leucosin to 0.43 per cent.; there thus remains 1.76 per cent. to be divided between edestin and proteoses.

Insoluble in salt solution	2.44 per cent.
Gliadin, soluble in alcohol	4.00 "
Leucosin, soluble in water	0.43 "
Edestin and Proteose, soluble in salt solution	1.76 "
	8.63 "

ZIRCONIUM SULPHITE.

BY F. P. VENABLE AND CHARLES BASKERVILLE.

Received March 30, 1895.

VERY little is recorded in the text-books on chemistry with regard to this compound of zirconium. Berthier is reported as having examined it and found it to be a white insoluble body, slightly soluble, however, in an aqueous solution of sulphurous acid, from which it is thrown down again upon boiling. Whether this was what is commonly known as the neutral, or the acid, or a basic sulphite, is not recorded. It is highly probable that with so weak an acid as sulphurous acid, zirconium would form under these circumstances only basic compounds. We may state with regard to our own work that we have been unable with one exception to form any sulphite corresponding to the acid or the neutral. Only very indefinite compounds or mixtures of the sulphite with the hydroxide have come into our hands, as a rule.

The subject was first brought to our attention by the study of the reaction utilized by Baskerville for the quantitative separation of zirconium from iron and aluminum.[1] It was also put into use by him for shortening the method of preparing the pure zirconium chlorides.[2] The reaction in question is that which takes place when a nearly neutral solution of zirconium chloride is boiled with sulphur dioxide in excess.

Several points of interest were observed as to this reaction. It was found that when a solution of the sulphate was used it was difficult to secure any precipitation by means of sulphur dioxide even with persistent boiling. The chloride was clearly

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[1] THIS JOURNAL, 16, 475.

[2] J. Elisha Mitchell, Scientific Society, 11, 85.

the best salt to use. The pure chloride was made up into approximately a two and a half per cent. solution and this was either very nearly neutralized by means of ammonia, or ammonia was added until there was a slight permanent precipitate. In the latter case the saturation of this solution with sulphur dioxide produced an immediate precipitate. If this were permitted to stand for some time the precipitate was redissolved, the remaining liquid being only slightly clouded. This re-solution was probably due to the hydrochloric acid liberated and also to the excess of sulphurous acid present. If this solution of zirconium chloride saturated with sulphur dioxide were diluted with several times its volume of water and boiled from fifteen to thirty minutes, a heavy white precipitate was produced. This was quite easily filtered by means of an unglazed porcelain suction filter. The precipitate was washed several times and finally dried over sulphuric acid in a desiccator. The analysis gave:

Zirconium dioxide...........	61.10	61.75	61.75	61.00	....	....
Sulphur dioxide............	....	....	....	....	22.24	22.20

Ratio of zirconium to sulphur dioxide is 2 : 1, approximately.

Ratio of zirconium to sulphur dioxide in the neutral sulphite, $Zr(SO_3)_2$, is 1 : 1.4.

This substance when so dried was perfectly white and quite hard. It was powdered with some difficulty in an agate mortar and resembled very much finely divided silica.

It was sometimes noted that the precipitate formed on passing the sulphur dioxide into the solution of zirconium chloride was partially dissolved upon the prolonged passage of the gas. To determine in how far the liberated hydrochloric acid was the agent causing this re-solution, some zirconium hydroxide, freshly precipitated by means of ammonium hydroxide, was washed free from hydrochloric acid and was then treated with a concentrated and freshly prepared solution of sulphur dioxide. This was allowed to stand during two or three months and was frequently shaken. The solid at the bottom of the flask separated into two layers, the gelatinous hydroxide settling first and upon this a white finely divided substance formed. The supernatant liquid was found to contain zirconium. The white layer was separated from the hydroxide and analyzed. It contained:

Zirconium dioxide	15.05	15.53	....
Sulphur dioxide	....	....	4.86
Water (blast-lamp)	2.78	3.03	....
Water, at 95° C	77.41	76.33	...
	100.10	99.75	

Ratio of zirconium to sulphur dioxide is 2.2 : 1.

This substance apparently came to a constant weight on drying in a steam-bath at 95° C.

A somewhat peculiar product was obtained during an attempt at filtering the precipitated sulphite. It filtered very slowly and in the course of a few hours a layer of a watery liquid formed above the white sulphite. This was allowed to stand several days and turned into a solid jelly. This was noticed several times. The thickness of the jelly-like layer would, of course, depend upon the amount of moisture in the precipitate but several times it was half an inch or more in thickness. This body was analyzed in the moist condition after simply drying between filter-paper. It gave :

Zirconium dioxide	20.02	20.65	....	....
Sulphur dioxide	....	....	5.19	5.51
Water (blast-lamp)	9.14	8.53	....	....
Water, at 95° C.	65.65	65.22	....	....
	100.00	99.91		

Ratio of zirconium and sulphur dioxide is here 3 : 1.

A portion of this jelly was brought to constant weight by heating for a number of hours in a steam-bath. About sixty-five per cent. of the original weight was lost and the body assumed a translucent appearance like dried gelatine. The analysis of this gave :

Zirconium dioxide	59.34	....
Sulphur dioxide	....	11.46
Water (blast-lamp)	29.20	...
	100.00	

Ratio of zirconium to sulphur dioxide is 4 : 1.

The analysis shows that some of the sulphur dioxide was lost on drying.

