this happens bring the blast into action and ignite to constant weight. The weight finally accepted must not change even after half an hour's ignition. Upon this requirement especial stress must be laid. Pure magnesium pyrophosphate does not suffer any loss even after several hours' ignition, nor does a good platinum crucible. To the weighed amount of pyrophosphate add the correction given in the table. Multiplication of the sum by 64 gives the amount of phosphoric acid in the weight taken for analysis.

CORRECTION FOR PHOSPHORIC ACID DETERMINATION.

Found, $Mg_2P_2O_7$ in grams.	Lost, milligrams $Mg_2P_2O_7$.	Found, $Mg_2P_2O_7$ in grams.	Lost, milligrams $Mg_2P_2O_7$.
0.10	0.6	0.24	4.0
0.12	0.8	0.25	4.2
0.14	1.2	0.26	4.6
0.15	1.4	0.27	5.0
0.16	1.6	0.28	5.5
0.17	2.4	0.29	6.1
0.18	2.6	0.30	6.8
0.19	3.2	0.31	7.6
0.20	3.5	0.32	8.6
0.21	3.6	0.33	9.6
0.22	3.8	0.34	10.6

When phosphoric acid is to be estimated as pyrophosphate it must always be first separated as molybdate, even when the original solution contained no bases capable of forming insoluble phosphates, as otherwise these corrections will not be applicable.

Using these corrections, the estimation of phosphoric acid becomes one of the most accurate of known analytical methods.

EXPERIMENTS ON A FERRO-TUNGSTEN.

BY JAMES S. DE BENNEVILLE.

Received February 28, 1894.

IN making an analysis of a ferro-tungsten rich in tungsten the chemical behavior of a residue insoluble in acids and apparently not decomposed by fused solvents led me to believe that it was metallic tungsten. The time available was limited and the few experiments made were hasty and at intervals, and in a private communication describing the method pursued in analysis I called attention to the insufficient basis on which the analysis rested and the necessity for further investigation. The work involved in this paper was undertaken to determine, if possible, whether tungsten existed uncombined in the alloy and whether any definite ratio between tungsten and iron could be shown or alloys separated. The results showed that what was taken to be tungsten was a rich tungsten alloy the iron of which was not attacked by acids and which in its indifference toward chemical reagents resembled metallic tungsten.

The method of analysis adopted was directed toward determining how different solvents would act on the alloy. The steps taken were from the less to the more energetic reagent and consisted in 1. Attack by strong hydrochloric acid and determination of the iron and tungsten so removed in solution. 2. Fusion of the residue with a mixture of alkali carbonate and nitrate. 3. Action of solution of silver nitrate on the alloy.

The results based on sixteen analyses showed the alloy to be very heterogeneous. The sample was in the form of small fragments showing to the eye the differentiation throughout the mass and even the fragments themselves had not the same appearance, some of them having a number of cleavage planes of a pyritous appearance. In making these later analyses no effort was made to obtain a uniform sample, but the contrary, for the object sought was to ascertain whether all the iron was alloyed with tungsten or *vice versa;* and whether iron and tungsten were present as such dissolved in a true alloy.

A marked regularity was shown in the amount of tungsten dissolved on treating the alloy with ammoniacal silver nitrate solution. However, on digesting with neutral solution of silver nitrate no tungstic acid separated and the silver precipitated was in proportion to the iron dissolved. This absence of tungstic acid from the residue pointed to the fact that all the tungsten was in the form of alloy. The small quantity of iron separated did not calculate to any definite ratio with the tungsten acted on by the silver salt. Part of the iron was probably due to the steel mortar in which, owing to its great hardness, it was necessary to crush the alloy. This would vitiate any calculation.

