

above; but Mallet made no investigation into the constitution of the compound which he prepared in this manner.

A nitride of thorium has been prepared by Chydenius¹ by a procedure identical with that used in the preparation of the first zirconium nitride above described. This nitride of thorium is spoken of as a white amorphous powder, and behaves in a manner very similar to the zirconium compound. Thus the analogy existing between these two elements is once more strikingly manifested.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 35.]

IV. ON THE SEPARATION OF IRON FROM ZIRCONIUM AND CERTAIN OTHER ALLIED METALS.

BY J. MERRITT MATTHEWS.

Received September 2, 1898.

THOUGH there have been several methods proposed in the past for the separation of iron from zirconium, still chemists have not considered that this problem has, as yet, been satisfactorily solved. All methods which have been recommended for the quantitative separation of these two metals have proved, in some particular, to be untrustworthy, for in all of them traces of iron appear to remain with the zirconium with great pertinacity.

As it may be of interest in connection with the present subject, a brief résumé will here be given of the principal methods which have hitherto been proposed for the separation of iron from zirconium.

Bailey,² by the use of a moderately concentrated solution of hydrogen peroxide precipitates Zr_2O_3 , whereas neither iron, aluminum, nor titanium salts are precipitated by this reagent. No accurate results, however, have been worked out by this method.

Berlin³ observes that if zirconium dioxide, contaminated with iron, is fused with sodium carbonate to a white heat, and the fusion treated with hydrochloric acid, the iron salt dissolves,

¹ *Jsb. Chem.*, 1863, 194.

² *J. Chem. Soc.*, 49, 481.

³ *J. prakt. Chem.*, 58, 147.

leaving the zirconium dioxide undissolved. Scheerer¹ claims that by this fusion a sodium zirconate is formed at first, which is subsequently decomposed on washing with water. Some of the zirconium, however, will go into the solution with the iron; and on the other hand, the zirconium dioxide will still be slightly contaminated with traces of ferric oxide.

Stromeyer² applies Chancel's method³ for the separation of iron from aluminum to its separation from zirconium. By boiling with sodium thiosulphate, zirconium hydroxide is precipitated, while the iron remains in solution. Hermann,⁴ however, says that this procedure results in the formation of a zirconium hyposulphite; and traces of iron still continue with the zirconium. For an approximate separation, however, this seems to be a good one.

Rivot⁵ recommends the reduction of the iron to the metallic condition, by heating in a current of hydrogen. But it is very doubtful if all of the iron will be eliminated from the zirconium dioxide by this means.

Berthier⁶ uses ammonium hydroxide and sulphide, which precipitates ferrous sulphide, FeS , and zirconium hydroxide, $\text{Zr}(\text{OH})_4$; when this mixture is treated with sulphurous acid, the ferrous sulphide dissolves; the filtrate may contain some zirconium salt which, on heating, is precipitated from the iron as hydroxide. Hermann claims that this method does not give zirconium dioxide free from iron. Henneberg⁷ obtains a zirconium dioxide pure, except in that portion which is precipitated on heating.

Hermann claims to have obtained very pure zirconium dioxide by treating a solution of the chloride with a corresponding amount of ammonium oxalate, and igniting the precipitate. But in this method the amount of zirconium must be known beforehand, in order to calculate the quantity of ammonium oxalate to be added, as any excess of the latter reagent will dissolve the precipitate.

¹ *Pogg. Ann.*, 59, 48.

² *Ann. Chem. Pharm.*, 113, 127.

³ *J. prakt. Chem.*, 74, 471.

⁴ *Ibid.*, 97, 340.

⁵ *Ann. chim. phys.*, 17, 244.

⁶ *Ibid.*, 50, 362.

⁷ *J. prakt. Chem.*, 38, 508.

Dubois and Silveria observe that if impure zirconium hydroxide is boiled with oxalic acid, the iron oxalate formed is easily soluble, whereas the zirconium oxalate is insoluble. But Berlin¹ found that the zirconium oxalate is somewhat soluble in oxalic acid, which fact vitiates this method.

