[Contributions to the Chemistry of Zirconium, No. 7]

A REVISION OF THE ATOMIC WEIGHT OF ZIRCONIUM.[1]

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Received January 6, 1898.

I. PURIFICATION OF THE MATERIAL.

PREPARATORY to entering upon the revision of the atomic weight of zirconium, a study was first made of the best method of decomposing zircons and securing pure preparations.[2] The pulverized zircons were fused in nickel crucibles with sodium hydroxide and sodium fluoride. The melt was washed, dissolved in hydrochloric acid and filtered from some of the silica and from undecomposed zircon. This filtrate was evaporated to dryness to render the silica insoluble, again dissolved in diluted hydrochloric acid and filtered, and this was repeated two or three times. The further purification consisted in precipitation by ammonium hydroxide, washing, and re-solution in hydrochloric acid, followed by repeated crystallizations from boiling concentrated hydrochloric acid. After it had been thus purified it was found that traces of silica were still present. To remove these, the chloride was dried, ignited, and the powdered zirconia was again and again treated with hydrofluoric acid. After driving this off the zirconia was again melted with potassium hydroxide (purified by alcohol), taken up with hydrochloric acid and subjected once more to crystallization from strong hydrochloric acid. These crystallizations varied in number from twenty to thirty odd, and if those which preceded the second fusion are to be taken into account, exceeded sixty in all. Just before using in the series of determinations of the atomic weight, this purified chloride was filtered by means of an unglazed porcelain suction filter which had been cleaned by boiling for several days in strong hydrochloric acid and then standing three days in fresh cold hydrochloric acid. The last acid was entirely free from color. This filter was kept under distilled water when not in use. The filtration had to be carried out with hot solutions, but the liquid was not in contact with the filter more than five or six minutes.

When this work was undertaken it was believed that the substance under examination was zirconium tetrachloride. This

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[1] Read at the Washington Meeting.

[2] *J. Anal. Appl. Chem.*, 5, 551-554.

belief was based on the work of Linnemann and upon my own determinations of the zirconia, these agreeing fairly well with the amount required for $ZrCl_4$. At the close of the determinations of zirconia recorded later, some determinations of the chlorine present were made and were found not to agree at all with the amount requisite for the supposed formula. The matter did not seem easy of explanation, and the work was laid aside until time could be gotten for a more thorough study of this body. My study of the oxychlorides of zirconium has shown that there are at least three:

$ZrOCl_2.3H_2O$ when crystallized from strong hydrochloric acid.

$ZrOCl_2.8H_2O$ when crystallized from water.

$ZrOCl_2.6H_2O$ when precipitated by hydrochloric acid from an aqueous solution.

All of these, dried in a stream of hydrogen chloride at 100°–125°, have the formula $ZrOCl_2.3H_2O$, and this water is lost only by heating from 180° to 210°.

The liquid filtered as above is clear and bright and soon begins to deposit groups of needle-like crystals, or it crystallizes to a solid mass if a large amount of the salt is present. In several cases the crystallization was repeated two or three times from acid after this filtration, but no perceptible difference was made in the results. These crystals take up a considerable amount of acid which cannot be drained off. In this acid they easily melt, and if the excess is removed under a stream of hydrochloric acid gas the chloride can be gotten in the form of a dry white powder. The oxychloride can be thus dried without decomposition under a stream of hydrochloric acid gas at the temperature of 100°–125° C. to $ZrOCl_2.3H_2O$. As the difficulty in drying this salt was the main stumbling block in the way of previous workers, interfering with its use for atomic-weight work, the removal of this obstacle seemed to place it among the most suitable of the compounds to be used for the purpose. A full account of the examination of the chlorides will be published shortly. Other compounds have been examined also in the progress of this work, and though they may be used hereafter, they have seemed to me to present more difficulties than the chloride, and so this has been taken first.

PREVIOUS DETERMINATIONS OF THE ATOMIC WEIGHT.

It is perhaps best to give here a brief outline of previous determinations of the atomic weight of zirconium. Six such series have come under my notice. In three of these the sulphate was used, and in the others the chloride and the double fluoride of zirconium and potassium were used, and in one the selenate.

The determinations of Hermann,[1] by means of the chloride, can be dismissed as untrustworthy, because of his failure to overcome the difficulties inherent in the use of the chloride as shown by Bailey's work and my own.

The work of Marignac upon the double fluoride I am not in a position to criticise properly, except in so far as to say that his analyses are not very numerous, and that they show a range of nearly three units in the atomic weight.

