HCl$
WO_3	74.97%	76.36%	75.01%	76.09%
HCl	23.95%	23.24%	24.00%	23.91%

According to the above results, it seems that the experimental formula of the crystal is $WO_3 \cdot 2HCl$ or $\left[WO \begin{smallmatrix} (OH)_2 \\ Cl_2 \end{smallmatrix} \right]$. Judging from the components of the crystal, the reaction between tungstic acid and concentrated hydrochloric acid solution may be shown as follows:—



The white tungstic acid having more than one molecule of water, which is a product of decomposition of tungstic salts, forms a soluble chemical compound with concentrated hydrochloric acid solution. If yellow tungstic acid having a single molecule of water is formed in the solution, the above mentioned reaction does not take place, but the yellow tungstic acid is precipitated, as it is insoluble in concentrated hydrochloric acid. The white tungstic acid produced right after decomposition has the property of turning immediately into yellow tungstic acid. To insure that the reaction in formula (5) will take place, the property of the newly formed tungstic acid of dissolving in concentrated hydrochloric acid immediately after its formation must be utilized. By adding concentrated sulphuric acid, water produced as the result of the reaction (5) is removed, thus stimulating further formation of $WO_3 \cdot 2HCl$. This compound being insoluble in conc. sulphuric acid is thrown out of solution as crystalline precipitates (Fig 2.).

Article 3. Separation of Tungstic Acid from Hydrochloric Tungstic Acid Solution.

As tungstic acid exists in the solution in a very unstable condition, as stated in Article 2, it is very simple to separate it out of the solution as a precipitate: the desired result can be obtained by simply reducing the concentration of the hydrochloric acid in the solution.

There are two methods for reduction of concentration—(1) dilution with water and (2) dilution by distilling off hydrochloric acid from the solution.

The comparative results of these two methods are shown in Table No. 4. and Fig 3. (A & B).

Table No. 4—A
Dilution with water.

Concentration of <i>HCl</i> in Solution	12 <i>N</i>	11.5 <i>N</i>	11 <i>N</i>	10.5 <i>N</i>	10 <i>N</i>	9 <i>N</i>	8 <i>N</i>	7 <i>N</i>
Amount of separated <i>WO</i> ₃	0%	3%	27%	73%	87%	93%	98%	100%

Table No. 4—B
Dilution by hydrochloric acid distillation.

Concentration of <i>HCl</i> in Solution	12 <i>N</i>	11.5 <i>N</i>	10.8 <i>N</i>	10.4 <i>N</i>	9.5 <i>N</i>	8.7 <i>N</i>	7.8 <i>N</i>	7 <i>N</i>
Amount of separated <i>WO</i> ₃	0%	3%	16%	66%	85%	95%	98%	100%

Fig. 3—A Dilution with water.

Relation between hydrochloric acid concentration and amount of *WO*₃ precipitated.

