

XXIV. *On the Nitroprussides, a New Class of Salts.**By Dr. LYON PLAYFAIR, F.R.S., F.C.S.*

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1. IN an inquiry into the constitution of the prussides, I found it necessary to examine into the somewhat anomalous action of nitric acid on the yellow prusside of potassium. This examination has led to the discovery of a singular class of compounds, which form the subject of the present memoir.

The previous knowledge on the action of nitric acid on the prussides may be summed up very briefly. THOMSON* examined the gases produced during the action, and recognized them to be nitrogen, cyanogen, nitric oxide, and carbonic acid, while the residue was believed to consist of perntrate of iron and nitrate of potash. DOBEREINER† remarked that previous to the complete decomposition of the prussides, a strong coffee-coloured liquid was produced, which, after neutralization, precipitated protosalts of iron of a dark blue colour. GMELIN‡, to whom chemistry was already indebted for important discoveries in the prussides, observed that the coffee-coloured liquid noticed by DOBEREINER was rendered of a magnificent purple or blue colour on the addition of an alkaline sulphide. The same fact was noted by Mr. MERCER§ of Oakenshaw, without his being aware that it had already been remarked by GMELIN. CAMPBELL||, in repeating GMELIN's experiment, threw out the intelligent suggestion that the purple colour might be due to the production of a sulphuret of nitrogen, which GREGORY¶ had already remarked produced an amethystine colour when mixed with an alcoholic solution of potash. SMEE**, in an examination of the action of nitric acid on the prussides, observes that ferridcyanide is produced, nitric oxide being evolved.

I am not aware of any further knowledge on this subject; and as it is far from being sufficiently extended, a new examination was desirable.

2. When dissolved ferrocyanide of potassium is digested with diluted nitric acid, a coffee-coloured liquid is produced, having the characters ascribed to it by DOBEREINER and GMELIN. The addition of this acid solution to sulphide of potassium dissolved in water causes a precipitation of sulphur and the production of various colours, from a pink to a violet or blue shade. When the acid liquid is neutralized with potash, it

* As quoted by GMELIN, Handbuch, Band iv. s. 370.

† SCHW. J. xxvi. p. 305.

‡ Ann. Pharm. Bd. xxviii. s. 57, and Memoirs of Chem. Soc. vol. i. p. 41.

§ Unpublished Letter.

|| Handbuch, B. i. s. 167.

¶ TURNER'S Chemistry, p. 343.

** Phil. Mag. xvii. 194.

immediately produces the most intense purple coloration with a soluble sulphide*. The action of nitric acid on the pounded salt is similar, but much more violent than that experienced with the solution. Nitric oxide is at first evolved, but it soon ceases if the mixture be kept cool, and it is followed by the copious escape of cyanogen gas, accompanied by hydrocyanic acid, and a gas of peculiar pungency, apparently hydrated cyanic acid; more or less nitrogen and carbonic acid are also found in the escaping gases. The dark red solution remaining after the action, deposits, on cooling, abundance of nitrate of potash, and, under the most favourable circumstances, about 5 per cent. of a peculiar *white substance*, afterwards to be described. The red-coloured solution now precipitates protosalts of iron of a dark blue colour, or if it has been heated for a short time, or even stood in the cold for some days, of a dark green, and sometimes of a slate colour. A dark green precipitate is also produced on the addition of salts of copper. The same precipitates are obtained from the neutralized as from the acid solution. Such were the preliminary observations made on repeating DOBEREINER'S experiment.

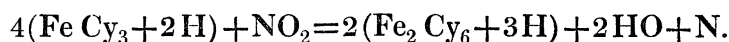
One important fact was observed in this preliminary trial, viz. that nitric oxide disappeared during the action, and in fact only occurred when the transformation was so violent as to escape control. This gas was therefore probably one important cause of the change, and it therefore became necessary to examine its action on the cyanides, as a more simple means of eliciting its mode of action.

3. The first obvious experiment was to ascertain whether cyanide of potassium charged with nitric oxide would produce prussides exerting the remarkable colouring action on the sulphides. Nitric oxide is in fact readily absorbed by cyanide of potassium, the solution becoming red-coloured and depositing a black substance resembling paracyanogen. This red-coloured solution did not of itself give any colour when mixed with a sulphide. It was now converted into a prusside by the addition of protosulphate of iron. The resulting prusside was now found to strike a magnificent purple colour with a soluble sulphide. The same coloration was obtained when a prusside was made from common cyanide of potassium added to a solution of protosulphate of iron, through which nitric oxide had been passed. It was obvious from these experiments that nitric oxide was one of the great causes of the change experienced by the prusside.

4. The action of nitric oxide on the prussides themselves was now examined. It was found that nitric oxide could be passed through a solution of ferrocyanide of potassium without producing any sensible change. But when the prusside was mixed with sufficient acid to take up its alkaline base, it was now found that nitric oxide was freely absorbed by this mixture when heated, though not in the cold; and that

* The intensity and beauty of this coloration render the nitroprussides the most sensible of all tests for the presence of the minutest trace of a soluble sulphide. The presence of quantities insensible to ordinary tests is at once strongly exhibited by the use of this colouring agent.

the resulting liquid exhibited the strong coloration with sulphides. Ferrocyanide of lead, or any other ferrocyanide, gave, when mixed with strong acids, a similar result. It was therefore obvious that the peculiar compound might be obtained from pure hydroferrocyanic acid. The latter acid was prepared from prusside of lead by sulphuretted hydrogen, the excess of the latter being removed by the addition of a little more lead salt. The filtered ferrocyanic acid was found to suffer no change when exposed to the action of nitric oxide in the cold; but when the solution was kept in a water-bath and the gas led through it, a change was observed. This, however, at first merely consisted in the transformation of ferrocyanic to ferridcyanic acid,—

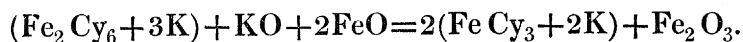


Until this change was completed not the least coloration took place on mixing the acid liquid with a sulphide. When, however, the acid no longer gave prussian blue with perchloride of iron, it began to assume a red colour, continuing to evolve a gas, and it now exhibited, after neutralization, the peculiar coloration with sulphides. It now gave a blue precipitate with protosulphate of iron, like ordinary ferridcyanic acid. This blue precipitate became paler in colour as the gas continued to stream through the hot solution, until finally the addition of the iron salt gave a precipitate of a *clear salmon colour*. Here then was the acid* of the new compounds, and its salts were obtained by neutralization with the respective bases. This process was a great step in the inquiry, because it enabled the distinctive characters of the nitroprussides to be determined. At the same time it was not fitted to procure the salts in sufficiently large quantities for examination. By showing however what was to be looked for, it enabled a more complete examination to be made of the products of oxidation of the prussides by nitric acid, with a view to the separation of the nitroprussides from the ferridcyanides, with which they were obviously mixed.

5. It was observed that the oxidized prusside required a very small quantity of protosulphate of iron for its complete precipitation. One double equivalent of ferrocyanide of potassium ($\text{Fe}_2 \text{Cy}_6 + 4\text{K}$) was oxidized with 3 equivs. of nitric acid diluted with its own volume of water. The dark red, almost black liquid, was diluted with water and treated with a known quantity of sulphate of iron dissolved in water. Prussian blue was formed, but it remained in *solution*, forming a dark blue soluble fluid, of great beauty and intensity. When the added sulphate of iron amounted to one equivalent, that is to one-fourth of the potassium originally in the prusside, the prussian blue became insoluble and was thrown on a filter and washed. It was obvious from this experiment that there must be a potassium salt in combination with the prussian blue, because the quantity of iron salt added was quite insufficient to unite with the iron and cyanogen of the radical. This idea was confirmed by

* On neutralizing this nitroprussic acid with carbonates, the resulting salts were found to be accompanied by a nitrate, although the nitric oxide had previously been passed through water in a washing-bottle.

finding that 2 equivs. of sulphate of copper were required to effect the precipitation, which 1 equiv. of sulphate of iron had effectually done. To separate the potassium salt present in the latter case, the precipitated prussian blue, after being washed with cold water, was mixed with water and boiled. The whole was now thrown on a filter, and a solution of a fine ruby-red colour passed through. This solution gave a salmon-coloured precipitate with a protosalt of iron. This precipitate does not readily occur in an acid liquid, and hence the addition of the iron salt to the original oxidized solution does not effect a complete precipitation, the filtrate from it being yellow from dissolved nitroprusside of iron. There being always some nitroprusside of iron along with the prussian blue, the simple treatment with hot water does not wholly economise the products, as it only separates the salt of potassium. The mixture may therefore be decomposed by caustic potash, which, added in sufficient quantity, forms peroxide of iron, and ferrocyanide instead of ferridcyanide,—



The ferrocyanide may now be separated from the nitroprusside, either by precipitation by alcohol, or by the addition of nitrate of lead. These plans were not however so advantageous as the simple means of separation given above. That method was followed for some time until the examination of the nitroprussides threw some light on their properties and composition; it was then found that a process yielding a much larger product of the new compound, might be invented. The following study was therefore made of the products arising from the oxidation of the prussides by nitric acid. The knowledge thus obtained led, as was expected, to a very economical and simple means of obtaining the nitroprussides in large quantities.

6. As nitric oxide was one of the most important means of producing the conversion of prussides into nitroprussides, it was necessary to operate so as to prevent its escape. This was done by keeping the mixture of acid and prusside well-cooled at the first part of the action. Nitric oxide is almost always evolved at first, but it soon diminishes to nothing as the action proceeds. A copious evolution of gas takes place. The escaping gas burns with the characteristic purple flame of cyanogen. Led through protosulphate of iron, after the first violent action has ceased, no blackening is perceived, so that nitric oxide has ceased to be evolved. Led into caustic barytes, carbonate of barytes is precipitated, and the solution is found to contain cyanide of barium and cyanate of barytes. When the gas is collected over mercury and potash is thrown into the tube containing it, a portion of gas still remains unabsorbed and is easily recognized as nitrogen. When the escaping gas is led into water it is dissolved in considerable quantity, and the water now smells strongly of cyanogen and of a peculiar pungent gas, which appears to be hydrated cyanic acid. The gas treated with ammonia deposits azulmic acid, and the usual products of the transformation of cyanogen. The following process is found best adapted for the

preparation of the nitroprusside. Nitric acid of commerce is diluted with its own bulk of water, and the quantity of it necessary to neutralize 53.3 grs. of carbonate of soda (1 equiv.) is ascertained by the alkalimeter. This quantity denotes 1 equiv. of acid.

Ferrocyanide of potassium is now reduced to powder and is placed in a convenient vessel, and for every 422 grs. of the salt used (that is for 1 equiv. $\text{Fe}_2\text{Cy}_6\text{4K}+6\text{HO}$) 5 equivs. of the acid are employed. This quantity of acid is found to produce an economical result, but it is very remarkable that one-fifth of the quantity, or 1 equiv., is sufficient to convert a large portion of the prusside into nitroprusside. This is the more remarkable, because there are four available equivalents of potassium, and it was to be expected that nitrate of potash would be produced. This however is not the case, 1 equiv. of nitric acid effecting oxidation to a considerable extent on a double equivalent of yellow prusside. The five equivalents of acid mentioned above are at once poured on the prusside, as the cooling effect of the whole reduces the violence of the action. The mixture assumes a milky appearance, but soon the salt dissolves with a brownish-red colour like coffee, the mixture of gases already described being freely evolved. When the solution is complete, it is found to contain ferridcyanide of potassium mixed with a nitroprusside and nitrate of potash. It is now removed into a bolt-head and digested in the water-bath. It continues to evolve gas, and after a time it no longer yields prussian blue with sulphate of iron, but forms a dark green or a slate-coloured precipitate. The solution is now removed from the water-bath and is allowed to cool, during which abundance of nitrate of potash crystallizes out, and always more or less of a peculiar white substance. The dark coffee-coloured mother-liquor is now neutralized with carbonate of soda or carbonate of potash, according as salts of sodium or potassium are desired. The neutralized solution shows the presence of iron existing as a base, for prussian blue is precipitated on the addition of a prusside. The neutral solution is now boiled, and it deposits generally a green precipitate, though occasionally one of a brown colour; and the filtrate is found to be of a dark ruby-red, containing only nitroprusside of the base employed and a nitrate. The latter is separated by crystallization in the manner pointed out under the respective salts. Nitroprusside of sodium being most easily prepared, is recommended as the product of the process here given.

Some practical difficulties may be mentioned so as to prevent disappointment in the preparation. A carbonate of and not the caustic alkali should be employed in the neutralization. When the latter is used, the solution of nitroprusside is apt to be mixed with ferrocyanide. When this takes place an addition of acid serves to remove the impurity, as some of the precipitated oxide of iron is dissolved, and forming prussian blue with the ferrocyanide, removes it from the solution. This impurity may also be removed by the addition of nitrate of lead, which precipitates the prusside but not the nitroprusside; or it may be taken away by the gradual addition of

sulphate of iron, which removes the ferrocyanide before precipitating the nitroprusside. When the quantity last added precipitates the solution of a salmon colour, the impurity has been removed*.

Red prusside (ferridcyanide) of potassium may be used in the preparation exactly as described for the yellow prusside.

7. The following experiments were made in order to ascertain approximately how much nitroprusside was formed by the process now described. 105·5 grs. crystallized ferrocyanide of potassium were digested with $1\frac{1}{2}$ equiv. of nitric acid. After digestion the liquid was neutralized with carbonate of soda and boiled, the resulting green precipitate being collected on a weighed filter. The filtrate was precipitated by a salt of copper, and the nitroprusside of copper was collected and weighed.

