LXIII.—*The Composition of Prussian Blue and Turnbull's Blue.*

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We are indebted to Dr. Williamson for the most satisfactory preparation and analyses of these two compounds. On his authority, the two substances are generally regarded as dissimilar in composition, and are respectively designated by the formulæ Fe_7Cy_{18} and Fe_5Cy_{12} (*Mem. Chem. Soc.*, **3**, 125). It has, however, been conjectured by Reindel (*J. pr. Chem.*, **102**, 38) and others that these two compounds are identical. This view has been based on the oxidising power of ferricyanide of potassium on the one hand and the reducing power of ferrocyanide of potassium on the other, either of which might account for the supposed identity in composition.

Thus, we might have—

$$2K_3Fe'''Cy_6 + 3FeCl_2 + H_2O = 2HK_3Fe''Cy_6 + FeO + Fe_2Cl_6$$
$$= Fe'''_2Fe''(Fe''Cy_6)_2 + H_2O + 6KCl,$$

and

$$\begin{cases} 2K_4Fe''Cy_6 + Fe_2Cl_6 = Fe'''_2K_2(Fe''Cy_6)_2 + 6KCl \\ Fe'''_2K_2(Fe''Cy_6)_2 + FeCl_2 = Fe'''_2Fe''(Fe''Cy_6)_2 + 2KCl, \end{cases}$$

while, on the other hand—

$$2K_4Fe''Cy_6 + Fe_2Cl_6 + FeCl_2 = 2K_3Fe'''Cy_6 + 3FeCl_2 + 2KCl$$
$$= Fe''_3(Fe'''Cy_6)_2 + 8KCl,$$

the action of the ferrous salt on the ferricyanide being a case of double decomposition.

Skraup has shown (*Annalen*, **186**, 371) that soluble Prussian blue, $Fe'''_2K_2(Fe''Cy_6)_2$, may be prepared either by the action of a ferrous salt on ferricyanide of potassium or by the action of a ferric salt on ferrocyanide of potassium, and that the two compounds so obtained are identical. He also states that by the action of a ferrous salt on this compound (soluble blue), Turnbull's blue, Fe_5Cy_{12}, is obtained, and by the action of a ferric salt Prussian blue, Fe_7Cy_{18}, is produced. But with regard to the latter, the analysis he gives, though nearer the formula Fe_7Cy_{18} than Fe_5Cy_{12}, is yet so different as to be almost valueless. Thus he finds a percentage of Fe = 32·85 per cent., of C = 20·33 per cent. This gives the ratio of Fe : C as 1·61 : 1—whereas the formula Fe_7Cy_{18} demands 1·81 : 1. He further states that whether the compound Fe_5Cy_{12} or Fe_7Cy_{18}, is formed in the manufacture of Prussian blue depends entirely on the amount of oxidising agents present. Skraup also studied the conditions under which oxidation and reduction respectively took place when the double cyanides of

iron and potassium were mixed with iron oxides (or hydrates). He found that ferric hydrate was speedily reduced by ferrocyanide of potassium to ferroso-ferric hydrate at the ordinary temperature. If, therefore, a corresponding reduction takes place when an iron salt is used instead of the hydrate—we should have a mixture of ferric and ferrous salts which would be in the proportion necessary (according to the equations already given). It was therefore of interest to see whether or no these two compounds would prove to be identical when prepared under like conditions, and when all precautions were taken to prevent oxidation. The method adopted was as follows: Prussian blue was made by the action of ferric chloride on hydroferrocyanic acid. The acid was prepared by the action of dilute sulphuric acid on lead ferrocyanide, as by this means the whole experiment of making the Prussian blue could be effected at one operation. The water in which the lead ferrocyanide was suspended had by long-continued boiling been freed from air, and the dilute acid was also similarly freed from air. The experiment was conducted in an atmosphere of carbon dioxide, and carried on in the cold throughout. The precipitate of Prussian blue, after being washed by decantation, was thrown on to a filter, thoroughly washed, and then dried over sulphuric acid in a vacuum. The substance was tested, and found to be quite free from alkali. Analyses gave the following results:—

I.
0·3838 gram gave 0·2773 CO_2 = 19·71 per cent. C.
0·3857 ,, ,, 0·2797 CO_2 = 19·78 ,, C.
0·7695 ,, ,, 0·3915 Fe_2O_3 = 35·63 ,, Fe.
This gives ratio of Fe to C as 1·80 : 1.

II.
0·3563 gram gave 0·2574 CO_2 = 19·70 per cent. C.
0·3583 ,, ,, 0·2583 CO_2 = 19·66 ,, C.
0·7146 ,, ,, 0·3654 Fe_2O_3 = 35·79 ,, Fe.
This gives ratio of Fe to C as 1·82 : 1.

Taking the mean of these analyses, we get the ratio of Fe : C as 1·81 : 1, which is exactly what is required by the formula Fe_7Cy_{18}. (I) and (II) were from the same preparation, but in slightly different states of hydration.

Turnbull's blue was prepared in a manner exactly similar by acting on ferrous sulphate with hydroferricyanic acid. The acid was prepared from lead ferricyanide by decomposing a saturated solution of it with sulphuric acid. Precisely similar precautions were taken as in the case of Prussian blue. Analysis showed—

I.
0·3553 gram gave 0·2349 CO_2 = 18·00 per cent. C.
0·3540 ,, ,, 0·2347 CO_2 = 18·01 ,, C.
0·7093 ,, ,, 0·3505 Fe_2O_3 = 34·59 ,, Fe.
This gives the proportion of Fe to C as 1·92 : 1.

II. { 0·3286 gram gave 0·2160 CO_2 = 17·93 per cent. C.
0·3334 „ „ 0·2190 CO_2 = 17·91 „ C.
0·6620 „ „ 0·3267 Fe_2O_3 = 34·54 „ Fe.

This gives the ratio of Fe : C as 1·93 : 1.

Taking the mean result, we get the ratio of Fe to C as 1·93 : 1. The ratio required for the formula Fe_5Cy_{12} is 1·94 : 1.

(I) and (II) were not exactly in the same state of hydration.

These results, then, clearly show that the formulæ given by Williamson are correct, and that the two blues are not identical in composition. The water present in the compound has not been included in the formula, because no particular stage of hydration was accompanied by any characteristic physical properties. In well-dried samples, the amount in Prussian blue was about 22 per cent., corresponding approximately with the formula $Fe_7Cy_{18},14H_2O$; in Turnbull's blue about 26 per cent., corresponding with about $Fe_5Cy_{12},12H_2O$—but in neither case were the results more than approximate.

In estimating the iron, the fixed residue, after ignition, was dissolved in strong hydrochloric acid (with a little nitric acid), and precipitated by ammonia. The fixed residue in similar analyses has often been erroneously regarded as ferric oxide, but I found that in one case 0·3162 gram fixed residue yielded 0·3268 gram ferric oxide. It will, therefore, be readily seen that results obtained by regarding the fixed residue as ferric oxide would be valueless when considering two substances so nearly alike in composition as these two blues.