Classen² gives an electrolytic separation of iron from zirconium; but by his method the zirconium is only determined by difference.

Another method which has been recommended is to boil the impure zirconium salt with a solution of potassium sulphate, when a basic sulphate of zirconium will be precipitated. The precipitation, however, is never complete, as the filtrate always contains some of the zirconium.

It will be seen by this short review that the separation of iron from zirconium is by no means a positive certainty, as there seems to be a great many conflicting opinions entertained by the different authorities.

DETAILS OF THE METHOD FOR THE SEPARATION OF IRON FROM ZIRCONIUM.

On introducing a small quantity of water into an ethereal solution of zirconium tetrachloride, it was noticed that a white precipitate was formed, insoluble in excess of ether. This precipitate was no doubt an oxychloride of zirconium, and analyzed in accordance with the well-known hydrated chloride, $ZrOCl_2 \cdot 8H_2O$.

I. 0.1682 gram material gave :

0.1492 gram silver chloride = 21.93 per cent. chlorine.

0.0645 gram zirconium dioxide = 28.34 per cent. zirconium.

II. 0.1276 gram material gave :

0.1181 gram silver chloride = 21.86 per cent. chlorine.

0.0488 gram zirconium dioxide = 28.26 per cent. zirconium.

	Calculated for $ZrOCl_2 \cdot 8H_2O$.	Found.	
		I.	II.
Chlorine.....	22.05	21.93	21.86
Zirconium.....	28.18	28.34	28.26

On testing this precipitate with a solution of potassium thiocyanate, not a trace of iron was indicated, although the zir-

¹ *J. prakt. Chem.*, 58, 145.

² *Ber. d. chem. Ges.*, 14, 2783.

conium tetrachloride used in the solution showed a decided contamination by iron under the same conditions.

With this sharp distinction in solubilities of the hydrated salts of zirconium and iron in ether as a basis, a simple and accurate separation of these two elements was immediately suggested.

Weighed quantities of the chlorides of zirconium and iron were mixed together. Previous analyses of these salts were made in order to determine their respective percentages of zirconium and iron. The mixed salts were dissolved in water and carefully evaporated to dryness on a water-bath; after cooling they were treated with absolute ether, and dry hydrochloric acid gas was passed through the liquid. Experience proved that this latter treatment was necessary to effect a rapid and complete solution of the iron salt by the ether, as the ferric chloride on evaporation to dryness evidently forms basic compounds of indefinite composition which are difficultly soluble in ether. The solution was rapidly filtered, and the residue washed with absolute ether several times to insure the removal of the last traces of the iron salt. The residue was then dissolved in water, and the zirconium determined by precipitation as hydroxide by means of ammonium hydroxide; drying the precipitate, igniting and weighing as zirconium dioxide, ZrO_2 . The ether was evaporated or distilled from the filtrate, and the residue dissolved in water, with the addition of a few drops of hydrochloric acid if necessary; and the iron was determined by precipitation with ammonium hydroxide, drying the precipitate, igniting, and weighing as ferric oxide, Fe_2O_3 .

On testing the aqueous solution of the residue containing the zirconium with potassium thiocyanate solution, not a trace of iron was discovered, showing that the separation had been a complete and successful one.

Several analyses were made, using varying relative amounts of the zirconium and iron salts.

I. 0.1824 gram ferric chloride with 0.1262 gram zirconium tetrachloride gave:

0.0540 gram ferric oxide = 29.50 per cent. ferric oxide.

0.0615 gram zirconium dioxide = 48.89 per cent. zirconium dioxide.

II. 0.1763 gram ferric chloride with 0.1890 gram zirconium tetrachloride gave :

0.0524 gram ferric oxide = 29.55 per cent. ferric oxide.

0.0920 gram zirconium dioxide = 48.83 per cent. zirconium dioxide.

III. 0.3064 gram ferric chloride with 0.1620 gram zirconium tetrachloride gave :

0.0910 gram ferric oxide = 29.60 per cent. ferric oxide.

0.0788 gram zirconium dioxide = 48.79 per cent. zirconium dioxide.