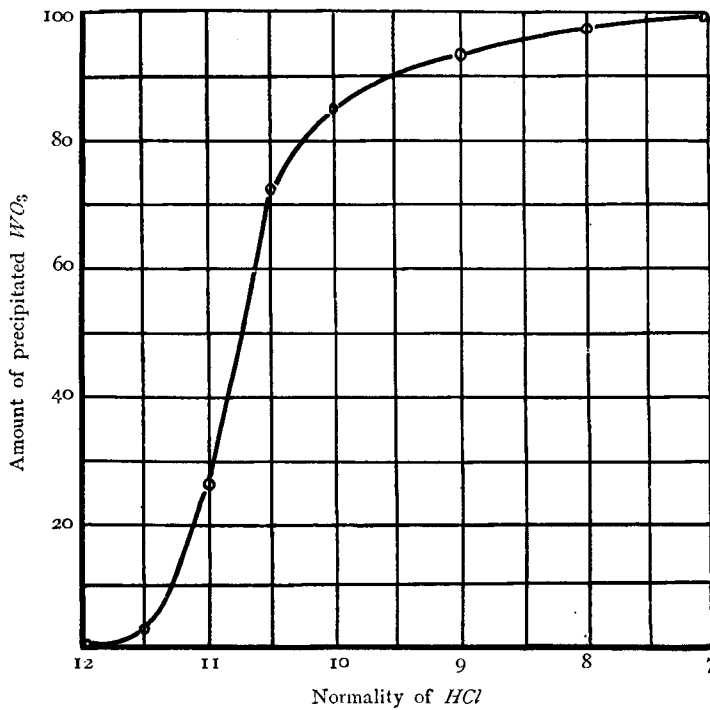
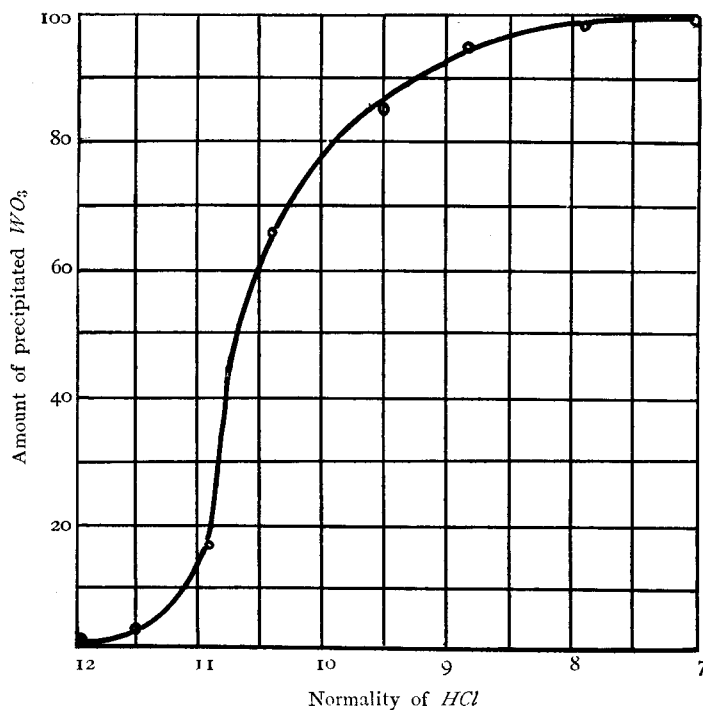


Fig. 3—B Dilution by hydrochloric acid distillation.
Relation between hydrochloric acid concentration
and amount of WO_3 precipitated.



By adding water to the solution, hydrochloric acid is diluted, causing separation of tungstic acid from the solution: the relation between the degree of concentration of the hydrochloric acid and the amount of the tungstic acid precipitated as trioxide (WO_3) is shown in Table No. 4—A.

If the same solution is heated, distillation of hydrochloric acid takes place causing decrease of its concentration, making tungstic acid precipitate. The results are presented in Table No. 4—B.

In Table No. 4. and Fig. 3. A & B, the quantity of tungstic acid precipitated due to reduction of hydrochloric acid concentration is presented in percentage, taking the amount of tungsten trioxide in 12 normal hydrochloric acid solution as 100%. Precipitation is completed when normality of solution is reduced to 7. It is to be noted that at 10.5 normal the

amount of the precipitate starts to increase rapidly: the characteristic of the curve resembles that of the solubility curve of tungstic acid in Fig 1. This characteristic shows also that the solution is not a simple hydrochloric acid solution of tungstic acid. The size of the individual particles of the precipitate produced by hydrochloric acid distillation is larger than that obtained by dilution with water and it may be washed more easily. It is almost pure, occluding no injurious impurity.

CONCLUSION.

1. Tungstic acid, separated from its salts, is soluble in concentrated hydrochloric acid. The percentage of solubility may be increased as high as 12 % (calculated as tungstic trioxide), provided that the freshly separated tungstic acid comes in contact with conc. hydrochloric acid immediately after its separation: solubility depends greatly upon the degree of concentration of the solvent, a sudden increase in solubility taking place at 10.5 normal.

2. Forming a chemical compound such as $WO_3 \cdot 2HCl$, tungstic acid dissolves in conc. hydrochloric acid solution. So, the former is again easily separated from the solvent by merely reducing the concentration of the latter.
