made depending upon the different affinities of the coloring principles of bark and fustic for alum and tin mordants, but in none of them could any admixture with quercitron bark extract be detected.

The conclusions drawn from these analyses and comparisons were that I was made entirely by the "open-extraction" method; II was made by the "closed-extraction" method, using five to eight pounds pressure; and that III was extracted in open vessels, but that the changes of "waters" was done under pressure. The reason for the latter conclusion was that, while the ash percentage was low, the "extractive matter," or organic matter insoluble in alcohol was very high and the only way that this could happen would be by opening up the fiber of the wood, as is the case in open boiling and then applying pressure, which carried this "extractive matter" into the extracting liquor. These conclusions were subsequently borne out by experiments.

CAMDEN, N. J., April 6, 1895.

THE TUNGSTATES AND MOLYBDATES OF THE RARE EARTHS.

BY FANNY R. M. HITCHCOCK.

[*Continued from page 494.*]

b. Five cc. of the cerium sulphate solution were diluted to sixty cc., and brought to boiling, when alcohol was added, five cc. at a time, until sixty-five cc. had gone in, but the solution still remained clear. To this hot solution the cerium sulphate solution was added in the same way as the alcohol had been. The first addition of five cc. caused a precipitate to form, which redissolved at once. The second addition of five cc. caused a precipitate which dissolved again very slowly, and with the third addition the cerium sulphate came down in fine needles.

It was evident that the amount of alcohol which had been used in experiments 8, 9 and 10, with the sodium molybdate, had not been sufficiently great to cause by itself the precipitation of the cerium sulphate. The experiments were, therefore, repeated, the conditions being slightly varied.

Experiment 11. Ten cc. sodium molybdate solution were diluted to 100 cc., and fifteen cc. of the cerium sulphate solution added. To this, in the cold, fifty cc. of ninety-five per cent. alcohol were added very gradually, and with constant stirring. The whole was allowed to stand for half an hour, when the precipitate was filtered off, washed, first with fifty per cent. alcohol, then with thirty per cent., and finally with pure water, ignited, and weighed. The results obtained were the best of all the series.

Wt. obtained.	Calculated.	Difference.
0.1620 gram.	0.1629	—0.0009

The ignited precipitate dissolved in hydrochloric acid gave no trace of sulphuric acid when tested with barium chloride.

Experiment 12.—This was a duplicate of No. 11, except that the final washing was done with twenty per cent. alcohol instead of pure water. The washing was continued until there was no reaction with barium chloride for sulphuric acid.

Wt. obtained.	Calculated.	Difference.
0.1799 gram.	0.1629	+0.0170

The precipitate was tested as before, and proved to contain cerium sulphate.

Experiment 13.—Ten cc. of sodium molybdate solution were diluted to 185 cc. and fifty cc. of ninety-five per cent. alcohol added, followed by fifteen cc. of cerium sulphate solution. After standing an hour the precipitate was filtered off, and washed in the same manner as in No. 12.

Wt. obtained.	Calculated.	Difference.
0.1644 gram.	0.1629	0.0015

From the precipitate barium sulphate equivalent to 0.00146 gram of cerium sulphate was obtained, and the filtrate gave 0.0007 gram of molybdenum trisulphide.

Experiment 14.—This was a duplicate of No. 13.

Wt. obtained.	Calculated.	Difference.
0.1708 gram.	0.1629	0.0079

The precipitate yielded the equivalent of 0.0090 gram of cerium sulphate with barium chloride.

With hydrogen sulphide a precipitate of molybdenum trisulphide was given by all the filtrates from the experiments described above, the amount varying in wide limits. While alcohol diminished the solubility of the cerium molybdate formed, the advantage gained was more than counterbalanced by the tendency of the molybdate to carry down with it cerium sulphate in the presence of alcohol.

SODIUM TUNGSTATE AND CERIUM SULPHATE.

The solution of sodium tungstate used contained 27.07 grams in one liter. But few experiments were made, the results obtained being similar to those with sodium molybdate. Precipitation in a water solution alone was very incomplete, the precipitate persistently running through the filter, so that no definite results could be obtained in this way. When alcohol was used better results were obtained, the filtrate coming through clear.