It was found by various trials that perfectly uniform results could not be obtained, the amount and even the composition of the precipitate† on boiling varying with the conditions of the preparation. The two following experiments may be taken as giving mean results:—

I. 105·5 grs. yellow prusside gave 8·275 green precipitate, yielding on incineration 7·95 grs. peroxide of iron; the filtrate gave 48·90 grs. nitroprusside of copper.

II. 105·5 grs. yellow prusside gave 8·32 grs. green precipitate, yielding by calculation 6·30 grs. peroxide of iron; the filtrate gave 46·12 grs. nitroprusside of copper.

Taking the mean of the two experiments, 105·5 grs., or one-fourth of the double equivalent of yellow prusside, yield 8·297 grs. green precipitate containing 4·984 grs. iron; the filtrate yields 47·51 grs. nitroprusside of copper. But before drawing deductions, it is necessary to know the composition of the green precipitate. It consists of a mixture of prussian blue, nitroprusside and peroxide of iron, this mixture not being constant. However, to take a special case as an example,—

22·26 grs., calcined and treated with nitrate of ammonia, gave 13·62 grs. peroxide of iron, or 42·83 per cent. of metallic iron.

9·49 grs. burned with oxide of copper, gave 4·13 grs. carbonic acid and 0·96 gr. water; the carbon is therefore 11·87 per cent., the water 10·11.

35·02 grs. treated by caustic potash, gave, when neutralized by acetic acid, a red

* It is perhaps needless to remark, that when the ruby-red solution free from prussides has been obtained by any of the processes above described, it may be used at once for the precipitation of the insoluble nitroprussides.

† The composition of the precipitates varies considerably. If on neutralizing the acid solution an excess of alkali be added, the addition of an acid gives a slaty precipitate, which consists mainly of oxide of iron mixed with prussian blue. Under somewhat similar conditions, I believe, though on this subject I am not certain, the precipitate on boiling, instead of being green, is brown, like oxide of iron. On washing and exposure to the air it becomes green.

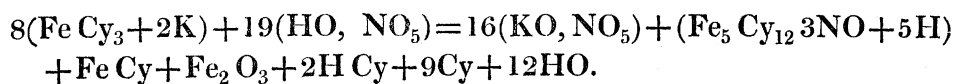
In an experiment where this precipitate came, 105·5 grs. yellow prusside gave 5·83 grs. of a brown precipitate, and 50·66 grs. of nitroprusside of copper. In another experiment with a like quantity, 4·755 grs. of the brown precipitate were obtained.

filtrate, from which the ferrocyanide of potassium was precipitated by alcohol; the filtrate from this had all the properties of nitroprusside of potassium, and gave by precipitation with sulphate of copper 13·98 grs. nitroprusside of copper, equal to 13·24 grs. nitroprusside of iron, or 37·80 per cent.

The reactions in the preparation of the nitroprusside may now be approximatively explained.

By reference to the ascertained composition of the nitroprussides, it will be seen that the 47·51 grs. of the copper nitroprusside obtained from the 105·5 grs. of yellow prusside, are equal to 35·69 grs. anhydrous nitroprussic acid: this quantity contains 9·66 grs. of iron. Now 14 grs. iron were present in the yellow prusside used, so that about two-thirds of the iron have been converted into nitroprussic acid. The other third is in the green precipitate, which was found to contain 4·98 iron; if it had been one-third it should have been 4·66; of this quantity 1·19 is as nitroprusside of iron, and therefore 0·59 as nitroprussic acid. Hence we have out of the 14 grs. iron present in the ferrocyanide 10·25 grs. converted into nitroprussic acid, or very nearly three-fourths; the remaining one-fourth is partly as prussian blue and oxide of iron, and partly as the basic iron in the nitroprusside of iron.

The quantity of carbon or of cyanogen converted into nitroprusside has now to be examined. The 47·51 grs. copper nitroprusside contain 9·93 grs. of carbon, that in the nitroprusside of iron of the green precipitate would amount to 0·60, hence the carbon converted into nitroprussic acid is 10·53. There were 3 equivs. or 18 grs. of carbon in the yellow prusside, of which about $1\frac{3}{4}$ equiv. has been converted into nitroprusside; of the remaining $7\frac{1}{2}$ grs. carbon or 16·2 grs. cyanogen, about 0·38 gr. carbon or 0·823 gr. cyanogen remain in the green precipitate as a cyanide, the remainder escaping as a gas. It is true that the results here given only form a rude approximation, but they denote sufficiently the final, though not all the intermediate changes which occur; the ultimate action may be expressed by the following equation:—



Thus 8 equivs. ferrocyanide of potassium lose their potash by 16 equivs. of nitric acid, and the hydroferrocyanic acid formed is oxidized at the expense of 3 equivs. nitric acid, the 3 equivs. of nitrous oxide thus formed entering into the constitution of nitroprussic acid, 12 equivs. of water being formed by the oxidation. Of the cyanogen, 12 equivs. remain in the nitroprussic acid, 2 equivs. escape as hydrocyanic acid, 9 equivs. as cyanogen, and 1 equiv. remains united with iron as a cyanide. This scheme would require 10·04 grs. of the iron experimented on to be converted into nitroprussic acid, and direct experiment gave 10·2 grs. We should indeed find 1·8 gr. cyanogen in the cyanide of iron*, whereas only 0·823 gr. cyanogen was found

* The empirical formula Fe Cy represents the actual proportion of iron and cyanogen in certain prussian blues, although the elements are not arranged according to this simple expression.

in this state; but when we consider the small quantity present and the variable nature of prussian blues, such a discordance is not fatal to the correctness of an explanation, which is only given as an approximation.

8. It has already been mentioned that carbonic acid was one of the products evolved as a gas. This acid scarcely appears at all when the quantity of nitric acid used is only 1 equiv. for every 4 equivs. of potassium in the prusside. On the contrary, it is a very marked product when 5 equivs. are employed. Precisely under the same circumstances that the carbonic acid is least in quantity, does the peculiar white substance, already referred to, augment, and when the carbonic acid is greatest, as when five equivalents of nitric acid are used, then scarcely any of the white substance is observed. The carbonic acid is therefore obviously a product of the oxidation of the white substance. Five per cent. of the white substance were obtained when one equivalent of nitric acid was used to oxidize an amount of yellow prusside containing 4 equivs. of potassium; to ensure this, the largest quantity obtained by experiment, the action of the acid on the prusside must be as subdued as possible. The white substance is found with the nitrate of potash, which has deposited from the oxidized liquid, and is separated from it by the solution of the latter in water. The white substance is scarcely at all soluble in cold water, and therefore may be collected and purified by repeated solutions in boiling water, in which it is only very sparingly soluble, and deposits itself, on cooling of the solution, as a white crystalline precipitate. It may also be sublimed without change between two watch-glasses. The following analyses of this white substance show its composition. Analyses I. II. were made upon a specimen purified by sublimation; III. IV. upon a specimen purified by solution.

- I. 5.05 grs. gave 5.004 grs. carbonic acid and 2.094 grs. water.
- II. 7.835 grs. gave 7.850 grs. carbonic acid and 3.236 grs. water.
- III. 5.947 grs. gave 5.95 grs. carbonic acid and 2.46 grs. water.
- IV. 6.992 grs. gave 6.95 grs. carbonic acid and 2.886 grs. water.

The nitrogen analyses were made by WILL and VARRENTRAPP'S plan, the portions used in analysis being in one case purified by sublimation and in the other by solution:

- 4.345 grs. gave 21.835 grs. platinum salt.
- 7.027 grs. gave 35.74 grs. platinum salt.

	Purified by sublimation.		Purified by solution.				Calculated.
Carbon	27.024	27.324	27.255	27.108	2	12	27.27
Nitrogen	31.583	31.583	31.961	31.961	1	14	31.81
Hydrogen	4.607	4.589	4.594	4.586	2	2	4.54
Oxygen	36.786	36.584	36.190	36.345	2	16	36.38
	<u>100.000</u>	<u>100.000</u>	<u>100.000</u>	<u>100.000</u>			<u>100.00</u>

The carbon is to the nitrogen as 2 : 1, or in the same proportion as cyanogen. In

fact the formula $Cy+2HO$ correctly represents the composition, and the substance may be supposed to be formed by the union of cyanogen in its nascent state with 2 equivs. of water. When this white substance is treated with acids, it is converted into oxalic acid and ammonia. This fact, together with the analysis, proves it to be OXAMIDE*. Its occurrence in a process of oxidation is very surprising, and perhaps may throw some doubts on the theoretical composition ascribed to it, $2CO+NH_2$. There is little doubt that this substance is the same as that observed by VAUQUELIN† in a watery solution of cyanogen, which however was not analysed by him. The description which he gives applies closely to oxamide. WÖHLER‡ also observed two substances in a watery solution of cyanogen, one of which may be this body. The appearance of carbonic acid is now explained, as it is obviously due to an oxidation of the oxalic acid produced by the transformation of the oxamide.

SECTION II.—*General remarks on the Nitroprussides.*

9. The nitroprussides are salts with characters so decided, that they cannot be confounded with any known series of compounds. They are generally highly coloured—the salts of potassium, ammonium, sodium, barium, calcium and lead being of a dark red or ruby colour; they are readily soluble in water, and communicate a dark red colour to the solution. Alcohol does not precipitate these salts from their solutions. The soluble nitroprussides crystallize readily, yielding large and well-defined crystals. The nitroprussides of copper, zinc, iron, nickel, cobalt and silver, are either wholly or nearly insoluble.

The following Table exhibits some of the characteristic reactions of a soluble nitroprusside:—

Reagents.	Behaviour of the nitroprusside.
Sulphides of the alkaline metals	Magnificent transitory purple colour.
Sulphuretted hydrogen	Produces prussian blue, a prusside and peculiar compound.
Neutral salts of lead	No change.
Basic salts of lead	White precipitate, after a time in strong solution.
Persalts of mercury	No change.
Proto- and persalts of tin	No change.
Salts of zinc	Light salmon-coloured precipitate.
Salts of copper	Light green precipitate.
Salts of nickel	Dirty white precipitate.
Salts of cobalt	Flesh-coloured precipitate.
Protosalts of iron	Salmon-coloured precipitate.
Persalts of iron	No change.
Caustic alkalies	Turn the red coloured solutions of an orange colour.

The beautiful colour immediately produced on the addition of a soluble sulphide, is a most marked character of the nitroprussides. This purple coloration is most in-

* In the descriptions of oxamide, it is usual to state that all acids convert it into oxalic acid and ammonia. It is however very readily soluble in concentrated sulphuric acid, from which it is again precipitated unchanged by the addition of water.

† Ann. de Chim. et de Phys. ix. 113; xxii. 132.

‡ Pogg. Ann. xv. 627.

tense, and enables the detection of the most minute quantity of either reagent. As a test for the presence of sulphides it is wonderfully useful, enabling minute quantities of them to be found in circumstances where the ordinary means of testing altogether fails to denote their presence. This purple coloration is however only transitory, the compound soon breaking up into various substances, among which, hydrocyanic acid, ammonia, nitrogen, oxide of iron, a ferrocyanide, a sulphocyanide and a hyponitrite may be recognized.

The soluble nitroprussides are decomposed when sulphuretted hydrogen is passed through them, oxide of iron, prussian blue, sulphur, a ferrocyanide, and a peculiar sulphur compound being among the products of decomposition.

The alkalies decompose the soluble nitroprussides when their solutions are mixed together and boiled. The products of the transformation in this case are oxide of iron, nitrogen, a ferrocyanide and a hyponitrite. An excess of ammonia, even in the cold, gradually decomposes the nitroprussides, nitrogen gas being evolved, and a peculiar uncrystallizable black compound remains as the result of the decomposition.

Sulphurous acid, the sulphites and hyposulphites exert no apparent action on the nitroprussides. They are however wholly decomposed by boiling them with concentrated sulphuric acid; during this decomposition, the peculiar purple colour due to sulphides is observed.

Chlorine does not produce any change when passed through solutions of the nitroprussides.

Prussian blue dissolves in an excess of some of the nitroprussides, forming a beautiful blue solution; when the prussian blue is in excess, it is able, under certain circumstances (see § 5), to remove the soluble nitroprusside from solution, but it again yields it up to boiling though not to cold water.

Some of the nitroprussides are very permanent and suffer no change in solution, either by exposure to the air or by the action of heat. Several, on the contrary, especially nitroprussic acid, the nitroprussides of barium, calcium and ammonium, decompose partially, either when their solutions are long kept, or speedily when they are boiled. Some of the products of decomposition are dissolved by the still undecomposed nitroprusside, and cannot be again separated from them by crystallization.

After this general idea of the habits of the nitroprussides, their individual salts and their transformations may be more easily studied.

Nitroprussic Acid.

10. This acid may be obtained in solution by decomposing nitroprusside of silver with an equivalent quantity of hydrochloric acid, or by precipitating nitroprusside of barium with an equivalent quantity of sulphuric acid. It may also be obtained, but in a less pure state, by precipitating nitroprusside of potassium dissolved in a small quantity of water, and diluted with several times its volume of alcohol, with an alco-

holic solution of tartaric acid, the quantity of the latter being just sufficient to form bitartrate of potash with the potassium; but as the acid dissolves some of the latter salt, this process does not yield a pure product.

A dark red-coloured solution, strongly acid, is obtained by these methods. Ether does not precipitate the acid as it does ferrocyanic acid. Soon however the solution begins to form hydrocyanic acid, and either to deposit oxide of iron or to hold iron in solution, which may be detected by a prusside. When this change has taken place, evaporation *in vacuo* over sulphuric acid yields crystals of the acid, which is however found to contain a small quantity of an impurity, probably of a cyanide of iron, which cannot be separated by crystallization, or any other of the numerous methods tried. The amount of this impurity is from 2 to 3 per cent. This crystalline acid belongs to the oblique system, and its crystals are described and measured in a further part of this paper, together with its analyses. It possesses all the properties of nitroprussic acid, and only differs by containing this small quantity of impurity. The perfectly pure acid in crystals has not been obtained, notwithstanding very many efforts to obtain this desirable result. *Vide* page 499.

