

VI. *On the Ferrocyanides.* By R. CORBETT CAMPBELL.
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IT is well known that the yellow prussiate of potash, heated by itself in close vessels, is decomposed into cyanide of potassium, carburet of iron, and nitrogen gas. I have observed that, heated in contact with the air, the products of the decomposition are very different. The cyanide of potassium takes oxygen from the air, and is thereby converted into cyanate of potash, while the cyanide of iron is decomposed, converting the iron into an oxide. The absorption of oxygen is caused by the presence of the cyanide of iron, for cyanide of

potassium, heated by itself in contact with the air, does not become changed into cyanate of potash. I believe that a process for cyanate of potash may be founded on the above observation, preferable to the common one with oxide of manganese; for it has been proved that this oxide is not essential in the process, and it not unfrequently happens that a large quantity of the cyanide of potassium is converted into carbonate of potash. Sometimes also a little manganese dissolves along with the cyanate.

For the preparation of this salt, then, without the use of manganese, the powdered and dried prussiate of potash is heated almost to redness, in a flat iron vessel, with constant stirring of the melted mass. Some ammonia is evolved, which results from the action of the moisture of the air, for the substance itself contains no hydrogen. The melted mass should be taken out with an iron spatula, allowed to cool, reduced to powder, and again fused; because the melting cyanate of potash is apt to protect little bits of the yellow prussiate from the action of the air. If the heating be properly conducted, not a particle of cyanide of potassium will be formed. The cyanate of potash is dissolved out with hot alcohol filtered and crystallized. The undecomposed prussiate of potash remains undissolved.

The double salt of ferroproussiate of potash and lime acts under heat exactly like the ferroproussiate of potash itself. Well dried and set on fire, it continues to burn, until the alkaline and earthy cyanides are converted into cyanates, and the iron into oxide. The reason that the double salt continues to burn is to be found in the porous state of the mass, which offers no obstacle to the free access of air; whereas the yellow prussiate alone fuses, and prevents the progress of the combustion.

The ferrocyanide of zinc, which always contains some ferroproussiate of potash in chemical combination, likewise continues to burn, and affords cyanate of potash and the oxides of the metals.

When the double salt of potash and lime is heated in the air as above mentioned, and then dissolved in water, the solution possesses the remarkable property of becoming pink in the sun's rays, and again becoming colourless in darkness. Neither cyanate of lime nor cyanate of potash, together or singly, or mixed with prussiate of potash, show this reaction. It is hence probable that this solution owes the above-mentioned property to the admixture of some foreign substance, present probably in a very small quantity. All attempts to isolate any such substance were fruitless.

As the shade of colour in the above solution is exactly that of a solution of permanganate of potash, the solution and the substances used were tested for manganese. They contained none. The reactions of this solution too stand in contradiction with some of those of the permanganates. The presence of ferrocyanide of potassium is essential to the production of the pink in the sun's rays, but the action of the same salt on permanganate of potash is first to reduce it to the green manganate, and by further addition of the prussiate to oxide of manganese. As the prussiate of potash of commerce often contains traces of sulphocyanide of potassium, the experiments were repeated with prussiate of potash, that had been washed with hot alcohol, and by this means all sulphocyanide removed; but no difference was observed in the result.

It is further clear, that this salt, even if it were present in the prussiate of potash, could take no part in the above-mentioned reaction, for it gives no precipitate with a lime salt, with or without the presence of prussiate of potash. An alkaline state of the liquid is essential to the production of the pink in the sun's rays; so is likewise the presence of a ferrocyanide. If a solution of nitrate of copper be added to a solution of the heated double salt, till all ferrocyanide be removed, and then the excess of copper precipitated by carbonate of potash, the solution will have lost entirely the property of becoming coloured in the sun's rays, but will recover it on the addition of a few drops of a solution of yellow prussiate of potash.

The air exercises no influence on these changes; they take place equally distinctly in closed vessels.