IV. 0.6564 gram ferric chloride with 0.2544 gram zirconium tetrachloride gave :

0.1931 gram ferric oxide = 29.36 per cent. ferric oxide.

0.1240 gram zirconium dioxide = 48.78 per cent. zirconium dioxide.

V. 0.1276 gram ferric chloride with 0.6924 gram zirconium tetrachloride gave :

0.0390 gram ferric oxide = 29.70 per cent. ferric oxide.

0.3385 gram zirconium dioxide = 49.04 per cent. zirconium dioxide.

On analyzing the ferric chloride used it gave 29.44 per cent. ferric oxide, while the zirconium chloride gave 48.97 per cent. zirconium dioxide. The latter salt also showed a contamination by iron equivalent to 0.16 per cent. ferric oxide, and in the percentages given in the above analyses, an allowance is made for this correction.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide.....	29.44	29.50	29.55	29.60	29.36	29.70
Zirconium dioxide .	48.97	48.89	48.83	48.79	48.78	49.04

In making a practical use of this separation it is only necessary to obtain the two metals in solution in the form of chlorides and then the details as already given may be applied.

ON THE DELICACY OF THE SEPARATION OF IRON FROM ZIRCONIUM.

The fact that zirconium oxychloride is perfectly white in color should not be taken as a final indication that it is absolutely free from traces of iron ; and this should be borne in mind in the preparation of salts for atomic weight determinations. In order

to establish the accuracy of the method which has been described for the separation of iron from zirconium, a series of delicate experiments was carried out with the object of determining approximately the quantity, if any, of iron still remaining with the zirconium salt.

Zirconium tetrachloride, contaminated with iron, was treated with a little water in order to convert it into the oxychloride; it was then digested with ether, and a drop of hydrochloric acid added. The ether was filtered off and the perfectly white residue of zirconium oxychloride was washed several times with absolute ether to insure the removal of the last traces of the iron salt.

A solution of ferric chloride was made, one cc. of which contained 0.000001 gram ferric chloride. This was called solution No. 1.

Another solution of ferric chloride was made, one cc. of which contained 0.0000005 gram ferric chloride. This was called solution No. 2.

One cc. of solution No. 1 was placed in a test-tube, and to this were added one cc. of hydrochloric acid (sp. gr. 1.17), and one cc. of a solution of ten grams ammonium thiocyanate in 100 cc. of water, and the volume of the liquid was made up to ten cc. A slight pink color was noticed. One cc. of solution No. 2 was treated in the same manner, and a just perceptible pink tinge was observed.

One-tenth gram of zirconium tetrachloride was dissolved in five cc. of water, and treated as above; a dark red color immediately appeared.

One-tenth gram of the zirconium oxychloride as freed from iron, was dissolved in five cc. of water, and treated in a similar manner; a very slight pink tinge was perceptible. On comparing this with solutions No. 1 and No. 2, it was found that the intensity of coloration of the zirconium oxychloride solution was between that of the two iron solutions. From this it is to be concluded that the ratio between the amount of iron salt and that of the zirconium salt present in the zirconium oxychloride is approximately between the limits of 1 : 200,000 and 1 : 100,000.

The tetrachloride of zirconium, before its separation from iron, showed a percentage of the latter equivalent to about 0.16

per cent. ferric oxide. By the above comparison this percentage appears to be reduced to something approximately between the limits of 0.001 and 0.0005 per cent. The solution of hydrochloric acid used in these experiments was purified to such an extent that one cc., when treated with one cc. of the ammonium thiocyanate solution, on dilution to ten cc. gave no perceptible pink coloration.

The observations of those delicate tints were made immediately after mixing the solutions, and by comparison with an equal volume of distilled water. On standing for a time the colors were apparently discharged.

As thorium, cerium, and titanium belong to the same group as zirconium, and form corresponding hydrated oxychlorides insoluble in ether, the same method was applied in the separation of iron from these metals as with zirconium, and very good results were obtained. The method was carried out in every particular as already described, and was also extended to include lanthanum, neodymium, and praseodymium, as their hydrated chlorides were found to be insoluble in ether.

