of any thermometer will then consist simply in a series of dilutions (sixteen are obviously needed to cover 4° in 0.25° steps). This experimental work is very easily done, and with the adiabatic calorimeter is capable of great accuracy. Of course other reactions also, besides the heat of dilution of hydrochloric acid, could be used for this purpose, after they had been properly studied. Heat of neutralization of acids may be especially convenient. In case any interval appeared to be especially abnormal, it could be subdivided still further by a yet feebler reaction. We have already made further progress along these lines, and hope soon to publish a more complete account, which we hope may be really useful to chemists and physicists dealing with the difficult subject of exact thermometry.

We are greatly indebted to the Carnegie Institution of Washington, whose liberal grant alone made the work possible at this time.

Summary.

A new method for subdividing accurately any given interval on the thermometer scale is presented. This method depends upon the execution of a given simple reaction step by step over the range in question, somewhat analogously to the calibration of a buret with the Ostwald calibrator. Allowance must be made, of course, for the temperature-coefficient of the reaction, and other details dependent upon changing heat-capacity. The method is peculiarly suitable for the standardizing of short ranges, such as those used in thermochemistry.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE SEPARATION OF TUNGSTEN FROM MOLYBDENUM.[1]

BY EDWARD ELLSWORTH MARBAKER.

Received October 8, 1914.

With the extensive introduction of tungsten and molybdenum into industrial chemistry in the form of the special steels and the filament of the incandescent electric lamp, the importance of these metals has been greatly increased from the standpoint of the analytical chemist.

It is a well-known fact that molybdenum always accompanies tungsten in its ores, and it shows a marked tendency to remain with the tungsten throughout the process of manufacture. This amount of molybdenum, although small, interferes to a great extent with the determination of the tungsten, and hence one of the important problems in modern analysis is to devise a separation of the two metals which will be easy to carry out and also be of the highest accuracy. Up to the present time there have

---

[1] From the author's Ph.D. thesis, 1914.

been suggested methods for the attainment of this end: Rose,[1] Pechard,[2] Smith and Reugenberg,[3] Ibbotson and Brearley.[4] In 1911, Mdivani[5] announced a new method for the determination of tungsten which was based on the observation of Anthon,[6] that when a tungstate solution is treated with a solution of stannous chloride, a yellow precipitate of normal tin tungstate, $SnWO_4$, is formed, which is changed to the blue oxide of tungsten, W_2O_5, on the addition of concentrated hydrochloric acid. Mdivani added to the tungstate solution, a solution of stannous chloride in concentrated hydrochloric acid and then boiled for a few minutes. The blue oxide was precipitated and, after settling, was filtered off, washed with hot water, dried, ignited to tungsten trioxide and weighed as such.

1. An Effort to Reproduce the Results of Mdivani.

Mdivani made up a solution for analysis by dissolving 2 g. of pure tungsten trioxide in strong ammonia and diluting to one liter. He treated 50 cc. of this solution, which contained 0.1 g. of WO_3, with 20 cc. of a solution containing 50 g. of crystallized stannous chloride in 200 cc. concentrated hydrochloric acid. The blue precipitate which was thrown down was boiled up for a few minutes and then allowed to settle, after which it was washed by decantation with hot distilled water and finally ignited and weighed as tungsten trioxide.

A weighed sample of pure tungstic acid, which had been prepared for the purpose of making ductile tungsten lamp filament, was treated with strong ammonia. The attack was not complete, showing that the purity of the substance was doubtful; but the solution was filtered and made up to one liter. Samples of this solution were analyzed by evaporating to dryness three times with hydrochloric acid and nitric acid, baking at about 120° for fifteen minutes after each evaporation, then washing on to a filter with a hot ammonium nitrate solution, finally igniting and weighing. Fifty cc. of the solution were thus found to contain 0.1422 g. WO_3. This value was obtained as the average of ten closely agreeing determinations.

