

3. The most probable value (obtained by extrapolation to zero concentration of acetic acid) of the equilibrium constant (omitting the concentration of the water) for the reaction as written above is 950 ($= 1/10.5 \times 10^{-4}$); this corresponds to a velocity constant for the acetylation of 0.0089 liters per mol per hour.

In conclusion we wish to express our gratitude to Prof. H. C. Biddle for his many helpful suggestions.

BERKELEY, CALIFORNIA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA.]

THE ATOMIC WEIGHT OF ZIRCONIUM.

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Received June 8, 1917.

As the results of our work involve a considerable change in the atomic weight of zirconium, it is well to give a brief review of the previous determinations of this constant.

TABLE I.¹
Previous Determinations of the Atomic Weight of Zirconium.

	Date.	Chemist.	Ratio.	Number of analyses.	Atomic weight.
1.	1825	Berzelius ²	Zr(SO ₄) ₂ :ZrO ₂	6	89.46
2.	1881	Weibull ³	Zr(SO ₄) ₂ :ZrO ₂	7	89.54
3.	1889	Bailey ⁴	Zr(SO ₄) ₂ :ZrO ₂	8	90.65
4.	1881	Weibull ³	Zr(SeO ₄) ₂ :ZrO ₂	5	90.79
5.	1860	Marignac ⁵	K ₂ ZrF ₆ :K ₂ SO ₄	4	90.03
6.	1860	Marignac ⁵	K ₂ ZrF ₆ :ZrO ₂	4	91.54
7.	1898	Venable ⁶	ZrOCl ₂ .3H ₂ O:ZrO ₂	10	90.81
8.	1844	Hermann ⁷	ZrCl ₄ :?	1	88.64
9.	1844	Hermann ⁷	2ZrOCl ₂ .9H ₂ O:?	2	89.98

We believe that little dependence is to be placed upon any of these figures. In the first three, zirconium sulfate is used. It is now well known that this substance cannot be freed from water without losing some sulfur trioxide. In addition it is difficult to prepare pure, especially avoiding the products of hydrolysis.

The series of determinations in No. 7 was carried out by one of us in 1898 and at the time of publication several sources of error were pointed out and a promise given of further work on the subject. Circumstances have prevented the fulfillment of the promise until now. The most serious

¹ Clark, "Constants of Nature," p. 287 (1910).

² *Ann. Physik.*, [1] 4, 126 (1825).

³ *Lund. Arsschrift*, 18 (1881-2).

⁴ *Chem. News*, 60, 6, 17, 32 (1889).

⁵ *Ann. chim. phys.*, [3] 60, 270 (1860).

⁶ THIS JOURNAL, 20, 119 (1898).

⁷ *J. prakt. Chem.*, 31, 75 (1844).

objection was that the compound taken was a hydrate. Relying upon the statement of Linnemann¹ and the results of the first tentative analyses, the hydrate of zirconium oxychloride was supposed to be the tetrachloride. Somewhat singularly $ZrCl_4$ ($x + 141.8$) and $ZrOCl_2 \cdot 3H_2O$ ($x + 140.9$) give about the same percentage of ZrO_2 and the mistake was found out only when it came to the determination of chlorine.

One inherent source of error and a considerable one in all the above determinations lies in the loss of ZrO_2 on ignition. This oxide is so finely divided that it is swept off even on gentle ignition. Various means of remedying this have been tried, including the use of ammonium salts, but none of these methods suffice to prevent the loss. The loss of ZrO_2 would lower the atomic weight and hence it is not surprising that our results show a large increase over the International Committee's figure, 90.6, obtained from an arbitrary combination of the figures given in the above table.

It was decided that the most suitable compound for our purpose was zirconium tetrachloride and we wished, if possible, to determine both components. For reasons to be stated later it will be seen that we were only partially successful in this end and so only one of the methods will be given in detail at this time. The present paper will describe our experiments in determining the ratio $4Ag:ZrCl_4$.

Purification of Zirconium Chloride.

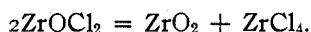
Through the kindness of the Welsbach Company, of Gloucester, N. J., we received a considerable quantity of wet zirconium hydroxide said to be freed from the rare earths. It gave no test for sulfates, which we wished to avoid, but contained appreciable amounts of iron and silica. As it had been prepared from North Carolina zircons, the other possible impurities were known from previous analysis and the same general methods of preliminary purification were followed as in the earlier work.