In 1825 Berzelius ignited the sulphate and gave six determinations of the ratio of the sulphate to the oxide. In some of the experiments he also precipitated the zirconium hydroxide by means of ammonium hydroxide and determined the sulphuric acid in the filtrate by precipitation with barium chloride.

Mats Weibull also used the sulphate and reports seven experiments with an entire consumption of 8.2335 grams. Bailey's own determinations number eight, using in all more than sixteen grams. He gives full data as to his work, and it is well done and merits very careful attention. The following table is copied from his article.[2] The figures have been recalculated to the basis of $O = 16$.

	Mean.	Maximum.	Minimum.	
$Zr : Cl$	88.77	....	....	Hermann
$ZrO_2 : HCl$	90.14	90.98	89.29	Hermann
$K_2ZrF_6 : K_2SO_4$	90.53	92.80	90.06	Marignac
$ZrO_2 : K_2SO_4$	90.64	91.26	90.24	Marignac
$K_2ZrF_6 : ZrO_2$	90.8	91.3	89.9	Marignac
$Zr(SO_4)_2 : ZrO_2$	89.45	92.65	89.27	Berzelius
$Zr(SO_4)_2 : ZrO_2$	89.48	90.38	89.13	Mats Weibull
$Zr(SO_4)_2 : ZrO_2$	90.65	90.78	90.46	Bailey

It is manifest that the determinations based upon the ignition of the sulphate are the only ones worthy of further attention. A

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[1] *J. prakt. Chem.*, 31, 77.

[2] *Chem. News*, 60, 17.

brief criticism of these is necessary. First, as to Mats Weibull, Bailey says that the temperature used by him in freeing the sulphate from the excess of sulphuric acid was some 50° too low. This would of course give him variable and low results. Berzelius does not give exact data as to temperature used, but he seems to have heated the sulphate too high in driving off the excess of acid. Possibly more stress is to be laid upon the question of the purity of his sulphate and the correctness of the assumption that he had in hand the normal sulphate.

Bailey concludes from his experiments that the sulphate is stable up to 400° C., and that the excess of sulphuric acid can be completely driven off by the use of a temperature between this and 350° C. He further states that a mixture of the salt and free acid, as prepared by him, when heated to this temperature until constant, yields the normal sulphate. It must be said that he gives no proofs of this beyond the amount of zirconia found in his atomic weight determinations.

Whilst certain criticisms of the work of Bailey have occurred to me, I will refrain from mentioning them until I have had opportunity to repeat his experiments and so make myself more familiar with the details of his method.

One criticism I can venture upon now, however. I doubt whether it is possible to ignite, without loss, zirconia along with ammonium carbonate, as was done by Berzelius and by Bailey to remove the "last two or three milligrams of sulphuric acid." I have not ventured to use this method in getting rid of the chlorine which is held just as tenaciously as the sulphuric acid, as I feel sure that it could not be done without loss. Bailey adopted extraordinary precautions to prevent this loss, but it seems to me that it is not the currents of the external atmosphere, as he maintains, which are to be most avoided, but the mass of escaping vapor of the ammonium salts. It is easily possible for him to have lost several milligrams of the finely-divided zirconia in his way, and as he states, each milligram was equivalent to a variation of 0.25 in the atomic weight.

THE WEIGHINGS.

In the following experiments the amounts of substance used varied from one to five grams. To avoid the disadvantage of a small error causing a large variation in the result, I would gladly have used larger amounts of the chloride, but many difficulties met me there. The purification of the zirconium chloride is slow and costly. It is best carried out in small portions of a few grams at a time. Some fifty grams have constituted the stock at my command. The drying of large portions and the subsequent ignition would be exceedingly tedious and time consuming, besides requiring such apparatus as could not be well afforded. Five or six grams have been about the largest amounts that could be well handled at one time. Even such an amount as that required from sixteen to twenty days for the completion of the experiment. It could not safely be hurried through in shorter time.

The weighings were carried out upon an excellently constructed Sartorius balance, intended for a load of 200 grams. The heaviest apparatus used weighed less than sixty grams. The weights were corrected by one which had been compared with the standard at Washington. All objects were weighed against a tare of as nearly the same size, form, and weight as possible, all of the flasks, crucibles, etc., being made in pairs. This partly avoided the necessity for a reduction of the weighings to a vacuum and corrections for moisture, pressure, etc. Such corrections would have had little meaning in comparison with the other inaccuracies of the process and manipulation, and could only serve to give a false appearance of excessive accuracy. The objects were left one-half hour in the balance-case before weighing, experiments having shown that this time was sufficient. Of course the adjustment of the balance was carefully watched, and the balance, which has been used very little, was put to no other use during the progress of these experiments.

METHOD OF WORK.