The results, under I, were obtained by the following method: The fragments of the alloy were powdered separately in a steel mortar and passed through a sixty mesh sieve. Weighed portions were then extracted by strong hydrochloric acid (sp. gr. 1.20) until the acid no longer acted. In this solution iron and tungsten were determined. The residue was fused with a mixture of sodium carbonate and nitrate and the fusion lixiviated in water. Decomposition was complete. Iron and tungsten were determined. The results obtained were as follows:

I. TO ONE GRAM.

No.	1	2	3	4
Acid extract, iron	0.3648	0.3779	0.3631	0.3853
Acid extract, tungsten..	0.0233	0.0309	0.0217	0.0282
Residue, iron...........	0.1786	0.1762	0.1669	0.1416
Residue, tungsten......	0.4333	0.4057	0.4390	0.4626

Taken in connection with II this table appears to show that part of the alloy is readily attacked by acid, iron being dissolved and the tungsten left behind in the residue. This is indicated by the small quantity of free iron (see II) in the majority of the samples taken for analysis. Any large quantity of unalloyed iron would be shown very positively. This does not show necessarily the separation of an easily decomposed alloy from others less readily attacked. Other facts, given later, indicate that this alloy is an unsaturated compound and that a still higher percentage of tungsten than given in these analyses can be held chemically combined with the iron, but the higher valency exercised by the iron in these rich tungsten compounds may not be the most stable.

It was sought to ascertain how the alloy would act toward silver solution. Four reactions were involved. 1. Metallic iron, reducing silver from its salts in the ratio of Fe:2Ag. The reaction takes place in neutral solution. 2. Metallic tungsten and silver salt in neutral solution. 3. Metallic tungsten and silver salt in ammoniacal solution. 4. Action of the tungsten in this alloy on the silver salt. In the neutral solution of silver nitrate tungsten is converted into tungstic acid and silver is reduced. Silver tungstate is also formed. After washing the precipitated tungstic acid and silver free from excess of silver nitrate and dissolving in ammonia the black silver sulphide was obtained by ammonium sulphide. The quantity was small but this salt is somewhat soluble in water[1] and washing must have removed some portion of it. The main bulk of the flocculent white precipitate is tungstic acid. In the ammoniacal solution of silver nitrate the tungstic acid formed dissolves leaving silver as residue.

The results obtained from experiments carried out on this line indicated the amount of free iron and by dissolving it out left the residue ready for further treatment. The alloyed ferrotungsten did not appear to be attacked by the silver nitrate, which was to be expected from the strong affinity of iron for tungsten. In two analyses, however (18 and 19), in which a large quantity of iron replacing silver was found, the tungsten instead of dropping to a low percentage remained near the average found in nearly all the analyses, forty per cent. This looks as if the alloyed ferro-tungsten had been attacked by the reagent, but it can be explained on the ground of segregation. Crookes[2] in criticising Schöffel's method for chrome and tungsten steels by solution of the iron in copper ammonium chloride notes the fact that steels containing a high percentage of chromium (eight per cent.) or tungsten (twelve per cent.) are but slightly attacked.

To make use of the reaction that in ammoniacal solution of silver nitrate tungsten replaces silver in the ratio of W : 6Ag the following analytical method was adopted:

Weighed portions of the alloy were digested for thirty hours with a neutral solution of silver nitrate. This solution was decanted from the heavy residue and washed by decantation with water. After removal of the excess of silver, iron was determined in this solution giving the quantity of free iron. It was noticeable that in nearly all the analyses this was very small and in part was due probably to fragments from the mortar. In two of the analyses this "free iron" is a considerable percentage of the whole and cannot be put down to that cause. After removal of the neutral silver salt the residue was digested for from thirty-six hours to a week with an excess of ammoniacal solution of silver nitrate. This solution was filtered and the residue

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[1] E. F. Smith and Bradbury, *J. Anal. Appl. Chem.*, 5, 486.

