V.—*On Certain Bismuth Compounds.* (Part V.)

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1. IN the fourth part of the present series of papers I described the action of potassium ferrocyanide upon a nearly neutral solution of bismuth nitrate. This action results in the formation of bismuth ferrocyanide, $\text{Bi}_4\cdot 5\text{FeCy}_6$, a salt which, when moist and containing traces of nitric acid, readily undergoes decomposition by the action of the air.

The results of the analyses of the greenish-blue substance produced by acting on bismuth ferrocyanide with very dilute nitric acid were most readily explained on the assumption that this substance is tolerably pure bismuth ferricyanide, $\text{Bi}_3\cdot 5\text{FeCy}_6$ (*Chem. Soc. J.*, vol. i, 1877, p. 655).

2. I have now succeeded in preparing pure bismuth ferricyanide by precipitating a nearly neutral cold solution of bismuth nitrate with an excess of potassium ferricyanide, washing the precipitate with cold water by decantation, and drying over sulphuric acid *in vacuo*.

3. The salt as thus prepared presented the appearance of a tawny-yellow amorphous powder with a shade of green. It was analysed by the process described in my former paper, viz., decomposition by strong sulphuric acid, separation of bismuth by precipitation with much water, and titration of iron, after reduction, by means of permanganate. I find that instead of separating bismuth from the whole of the liquid obtained by adding water to the mass from which sulphuric acid has been for the most part expelled, it is preferable to add to this mass such a quantity of dilute sulphuric acid as suffices

to form a clear solution, to make this solution up to a determinate volume (say to $\frac{1}{2}$ a litre), to withdraw an aliquot portion for the estimation of iron, to add ammonia to the remainder until the precipitate which is produced has a pale yellowish-red tint, and then to add three or four drops of acid and a considerable quantity of water. After standing some time the precipitated bismuth salts are collected, washed once or twice and dissolved in the minimum quantity of hot nitric acid. The bismuth is then determined by the ordinary gravimetric process, or by the improved volumetric method described by me in vol. I of the Society's Journal for 1877, p. 658.

As the analyses given in my former paper of the somewhat decomposed bismuth ferricyanide evidently pointed to the formula, $\text{Bi}_3\cdot 5\text{FeCy}_6$, I have not thought it necessary to make more than a single analysis of the purer preparation.

0.2793 gram gave 0.112 gram $\text{Bi}_2\text{O}_3 = 0.1005$ gram Bi.

0.468 „ used 8.5 c.c. permanganate = 0.0744 gram Fe.

(1 c.c. permanganate = 0.00876 gram Fe).

Calculated for $\text{Bi}_3\cdot 5\text{FeCy}_6$.		Found.
Bismuth	= 37.29	37.18
Iron	= 16.59	15.91
Cyanogen	= 46.12	46.91 (by difference)
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100.00		100.00

4. Ferricyanide of bismuth, whether in a dry or moist condition, is unaltered in air, even after many days. If it be suspended in water and the water be boiled, hydrocyanic acid is evolved, the water acquires an acid reaction, and a green, then a greenish-blue, and finally a blue salt (or salts) is produced. The presence of small quantities of acid, more especially of nitric acid, materially hastens this decomposition of the ferricyanide. When the salt is dried at 100° it undergoes partial decomposition, with evolution of hydrocyanic acid and production of greenish-yellow substances.

5. The action of chlorine and of bromine upon ferro- and ferricyanide of bismuth respectively is interesting.

In the hope of being able to prepare ferri- from ferrocyanide of bismuth by a method other than that already described, viz., boiling with dilute nitric acid, I suspended a quantity of the nearly pure ferrocyanide (still containing traces of potash) in cold water, and passed chlorine into the mixture until the blue colour of the original salt had entirely disappeared. The liquid was now of a brownish-red colour and contained a quantity of nearly white solid matter which quickly settled to the bottom of the vessel. After filtration and wash-

ing this solid matter was found to contain bismuth and chlorine, but not a trace of iron either in the form of ferro- or ferricyanide, or of oxide. The filtrate showed the reactions of hydroferricyanic acid, but was free from hydroferrocyanic acid; on evaporation over sulphuric acid it yielded crystals of potassium ferricyanide. No bismuth could be detected in the filtrate.

6. I performed a similar experiment, keeping the water in which the ferrocyanide was suspended at the boiling point; the result was altogether different from that detailed in par. 5. The colour of the light yellow ferrocyanide slowly changed to pale blue, then to green-blue, and finally to deep blue. The supernatant liquid showed the reactions of hydroferro- and hydroferricyanic acids: it contained no bismuth. An examination of the coloured substances produced in this reaction showed that they probably consisted of more or less pure bismuth ferricyanide mixed with varying quantities of some form of prussian blue and also with bismuth oxychloride.

7. Another quantity of the ferrocyanide which contained traces of potash was suspended in cold water to which bromine was added, the whole being shaken up from time to time. Judging from the colour of the solid and liquid portions, there appeared to be a slow change of ferro- into ferricyanide of bismuth; after some hours, however, the main resultant of the action was a white precipitate containing bismuth and bromine, and a supernatant reddish-yellow liquid which exhibited the reactions of hydroferricyanic acid.

8. An experiment similar to that described in par. 6 was carried out, substituting bromine for chlorine; the result was analogous with that obtained when chlorine was employed.