The purified chloride was introduced into a small glass flask having a capacity of 100 cc. This was provided with a glass stopper ground to fit, and also a second one with two tubes arranged for the passage of the hydrochloric acid gas. The arrangement of the tubes was similar to that in an ordinary ether wash-bottle, though both tubes outside were bent downwards and had little bulbs blown in them for catching moisture, etc. A Thörner bath was found to be very convenient for keeping these flasks at 100° C. The hydrochloric acid was prepared by allowing sulphuric acid to drop into a large flask containing the hydrochloric acid. The gas thus obtained in a regular stream, was passed through a wash-bottle containing sulphuric acid and then through towers filled with glass beads kept moist with concentrated sulphuric acid.

The drying took from fifty to one hundred hours (in some extreme cases). If the stream of gas was rapid the temperature could rise to 110° or even higher without decomposition of the chlorine. A much lower temperature caused this decomposition if the stream was insufficient to keep the flask full of gas. A number of experiments were carried out showing these facts. Indeed, two in the series of determinations were lost by the stream of gas becoming too slow or altogether ceasing for a short while. (Experiments VI and VIII.) It was thought from experiments at first that where this decomposition had begun it was impossible to secure a constant weight of the residue, but this is certainly not true where the decomposition has been only slight. Of course this introduces a chance for error in the method. The drying must be watched quite closely, and not more than eight or ten hours of drying could be easily managed in a day.

At first it was feared to remove the atmosphere preparatory to weighing, and efforts were made at weighing the flasks full of hydrogen chloride. These results were too low and varied among themselves, so that it was evidently impracticable to carry out the experiments in this way. It was found that the hydrochloric acid could be replaced by dry air. The flask was removed from the bath and dry, pure air passed through it for half an hour. It is of course essential that the air be carefully dried. The tubes are then removed and the glass stopper quickly fitted in its place. It is then ready for placing in the balance-case. The chloride is deliquescent and some trouble in weighing was experienced. If the stopper was well ground there was no appreciable change in the weight in from twenty to forty minutes after placing upon the balance. The loss of weight in the latter part of the drying was very slow. The weighings were taken at intervals of from six to eight hours' heating. The number of weighings necessary before constancy was secured served as a safeguard against error. A series of such weighings is given further on.

After drying, the chloride was dissolved in a small amount of water (redistilled) and this solution, with rinsings, transferred to a platinum crucible. It was evaporated to dryness upon a water-bath, with due precautions against dust, etc., was next heated gradually upon a sand-bath until most of the chlorine had been driven off, and was then slowly raised to the highest temperature attainable by the Bunsen burner. During this latter part of the operation the cover was kept on. Three or four days were thus consumed, the gradual heating giving a coherent flinty mass of glistening semi-translucency which could be safely heated by the water-blast without loss. During the driving off of the chlorine the platinum crucible was more or less attacked, but as this was before the lid was on, there was little chance of loss from this source. This corroded platinum was probably the reddish-brown decomposition product mentioned by Bailey as coming from the ignition of the oxychloride.

The last of the chlorine was driven off by heating with a water-blast for from forty-five to seventy hours. The last weighings were made at intervals of from six to twenty hours and were recorded as constant if they agreed within 0.00005 of a gram. A series of weighings is here given as an example. Experiment No. II, or the first one successfully carried out in the series, is taken for the purpose.

Weights of zirconium chloride:	March 28	5.25910
“ “ “ “	“ 29	5.25786
“ “ “ “	“ 30	5.25760
“ “ “ “	April 1	5.25762
Weights of zirconium oxide:	April 11	2.78759
“ “ “ “	“ 12	2.78724
“ “ “ “	“ 13	2.78583
“ “ “ “	“ 15	2.78517
“ “ “ “	“ 16	2.78452
“ “ “ “	“ 17	2.78451

This zirconia was examined for chlorine in most of the analyses and was found to be free from it. In the last three experiments reported in the series, the ignited residue was treated with hydrofluoric acid. Ignition after this treatment was very difficult, as the mass was not compact and coherent. The finely divided zirconia was lost in spite of the most careful treatment. The first was lost altogether and the weighing was not carried out. The second showed, upon the lid signs of the powdered zirconia having been swept out. The total loss of weight, however, was less than one milligram. This could readily be attributed to the zirconia and pointed to the absence of silica unless in insignificant traces.

I think great purity may be claimed for the preparations used in the analyses. Crystallizing from hot hydrochloric acid is apt to remove most known impurities, and they were eliminated beyond the possibility of detection by the ordinary tests. The analyses were not made from the same preparation, but from small quantities prepared at different times and some crystallized ten or a dozen times more than others, yet no appreciable difference could be detected in the results. That these results are not in close accord with one another, is due in part to the deliquescence of the chloride and to the risks involved in the prolonged heating of the oxide.

