AN EXAMINATION OF THE CHLORIDES OF ZIRCONIUM.

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A ZIRCONIUM chloride of definite composition would prove a valuable compound for determining the atomic weight of the element. There are several difficulties in the way of securing such a compound.

1. The tendency to form basic chlorides.
2. The ease with which hydrochloric acid is lost through the action of heat and of dehydrating agents.
3. The presence of free hydrochloric acid.
4. The deliquescent nature of the chlorides.

It is particularly desirable that the conditions under which a definite chloride can be formed should be discovered, as zirconium seems to yield no very satisfactory compounds for the determination of the atomic weight. There have been many efforts at finding out these exact conditions.

Most text-books state that anhydrous, pure zirconium tetrachloride can be prepared by passing dry chlorine over a mixture of charcoal and zirconia heated to a high temperature. Hermann used this sublimed zirconium chloride for the determination of the atomic weight. As Clarke says, however, little confidence can be placed in his results. Bailey[1] has recorded that even with great care to avoid the presence of moisture he was unable to prevent the formation of oxychlorides. He also says that in no case was it found possible to prepare the chloride free from iron and silica. The necessity for the presence of these in the materials used or in the resulting compounds is not very apparent. I have as yet had no opportunity of repeating his experiments.

The chlorides most commonly worked with, have been those formed by the solution of the hydroxide in hydrochloric acid, followed by precipitation or crystallization from concentrated hydrochloric acid.

Berzelius attempted to remove the excess of hydrochloric acid

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

by heating the salt to 60° C. but was not able to obtain a definite compound. Two analyses gave

ZrO_2	0.332	0.485
AgCl	0.661	1.096

The silver chloride should be about two and one-third times as much as the oxide.

Paykull dried the salt between filter paper and found the composition of the crystals to be $ZrOCl_2.8H_2O$, the amorphous form precipitated by hydrochloric acid being $2ZrOCl_2.13H_2O$.

Endemann has described basic or oxychlorides $Zr_3O_4Cl_4$, ZrOClOH, and $Zr_8O_8Cl_7(OH)_9$; Troost and Hautefeuille have described others, $Zr_2O_3Cl_2$ and Zr_2OCl_6. In fact water is so easily taken up and hydrochloric acid lost that a large number of such indefinite compounds might be prepared by slightly varying the conditions.

Nylander[1] made a series of attempts at dehydrating the chloride. He prepared the chloride by dissolving the hydroxide in hydrochloric acid and evaporating to crystallization. The salt formed white needles, easily soluble in water. They were washed with alcohol and for analyses I and II were pressed between filter paper; III and IV were dried over sulphuric acid. The results were as follows:

	I.	II.	III.	IV.
Zr	27.56	25.69	30.11	31.78
Cl	21.58	21.58	23.06	23.80
Loss (H_2O)	50.86	52.78	46.83	44.12

or calculated on a dry basis:

Zr	56.08	54.41	56.63	57.18
Cl	43.02	45.59	43.37	42.82

Again preparations were made as before. I was dried between filter paper, II over sulphuric acid, III was pressed between filter paper and then dried over sulphuric acid, IV was dried a long time over sulphuric acid. The analyses gave the following:

	I.	II.	III.	IV.
Zr	28.52	34.91	37.78	35.69
Cl	21.93	26.09	25.87	21.74
Loss	49.55	39.10	36.35	42.57

or calculated on a dry basis:

Zr	56.93	57.23	59.34	62.14
Cl	43.07	42.77	40.66	37.86

Lastly he allowed a solution of the chloride to evaporate over

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[1] Bidrag till kännedomen om Zirkonjord. Inaug. Diss. Lund, *1864*.

sulphuric acid washed the crystals obtained with alcohol and pressed them between filter paper. Analyses gave:

Zr	27.94	28.74
Cl	27.32	26.67
Loss	44.74	42.62

or calculated on a dry basis:

	Found			Theory.
Zr	50.56	50.04	Zr	38.50
Cl	49.44	49.96	Cl_4	61.50

The above results show that his preparations were indefinite oxychlorides or mixtures in varying proportions of zirconium tetrachloride and oxychloride.

Bailey repeatedly crystallized the chloride from hydrochloric acid, washed it with hydrochloric acid and then removed the free acid.