THORIUM FROM IRON.

The thorium salt used was the chloride, and its analysis gave 60.79 per cent. thorium dioxide, and was not appreciably contaminated with iron, so no correction was necessary in the percentages found.

I. 0.5608 gram thorium tetrachloride with 0.2246 gram ferric chloride gave :

0.3418 gram thorium dioxide = 60.95 per cent. thorium dioxide.

0.0657 gram ferric oxide = 29.25 per cent. ferric oxide.

II. 0.2681 gram thorium tetrachloride with 0.4625 gram ferric chloride gave :

0.1628 gram thorium dioxide = 60.72 per cent. thorium dioxide.

0.1364 gram ferric oxide = 29.53 per cent. ferric oxide.

III. 0.5072 gram thorium tetrachloride with 0.3217 gram ferric chloride gave :

0.3075 gram thorium dioxide = 60.63 per cent. thorium dioxide.

0.0952 gram ferric oxide = 29.59 per cent. ferric oxide.

IV. 1.0368 grams thorium tetrachloride with 0.7241 gram ferric chloride gave :

0.6318 gram thorium dioxide = 60.94 per cent. thorium dioxide.

0.2137 gram ferric oxide = 29.51 per cent. ferric oxide.

V. 0.1193 gram thorium tetrachloride with 0.6976 gram ferric chloride gave :

0.0720 gram thorium dioxide = 60.35 per cent. thorium dioxide.

0.2062 gram ferric oxide = 29.58 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide	29.44	29.25	29.53	29.59	29.51	29.58
Thorium dioxide	60.79	60.95	60.72	60.63	60.94	60.35

CERIUM FROM IRON.

Cerium chloride was used, and its analysis gave 61.11 per cent. cerium dioxide.

I. 0.1098 gram cerium chloride with 0.3510 gram ferric chloride gave :

0.0669 gram cerium dioxide = 60.93 per cent. cerium dioxide.

0.1044 gram ferric oxide = 29.74 per cent. ferric oxide.

II. 0.1930 gram cerium chloride with 0.2574 gram ferric chloride gave :

0.1178 gram cerium dioxide = 61.04 per cent. cerium dioxide.

0.0758 gram ferric oxide = 29.45 per cent. ferric oxide.

III. 0.2240 gram cerium chloride with 0.2642 gram ferric chloride gave :

0.1367 gram cerium dioxide = 61.03 per cent. cerium dioxide.

0.0784 gram ferric oxide = 29.67 per cent. ferric oxide.

IV. 0.7532 gram cerium chloride with 0.1024 gram ferric chloride gave :

0.4598 gram cerium dioxide = 61.05 per cent. cerium dioxide.

0.0301 gram ferric oxide = 29.39 per cent. ferric oxide.

V. 0.1262 gram cerium chloride with 0.8436 gram ferric chloride gave :

0.0774 gram cerium dioxide = 61.33 per cent. cerium dioxide.

0.2489 gram ferric oxide = 29.52 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide	29.44	29.74	29.45	29.67	29.39	29.52
Cerium dioxide	61.11	60.93	61.04	61.03	61.05	61.33

TITANIUM FROM IRON.

Titanium chloride was the salt used, and on analysis this gave 57.17 per cent. titanium dioxide.

I. 0.1060 gram titanium chloride with 0.2224 gram ferric chloride gave :

0.0604 gram titanium dioxide = 56.98 per cent. titanium dioxide.

0.0660 gram ferric oxide = 29.68 per cent. ferric oxide.

II. 0.2588 gram titanium chloride with 0.2508 gram ferric chloride gave :

0.1474 gram titanium dioxide = 56.95 per cent. titanium dioxide.

0.0736 gram ferric oxide = 29.35 per cent. ferric oxide.

III. 0.6532 gram titanium chloride with 0.1086 gram ferric chloride gave :

0.3728 gram titanium dioxide = 57.08 per cent. titanium dioxide.

0.0318 gram ferric oxide = 29.28 per cent. ferric oxide.