Nitroprusside of Sodium.

11. This salt is the most readily procured, in a crystallized state, of all the nitroprussides; it may be obtained by decomposing the nitroprussides of copper or iron by means of soda, filtering from the oxides of these metals and evaporating the solution by a gentle heat. When prepared from the iron salt, it is apt to contain a little iron in excess.

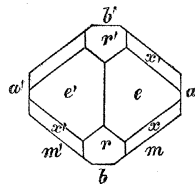
Nitroprusside of sodium is however most easily prepared in the following manner:—1 equiv. of yellow prusside of potassium is digested with 5 equivs. nitric acid, as described in page 481, until the solution precipitates salts of protoxide of iron of a slate colour. It is now neutralized with carbonate of soda, both solutions being employed cold. The neutralized liquid is now boiled, and the green precipitate is separated by filtration from the dark red-coloured solution. This is now evaporated down and again filtered from a brown precipitate which falls during evaporation. The nitrates of soda and potash are allowed to crystallize out.

The dark red solution is now evaporated on the sand-bath, and during evaporation prismatic crystals separate from the hot solution. These are removed, dissolved in water, and again crystallized by allowing the solution to cool. The reason of taking the crystals from the hot solution in the first instance is to obtain them uncontaminated with the nitrates, which are more soluble in hot water than this nitroprusside. By this process any quantity of the nitroprusside of sodium may be obtained in fine large ruby-coloured crystals.

Properties.—This salt crystallizes in fine ruby-coloured prisms, which have been measured by Prof. MILLER.

Symbols:— a 100, b 010, e 101, r 011, m 110, x 211. x is common to the zones em , ra .
The angles between the normals to the faces are,—

ba	90°	$0'$
ea	68	16
ee'	43	28
rb	62	26
rr'	55	8
ma	52	38.5
mb	37	21.5
mm'	74	43
rm	68	25
re	34	34
em	77	1
xm	49	24
en	27	37



Nitroprusside of sodium resembles very much in appearance the ordinary red prusside of potassium when the latter salt is crystallized from alkaline solutions*.

Nitroprusside of sodium is not at all deliquescent, but is very soluble in water, dissolving in $2\frac{1}{2}$ times its weight of water † at 60° . It is still more soluble in hot water, but appears to have a point of less solubility at a particular temperature, for it may easily be crystallized by keeping its hot solution on the sand-bath, while it may not do so on cooling.

It is decomposed by mixing it with excess of alkali, and suffers the singular transformations with sulphurets of the alkaline metals which have been already alluded to. It undergoes no change in weight when heated to 212° , and therefore does not lose water in the water-bath.

The following analyses were made by heating the salt with sulphuric acid, and estimating the iron as peroxide, the sodium as sulphate of soda:—

Analyses I. and II. were made upon a salt obtained by acting on nitroprusside of iron with caustic soda. Analyses III. and IV. from a salt prepared from nitroprusside of copper. Analyses V. VI. and VII. from the process last described, by acting on yellow prusside of potassium with nitric acid and neutralizing with carbonate of soda; and analyses VIII. and IX. from another preparation in the same way.

- | | | |
|---|-----|---|
| { | I. | 11.800 grs. gave 3.300 grs. peroxide of iron and 5.870 grs. sulphate of soda. |
| | II. | 10.300 grs. gave 2.930 grs. peroxide of iron and 5.000 grs. sulphate of soda. |

* Red prussiate of potash crystallizes more easily and with much greater beauty from alkaline than from neutral or acid solutions; the reason being that the excess of alkali decomposes a small quantity of a green precipitate, which crystallizes along with it.

† 50.12 grs. saturated solution at 60° gave 14.46 salt; in another experiment 42.88 grs. solution gave 12.45 grs. salt, both being dried in water-bath.

- III. 13·767 grs. gave 3·813 grs. peroxide of iron and 6·440 grs. sulphate of soda.
- IV. 21·536 grs. gave 5·932 grs. peroxide of iron and 10·410 grs. sulphate of soda.
- V. 19·610 grs. gave 5·470 grs. peroxide of iron and 9·890 grs. sulphate of soda.
- VI. 13·545 grs. gave 3·740 grs. peroxide of iron and 6·450 grs. sulphate of soda.
- VII. 15·740 grs. gave 4·420 grs. peroxide of iron.
- VIII. 13·788 grs. gave 3·880 grs. peroxide of iron and 6·710 grs. sulphate of soda.
- IX. 25·155 grs. gave 7·028 grs. peroxide of iron and 12·120 grs. sulphate of soda.

The combustions were made with chromate of lead.

- I. 9·188 grs. gave 6·870 grs. carbonic acid and 1·300 gr. water.
- II. 8·580 grs. gave 6·315 grs. carbonic acid and 1·224 gr. water.
- III. 13·815 grs. gave 10·080 grs. carbonic acid and 1·780 gr. water.
- IV. 8·765 grs. gave 6·570 grs. carbonic acid and 1·280 gr. water.
- V. 12·010 grs. gave 8·790 grs. carbonic acid and 1·450 gr. water.
- VI. 15·070 grs. gave 10·790 grs. carbonic acid and 1·820 gr. water.
- VII. 9·000 grs. gave 6·580 grs. carbonic acid and 1·110 gr. water.
- VIII. 8·645 grs. gave 6·340 grs. carbonic acid and 1·184 gr. water.
- IX. 10·921 grs. gave 8·035 grs. carbonic acid and 1·309 gr. water.

The nitrogen in this salt was determined by DUMAS' quantitative method, an air-pump being used, so as to facilitate the expulsion of air from the apparatus.

I. 7·903 grs., by DUMAS' quantitative method, gave 117 CC. gas; thermometer 11°·1 C.; barometer 30·415 inches. Hence the nitrogen is 27·781 per cent.

II. 4·6 grs., also treated by DUMAS' method, gave 68 CC. gas; thermometer 45° FAHR.; barometer 30·742 inches. Per-centage of nitrogen 28·79.

	From Iron Salt.		From Copper Salt.		From Prusside of Potassium.				
Iron	19·576	19·912	19·387	19·281	19·525	19·320	19·56	19·69	19·59
Sodium	16·114	15·718	15·160	15·795	16·348	15·88	15·90	15·76
Carbon	20·392	20·073	19·899	20·442	19·960	19·530	19·94	20·00	20·06
Hydrogen	1·572	1·585	1·437	1·622	1·340	1·340	1·37	1·52	1·33
Nitrogen	42·346	42·712	27·781 16·336	42·860	28·790 14·037	43·25	42·89	43·26
Oxygen									
	100·000	100·000	100·000	100·000	100·000		100·00	100·00	100·00

In order to estimate the water with more precision than can be done in an organic analysis, a portion of salt was heated in an F tube to which a chloride of calcium tube was attached; 9·52 grs. gave 1·20 gr. water, equal to 1·40 hydrogen per cent.

The above analyses correspond to the following calculated formula:—

	Calculation.
5 Iron	140
5 Sodium	116
24 Carbon	144
15 Nitrogen	210
10 Hydrogen	10
13 Oxygen	104
	<hr/>
	724
	<hr/>
	100·00

It is obvious that if the analyses would authorise 25 eqvts. of carbon instead of 24, a very much more simple formula might be given. The mean proportion of iron to carbon is 19.54 : 20.03, while the proportion, 5 eqvts. : 25 eqvts. or 1 : 5, would require 19.54 : 20.93 of carbon. Throughout all the salts, this less quantity of carbon refuses to enrol itself in the simple proportion of 1 : 5, and necessitates the use of the much more complex one of 5 : 24. The above formula may be expressed as $\text{Fe}_5 \text{Cy}_{12} 3\text{NO}, 5\text{Na} + 10\text{HO}$.

Nitroprusside of Potassium.

12. This salt may be obtained in several ways.

1. By acting upon prusside of potassium with nitric acid, exactly as described under nitroprusside of sodium, but the neutralization of the acid is effected by carbonate of potash, instead of carbonate of soda as therein described. The nitrate of potash is crystallized out and the mother-liquor is put in the hot chamber to crystallize.

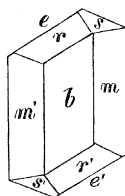
2. It may be prepared from the nitroprusside of iron, or better from the copper salt, by decomposing it with caustic potash, care being taken to keep the nitroprusside in excess.

Properties.—This salt, from its great solubility, is somewhat difficult to crystallize. It is apt to deposit in an amorphous form; but this may be avoided by a little practice, and fine large crystals may be obtained. These crystals belong to the oblique system, and have been measured by Prof. MILLER.

Symbols:— b 010, m 110, s 012, e $\bar{1}$ 01, r $\bar{1}$ 11.

Angles between normals to the faces:—

ab	30°	$0'$
rb	54	5
mb	49	46
sb	68	52
em	113	55
es	57	7
sm	69	3



The axis of the zone mb , makes an angle of $57^\circ 56'$ with that of the zone rb , and an angle of $71^\circ 0'$ with the axis of the zone sb .

This salt dissolves in its own weight of water at 60° ; 60.06 grs. of a saturated solution of this salt evaporated in the water-bath left 30.40 grs. of the salt. It is not precipitated from its solution by alcohol. With caustic potash it unites and forms a salt which is described in a further part of the paper. Nascent hydrogen does not decompose it. Hydrogen, chlorine and sulphurous acid were passed through both cold and hot solutions of the salt without effecting any change. It is slightly deliquescent, and acquires a greenish shade when exposed to light; its solutions on long keeping deposit prussian blue and become partially decomposed.

The crystals of this salt are of a dark red colour.

The analysis was made by decomposing the salt by Nordhausen sulphuric acid. The following estimations give the amount of water lost in the water-bath :—

- I. 14·865 grs. lost 1·765 grs., or 11·873 per cent.
- II. 15·455 grs. lost 1·855 grs., or 12·002 per cent.
- III. 12·430 grs. lost 1·480 grs., or 11·906 per cent.
- IV. 20·155 grs. lost 2·245 grs., or 11·138 per cent.

Mean . . . 11·730

The inorganic analyses yielded the following results :—

- I. 23·905 grs. gave 6·479 grs. peroxide of iron and 13·837 grs. sulphate of potash.
- II. 20·145 grs. gave 5·525 grs. peroxide of iron and 12·105 grs. sulphate of potash.
- III. 13·015 grs. gave 3·550 grs. peroxide of iron and 7·660 grs. sulphate of potash.
- IV. 12·945 grs. gave 3·536 grs. peroxide of iron and 7·600 grs. sulphate of potash.
- V. 17·195 grs. gave 4·832 grs. peroxide of iron.

The organic analyses were made with chromate of lead.

- I. 7·475 grs. gave 0·448 gr. water and 5·403 grs. carbonic acid.
- II. 7·122 grs. gave 0·425 gr. water and 5·105 grs. carbonic acid.

	I.	II.	III.	IV.	V.	Mean.
Iron . .	18·972	19·198	19·093	19·120	18·901	19·056
Potassium	25·947	26·934	26·385	26·388	26·413
Carbon .	19·712	19·548	19·630
Hydrogen	0·665	0·663	0·664
Nitrogen } Oxygen . }	34·704	33·657	34·237
	100·000	100·000				100·000

These results may be expressed by the following calculation :—

	Calculated.	Mean.
5 Iron	140	18·92
5 Potassium . .	195	26·35
24 Carbon . . .	144	19·46
3 Hydrogen . . .	3	0·40
15 Nitrogen . . .	210	28·38
6 Oxygen	48	6·49
	740	100·00
		100·000

According to this calculation the formula of the salt dried at 212° is Fe₅ Cy₁₂ 3NO, 5K+3HO; the salt loses in the water-bath 11·73 per cent. of water; had it lost 12·7 per cent. this would have corresponded to 12 eqv.; 11 eqv. would yield a loss of 10·6 per cent.

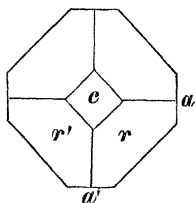
Nitroprusside of Barium.

13. This salt is obtained by decomposing nitroprusside of copper by caustic barytes, avoiding an excess of the latter. On filtration a dark red-coloured solution passes through. When evaporated under the air-pump, it forms fine large pyramidal crystals. The following measurements have been made by Prof. MILLER of Cambridge:—

Symbols:— a 100, c 001, r 111.

Angles between normals to the faces:—

ac	90°	$0'$
aa'	90	0
rc	44	35
rr'	59	30
ra	60	15



This salt, out of a strong solution, also frequently crystallizes in flattened prisms; no doubt as a different hydrate.

Nitroprusside of barium is of a dark red colour, is easily soluble in water, and is not deliquescent. It deposits a brown precipitate on boiling, resembling oxide of iron, but which, in the specimen examined, also contained barytes. The salt, after it has experienced this change, crystallizes in the same form, but with impurities which cannot be separated by filtration or crystallization. Analyses of this altered salt are given, page 504.

The salt crystallized in the air-pump lost water in water-bath.

20·415 grs. lost at 212° 3·110 grs. water = 15·233 per cent.

24·455 grs. lost at 210° 3·648 grs. water = 14·917 per cent.

The analyses were made by acting upon the salt by sulphuric acid in the usual way.

I. 20·791 grs. gave 12·173 grs. sulphate of barytes and 4·180 grs. oxide of iron.

II. 17·240 grs. gave 10·198 grs. sulphate of barytes and 3·480 grs. oxide of iron.

The combustions were made with chromate of lead.