A solution of stannous chloride was made according to the directions of Mdivani. Twenty cc. of the tin solution were added to 50 cc. of the ammonium tungstate solution, and the resulting blue precipitate was boiled for a few minutes and washed according to the directions of Mdivani. The pure water recommended for washing was found to be inadequate because it caused the formation of basic tin salts which could not be

---

[1] Rose, Treadwell-Hall, *Analytical Chemistry,* II, 3d ed., 1911, p. 296.

[2] Pechard, *Ibid.,* 295; *Compt. rend.,* 114, 173 (1892).

[3] Smith and Reugenberg, THIS JOURNAL, **22,** 772 (1900); Treadwell-Hall, 293.

[4] Ibbotson and Brearley, *Chem. News,* 81, 13 (1900).

[5] Mdivani, *Bull. Soc. Chem.,* [4] **9,** 122 (1911).

[6] Anthon, Dammer, *Handbuch,* 3, 659 (1893); *J. prakt. Chem.,* **9,** 341 (1836).

washed out and hence gave rise to high results. This was easily remedied by washing the precipitates with a solution of hydrochloric acid made by adding 50 cc. of strong acid to a liter of boiling distilled water. The washed precipitates were thus entirely free from tin.

Four determinations resulted as follows:

WO_3 present, 0.1422 g.; WO_3 found, 0.1392, 0.1386, 0.1390 and 0.1387 g.

To determine the cause of these low results, the filtrate from one of the determinations, which was perfectly clear and colorless, was evaporated to dryness. Blue oxide of tungsten separated. This showed that either the precipitation had not been complete or that the acid of the wash water had caused some of the oxide to pass into solution. Subsequent results indicated that the latter was not the case. The small amount of blue oxide was transferred to a filter and washed with the dilute acid until the filtrate gave no test for tin on the addition of ammonia. The filter and its contents were then ignited, but instead of obtaining a small amount of yellow tungsten trioxide, there was present a mixture of the yellow oxide and a white substance which proved to be tin oxide. This would indicate that a combination had taken place between the tin and the tungsten, because all of the tin had been washed out of the precipitate so far as the tests on the filtrate showed. In order to eliminate the small amount of tin, the residue was carefully treated with ammonium chloride, as recommended by Rammelsberg,[1] which causes the tin to volatilize as stannic chloride, leaving the tungstic acid behind. The weight of this residue added to that of the main portion of the oxide brought the result into agreement with the theoretical.

2. The Action of Mdivani's Reagent on a Mixture of Ammonium Tungstate and Ammonium Molybdate.

When stannous chloride was added to a solution of ammonium molybdate a brown precipitate appeared. This rapidly dissolved in the excess of the reagent, the solution assuming a characteristic orange color, due to the reduction of the MoO_3 to Mo_2O_3. This is very different from the reaction which takes place in the tungstate solution, hence it seemed possible to effect a separation.

A solution of molybdenum trioxide in ammonia was made up and analyzed by the method of Chatard.[2] Ten cc. of the solution were found to contain 0.1164 g. MoO_3.

A solution containing 0.1164 g. MoO_3 and 0.1422 g. WO_3 was treated with 20 cc. of the tin solution and the resulting precipitate of W_2O_5 handled as outlined before. It was washed with the acid wash water until the washings gave no test for tin. The filter and its contents were ignited and weighed. A fairly close value for the tungsten was obtained.

[1] Rammelsberg, *Chem. News*, **9**, 25 (1864).

[2] Chatard, *Ibid.*, **24**, 175 (1871).

