

cases this frothing is due to decomposition of the non-sugars. This is a subject that will be looked into.

Whatever may have been the initial cause of heat, whether fermentation or decomposition due to the treatment, there can be no doubt that there was a violent manifestation of heat most destructive in its effects.

THE FERROCYANIDES OF ZINC AND MANGANESE.¹

BY G. C. STONE AND D. A. VAN INGEN.

Received May 15, 1897.

OUR work on ferrocyanides was undertaken more to try to reconcile the very discordant statements that have been made about its value as a means for the volumetric determination of zinc than to determine the exact composition of the salts. We therefore have merely tried to determine the influence of temperature and acidity on the composition of the precipitates formed when potassium ferrocyanide is added to the solution of a salt of zinc or manganese. The simplest method for this is to add to a known amount of a zinc solution an excess of a ferrocyanide solution, the strength of which has been accurately determined by titration with permanganate and to determine the excess of ferrocyanide not precipitated by the zinc by titration with permanganate. We found that it was practically impossible to filter the ferrocyanides of either zinc or manganese, but by diluting to a known volume, allowing the precipitate to settle and titrating an aliquot portion, we obtained results that agreed with each other, provided the excess of ferrocyanide remained the same; but with varying excesses the ratio of zinc to ferrocyanogen in the precipitate fell irregularly as the excess of ferrocyanide increased. With manganese this method also failed, as we found that the ferrocyanides of manganese were somewhat soluble in water, rather more so in potassium ferrocyanide and entirely soluble in strongly acid solutions.

We next tried precipitating zinc and manganese in neutral, strongly acid solutions, both hot and cold, and in cold slightly acid ones. The precipitates were washed by decantation. Most of them settled very slowly, especially when nearly washed. We found that they settled much more rapidly if some other salt

¹ Read at the meeting of the New York Section, May 7, 1897.

was present, and in most cases added barium chloride, as it caused the precipitate to settle comparatively rapidly and did not react with it. Even then the washing was very tedious, requiring several days. The zinc salts were much easier to wash than the manganese, and it was possible to test the completeness of the washing, as they are not appreciably soluble in water; but with manganese it was impossible to tell when the washing was complete, owing to the solubility of the manganese ferrocyanides. We therefore washed all the manganese precipitates several times more than we found necessary for the zinc, but even then felt somewhat doubtful of the result in some cases.

We found the best test for soluble ferrocyanides was a very dilute solution of cobalt nitrate, so dilute that two or three drops of it on a white porcelain plate showed no color. In applying the test the best way is to put a drop of a dilute solution of cobalt on a watch-glass and shake it off so that only a very minute drop, or no visible *drop* remains, then add two or three drops of water and a few drops of the solution to be tested. Hold the watch-glass at about the level of the eye and look across the surface towards a window; a faint green can be seen if even a trace of ferrocyanide is present. If the cobalt solution is not very dilute, its color, red, neutralizes the green, and it does not show. Testing the delicacy of this reaction with known amounts of ferrocyanide, we found that one cc. of a solution containing 0.000009 gram of potassium ferrocyanide showed a color, when compared with distilled water; but with one containing 0.000007 gram no color could be seen. Ferric chloride is nearly, but not quite, as delicate as cobalt; uranium is much less delicate.

Having washed our precipitates, we dried them and heated a weighed portion in a porcelain crucible, at first gently, then very strongly, to decompose the organic matter; dissolved in hydrochloric acid and boiled with potassium chlorate to oxidize the iron; precipitated the iron by barium carbonate; dissolved the precipitate; reduced the iron by hydrogen and determined it by titration with potassium permanganate. In the filtrate from the iron we determined the manganese by titration with permanganate. The zinc we separated from the excess of barium by pre-

precipitation as sulphide, converted to phosphate and weighed as pyrophosphate; or, we removed the barium as sulphate and determined the zinc as pyrophosphate in the filtrate. The atomic weights used were those given in this Journal, 18, 213 (March, 1896), where oxygen equals 16. They are: Carbon, 12.01; hydrogen, 1.008; iron, 56.02; manganese, 54.99; nitrogen, 14.04; phosphorus, 31.02; potassium, 39.11; and zinc, 65.41. We did not attempt to determine more than the ratio of zinc or manganese to iron, which, of course, is the same as the ratio of ferrocyanide.

A zinc salt precipitated from a neutral solution in the cold, the amount of ferrocyanide used being slightly in excess of what was required to form zinc ferrocyanide with the zinc present, gave a ratio of 287 atoms of zinc to 285 atoms of iron. A second similar precipitate gave a ratio of 702:692. In both cases the ratio is practically 1:1, giving the empirical formula $ZnK_2Fe(CN)_6$.