I. 8·539 grs. gave 1·208 gr. water and 4·665 grs. carbonic acid.

II. 10·068 grs. gave 1·132 gr. water and 5·580 grs. carbonic acid.

	I.	II.			Calculated.
Iron . .	14·073	14·129	5	140	14·05
Barium .	34·446	34·791	5	343	34·43
Carbon .	14·899	15·075	24	144	14·45
Hydrogen	1·571	1·249	15	15	1·50
Nitrogen	} 35·011	} 34·756	15	210	} 35·57
Oxygen			18	144	
	<hr/> 100·00	<hr/> 100·00		<hr/> 996	<hr/> 100·00

In the above analysis the proportion of carbon to the iron is higher than obtained with the other salts, but the error is usually on this side when chromate of lead, as in this instance, is used in the combustion. It will also be seen in a further part of the paper, that a carbonaceous impurity, probably an attached cyanide, not separable by crystallization, but removed when it is converted into a silver salt, is produced when a solution of this salt is kept for some time, and it is possible that a small portion may be present in the salt analysed. If we could be assured of the absence of all impurity, which it will be afterwards seen that it is difficult to believe from the variable composition of this salt, it is obvious that the above analyses might be much more simply expressed by the following calculation:—

	Calculated.
2 Iron 56	14·03
2 Barium 137	34·33
10 Carbon 60	15·03
6 Hydrogen 6	1·50
6 Nitrogen 84	} 35·11
7 Oxygen 56	
<hr style="width: 50%; margin-left: auto; margin-right: 0;"/> 399	<hr style="width: 50%; margin-left: auto; margin-right: 0;"/> 100·00

On the first formula the dried salt would be $\text{Fe}_5\text{Cy}_{12}\text{3NO}, 5\text{Ba}+15\text{HO}$, on the second $\text{Fe}_2\text{Cy}_5\text{NO}, \text{Ba}_2+6\text{HO}$. The water lost in the water-bath would in the first case correspond to 20 equivs., in the latter case to 8 equivs.

Nitroprusside of Silver.

14. This salt may be prepared by adding nitrate of silver to any of the soluble nitroprussides.

The colour of the salt varies according to its state of preparation, from a fleshy white to a pale buff. When dry it has a flesh colour. It is insoluble in water, alcohol and nitric acid. Hydrochloric acid decomposes it with the formation of nitroprussic acid and chloride of silver. The caustic alkalies decompose it, as they do the soluble nitroprussides generally: ammonia dissolves nitroprusside of silver, but it soon deposits white crystals, which are apt to be contaminated by oxide of iron. These white shining crystals are a compound of the salt with ammonia, and are quickly decomposed, even by water alone, but very readily by water acidulated with nitric acid. Ammonia is now found in solution and nitroprusside of silver remains. If ammonia and nitroprusside of silver be boiled together, a total decomposition takes place.

The salt was decomposed by sulphuric acid, the silver estimated as a chloride and the iron as peroxide. Each salt analysed was prepared at different times.

I. 14·788 grs. gave 2·749 grs. oxide of iron and 9·925 grs. chloride of silver.

II. 22·838 grs. gave 4·220 grs. oxide of iron and 15·180 grs. chloride of silver.

III. 16·675 grs. gave 3·115 grs. oxide of iron and 11·09 grs. chloride of silver.

IV. 26·545 grs. gave 4·970 grs. oxide of iron and 17·78 grs. chloride of silver.

The combustions were made in the usual way.

- I. 8.350 grs. gave 0.252 gr. water and 4.045 grs. carbonic acid.
- II. 8.385 grs. gave 0.234 gr. water and 4.150 grs. carbonic acid.
- III. 7.900 grs. gave 0.183 gr. water and 3.820 grs. carbonic acid.
- IV. 9.415 grs. gave 0.120 gr. water and 4.577 grs. carbonic acid.

As this salt was well calculated to give correct knowledge with regard to the composition of the nitroprussides generally, the nitrogen was carefully determined by the three best processes, viz. those of DUMAS, LIEBIG and BUNSEN.

I. Quantitative estimation of nitrogen :—

6.808 grs. salt gave 69 C. C. nitrogen gas, the thermometer being 7°·7 C. and the barometer 30.094 inches. This makes the nitrogen 19.299 per cent.

II. LIEBIG'S method :—

Tubes.	Vol. mixed gases.	Vol. after absorption.	Vol. of carbonic acid.
1.	21.0	8.15	12.85
2.	18.4	7.3	11.1
3.	24.0	9.25	14.75
4.	20.15	7.45	12.70
5.	13.3	5.35	7.95
6.	26.20	9.2	17.0
	<u>123.05</u>	<u>46.70</u>	<u>76.35</u>

Hence the proportion of nitrogen to carbonic acid is as 1 : 1.63. This, calculated on 13.288, the mean quantity of carbon, gives 19.02 per cent.

BUNSEN'S method :—

	Obs. vol.	Barom. inches.	Therm.	Col. merc.
Vol. of mixed gases (moist) .	110.8	757.7	16.2 C.	217.0
Vol. after absorption (dry) .	46.2	761.9	16.2	218.0
Corrected vol. of mixed gases . . .			66.801	
Corrected vol. of nitrogen			<u>25.800</u>	
Vol. of carbonic acid				<u>41.001</u>

Hence the proportion of nitrogen to carbonic acid is as 1 : 1.589, which calculated on 13.288 carbon, gives 19.512 per cent.

	I.	II.	III.	IV.	Mean.		Calculated.
Iron . . .	13.012	12.934	13.076	13.106	13.032	5 140	13.011
Silver . . .	50.546	50.000	49.925	50.040	50.128	5 540	50.185
Carbon . . .	18.211	13.508	13.177	13.257	13.288	24 144	13.382
Hydrogen . . .	0.330	0.310	0.250	0.140	0.257	2 2	0.185
Nitrogen . . .	19.299	19.020	19.512	} 23.457	19.277	15 210	19.516
Oxygen . . .	3.602	4.228	4.060		4.118	5 40	3.721
	<u>100.000</u>	<u>100.000</u>	<u>100.000</u>	<u>100.000</u>	<u>100.000</u>	<u>1076</u>	<u>100.000</u>

With a quantity of hydrogen so small as that in the above analysis, it is difficult to obtain accordant results in an organic analysis. A portion of well-dried salt was therefore heated in an F tube, to which a tube filled with chloride of calcium was attached.

5·375 grs. gave 0·085 gr. water, equal to 0·175 H. per cent.

4·000 grs. gave 0·065 gr. water, equal to 0·180 H. per cent.

It is therefore quite certain that the silver salt dried at 212° still retains 1½ per cent. of water. It loses however this water at a higher heat and becomes anhydrous. The formula of the silver salt is therefore $\text{Fe}_5\text{Cy}_{12}\text{3NO}, \text{Ag}_5+2\text{HO}$.

Nitroprusside of Copper.

15. This salt is obtained by adding a solution of a copper salt to that of a nitroprusside. As it is insoluble in cold water, and almost entirely so in hot, it may be washed to any extent.

It is of a pale green colour, which changes to slate colour when exposed to light in the moist state. It is quite insoluble in alcohol. It is decomposed by the caustic alkalies, first passing into a dark brown basic nitroprusside, and then into oxide of copper and a soluble nitroprusside.

Nitroprusside of copper, dried in the hot chamber at about 100° FAHR., still lost weight in the water-bath.

45·60 grs. lost in water-bath 4·525, or 9·922 per cent.

25·12 grs. lost in water-bath 2·870, or 11·425 per cent.

The analysis of the dried salt was made by decomposing it with sulphuric acid, and estimating the two metals as oxides, after separating them in the usual way by sulphuretted hydrogen.

I. 22·24 grs. gave 6·325 grs. oxide of copper and 6·515 grs. peroxide of iron.

II. 21·00 grs. gave 6·018 grs. oxide of copper and 6·120 grs. peroxide of iron.

The combustions were made with chromate of lead and with oxide of copper.

I. 8·100 grs. gave 0·230 gr. water and 6·343 grs. carbonic acid.

II. 7·977 grs. gave 0·240 gr. water and 6·217 grs. carbonic acid.

III. 9·887 grs. gave 0·330 gr. water and 7·694 grs. carbonic acid.

IV. 11·507 grs. gave 0·320 gr. water and 8·936 grs. carbonic acid.

The nitrogen was determined in three different ways.

I. DUMAS' quantitative method:—

6·226 grs. gave 98 CC. nitrogen gas. Barom. 30·105 inches. Therm. 8°·8 C.

II. BUNSEN'S method:—

	Vol.	Barom. inches.	Therm.	Col. merc.
Vol. mixed gases (moist) .	246·3	29·988	15·6	219·7
Vol. after absorption (dry) .	121·1	30·069	15·4	348·0

Corrected vol. of mixed gases . . .	123·180
Corrected vol. of nitrogen	47·491
	<hr/>
Corrected vol. of carbonic acid . . .	75·689

Hence the proportion of nitrogen to carbonic acid is 1 : 1·593, which calculated on the mean quantity of carbon (21·25), yields 31·12 per cent. nitrogen.

III. LIEBIG'S method:—

Tubes.	Vol. mixed gases.	Vol. after absorption.	Vol. of carbonic acid.
1.	21·2	8·0	13·2
2.	22·4	9·1	13·3
3.	26·0	10·4	15·6
4.	21·7	8·2	13·5
5.	28·3	10·6	17·7
6.	17·9	6·7	11·2
7.	22·2	8·2	14·0
8.	19·8	7·5	12·3
9.	20·0	8·0	12·0
10.	22·7	9·0	13·7
11.	28·0	10·8	17·2
12.	19·2	7·3	11·9
13.	14·6	5·4	9·2
	<hr/>	<hr/>	<hr/>
	284·0	109·2	174·8

Hence the proportion of nitrogen to carbonic acid is 1 : 1·60.

	I.	II.	III.	IV.	Mean.			Calculated.
Iron . . .	20·506	20·400	20·453	5	140	20·43
Copper . .	22·708	22·880	22·794	5	158	23·06
Carbon . .	21·351	21·255	21·222	21·179	21·251	24	144	21·02
Hydrogen .	0·315	0·309	0·371	0·308	0·325	1	1	0·14
Nitrogen .	29·856	31·120	30·980	30·652	15	210	30·65
Oxygen . .	5·264	4·036	4·515	4	32	4·70
	<hr/>	<hr/>			<hr/>		<hr/>	<hr/>
	100·000	100·000			100·000		685	100·00

The formula of the copper salt is therefore $\text{Fe}_5 \text{Cy}_{12} 3\text{NO}, \text{Cu}_5 + \text{HO}$.

Nitroprusside of Iron.

16. This salt is obtained by adding sulphate of the protoxide of iron to a soluble nitroprusside. When the solutions are dilute the precipitate does not at first appear; as however it is very sparingly soluble, it may be purified by washing either with hot or cold water.

This salt is a salmon-coloured precipitate, nearly though not absolutely insoluble in water; it is more soluble in water rendered acid by nitric acid. It is decomposed by caustic alkalis, with the precipitation of oxide of iron and the formation of a

soluble nitroprusside. Before however being completely decomposed, a dark-coloured basic nitroprusside of iron is produced.

A salt dried in the hot chamber, at a temperature about 90° FAHR., still lost water when exposed in the water-bath:—

14·162 grs. lost at 212° 2·890 grs., or 20·406 per cent.

10·893 grs. lost at 212° 2·320 grs., or 21·298 per cent.

17·500 grs. lost at 212° 3·545 grs., or 20·257 per cent.

In the two first analyses given below, the iron was determined by decomposing the salt by sulphuric acid, oxidizing with nitric acid and precipitation by ammonia. The third estimation was by calcination, a little nitrate of ammonia being used to effect complete oxidation.

I. 18·075 grs. gave 9·917 grs. peroxide of iron.

II. 30·935 grs. gave 16·900 grs. peroxide of iron.

III. 9·220 grs. gave 4·995 grs. peroxide of iron.

The combustions were performed with chromate of lead.

I. 7·218 grs. gave 0·717 gr. water and 5·255 grs. carbonic acid.

II. 7·347 grs. gave 0·810 gr. water and 5·360 grs. carbonic acid.

III. 6·360 grs. gave 0·693 gr. water and 4·695 grs. carbonic acid.

The nitrogen was determined by DUMAS' quantitative method.

5·427 grs. gave 86 CC. nitrogen gas, the thermometer being 48°·7 FAHR. (9·4 Cent.) and the barometer 29·285 inches.

	I.	II.	III.	Mean.			Calculated.
Iron	38·406	38·241	37·922	38·189	10	280	38·35
Carbon . . .	19·855	19·896	20·136	19·962	24	144	19·72
Nitrogen . .	29·285	29·285	29·285	29·285	15	210	28·76
Hydrogen .	1·103	1·224	1·210	1·179	8	8	1·09
Oxygen . .	11·351	11·354	11·447	11·385	11	88	12·08
	<u>100·000</u>	<u>100·000</u>	<u>100·000</u>	<u>100·000</u>		<u>730</u>	<u>100·00</u>

The formula of the iron salt, dried at 212°, would therefore be



Nitroprusside of Zinc.

17. This salt is prepared by precipitating one of the soluble salts of zinc by a nitroprusside. It is a salmon-coloured precipitate, of a more fleshy colour than the iron salt. When formed slowly, as when muriatic acid and zinc are made to act on nitroprusside of soda, it is of a deep orange colour.

Nitroprusside of zinc is very slightly soluble in cold water, rather more so in hot water. In its behaviour to reagents it acts exactly like the iron nitroprusside. It was analysed by decomposing it with sulphuric acid, separating the iron by succinate of ammonia and determining the zinc as a carbonate.

I. 24.14 grs. gave 6.92 grs. peroxide of iron and 6.70 grs. oxide zinc.
 9.43 grs. gave 7.10 grs. carbonic acid and 0.335 gr. water.