It was assumed at this point that the precipitate of tungstic acid contained no molybdenum, but a careful test was made to determine whether the filtrate containing the molybdenum contained any tungsten. This test was carried out as follows: An excess of metallic zinc was added to the solution and the tin was precipitated as metal. The solution changed color from orange to green. It was decanted from the tin, which was present in the form of a porous cake, and the tin washed several times with hot water. The clear green liquid was then evaporated on the hot plate, during which process the color changed to brown again. When the bulk of the solution had been decreased to about 150 cc. a few drops of nitric acid were added. It rapidly became colorless, showing that the molybdenum had been oxidized to the form of molybdate. Ammonia was then added in great excess. The precipitate of zinc hydroxide which first appeared dissolved in excess, leaving a small precipitate of iron and tin hydroxides. This was filtered out and reprecipitated. The filtrate was added to the main solution and the whole treated with acid to the point of neutrality. A small amount (3–5 cc.) of acetic acid was then added, followed by an excess of lead acetate. A precipitate of lead molybdate was formed which after settling, was filtered, washed with dilute acetic acid, ignited and weighed. This weight proved to be lower than the theoretical but the loss could not be accounted for, although the precipitate of tin metal, the iron and tin precipitate, and the filtrate from the lead molybdate were all tested with zinc and sulfocyanide, but no evidence of molybdenum was observed.

The ignited residue of lead molybdate was then tested with hydrochloric acid, according to the method of separation suggested by Ibbotson and Brearley.[1] The solution of the residue was complete, but on dilution no tungstic acid separated out, thus showing that the molybdenum was not contaminated with any tungsten and that, so far as the tungsten was concerned, the separation was complete.

It was found in other determinations, carried out in the same way, that the weight of the tungstic oxide was high, although all the tin had been removed by careful washing. The high results must then have been due to a small amount of molybdenum left in the tungsten. The precipitate of W_2O_5 was dissolved in ammonia containing a little hydrogen peroxide and reprecipitated with a second portion of the tin solution. The precipitation at this point was never complete, because the filtrate had a blue color. This was evaporated to dryness, the W_2O_5 washed out and ignited with ammonium chloride and finally weighed. This weight was added to that of the main precipitate and the sum of the two gave a somewhat low result, due probably to unavoidable losses in the process of analysis.

---

[1] Ibbotson and Brearley, *Chem. News*, **81**, 13 (1900).

A series of results follows:

Gram WO_3 present.		Gram WO_3 found.	Gram WO_3 present.		Gram WO_3 found.
0.1422		0.1426	0.1422	Reprecipitated	0.1412
0.1422		0.1414	0.1422		0.1405
0.1422		0.1429	0.1422		0.1414
0.1422		0.1434	0.1422		0.1434
0.1422		0.1432	0.1422		0.1428
0.1422	Reprecipitated	0.1404	0.1422		0.1415
				Average,	0.1422

These results indicate a possible separation of tungsten from molybdenum, although they are not particularly concordant. The molybdenum was not determined, because at the moment there was no method available for the separation of the molybdenum from extremely large amounts of tin.

3. The Action of Mdivani's Reagent on a Mixture of Sodium Tungstate and Sodium Molybdate.

Mdivani states in his paper that the quantitative precipitation of tungsten may be carried out as well in solutions of sodium and potassium tungstate and molybdate as in solutions of the ammonium salts.

The solution of sodium tungstate used was made from a portion of the salt which had been prepared by fusing together the theoretical amounts of pure WO_3 and Na_2CO_3 and crystallizing the product. The solution contained 0.1489 g. WO_3 in each 10 cc. The solution of sodium molybdate was made by dissolving a sample of a salt, which had been made by Schuchardt, and afterwards recrystallized several times. This solution contained 0.1200 g. MoO_3 in each 10 cc.

A sample of the tungstate solution was measured out and treated with the usual amount of Mdivani's reagent. The blue precipitate appeared and was filtered off. The filtrate was colored blue, showing that the precipitation had not been complete. Several attempts were made to improve this precipitation by adding more reagent than usual and also by the addition of ammonium chloride, but without any favorable results.

A solution containing both tungstate and molybdate was then treated in the usual manner with the tin solution in order to determine the effect of the presence of sodium molybdate. The blue precipitate of W_2O_5 came down well and was weighed after filtering and washing. The filtrate in this case was orange colored, on account of the molybdenum present. A series of ten determinations was made and the results were so concordant and near the theoretical that it shows conclusively that for the amounts of tungstate and molybdate present a separation of tungsten and molybdenum can be effected by means of an acid stannous chloride solution. The results follow:

Gram MoO_3 present.	Gram WO_3 present.	Gram WO_3 found.
0.1200	0.1489	0.1492
0.1200	0.1489	0.1489
0.1200	0.1489	0.1490
0.1200	0.1489	0.1486
0.1200	0.1489	0.1486
0.1200	0.1489	0.1489
0.1200	0.1489	0.1492
0.1200	0.1489	0.1486
0.1200	0.1489	0.1489
0.1200	0.1489	0.1489

As in the case of the separation of tungsten and molybdenum using the ammonium salts, the molybdenum was not determined.