Two lots precipitated from cold neutral solutions, in which the zinc was in excess, gave ratios of 501:511, and 700:684, which also gives the formula $ZnK_2Fe(CN)_6$.

The next precipitate was formed in a cold solution containing five cc. per hundred of hydrochloric acid. Two portions of this were analyzed giving ratios of 160:113 and 318:227, or in both cases 100:71, this would make the formula $Zn_{10}K_8(Fe(CN)_6)_7$, about an average of two of the other salts found.

The next two were precipitated from hot solutions, *A* was neutral and *B* contained five cc. of hydrochloric acid per hundred. *A* gave a ratio of 189:136, and *B* of 176:135; in both cases nearly 4:3, making the formula $Zn_4K_3(Fe(CN)_6)_3$.

We precipitated the next lot in a dilute solution containing one cc. of dilute (1:6) hydrochloric acid in each hundred, these being the conditions under which we precipitate zinc and manganese in the volumetric method we use. This gave us ratios of 175:131 and 174:130, giving the formula $Zn_3K_4(Fe(CN)_6)_3$.

The last zinc salt which we analyzed was bought from a dealer in chemicals as $Zn_2Fe(CN)_6$. It gave us ratios of 169:115 and 170:116, giving the formula $Zn_3K_2(Fe(CN)_6)_2$.

With manganese the results were not quite as satisfactory, owing to the impossibility of being sure that the precipitates

were completely washed. In the precipitates that received the most washing we found the simplest ratios of manganese to iron.

Two lots precipitated from cold neutral solutions, *A* containing more and *B* less ferrocyanide than would form $\text{Mn}_2\text{Fe}(\text{CN})_6$, gave ratios of, *A* 555 : 594, and *B* 941 : 991, slightly more than 1 : 1, making the formula $\text{Mn}_{20}\text{K}_{44}(\text{Fe}(\text{CN})_6)_{21}$, or more probably $\text{MnK}_2\text{Fe}(\text{CN})_6$.

The next were precipitated from cold solutions containing five cc. of hydrochloric acid per hundred; they gave ratios of 155 : 116 and 309 : 233, or 4 : 3, making the formula $\text{Mn}_4\text{K}_4(\text{Fe}(\text{CN})_6)_3$.

The next solutions were hot, *A* containing five cc. hydrochloric acid per hundred and *B* being neutral. The ratios were: *A* 148 : 161, and *B* 144 : 135, giving the formula $\text{Mn}_{10}\text{K}_{24}(\text{Fe}(\text{CN})_6)_{11}$, and $\text{Mn}_{20}\text{K}_{36}(\text{Fe}(\text{CN})_6)_{19}$; in both cases it should probably be $\text{MnK}_2\text{Fe}(\text{CN})_6$.

The last of the manganese salts were prepared under the conditions we have in our volumetric method, a cold solution containing one cc. of dilute (1 : 6) hydrochloric acid in one hundred cc. They gave ratios of 141 : 140 and 142 : 140— $\text{MnK}_2\text{Fe}(\text{CN})_6$.

It being evident from the preceding that both zinc and manganese form different salts under varying conditions, we next tried whether the different indicators which have been proposed for volumetric analysis showed the same salt, and whether any one indicator showed different salts under different conditions. The indicators which we have seen proposed are ferric salts, uranium, cobalt, copper, and platinum. In testing we used zinc and manganese solutions, in which the metals had been very carefully determined gravimetrically, and a solution of potassium ferrocyanide which had been titrated with permanganate, and the ferrocyanide value calculated from the iron value. The variables were the proportions of acid, the temperature, the dilution of the indicator, and the way the solution and indicator were brought together.

In a cold solution containing one-seventh cc. of hydrochloric acid in one hundred, uranium, when a drop of it was mixed with a drop of the solution on a porcelain plate, showed the reaction when the quantities of zinc and ferrocyanide were sufficient to form $\text{Zn}_2\text{Fe}(\text{CN})_6$.

In a hot solution containing ten cc. of hydrochloric acid,

uranium, used as in the last case, gave the reaction with $Zn_3K_2(Fe(CN)_6)_2$.

In a cold solution containing one-seventh cc. of acid, uranium gave a reaction for $Zn_4K_4(Fe(CN)_6)_3$, when drops of it and the solution were placed side by side on filter paper so that the uranium did not touch the precipitate, but only the clear solution that filtered from it. Under the same conditions copper and ferric chloride gave the reaction at the same point.