Experiment 1.—Ten cc. sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of ninety-five per cent. alcohol added. The whole was brought to boiling when twenty-five cc. cerium sulphate solution were added. A dense, flocculent yellow-white precipitate came down at once, subsiding rapidly; it was filtered and washed with twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3266 gram.	0.3144	0.0122

Experiment 2.—Ten cc. of sodium tungstate solution were diluted with distilled water to 100 cc. and twenty-five cc. of ninety-five per cent. alcohol added, followed by twenty-five cc. of cerium sulphate solution in the cold. A bluish white precipitate formed, which on standing acquired a yellow tint. This was filtered cold and washed with twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3125 gram.	0.3144	—0.0019

Experiment 3.—Ten cc. of sodium tungstate solution were diluted to 100 cc. and twenty-five cc. of ninety-five per cent. alcohol added. The whole was brought to boiling and twenty-five cc. cerium sulphate added. The precipitate was washed with hot twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3322 gram.	0.3144	0.0178

The precipitate from all three solutions contained cerium sulphate, and the filtrates all showed traces of tungsten.

The next salts taken up were the two very rare ones, neodymium chloride and praseodymium chloride. For the material used I am indebted to the courtesy of Professor Waldron Shapleigh, of the Welsbach Light Company, Gloucester, N. J. The material given me consisted of the oxides prepared from the oxalates by ignition. These oxides are considered by v. Welsbach[1] to be the peroxides, and the formulas Nd_4O_7 and Pr_4O_7 have been assigned to them.

Nd_4O_7 is a light brown powder, while Pr_4O_7 is dark brown, almost black. Both dissolve readily in hydrochloric acid with evolution of chlorine, and form sesquichlorides. Neodymium chloride, Nd_2Cl_6, forms a rose colored solution while the corresponding praseodymium salt is pale green in color. The solutions used were prepared by evaporating the chlorides prepared from the oxides to dryness, taking up with water and again evaporating until all the hydrochloric acid was expelled. The residue was dissolved in water and filtered off from a little insoluble material which was probably a basic salt. About half a gram of the oxide was taken, and from it 100 cc. of the chloride solution was prepared.

The tungstates obtained from these salts by precipitation with sodium tungstate were gelatinous, and very difficult to filter and wash, showing a strong tendency to pass through the pores of the filter-paper.

For this reason a double filter was always used, and even with this precaution it was necessary to use as little pressure as possible with the filter-pump, and yet secure filtration. Even with the filter-pump the washing was very slow, and generally consumed a day at least, sometimes longer, although the quantities of material used were very small. The best results were obtained by washing first by decantation, and then on the filter.

The molybdates are gelatinous when first precipitated, but on heating they gradually become granular, and are then easily filtered and washed.

The neodymium tungstate has a very pale rose tint before ignition, which changes to a lavender color after ignition. The praseodymium tungstate has a decided greenish yellow tint both before and after ignition. The colors of the molybdates were similar to those of the tungstates, but deeper in tint.

The tendency of the precipitates to adhere to the sides of the beaker was a serious source of error at first; particularly after boiling, when it seemed impossible to remove them entirely. If not heated above 70° C. a piece of moist filter will remove the

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[1] *Wien. Monatsheft*, **6**, 477, *1885*.

adherent precipitate better than anything; in most cases it removes it perfectly, while a rubber is useless.

The ignitions were all made with free access of air, and were continued for at least two hours. Apparently no reduction of the molybdic acid takes place, as a second ignition after moistening with ammonium nitrate or with nitric acid, causes no change in the weight.

The solubilities were determined by the Victor Meyer method.[1] It will be noticed that with the praseodymium salts the solubility increases with a rise in temperature, the increase being more marked with the tungstate than with the molybdate.

With neodymium tungstate the solubility decreases as the temperature rises, while with the molybdate it increases under the same conditions. Slight though the solubility is, it is sufficiently great to cause decided error in the results when such small quantities are taken as were used in the experiments here recorded.

It was found very difficult at first, when analyzing the salts, to obtain a constant weight for the oxides, the results being all higher than theory required. The method finally adopted proved very satisfactory. The precipitated oxalate was strongly ignited together with the filter-paper, in a covered platinum crucible, for half an hour, cooled, and moistened with saturated solution of oxalic acid, then ignited again in the covered crucible.