The tungsten trioxide obtained in the foregoing analyses was tested for molybdenum by the method of Debray[1] by passing over it dry hydrogen chloride at a temperature of 200°. A slight sublimate of the compound $MoO_3.2HCl$ was formed, proving that a little molybdenum was present. On subsequent analysis by the method of Chatard it was found that the molybdenum contained in the tungsten trioxide from six determinations amounted to less than one milligram of MoO_3.

The fact that the separation takes place so easily is so at variance with the usual experience of analysts of tungsten compounds that it seemed very remarkable that the molybdate actually aids the precipitation of the tungsten, as it will be remembered that the precipitation of W_2O_5 from the tungstate alone is never complete. This was so peculiar that the effect of other salts on the precipitation was tried. The results of these tests were as follows:

Salt present.	Gram WO_3 present	Gram WO_3 found.
0.1 g. K_2SO_4	0.1489	0.1481
0.1 g. K_2SO_4	0.1489	0.1488
K_2CrO_4	0.1415	0.1414
0.2 g. NaCl	0.1489	0.1487
0.2 g. NaCl	0.1489	0.1494

The filtrate from the tungsten in all of the foregoing determinations, except that containing chromium, was perfectly colorless. These results show that an accurate estimation of the tungsten in sodium tungstate can be made by the addition of any of the salts mentioned in the table.

In order to determine the availability of the method various amounts of sodium tungstate and sodium molybdate were taken. The results appear in the following table:

Gram MoO_3 present.	Gram WO_3 present.	Gram WO_3 found.
0.1200	0.0089	0.0089
0.1200	0.0149	0.0151
0.1200	0.0596	0.0592
0.1200	0.0900	0.0900

---

[1] Debray, *Compt. rend.*, **46**, 1101 (1858).

Gram MoO_3 present.	Gram WO_3 present.	Gram WO_3 found.
0.1200	0.1200	0.1200
0.1200	0.1788	0.1786
0.1200	0.2100	0.2101
0.1200	0.2400	0.2397
0.1200	0.2700	0.2700
0.1200	0.3000	0.2998
0.0121	0.1500	0.1496
0.0241	0.1500	0.1497
0.0482	0.1500	0.1500
0.0724	0.1500	0.1504
0.0965	0.1500	0.1499

4. The Determination of the Molybdenum in the Filtrate from the Blue Oxide.

The filtrate from the tungsten contains all the molybdenum and a large amount of tin in the form of stannous and stannic chlorides. The tin was removed from the solution by means of metallic zinc, the filtrate was evaporated down to a small bulk, oxidized with nitric acid and treated with an excess of ammonia. The zinc hydroxide which was thrown down dissolved in excess. The molybdenum was then precipitated by lead acetate after the solution had been almost neutralized with HCl and finally treated with a small excess of acetic acid. The precipitate of lead molybdate was allowed to settle, filtered, washed with hot dilute acetic acid, and finally weighed. In every case the result was low.

Since the foregoing procedure failed to solve the problem of determining the molybdenum, a careful review of the literature was taken up in the hope that a method for determining molybdenum in a hydrochloric acid solution had been devised. Nothing of this nature was found in connection with any gravimetric method, but the discussion of the volumetric methods seemed to offer a means of solving the problem.

