

Our analytical examination has not been, and cannot well be continued further than to afford the results cited above; hence we prefer not to express a positive opinion as to the probable combinations of the constituents as they occur in the rail, nor do we feel able to offer any explanation as to how the changes in composition have been brought about. Merely for comparison with Herting's results, we present our own, calculated upon the same basis, except that the silicon is calculated as oxide.

They are as follows :

	Outer shell. Per cent.	Inner core. Per cent.
Carbon	9.50	16.00
Silica.....	12.45	22.55
Phosphoric anhydride	8.25	8.60
Ferrous sulphide.....	6.30	2.00
Ferrous sulphate.....	11.15	3.20
Magnetic oxide (Fe_3O_4).....	46.80	49.20

The writers wish to express their obligations to Mr. J. B. Dil-
lingham, and Prof. W. H. Niles, through whose courtesy they
came into possession of the fragment of the rail, and to whom
they are indebted for information as to its history.

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[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM, No. 6.]

THE OXALATES OF ZIRCONIUM.

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THE text-books of chemistry make either very little or no reference to the oxalates of zirconium. Beyond an occasional reference to the oxalate or basic oxalate gotten by precipitating with oxalic acid or an oxalate, we can find little mention of these compounds. Behrens, in his microchemical work, speaks of an oxalate prepared as colorless pyramids by precipitating a solution of zirconium sulphate with potassium binoxalate, but no analyses are given, and the crystals could scarcely have been the pure oxalate. Paykull¹ speaks of double oxalates being prepared with the alkaline oxalates (1:2) and of his failure to prepare the neutral oxalate. His methods, and indeed full results, are unknown to us, as we did not have access to the original paper.

We may summarize the work which follows in the succeeding pages by saying that we found it possible to prepare the basic oxalates by precipitation. This was usually in the form of

¹ *Ofv. af. Vet. Ak. Förhändl. ref. in Ber. d. chem. Ges., 12, 1719.*

$Zr(C_2O_4)_2 \cdot Zr(OH)_4$, though other ratios were gotten. The neutral oxalate we did not succeed in preparing, but instead the tendency seems to be toward the formation of the acid oxalate, $Zr(C_2O_4)_2 \cdot H_2C_2O_4 \cdot 8H_2O$. This tendency toward the formation of acid salts was shown also in the double oxalates. Two of these were prepared. For sodium, $Zr(C_2O_4)_2 \cdot 3Na_2C_2O_4 \cdot H_2C_2O_4 \cdot 5H_2O$, and for potassium the salt $[Zr(C_2O_4)_2]_2 \cdot (K_2C_2O_4)_2 \cdot H_2C_2O_4 \cdot 8H_2O$. The oxalate with ammonium as a constituent was not so easy of preparation in a pure state. The compound secured was $Zr(C_2O_4)_2 \cdot 2(NH_4)_2C_2O_4$. The experiments and analyses are given in detail.

ZIRCONIUM OXALATES.

The Oxalate Gotten by Precipitation.—On the addition of a saturated solution of oxalic acid to a slightly acid solution of zirconium chloride until no further precipitation occurred, a gelatinous precipitate formed which had very nearly the composition $Zr(C_2O_4)_2 \cdot 2Zr(OH)_4$. Analysis I gave Zr, 46.39, and C_2O_4 , 30.89, instead of the theoretical 46.40 and 30.93 respectively. The filtrate from this was turbid, and on standing yielded another precipitate which had nearly the composition $2Zr(C_2O_4)_2 \cdot 3Zr(OH)_4$.

These basic oxalates are very difficultly soluble in acids, and of extremely fine subdivision, settling slowly and passing through even the best filters. It does not seem probable that they could be secured of very constant composition. Probably basic oxalates with many different ratios between the oxalate and the hydroxide might be secured. On drying at 100° , or even a little lower, the oxalic acid is gradually volatilized and lost. This is true of all the oxalates and double oxalates prepared so that the only mode of drying these preparations was between filter paper.

The Acid Oxalate Prepared by Crystallization.—In preparing this oxalate, zirconium hydroxide was dissolved in oxalic acid. The hydroxide is quite soluble in oxalic acid, and a concentrated solution is readily obtained. A considerable excess of the acid is required to hold the oxalate thus formed in solution. If this solution be acidified by means of hydrochloric acid a very fine precipitate is obtained settling very slowly, easily passing through the best filter papers and insoluble even in a considera-

ble excess of the acid, but soluble in concentrated sulphuric acid. This precipitate was not analyzed, nor were the exact conditions of its formation determined, as its examination did not promise results of sufficient importance to justify overcoming the difficulties in the way.