The hydroxide was dissolved in concentrated hydrochloric acid, the solution filtered and concentrated to crystallization of the oxychloride. It was then recrystallized from hot concentrated hydrochloric acid until potassium sulfocyanate failed to give any test for iron. Beyond this point the crystallization was carried out eight or ten times, making a total of forty or more crystallizations. These later crystallizations were done in quartz vessels. No absorption spectrum could be obtained and the flame spectrum showed only faint sodium lines. The crystals were then dissolved in the least possible amount of distilled water in quartz vessels and most of the silica filtered off. The oxychloride was recrystallized several times from water and allowed to dry over sodium hydroxide or sulfuric acid. As will be seen from the method of preparing the zirconium chloride, the purification was carried still further by means of fractional sublimation.

¹ *Monatsh.*, 6, 335 (1885).

In preparing zirconium chloride, two methods seemed open to us:

1. The dissociation of the oxychloride by heat,



2. The action of chlorine and carbon tetrachloride on ZrO_2 . The first method has been used by Chauvenet¹ and also by Lely and Hamburger;² and the dissociation was said to take place at about 600° . It was necessary to dehydrate the oxychloride under a stream of dry hydrochloric acid gas³ at about 200° . In spite of all precautions the yield obtained by us was less than 10% of the theoretical and so this method was abandoned. A few grams of the tetrachloride, however, were prepared in this way and two analyses by the nephelometer method were partially carried out. As the results of the incomplete analyses corresponded to an atomic weight of about 92, they were discontinued under the impression that the preparation was not suitable for analysis. Doubtless there was present a trace of finely divided ZrO_2 in the samples taken. It is interesting to note that Bailey⁴ in some preliminary work with the oxychloride obtained results which gave figures over 92 and which he also concluded were "undoubtedly too high." In passing we may mention that the dissociation takes place at a much lower temperature than that given by the authors cited. It was found to begin at $300-350^\circ$ and to be abundant at 420° .

The second method, namely, the action of a stream of chlorine loaded with CCl_4 vapor upon the heated oxide, was first given by Demarçay⁵ who, however, added few details as to apparatus, temperature, etc. Lothar Meyer and Wilkens⁶ reported in the same year that they found it impossible to prepare the tetrachloride by this method. Lely and Hamburger⁴ in the article already cited used the method and gave the reaction temperature as 800° , using on that account a porcelain tube enclosed in one of iron.

The difficulties in the use of materials other than glass were so great that we were deterred from attempting this method until convinced of the impracticability of the dissociation method. A preliminary trial, however, showed that the reaction in the Demarçay method began at a little over 300° and was quite rapid at $450-500^\circ$. Therefore ordinary glass could be used and the connections easily made, all glass parts being fused together.

The apparatus was constructed as follows: For the chlorine generator an ordinary Erlenmeyer flask was fitted with a separatory funnel whose

¹ *Compt. rend.*, 154, 1234 (1912).

² *Z. anorg. Chem.*, 87, 209 (1914).

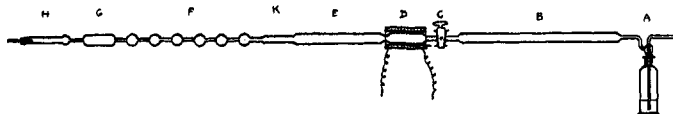
³ In regard to the preparation of HCl the best method is to drop the concentrated solution through a separatory funnel drawn to a fine opening and ending beneath the surface of concentrated H_2SO_4 . This is a reversal of the usual method.

⁴ *Loc. cit.*

⁵ *Compt. rend.*, 104, 1136 (1887).

⁶ *Ber.*, 20, 681 (1887).

tube was drawn out to a small opening, the end coming within one or two inches of the bottom. Concentrated hydrochloric acid could thus be dropped upon solid potassium permanganate and the stream of gas easily regulated. The reaction continued uniformly for many hours with little attention. The gas was passed through a CaCl_2 -tube and then bubbled through carefully purified and dried CCl_4 in a glass-stoppered wash-bottle (A). The tube from this was sealed to a P_2O_5 -tube (B) 50 cm. long and this to a T-tube (C) with a three-way glass cock. The T-tube was sealed to the generator in which ZrCl_4 was formed. For the generator a



Carius tube was drawn out and a 6 mm. tube sealed on for attachment to the three-way cock. About 5 inches of the Carius tube served as a generator (D); at this point it was constricted. Sixteen inches of the Carius tube (E) served for gathering the ZrCl_4 . A tube 8 mm. in diameter and 10 cm. long was attached to this as a dust trap (K) and to this the string of bulbs (F) was sealed on (usually six or eight bulbs). At the end of the bulbs a 50 cc. pipet bulb (G) was sealed for the waste and then a P_2O_5 -tube (H) was attached by rubber and was connected with the outlet for the escape of chlorine.

