

the process again resumed by bringing the cooled iron in contact with the electrolyte.

It is necessary to make this change fairly rapidly, as the temperature of the bath must not be allowed to fall much from that at which the electrolysis takes place. From time to time molten calcium chloride is added to the bath and the process may, in this way, be carried on for a considerable length of time.

Under any circumstances it was found that there was a very considerable loss of the metal due either to oxidation or to recombination of it with the chlorine from the anode. Some experiments were therefore tried with a view to preventing this loss. The kathode was so constructed that the iron rod was surrounded with a graphite bell, the rod being insulated by mica bushings from contact with the graphite. The space inclosed by the bell was about 50 cc. and it was thought probable that the calcium would collect in this space out of contact with the air and away from the influence of the chlorine from the anode. It was found, however, that this arrangement did not give good results, probably from the fact that graphite was used as a material for the bell, as short-circuiting took place soon after it was put in operation. As soon as the bell becomes a conductor it merely acts as a large kathode, decreasing the current density at this point to such a degree that good results are impossible.

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## POTASSIUM MERCURIC FERROCYANIDE.

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ON ADDING a solution of potassium ferrocyanide to a solution of mercuric chloride, a yellowish precipitate is at first obtained, which, on standing, turns blue. A qualitative examination of this blue precipitate led me to consider it as potassium mercuric ferrocyanide. On looking into the literature I found no mention of a compound such as I supposed that I had obtained. Kane<sup>1</sup> obtained a compound  $K_4Fe(CN)_6 + 3Hg(CN)_2 + 4H_2O$  by acting upon a hot solution of mercuric cyanide with potassium ferrocyanide. Loewe<sup>2</sup> obtained the same compound by shaking a moderately concentrated solution of potassium

<sup>1</sup> J. pr. Chem. 19, 405.

<sup>2</sup> Jsb. Chem. 1857, p. 273.

ferricyanide with mercury. Bunsen<sup>1</sup> obtained a salt,  $\text{Hg}_2\text{Fe}(\text{CN})_6\text{NH}_3 + \text{H}_2\text{O}$ . Pattison-Muir<sup>2</sup> mentions the fact that when a solution of potassium ferrocyanide is added to a solution of a mercuric or mercurous salt, precipitates of unknown composition are obtained.

In the first attempts to isolate the compound aqueous solutions of both mercuric chloride and potassium ferrocyanide were used, but it was found that on adding the ferrocyanide solution to the mercuric chloride solution at room temperature the precipitate formed would run through the filter-paper. When the precipitation is performed at boiling temperature a more flocculent precipitate is obtained, but the decomposition of the compound formed is also more rapid. The precipitation was then tried in hot solutions in an atmosphere of carbon dioxide. With proper precautions and a specially constructed apparatus this would probably have been successful. But at this time it was found that when an aqueous solution of potassium ferrocyanide is added to a solution of mercuric chloride in an equal mixture of alcohol and ether a heavy precipitate is formed which settled very rapidly at room temperature. An attempt was made to replace the aqueous potassium ferrocyanide solution by solid potassium ferrocyanide, but under these conditions the reaction does not take place. When a solution of potassium ferrocyanide is added to a mixture of alcohol and ether not containing any mercuric chloride, the potassium ferrocyanide will be precipitated. Also, if water is added to an alcohol-ether solution of mercuric chloride a precipitate is obtained. Hence, besides the new compound a great quantity of mercuric chloride and potassium ferrocyanide were precipitated. The method finally employed for obtaining the compound was as follows: Fifteen to 20 grams of mercuric chloride were dissolved in about 100 cc. of a mixture of one volume of absolute alcohol to one volume of ether. Eight to 10 grams of potassium ferrocyanide, finely ground, were dissolved in the least possible quantity of water. This latter solution was poured into the mercuric chloride solution and the precipitate allowed to settle. The supernatant alcohol and ether was filtered through a Buchner funnel and a fresh portion of alcohol and ether poured on the precipitate, and

<sup>1</sup> Pogg. Ann. 34, 139.