IV. 0.3549 gram titanium chloride with 0.7643 gram ferric chloride gave :

0.2033 gram titanium dioxide = 57.28 per cent. titanium dioxide.

0.2253 gram ferric oxide = 29.48 per cent. ferric oxide.

V. 0.1083 gram titanium chloride with 0.9212 gram ferric chloride gave :

0.0617 gram titanium dioxide = 56.97 per cent. titanium dioxide.

0.2720 gram ferric oxide = 29.53 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide	29.44	29.68	29.35	29.28	29.48	29.53
Titanium dioxide ..	57.17	56.98	56.95	57.08	57.28	56.97

LANTHANUM FROM IRON.

The lanthanum chloride used in the analyses gave 50.20 per cent. lanthanum oxide, La_2O_3 .

I. 0.2968 gram lanthanum chloride with 0.1465 gram ferric chloride gave :

0.1485 gram lanthanum oxide, La_2O_3 , = 50.03 per cent. lanthanum oxide.

0.0435 gram ferric oxide = 29.69 per cent. ferric oxide.

II. 0.4541 gram lanthanum chloride with 0.7105 gram ferric chloride gave :

0.2274 gram lanthanum oxide, La_2O_3 , = 50.08 per cent. lanthanum oxide.

0.2098 gram ferric oxide = 29.53 per cent. ferric oxide.

III. 0.1079 gram lanthanum chloride with 0.6514 gram ferric chloride gave :

0.0539 gram lanthanum oxide, La_2O_3 , = 49.95 per cent. lanthanum oxide.

0.1926 gram ferric oxide = 29.57 per cent. ferric oxide.

IV. 0.7525 gram lanthanum chloride with 0.1024 gram ferric chloride gave :

0.3769 gram lanthanum oxide, La_2O_3 , = 50.09 per cent. lanthanum oxide.

0.0304 gram ferric oxide = 29.68 per cent. ferric oxide.

V. 0.5048 gram lanthanum chloride with 0.5025 gram ferric chloride gave :

0.2539 gram lanthanum oxide, La_2O_3 , = 50.30 per cent. lanthanum oxide.

0.1485 gram ferric oxide = 29.55 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide	29.44	29.69	29.54	29.57	29.68	29.55
Lanthanum oxide, La_2O_3	50.20	50.03	50.08	49.95	50.09	50.30

PRASEODYMIUM FROM IRON.

The salt used was praseodymium nitrate, and its analysis gave 43.33 per cent. praseodymium oxide, Pr_2O_3 .

I. 0.5308 gram praseodymium nitrate with 0.4245 gram ferric chloride gave :

0.2293 gram praseodymium oxide, Pr_2O_3 , = 43.20 per cent. praseodymium oxide.

0.1261 gram ferric oxide = 29.70 per cent. ferric oxide.

II. 0.5090 gram praseodymium nitrate with 0.3596 gram ferric chloride gave :

0.2198 gram praseodymium oxide, Pr_2O_3 , = 43.18 per cent. praseodymium oxide.

0.1064 gram ferric oxide = 29.59 per cent. ferric oxide.

III. 0.1085 gram praseodymium nitrate with 0.7240 gram ferric chloride gave :

0.0465 gram praseodymium oxide, Pr_2O_3 , = 42.86 per cent. praseodymium oxide.

0.2139 gram ferric oxide = 29.54 per cent. ferric oxide.

IV. 0.6849 gram praseodymium nitrate with 0.1096 gram ferric chloride gave :

0.2960 gram praseodymium oxide, Pr_2O_3 , = 43.33 per cent. praseodymium oxide.

0.0323 gram ferric oxide = 29.43 per cent. ferric oxide :

V. 0.2532 gram praseodymium nitrate with 0.2485 gram ferric chloride gave :

0.1092 gram praseodymium oxide, Pr_2O_3 , = 43.13 per cent. praseodymium oxide.

0.0735 gram ferric oxide = 29.58 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide	29.44	29.70	29.59	29.54	29.43	29.58
Praseodymium oxide, Pr_2O_3 ...	43.33	43.20	43.18	42.86	43.22	43.13

NEODYMIUM FROM IRON.