In charging the trap was first well packed with glass wool and then the constriction between the collecting chamber and generator was plugged with wool and the latter was nearly filled with ZrO_2 . It was plugged at the far end and sealed to the rest of the train. The whole was heated to $400\text{--}500^\circ$ for several hours under a current of dry air until no moisture was left. The remainder of the train was then sealed on and dried.

To get a good dust trap to hold back all solid particles, especially the finely divided ZrO_2 which at first gave us much trouble, we made use of glass wool. It may be stated that several samples of wool failed on account of the ease with which they splintered and allowed particles of glass to be swept on into the receiving bulbs. Quartz wool proved especially brittle.

The tubing for the bulbs had an internal diameter of 4 mm. and the bulbs were 3.8 cm. apart and had a diameter of about 3 cm. All connections were therefore of glass from the CCl_4 flask to the exit. The temperature maintained for the reaction was $450\text{--}500^\circ$ and the current of gas was passed through about as rapidly as the bubbles could be counted. The yield was about 1 g. per hour. The material collected in the gathering tube. When the amount was judged sufficient it was sublimed past the heated dust trap into the bulbs. Such ferric chloride as was present revealed itself by its red color and being more volatile was driven forward into the

waste bulb. If carefully carried out the process of sublimation from bulb to bulb effectually got rid of all the iron, leaving a brilliantly white crystalline mass of zirconium tetrachloride, the individual crystals being water-clear. Our experience would indicate that this sublimation method is the only reliable means of separating the last traces of iron. All of our most carefully prepared samples by the crystallization method showed traces of iron under the sublimation method. It is therefore quite probable that none of the compounds used in previous atomic weight determinations were of satisfactory purity. The presence of iron would lower the apparent atomic weight.

All parts of the apparatus were carefully dried before beginning a running. Before sublimation the 3-way stopcock was shifted and chlorine introduced through a separate drying train so as to cut off the P_2O_5 -tube which might continue to hold some of the CCl_4 . As a later precaution this branch of the T-tube was sealed off. In the preliminary series air was used for the subliming gas, but fearing possible action on the chloride, chlorine was used in the later series. Finally dry air at room temperature displaced the chlorine. After distributing the $ZrCl_4$ among the bulbs, each bulb was sealed separately, drawing one end to a fine capillary and later when cool the capillary was broken and sealed again immediately, so as to have the air in the bulbs at room temperature and pressure.

To test the possible action of chlorine upon the glass bulbs well-dried chlorine was passed through a bulb at room temperature for two days and then replaced by air. A little water was introduced and silver nitrate solution added, but no precipitate nor opalescence formed. In a later experiment, after the data in this paper had been completed, the same experiment was tried under conditions similar to actual working conditions. The bulb was heated an hour while dry chlorine was passed through. After displacing the chlorine by air, the tube was washed with water and silver nitrate solution added. An appreciable precipitate of silver chloride formed, showing that chlorine combines with the constituents of the glass. This, of course, is a serious source of error and some means of avoiding this source of contamination will be sought in further work. It is interesting to observe that the possible chlorides are sodium chloride and calcium chloride. The combining weight of sodium is 23 and of calcium is 20, as against zirconium, about 23.

Heating Apparatus.—The generating tube was heated electrically. A sleeve 15 cm. long and of internal diameter slightly greater than the external diameter of the generating tube was put over the tube before the bulbs were sealed to the train. The form on which the sleeve was made consisted of another piece of a Carius tube around which numerous sheets of paper were wrapped. When the sleeve had been made the paper could be burned out and the sleeve could be slipped from the glass form. About

20 feet of nichrome wire (No. 24) were wrapped around the form, asbestos cord serving to keep the wire in place. Cords were passed over and under the successive coils of wire, and about 6 such double cords were used at equal intervals around the sleeve. At this stage the arrangement resembled somewhat the weave of a basket. Then a paste was spread over the cords and coils, the paste being made by mixing with water the asbestos fibre which is used for insulating steam pipes. In order to give rigidity to the sleeve short heavy wires were laid longitudinally over the sleeve and these were wrapped with more asbestos cord in order to keep them in place. Then more asbestos paste was spread over the whole surface so as to conceal the cord and heavy wire stays. The whole system was dried in a hot-air current and finally an electric current was passed through the wire. After the sleeve had been thoroughly dried, the paper charred and it was possible to slip the sleeve from the tubing.