A temperature of 120° Fahr. destroys the colour, but on cooling and re-exposure to the sun's rays, the colour again appears. By evaporation in the rays of the sun, a pink salt is obtained. The presence of cyanate of potash is not essential to the production of the colour; if muriatic acid be added to the solution until all cyanic acid be destroyed or removed, and then supersaturated with alkali, the solution possesses the colouring property as strong as before. Another proof that cyanate of potash is not essential, is that the double salt of ferroproussiate of lime and potash heated in closed vessels, and dissolved in water, shows likewise the same reaction, although containing no cyanate of potash.

I have already stated, that the investigation undertaken with the view of isolating the colouring substance in these experiments, was without success; nevertheless some observations were made which seem to stand in relation to this subject.

It has often been remarked, that, on adding an acid to the solution of the heated double salt, a minute quantity of a reddish powder is precipitated. This powder contains iron; it is decolorized by carbonate of potash, but the colour is not reproduced by exposure to the sun. The solution from which this powder has been precipitated, on being saturated with alkali, and exposed to the sun's rays, is found not to have lost the colouring property. I suspect that this red powder is the same as is observed to be precipitated from some specimens of commercial prussiate of potash, on the addition of strong acetic acid. Prussiate of potash is sometimes observed in commerce of a darker tint than usual, and it is this variety which frequently shows the above-mentioned reaction.

If a solution of cyanide of ammonium be added to a solution of acetate of copper, a compound of copper and cyanogen is precipitated, not analogous in its composition to the cyanide from which it is precipitated. The supernatant solution becomes pink-coloured for a few seconds. In order to see if this reaction result from the action of the free cyanogen on the cyanide of ammonium, a stream of this gas was sent through a solution of the salt. It became first yellow, and then red, but a different red from that mentioned in the reaction with the copper salt.

Professor Liebig pointed out to me another instance of a fugitive pink colour occurring in a cyanogen compound, which Prof. Gmelin of Heidelberg has mentioned in his *System of Chemistry*. When strong nitric acid is added to pounded yellow prussiate of potash, and slightly heated, much cyanogen gas is evolved; when the heat is not too strongly applied, neither prussic acid nor nitrous acid are remarked. The mass becomes black, and is quite soluble in water: if there be added to this solution, first, an excess of potash, and then some drops of sulphuret of potassium, the solution becomes beautifully pink-coloured, disappearing after the lapse of a few seconds.

It differs from the pink colour observed as occurring in the solution of the heated double salt when exposed to the sun, in its action to sulphuretted hydrogen. This gas, or an alkaline sulphuret, instantly destroys the colour resulting from the action of light, while an alkaline sulphuret is essential to the production of the other. The pink colour of the solution to which sulphuret of potassium has been added, becomes soon purple, and afterwards deposits a blue substance, which long kept in the solution becomes white. This blue precipitate cannot be prussian blue, for it is produced in an alkaline solution, and is instantly decolorized by acids. It is possible that

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the above pink solution owes its colour to the same substance as is present in Gregory's solution of sulphuret of azote in caustic potash.

I have brought forward these different instances of coloration occurring in cyanogen compounds, because they seem to point out the existence of a yet unexamined class of prussiates.

On the Acid Cyanurate of Potash.

Mineral acids, as well as acetic acid, were found to have the power of converting the neutral cyanate of potash into the acid cyanurate. The essential circumstance in this process is that the solution of the cyanate of potash be concentrated. The process above described for making cyanate of potash by calcining in the air the yellow prussiate of potash, affords a ready means of making this salt easily, and in quantity. The roasted prussiate is digested with cold water, filtered, and muriatic acid, added to the precipitated salt, is dissolved in hot water, and crystallized by cooling.

The foregoing experiments were partly confirmed and partly originally performed in the laboratory at Giessen, in 1838.

This paper is the only scientific memorial of its amiable author, who died about two years ago, at an early age, but mature enough to have endeared him to many men of science, and to have indicated promise of scientific eminence. He will be most remembered by his friends for a marked rectitude of mind, combined with an uncommon ardour; evincing itself in the warmth of kindly feelings and in the enthusiasm of scientific pursuits.—T. C.