It will be seen then that these different preparations show a very varying ratio of the zirconium to the sulphur dioxide and in no case approach to the ratio of the neutral sulphite (1 : 1.4). They are, therefore, to be looked upon as either mixtures of the sulphite and hydroxide or very unstable compounds. The jelly-like substance mentioned last gives more promise of being a chemical individual; still it has not been thought legitimate to attempt the calculation or assignment of a formula to it.

A last attempt at preparing the neutral sulphite was made by placing some of the excess of sulphurous acid, which had been standing over the precipitated zirconium sulphite, in a dessiccator and allowing it to evaporate over sulphuric acid. The bulk of liquid decreased from about 200 cc. to five to ten cc. and then hard, white, warty crystals began to form, which were quite difficult to remove from the crystallizing dish. In appearance they resembled zirconium sulphate. The solution had lost the odor of sulphur dioxide. The time consumed in the evaporation was several months.

The crystals were dried upon filter-paper and yielded, on analysis,

Zirconium......24.47 per cent.: on a dry basis, 36.43.
Sulphur dioxide 34.54 “ “ “ “ “ 51.42.

Calculated for $Zr(SO_3)_2$, Zr 36.25; SO_2 51.20. These crystals then seem to be a hydrated sulphite of the composition $Zr(SO_3)_2.7H_2O$.

The nature of the precipitate gotten by means of sodium sulphite was also examined. The sulphite used was fairly pure. The zirconium chloride solution was distinctly acid and the mixed solution was acid. A transient precipitate was produced in the cold on mixing the two. On heating, a good flocculent precipitate was formed which settled well and was easily filtered. The precipitate looked like the hydroxide, rather than the white sulphite already described. The analysis gave:

Zirconium dioxide........	5.75	5.75	....	....
Sulphur dioxide..........	....	....	1.05	1.004

Ratio of zirconium and sulphur dioxide is 4:1.

Chancel[1], in giving a method of separation of iron from zirconium, states that by means of a boiling solution of sodium thio-

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[1] *Ann. d. Chem. u. Pharm.*, 108, 237; Watt's Dictionary, 5, 1081, *1877*.

sulphate the zirconium is precipitated as thiosulphate. Stromeyer[1] stated that if a dilute zirconium chloride solution be neutralized by sodium carbonate in the cold and sodium thiosulphate added until the solution was decolorized and then boiled as long as sulphur dioxide came off, the zirconium would be precipitated as oxide (meaning doubtless hydroxide).

To test these observations a solution of zirconium chloride was neutralized by ammonia and an excess of sodium thiosulphate was added in crystals. A precipitate began to be formed directly. This was washed eight or ten times by decantation, filtered, the precipitate dried by absorption paper, and analyzed. It gave:

Zirconium dioxide	19.66	20.50	....	....
Sulphur dioxide	....	....	4.03	4.14
Water (blast-lamp)	16.05	16.41	....	....
Water, at 95° C	60.11	58.58	....	....
	99.85	99.61		

Percentage of zirconium on a water-free basis is 75.
Percentage of zirconium calculated in $Zr(S_2O_3)_2$ is 21.95.

A second experiment was carried out with an acid solution of zirconium chloride. The sodium thiosulphate crystals were added in the cold and when completely dissolved the solution was heated to boiling. This precipitate on analysis gave:

Zirconium dioxide	21.74	20.73	....	....
Sulphur dioxide	....	....	5.33	5.41
Water (blast-lamp)	9.72	8.64	....	....
Water, at 95° C	63.28	65.37	....	....
	100.07	100.15		

Finally another portion was taken, precipitated with an excess of sodium thiosulphate, and boiled until there was no longer any odor of sulphur dioxide. This precipitate was analyzed:

Zirconium dioxide	47.01	47.19	....	....
Sulphur dioxide	....	....	6.90	6.95
Water (blast-lamp)	21.41	21.14	....	....
Water, at 95° C	24.16	24.72	....	....
	99.48	100.01		

The low percentage of water here was due to the exposure of

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[1] *Ibid*, 113, 127.

the precipitate in a warm room and its consequent partial drying. There is no evidence here nor in the previous cases of the formation of any definite thiosulphate and we would question its existence under ordinary conditions. There is no evidence of the formation here of an hydroxide as one of the authors quoted states. Basic salts seem to be the only products.

UNIVERSITY OF NORTH CAROLINA,
March, 1895.

ON SOME CONDITIONS AFFECTING THE ACCURACY OF THE DETERMINATION OF POTASH AS POTASSIUM PLATINICHLORIDE.

BY A. L. WINTON, Connecticut Agricultural Experiment Station.

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IN the course of some determinations of potash in potassium chloride, made by direct evaporation with platinum solution preliminary to a further study of methods, it was observed that the potassium platinichloride was more finely divided and the results were higher when the solution of the potash salt was concentrated on adding the reagent, than when it was dilute.

In order to ascertain the real connections of the facts observed, I then made a series of experiments which were all conducted in exactly the same way, except for the kind of dish used, the dilution of the solution of potassium chloride on adding the platinum solution, the presence or not of added hydrochloric acid, the temperature of the water-bath, and the strength of alcohol used for washing.

The potassium chloride used was from a lot sent by Dr. H. J. Wheeler, Reporter on Potash, for the Association of Official Agricultural Chemists. After being finely ground, it contained 0.45 per cent. of moisture, which was determined by heating below a red heat over a lamp until constant weight was secured. In each case, approximately one-half gram was weighed out from a weighing bottle. After solution in water and adding platinum solution, the mixture was evaporated to a pasty condition, and about twenty-five cc. of alcohol were added and allowed to stand on the potassium platinichloride for one hour with repeated stirring. The precipitates were then collected in