[2] Crookes "Select Chemical Methods," pp. 217-219.

washed with water. Silver was removed from the ammoniacal solution by ammonium sulphide and tungsten determined in the filtrate. The residue from the treatment with the silver salt was dried and ignited. Silver was removed by nitric acid and the final residue obtained was fused with a mixture of sodium carbonate and saltpeter. Tungsten was precipitated from the neutral solution of alkali tungstate as mercurous salt. Iron was determined where found. This method of analysis separated the constituents into 1. Iron replacing silver. 2. Tungsten replacing silver. 3. Unattacked iron and tungsten.

The experimental results tabulated were:

III. 9–12 with neutral solution of silver salt; 13–15 with ammoniacal solution of silver salt; 16–20 with neutral and subsequently ammoniacal solution of silver salt.

III. Calculated to One Gram. Alloy Treated with Silver Salt.

No.	Total iron. A.	Total tungsten. B.	"Free" iron. C.	"Free" tungsten. D.	Residual iron. E.	Residual tungsten. F.	A : B less "free" iron ratio. G.
9	0.4068	0.5758	0.0070	....	0.3998	....	7:3
10	0.4698	0.5081	0.0150	....	0.4548	....	3:1
11	0.5919	0.3889	0.0072	....	0.5847	....	5:1
12	0.5199	0.4552	....	0.0453	....	0.4099	..
13	0.6861	0.2986	....	0.0586	....	0.2400	..
14	0.6207	0.3700	....	0.0692	....	0.3008	..
15	0.5118	0.4789	0.0121	0.0399	0.4997	0.4390	0.7:2
16	0.4075	0.5842	0.0281	0.0522	0.3794	0.5320	0.2:1
17	0.5227	0.4680	0.0561	0.0367	0.4666	0.4313	3.26:1
18	0.5221	0.4686	0.3147	0.0626	0.2074	0.4060	3:2
19	0.4847	0.4933	0.3430	0.0535	0.1444	0.4398	1:1
20	0.5178	0.4689	0.0150	0.0534	0.5028	0.4155	7:2

The term "free" iron and "free" tungsten is used to indicate the quantity of those metals replacing silver in the silver solution.

The variation in the analytical results appears to show that we have to deal with a number of alloys and these not distributed evenly through the mass. The small quantity of iron replacing silver in silver nitrate indicates that the iron is in combination with the tungsten and not a number of more or less complex alloys dissolved in a matrix of metallic iron. Nos. 18 and 19 can be attributed to segregation on cooling, such segregation taking place when the mass was not very liquid in which case the separated and unalloyed iron would surround a rich tungsten alloy. Schneider[1] separated from a high tungsten iron what appeared to be two alloys corresponding to the formulas Fe_3W and Fe_8W. If iron be regarded as divalent the saturation point of tungsten would be reached in the formula Fe_3W (taking tungsten as hexavalent). If iron be regarded as octovalent the saturation formula would be Fe_3W_4. Howe in his "Metallurgy of Steel" states that "tungsten unites with iron apparently in all proportions at least up to eighty per cent." The following table of analyses is taken from his work quoted, p. 81:

No.	1.	2.	3.	4.	5.	6.
Tungsten	37	77.8	53.1	29.12	24.25	28.18
Iron	63	16.4	43.4	67.93	30.	68.36
Manganese	..	5.8	3.5	but little	41.50	0.99
Silicon	..	....	....	0.61	....	0.23
Carbon	..	....	....	1.17	5.65	1.88
Phosphorus	..	....	....	....	0.14	0.008

The description given of No. 3, "platinum gray, hard, brittle, lamellar completely fusible" would in the first three qualities apply directly to the ferro-tungsten under consideration. Analysis No. 2 very closely approximates the formula Fe_3W_4 and if no alloy of iron and tungsten, in combination, containing a higher percentage of tungsten, exists, it would point strongly to the octovalency of iron in its combinations with this element as metal. The other analyses, including those of the ferro-tungsten under consideration would be unsaturated compounds. This valency has been shown to belong to other members of this family. Ruthenium and osmium in their oxides, iron in ferric acid, appear as hexavalent and the existence of the ammonia cobalt salts indicate a still higher valency for a metal closely allied to iron.[2]

Mendelejeff compares alloys to solutions as indefinite unstable compounds. In solutions in which there is free communication within the bounds of the liquid on alteration in temperature a change in molecular composition occurs as is shown by the separation of definite salts limited by such temperature. An alloy in the fused state is then analogous to a solution and when during

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[1] Howe's Metallurgy of Steel, p. 81.