The temperature inside the sleeve was obtained by a preliminary calibration. A Carius tube similar to the one used as generator was placed in the sleeve and a nitrogen-filled thermometer reading to 550° was placed in the tube, so that the bulb of the thermometer was about opposite the center of the sleeve. Then by obtaining readings on the thermometer and on an ammeter in the electric circuit it was possible to prepare a table for the instrument whereby the temperature could be read from the ammeter reading. Of course, each sleeve having different radiation would have to be calibrated. Any desired temperature could be obtained by regulating a carbon compression rheostat in the circuit. The readings of the ammeter are of no value here as we used a 2-ampere scale instrument, with a shunt of unknown resistance, which cut down the ammeter reading to the range of the instrument. Sleeves made as described gave entire satisfaction.

Determination of Zirconium.

In determining an atomic weight it is manifestly important to make a complete analysis of the compound chosen and thus get as many ratios as possible and have the assurance as to the entire composition. The determination of zirconium, which gives the ratio hitherto chiefly relied upon, presents serious difficulty on account of the ease with which the finely divided zirconia is lost. Methods used by some who have preceded us in this work were tried but we were unable to prevent the loss. The addition of ammonium salts failed to prevent it. Indeed, one would naturally suppose that these salts on volatilizing would carry off still more zirconia.

The following method was devised which succeeded in avoiding loss of zirconia but failed on another account, namely, the lack of completion in driving off the chlorine. We hope to remedy this difficulty at some future time but we have concluded to report the present work independent

of this ratio. We report the details of the method, however, as it may prove useful to others engaged in similar work.

The bulb containing zirconium tetrachloride had both side tubes scratched with a file about 1 cm. from the bulb. After weighing the bulb, the ends of these tubes were cracked off by means of an electrically heated platinum wire. This could be done very cleanly without the loss of glass. It was carried out over a weighed platinum dish. All ends were carefully washed and the washings transferred to another platinum dish. The bulb was placed in the latter dish and the dish in a desiccator the bottom of which was covered with water. The hydrolysis went on slowly and after two or three days the material could be dissolved out of the bulb without the formation of clouds of hydrochloric acid, which might have entailed loss. The solution and washings contained in the platinum dish were evaporated on a water bath protected by an inverted funnel until the volume was reduced to 5 or 10 cc. It was then introduced into the weighing flask by means of a 2 cc. pipet.

The weighing flask was of quartz with two tubes bent at right angles but in line with one another and had a capacity of about 30 cc. The mouths of the tubes were ground inside and fitted with quartz stoppers. Several of these flasks were made to order. One was kept in the balance case as a counterpoise.

The flask containing the solution was suspended from a glass rod by platinum wires in an electric oven. The evaporation was carried out without visible ebullition at a temperature under 100°. The temperature could be gradually increased by lowering the flask into the oven. The oven was a box of asbestos board with a coil of nichrome wire in the bottom. Much of the water and hydrochloric acid was thus driven off. When nearing the end of the evaporation superheated steam was passed through the flask. For this purpose an ordinary 250 cc. distilling flask was used. An electrically heated nichrome coil introduced into the water caused internal boiling while the side tube surrounded by another heated coil of nichrome wire gave the needed additional heat. Oven and steam generator had each a carbon compression rheostat in the circuit to regulate the heating. There was no spitting or loss during this operation. As the mass approached dryness bubbles slowly formed and the vapors escaped. Finally a glistening mass was left. The temperature was raised to about 125° and the heating continued for some hours. Then by steps it was raised to 390–400° until the escaping steam showed little or no hydrochloric acid. Further heating under steam was then done over a Scimatco burner until three separate tests at intervals of a half hour showed no HCl. This test was made by letting the escaping steam condense for about a minute upon a small test tube containing cold water. The drops

were collected on a watch glass and silver nitrate solution added. The test is very delicate.

After this treatment the flask could be heated for hours over a blast lamp and brought to a fairly constant weight. The residue was hard and glistening as if vitrified. No test for chlorine was obtained when the powdered mass was boiled with water. On fusion with sodium hydroxide, prepared from metallic sodium, appreciable amounts of chlorine were found. Hence all results obtained by this method were too high. They are given here, however, because of their bearing on the other ratio.