The excess of weight in the earlier analyses being greater than was called for by oxidation to the peroxides, Nd_4O_7 and Pr_4O_7, the following experiments were made to determine how much oxygen would be taken up by the oxides after they had been reduced to the sesquioxides. In the analyses of neodymium molybdate, the theoretical amount required for the quantity taken was 0.0865 gram; the amount obtained was 0.0863 gram. This was heated in a platinum crucible with a Bunsen burner, the flame being applied at the back of the crucible, while the oxide was drawn forward to prevent any action of reducing gases, as far as possible. The cover of the crucible was bent and placed so as to cause a current of air to pass over the oxide.

[1] *Ber. d. chem. Ges.*, 8, 998, *1875*.

From time to time the crucible was cooled and weighed. The following table shows the gain in weight observed and the length of time for which the heat had been applied. It is assumed that the weight first taken represents the sesquioxide, and the atomic mass is taken as 140.5.

Time of heating.	Weight.	Gain.	Oxide.
0 hours.	0.0863 gram.	0.0000	Nd_2O_3.
4 "	0.0888 "	0.0025	Nd_4O_7.
5 "	0.0892 "	0.0029	
7½ "	0.0906 "	0.0043	Nd_2O_4?
10½ "	0.0937 "	0.0074	
16 "	0.0958 "	0.0095	
22 "	0.0997 "	0.0134	Nd_2O_6?
27½ "	0.1035 "	0.0172	Nd_2O_7?
30½ "	0.1036 "	0.0173,	

The oxide on first heating changed to light brown, the color of the superoxide prepared by the Welsbach Company; as the heat was continued it grew lighter in color, until, when it had attained its maximum weight, it was almost pure white.

If the flame be placed directly under the oxide, it loses weight and gradually passes into the brown "superoxide," Nd_4O_7.

A similar experiment with praseodymium sesquioxide, Pr_2O_3, gave the following results:

Time of heating.	Weight.	Gain.	Oxide.
0 hours.	0.0668 gram.	0.0000	Pr_2O_3.
4 "	0.0706 "	0.0038	Pr_2O_4?
6 "	0.0722 "	0.0054	
8 "	0.0730 "	0.0062	Pr_2O_5?
11 "	0.0745 "	0.0077	
13 "	0.0749 "	0.0081	

The atomic mass of praseodymium is taken at 143.5. The color of the oxide changed in the same way as that of neodymium, passing rapidly into the black peroxide Pr_4O_7 of Welsbach, then slowly changing to a reddish brown, and gradually becoming quite light in color. Whether it would be possible to increase the weight still more by heating small quantities for a long period of time, can only be determined by experiment; but the indications point to the existence of praseodymium trioxide PrO_3, as the increase in weight obtained is greater than that required for Pr_2O_6.

It would appear that the oxide Nd_2O_7 can be formed, improbable as it may seem, and that it is comparatively stable.

If it is really Nd_2O_7, neodymium is properly classed with manganese in the seventh group. It would be interesting to know if by reduction the monoxide NdO could also be formed.

SODIUM TUNGSTATE AND PRASEODYMIUM CHLORIDE.

The solution of sodium tungstate contained five grams in one liter.

Experiment 1.—Ten cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of ninety-five per cent. alcohol were added, followed by five cc. of praseodymium chloride solution in the cold. A precipitate formed at once, and the whole was boiled for an hour. It was then filtered, washed with hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

Wt. obtained.	Calculated.	Difference.
0.0579 gram.	0.0586	—0.0007

Experiment 2.—Ten cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of alcohol added. The whole was brought to boiling, and five cc. of the praseodymium chloride solution added, after which the boiling was continued for an hour. The precipitate was then filtered off, and washed with cold water containing twenty per cent. of alcohol. The filtrate showed a slight opalescence, which was not removed by refiltering.

Wt. obtained.	Calculated.	Difference.
0.0540 gram.	0.0586	—0.0046

Experiment 3.—Twenty cc. of the sodium tungstate solution were diluted with seventy-five cc. of distilled water, and five cc. of the praseodymium chloride added. The whole was then boiled for an hour, allowed to cool, and filtered cold, the washing being done with cold water.

Wt. obtained.	Calculated.	Difference.
0.1091 gram.	0.1172	—0.0081

Experiment 4.—Twenty cc. of sodium tungstate solution were diluted to 100 cc. with distilled water, and five cc. of the praseodymium chloride solution added. The whole was allowed to

stand for twelve hours, then brought to boiling, filtered hot, and washed with boiling water.