<sup>2</sup> Watts' Dict., Vol. 2, p. 335.

the flask shaken. Again the alcohol and ether were decanted. Now cold water was poured on the precipitate, which does not settle so rapidly as at first, probably because the greater part of the mercuric chloride had been removed by the alcohol-ether treatment. The whole precipitate was then transferred to the filter-paper and by means of a filter-pump washed within a few minutes with a liter of water cooled to  $0^{\circ}\text{C}$ . It was again carefully washed with alcohol and ether and dried at  $100^{\circ}\text{C}$ . The compound which was obtained was a fine powder with only a very faint blue tinge.

With the substance thus prepared the analysis was made as follows: One-half gram was dissolved in 5 cc. of nitric acid (sp. gr. 1.4) and 2 cc. sulphuric acid (sp. gr. 1.8). It was boiled until white fumes of sulphuric acid were given off. Water was now added and the solution warmed until everything had dissolved. After cooling, the mercury was precipitated as the sulphide and weighed as such on a weighed filter-paper. In the filtrate, after oxidation, the iron was precipitated as hydroxide and weighed as the oxide.

Another portion of 0.5 gram of the substance was analyzed for potassium in the following manner. The decomposition was affected in the same way as mentioned above with the exception that only 1 cc. of sulphuric acid was added. The containing crucible was heated until all the sulphuric acid had been driven off. After the addition of a few cubic centimeters of hydrochloric acid, heat was again applied. The solution was now transferred to a porcelain dish, the mercury and iron removed as before and the resulting solution evaporated to dryness in a weighed platinum dish. After driving off the ammonium chloride, a few drops of sulphuric acid were added and the dish again heated until the excess of sulphuric acid was removed. Finally the temperature was raised until the platinum dish assumed a dull red color. The potassium was thus determined as the sulphate.

For the determination of the cyanogen, 0.5 gram of the compound was decomposed by boiling with 3 grams of yellow mercuric oxide for half an hour. After filtering off the excess of mercuric oxide, and also the iron hydroxide formed, 50 cc. of an ammoniacal zinc sulphate solution were added to the filtrate. A solution of hydrogen sulphide is now added. A black precipitate of mercuric sulphide first comes down. The ammoniacal zinc

sulphate solution serves as an indicator, as zinc only comes down as the sulphide after all the mercury has been precipitated. The end-point then is indicated when, on a fresh addition of hydrogen sulphide solution to the supernatant solution, a pure white precipitate is obtained. The mixture of mercuric and zinc sulphides is now filtered, an excess of silver nitrate added and the solution acidified with nitric acid. The precipitated silver cyanide is filtered, dried, ignited and the silver weighed. From the quantity of silver found the cyanogen is calculated.

The following results, compared with the theoretical percentages of the elements in the compound  $K_2HgFe(CN)_6$ , agree very closely.

	Found. Per cent.	Calculated. Per cent.
Potassium .....	15.82	15.91
Mercury .....	40.63	40.61
Iron .....	11.45	11.40
Cyanogen.....	31.78	31.81
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	99.68	99.73

There is therefore no doubt that the above formula must be attributed to the compound. Only a few of the chemical properties of the compound were investigated. With hydrochloric acid the compound becomes blue, with formation of Prussian blue, mercuric chloride and hydroferrocyanic acid. A similar reaction occurs more slowly when the compound is boiled with water. When acted upon by sodium hydroxide, ferric hydroxide, mercuric oxide and potassium ferrocyanide were obtained. The compound is not soluble in water, but a solution of potassium ferrocyanide in water dissolves considerable quantities, probably with formation of a more complex compound. An attempt to isolate a similar compound by acting upon a solution of a mercurous salt with a solution of potassium ferrocyanide has not thus far been successful.