On evaporating the acid solution of the oxalate the excess of oxalic acid first crystallized out. In the various preparations made, the first one or two crops of long crystals were found to be nearly pure oxalic acid, and were rejected. Then the form of the crystals changed to small granular or prismatic masses, and with each succeeding crop of crystals the percentage of zirconium increased, reaching speedily an approximately constant ratio. No difference in the form of the crystals in these different crops could be detected on superficial examination, and hence it was impossible to distinguish between the zirconium oxalate and the oxalic acid almost free of zirconium, except by analysis. In no case was the normal oxalate secured. The analyses showed a tendency toward the formation of an acid oxalate and to mixtures of this with the normal oxalate. These mixtures were gotten in the later crystallizations, but the last crystallization, when nearly the whole would solidify into a crystalline mass, showed decreased percentages of zirconium. It is possible that larger amounts than we had at our disposal would enable one to so fraction the crystallizations as to secure a pure oxalate. It is, however, questionable whether the normal oxalate can exist in solution without admixture with some oxalic acid.

Four series of crystallizations were made, and in two cases fairly abundant crops of crystals corresponding to the acid oxalate were obtained. In each series enough of the zirconium hydroxide was taken to form about twenty grams of the oxalate.

	First series. Sixth fraction. II.	Second series. Fifth fraction. III.	$Zr(C_2O_4)_2 \cdot H_2C_2O_4$.
Zr	25.44	25.28	25.53
C_2O_4	74.55	74.72	74.47

These are calculated upon the water-free basis. The crystals contained 29.34 and 29.27 per cent. of water respectively, where the salt $Zr(C_2O_4)_2 \cdot H_2C_2O_4 \cdot 8H_2O$ contains 28.90 per cent. Other crops of crystals contained percentages of zirconium not varying greatly from these given above as 28.14, 27.62, 24.9, 23.83.

The percentage of zirconium in the normal oxalate is 33.96.

ZIRCONIUM SODIUM OXALATE.

The addition of sodium oxalate to a slightly acid solution of zirconium chloride gives a gelatinous white precipitate. Most of this dissolves in an excess of the oxalate. The undissolved portion settles to the bottom, and after prolonged standing, a second layer of a more powdery appearance forms. This can also be gotten by concentration of the filtrate from the first precipitate. Analysis showed that the first gelatinous precipitate was chiefly $Zr(OH)_4$. The second precipitate was a double oxalate of zirconium and sodium, but was either of inconstant composition (varying ratios of sodium to the zirconium), or was decomposed by the washing.

The analyses, calculated on a dry basis, gave:

	IV.	V.	VI.
Zr	53.12	46.86	41.98
Na.....	9.16	4.10	1.07
C_2O_4	38.06	39.64	42.95

If the solution made with the excess of sodium oxalate was diluted considerably with water, a gelatinous precipitate was formed, very fine and insoluble. Precipitates were also formed by the addition of hydrochloric acid. This mode of forming the double oxalate was abandoned, and the following method was adopted with greater success. Zirconium hydroxide was dissolved in an excess of oxalic acid, and to this a concentrated solution of sodium hydroxide was added, bringing it nearly to neutralization. When the solution was concentrated an abundant crop of crystals was obtained on cooling, a good deal of heat being evolved in the mixing. Further evaporation yielded other crops of crystals. These were washed, dried between filter paper and analyzed. The results are given in the following table:

	VII.	VIII.	IX.	Calculated.
Na	18.14	17.46	17.75	18.19
Zr	12.59	12.66	12.78	11.93
C_2O_4	69.27	66.89	69.47	69.88

These results show a somewhat wide variation from those calculated. This probably arises from the fact that the fractions were not composed of the crystals of a single kind of oxalate, but had other oxalates mixed with them in small amounts. Examined under a magnifying glass they seemed to be homo-

geneous, but the different crops could not be distinguished from one another. They were all small, hard prismatic crystals, somewhat difficultly soluble in water. One set of crystals, the analysis of which is reported under VII in the above table, was redissolved in water and recrystallized. On analysis it yielded the following results:

	VII.	XI.
Na	18.14	18.19
Zr	12.59	12.71
C ₂ O ₄	69.27	69.10

These were calculated upon a water-free basis. The crystals from the various crops mentioned above did not contain a very constant amount of water, but ranged from 9.13 to 11.06. The calculated amount of water in $Zr(C_2O_4)_2 \cdot 3Na_2C_2O_4 \cdot H_2C_2O_4 \cdot 5H_2O$ is 10.62. It would seem, therefore, that the tendency, when this method of formation is adopted, is toward the formation of crystals containing free oxalic acid and with the sodium and zirconium oxalates bearing a ratio of three to one.

ZIRCONIUM POTASSIUM OXALATE.

The curdy precipitate gotten by precipitating zirconium chloride with normal potassium oxalate is insoluble in an excess of either of the substances. The precipitate first obtained is an impure zirconium hydroxide, containing only small amounts of oxalic acid. The supernatant liquid on concentration yields needle-like crystals of potassium oxalate, carrying only traces of zirconium. After the separation of a good deal of this potassium oxalate, further concentration yielded a gelatinous substance having the composition (XII): Zr, 39.34; K, 5.06; C₂O₄, 43.05; which seems to be a basic zirconium oxalate, mixed or united with a small proportion of potassium oxalate. If the potassium be calculated as potassium oxalate and subtracted, the composition of the remainder would be approximately $Zr(OH)_2 \cdot Zr(C_2O_4)_2$.