				Calculated.
Iron	20.07	5	140	20.11
Zinc	22.26	5	160	22.98
Carbon	20.53	24	144	20.69
Hydrogen	0.39	2	2	0.28
Nitrogen }	36.75	15	210	35.94
Oxygen }		5	40	
	<hr/>		<hr/>	<hr/>
	100.00		696	100.00

This analysis would lead to the formula $\text{Fe}_5 \text{Cy}_{12} 3\text{NO} \text{Zn}_5 + 2\text{HO}$.

SECTION III.—*Changes experienced by certain Nitroprussides when their solutions are heated or kept.*

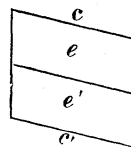
18. Several of the nitroprussides, especially nitroprussic acid, nitroprussides of ammonium, barium and calcium, deposit either prussian blue or oxide of iron when their solutions are heated or are kept for some time. The residual liquid, after evaporation, yields crystals of the same shape and exactly of the same properties as before. Analysis however shows that some change has resulted in their composition, for the iron or electro-negative metal is now in greater than atomic proportion to the electro-positive metal. The proportion of carbon is also somewhat different. Still the difference in composition is not very considerable, although decidedly marked; it is not however sufficient to cause any obvious alteration in their general properties. In fact, there is an attached impurity, probably a cyanide of iron, which cannot now be removed by crystallization, precipitation, digestion with nitric acid, or any of the ordinary means of purification. This impurity, if it be one, remains so obstinately attached that all methods of purification have quite failed to remove it. This circumstance, before it was understood, had thrown the greatest difficulties in the way of the inquiry, and protracted it to a most tedious length by preventing the attainment of accordant results. It is to prevent the like inconvenience to those who repeat these experiments that this section of the paper is specially devoted. Attention has previously been drawn to the fact, that the nitroprussides form chemical compounds with the cyanides of iron. This seems to be a case of the same kind, but of more ultimate union. The impurity or chemically attached cyanide in this case appears to be Fe Cy_2 , or perhaps $\text{Fe Cy} + \text{H Cy}$, judging from analysis only, for its separation has not been accomplished. The proportion in which it is present is very small, generally only 2(Fe Cy_2) to 7 equivs. of a nitroprusside, or if it be a chemical compound, $7(\text{Fe}_5 \text{Cy}_{12} 3\text{NO} + 5\text{R}) + \text{Fe}_2 \text{Cy}_4$. Still as the crystalline form and all the properties of the nitroprussides remain unchanged, we can scarcely view its presence in any other light than as an impurity. Several of the nitroprussides, viz. nitroprussic

acid and the nitroprussides of ammonium and calcium, have not yet been obtained free from this impurity, and are therefore described in this section.

Nitroprussic Acid.

19. The mode of preparation of this acid has been already described at page 486. It is however most readily prepared from nitroprusside of silver by adding to it as much hydrochloric acid as suffices to form chloride of silver with the silver in the salt. The dark red solution thus obtained soon evolves hydrocyanic acid, even in the cold, and after a time prusside of potassium indicates the presence of iron in solution. If the solution be heated, it deposits abundance of a brown precipitate resembling oxide of iron. When the latter is separated by filtration, and the solution is evaporated *in vacuo* over sulphuric acid, crystals are formed and may be separated; they must be dried over sulphuric acid, as they are exceedingly deliquescent. These crystals belong to the oblique system, but on account of their excessive tendency to deliquesce, it is difficult to measure their angles with accordant results. The angles between normals to the only faces which gave results to be depended on, are stated by Prof. MILLER to be as follows:—

ec	$36^{\circ} 57'$
$e'c'$	$36 57$
ee'	$106 6$



It will be seen that the equality of the angles ec and $e'c'$ is a tolerably certain indication that the crystals belong to the oblique system.

The acid made by the action of hydrochloric acid on nitroprusside of silver, and evaporated over sulphuric acid in the cold, crystallized (light being excluded) without the deposition of oxide of iron, but the smell of hydrocyanic acid, accompanied by a peculiar pungent smell, was strongly perceptible. Analysis shows that these crystals are the same as those obtained from a boiled solution.

Properties of the Crystallized Acid.—The crystallized acid is of a dark red colour, and has a very acid reaction, the crystals being generally flattened and of tolerable size. They are quite as deliquescent as chloride of calcium. They dissolve to a large extent in water, and are also soluble in alcohol and in ether. They may be dried in the water-bath without change, but their aqueous solution cannot be boiled without decomposition.

The following analyses were made on crystals obtained from a boiled solution, and were dried at 212° . The acid was that made by the action of hydrochloric acid on the silver salt. Nos. I. II. and III. were preparations made at distinct times.

The iron was determined by calcination and by treating the residual oxide with nitrate of ammonia.

- I. 2.345 grs. gave 0.800 gr. peroxide of iron.
- II. 3.915 grs. gave 1.325 gr. peroxide of iron.
- III. 3.580 grs. gave 1.220 gr. peroxide of iron.

The combustions were made in the usual way.

- I. 7.720 grs. gave 7.005 grs. carbonic acid and 1.175 gr. water.
 II. 10.810 grs. gave 9.880 grs. carbonic acid and 1.665 gr. water.
 III. 4.385 grs. gave 3.980 grs. carbonic acid and 0.700 gr. water.

An estimation of nitrogen by BUNSEN'S method gave the following result :—

	Obs. vol.	Barom. inches.	Therm.	Col. Merc.
Vol. of mixed gases (moist) . .	89.5	29.994	7.0 C.	152.7
Vol. after absorption (dry) . .	37.4	30.015	9.2 C.	205.2
Corrected vol. of mixed gases . . .			52.995	
After absorption of carbonic acid . .			20.570	
Nitrogen			<u>32.425</u>	

Hence the proportion of nitrogen to carbonic acid is 1 : 1.576.

	I.	II.	III.	Mean.		Calculated.
Iron	23.88	23.69	23.85	23.80	5 140	24.26
Carbon	24.74	24.92	24.75	24.80	24 144	24.95
Hydrogen	1.69	1.71	1.77	1.72	11 11	1.90
Nitrogen	36.73	36.73	36.73	36.73	15 210	36.39
Oxygen	12.96	12.95	12.90	12.95	9 72	12.50
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>		<u>100.00</u>
					577	

The calculated result, especially as regards the hydrogen, is not sufficiently close to be the true expression of the analysis, but it is here given to show how far the acid differs from pure nitroprussic acid. It is indeed probable that the acid dried at 212° only contains 10 equivs. of water.

The acid is so remarkably deliquescent that it is very difficult to ascertain how much the crystals lose in the water-bath. The following analysis of the salt dried *in vacuo* over sulphuric acid shows a higher state of hydration. The sample analysed had never been heated, even in solution, so that it evaporated without the deposition of oxide of iron. Still the oxide was detected in the mother-liquor by ferrocyanide of potassium.

- I. 3.225 grs. gave 1.010 gr. peroxide of iron.
 II. 3.235 grs. gave 1.020 gr. peroxide of iron.
 I. 5.830 grs. gave 5.020 grs. carbonic acid and 1.09 gr. water.
 II. 8.225 grs. gave 7.060 grs. carbonic acid and 1.51 gr. water.

	I.	II.	Mean.
Iron	21.92	22.07	21.99
Carbon	23.48	23.32	23.40
Hydrogen	2.07	2.03	2.05
Nitrogen	} 52.53	52.58	52.56
Oxygen			
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

A silver salt made from the well-crystallized acid showed that the iron was in excess, and that the carbon was in the usual proportion (see p. 506). The analyses of these silver salts are given further on, in order to avoid repetition. The discussion as to the constitution of the acid is also deferred to that place.

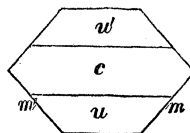
Nitroprusside of Ammonium.

20. When ammonia is added to an excess of nitroprusside of iron the latter is decomposed, oxide of iron being precipitated, but during the action nitrogen gas is evolved. If the red-coloured solution caused by filtration be evaporated in the air-pump, a difficultly crystallizable salt is obtained, which very readily decomposes, turning blue in the water-bath, and even when dried over sulphuric acid *in vacuo*. This salt is probably the true nitroprusside of ammonium, but it has not been obtained pure for analysis. If a solution of this salt be heated, prussian blue is deposited, and the filtered dark-red liquid, being evaporated by a gentle heat, now crystallizes in a warm place very readily, and in fine large red crystals, which are so dark as to be almost of a black colour. These have been measured by Prof. MILLER; they are prismatic, but the angles given are only approximative, the faces of the crystal examined being imperfect.

Symbols:—*c* 001, *m* 110, *u* 011.

Angles between normals to the faces:—

<i>mc</i>	90° 0'
<i>mm'</i>	88 4
<i>uc</i>	55 3
<i>uu'</i>	110 6



They are twin crystals, the twin faces being *m*.

This salt is very soluble in water, from which it is not precipitated by alcohol. It is very slightly deliquescent. The salt dried in air loses water in the water-bath.

18·648 grs. lost at 212° 2·928 grs., or 15·701 per cent.

10·915 grs. lost at 212° 1·800 gr., or 16·491 per cent.

11·502 grs. lost at 212° 1·948 gr., or 16·936 per cent.

45·400 grs. lost at 212° 6·850 grs., or 15·088 per cent.

16·054

The iron was determined by calcination.

I. 10·905 grs. gave 3·455 grs. peroxide of iron.

II. 12·954 grs. gave 4·070 grs. peroxide of iron.

The combustions made with chromate of lead gave the following results:—

I. 9·822 grs. gave 2·903 grs. water and 8·251 grs. carbonic acid.

II. 12·765 grs. gave 3·682 grs. water and 10·494 grs. carbonic acid.

III. 7·215 grs. gave 2·010 grs. water and 6·020 grs. carbonic acid.

The nitrogen was determined by DUMAS' quantitative method.

I. 4.494 grs. salt gave 112 C.C. gas, the therm. being $47^{\circ}\frac{1}{2}$ FAHR., barom. 29.844 in.
 II. 3.372 grs. salt gave 83 C.C. gas, the therm. being 50° FAHR., barom. 29.550 in.

This, calculated on 22.7 per cent. carbon, gives 43.619 per cent. nitrogen.

Again, 8.747 grs. salt distilled with a weak solution of soda, gave a distillate which, collected in hydrochloric acid, yielded 15.021 grs. platinum salt.

	I.	II.	III.	Mean.
Iron	22.177	21.993	22.085
Carbon	22.901	22.420	22.755	22.692
Hydrogen . . .	3.283	3.204	3.095	3.194
Nitrogen . . .	46.894	45.076	45.985
Oxygen	4.745	7.307	6.044
	100.000	100.000		100.000

The ammonium per cent. from the amount of platinum salt is 13.872.

It is obvious that there is little hydrogen as water, for the greatest part is required to make up the ammonium (13.872 per cent. requires 3.08 hydrogen). Reserving, as in the other cases, the discussion as to the cause of difference between this salt and the pure nitroprusside, it will be convenient to give the calculation for nitroprusside of ammonium, of which the formula would be $Fe_5Cy_{12}3NO, 5NH_4+2HO$.

5 Iron	140	22.36
24 Carbon	144	23.00
20 Nitrogen	280	44.72
22 Hydrogen	22	3.51
5 Oxygen	40	6.41
	626	100.00

The hydrogen, but not the other constituents, would agree better with the above formula minus 2 equivs. of water ; the hydrogen by the latter would be 3.28 per cent.

Nitroprusside of Calcium.

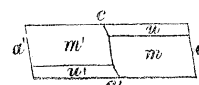
21. To prepare this salt, nitroprusside of iron or of copper is decomposed by milk of lime, the nitroprusside being kept in decided excess. A dark red solution is obtained, which on evaporation, even at a gentle heat, deposits prussian blue. When sufficiently concentrated the solution yields crystals of a dark red colour, and of considerable lustre. The crystals belong to the oblique system. They have been approximatively measured by Prof. MILLER.

Symbols:—*a* 100, *c* 001, *m* 110 ; there are besides one or two faces in the zone *c m c'*, the symbols of which have not been found.

Cleavage *a* very perfect.

Angles between normals to faces approximately:—

<i>ac</i>	$82^{\circ} 0'$
<i>ma</i>	$70^{\circ} 0'$
<i>mm'</i>	$40^{\circ} 0'$



The values of *cu* were extremely discordant. In the best crystals, the angle between normals to *cu* was found to be $71^{\circ} 41'$.

Nitroprusside of calcium is very soluble in water, and in its behaviour to reagents is exactly the same as the soluble nitroprussides already described. By the mean of two experiments the crystallized salt lost 17.85 per cent. of water in the water-bath at 212° .

The salt was analysed by fusion with nitrate of ammonia, the iron and lime being determined in the usual way.

13.29 grs. gave 4.004 grs. peroxide of iron and 4.698 grs. carbonate of lime.

8.33 grs. burned with chromate of lead gave 6.56 grs. carbonic acid and 0.82 water.

				Calculated.
Iron	21.09	5	140	21.11
Calcium	14.14	5	100	15.08
Carbon	21.47	24	144	21.71
Hydrogen	1.09	5	5	0.75
Nitrogen	42.21	{ 210	210	41.35
Oxygen				
	100.00		663	100.00

It will be seen that this salt belongs to the class which has dissolved some of the cyanide of iron resulting from its partial decomposition, and that therefore the electro-positive metal is in too small quantity. Allowing for this impurity, which cannot be removed, it is probable that the pure nitroprusside of calcium has the formula $Fe_5 Cy_{12} 3NO, Ca_5 + 5HO$. The loss of water in the water-bath corresponds to 15 equivs., which ought to have given the loss as 17 per cent. In one experiment it lost 17.44 per cent., in another 18.26. We may conclude that the formula of the crystallized salt is $Fe_5 Cy_{12} 3NO, Ca_5 + 20HO$.