(1) By washing with a mixture of one part alcohol and ten parts of ether.

(2) By gently heating the salt.

(3) By exposing the finely divided salt at ordinary temperatures in a vacuous desiccator over potash until no hydrochloric acid appeared when air was passed over it.

The analysis was performed by dissolving the salt in water and precipitating the zirconia with ammonia, then acidulating with nitric acid and precipitating the chlorine by means of silver nitrate. By method (2) a constant and progressive diminution of chlorine was observed. Therefore no analyses were made. For the other methods he gives the results of the analyses by a statement of the relation of ZrO_2 to AgCl.

	ZrO_2	:	AgCl
Berzelius determination	1	:	1.991
" "	1	:	2.260
Bailey's method 1	1	:	2.206
" " "	1	:	2.179
" " "	1	:	2.226
" " "	1	:	2.260
" " 2	1	:	2.264
" " " without washing	1	:	2.245
" " "	1	:	2.309
" " "	1	:	2.285
$ZrOCl_2$	1	:	2.350

These preparations are evidently mixtures also.

Hermann[1] states that the hydrated chloride, gotten in crystals on evaporating its aqueous solution, becomes opaque at 50° C., giving off part of the water and half of the hydrochloric acid and leaving a basic chloride or oxychloride, $ZrCl_4.ZrO_2.18H_2O$ or $ZrOCl_2.9H_2O$. The same compound is obtained in stellate groups of white silky prisms on evaporating a solution of the chloride. These crystals when heated become white and turbid and are converted into the anhydrous dioxychloride, $ZrCl_4.2ZrO_2$.

The conditions here are inexact and though Hermann may have obtained these compounds he would doubtless find it difficult to prepare them again. While it is perfectly true that an oxychloride is formed on the evaporation of an aqueous solution of the chloride, I have been unable to obtain the compounds he mentions. Linnemann[2] maintains that crystallization from hydrochloric acid (sp. gr. 1.17) and treatment with alcohol and ether gives a fine, crystalline, snow white, silky body, leaving fifty per cent. of its weight on ignition and therefore very nearly pure $ZrCl_4$ which should leave 52.5 per cent. He claims that this is "chiefly a neutral, not a basic compound.

My own experiments on the dehydration of this salt have extended over the past two years, as opportunity was afforded. Several series of experiments were undertaken, some along the lines attempted by others, and others by methods not tried before. In all the purified chloride obtained by repeated crystallization from hydrochloric acid was used, the salt being still wet with the excess of the acid. There was no attempt at drying this between filter paper. The method of preparing this salt has been fully described in a previous paper in the *Journal of Analytical and Applied Chemistry*, **5**, 551.

In the first experiment this chloride was washed once with water and then put in a desiccator and dried over calcium chloride (porous desiccated). It remained in the desiccator about seven months. Even after this lapse of time it still continued to show a slight loss in weight. It yielded on analysis 48.84 per cent. ZrO_2.

Another portion was placed in a jar over solid lumps of sodium hydroxide. After six weeks the loss was very slight. Careful

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[1] Watts' Dict., 5, 1080.

[2] *Chem. News.*, 52, 224.

ignition left a residue of ZrO_2 equivalent to 42.99 per cent. of the original weight. There was found to be 24.44 per cent. of chlorine present.

Again a portion was placed over calcium chloride and dry air was drawn over it at the rate of about fifty liters in the twenty-four hours for six months. After the first two months it was examined weekly by the interposition of a flask containing silver nitrate to see whether hydrochloric acid was still coming off. Even after the lapse of so long a time as this it was found that the loss of hydrochloric acid continued, although it was slight. On analysis this gave ZrO_2 42.28 per cent., and Cl 24.35 per cent. Although the results in this and the experiment immediately preceding correspond fairly well, they are unsatisfactory as they point either to a mixture of chlorides or an oxychloride of very complicated formula and hence unsuited for the ultimate aim of the research.

Lastly a portion was placed over concentrated sulphuric acid and the atmosphere above it exhausted occasionally. This was kept up during two months of summer weather. The loss in the last fifteen days was about 0.02 per cent. of the whole. The mass was powdery with a slightly discolored crust. It was all soluble in water, however, and yielded a clear colorless solution. It contained 53.30 per cent. of ZrO_2. This corresponds very nearly to the formula $ZrCl_4$, and is altogether at variance with the results obtained by Nylander and with the assertion made by Hermann that half of the hydrochloric acid was lost over sulphuric acid.