Wt. obtained.	Calculated.	Difference.
0.1136 gram.	0.1172	—0.0036

The filtrate was boiled for an hour with fifty cc. of ninety-five per cent. alcohol, but no additional precipitate was obtained.

Experiments 5 and *6*.—Twenty cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and five cc. of the praseodymium chloride solution added, followed by fifty cc. of ninety-five per cent. alcohol. The whole was then boiled, filtered while hot, and washed with hot water containing thirty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
Experiment 5.	0.1200 gram.	0.1172	0.0028
" *6*.	0.1230 "	0.1172	0.0058

Experiments 7, *8*, and *9*.—Thirty cc. of the sodium tungstate solution were diluted to seventy-five cc. with distilled water, and six cc. of the praseodymium chloride added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was heated to 60° C. for half an hour, filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
Experiment 7.	0.1733 gram.	0.1758	—0.0025
" *8*.	0.1730 "	0.1758	—0.0028
" *9*.	0.1724 "	0.1758	—0.0034

The precipitates after ignition showed traces of the blackish-brown praseodymium peroxide Pr_4O_7. The filtrate was tested with hydrogen sulphide, but gave no reaction for tungsten.

Experiments 10, *11*, *12*, *13*, and *14*.—Thirty cc. of the sodium tungstate solution were diluted to seventy-five cc. with distilled water, six cc. of the praseodymium chloride solution, and twenty-five cc. of alcohol added, and the whole heated for two hours at a temperature of 60° C. The precipitate was filtered off while the solution was hot, and was washed with 150 cc. hot water, containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
Experiment 10.	0.1715 gram.	0.1758	—0.0043
" *11*.	0.1712 "	0.1758	—0.0046
" *12*.	0.1713 "	0.1758	—0.0045
" *13*.	0.1712 "	0.1758	—0.0046
" *14*.	0.1713 "	0.1758	—0.0045

The ignited precipitates appeared to be homogeneous, no traces of Pr_4O_7 showing.

The filtrates were all tested for tungsten with hydrogen sulphide, but no tungsten trisulphide was obtained. This test is not of much value, however, when alcohol is present, as that will prevent the precipitation of tungsten as sulphide to a great extent, so that small quantities will escape detection, unless the alcohol is removed by evaporation before the hydrogen sulphide is used. The precipitaton of molybdenum does not seem to be hindered under the same conditions, the hydrogen sulphide bringing down minute traces in a solution containing thirty-three per cent. of alcohol

As the error is constant, and the condition of precipitation the same for all the numbers of this series of experiments, it is probably due to the solubility of praseodymium tungstate in water containing alcohol.

ANALYSIS OF PRASEODYMIUM TUNGSTATE.

One-tenth of a gram of the salt was fused with three grams of equal parts of sodium carbonate and sulphur. The fused mass was taken up with water, the gray-green insoluble residue filtered off, and washed with cold water; the filtrate was acidified with hydrochloric acid, the precipitated tungsten trisulphide filtered off on a tared filter, and dried in the air-bath at 100° C. until a constant weight was obtained.

When allowance is made for the molybdic acid present in sodium tungstate the amount of sulphide obtained must be lower than that called for by theory for pure praseodymium tungstate. The praseodymium oxide should be slightly higher in amount.

To estimate the oxide the insoluble residue from the fusion was dissolved in hydrochloric acid, precipitated with oxalic acid and ammonium hydroxide, and ignited in a covered crucible as already described.

	Wt. obtained.	Calculated.	Theoretical.
Pr_2O_3	0.0334 gram.	0.0331	0.0325
WS_3	0.0806 "	0.0808	0.0814

These results leave no doubt but that the constitution of this salt is correctly represented by the formula $Pr_2(WO_4)_3$.

To determine the solubility of the salt, praseodymium chloride was precipitated by sodium tungstate in aqueous solution; the precipitate with the solution was heated to 60° C. for two hours before filtering, and was washed with hot water until silver nitrate showed no trace of chlorine. The precipitate was dried in the air for a week, and then finely powdered. Portions of the salt were mixed with distilled water at different temperatures, about eighty cc. of water being taken for each portion, and then allowed to stand for two hours, the temperature being kept constant and the liquid frequently stirred. At the end of two hours they were filtered into weighed porcelain crucibles, evaporated to dryness, ignited, and weighed.