SOURCES OF ERROR.

Five main sources of error have occurred to me apart from any question as to the purity of the material.

1. The deliquescence of the chloride.
2. The loss of the finely divided zirconia.
3. The corrosion of the platinum crucibles.
4. The attack of the glass flasks by the gaseous and liquid hydrochloric acid. It is very evident that the glass vessels would suffer when subjected to the action of hydrochloric acid during such prolonged periods. The weighings easily revealed the extent of this action. It was found to vary with different flasks. For instance, flask I lost 0.00116, 0.00031, 0.00023, and 0.00078 gram. On the other hand, flask IV weighed after the first experiment only 0.00011 gram less, and after the next two experiments the loss was 0.00013, and the total loss during three experiments was 0.00024. This is probably transferred mainly as alkaline chlorides to the crucibles and is there volatilized. Sodium could readily be detected upon the lid of the crucible

after partial ignition. Of course if all is volatilized then no error is introduced into the experiment, but there may be some non-volatile material also transferred from the flasks. The total amount is so small that the error cannot be a large one.

5. Substances carried into the drying flasks by the stream of gas. Much care was taken to avoid error from this source. The main danger lay in the necessity for the use of some rubber connections. Vulcanized rubber was used. It was freed from excess of sulphur and was replaced by fresh pieces when attacked by the gas. The dry gas does not attack rubber very rapidly. Gaseous sulphur compounds, coming from the sulphuric acid, used in preparing and drying the hydrogen chloride, were probably carried through the drying flasks, but there seems to be no probability of their causing a decomposition of the oxychloride.

THE DETERMINATIONS.

All analyses which were completed under the proper conditions of the method, as already given, are here reported. Experiment III became contaminated from the iron support during the prolonged heating and came out consequently a little high, giving the ratio of ZrO_2 : $ZrOCl_2.3H_2O$ as 53.12. In most of the subsequent analyses the ignition was carried out with the crucible suspended in a platinum wire cage from a glass support. Experiments VI and VIII were dried with an insufficient stream of gas, as already stated, and hence were partially decomposed. They gave 53.57 and 53.8, respectively. The remaining analyses follow :

	$ZrOCl_2.3H_2O$.	ZrO_2.	Ratio.
II	5.25762	2.78450	52.961
IV	3.53994	1.87550	52.981
V	3.25036	1.72435	53.051
VII	1.52245	0.80708	53.012
IX	2.98802	1.58274	52.969
X	2.11371	1.11920	52.949
XI	2.38139	1.26161	52.978
XII	1.90285	1.00958	53.055
XIII	2.61847	1.38658	52.954
XIV	1.07347	0.56840	52.951
	26.64828	14.11953	52.986

Calculating these for the ratio $ZrOCl_2.3H_2O : ZrO_2$, taking $H = 1.008$, $O = 16$, and $Cl = 35.45$. we have the following:

Maximum ratio......	53.055	Atomic weight......	91.12
Mean "	52.986	" "	90.78
Minimum "	52.951	" "	90.61

The atomic weight as determined by Bailey is 90.65. The mean value given in Clarke's Recalculation is 90.40. I purpose repeating the determinations with the oxychloride, with such modifications as have occurred to me since the completion of the above work.

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THE SURFACE-TENSIONS OF AQUEOUS SOLUTIONS OF OXALIC, TARTARIC, AND CITRIC ACIDS.

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Received January 5, 1898.

IN the determination of the surface-tensions of the solutions of citric, oxalic, and tartaric acids, the apparatus described in a previous number of this Journal[1] was employed. The "apparatus constant" was ascertained directly before and after a series of determinations, Ramsay and Shields'[2] data for water being taken as the standard; the variation, when there was one, which seldom happened, affected only the decimal places after the second. At least five readings of the adjustment of the tubes were made for every solution, and their average taken. The specific gravity of the solutions were determined to one or two figures in the fourth decimal place and were referred to water at temperature of its maximum density.

The thermometer had been tested by the Physikalische Reichsanstalt, at Berlin, and found to be without appreciable error in the neighborhood of 20°.

The acids were the purest obtainable and were recrystallized once or twice.

The solutions were prepared by dissolving the solid acids so as to form almost saturated solutions, and then diluting this stock solution; their surface-tensions were measured very soon after they were made up, although it was found that that phys-

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[1] This Journal, 18, 514.

[2] *Ztschr. phys. Chem.*, 12, 471. Surface-tension for water at 15° was taken to be 71.27 dynes per cm.