Cobalt was tried, using a strong solution, placing a drop on porcelain and a drop of the solution by it, so that the two touch, but do not mix. The reaction was for $Zn_4K_4(Fe(CN)_6)_3$. When the solution was *mixed* with *very* dilute cobalt, the reaction was for $Zn_3K_2(Fe(CN)_6)_2$. Both of the solutions tested with cobalt were cold and contained one-seventh cc. hydrochloric acid per hundred.

Platinum was not tried. Dr. Miller¹ states that when used with a hot acid solution it gives the reaction with $Zn_3K_2(Fe(CN)_6)_2$. He says it does not work with a cold solution.

With manganese we tried only three indicators. In all cases the solutions were cold and contained one-seventh cc. of hydrochloric acid per hundred. Strong cobalt and uranium on paper gave the reaction for $MnK_2Fe(CN)_6$; very dilute cobalt gave it for $Mn_3K_2(Fe(CN)_6)_2$.

Of the different indicators tried we found cobalt the most satisfactory, as it shows the reaction as soon as the drops touch, while all the others require an appreciable time for it to develop.

It will be seen that all the salts shown by the indicators, all but the third of the zinc series, and, we may add, twenty-three out of twenty-eight, in which we tried to determine the ratios by adding an excess of ferrocyanide and titrating it, are salts having nearly the general formula $K_4Fe(CN)_6, nR''_2Fe(CN)_6$, which is possibly the formula of these salts. Nearly all of those which contain more than one atom of the heavy metal agree fairly with the formula $R_nK_{2n-4}(Fe(CN)_6)_{n-1}$, the salt with one atom being the common difference of the series $R''K_2Fe(CN)_6$. It would, of course, require much more work than the limited time at our disposal has permitted to establish the correctness of either.

¹ This Journal, 18, 1100.

In using ferrocyanide as a reagent for volumetric analysis, it is of the utmost importance to keep all of the conditions absolutely uniform. Provided this is done the results are good, but if there is any variation they are liable to be entirely incorrect.

The following table gives the analytical results in detail :

TABLE.

Excess.	Hydrochloric acid. cc.	Temper- ature.	Zinc.	Iron.	Zinc.	Iron.	Zn : Fe
			Grams.	Grams.	Atoms.	Atoms.	:: 100 :
Fe(CN) ₆	0	Cold	0.01875	0.01596	287	285	99
Fe(CN) ₆	0	"	0.04598	0.03878	702	692	98
Zn	0	"	0.03280	0.02866	501	511	102
Zn	0	"	0.04579	0.03831	700	684	98
Fe(CN) ₆	5	"	0.10500	0.06368	160	113	70
Fe(CN) ₆	5	" (a)	0.42268	0.05098	318	227	71
Fe(CN) ₆	0	Hot	0.12392	0.07616	189	136	72
Fe(CN) ₆	5	"	0.11500	0.07575	176	135	76
Fe(CN) ₆	½	Cold	0.11469	0.07367	175	131	75
Fe(CN) ₆	½	"	0.11414	0.07287	174	130	75
Bought as Zn ₂ Fe(CN) ₆			0.11053	0.06497	169	115	78
Bought as Zn ₂ Fe(CN) ₆			0.11157	0.06508	170	116	67
			Manganese. Grams.		Manganese. Atoms.		Mn : Fe :: 100 :
Fe(CN) ₆	0	Cold	0.03050	0.03330	556	594	107
Mn	0	"	0.51763	0.55500	941	991	105
Fe(CN) ₆	5	"	0.08522	0.06540	155	116	75
Fe(CN) ₆	5	" (b)	0.03408	0.05252	309	233	75
Fe(CN) ₆	5	Hot	0.08139	0.09010	148	161	109
Fe(CN) ₆	0	"	0.07938	0.07547	144	135	94
Fe(CN) ₆	½	Cold	0.07757	0.07844	141	140	99
Fe(CN) ₆	½	"	0.07788	0.07862	142	140	99

(a) Zinc and iron determined in different portions.

(b) Manganese and iron determined in different portions.

[CONTRIBUTION FROM THE ANALYTICAL LABORATORIES OF COLUMBIA UNIVERSITY.]

ON THE FERROCYANIDES OF ZINC AND MANGANESE.¹

BY EDMUND H. MILLER AND J. A. MATHEWS.

Received May 12, 1897.

INTRODUCTION.

THE work to be described was undertaken to determine whether the precipitates formed by adding potassium ferrocyanide to solutions of zinc or manganese are normal ferrocyanides, as given by many authorities, or double potassium ferro-

¹ Read at the meeting of the New York Section, May 7, 1897.