On adding potassium binoxalate to a solution of zirconium chloride a white curdy precipitate was obtained which was not completely soluble in excess of the binoxalate. The somewhat turbid solution was filtered and evaporated. Large crystals resembling those of oxalic acid formed. These were separated, and on analysis proved to be oxalic acid. At the same time a number of small crystals were formed, which were mechanically

separated, washed and dried. These were analyzed and are reported under XIII. A further crop was gotten from the mother liquor, and the analysis is given under XIV.

	XIII.	XIV.
Zr.....	19.59	17.99
K.....	16.18	13.91
C ₂ O ₄	64.23	68.09

The curdy precipitate, which first formed, was also examined and found to have the composition $Zr(C_2O_4)_2 \cdot 2Zr(OH)_4$.

The addition of a solution of potassium tetroxalate to zirconium chloride gave a gelatinous precipitate of zirconium oxalate (basic), carrying a little potassium oxalate. Subtracting the potassium oxalate, the percentages (XVI) Zr, 39.09 and C₂O₄, 38.63 are left, which are not very different from the figures gotten for the precipitate from potassium oxalate (neutral).

This curdy gelatinous precipitate was dissolved in excess of tetroxalate and the solution placed over sulphuric acid to crystallize, and yielded crystals having the composition (XVII): Zr, 20.85; K, 16.72; and C₂O₄, 62.31. As will be seen, these are not far from the 1 : 2 zirconium potassium oxalate, with excess of oxalic acid.

When potassium hydroxide was added to a solution of zirconium oxalate in oxalic acid until nearly neutral and then set aside for crystallization, various crops of crystals were gotten, as in the case of the double sodium oxalates. These crops of crystals were similar in appearance to the sodium crystals. They were analyzed and showed fairly constant composition.

	XVIII.	XIX.	XX.	XXI.	$\frac{(Zr(C_2O_4)_2)_2}{(K_2C_2O_4)_2 \cdot H_2C_2O_4}$
Zr.....	18.08	19.25	19.83	18.47	18.95
K.....	16.41	16.35	14.84	14.46	16.34
C ₂ O ₄	66.51	64.40	65.33	67.07	64.71

The three previous analyses may also be referred to here as having approximately the same composition. See Analyses XIII, XIV, XVII. These are calculated as water-free. In the Analyses XVIII and XIX the percentages of water were 12.99 and 12.38. These would correspond to the formula $(Zr(C_2O_4)_2)_2 \cdot (K_2C_2O_4)_2 \cdot H_2C_2O_4 \cdot 8H_2O$. In this case, as in the zirconium oxalates and the sodium oxalates, the crystals seem to form only along with free oxalic acid, giving acid salts.

ZIRCONIUM AMMONIUM OXALATES.

The addition of a solution of ammonium oxalate to the slightly acid solution of zirconium chloride gave a heavy gelatinous pre-

precipitate which was soluble in excess of ammonium oxalate and proved to be zirconium hydroxide with more or less zirconium oxalate and small amounts of ammonia. The filtrate from this precipitate was evaporated slowly and a fine crystalline powder obtained. This contained (XXII) Zr, 42.17 per cent. and C_2O_4 , 39.86 per cent. This is in fair agreement with $Zr(C_2O_4)_2 \cdot Zr(OH)_4$. When ammonium oxalate is added until the first gelatinous precipitate is redissolved and then evaporated to crystallization, different crops of crystals can be gotten containing various amounts of ammonia. These did not seem to have any regular composition in our experiments and were looked upon as basic zirconium oxalates with varying amounts of ammonium oxalate present. Thus for one of these the figures (XVIII) Zr, 31.48; NH_3 , 7.14; and C_2O_4 , 61.38 were gotten.

Abandoning this method and using the one adopted in the cases of the sodium and potassium double oxalates, a more favorable result was obtained. Zirconium hydroxide was dissolved in excess of oxalic acid and then this was nearly neutralized by means of ammonium hydroxide. Analyses of these crops of crystals follow :

	XXIV.	XXV.	$Zr(C_2O_4)_2 \cdot 2(NH_4)_2C_2O_4$.
Zr	16.55	16.66	17.58
NH_3	14.46	13.35	13.28
C_2O_4	69.99	69.99	68.94

While these do not show that the crystals had been thoroughly purified, the results indicate that the composition is one zirconium oxalate to two ammonium oxalate. On recrystallizing one of these crops of crystals, zirconium hydroxide was observed to separate when the solution was heated (to evaporate to crystallization), and the crystals which were obtained consisted of ammonium oxalate alone.

In general it may be stated that the zirconium oxalate fails to show any decided tendency to enter into clearly defined combinations with the alkaline oxalates, exhibiting rather a power of crystallizing along with them in mixtures of any proportions. It can only be said at best that under the conditions of our experiments certain ratios seem to be preferred, and appeared more persistently. In all cases the crystals formed from oxalic acid solutions, and this free oxalic acid crystallized with them, giving acid oxalates.