Altered Nitroprusside of Barium.

22. When a solution of nitroprusside of barium is boiled, it deposits a brown precipitate containing both iron and barium*. The solution now crystallizes either in pyramidal or in prismatic crystals, that is, in the first state when crystallized slowly, in the second when deposited quickly from a hot solution. It is now found that the salt is inconstant in composition, different preparations giving very discordant results. The salt is however peculiarly difficult to dry, having to be kept in the water-bath for days before it ceases to lose weight; it abstracts water when dried most speedily from the atmosphere.

It is found that the carbon is increased in a marked degree. The following two specimens were made at different times and analysed. Analyses I. and II. were made

* The barytes used in decomposing the nitroprusside of copper was that made by boiling peroxide of manganese with sulphuret of barium. It always contains a little hyposulphite, and the brown precipitate was found to contain sulphate of barytes.

on the same specimen, but crystallized over again for analysis II. No. III. is on a totally different specimen.

I. 14.40 grs. gave 8.62 grs. sulphate of barytes and 3.12 grs. oxide of iron.

II. 15.90 grs. gave 10.17 grs. sulphate of barytes and 3.68 grs. oxide of iron.

III. 14.135 grs. gave 8.47 grs. sulphate of barytes and 3.06 grs. oxide of iron.

The combustions were made with chromate of lead.

I. 11.735 grs. gave 7.730 grs. carbonic acid and 1.390 gr. water.

II. 10.610 grs. gave 7.145 grs. carbonic acid and 0.700 gr. water.

III. 14.045 grs. gave 8.800 grs. carbonic acid and 1.900 gr. water.

	I. 1st Crystallization.	II. 2nd Crystallization.	III. New portion.
Iron	15.16	16.27	14.76
Barium	35.57	37.59	37.85
Carbon	17.96	18.34	17.08
Hydrogen	1.31	0.73	1.50

But a new portion of barytes salt did not give the same result; the portion analysed was in prismatic crystals, and crystallized twice.

I. 11.65 grs. gave 6.58 grs. sulphate of barytes and 2.49 grs. oxide of iron.

II. 17.22 grs. gave 9.83 grs. sulphate of barytes and 3.58 grs. oxide of iron.

I. 6.87 grs. gave 3.87 grs. carbonic acid and 0.52 gr. water.

II. 13.62 grs. gave 7.44 grs. carbonic acid and 0.69 gr. water.

	IV. 1st Crystallization.	V. 2nd Crystallization.
Iron	14.96	14.55
Barium	33.23	33.60
Carbon	15.41	16.38
Hydrogen	0.83	0.55

Another portion, in flat prismatic crystals, made by neutralizing nitroprussic acid with carbonate of barytes, gave the following results:—

12.33 grs. gave 6.61 grs. sulphate of barytes and 2.42 grs. peroxide of iron.

6.60 grs. gave 4.005 grs. carbonic acid and 1.040 gr. water.

	VI.
Iron	13.73
Barium	31.53
Carbon	16.52
Hydrogen	1.75

In this case the salt lost no more in the water-bath, although this was to have been expected from its larger quantity of hydrogen.

In all these cases the specimens were excellently crystallized, and yet there is a

greater or less quantity of a foreign substance prevailing in all, and producing results so very discordant. In the first two portions analysed the barium is to the carbon (37·01 : 17·79) almost exactly as 1 equiv. : $5\frac{1}{2}$ equivs., and the iron is to the carbon, sensibly though not so exactly, in the same proportion. In analysis VI., the iron is to the carbon as 28 : 33·7, or rather more than 1 : $5\frac{1}{2}$, while the barium is to the carbon as 1 : 6. Again, in analyses IV. and V., the iron is to the carbon as 1 : 5, and the barium to the same element 1 : $5\frac{1}{2}$.

Finally, it will be seen further on that the silver salt made from these altered salts of barium do not contain this excess of carbon. The filtrate from the silver salts yields on evaporation and incineration a small quantity of a black ash, but the quantity being so small the nature of the substance could not be ascertained. We can scarcely suppose that it is a ferrocyanide, because we should have expected to have it precipitated by nitrate of silver, even though it could not be recognized by its usual tests. It would be useless without further information to speculate upon the probable nature of the impurity. Sufficient however has been shown to prove that the most complicated results may attend the analysis of specimens of nitroprusside of barium prepared from solutions which have been heated and thus partially decomposed.

Altered Nitroprusside of Sodium.

23. The previous analyses of the crystallized nitroprussic acid and of the nitroprussides of ammonium and barium, and the composition of the silver salts prepared from them, show a want of accordance between the iron in the electro-negative constituent and the metal in the electro-positive one. The iron in all these cases is about half a per cent. in excess, therefore not sufficient to be considered as being in atomic proportion. It was thought, from the very distinct crystallization of the sodium salt, that this excess might not accompany it if prepared from the respective silver salts of the above compounds. Accordingly the silver salt was decomposed by an equivalent quantity of hydrochloric acid. The resulting solution was neutralized with carbonate of soda and crystallized. Analyses I. and II. were made on a salt thus prepared from crystallized nitroprusside of barium. Analysis III. on a salt similarly made from nitroprusside of ammonia. Again, when we refer to the action of caustic soda on the nitroprussides, it was obvious that by using a less quantity of the alkali than sufficed to effect the complete decomposition, a nitroprusside with a similar impurity in solution was to be expected.

Analysis IV. was made on a specimen thus prepared, and its accuracy is confirmed by a future analysis of a silver salt.

- | | |
|---|---|
| { | I. 13·695 grs. gave 3·72 grs. peroxide of iron. |
| { | II. 20·93 grs. gave 5·72 grs. peroxide of iron and 9·93 grs. sulphate of soda. |
| | III. 15·35 grs. gave 4·25 grs. peroxide of iron and 7·10 grs. sulphate of soda. |
| | IV. 11·13 grs. gave 3·07 grs. peroxide of iron and 5·06 grs. sulphate of soda. |

The combustions were made with chromate of lead.

- II. 13.34 grs. gave 9.74 grs. carbonic acid and 1.58 gr. water.
 III. 14.475 grs. gave 10.68 grs. carbonic acid and 1.67 gr. water.
 IV. 6.730 grs. gave 5.33 grs. carbonic acid and 1.01 gr. water.

	From barium salt.		From ammonium salt. III.	By action of caustic soda. IV.
	I.	II.		
Iron . . .	19.00	19.12	19.38	19.30
Sodium		15.37	15.00	14.72
Carbon		19.91	20.12	21.59
Hydrogen.		1.31	1.21	1.65
Nitrogen . . . } . . .		44.39	44.29	42.74
Oxygen . . . }				
		100.00	100.00	100.00

It will be seen from these analyses that the excess of iron still remains, and this is further confirmed by silver salts again made from them and analysed. It will also be observed that in specimen IV. we have the same remarkable increase in carbon as observed in the barium salt; the sodium is to the carbon as $1 : 5\frac{1}{2}$, which is exactly the proportion found in the latter salt; but this excess of carbon does not go down with a silver salt made from it.

Examination of the Silver Salts made from the altered Nitroprussides.

24. To save unnecessary repetition, the numerous analyses made of the silver salts are here brought together, although it might have been more distinct to have introduced them under the respective salts from which they were made. The reason for converting them into silver salts was, that from the high atomic weight of silver and its accuracy of determination, the atomic accordance or disagreement between it and the iron could more readily be perceived.

Analyses I. II. and III. were made on three different preparations of silver salt made from three different specimens of crystallized nitroprussic acid, by adding the latter to nitrate of silver.

Analysis IV. was made upon a portion of II. treated on sand-bath with strong nitric acid in the hope of dissolving out the excess of iron. A very small quantity of iron was detected in solution by prusside of potassium.

Analysis V. was made on the silver salt prepared from crystallized nitroprusside of ammonia.

Analyses VI. and VII. from silver salt precipitated from crystallized nitroprusside of barium, which contained 17.96 grs. of carbon, or in which the barium was to the carbon as $1 : 5\frac{1}{2}$.

Analysis VIII. On previous silver salt digested on the sand-bath with strong nitric acid to dissolve out excess of iron.

Analysis IX. On silver salt made from the crystallized sodium salt (No. 2) containing 19.91 grs. carbon.

Analysis X. Silver salt prepared from sodium salt (No. 4) containing 21.59 carbon, or in which the sodium was to the carbon as 1 : 5½. In order if possible to remove the excess of iron, the salt was first precipitated by sulphate of copper and washed, the copper salt was now decomposed by soda and crystallized, and the silver salt was precipitated from this newly-crystallized portion.

- | | |
|--|--|
| { | I. 19.605 grs. gave 3.77 grs. peroxide of iron and 12.86 grs. chloride of silver. |
| | II. 16.795 grs. gave 3.24 grs. peroxide of iron and 10.94 grs. chloride of silver. |
| | III. 13.580 grs. gave 2.60 grs. peroxide of iron and 8.79 grs. chloride of silver. |
| | IV. 6.765 grs. gave 1.35 gr. peroxide of iron and 4.355 grs. chloride of silver. |
| | V. 14.68 grs. gave 2.80 grs. peroxide of iron and 9.44 grs. chloride of silver. |
| { | VI. 13.16 grs. gave 2.43 grs. peroxide of iron and 8.535 grs. chloride of silver. |
| | VII. 24.41 grs. gave 4.54 grs. peroxide of iron and 15.79 grs. chloride of silver. |
| VIII. 15.21 grs. gave 2.88 grs. peroxide of iron and 9.89 grs. chloride of silver. | |
| IX. 13.60 grs. gave 2.60 grs. peroxide of iron and 8.80 grs. chloride of silver. | |
| X. 8.81 grs. gave 1.69 gr. peroxide of iron and 5.59 grs. chloride of silver. | |

The combustions were made partly with chromate of lead, partly with oxide of copper.

- | |
|--|
| I. 12.05 grs. gave 6.08 grs. carbonic acid and 0.10 gr. water. |
| II. 12.195 grs. gave 6.10 grs. carbonic acid and 0.08 gr. water. |
| IV. 8.10 grs. gave 4.03 grs. carbonic acid and 0.09 gr. water. |
| V. 10.35 grs. gave 5.13 grs. carbonic acid and 0.21 gr. water. |
| VI. 14.52 grs. gave 7.18 grs. carbonic acid and 0.05 gr. water. |
| VIII. 9.56 grs. gave 4.85 grs. carbonic acid and 0.04 gr. water. |
| IX. 10.835 grs. gave 5.50 grs. carbonic acid and 0.10 gr. water. |

	I. II. III.			IV.	V.	VI. VII.		VIII.	IX.	X.	Mean.
Iron	13.46	13.50	13.40	13.97	13.35	12.92	13.01	13.25	13.38	13.42	13.36
Silver	49.42	49.02	48.71	48.46	49.50	48.67	48.69	48.93	48.70	47.77	48.78
Carbon.....	13.75	13.64	13.56	13.43	13.48	13.82	13.84	13.64
Hydrogen	0.09	0.07	0.12	0.22	0.03	0.04	0.10	0.09
Nitrogen } Oxygen }	23.28	23.77	23.89	23.50	24.90	23.96	23.98	24.13
	100.00	100.00		100.00	100.00	100.00		100.00	100.00		100.00

If we assume the mean iron, 13.36, to represent the true quantity, then the silver to correspond to it in atomic proportion should have been 51.53, whereas there is only 48.78. Hence there is 0.72 of iron in excess over the equivalent quantity; this excess corresponds to $\frac{1}{18}$ th of an equivalent. Again, supposing the carbon to be in the same proportion to the silver as in the nitroprussides, there should have been 13.0, so that there is an excess of 0.64. The excess of iron and of carbon is therefore almost exactly as 1 equiv. : 4 equivs., or viewing the carbon as representing cyanogen as 1 : 2. On this view the amount of impurity in the silver salt is 2.10 per cent. Calculating the mean analysis deprived of this supposed impurity, we have

		Theory of nitroprusside of silver.
Iron	12·92	13·01
Silver	49·81	50·18
Carbon	13·28	13·38
Hydrogen	0·097	0·18
Nitrogen }	23·02	23·25
Oxygen }	23·02	23·25
	100·00	100·00

In the previous calculation the cyanide supposed to be present is Fe Cy_2 ; this only denotes the proportion of iron to the cyanogen; it is possible though less probable that it might be $2(\text{Fe Cy} + \text{HCy})$. In this case we might suppose the analysed silver salts to contain this cyanide somewhat in the following proportion: 7 equivs. nitroprusside to 1 equiv. of the supposed cyanide. On this supposition the calculated and actual numbers would be as follows:—

	Calculated.	Mean.
Iron	13·50	13·36
Silver	49·26	48·78
Carbon	13·76	13·64
Hydrogen	0·20	0·09

It is not however to be supposed that this cyanide is present as a chemical compound in the above proportion, as the differences in the analyses show that it occurs in varying and not very definite proportions.

It would indeed appear that the barium and sodium nitroprusside contained a body in which the iron and cyanogen are in the same proportion as in ferrocyanogen (Fe Cy_3). But as the silver salt precipitated from them does not contain an excess of carbon, it can scarcely be supposed that this would not be precipitated. But in fact there are no data further than the mere ultimate analyses upon which reasoning can be founded with regard to this dissolved and combined foreign substance in the partially decomposed nitroprussides. As however all their essential characters and their crystalline form remain altogether unaltered, we cannot view the foreign substances as more than accidental.