Atomic weight from the ratio $ZrCl_4 : ZrO_2$, 92.07, 92.17, 92.30, 92.19, 92.04, 92.24, 92.21, 91.95. Average, 92.12.

Of course an average of these results would have no special meaning, but it is given for purposes of comparison.

Determination of the Ratio $4Ag : ZrCl_4$.

Purification of Materials.

Water.—All the water used in this work was the distilled water of the laboratory which was redistilled from dilute alkaline permanganate solution, the first and last portions of the distillate being rejected. The still was in a basement room in which there was little danger of chlorine or hydrochloric acid fumes. The still was entirely of glass, as small quantities of the components of the glass would cause no error in the precipitation of chlorine by silver. Further, every flask of water used in the work was tested by the delicate nephelometric test for chlorides.

Nitric Acid.—The ordinary concentrated nitric acid of the laboratory was found to contain appreciable quantities of chlorides. To prepare nitric acid free from chlorides, the acid was distilled from a glass flask into a glass condenser, all connections being of glass. Only the intermediate third of the distillate was used. This distillate was also tested for chlorine by the nephelometer and found to be free from chlorides.

Silver.—The silver used was from silver residues, which, after washing, were dissolved in concentrated ammonia water. After settling, the clear solution was drawn off and the silver chloride was precipitated by neutralizing the ammonia with hydrochloric acid. The precipitate was then washed several times by decantation and then on a Büchner funnel by suction. The silver chloride was reduced by an alkaline solution of milk sugar. The reduced silver was washed with water several times and then dissolved in nitric acid. Any unreduced silver chloride was removed by filtration. The clear silver nitrate solution was then evaporated to crystallization and large crystals obtained. These were dissolved in redistilled water and an electric current passed between platinum electrodes. The cathode became coated with large crystals of silver which were frequently removed by shaking the electrode over a tube of pure water. By taking only the loosely adhering crystals, there seemed to be no danger

of getting any of the silver contaminated with platinum from the electrodes.

The silver was then fused into globules in an atmosphere of electrolytic hydrogen. For this purpose a quartz tube was wrapped with about 8 feet of the nichrome wire alternately with asbestos cord. More asbestos cord was wrapped around this in order to reduce heat losses. A porcelain boat containing purified magnesia was used as a support for the grains of silver. The magnesia was made from ignited magnesium nitrate prepared from the ordinary nitrate by three or four recrystallizations. The beads of silver were then brushed vigorously with an assay brush and were etched with nitric acid in order to remove any adhering magnesia. After washing with redistilled water the beads were dried in a Carius tube at 500° and 2 mm. pressure. The beads were kept in a weighing bottle under an inverted beaker. In order to obtain any required amount of silver it was found advantageous to weigh each bead to the nearest milligram, and then any required weight could be obtained by trying various combinations of the individual weights. In this way it was not necessary to cut small pieces from the silver to make up the required weight.

Balance and Weights.—A Voland balance sensitive to 0.02 mg. was used for all the weighings, at least one hour elapsing between time of placing the object on the balance pans and the time of final balancing. The balance was mounted on a masonry pillar on the basement floor in an interior room, and was protected by a large glass pane above and by curtains around the sides. Between the glass pane and an electric bulb above it, there was a large crystallizing dish half filled with water in order to absorb the heat rays from the bulb.

The weights were platinum plated or of platinum, and were calibrated by the Bureau of Standards.

Density of Zirconium Chloride and Zirconium Oxide.

In order to introduce corrections for buoyancy, it was necessary to determine the specific gravity of zirconium chloride and of zirconium oxide (for the method already described).

The density of zirconium chloride was found from the following data:

Weight of pycnometer.	22.087
Weight of pycnometer and sample.	22.878
Weight of pycnometer sample and CCl_4 to fill.	38.303
Weight of pycnometer and CCl_4 to fill.	37.960

The density is found to be 2.803. Carbon tetrachloride could be used as the liquid, as it was found to have no action on zirconium chloride. No residue was left when 4 cc. of CCl_4 were evaporated after shaking with zirconium chloride.

A similar experiment with ZrO_2 gave as its density 5.49.

Determination of Chlorine.