Randall[1] has shown that when a molybdate solution is passed through a Jones reductor and the reduced solution is caught in a ferric ammonium sulfate solution, decolorized by phosphoric acid, that the ferric iron oxidizes the molybdenum, and the ferrous iron thus formed may be titrated with standard potassium permanganate. This investigator proved that the molybdenum is completely reduced to the form of Mo_2O_3. Accordingly, a determination was carried out as follows: A portion of the sodium molybdate solution was measured out and treated with about 20 cc. of Mdivani's reagent. This gave rise to an orange colored solution, to which were added about 5 g. of pure 20-mesh zinc. The tin was deposited on the zinc as metal, and the green supernatant liquid was poured off, the tin washed with hot water, and then the solution and washings were heated to about 60°.

The reductor flask was charged with 20 cc. of the ferric alum solution

---

[1] Randall, *Am. J. Sci.*, [4] **24**, 313 (1907).

and 20 cc. of the "titrating solution."[1] Fifty cc. of dilute hydrochloric acid (2.5% by vol. of the concentrated acid heated to 60°) were passed through the reductor, followed by the solution containing the molybdenum, and then 150 cc. of the warm acid and finally 150 cc. of hot distilled water.

The flask was removed from the reductor and the titration was carried out in the usual way with the permanganate[2] solution. The molybdenum solution before entering the reductor is green, while in the reductor the reduction is completed, although there is no noticeable change in color. When the green solution enters the ferric solution the color changes to red. This red solution is titrated with permanganate, but the red color offers no obstacle because, as the permanganate is added, this color disappears, and toward the end of the titration the color of the solution is a faint bluish green in which the end point is very easily seen. The end point has to be taken very quickly, as it is not at all permanent. However, the titration is one which is very easily carried out.

A number of such determinations were made with the following results:

Gram MoO_3 present.	Gram MoO_3 found.	Gram MoO_3 present.	Gram MoO_3 found.
0.1500	0.1505	0.1350	0.1354
0.1500	0.1505	0.1635	0.1632
0.1470	0.1476	0.1200	0.1198
0.1500	0.1498	0.1050	0.1051
0.1500	0.1498	0.1800	0.1801

They show that the separation of tin from molybdenum by means of metallic zinc is quantitative and that the method may be used to determine the molybdenum in the filtrate from the tungsten in the method of separation under consideration.

5. The Separation of Tungsten from Molybdenum.

The two processes outlined in the third and fourth sections of this paper were combined, and both constituents of the mixture of sodium tungstate and molybdate were determined.

The separation worked very well with quantities up to and including 0.3000 g. of each constituent. More than this amount gave rise to high results unless an inordinate amount of time was consumed in washing out the molybdenum from the tungsten. The high results can be more quickly corrected by treating the ignited residue of WO_3 with as many cc. of concentrated hydrochloric acid as there are centigrams of the residue and boiling for a few minutes. Then this may be diluted with three times its volume of hot water and allowed to settle. This process removes the contaminating molybdenum and leaves the tungsten pure. The filtrate containing the small amount of molybdenum is of course

---

[1] This consisted of 90 g. manganous sulfate, 650 cc. distilled water, 175 cc. syrupy phosphoric acid and 175 cc. concentrated sulfuric acid.

[2] Standardized against ferrous ammonium sulfate and also oxalic acid.

added to the main molybdenum solution. There seem to be no limits to the applicability of the molybdenum titration. When large amounts of molybdenum were present it was found advisable to make up to 250 cc. and work with portions of 50 cc. each. The latter method proved to be a great factor in reducing the time of the determination.

When moderate samples are used the whole process, involving the determination of both the constituents, can be carried out in about three hours. The greater part of this time is consumed in washing the tungsten precipitate and in evaporating the filtrate containing the molybdenum to a bulk which may be easily handled.

The results of ten complete separations follow:

Gram WO_3 present.	Gram MoO_3 present.	Gram WO_3 found.	Gram MoO_3 found.
0.1005	0.1005	0.1001	0.1010
0.1500	0.1500	0.1496	0.1498
0.2000	0.2000	0.2004	0.1995
0.2520	0.2505	0.2526	0.2499
0.3015	0.3000	0.3016	0.2997
0.3500	0.3500	0.3508	0.3502
0.4005	0.4005	0.4008	0.3995
0.4500	0.4500	0.4508	0.4495
0.4995	0.4995	0.4999	0.4994
0.3000	0.3000	0.3000	0.2996

Summary.