The results obtained are given below:

Temperature.	Wt. of solution.	$Pr_2(WO_4)_3$.	Solubility.
20° C.	39.3817 grams.	0.0000	0:00000
20° C.	44.6541 "	0.0000	0:00000
75° C.	44.2312 "	0.0019	1:23300
75° C.	40.1484 "	0.0018	1:22300

SODIUM MOLYBDATE AND PRASEODYMIUM CHLORIDE.

The solution of sodium molybdate used contained 8.51 grams in one liter.

Experiments 1–6.—Twenty cc. of the sodium molybdate solution were diluted to seventy cc. with distilled water, then twelve cc. praseodymium chloride solution were added, followed by twenty-five cc. of alcohol. The whole was heated for two hours at a temperature of 65° C. The precipitate was then filtered off and washed with 150 cc. of hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

	Wt. obtained.	Calculated.	Difference.
Experiment 1.	0.2093 gram.	0.2101	—0.0008
" *2.*	0.2094 "	0.2101	—0.0007
" *3.*	0.2096 "	0.2101	—0.0005
" *4.*	0.2084 "	0.2101	—0.0017
" *5.*	0.2084 "	0.2101	—0.0017
" *6.*	0.2080 "	0.2101	—0.0021

The precipitates numbered 1, 2, and 3, all showed traces of praseodymium oxide Pr_4O_7; the others seemed to be homogeneous.

The filtrates were all tested for molybdenum, with zinc, hydrochloric acid and potassium thiocyanate, but none was found. Alcohol does not interfere with the delicacy of this test.

The ignited salt was analyzed, the molybdic acid being determined by the Pechard method, while the praseodymium oxide was determined in the residue, after the molybdic acid was expelled, by the same method as had been pursued with the tungstate.

	Wt. obtained.	Calculated.
WO_3	0.1135 gram.	0.1127
Pr_2O_3	0.0874 "	0.0873

The amount taken for analysis was two-tenths of a gram, and the resuts show the correct formula to be $Pr_2(MoO_4)_3$ corresponding to that found for the tungstate.

The solubility of praseodymium molybdate was determined with the following results:

Temperature.	Wt. of solution.	$Pr_2(MoO_4)_3$.	Solubility.
23° C.	71.4000 grams.	0.0011	1:65820
75° C.	69.8000 "	0.0010	1:69800

PRECIPITATION OF TUNGSTIC ACID WITH NEODYMIUM CHLORIDE.

The solution of sodium tungstate used contained five grams in one liter.

Experiments 1 and 2.—Twenty cc. of the sodium tungstate were diluted to 100 cc. with distilled water and five cc. of the neodymium chloride added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was brought to boiling, filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

The filtrates were opalescent, and repeated filtrations failed to render them clear. The precipitates, after ignition, appeared to be homogeneous.

	Wt. obtained.	Calculated.	Difference.
Experiment 1.	0.1117 gram	0.1167	—0.0050
" *2.*	0.1126 "	0.1167	—0.0041

Experiments 3 and 4.—Ten cc. of the sodium tungstate solution diluted to fifty cc. with distilled water, and three and one-half cc. of neodymium chloride solution added were heated to boiling, filtered while hot, and the precipitate washed with hot water.

	Wt obtained.	Calculated.	Difference.
Experiment 3.	0.0595 gram.	0.0583	0.0012
" *4.*	0.0573 "	0.0583	—0.0010

Experiments 5–16.—These experiments were duplicates of 3 and 4, excepting that the solutions were heated to 80° C. instead of to boiling. No alcohol was added, and the precipitates were washed with hot water. The precipitates showed traces of the brown peroxide, Nd_4O_7.