Neodymium nitrate was used, and its analysis gave 42.20 per cent. neodymium oxide, Ne_2O_3 .

I. 0.1763 gram neodymium nitrate with 0.4286 gram ferric chloride gave :

0.0740 gram neodymium oxide, Ne_2O_3 , = 41.97 per cent. neodymium oxide.

0.1261 gram ferric oxide = 29.42 per cent. ferric oxide.

II. 0.6389 gram neodymium nitrate with 0.1842 gram ferric chloride gave :

0.2688 gram neodymium oxide, Ne_2O_3 , = 42.07 per cent. neodymium oxide.

0.0540 gram ferric oxide = 29.32 per cent ferric oxide.

III. 0.7246 gram neodymium nitrate with 0.7562 gram ferric chloride gave :

0.3051 gram neodymium oxide, Ne_2O_3 , = 42.11 per cent. neodymium oxide.

0.2229 gram ferric oxide = 29.48 per cent. ferric oxide.

IV. 0.1545 gram neodymium nitrate with 0.2046 gram ferric chloride gave :

0.0645 gram neodymium oxide, Ne_2O_3 , = 41.75 per cent. neodymium oxide.

0.0610 gram ferric oxide = 29.81 per cent. ferric oxide.

V. 0.2081 gram neodymium nitrate with 0.7680 gram ferric chloride gave :

0.0869 gram neodymium oxide, Ne_2O_3 , = 41.76 per cent. neodymium oxide.

0.2271 gram ferric oxide = 29.57 per cent. ferric oxide.

	Used.	I.	II.	Found. III.	IV.	V.
Ferric oxide	29.44	29.42	29.32	29.48	29.81	29.57
Neodymium oxide, Ne_2O_3	42.20	41.97	42.07	42.11	41.75	41.76

The praseodymium and neodymium salts existing originally as nitrates, were evaporated to dryness with hydrochloric acid in order to convert them into the chloride form.

GENERAL REMARKS.

Gooch and Havens, in the *American Journal of Science* for December, 1896, describe a method for the separation of aluminum from iron by treatment with anhydrous ether saturated with hydrochloric acid gas. The hydrated chloride of aluminum remains insoluble, whereas the ferric salt is completely dissolved. This method is practically the same as the one herein described for the separation of iron from zirconium and the other rare earths; but the results of this present research were mostly obtained in October and November, 1896, before the writer was aware of the contemporaneous work of Gooch and

Havens. These latter writers also describe a separation of aluminum from glucinum by the same method.¹

The use of absolute ether may militate somewhat against the practical application of this method to general analytical purposes; since in the case of most of the metals experimented upon, very good separations are already known which do not require the use of a reagent both difficult and unpleasant to manipulate. This method, however, is especially recommended for the separation of iron from zirconium, the separations of the other metals being only tried as a matter of interest through the analogy existing between those metals and zirconium. A point, however, which may prove of practical importance, and which it is most desirable to emphasize here, is that by carefully following out the procedure herein described, zirconium oxychloride and dioxide may be easily and quickly prepared perfectly free from iron. This fact may be of considerable importance and utility in the preparation of zirconium compounds for use in atomic weight determinations, where a high degree of purity is absolutely necessary in order to obtain authentic results.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE LABORATORY OF THE NORTH DAKOTA AGRICULTURAL COLLEGE, NO. I.]

THE PROTEIDS OF CREAM.

BY E. F. LADD.

Received September 28, 1898.

IN some preliminary work in the chemistry of ripening cream for butter-making, several methods for the separation of proteids were tried, some of which were not suited to this work, and the results may be of interest, if not of value, to other workers in the same line. In the work here presented it was not our purpose to determine each of the individual proteids that cream might contain, but rather to learn something of the changes that take place in the proteids of cream during the process of ripening.

For our purpose the proteids of milk were divided into four groups, casein, albumen, albumoses, and peptones; that is, the

¹ *Am. J. Sci.*, August, 1897.