9. The action of chlorine upon bismuth ferricyanide when suspended in cold and in boiling water respectively is analogous with the action of the same gas upon bismuth ferrocyanide; the decomposition of the ferricyanide is not, however, in either case so rapid as that of the ferrocyanide. The action of bromine upon the ferricyanide when suspended in boiling water is analogous with, but less energetic than, the action of the same element upon the ferrocyanide under the same conditions. If, however, ferricyanide of bismuth be suspended in cold water to which bromine is added, a complete decomposition of the salt slowly ensues, a reddish-white precipitate is produced which contains the whole of the iron and bismuth originally present in the ferricyanide, while the supernatant liquid shows no traces either of hydroferro- or hydroferricyanic acid.

10. I have examined the action of chlorine and bromine respectively upon ferro- and ferricyanide of bismuth in the presence of cold and of hot solutions of caustic soda.

The ferrocyanide is completely decomposed with the precipitation

of the whole of the bismuth and iron which it originally contained. This decomposition is more rapid with bromine than when chlorine is employed; it is also more rapid in presence of hot than of cold caustic liquids. The first portions of the precipitate which is produced contain the whole of the bismuth, the solution at the same time giving the reactions for hydroferricyanic acid. If the supernatant liquid be decanted and be warmed with addition of more chlorine or bromine the decomposition is more rapid than if the action be allowed to proceed in contact with the precipitate which is at first produced. Bismuth ferricyanide is not so readily decomposed as the ferrocyanide by either chlorine or bromine in presence of caustic soda, whether hot or cold. Indeed I did not succeed in accomplishing the complete decomposition of the salt by means of chlorine even after many hours' treatment. By using a considerable excess of alkali and digesting with bromine in the cold, then pouring off the supernatant liquid, adding more bromine and gently warming, and repeating this process several times, I succeeded in effecting the complete decomposition of bismuth ferricyanide.

11. These reactions of the two double cyanides with chlorine and bromine may obviously be applied for the analysis of these salts. Bismuth ferrocyanide may be readily analysed by adding a considerable excess of caustic soda, followed by addition of bromine and heating, until the supernatant liquid when poured off from the precipitate and boiled becomes colourless; the precipitate is then collected, washed, and dissolved in sulphuric acid. The solution is divided into two portions; in one iron is determined by means of permanganate, after reduction by zinc; in the other bismuth is separated from iron, as already described, and is determined. The alkaline filtrate (containing bromine) separated from the precipitated iron and bismuth oxides may then be employed for the determination of cyanogen. This determination is most conveniently performed by the use of a standard solution of silver nitrate.

If it be desired to analyse bismuth ferricyanide by a similar process, it is advisable to digest the salt with water and bromine in the cold for some time, then to add caustic soda, to continue the digestion, to pour off the clear liquid, to add more bromine, and finally to gently warm this liquid until the decomposition is complete. The process is more applicable for the analysis of the ferro- than of the ferricyanide of bismuth.

12. Strong nitric acid when added to bismuth ferrocyanide, without warming, quickly causes the formation of bismuth ferricyanide; if the temperature be raised hydrocyanic acid is evolved and the greater part of the salt present passes into solution, evidently, however, only after undergoing decomposition.

13. If bismuth ferricyanide be suspended in water to which sodium amalgam is added the colour of the suspended salt gradually becomes paler, until an almost colourless substance is produced, which, from its general reactions, I have no doubt is bismuth ferrocyanide.

14. The action of chlorine and bromine upon ferro- and ferricyanide of bismuth respectively, as also the action of nitric acid upon the former and of sodium amalgam upon the latter salt, is, I think, in keeping with the general analogies existing between ferro- and ferricyanides. Most probably the first action of the halogens upon the ferrocyanide is to withdraw part of the bismuth with the production of hydroferrocyanic acid and bismuth ferricyanide. Hydroferrocyanic acid, it is well known, readily undergoes decomposition in the air, yielding some form of prussian blue. In the manufacture of ferricyanide of potassium the formation of a green salt is frequently noticed. This green salt, or a salt of analogous composition, would appear to be produced in many of the actions which I have described in the preceding paragraphs.

The decomposition of bismuth ferrocyanide by chlorine in presence of cold water appears at first sight to be more complete than the decomposition of the same salt by chlorine in presence of boiling water. I believe, however, that the apparent anomaly is explained by regarding—as indeed analysis shows that we must regard—the former decomposition as resulting in the production of bismuthyl chloride and hydroferrocyanic acid, while at the high temperature of the second reaction the hydroferrocyanic acid is quickly decomposed with the production of some form of prussian blue which colours the precipitated bismuthyl chloride. The rapid decomposition of the hydroferrocyanic acid produced, with subsequent precipitation of a form of prussian blue, will naturally tend to prevent the action of the chlorine upon the undecomposed ferrocyanide. The blue or green substance produced when chlorine is passed into boiling water in which bismuth ferrocyanide is suspended will therefore probably contain bismuth, ferricyanide, undecomposed ferrocyanide, bismuth oxychloride, and a form of prussian blue.

15. Ferrocyanide and ferricyanide of bismuth when heated in closed crucibles over a Bunsen lamp yield a black-brown mass containing iron, bismuth, carbon, and small quantities of cyanogen.