SECTION IV.—*Action of Caustic Alkalies on the Nitroprussides.*

25. When a dissolved caustic alkali, such as potash or soda, is added to a solution of a nitroprusside, the dark red colour of the solution changes to an orange-yellow. If both solutions have been moderately dilute, no oxide of iron is precipitated, nor is ammonia evolved. The addition of alcohol to the orange-yellow liquid causes the precipitation of an aqueous solution of a new salt. This salt may be procured in a solid state as follows. Nitroprusside of potassium is dissolved in water and double its volume of alcohol is added. Caustic potash is now added to this solution, and a yellow curdy precipitate is obtained. This precipitate is washed with alcohol to free it from an excess of either of the reagents, but it is almost impossible to remove the last traces.

The salt is now pressed between folds of bibulous paper and dried *in vacuo* over sulphuric acid. It may be called nitroprusside of potassium and potash.

This salt is of a bright yellow colour and of crystalline appearance. It is very sparingly soluble in alcohol, but very soluble in water, to which it gives a strong alkaline reaction. It precipitates salts of lead of a fine yellow colour like the chromate of lead. Salts of iron are precipitated of a yellowish brown, and salts of copper of a brown colour. On the addition of an acid, the excess of potash is removed and nitroprusside of potassium remains in solution; the salt therefore is a compound of a nitroprusside with potash. It will not crystallize *in vacuo*, its solution decomposing with the deposition of an oxide of iron, and with the escape of a gas which communicates a pink colour to the sulphuric acid used for the evaporation in the air-pump. The salt heated in a tube evolves nitric oxide and ammonia, and leaves a black residue which yields to water an alkaline solution of a nitroprusside. When its solution in water is boiled, complete decomposition takes place, a ferrocyanide, oxide of iron, nitrite and oxalate of potash being produced.

It is almost impossible to obtain it free from uncombined nitroprusside, which is observed to remain in solution when a salt of lead is added to it. If potash in excess be used, it is equally difficult to remove the excess by washing. The analyses therefore give only approximative results; they were made in the usual way by decomposing the salt with fuming sulphuric acid.

I. 17·350 grs. gave 3·440 grs. peroxide of iron and 14·32 grs. sulphate of potash.

II. 37·870 grs. gave 7·345 grs. peroxide of iron and 30·53 grs. sulphate of potash.

The combustions were made with chromate of lead.

I. 14·075 grs. gave 7·765 grs. carbonic acid and 1·015 gr. water.

II. 13·71 grs. gave 7·490 grs. carbonic acid and 0·985 gr. water.

The samples of salt analysed were made at different times.

	I.	II.	Mean.			Calculated.
Iron	13·87	13·57	13·72	5	140	14·38
Potassium . .	37·00	36·14	36·57	9	351	36·07
Carbon . . .	15·04	14·89	14·96	24	144	14·79
Hydrogen . .	0·80	0·79	0·79	8	8	0·82
Nitrogen } . .	33·29	34·61	33·96	{ 15	210 }	33·94
Oxygen } . .						
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00		<hr/> 973	<hr/> 100·00

Hence this salt differs from nitroprusside of potassium by containing 4 atoms of potash attached. Its formula is therefore $\text{Fe}_5 \text{Cy}_{12} 3\text{NO K}_5 + 4\text{KO} + 8\text{HO}$. There is little doubt that it might, when quite free from nitroprusside, contain an additional equivalent of potash.

It has been stated that a solution of this salt is decomposed on boiling. Oxide of iron falls down, nitrogen escapes, and the solution is now found to contain ferrocyanide of potassium, nitrite of potash and traces of oxalate of potash.

26. The products of transformation were determined (1) by precipitating the ferrocyanide by alcohol; (2) by adding nitrate of lime to precipitate the oxalate*, which was always accompanied by a minute quantity of a pink compound containing cyanogen and iron; (3) by examining the liquid which remained, and was found to evolve nitric oxide on the addition of an acid. It gave a precipitate with nitrate of silver, which, though sparingly soluble in cold water, dissolved in hot water and crystallized on cooling; 13·25 grs. of the crystalline salt thus obtained, treated with hydrochloric acid, gave 12·33 grs. chloride of silver, or 70·03 per cent. Nitrite of silver (AgO, NO_3) contains 70·12 per cent.

In examining the relative quantities of these products of transformation, recourse was first had to the yellow salt itself. But as this generally contained a little nitroprusside, and as the products of decomposition varied with the period of ebullition, on account of the slower action from the insufficient quantity of alkali, it was found more accurate to examine the transformations by acting upon a solution of nitroprusside with an excess of alkali. Without therefore giving the details of the experiments on the yellow salt itself, some of the general results may be stated; from these it will be seen that the quantities of oxide of iron and of prusside produced vary according to the conditions of the experiment, principally according to the longer or shorter period of ebullition. 100 parts of the yellow salt gave, on boiling its aqueous solution,—

	I.	II.	III.	IV.	V.
Peroxide of iron	3·0	3·58	3·0	3·56	2·71
Ferrocyanide of potassium .	60·86	60·59	59·48	68·83	64·50

In all these cases there was more or less nitroprusside of potassium undecomposed. The amount of oxalate of potash found in solution varied from 0·97 to 1·5 per cent.

The transformation was now examined in the following manner. A weighed quantity of a nitroprusside was dissolved in water and boiled, caustic potash or caustic soda (according as the nitroprusside was a salt of potassium or sodium) being added to the boiling solution, until a drop taken out gave, after being neutralized, no purple colour with a sulphide. The precipitated oxide of iron was now collected and weighed. The filtrate was precipitated by alcohol, and the prusside collected and determined on a weighed filter. The filtrate was now neutralized with acetic acid, and chloride of calcium added, but the oxalate of lime was generally not in sufficient quantity to collect and weigh, mere traces being obtained. It was now attempted to estimate the amount of nitrate by the process described by NESBIT for analysing nitrates†, that is, by converting its nitrogen into ammonia by zinc and muriatic acid, the hydrogen being slowly evolved. The ammonia thus formed was separated

* To prove that this was an oxalate, a portion was precipitated by nitrate of lead from the solution after precipitation by alcohol. The precipitate was of a pink colour, and was now decomposed by sulphuretted hydrogen, neutralized by pure carbonate of soda, and again precipitated as a lead salt, which was now quite white. Calcined with nitrate of ammonia, 1·660 gr. gave 1·250 gr. oxide of lead, or 75·3 per cent. Oxalate of lead contains 75·5 per cent.

† Memoirs of Chemical Society.

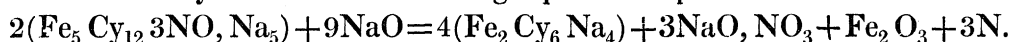
by distillation with caustic soda, collected in muriatic acid and determined as chloride of platinum and ammonia. This process did not however give constant results in my hands, probably from the difficulty of preventing the escape of nitric oxide on adding an acid to the nitrite. The nitrite was therefore determined by loss. In one case only did I, by the above process, obtain a result approaching the quantity of nitrite in solution.

17·24 grs. of nitroprusside of sodium were dissolved in water, the solution was boiled and caustic soda added, keeping the solution distinctly alkaline after ebullition had continued for some time. It yielded 0·92 gr. peroxide of iron, and 14·85 grs. ferrocyanide of sodium; the residual liquid, treated according to NESBIT'S plan, only gave 2·57 grs. platinum salt.

Iron precipitated	3·73 per cent.
Iron in prusside	15·08 per cent.
	18·81

Hence all the iron, except about 0·5 per cent., is found in the oxide of iron and in the prusside; the remainder is probably in the minute quantity of pink salt alluded to above. The carbon contained in the prusside amounts to 20·3; so that the total quantity of cyanogen has gone down in that form, the carbon in the nitroprusside being 20·0 per cent.

It will be seen that the iron precipitated as peroxide of iron is one-fourth that retained in the ferrocyanide. The following equation expresses the transformation:—



Or expressed in another way,—

4 equivs. ferrocyanide of sodium	$\text{Fe}_8 \text{Cy}_{24} \text{Na}_{16}$
3 equivs. nitrite of soda	$\text{Na}_3 \text{N}_3 \text{O}_{12}$
1 equiv. peroxide of iron	$\text{Fe}_2 \text{O}_3$
3 equivs. nitrogen	N_3
	$\text{Fe}_{10} \text{Cy}_{24} \text{Na}_{19} \text{N}_6 \text{O}_{15}$

The first change is obviously to form ferrocyanide of sodium, 6 equivs. of oxygen passing over to the nitrous oxide; this, with the oxygen in the latter, would make 4 equivs. nitrous acid; but the 2 equivs. of iron liberated require 3 of oxygen to form peroxide, which it receives at the expense of the nitrous acid, leaving therefore 3 equivs. of that acid to unite with soda, the remaining 3 equivs of nitrogen escaping as a gas. During the ebullition no ammonia can be detected, either by smell or by turmeric paper.

SECTION V.—*Action of an Alkaline Sulphide on a Nitroprusside.*

27. It has been repeatedly mentioned, that when solutions of nitroprusside of potassium or sodium and of the corresponding sulphides are mixed together, the most magnificent purple colour is produced. This colour however is very transitory and cannot be preserved in an aqueous solution. The purple or blue compound may

however be obtained in a solid state when alcoholic solutions of the two salts are employed. In order to obtain it in this state, nitroprusside of sodium is dissolved in the smallest possible quantity of water, and to this solution is added four or five times its bulk of alcohol. An alcoholic solution of neutral sulphide of sodium (the sulphide obtained by reducing the sulphate with hydrogen) is now added to the alcoholic solution of nitroprusside, the addition being stopped before the supernatant liquid gives a decidedly black reaction on lead paper. The mixed solutions acquire a magnificent purple blue colour. On stirring the mixture, an aqueous solution of the purple compound falls down in oily drops. After this has settled, the alcohol is decanted, and the blue solution is washed repeatedly and quickly with alcohol by decantation. It is now, as rapidly as possible, put *in vacuo* over sulphuric acid, when it soon parts with its water and becomes solid. It usually dries to a dirty green powder, which is a mixture of the purple compound with the products of its decomposition. It may however, though this is rare, dry quite unchanged in its character, being still of a fine blue colour and dissolving entirely in water with all its magnificent purple blue shade. It cannot then be dried in the water-bath, where it quickly decomposes and becomes green.

The following analysis was made on two portions which were dried in the air-pump, until they ceased to lose weight and had all their properties unchanged. They were oxidized by nitrate of ammonia; the residue was dissolved in nitric acid. The iron was precipitated as peroxide, the sulphur estimated as sulphate of barytes, and the soda as a sulphate.

I. 14·210 grs. gave 3·420 grs. peroxide of iron, 5·710 grs. sulphate of barytes and 9·38 grs. sulphate of soda.

II. 8·99 grs. gave 3·88 grs. sulphate of barytes and 6·62 grs. sulphate of soda, the iron being accidentally lost.

The combustion was made by chromate of lead, peroxide of lead being used to arrest the sulphurous acid.

I. 6·20 grs. gave 3·855 grs. carbonic acid and 0·440 gr. water.

II. 10·565 grs. gave 6·810 grs. carbonic acid and 0·675 gr. water.

	I.	II.	Mean.
Iron	16·84	16·84	16·84*
Sodium	21·37	23·84	22·60
Sulphur	5·51	5·92	5·71
Carbon	16·95	17·58	17·27
Hydrogen	0·78	0·71	0·74
Nitrogen }	38·55	35·11	36·84
Oxygen }			
	100·00	100·00	100·00

* It should be stated that in many analyses of this compound in its partially decomposed state, the most discordant results were obtained. The two analyses here adduced were made on the only specimens which appeared to be unchanged; in all the other cases the compound had become green and therefore was decomposed, as it no longer dissolved in water with its characteristic purple tint.

In such a variable compound as this, close results can scarcely be looked for in two analyses. As an approximation, however, it will be seen that the iron is to the sodium as 5 : 8, and to the sulphur as 5 : 3.

The blue unchanged compound gives with protosulphate of iron a beautiful precipitate of the same purple blue colour as itself, but this is decomposed by washing. With salts of lead it gives a brownish yellow precipitate, with salts of copper a brown precipitate, both these being obviously products of decomposition.

28. The purple blue compound dissolved in water speedily becomes red, and when in this state, a salt of lead throws down a pinkish red precipitate. This red solution however soon decomposes, a brownish precipitate falling, and the yellow colour due to a prusside being seen in the solution. If the sulphide originally employed contained sulphuretted hydrogen, a soluble prussian blue is also found in the liquid. During these changes, ammonia, hydrocyanic acid, and a gas possessing the properties of nitrogen are given off. In fact, on mixing the solutions of sulphide and nitroprusside, it is difficult, even by keeping the solutions quite cold, to prevent the formation of a little ammonia and escape of nitrogen. The solution of the purple compound in water decomposes even under the air-pump, depositing the brown precipitate, and it does so immediately when it is boiled.

When the solution is filtered from the brown precipitate, the addition of alcohol separates ferrocyanide of sodium. The alcoholic filtrate strikes a blood-red colour with a persalt of iron, and with sulphuric acid evolves nitric oxide, which is immediately rendered sensible by a protosalt of iron, a nitrite being thus shown to be in solution. Ammonia cannot be detected in the solution, neither does it appear to any great extent when the transformation takes place in the cold, though it always does so when ebullition is used to hasten the transformation. It therefore appears to be the product of an after action.

The brown precipitate is first to be examined. It is found to consist of peroxide of iron and sulphur, the latter remaining when the former is dissolved out by an acid. It was analysed by oxidation with nitromuriatic acid. 7.21 grs. gave 16.90 grs. sulphate of barytes, equal to 2.33 grs. of sulphur, and 4.22 grs. peroxide of iron, the rest being water. Hence the proportion of sulphur to iron in equivalents is nearly as 4 : 3; the proportion for 2.33 sulphur would yield 3.0 iron, while 2.95 was found by the experiment.