	Wt. obtained.	Calculated.	Difference.
Experiment 5.	0.0575 gram.	0.0583	—0.0008
" *6.*	0.0575 "	0.0583	—0.0008
" *7.*	0.0593 "	0.0583	+0.0001
" *8.*	0.0600 "	0.0583	0.0017
" *9.*	0.0585 "	0.0583	0.0002
" *10.*	0.0586 "	0.0583	0.0003
" *11.*	0.0590 "	0.0583	0.0007
" *12.*	0.0585 "	0.0583	0.0002
" *13.*	0.0585 "	0.0583	0.0002
" *14.*	0.0581 "	0.0583	—0.0002
" *15.*	0.0584 "	0.0583	0.0001
" *16.*	0.0597 "	0.0583	0.0014

Experiments 17 and 18.—Thirty cc. of the sodium tungstate solution were diluted to seventy cc. with distilled water and six cc. of the neodymium chloride solution added, followed by twenty-five cc. of alcohol. The whole was heated to 70° C., filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
Experiment 17.	0.1724 gram.	0.1749	—0.0025
" *18.*	0.1745 "	0.1749	—0.0004

No. 18 showed slight traces of the peroxide Nd_4O_7.

Experiments 19–21.—These were prepared like the preceding solutions Nos. 17 and 18, but were heated to 60° C. instead of 70°.

The filtrates showed no trace of molybdenum when tested with zinc, hydrochloric acid, and potassium thiocyanate.

	Wt. obtained.	Calculated.	Difference.
Experiment 19.	0.1731 gram.	0.1749	—0.0018
" *20.*	0.1727 "	0.1749	—0.0022
" *21.*	0.1728 "	0.1749	—0.0021

A comparison of these results shows that the precipitation of tungstic acid by neodymium chloride is practically quantitative. Analyses of the salt made in the same manner as for praseodymium tungstate agreed closely with the theoretical requirements as regarded the neodymium oxide. The tungstic acid was invariably too low, and the different results were too discordant; the tungstic acid, therefore, was determined by difference; the weight of neodymium oxide found was 0.0651 gram, the amount required by theory being 0.0652 gram. From this was deduced the formula $Nd_2(WO_4)_3$ for the salt, which corresponds to the praseodymium tungstate.

The solubilities, determined as for the praseodymium salts, and under similar conditions were as follows:

Temperature.	Wt. of solution.	$Nd_2(WO_4)_3$.	Solubility.
22° C.	42.1032 grams.	0.0008	1:52630
65° C.	41.7117 "	0.0007	1:59580
98° C.	39.6286 "	0.0006	1:66040

SODIUM MOLYBDATE AND NEODYMIUM CHLORIDE.

The solution of sodium molybdate used contained 5.1080 grams in one liter.

Experiments 1-5.—Twenty cc. of the sodium molybdate solution were diluted to seventy cc. with distilled water; seven cc. of the neodymium chloride solution were added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was then heated to 65° C. for two hours, filtered hot, and the precipitate washed with 150 cc. of hot water containing twenty-five per cent. of alcohol.

The ignited precipitates showed no trace of the brown oxide Nd_4O_7, and the filtrates, when tested, gave no reaction for molybdenum.

	Wt. obtained.	Calculated.	Difference.
Experiment 1.	0.1260 gram.	0.1256	0.0004
" *2.*	0.1259 "	0.1256	0.0003
" *3.*	0.1260 "	0.1256	0.0004
" *4.*	0.1259 "	0.1256	0.0003
" *5.*	0.1258 "	0.1256	0.0002

An analysis of two-tenths of a gram of the salt made in the same way as the analysis of praseodymium molybdate gave the following results:

	Wt. obtained.	Calculated.	Difference.
Nd_2O_3	0.0863 gram.	0.0865	—0.0002
MoO_3	0.1134 "	0.1135	—0.0001

From these results the formula $Nd_2(MoO_4)_3$ is deduced for neodymium molybdate.

The solubility determinations gave the following results :

Temperature.	Wt. of solution.	$Nd_2(MoO_4)_3$.	Solubility.
28° C.	69.9311 grams.	0.0013	1:53790
75° C.	71.4279 "	0.0022	1:32466

A comparison of the results obtained shows that the precipitation of both tungstic and molybdic acids by neodymium salts is quantitative.

SODIUM TUNGSTATE AND LANTHANUM CHLORIDE.

The solution of sodium tungstate contained five grams in a liter.

Experiments 1 and 2.—Twenty cc. of sodium tungstate solution were diluted to seventy cc. with distilled water, and seven cc. of lanthanum chloride solution added, followed by twenty-five cc. of alcohol. The whole was heated for two hours at a temperature of 60° C., after which the precipitate was filtered off and washed with 150 cc. of hot water containing twenty-five per cent. of alcohol. The filtrate was clear and gave no reaction for tungsten with hydrogen sulphide. The ignited precipitates appeared to be homogeneous.