Tungsten and molybdenum, in the form of their sodium salts, may be quickly and easily separated, the course of analysis being as follows:

To a boiling solution containing the tungstate and molybdate of sodium in appropriate amounts add the tin solution (50 g. $SnCl_2.2H_2O$ dissolved in 200 cc. concentrated HCl) in the proportion of 20 cc. for each 0.15 g. WO_3 present. This amount of the reagent should be carefully regulated, because less will not effect a complete separation, and more will be correspondingly harder to handle in the determination of the molybdenum. The dilution of the solution for analysis should be kept between 60 cc. and 300 cc., depending on the amount of tungsten present. After boiling a few minutes allow the blue precipitate of W_2O_5 to settle and then pour the orange supernatant liquid through a filter. Wash the precipitate thoroughly by decantation with hot 5% hydrochloric acid until the washings give no test for molybdenum by the zinc and thiocyanate method. Bring the precipitate on the filter and allow to drain. If the amount of precipitate is small the filter may be ignited wet, but if the amount be large it is better to heat it until the greater part of the water has been driven off. Place the filter in a porcelain crucible and ignite gently to WO_3. Cool in a desiccator and weigh.

The filtrate and wash water are united and the whole evaporated to a small bulk. If the amount of tungsten and molybdenum taken has been large, cool and dilute to 250 cc. and use aliquot portions of 50 cc. To this solution add from 5–10 g. of 20 mesh zinc. The tin will come out as metal. Pour off the green solutions when the precipitation of the tin is complete (this takes about ten minutes), and wash the cake of tin several times with hot water. Unite the filtrate and wash water and heat to 60°. Pass through the reductor in the order named, 50 cc. dilute HCl,[1] the solution containing the molybdenum, 150 cc. 2.5% (vol. conc. HCl), and finally 150 cc. hot distilled water. These pass into the flask of the reductor, which has been previously charged with 20 cc. 10% ferric ammonium sulfate and 20 cc. of the "titrating solution." This solution is next titrated with approximately 0.1 N potassium permanganate and the amount required calculated to MoO_3.

If it is desired to determine the amount of tungsten in a sodium tungstate solution, add to that solution a quantity of sodium chloride solution, and proceed as when molybdenum is present.

A fairly accurate separation of tungsten and molybdenum may be effected when they are present as ammonium salts, but the method is not to be highly recommended.

UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, PA.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD COLLEGE.]

THE MOLECULAR WEIGHT OF SODIUM CARBONATE AND THE ATOMIC WEIGHT OF CARBON REFERRED TO SILVER AND BROMINE.

BY THEODORE W. RICHARDS AND CHARLES R. HOOVER.

Received November 19, 1914.

Investigations concerning radioactivity have increased rather than diminished the interest in atomic weights. The possibility indicated by recent research that variations in these figures may exist in radioactive elements[2] stimulates further research in all directions concerning these quantities; for such variations cannot be due to chance, but must have fundamental cause. To be sure, no valid evidence of variation in any value except that for lead has as yet been found; but whether or not the atomic weights vary in a few cases, they still probably remain the most fundamental figures which come within our scientific ken. Therefore, no amount of trouble is too great to secure complete and satisfactory knowledge of them.

---

[1] Containing 2.5% by volume of the strong acid.

[2] Richards and Lembert, THIS JOURNAL, **36**, 1329 (1914); also *Z. anorg. Chem.*, **88**, 429 (1914), and *Science* (June 5, 1914), p. 831. This conclusion has been supported also by Soddy (*Proc. Chem. Soc.*, **30**, 134 (1914)), by Maurice Curie (*Compt. rend.*, **158**, 1676 (1914)), and by Hönigschmid and Mlle. S. Horovitz (*Ibid.*, p. 1786); also *Z. Electrochem.*, **20**, 319 (1914).