This last experiment showed the possibility of securing pure zirconium chloride, provided the excess of hydrochloric acid could be removed. It was thought that this might be done by heating in an atmosphere of hydrochloric acid. A weighed flask was so arranged that it could be kept at a definite temperature while a stream of dry hydrogen chloride was passing through it. The temperature ranged from 100° to 110° C., and the chloride placed in the flask melted, solidifying again after the loss of the water and excess of hydrochloric acid. If the drying was done slowly enough, fine crystals of zirconium chloride were gotten which lost no further weight on being kept at 100° C. A more rapid drying left a hard white mass which was quite hygroscopic. Heating this mass for several days did not cause any diminution in weight, provided the flask was kept full of hydrogen chloride. If the mass was heated even a short time in the absence of hydrogen chloride then further heating caused a continuous loss of weight even in the presence of a rapid stream of hydrogen chloride. After this it was impossible to secure a constant weight.

This method of drying has been tried repeatedly on various preparations and I regard the facts stated above as showing conclusively that a neutral zirconium chloride can be prepared and dried.

Analyses of this chloride gave the following percentages of ZrO_2:

52.70 52.78 52.63

Experiments have already been begun with a view of utilizing this body in a series of experiments looking to a revision of the atomic weight of zirconium.

In connection with this subject it may be well to mention some improvements in the method of purifying zirconium chloride. (See *Journal of Analytical and Applied Chemistry*, **5**, 551.)

In the first place the separation from silica by evaporation to dryness is not complete. It is impossible to heat this chloride to the necessary temperature without such a decomposition as will render the zirconium chloride also insoluble. It is best then to make this separation as thorough as possible by heating, then to change the chloride into oxide by ignition and to treat this several times with hydrofluoric acid until the trace of silica is all driven off. This silica is too small in amount to interfere with ordinary uses but would have to be removed where perfect purity was demanded.

Again where the hydroxide is dissolved in dilute hydrochloric acid, or contained so much water that the acid was greatly diluted by it, it will be found that more or less of a white insoluble powder will form on evaporating, as recommended on a water-bath, and on subsequent treatment with boiling strong hydrochloric acid. By a careful arrangement of glass wool in a hot-water funnel the dissolved chloride can be filtered away from this insoluble mass. It seems to be quite insoluble in hydrochloric acid though easily dissolved by water. Analysis shows that this mass is $ZrOCl_2$ and with it was found, as an impurity, whatever silica the separation by heating failed to remove.

Lastly, my assistant, Mr. Baskerville, has shown that much time and hydrochloric acid will be saved if, in the solutions containing much iron, the zirconium hydroxide be first precipitated out by means of sulphur dioxide. This precipitate can then be dissolved in acid and purified by crystallization as already recommended.

Of course it need scarcely be mentioned that if silica has been removed by ignition and treatment with hydrofluoric acid, it will be necessary to fuse once more with caustic alkali and repeat the ordinary purification.

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SEPARATION OF ZIRCONIUM BY MEANS OF SULPHUROUS ACID.

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WHILE testing the accuracy of the various methods recommended for the estimation of zirconium I was led, because of the analogy of the elements, to try a method commonly used with titanium; *viz.*, prolonged boiling of a potassium bisulphate fusion in dilute solution with sulphurous acid in excess. On application of this method, however, on a solution of zirconium sulphate (prepared by dissolving the hydroxide in sulphuric acid), I failed even after boiling four hours with an excess of sulphur dioxide to obtain a precipitate, if the solution was acid. If the solution was nearly neutralized with ammonium hydroxide and then boiled with an excess of sulphur dioxide, after being greatly diluted, a precipitate was produced. This precipitation, however, was incomplete, even after boiling six hours or passing steam through the same for two or three hours. The precipitate too was very finely divided, running through all filter papers at my command. Therefore this method could not be used.

But an addition of sulphurous acid to a solution of zirconium chloride, even in a cold acid solution, a dense white precipitate was immediately noted. On boiling with an excess of sulphurous