The sealed bulb containing the sample of zirconium chloride prepared by the method described above, and a 50 cc. platinum dish were weighed, using another platinum dish and a similar glass bulb as counterpoises. The bulb was then placed in a 400 cc., wide-mouthed and glass-stoppered bottle with about 300 cc. of distilled water. With the ground-glass contact wet there is an excellent water seal. The bottle was then vigorously shaken so as to break the bulb. The contents of the bulb dissolved quickly and completely in the water and with larger samples there was an appreciable heating. After standing a half hour the solution and fragments of glass were separated by the following method: The solution was removed by a pipet which was discharged into a funnel provided with a filter paper having a small ash weight. The filtered solution was collected in a 2-liter measuring flask. The filter paper collected any minute fragments of glass that might be in suspension. The bottle and glass were washed six or eight times with water, each time removing as much of the water as possible. The larger pieces of glass were then placed in the platinum dish in which the bulb was weighed and the smaller pieces washed by numerous additions of water. The removal of glass from the bottle was hastened by the use of the index finger covered with the finger of a rubber glove. The washing was continued until no particles could be seen when the bottle containing a little water was held up to the light.

The glass in the platinum dish together with the filter paper containing glass fragments was dried in an oven at 100–110° for several hours. The paper was then held in a platinum wire and burned, allowing the ash and glass fragments to fall into the dish. The dish was heated over a burner for a few minutes until the paper was all ashed. The cooled dish was then placed on the balance pan and, after at least one hour, was weighed. It was then possible to obtain the weight of the sample, and from this the approximate equivalent weight of silver was calculated. In the calculation Zr was taken as 91.7, preliminary analyses having indicated that this was the approximate atomic weight. This calculated amount of silver to within 1 or 2 mg. was accurately weighed. The silver was then dissolved in nitric acid in a liter measuring flask with a long neck. For each g. of silver about 2 cc. of a solution of nitric acid were used, made by diluting the concentrated nitric acid with an equal volume of water. While the silver was dissolving the flask was inclined at an angle to the vertical of 30° and was partly stoppered. It was necessary to heat only very gently to cause the silver to dissolve and a few minutes' boiling removed the red nitrous fumes from the flask. This solution was then diluted to about 500 cc. and poured very slowly into the chloride solution diluted to about 1000 cc. During the mixing the precipitating flask was frequently shaken.

The silver nitrate was then washed from the flask by numerous washings. The precipitation was carried out in an interior room dimly lighted by one electric bulb. The precipitating flask was then set in a dark box for several days, before examining for an excess of silver or of chlorine. The method of balancing these constituents was that of Richards,¹ as was in great part the method described above. When one constituent was found deficient by the nephelometric method, a small quantity of it was added from a buret. One of the "correcting" solutions contained one mg. of silver per cc. as silver nitrate, and the other an equivalent amount of potassium chloride. After several "corrections" an exact balance was found and the analysis completed. For the final tests the solutions were cooled in ice so as to remove from solution as much as possible of the dissolved silver chloride, thereby making the comparison in the nephelometer more sensitive.

TABLE I.
(Cl = 35.458; Ag = 107.88.)

No.	Zirconium chloride.	Silver.	Ratio.	Atomic weight.
I 1	5.55372	10.26178	1.8477	91.71
I 3	3.78445	6.99198	1.8476	91.73
I 4	2.97546	5.49645	1.8473	91.77
II 1	7.22480	13.34222	1.8467	91.84
II 3	6.35532	11.73094	1.8459	91.95
II 4	6.78989	12.64259	1.8472	91.77
III 2	5.65352	10.44718	1.8481	91.68
IV 2	2.76975	5.11980	1.8485	91.62
IV 3	4.30337	7.95180	1.8478	91.70
IV 4	4.31934	7.98115	1.8478	91.70
IV 5	2.42721	4.48516	1.8479	91.69
IV 6	4.80724	8.87607	1.8464	91.88
IV 7	2.35598	4.35052	1.8466	91.85

Average, 91.76

In Table I there are given the results of all the completed analyses. The duplication of results even within any one series is not as close as we hoped to obtain. It is believed that the average of these results, 91.76, is not in error by more than 0.1 and that the present accepted value is over one unit too low. Also the values from the ratio $ZrCl_4 : ZrO_2$ run around 92.1, which is known to be high on account of the retention of chlorine by ZrO_2 . We therefore propose in this preliminary investigation the value, 91.76 ± 0.1 . Publication at this time is rendered necessary by the temporary interruption of the work, and we propose to endeavor later to remove some of the objections which we have pointed out.

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¹ THIS JOURNAL, 27, 459 (1905).