	Wt. obtained.	Calculated.	Difference.
Experiment 1.	0.1143 gram.	0.1160	—0.0017
" *2.*	0.1143 "	0.1160	—0.0017

The tungstate before ignition was of a delicate blue, almost white, and after ignition the color deepened slightly. The color of the molybdate was almost the same as that of the tungstate.

ANALYSIS OF LANTHANUM TUNGSTATE.

The first analysis was made by fusing with sodium carbonate and sulphur, then taking up in water, and filtering off the sodium sulphotungstate formed, from the insoluble lanthanum oxide; then decomposing the filtrate with hydrochloric acid and estimating the tungsten from the tungsten trisulphide found.

The results obtained were very satisfactory so far as the lanthanum oxide was concerned, but no good results were obtained for the tungstic acid.

The amount of the salt taken for analysis was one-tenth of a gram.

	Wt. obtained.	Calculated.
La_2O_3	0.0326 gram.	0.0321
WS_3	0.0606 "	0.0822

The same difficulty was encountered here that was met with in the analysis of neodymium tungstate, and the cause was not apparent. A second analysis by a different method was made, the same amount of material being taken. The lanthanum tungstate was decomposed with aqua regia, evaporated to dryness with hydrochloric acid three times, and the separated tungsten trioxide filtered off and dissolved in ammonium hydroxide; the filtrate was rendered ammoniacal, the solution of the tungstic acid added to it, and hydrogen sulphide passed through it until the liquid was deep yellow in color. The liquid was acidified with hydrochloric acid, and before neutralization was complete the color changed to a bright green, becoming red when completely acidified. On rendering it ammoniacal again, the green color reappeared.

Hydrogen sulphide was passed through the solution again for an hour, hydrochloric acid added, and the solution warmed; it gradually became colorless, and a light brown precipitate of tungsten trisulphide settled down.

This was treated in the usual manner and dried at 100° to constant weight.

	Wt. obtained.	Calculated.
WS_3	0.0640 gram.	0.0822

The filtrate was boiled until all the hydrogen sulphide was expelled, a few drops of nitric acid added, and then ammonium hydroxide; the precipitate of lanthanum hydroxide was evidently not pure, being yellow in color instead of white; it was filtered off, ignited, dissolved in aqua regia, evaporated to dryness, taken up with a little hydrochloric acid, followed by ammonia, and the treatment with hydrogen sulphide repeated. The yellow ammoniacal solution passed through the same color changes as before, when acidified. On heating, a dark red-brown precipitate formed which was filtered off, and washed with dilute hydrochloric acid, and then with alcohol. A great part of the precipitate dissolved in the alcohol to a dark red solution, the precipitate left on the filter-paper turning brown. This precipitate was ignited in a weighed porcelain crucible and evaporated with concentrated nitric acid until a constant weight was obtained. It had the appearance of tungstic acid.

Wt. obtained = 0.0073 gram.

The alcoholic filtrate was evaporated to dryness in a weighed porcelain crucible, and treated repeatedly with fuming nitric acid to oxidize any sulphur that might be present to sulphuric acid, which was removed by repeated evaporation with ammonium hydroxide. The substance remaining in the porcelain crucible had the appearance of molybdic acid. It was pale yellow in color, was readily soluble in ammonium hydroxide, and also dissolved in aqua regia to a bright yellow solution, separating out as a bright yellow powder on concentrating the solution. The yellow powder, when ignited, turned brown, but regained its color on cooling, finally, however, becoming lemon-yellow. When moistened with hydrochloric acid and heated, no blue color appeared. A faint orange-red solution was obtained by treatment with zinc, hydrochloric acid, and potassium thiocyanate. Heated on platinum foil with concentrated sulphuric acid no blue color was produced. The phosphorus bead was colorless, even after treating with tin on charcoal.

The weight obtained was 0.0076 gram. The second analysis gives the following results:

	Wt. obtained.	Calculated.
La_2O_3.	0.0326	0.0321
WO_3.	0.0613	0.0679
	0.0076	

This corresponds to the formula $La_2(WO_4)_3$ for lanthanum tungstate. The same salt was prepared by W. French Smith[1] by the precipitation of sodium tungstate with lanthanum salts.