It was now desirable to ascertain what proportion of iron was thrown down as ferrocyanide and how much remained in the brown precipitate. For this purpose a portion of a preparation, which had become green by standing in the air-pump, was first analysed in order to ascertain the relative proportion of its constituents, and it was then dissolved in water and boiled.

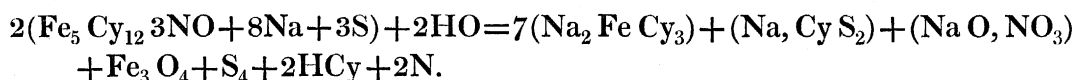
14.41 grs. gave 6.93 grs. sulphate of barytes, 17.68 grs. gave 3.55 grs. peroxide of iron and 10.00 grs. sulphate of soda. 6.025 grs. gave 3.31 grs. carbonic acid and

0·820 gr. water. Hence this changed purple compound, before complete transformation, contained in 100 parts,—

Iron	14·05
Sodium	18·33
Sulphur.	6·59
Carbon	14·98
Hydrogen	1·51
Nitrogen }	44·54
Oxygen }	
	100·00

11·31 grs. were now boiled in water, and 0·94 gr. of the brown precipitate was obtained by filtration, and 5·90 grs. of prusside of sodium were precipitated by alcohol. Hence of the total quantity of 1·58 gr. of iron present 1·08 gr. was found in the ferrocyanide, the remainder being in the brown precipitate. As the ferrocyanide of sodium is of constant composition, which the brown mixture is not, the iron in the latter is here estimated by loss and would amount to 0·50 gr. The proportion in equivalents is nearly, though not exactly, as 7 : 3, which would have made the iron in the brown precipitate 0·46 gr. instead of 0·50 gr..

Taking these proportions as leading to a general view of the transformation, it may be expressed by the following equation:—



The only point in which this transformation does not agree with experiment, is in the supposed production of ferrous-ferric oxide, whereas, when the brown precipitate is washed with acid, only peroxide of iron unaccompanied by protoxide of iron passes through. It is therefore probable that the oxidation of this oxide may give rise to the small quantity of ammonia observed, the oxygen from decomposed water uniting with it, and the nascent hydrogen with nitrogen to form ammonia. Allowing this to be the explanation of the disagreement with experiment, the following scheme may render the above equation more immediately intelligible. Two equivalents of the blue compound with 2 equivs. of water, by boiling, are resolved into—

- 7 equivs. ferrocyanide of sodium.
- 1 equiv. sulphocyanide of sodium.
- 1 equiv. nitrite of soda.
- 1 equiv. oxide of iron ($\text{FeO} + \text{Fe}_2\text{O}_3$).
- 4 equivs. sulphur.
- 2 equivs. hydrocyanic acid.
- 2 equivs. nitrogen.

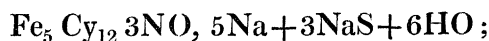
And probably the ferroso-ferric oxide is transformed at the expense of the oxygen of water into ferric oxide, the hydrogen forming ammonia with nitrogen,



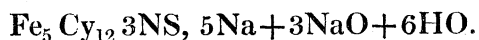
29. In giving the above equation, the blue sulphur compound was supposed to consist of nitroprusside of sodium with 3 equivs. of sulphuret of sodium attached. The following calculation shows that this is an expression of the analysis:—

	Calculated.	Mean experiment.
5 Iron . . . 140	17·36	16·84
8 Sodium . . 186	23·07	22·60
24 Carbon . . 144	17·86	17·27
3 Sulphur . . 48	5·95	5·71
6 Hydrogen . . 6	0·74	0·74
15 Nitrogen . . 210 } 9 Oxygen . . 72 }	35·02	36·84
806	100·00	100·00

The approximation is sufficiently near when the difficulty of getting the substance in at all a stable state is considered. Two views might be taken of the constitution of this singular compound (1), that it is nitroprusside of sodium with 3 equivs. of sulphuret of sodium attached—



but this would scarcely account for its extreme facility of decomposition; it may therefore be supposed that caustic soda is attached to the salt, as we have seen that it can be, in studying the action of alkalis on the nitroprussides, and that the sulphur has taken the place of the oxygen, thus:—



Either of these formulæ would suit the analysis; in support of the latter may be adduced the fact observed by GREGORY, that sulphuret of nitrogen in the presence of caustic alkalis acquires a deep transitory amethyst colour, which, on disappearing, evolved ammonia, a description exactly accordant with the present case.

Action of Sulphuretted Hydrogen on the Nitroprussides.

30. Sulphuretted hydrogen decomposes the soluble nitroprussides. The products of transformation are most conveniently obtained in the following way:—Nitroprusside of sodium is dissolved in the smallest possible quantity of cold water, and three or four times its volume of alcohol is added to the solution. Sulphuretted hydrogen is now passed through this alcoholic solution. Sulphur, prussian blue, and ferrocyanide of sodium, are very gradually precipitated; the action, however, is very slow, and must be long continued. The alcoholic solution is now of a reddish olive-brown colour. When the sulphuretted hydrogen has ceased to act, this supernatant brownish liquid gives no coloration when mixed with an alkaline sulphide.

If allowed to stand for a few hours, it deposits a little of the precipitates which it held in solution. After this the brown solution is found to contain neither ferrocyanide nor nitroprusside of sodium; a persalt of iron is slightly deepened in colour when mixed with it, showing the presence of a mere trace of a sulphocyanide. When this reddish-brown solution is evaporated in the water-bath, it deposits oxide of iron and sulphur, and becomes decomposed. Evaporated *in vacuo* over sulphuric acid it deposits, when nearly dry, black crystalline needles, but these seem to be a product of decomposition, and are mixed with oxide of iron and other substances; attempts were therefore made to ascertain the composition of the original substance by precipitating its solution by metallic salts. Bichloride of mercury produces a brown precipitate, sulphate of copper a pinkish brown, and nitrate of silver a black precipitate. But these were obviously products of decomposition, for during the precipitation nitric oxide is abundantly evolved. This is especially the case in the precipitate with silver. If that precipitate, after being washed, be now mixed with a small quantity of hydrochloric acid to take up the silver, sulphuretted hydrogen is evolved, protochloride of iron and abundance of sulphocyanic acid are now found in solution; the first is recognized by the prussian blue formed on adding red prusside of potassium, the second by the blood-red colour which it strikes with perchloride of iron. When nitrate of silver is added to the red-brown solution, the black precipitate already alluded to falls down, but at the same time the supernatant liquor had a reddish brown colour; on examining this it was found to contain a persalt and protosalt of iron, the dark coloration being due to the escaping nitric oxide. The amount of sulphur precipitated during the passage of sulphuretted hydrogen through the nitroprusside is about 17 per cent.; the amount of ferrocyanide of sodium and of prussian blue has been found to vary much.

From the difficulty of obtaining the products of transformation in a pure state, I have not yet been able to make direct quantitative examinations of the various substances formed; it is therefore impossible to express the transformation in the form of an equation. From some experiments now in progress, I trust, however, to overcome those difficulties which have prevented the completion of this study in time for the presentation of this paper.

On the Constitution of the Nitroprussides.

31. In the preceding part of the paper the analyses of the nitroprussides led to the extremely complicated formula $\text{Fe}_5 \text{C}_{24} \text{N}_{15} \text{O}_3 \text{R}_5$. This formula was *à priori* very improbable, and naturally led to the belief that an error in the estimation of the carbon forced its adoption. In fact, if 25 instead of 24 equivs. of carbon were present, the formula would resolve itself into the much simpler expression $\text{Fe}_2 \text{C}_{10} \text{N}_6 \text{O R}_2$. It is therefore important to review the evidence, in order to see whether the simple proportion of iron to carbon, 1 : 5, might be derived from it. The following table exhibits the proportion of iron and carbon found in the analyses of the respective salts:—

Name of salt.	Number of analyses furnishing the mean.	Quantity of iron. Mean.	Quantity of carbon. Mean.	Atomic relation of iron to carbon.
Nitroprusside of sodium	9	19.54	20.03	28 : 28.7
Nitroprusside of potassium	5	19.05	19.63	28 : 28.8
Nitroprusside of ammonium	3	22.08	22.69	28 : 28.7
Nitroprusside of silver	4	13.03	13.29	28 : 28.5
Nitroprusside of copper	4	20.45	21.25	28 : 29.0
Nitroprusside of iron	3	19.09	19.96	28 : 29.2
Nitroprusside of zinc.....	1	20.07	20.53	28 : 28.6
Nitroprusside of calcium	1	21.09	21.47	28 : 28.5
Nitroprusside of barium	2	14.10	14.98	28 : 29.7
Nitroprussic acid	3	23.80	24.80	28 : 29.1
Mean of the whole.....	35	192.30	198.63	28 : 28.9

Now the proportion of 1 equiv. of iron to 5 equivs. of carbon would require the proportion 28 : 30. This difference is too great to be due to any errors of observation, especially when it is remembered that these, in the case of a body containing much nitrogen, tend to increase and not to diminish the apparent quantity of carbon. The actual proportion found, 28 : 28.9, indicates, in equivalent, 5 equivs. iron to 24 equivs. carbon; this proportion would require 28 : 28.8; the slight excess found is in the direction of the known errors of observation.

These considerations forced the adoption of the complex formula given above. It will also be seen, from an examination of the analytical details, that the quantity of nitrogen corresponds to 6 equivs. for every 10 equivs. of carbon, or 15 equivs. for the 24 equivs. of carbon required by the formula. As 12 of these are in the state of cyanogen, as shown both by the transformation of the nitroprussides by alkalis and by sulphides, the remaining 3 equivs. must be in the form of an oxide of nitrogen. But the loss on the analyses does not admit the supposition that the oxide is nitric oxide, as might have been supposed, neither do the transformations countenance this idea. The oxygen is in the proportion of 3 equivs. for every 3 equivs. of nitrogen; the nitrogen not present as cyanogen must exist as nitrous oxide. This is unusual, and its functions must therefore be inquired into. It will at once be seen that if nitrous oxide is supposed to substitute and play the part of cyanogen, the iron and the non-electro-negative bodies with which it is associated are present in the same proportion as in the hypothetical radical ferrocyanogen; 5 equivs. ferrocyanogen have the formula $\text{Fe}_5 \text{Cy}_{15}$; 1 equiv. of nitro-ferrocyanogen has the formula $\text{Fe}_5 \text{Cy}_{12} 3\text{NO}$. The nitroprussides are therefore supposed to contain a ferrocyanogen in which 3 equivs. of cyanogen are substituted by 3 equivs. of nitrous oxide.

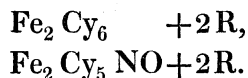
32. But the proportion of the electro-positive element in the nitroprussides is less than that existing either in the ferrocyanides or ferridcyanides. LIEBIG supposes these two latter compounds to differ by containing different radicals, one being twice the atomic weight of the other. It would be equally instructive to suppose that they both contain the same radical, but that, as in the case of the different phosphoric acids, one is quadribasic, while the other is tribasic.

Quadribasic prussides, $\text{Fe}_2 \text{Cy}_6 + 4\text{R}$, formula of ferrocyanides.

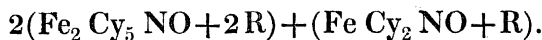
Tribasic prussides . . . $\text{Fe}_2 \text{Cy}_6 + 3\text{R}$, formula of ferridcyanides.

Bibasic prussides . . . $\text{Fe}_2 \text{Cy}_6 + 2\text{R}$, formula of undescribed compounds.

With regard to the last class, its existence must be yet considered hypothetical, but in searching for it, I have received sufficient encouragement to enable me to hope that I shall very shortly be able to establish it. Without presenting the analytical evidence to this effect, it can only be adduced as a probable hypothesis to explain the nitroprussides. The latter class of salts may be supposed to correspond to a bibasic class of prussides in which part of the cyanogen is replaced by nitrous oxide. Thus $5(\text{Fe Cy}_3 + \text{R}) = \text{Fe}_5 \text{Cy}_{15} + 5\text{R}$ correspond to 1 equiv. of a nitroprusside, $\text{Fe}_5 \text{Cy}_{12} 3\text{NO} + 5\text{R}$. The great approximation of the latter formula to the more simple expression $\text{Fe}_2 \text{Cy}_5 \text{NO} + 2\text{R}$, renders it singular that the small deficiency of carbon refuses to allow the formula to be thus expressed. In such a case this supposed bibasic prusside and the nitroprusside would stand in a very simple relation :



The complicated formula required by the analyses of all the nitroprussides might be resolved into $2(\text{Fe}_2 \text{Cy}_5 \text{NO} + 2\text{R}) + (\text{Fe Cy}_2 \text{NO} + \text{R})$, in which the latter member is constituted on the same type, but more cyanogen is displaced by the nitrous oxide. It will not excite surprise, after what has been learned in the previous inquiry as to the obstinate manner in which the nitroprussides unite with cyanides from which they are not removable by any means tried, that a salt constituted on the same type should unite with the true nitroprussides and form an integrant conjugate compound which is not broken up by crystallization. It appears therefore very probable that the true formula of the nitroprussides may in reality be $\text{Fe}_2 \text{Cy}_5 \text{NO} + 2\text{R}$, and that further research may eliminate this compound. Hitherto this has not been done, and the only formula which correctly expresses the analysis is $\text{Fe}_5 \text{Cy}_{12} 3\text{NO} + 5\text{R}$, which on theoretical, but on no other grounds, may be resolved into



I trust soon to be able to present to the Society another memoir on the prussides, which will confirm experimentally some of the views theoretically supported in the present communication ; but at present I submit the previous results with a view of drawing attention to this interesting class of salts, and with a perfect conviction that future research will simplify and explain the remarkably complex and unsatisfactory formulæ which I have been obliged to adopt, without believing them to be the correct expression of the constitution of the salts.