[2] Lothar Meyer, "Modern Theories of Chemistry," pp. 347, 348.

cooling segregation sets in the different alloys crystallize out from the mass. If the iron were present in such quantity that its saturation capacity for the tungsten would drop below divalency metallic iron would appear in this alloy but this is not the case.

The fact that iron does not replace silver in the silver nitrate or copper in the copper ammonium chloride shows a very strong affinity of iron for tungsten. If the bond between the iron and tungsten atoms was weak, or if there was merely a mechanical mixture, iron should replace silver in the neutral solution of the silver salt. This is based on the fact that "a positive element is separated from its combinations with a negative element by a stronger positive," and iron is more positive than silver.[1] Iron and tungsten are so separated in their properties as metal and semi-metal that an alloy of such constituents should be a very stable compound.

Metallic tungsten is left almost unattacked by hot acid. The action of aqua regia slowly converts it into tungstic acid. The acid must be used in small portions at a time and adhering tungstic acid removed by ammonia to prevent its protective action. Fusion with potassium bisulphate, or with caustic soda, or alkaline carbonate and saltpeter decomposes it.

In its action toward acids the alloy shows very strongly the influence of the tungsten. Acids do not act on it energetically as with carbon steel. To a degree this is to be expected but its inertness is almost as marked as with metallic tungsten. Hydrochloric acid dissolves out about two-thirds of the iron and a little tungsten. Nitric acid does the same. Part of the alloyed iron, therefore, appears to be attacked by acid solvents. Sulphuric acid barely acts upon it but fusion with potassium bisulphate (sulphuric acid at a red heat) decomposes the alloy completely. Aqua regia attacks it slowly but action is soon stopped by the tungstic acid forming a coating which must be removed to obtain further action on the alloy by the solvent. This chemical behavior points to a complex molecular structure. The formula Fe_3W_4 is purely empirical and the true formula is probably a very large multiple of this. If the fusibility and volatility of

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[1] Modern Theories of Chemistry, pp. 515-517.

compounds diminishes with increasing complexity of structure then in such difficultly volatile metals as tungsten, chromium, platinum, and other metals fusing at high temperatures, and in their alloys, the molecule (in the solid state) must be possessed of large molecular weight and corresponding inertness toward chemical action.[1]

I am indebted to Dr. Wahl, of Philadelphia, through Mr. Garrison, for the material on which these analyses were made.

THE DIRECT ESTIMATION OF CITRATE SOLUBLE PHOSPHORIC ACID.

By B. B. Ross.

Received December 18, 1893.

THE direct determination of citrate soluble phosphoric acid, as is well known, is effected in many European laboratories by precipitating it, as magnesium ammonium phosphate in the presence of the ammonium citrate employed in effecting its solution.

The lack of general applicability, together with other objections, which have been urged against this method, however, has caused its employment to be somewhat restricted and the process has met with little favor in this country.

The presence of the citric acid in the solution has, of course, prevented the direct application of the molybdate method, and several processes have been proposed for the elimination of the citric acid preparatory to the precipitation of the phosphoric acid by the molybdate solution. The writer some years since (Proceedings Association Official Agricultural Chemists, 1885,) proposed the removal of the citric acid by precipitation in the hot solution by means of calcium chloride.

A number of results reported at that time showed quite a close agreement with the figures obtained by the regular official method, but some later tests indicated a loss resulting from the retention of small quantities of calcium phosphate in the precipitate of calcium citrate.

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[1] "Modern Theories of Chemistry," pp. 131, 287. Ostwald "Outlines of General Chemistry," pp. 190, 191; in reference to potassium as solid p. 275.