The solubility of lanthanum tungstate in water was determined by the Victor Meyer method, the salt being prepared in the same way as the praseodymium tungstate.

Temperature.	Wt. of solution.	$La_2(WO_4)_3$.	Solubility.
27° C.	60.5580 grams.	0.0007	1:86510
65° C.	42.4678 "	0.0010	1:42467

SODIUM MOLYBDATE AND LANTHANUM CHLORIDE.

The solution of sodium molybdate used contained 8.51 grams in one liter.

Experiments 1–3.—Twenty cc. sodium molybdate solution were diluted to seventy cc. with distilled water, seven cc. of lantha-

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[1] "Ueber Didymium and Lanthanum." Inaugural Dissertation by W. French Smith. Göttingen, 1876.

num chloride solution added, followed by twenty-five cc. of ninety-five per cent. alcohol.

The precipitate, at first gelatinous, gradually became granular, and was filtered off, washed with 150 cc. hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

	Wt. obtained.	Calculated.	Difference.
Experiment 1.	0.2063 gram.	0.2083	−0.0020
" *2.*	0.2061 "	0.2083	−0.0022
" *3.*	0.2063 "	0.2083	−0.0020

The filtrates were clear and gave no reaction for molybdenum when treated with potassium thiocyanate in the presence of zinc and hydrochloric acid.

The solubility of the salt obtained was determined under the following conditions:

Temperature.	Wt. of solution.	$La_2(MoO_4)_3$.	Solubility.
25° C.	72.5500 grams.	0.0013	1:55800
85° C.	69.3474 "	0.0023	1:30150

ANALYSIS OF LANTHANUM MOLYBDATE.

The analysis was made in the same manner as with the other molybdates, the salt being decomposed in a current of dry hydrogen chloride gas. The molybdic acid was driven off very readily at first, but toward the close of the operation the full heat of the Bunsen burner was required. Two-tenths of a gram of the salt were taken for analysis, and results were as follows:

	Wt. obtained.	Calculated.
La_2O_3	0.0853	0.0856
MoO_3	0.1145	0.1144

From these results the formula $La_2(MoO_4)_3$ may be calculated for lanthanum molybdate.

Tests were now made with thorium chloride, potassium zirconium fluoride, and zirconium fluoride.

With thorium chloride no definite results could be obtained from either sodium molybdate or sodium tungstate; precipitates were formed with both salts even in quite dilute solutions, but they were slight in quantity, and ran through the filter in spite of every attempt to prevent it, whether filtered hot or cold. Neither alcohol nor ammonium salts made any difference in the behavior.

With the potassium zirconium fluoride no precipitate was obtained with either the sodium tungstate or molybdate.

With zirconium fluoride no results were obtained, the solutions remaining clear after standing several days.

Beyond these qualitative tests no work was done with the thorium or zirconium salts in connection with tungsten and molybdenum.

SUMMARY.

1. The tungstates and molybdates are precipitated quantitatively by nearly all the rare earths.

2. A separation of tungstic and molybdic acids is not possible through their combinations with the rare earths.

3. The non-precipitation of molybdic acid by uranyl solutions when tungstates are absent, and the almost complete precipitation of both when tungstic acid is also present is further evidence of the fact that we can scarcely hope to effect this separation by the method of precipitation.

4. The molybdates and tungstates of neodymium and praseodymium are new, and their constitution is correctly represented by the formula $Nd_2(MoO_4)_3$, $Nd_2(WO_4)_3$, and $Pr_2(MoO_4)_3$, $Pr_2(WO_4)_3$.

5. The solubility determinations indicate that tungstates and molybdates of the rare earths must be classed among the more difficultly soluble compounds.

6. Further research is required upon the methods to be followed in the separation of tungstic and molybdic acids from the oxides of the rare earths.

A NEW TABLE FOR THE QUALITATIVE SEPARATION OF THE METALS OF THE IRON GROUP.

By C. L. Hare.

Received April 15, 1895.

IN the qualitative separation of metals of the iron group much trouble has been experienced with the methods in general use for the separation of cobalt and nickel.

The methods commonly used for the separation of iron, aluminum, and chromium are also unsatisfactory.

The following compilation and application of methods recently worked up greatly simplifies and shortens the process for the qualitative separation of the metals of this group.